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Balancing macronutrient stoichiometry to alleviate eutrophication

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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

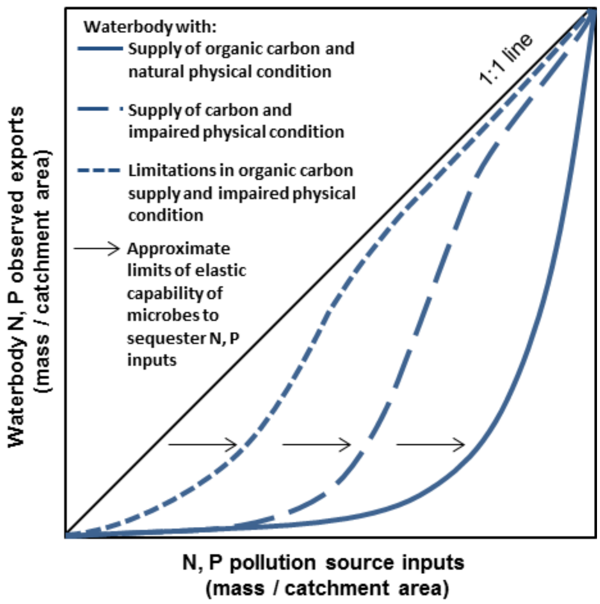

Figure 1. Conceptual model of resilience to nitrogen and phosphorus source inputs provided by river microbial nutrient processing mediated by organic carbon. In rivers, resilience to rising nutrient inputs is provided by physical and biochemical factors, crucially by microbial assimilation and longer-term 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

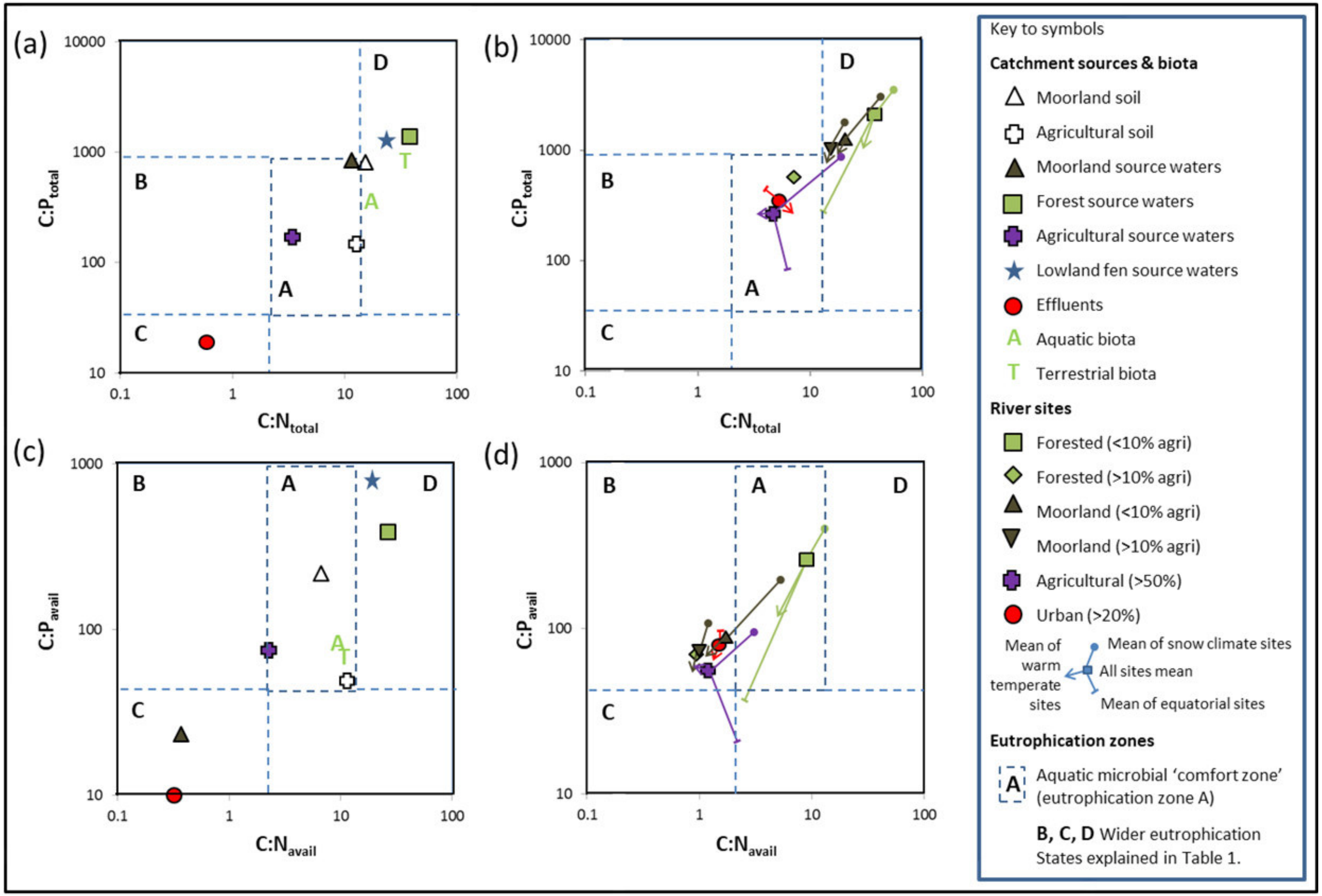
(a)
(b)
(c)
(d)
C:P$_{total}$
C:N$_{total}$
C:P$_{avail}$
C:N$_{avail}$
A
B
C
D
Key to symbols
Catchment sources & biota
Moorland soil
Agricultural soil
Moorland source waters
Forest source waters
Agricultural source waters
Lowland fen source waters
Effluents
Aquatic biota
Terrestrial biota
River sites
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.

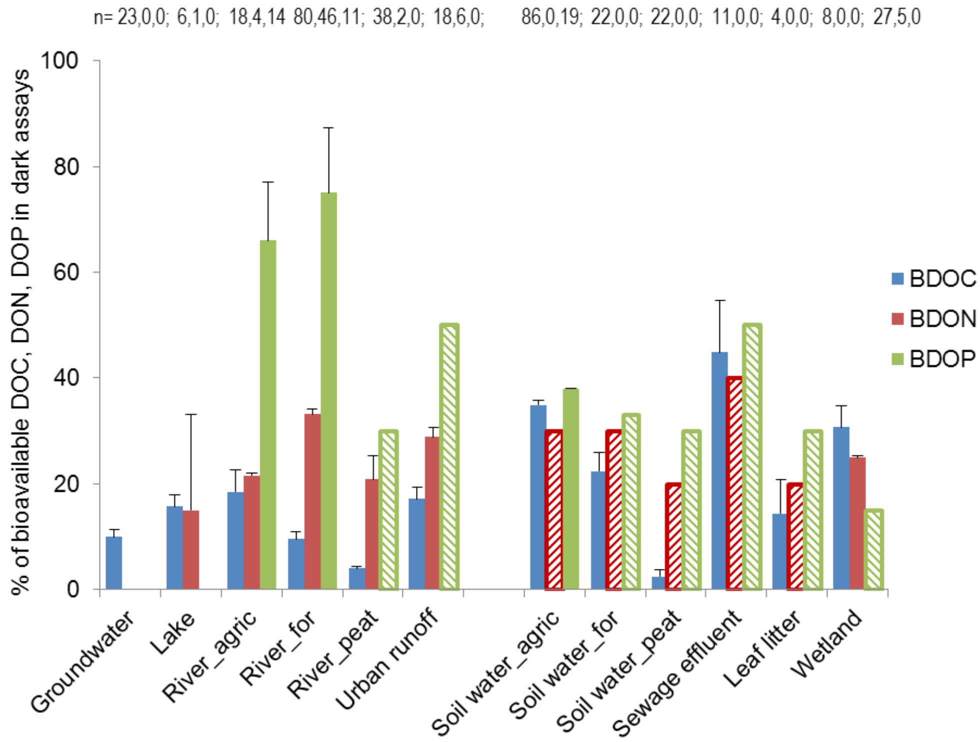

Figure 3. Summary of weighted means and variance for bioavailable proportions of dissolved organic C, N and P taken from literature metadata evidence and used for scaling available resources. Mean values are weighted by sample number (±1 weighted standard error, with stated n numbers indicating total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

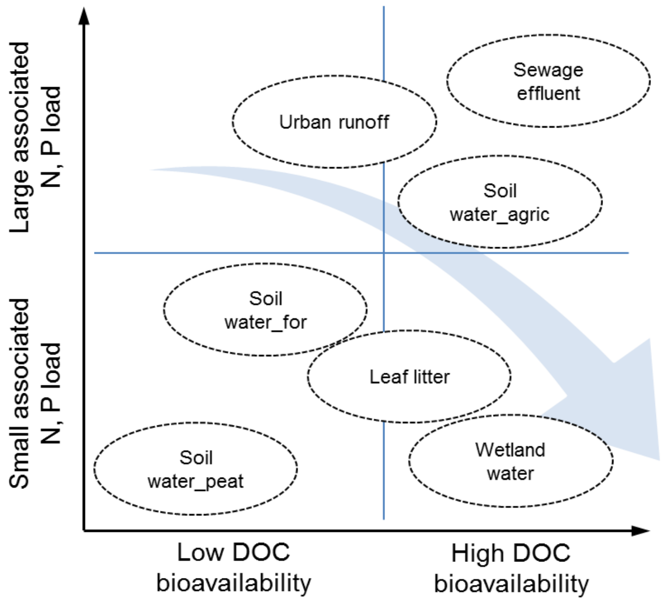

Figure 4. A conceptual matrix of catchment OC, N, P sources based on quadrants of low *vs* high available N, P load and low *vs* high DOC bioavailability (<20% and >20%, respectively) to demonstrate more and less appropriate forms of carbon for rebalancing. Wetland water and leaf litter provide optimum 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 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 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 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 C:P 994-10000, and C:N 11-100 C:P 47-10000	Abundant C-rich resources, relative to N and P, e.g. wetland or leaf litter available carbon.	Whilst microbial biomass is limited locally by lack of N, P, the beneficial C inputs drive microbial N and P sequestration potential down-river.

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

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Supplementary Material

Balancing macronutrient stoichiometry to alleviate eutrophication

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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.

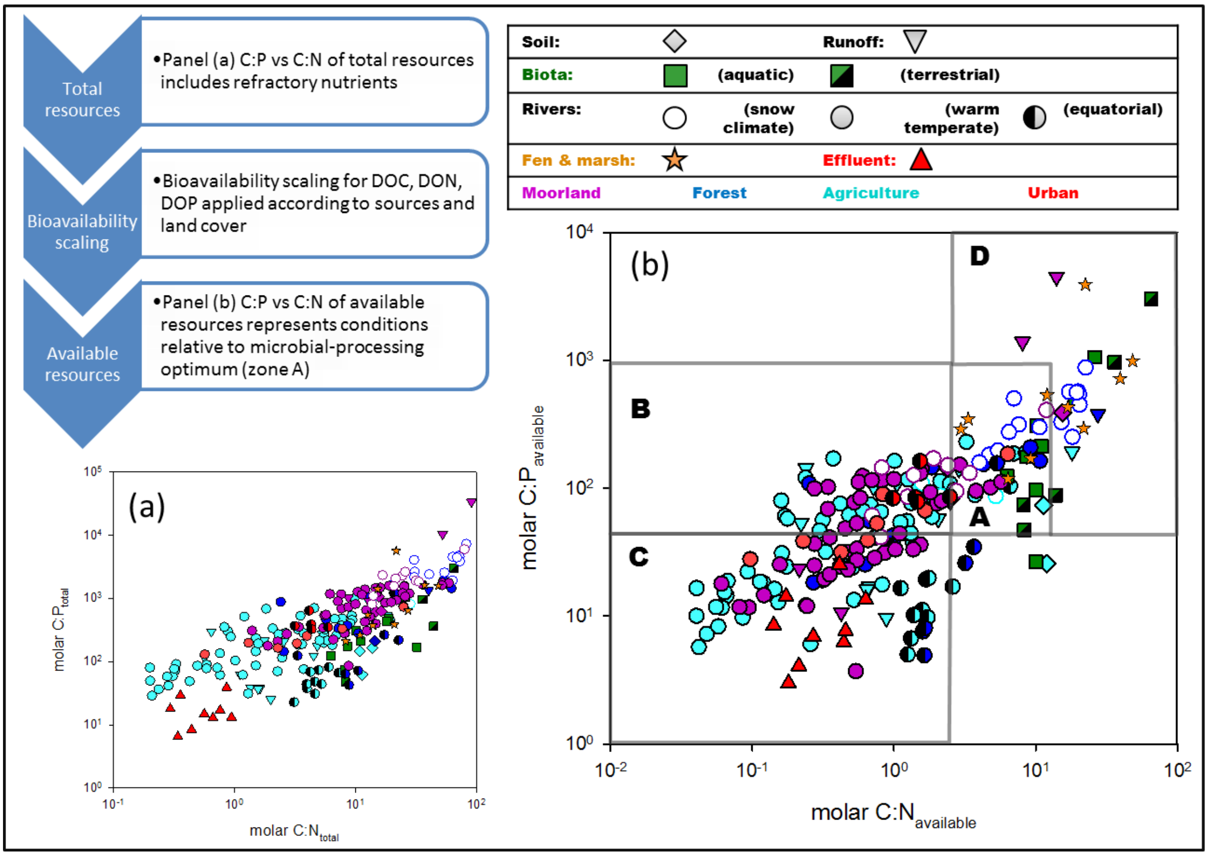
Data covered the latitudes 27-69°N and 3-46°S. Entries were compiled to single rows for either grouped data where key metadata such as land cover was not fully recorded, or individual sites to rows where full metadata was recorded; henceforth rows are termed database entries. Importantly, data were split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

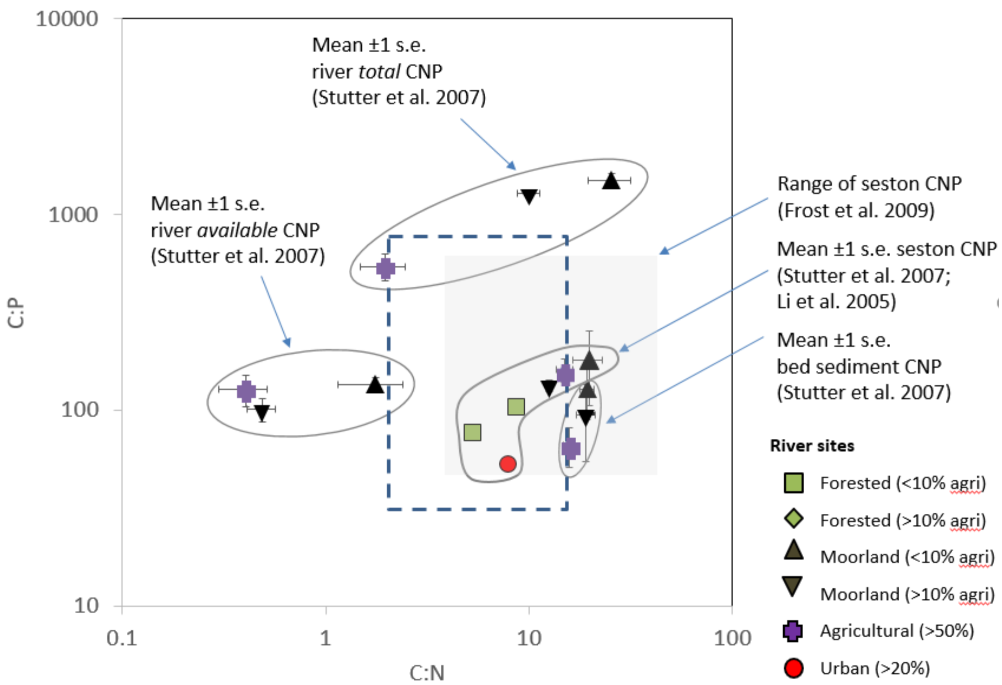


Table S1. Database of catchment nutrient sources, biological components and river ecosystem C, N and P concentrations, N and P speciation, C:N and C:P values used to construct Figure 2. Ratios of C:N and C:P refer to organic C forms only.

Component	n, spatial	Description	Country	Koppein climate zones	Land cover	Organic C, or DOC (µmol/kg)	Total N, or TDN (µmol/kg)	% org N	Total P, or TDP (µmol/kg)	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	11.4	62	M	12.0	26	22
Soil	6	Intensive grassland soil	UK	Cfb	Agr	4258333	390083	95	29038.7	10.9	147	M	11.4	74	22
Soil	10	Semi-natural soil	UK	Cfb	Peat	13166667	892176	95	21268.8	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	16.4	626	M	2.5	83	26
Soil		Elliott soil fulvic acid	US	Dfa	Peat	41766667	2678571	100	38709.7	15.6	1079	M	2.4	144	26
Runoff	9	Agricultural drainflow (Avon-Wye)	UK	Cfb	Agr	584	1033	15	5.0	0.6	117	M	0.2	53	25
Runoff	17	Arable drainflow	UK	Cfb	Agr	348	540	8	1.2	0.6	300	M	0.2	143	23
Runoff	11	Intensive grassland drainflow	UK	Cfb	Agr	456	178	21	2.2	2.6	209	M	1.0	109	23
Runoff	1	Riparian forest soil extract	UK	Cfb	For	4030	100	71	3.0	40.3	1343	M	27.4	381	23
Runoff	1	Upland pasture soil extract	UK	Cfb	Agr	1100	60	85	2.0	18.3	550	M	18.1	193	23
Runoff	4	Farm track runoff (Loddington)	UK	Cfb	Agr	663	137	46	3.7	4.8	178	M	2.5	79	25
Runoff	9	Rural paved roads	UK	Cfb	Agr	461	341	42	11.9	1.4	39	M	0.7	17	25

		runoff (Avon-Wye)													
Runoff	3	Arable surface runoff (Loddington)	UK	Cfb	Agr	818	154	50	3.0	5.3	273	M	2.9	142	25
Runoff	2	Arable field drain (Loddington)	UK	Cfb	Agr	753	425	19	3.4	1.8	220	M	0.7	103	25
Runoff	1	Farm yard runoff (Loddington)	UK	Cfb	Agr	1017	225	33	8.2	4.5	124	M	2.1	58	25
Runoff	3	Farm yard runoff (Avon-Wye)	UK	Cfb	Agr	1271	637	30	50.1	2.0	25	M	0.9	10	25
Runoff	12	Arable soil extract	UK	Cfb	Agr	490	440	11	7.8	1.1	63	M	0.4	26	19
Runoff	6	Intensive pasture soil extract	UK	Cfb	Agr	445	284	21	12.0	1.6	37	M	0.6	16	19
Runoff	12	Arable buffer soil extracts	UK	Cfb	Agr	790	487	17	20.9	1.6	38	M	0.6	16	19
Runoff	1	O hor podzol	UK	Cfb	Peat	3832	315	49	8.9	12.2	430	M	0.4	11	21
Runoff	1	AE hor podzol	UK	Cfb	Peat	4379	339	54	4.9	12.9	899	M	0.5	33	21
Runoff	63	Peatland springs	UK	Cfb	Peat	340	39	24	0.3	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	44.4	364	M	13.8	88	23
Biota_terrestrial	~410	Terrestrial plants	Global							36.0	968	M			7
Biota_terrestrial	Plant litter	Global								3000	M			15	
Fen and marsh	3	Bog	US	Dfc	We	2250	60	95	1.4	37.4	1626	Ob, C	48.2	987	8
Fen and marsh	3	Forested wetland	US	Dfc	We	2667	55	91	1.7	48.6	1593	Ob, C	39.4	719	8
Fen and marsh	3	Fen	US	Dfc	We	1217	58	74	3.1	21.1	387	Ob, C	21.8	294	8
Fen and marsh	1	Pristine wetland	US	Cfa	We	537	49	36	2.0	10.9	264	Ob, CN	3.0	290	24
Fen and marsh	1	Pristine wetland	US	Cfa	We	430	52	35	2.0	8.3	211	Ob, CN	3.3	348	24
Fen and marsh	3	Chapel Mires	UK	Cfb	We	1473	54	68	2.3	27.3	645	M	16.9	429	23
Fen and marsh	1	Wetland 2	G	Cfb	We	2914	134	91	0.5	21.8	5690	M	22.4	3908	10

Fen and marsh	1	Wetland 3	G	Cfb	We	1426	93	81	1.0	15.3	1408	M	12.0	535	10
Fen and marsh	1	Wetland 21	G	Cfb	We	1305	94	48	3.5	13.9	375	M	6.4	118	10
Fen and marsh	1	Wetland 24	G	Cfb	We	965	76	77	1.7	12.7	553	M	9.2	171	10
Effluent	32	Rural domestic septic tanks	UK	Cfb	Urb	3984	4213	6	305.1	0.9	13	M	0.4	6	16
Effluent	1	Hungerford STW	UK	Cfb	Urb	626	2123	10	35.0	0.3	18	M	0.1	8	14
Effluent	1	Marlborough STW	UK	Cfb	Urb	378	1058	12	12.9	0.4	29	M	0.2	14	14
Effluent	1	Newbury STW	UK	Cfb	Urb	458	812	10	31.0	0.6	15	M	0.3	7	14
Effluent	4	Sewage	Fr	Cfb	Urb	597000	785000	18	35200.0	0.8	17	Ob, C	0.6	13	17
Effluent	5	Sewage	Fr	Cfb	Urb	286000	645000	7	34400.0	0.4	8	Ob, C	0.2	4	17
Effluent	1	Tarland STW	UK	Cfb	Urb	990	1490	57	77.0	0.7	13	M	0.5	8	23
Effluent	1	Laurencekirk STW	UK	Cfb	Urb	310	360	6	8.0	0.9	39	M	0.4	25	23
Effluent	1	Rosemaud	UK	Cfb	Urb	550	1617	25	84.8	0.3	6	M	0.2	3	25
Biota_aquatic	268	River vascular plants	UK	Cfb		36500000	1921429	0	74193.5	19.0	492	M			6
Biota_aquatic	105	River bryophytes	UK	Cfb		34083333	1307143	0	32258.1	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	18.1	437	M	10.0	96	13
Biota_aquatic	6	Aquatic macrophytes: water extracts 1g:30mL)	Ch	Cfa		7141667	221429		41935.5	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_aq		Suwannee river	US	Cfa		438	835714	100	4193.5	52.5	10459	M	8.1	1396	26

uatic		humic acid				58333									
Biota_aquatic		Suwannee river fulvic acid	US	Cfa		43616667	478571	100	1290.3	91.1	33803	M	14.0	4508	26
River	1	River Dee main stem	UK	Cfb	Peat	402	16	45	0.3	25.5	1587	M	1.6	142	20
River	1	River Dee main stem	UK	Cfb	Peat	410	27	34	0.3	15.1	1243	M	0.8	115	20
River	1	River Dee main stem	UK	Cfb	Peat	422	35	25	0.3	12.0	1394	M	0.6	124	20
River	1	River Dee main stem	UK	Cfb	Peat	434	57	14	0.4	7.6	1165	M	0.3	102	20
River	1	River Dee, Tributary	UK	Cfb	Peat	465	13	64	0.3	36.0	1650	M	2.9	152	20
River	1	River Dee, Tributary	UK	Cfb	Peat	404	39	25	0.3	10.5	1279	M	0.5	77	20
River	1	River Dee, Tributary	UK	Cfb	For	388	161	7	0.4	2.4	887	M	0.3	109	20
River	1	River Dee, Tributary	UK	Cfb	Agr	144	162	2	0.5	0.9	302	M	0.2	60	20
River	1	River Dee, Tributary	UK	Cfb	Agr	413	199	7	1.2	2.1	338	M	0.4	76	20
River	1	River Dee, Tributary	UK	Cfb	Agr	304	252	4	0.6	1.2	516	M	0.2	120	20
River	1	River Dee, Tributary	UK	Cfb	Agr	229	278	3	0.6	0.8	354	M	0.2	80	20
River	1	River Dee, Tributary	UK	Cfb	Agr	835	182	18	1.2	4.6	707	M	1.0	163	20
River	1	River Dee, Tributary	UK	Cfb	Agr	529	290	9	0.8	1.8	688	M	0.4	171	20
River	1	A Hiraethlyn Pont Newydd	UK	Cfb	Agr	196	257	7	3.2	0.8	61	M	0.2	13	5
River	1	Afon Ddu Upper	UK	Cfb	For	894	17	62	0.5	53.7	1960	M	9.2	208	5
River	1	Carreg Ddefod	UK	Cfb	For	928	15	63	0.6	62.2	1449	M	10.7	163	5
River	1	Conwy above Serw	UK	Cfb	Peat	785	15	71	0.4	52.8	1766	M	4.8	101	5
River	1	Cwm-clorad-isaf	UK	Cfb	Agr	135	9	34	0.2	14.4	708	M	3.7	89	5
River	1	Cwm-Llanerch	UK	Cfb	Agr	500	51	54	0.5	9.8	1003	M	3.2	230	5
River	1	Dyffryn Mymbyr outlet	UK	Cfb	Peat	131	10	36	0.3	13.2	513	M	0.4	24	5
River	1	Eidda above confluence	UK	Cfb	Peat	329	43	16	0.5	7.7	693	M	0.4	41	5
River	1	Glasgwm 1	UK	Cfb	Peat	226	8	37	0.2	27.3	1221	M	1.5	36	5
River	1	Glasgwm at Penmachno	UK	Cfb	Peat	208	17	13	0.3	12.3	655	M	0.5	34	5
River	1	Glasgwm automatic sampler	UK	Cfb	Agr	331	13	37	0.3	26.0	1204	M	7.0	186	5
River	1	Gwahallwy	UK	Cfb	Peat	447	81	24	0.8	5.5	542	M	0.3	25	5
River	1	Gyffylog	UK	Cfb	Peat	198	142	10	0.6	1.4	310	M	0.1	18	5

River	1	Hiraethlyn automatic sampler	UK	Cfb	Peat	567	249	5	2.7	2.3	209	M	0.1	12	5
River	1	Lledr at Pont-Lledr EA25009	UK	Cfb	Peat	206	17	16	0.5	12.0	430	M	0.5	27	5
River	1	Llugwy at Betws	UK	Cfb	Agr	166	18	21	0.3	9.4	536	M	2.1	114	5
River	1	Machno at Roman Bridge EA25010	UK	Cfb	Agr	213	27	0	0.4	7.8	482	M	1.5	107	5
River	1	Merddwr at Pont Newydd EA25013	UK	Cfb	Peat	461	81	21	0.8	5.7	553	M	0.3	37	5
River	1	Nant Cwm Caseg Fraith	UK	Cfb	Peat	198	11	22	0.2	17.7	859	M	0.9	31	5
River	1	Nant Ddu	UK	Cfb	For	73	10	36	0.2	7.3	340	M	0.6	25	5
River	1	Nant-y-Brwyn Upper	UK	Cfb	Peat	116 4	20	74	0.7	59.4	1758	M	5.7	112	5
River	1	Nant-y-Coed	UK	Cfb	Peat	601	68	28	0.8	8.8	734	M	0.5	49	5
River	1	Nant-y-Rhiw-felen	UK	Cfb	Peat	324	172	9	1.8	1.9	178	M	0.1	12	5
River	1	Pennant Lodge	UK	Cfb	Agr	480	320	11	5.5	1.5	87	M	0.3	19	5
River	1	Pont ar Gonwy	UK	Cfb	Peat	816	16	57	0.5	52.0	1628	M	3.8	95	5
River	1	Trebeddau	UK	Cfb	Peat	328	96	16	0.9	3.4	355	M	0.2	25	5
River	1	Trib of Glasgwm 2	UK	Cfb	Peat	252	12	25	0.3	21.9	935	M	1.1	44	5
River	1	Trib of Glasgwm 4	UK	Cfb	Peat	190	8	34	0.3	25.0	751	M	1.4	33	5
River	1	Trib of Llynnau Mymbyr 1	UK	Cfb	Peat	74	11	32	0.3	6.6	223	M	0.2	12	5
River	1	Ysgubor Newydd	UK	Cfb	For	587	102	23	1.3	5.7	467	M	0.7	55	5
River	1	Lambourn, Boxford	UK	Cfb	Agr	117	560	8	4.0	0.2	29	M	0.0	6	14
River	1	Lambourn, E Shefford	UK	Cfb	Agr	114	565	7	1.4	0.2	81	M	0.0	17	14
River	1	Lambourn, Shaw	UK	Cfb	Agr	129	545	8	3.5	0.2	36	M	0.0	7	14
River	1	Pang, Bucklebury	UK	Cfb	Agr	180	631	7	4.3	0.3	41	M	0.1	8	14
River	1	Pang, Frilsham	UK	Cfb	Agr	126	626	7	2.5	0.2	50	M	0.0	10	14
River	1	Pang, Tidmarsh	UK	Cfb	Agr	186	564	8	2.0	0.3	92	M	0.1	19	14
River	1	Dun, Hungerford	UK	Cfb	Agr	136	418	8	1.9	0.3	72	M	0.1	14	14
River	1	Kennet, Clatford	UK	Cfb	Agr	192	621	5	3.3	0.3	59	M	0.1	12	14
River	1	Kennet, Mildenhall	UK	Cfb	Agr	161	579	6	2.8	0.3	58	M	0.1	12	14
River	1	Kennet Hungerford	UK	Cfb	Agr	148	464	6	1.9	0.3	77	M	0.1	15	14
River	1	Kennet, Woolhampton	UK	Cfb	Agr	187	438	7	3.8	0.4	49	M	0.1	10	14

River	1	Kennet, Fobney	UK	Cfb	Agr	240	405	8	2.7	0.6	90	M	0.1	18	14
River	1	River Avon	UK	Cfb	Agr	541	218	11	4.7	2.5	115	M	0.5	24	23
River	1	River Almond	UK	Cfb	Urb	555	424	4	2.8	1.3	199	M	0.2	39	23
River	1	Water of Leith	UK	Cfb	Urb	498	64	28	1.5	7.8	332	M	1.7	67	23
River	1	River Esk (Lothian)	UK	Cfb	Agr	331	97	15	1.8	3.4	183	M	0.7	41	23
River	1	River Tyne	UK	Cfb	Agr	296	253	9	4.8	1.2	62	M	0.2	12	23
River	1	River Devon	UK	Cfb	Agr	250	67	18	3.3	3.7	76	M	0.8	18	23
River	1	Allan Water	UK	Cfb	Agr	386	60	12	2.1	6.5	183	M	1.4	38	23
River	1	River Forth	UK	Cfb	Peat	288	18	0	0.2	16.1	1489	M	0.6	112	23
River	1	River Carron (Falkirk)	UK	Cfb	Agr	395	173	22	5.6	2.3	70	M	0.5	13	23
River	1	River Leven (Fife)	UK	Cfb	Agr	420	77	20	2.1	5.5	198	M	1.2	44	23
River	1	River Forth	UK	Cfb	For	513	60	19	1.4	8.6	376	M	1.0	43	23
River	1	River North Esk (Tayside)	UK	Cfb	Peat	294	108	13	1.1	2.7	274	M	0.1	15	23
River	1	River South Esk (Tayside)	UK	Cfb	Agr	196	130	11	0.8	1.5	236	M	0.3	57	23
River	1	Dighty Water	UK	Cfb	Urb	192	337	1	1.5	0.6	131	M	0.1	28	23
River	1	River Eden	UK	Cfb	Agr	353	489	6	4.4	0.7	80	M	0.1	16	23
River	1	River Tay	UK	Cfb	Peat	322	45	21	0.4	7.2	908	M	0.3	69	23
River	1	River Earn	UK	Cfb	Agr	401	72	19	1.5	5.5	261	M	1.2	55	23
River	1	Eye Water	UK	Cfb	Agr	369	395	0	1.5	0.9	249	M	0.2	58	23
River	1	Whiteadder Water	UK	Cfb	Agr	789	117	0	1.6	6.8	479	M	1.3	117	23
River	1	River Tweed	UK	Cfb	Agr	409	122	8	1.3	3.4	321	M	0.7	74	23
River	1	Urr Water	UK	Cfb	Agr	361	103	23	0.7	3.5	533	M	0.8	121	23
River	1	River Dee (Solway)	UK	Cfb	For	471	39	51	0.4	12.1	1146	M	1.8	145	23
River	1	River Cree	UK	Cfb	For	597	29	77	0.5	20.8	1234	M	4.3	154	23
River	1	Water of Luce	UK	Cfb	Peat	648	33	61	0.7	19.8	873	M	1.5	80	23
River	1	River Esk (Solway)	UK	Cfb	For	445	42	35	1.6	10.6	281	M	1.4	34	23
River	1	River Annan	UK	Cfb	Agr	203	77	21	0.7	2.6	285	M	0.6	67	23
River	1	River Nith	UK	Cfb	Agr	184	79	11	0.7	2.3	272	M	0.5	62	23
River	1	River Clyde	UK	Cfb	Agr	355	273	5	11.4	1.3	31	M	0.3	6	23
River	1	River Clyde	UK	Cfb	Urb	345	151	12	2.1	2.3	165	M	0.4	32	23
River	1	River Clyde	UK	Cfb	Urb	568	172	20	2.9	3.3	195	M	0.7	39	23

River	1	River Kelvin	UK	Cfb	Urb	442	103	17	1.2	4.3	376	M	0.8	90	23
River	1	White Cart Water	UK	Cfb	Urb	461	116	15	1.8	4.0	255	M	0.8	53	23
River	1	Black Cart Water	UK	Cfb	Agr	439	47	36	1.0	9.4	459	M	2.5	108	23
River	1	River Leven (Loch Lomond)	UK	Cfb	Peat	280	52	41	0.8	5.4	343	M	0.3	19	23
River	1	River Garnock	UK	Cfb	Agr	490	54	45	1.2	9.1	407	M	2.7	96	23
River	1	River Garnock	UK	Cfb	Agr	589	84	36	2.2	7.0	262	M	1.9	60	23
River	1	River Irvine	UK	Cfb	Agr	655	85	22	1.8	7.7	374	M	1.8	89	23
River	1	River Irvine	UK	Cfb	Agr	637	113	24	2.0	5.6	324	M	1.3	76	23
River	1	River Irvine	UK	Cfb	Urb	106 4	43	47	1.5	25.0	733	M	6.4	185	23
River	1	River Irvine	UK	Cfb	Agr	481	129	16	1.7	3.7	284	M	0.8	65	23
River	1	River Ayr	UK	Cfb	Agr	387	66	19	1.8	5.9	216	M	1.3	44	23
River	1	River Irvine	UK	Cfb	Agr	327	65	17	1.5	5.1	217	M	1.1	54	23
River	1	River Lochy	UK	Cfb	Peat	227	18	41	0.7	12.4	308	M	0.7	28	23
River	1	River Beauly	UK	Cfb	Peat	321	22	24	0.2	14.7	1461	M	0.7	116	23
River	1	River Carron (Wester Ross)	UK	Cfb	Peat	215	21	34	0.3	10.0	814	M	0.5	53	23
River	1	River Findhorn	UK	Cfb	Peat	717	26	56	0.6	28.0	1202	M	2.0	76	23
River	1	River Nairn	UK	Cfb	Peat	723	117	13	0.6	6.2	1180	M	0.3	99	23
River	1	River Ness	UK	Cfb	Peat	365	32	27	0.3	11.3	1150	M	0.6	84	23
River	1	River Conon	UK	Cfb	Peat	372	20	33	0.2	19.0	1591	M	1.0	118	23
River	1	River Shin	UK	Cfb	Peat	501	20	43	0.3	25.4	1554	M	1.5	131	23
River	1	Wick River	UK	Cfb	Peat	109 4	44	69	0.9	24.6	1211	M	2.2	79	23
River	1	River Thurso	UK	Cfb	Peat	739	29	54	0.7	25.7	1079	M	1.8	93	23
River	1	River Spey	UK	Cfb	Peat	276	34	39	1.0	8.2	285	M	0.5	23	23
River	1	River Lossie	UK	Cfb	For	443	173	8	3.1	2.6	145	M	0.3	18	23
River	1	River Dee (Grampian)	UK	Cfb	Agr	545	151	14	2.9	3.6	189	M	0.8	42	23
River	1	River Dee (Grampian)	UK	Cfb	Peat	317	39	12	1.1	8.2	279	M	0.4	21	23
River	1	River Dee (Grampian)	UK	Cfb	Peat	349	40	44	4.1	8.8	86	M	0.5	4	23
River	1	River Don	UK	Cfb	Agr	224	221	1	2.1	1.0	104	M	0.2	24	23
River	1	River Ythan	UK	Cfb	Agr	235	475	2	2.7	0.5	86	M	0.1	22	23

River	1	River Ugie	UK	Cfb	Agr	426	284	17	2.9	1.5	145	M	0.3	32	23
River	1	River Ugie	UK	Cfb	Agr	250	425	2	3.2	0.6	78	M	0.1	19	23
River	1	River Ugie	UK	Cfb	Agr	312	411	14	2.3	0.8	136	M	0.2	31	23
River	1	River Deveron	UK	Cfb	Agr	282	179	0	1.5	1.6	194	M	0.3	46	23
River	1	River Dee (Grampian)	UK	Cfb	Peat	348	24	54	0.9	14.7	399	M	1.0	33	23
River	1	River Irvine	UK	Cfb	Agr	971	37	54	1.3	26.1	762	M	8.5	190	23
River	1	Vargstugbäcken	Sw	Dfb	Peat	2333	29	93	0.4	79.7	6028	M	11.9	408	2
River	1	Stortjäcken outlet	Sw	Dfb	For	1833	26	96	0.4	71.3	4736	M	19.9	568	2
River	1	Kallkällsmyren	Sw	Dfb	For	2833	34	94	0.4	82.6	7319	M	22.5	878	2
River	1	Stormyrbäcken	Sw	Dfb	For	1917	26	96	0.4	72.5	4571	M	20.2	540	2
River	1	Övre Krycklan	Sw	Dfb	For	1167	21	96	0.5	54.4	2583	M	15.2	329	2
River	1	Kallkällsbäcken	Sw	Dfb	For	2250	31	96	0.6	73.3	3875	M	20.4	450	2
River	1	Langbäcken	Sw	Dfb	For	1500	24	97	0.8	63.6	1938	M	18.2	251	2
River	1	Risbäcken	Sw	Dfb	For	1917	30	94	0.4	63.9	4571	M	17.2	566	2
River	1	Västrabäcken	Sw	Dfb	For	1583	23	96	0.4	69.3	4462	M	19.5	561	2
River	1	Perhonjoki	F	Dfb	For	1280	51	73	0.9	25.1	1470	Ob, NP	4.7	182	18
River	1	Siikajoki	F	Dfb	For	1320	55	60	1.0	24.0	1376	Ob, NP	4.0	159	18
River	1	Oulujoki	F	Dfb	For	680	22	82	0.3	30.9	2656	Ob, NP	7.6	315	18
River	1	Iijoki	F	Dfb	For	680	34	94	0.4	20.0	1627	Ob, NP	5.4	197	18
River	1	Simojoki	F	Dfb	For	1560	51	84	0.4	30.6	4088	Ob, NP	7.0	503	18
River	1	Kalixälven	Sw	Dfb	For	430	14	79	0.2	30.7	2172	Ob, NP	6.5	274	18
River	1	Alterälven	Sw	Dfb	For	1020	25	92	0.4	40.8	2423	Ob, NP	10.6	300	18
River	1	Vantaanjoki River	F	Dfb	Peat	752	24	80	0.4	31.6	1928	Ob, CN	3.4	131	1
River	1	Vantaanjoki River	F	Dfb	Peat	624	25	75	0.3	24.6	2311	Ob, CN	2.4	151	1
River	1	Vantaanjoki River	F	Dfb	For	742	58	28	0.7	12.9	1003	Ob, CN	1.6	109	1

River	1	Vantaanjoki River	F	Dfb	Peat	1562	61	58	0.6	25.8	2647	Ob, CN	1.9	171	1
River	1	Vantaanjoki River	F	Dfb	Peat	1178	70	23	0.5	16.8	2356	Ob, CN	0.8	145	1
River	1	Vantaanjoki River	F	Dfb	For	880	58	43	1.1	15.3	800	Ob, CN	2.1	87	1
River	1	Vantaanjoki River	F	Dfb	Peat	2316	69	65	1.3	33.5	1853	Ob, CN	2.8	95	1
River	1	Vantaanjoki River	F	Dfb	Peat	1634	76	47	0.8	21.5	2068	Ob, CN	1.4	126	1
River	1	Vantaanjoki River	F	Dfb	Peat	1847	88	42	1.2	20.9	1579	Ob, CN	1.2	86	1
River	1	Vantaanjoki River	F	Dfb	For	5517	194	68	6.7	28.5	821	Ob, CN	5.2	87	1
River	1	Vantaanjoki River	F	Dfb	Peat	890	65	40	1.1	13.8	817	Ob, CN	0.8	41	1
River	1	Vantaanjoki River	F	Dfb	Peat	971	69	25	0.9	14.1	1103	Ob, CN	0.7	61	1
River	1	Concepcion	P	Af	For	662	31	87	0.5	21.1	1207	Ob, C	5.3	157	3
River	1	Abejitas	P	Af	Agr	222	11	69	0.5	19.4	458	Ob, C	6.6	104	3
River	1	Tambopata	P	Af	For	68	21	27	0.5	3.3	125	Ob, C	1.0	36	3
River	1	Capitão Anselmo	B	Aw	Agr	116	23	56	1.6	5.0	74	M	1.7	19	11
River	1	Carandaí	B	Aw	Agr	148	25	45	1.8	6.0	82	M	1.8	20	11
River	1	Mexerica	B	Aw	Agr	118	16	60	1.8	7.3	67	M	2.6	17	11
River	1	Nelson	B	Aw	Agr	61	15	71	1.6	4.0	38	M	1.7	9	11
River	1	São Caetano	B	Aw	Agr	166	39	35	2.4	4.2	68	M	1.1	17	11
River	1	Aguas Santas	B	Aw	For	72	9	72	1.1	8.3	64	M	1.6	8	11
River	1	Arenoso	B	Aw	For	361	21	79	1.4	17.3	267	M	3.7	35	11
River	1	Complexo Cafezinho	B	Aw	For	104	10	55	1.5	10.5	72	M	1.7	8	11
River	1	Correias	B	Aw	For	111	13	69	2.6	8.8	43	M	1.6	5	11
River	1	Mangue	B	Aw	For	247	11	43	1.1	22.8	219	M	3.2	26	11
River	1	Alves Melo	B	Aw	Agr	59	13	58	1.2	4.6	48	M	1.6	11	11
River	1	Capoeirinha	B	Aw	Agr	50	16	68	2.2	3.1	23	M	1.2	5	11
River	1	Darcy	B	Aw	Agr	77	20	58	1.7	4.0	44	M	1.4	10	11
River	1	Oficina de Agosto	B	Aw	Agr	70	13	54	1.6	5.3	44	M	1.7	10	11
River	1	Sossego	B	Aw	Agr	59	13	43	1.9	4.6	31	M	1.3	7	11
River	1	C. Palmital	B	Aw	Urb	828	139	83	2.4	5.9	351	M	2.5	86	11
River	1	C. Santo Antonio	B	Aw	Urb	945	220	68	2.4	4.3	391	M	1.4	84	11

River	1	Cel. Xavier Chaves	B	Aw	Urb	1219	295	76	1.9	4.1	641	M	1.5	163	11
River	1	Prados	B	Aw	Urb	1058	336	64	2.9	3.1	369	M	1.0	83	11
River	1	Ritápolis	B	Aw	Urb	927	213	70	2.8	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.

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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	n	BDOC		BDOP				Incubation time	Temperature	Methods	Ref	
(a) Dark only incubations														
(i) Groundwaters														
Gw	US	nd	14; 1	5						nd	20	b, f, h, p	Cfa	26
Gw	US	nd	8; 1	15						nd	20	b, f, h, p	Cfa	26
Gw	US	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								
(ii) Lakes														
L	Au	Agr	2; nd	18	(15-21)					28	20	a, f, h, p	Cfa	6
L	Au	Agr	3; nd	16	(5-27)					28	20	a, f, h, p	Cfa	6
L	US	For,Wet	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)								
(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	1; 1	10	(3-18)					1	20	c, f, n, r	Cfb	39
Le	Cz	For	1; 3	17	(1					42	20	a, f, i/l, p	Cfb	41

					3-23)									
Le	US	For	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								
(iv) Rivers; agricultural														
R	F	For(39),Agr(50)	1; 1	4						30	3	a, f, i, p	Dfb	4
R	F	For(39),Agr(50)	1; 1	13		68				30	15	a, f, k, p	Dfb	4
R	F	For(42),Agr(43)	1; 2	5		48				30	15	a, f, k, p	Dfb	4
R	F	For(39),Agr(49)	1; 6	0		20				30	15	a, f, k, p	Dfb	4
R	Au	Agr(90), Ur(10)	1; nd	39						28	20	a, f, h, p	Cfa	6
R	Au	Agr, Urb	5; nd	24	(9-38)					28	20	a, f, h, p	Cfa	6
R	US	For(23),Agr (74)	1; 1	26						0.05	20	b, f, j, p	Cfa	8
R	US	For(23),Agr (74)	1; 1	31						0.05	20	b, f, j, p	Cfa	8
R	Br	Agr, For	1; 2	31						10	20	a, f, h, p	Cfa	18
R	US	For(23),Agr (74)	1; 12	13	(2-37)					1.2	20	b, f, h, p	Cfa	26
R	Au	For(27),Agr(85),Urb(6)	1; 1	3		20				14	25	a, f, j, p	Csa	29
R	Au	For(22),Agr(67),Urb(25)	1; 1	13		44				14	25	a, f, j, p	Csa	29
R	US	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)	1; 1	3		1				6	25	a, f, j, p	Cfa	46
R	US	For(26),Agr(55),Wet(14),Ur(2)	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)								
(v) Rivers; forested														
R	Br	For(100)	1; 1	12						4	25	a, f, j, p	Af	1
R	Br	For(100)	1; 1	12						3	25	a, f, j, p	Af	1
R	F	For(46),Agr(19),Wet(3),Ur(10)	1; 4	11		10				18	4-18a	a, f, h, p	Dfb	3
R	F	For(36),Agr(25),Wet(19),Ur(5)	1; 4	9		22				18	4-18a	a, f, h, p	Dfc	3
R	F	For(89),Agr(0)	1; 1	4						30	3	a, f, i, p	Dfb	4

R	F	For(71),Agr(4)	1; 1	11						30	3	a, f, i, p	Dfb	4
R	F	For(67),Agr(13)	1; 1	4						30	3	a, f, i, p	Dfb	4
R	F	For(55),Agr(23)	1; 1	9						30	3	a, f, i, p	Dfb	4
R	F	For(47),Agr(23)	1; 1	5						30	3	a, f, i, p	Dfb	4
R	F	For(62),Agr(17)	1; 1	3						30	3	a, f, i, p	Dfb	4
R	F	For(89),Agr(0)	1; 1	12		17				30	15	a, f, k, p	Dfb	4
R	F	For(71),Agr(4)	1; 1	3		23				30	15	a, f, k, p	Dfb	4
R	F	For(67),Agr(13)	1; 1	6		23				30	15	a, f, k, p	Dfb	4
R	F	For(55),Agr(23)	1; 1	8		89				30	15	a, f, k, p	Dfb	4
R	F	For(74),Agr(8)	1; 3	7		18				30	15	a, f, k, p	Dfb	4
R	F	For(60),Agr(19)	1; 4	2		29				30	15	a, f, k, p	Dfb	4
R	F	For(51),Agr(18)	1; 5	2		46				30	15	a, f, k, p	Dfb	4
R	F	For(39),Agr(31)	1; 7	8		61				30	15	a, f, k, p	Dfb	4
R	F	For(46),Agr(35)	1; 8	8		92				30	15	a, f, k, p	Dfb	4
R	US	For(100)	1;9	15						40	25	a, f, h, p	Dfc	5
R	US	For(100)	1;9	5						40	25	a, f, h, p	Dfc	5
R	US	For(100)	1;9	35						40	25	a, f, h, p	Dfc	5
R	US	For(100)	1;9	15						40	25	a, f, h, p	Dfc	5
R	Sw	For(39-100),Wet	9; nd	4.4	(4-8)					11	20	a, f, h, q, r	Dfc	7
R	A	For, Peat	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; 12	7		12				30	20	a, f, h, p	Dfb	16
R	US	For(96), Wet(4)	1; 12	18		43				30	20	a, f, h, p	Dfb	16
R	US	For(96), Wet(4)	1; 12	17		42				30	20	a, f, h, p	Dfb	16
R	US	For(100)	1;9	15	(0-32)	37	(20-70)			14	10	a, f, i, p	Dfc	17
R	US	For(100)	1;9	14	(0-3	37	(5-60)			14	10	a, f, i, p	Dfc	17

					8)									
R	Ja	For, Agr, Urb	2; 2-8	31	(29-33)					45	20	a, f, h, p	Cfa	19
R	US	For	113; 3		(0-10)					13	12	a, f, j, p	Dfb	27
R	Au	For(84),Agr(10), Urb(6)	1; 1	1		4				14	25	a, f, j, p	Csa	29
R	Ch	For, Wet	8; nd	21	(15-30)	45	(29-57)			55	20	a, f, i, p	Dwb-Dfb	35
R	Sw, F	nd	13; 1			32	(8-72)			14	18-25a	a, f, j, p	Dfb-Dfc	36
R	Sw, F	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)	1; 6			36	(19-55)			14	20	a, f, k, p	Dfc	37
R	US	For, Upl	1; 6	20	(6-51)					28	15	a, f, j, r	ET	44
R	US	For, Wet	1; 6	15	(3-35)					28	15	a, f, j, r	ET	44
R	US	For, Wet	1; 5	17	(5-43)					28	15	a, f, j, r	ET	44
R	US	For(62), Wet(~20)	1; 16	22	(7-53)					28	15	a, f, j, r	Dfc	44
R	US	For(100)	1; 1	5		40				6	25	a, f, j, p	Cfa	46
R	US	For(83),Agr(0),Wet(0),Ur(2)	1; 1	1		1				6	25	a, f, j, p	Cfa	46
R	US	For(75),Agr(17),Wet(3),Ur(3)	1; 1	16		19				6	25	a, f, j, p	Cfa	46
R	US	For(64),Agr(20),Wet(0),Ur(6)	1; 1	7		33				6	25	a, f, j, p	Cfa	46
R	US	For(64),Agr(26),Wet(5),Ur(3)	1; 1	1		12				6	25	a, f, j, p	Cfa	46
R	US	For(52),Agr(25),Wet(0),Ur(5)	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)								

(vi) Rivers; peatland														
R	F	For(40),Agr(2),Peat(40),Ur(2)	1; 4	8		5				18	4-18a	a, f, h, p	Dfc	3
R	Si	Peat, For	15; 1	3	(1-6)					5	15	a, f, h, r	Dfc	13
R	Si	Peat, For	14; 1	5	(1-14)					5	15	a, f, h, r	Dfc	13
R	Si	Peat, For	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)	1; 6			37	(28-45)			14	20	a, f, k, p	Dfc	37
R	UK	Upl(100)	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)								
(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	2; 2	38						10	20	a, f, h, p	Cfa	18
R	Ja	Urb, For, Agr	7; 2-8	23	(3-31)					45	20	a, f, h, p	Cfa	19
R	Au	For(18),Agr(10),Urb(64)	1; 1	9		21				14	25	a, f, j, p	Csa	29
R	Au	For(32),Agr(18),Urb(36)	1; 1	17		23				14	25	a, f, j, p	Csa	29
R	Au	For(26),Agr(53),Urb(42)	1; 1	8		25				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(100)	1; 1	17		35				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(86),Agr(13)	1; 1	16		37				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(100)	1; 1	16		27				14	25	a, f, j, p	Csa	29
Ur	Au	Urb(98), Agr(3)	1; 1	7		46				14	25	a, f, j, p	Csa	29
R	US	For(19),Agr(10),Wet(0),Ur33)	1; 1	2		12				6	25	a, f, j, p	Cfa	46
Weighted means ±1 s.e. (n, spatial samples (n, studies))				17.1 ±2.3; n=18 (5)		28.8 ±1.9; n=6 (2)								
(viii) Soil water; agricultural														
S,r	NZ	Agr (P)	12; 1	38		100				49	20	a, f, n, p, r	Cfb	14

S,r	NZ	Agr (P)	12; 1	45		100				49	20	a, f, n, p, r	Cfb	14
S,r	NZ	Agr (P)	12; 1	58		100				49	20	a, f, n, p, r	Cfb	14
S,we	NZ	Agr (P)	12; 1	43		100				36	20	a, f, n, p, r	Cfb	14
S,we	NZ	Agr (P)	12; 1	39		100				36	20	a, f, n, p, r	Cfb	14
S,r	NZ	Agr (P)	1; 5					15	(8-20)	nd	37	a, f, o, p	Cfb	24
S,we	NZ	Agr (P)	9; 1					57	(15-85)	nd	37	a, f, o, p	Cfb	24
S,we	NZ	Agr (C)	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)	23; 1	10						nd	20	b, f, h, p	Cfa	26
S,we	UK	Agr (P)	1; 1	11	(0-15)					1	21	c, f, n, r	Cfb	39
Weighted means ±1 s.e. (n, spatial samples (n, studies))				34.9 ±0.9; n=86 (4)		nd								
(ix) Soil water; forested														
S,r	Sw	For	2; 16	30						21	20	a, f, i, p	Cfb	2
S,r	Sw	For	2; 16	10						21	20	a, f, i, p	Cfb	2
S,we	Sw	For	10; 1	39						21	20	a, f, i, p	Cfb	2
S,r	Sw	For	2; nd	9						11	20	a, f, h, q, r	Dfc	7
S,we	US	For	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	1; 1	3	(0-7)					1	20	c, f, n, r	Cfb	39
Weighted means ±1 s.e. (n, spatial samples (n, studies))				22.4 ±3.4; n=22 (5)		nd								
(x) Soil water; peatland														
S,r	Sw	Upland	2; nd	4						11	20	a, f, h, q, r	Dfc	7
S,we	Si	Peat	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								

(xi) Sewage effluent														
Se,t	Po	Ur	1; 5	35	(28-39)					21	20	a, f, p, s	Cfb	9
Se,t	Po	Ur	1; 5	24	(9-30)					21	20	a, f, p, s	Cfb	9
Se,r	Ja	Ur	5; 2-8	12	(3-16)					45	20	a, f, h, p	Cfa	19
Se,t	Fr	Ur	1; nd	74	(70-77)					45	20	a, f, h, p	Cfb	33
Se,t	Fr	Ur	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								
(xii) Lowland wetlands														
We	Au	For,Wet	7; nd	30	(23-40)					28	20	a, f, h, p	Cfa	6
We	US	Wet(100)	3; 8	32						30	26	a, g, i, p	Dfc	12
We	US	For(50),Wet(50)	3; 8	23						30	26	a, g, i, p	Dfc	12
We	US	Wet(100)	3; 8	42						30	26	a, g, i, p	Dfc	12
We	US	Wet(100)	5; 1	45	(24-69)					4	26	a, g, i, p	Cfa	23
We	Ja	Wet(100)	2; 1	18	(16-20)					nd	nd	a, g, i, p	Dfb	31
We	Sw	Wet,For	1 ;9			4	(2-6)			28	25	a, f, i, p	Cfb	38
We	US	Wet(19),Agr(1),For(80),Urb(0.1)	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)	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)	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)	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)								
(b) Light, or light:dark incubations (not included in statistical evaluation)														
R	US	For(3),Agr(28),Wet(12),Ur(28)	1; 1			7				5	nd	a, g, j, p	Cfa	22
R	Be	nd	14; 1							13	21	a, g, m, q	Cfb	42
R	US	For	1; 3			34	(28-44)			12	10-27a	a, g, k, p	Cfa	32
R	US	For	1; 3			23	(8-44)			12	10-27a	a, g, k, p	Cfa	32
R	US	For	1; 3			16	(0-34)			12	10-27a	a, g, k, p	Cfa	32
R	F	Agr(22-43)	12; 1					1		21	20	d, e, m, p	Dfb	10
R	F	nd	12; 1					36	(7-55)	21	20	d, e, m, p	Dfb	10
Ur	US	For(2),Agr(3),Ur(83)	1; 1			5				5	nd	a, g, j, p	Cfa	22
Ur	US	Ur	1; nd			10				5	nd	a, g, j, p	Cfa	21
Ur	US	Ur	1; nd			39				5	nd	a, g, j, p	Cfa	21
Ur	US	Ur(100)	1; 3			59	(42-73)			12	10-27a	a, g, k, p	Cfa	32
Ur	US	Ur(100)	1; 3							12	10-27a	a, g, k, p	Cfa	32
Ur	US	Ur(100)	1; 3							12	10-27a	a, g, k, p	Cfa	32
S,r	F	Agr (P)	11; 1					1		21	20	d, e, m, p	Dfb	10
S,r	F	For	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	5; nd					1	(0-0)	nd	24	a, e, m, q	Aw, Cfa,	20

													Dwc	
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.

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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: Agric	Urban	Forest	Wetland	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
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

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