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# Balancing macronutrient stoichiometry to alleviate eutrophication

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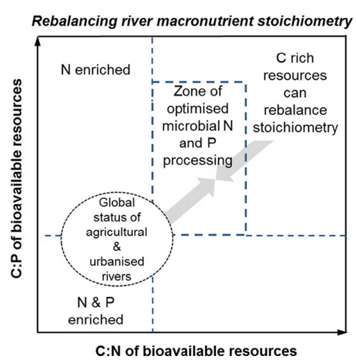
## HIGHLIGHTS

- Eutrophication assessment should examine balances of the macronutrients C, N and P.
- C:N and C:P stoichiometry was assessed in global catchment sources and river waters.
- Excesses of NP relative to organic C was associated with agriculture and urbanisation.
- Restoration of catchment C sources (e.g. wetlands) may drive microbial NP sequestration.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Reactive nitrogen (N) and phosphorus (P) inputs to surface waters modify aquatic environments, affect public health and recreation. Source controls dominate eutrophication management, whilst 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. Heterotrophic 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. We propose that the capability of streams and rivers to retain N and P may be improved by active stoichiometric rebalancing. Although autotrophic OC production contributes to heterotrophic rates substantial control on nutrient processing from allochthonous OC is documented for N and an emerging field for P. Hence, rebalancing should be done by reconnecting appropriate OC sources such as wetlands and riparian forests that have become disconnected from rivers concurrent with agriculture and urbanisation. However, key knowledge gaps require research prior to the safe implementation of this approach in management: (i) to evaluate system responses to catchment inputs of dissolved OC forms and amounts relative to internal production of autotrophic dissolved OC and aquatic and terrestrial particulate OC and (ii) evaluate risk factors in anoxia-mediated P desorption with elevated OC scenarios. Still, we find stoichiometric rebalancing through reconnecting landscape beneficial OC sources has

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considerable potential for river management to alleviate eutrophication, improve water quality and aquatic ecosystem health, if augmenting nutrient source control.



## 1. Introduction

Nutrient pollution is a primary cause of degraded water quality (Rockström et al., 2009; Dodds et al., 2009; Strokal 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 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. A large meta-analysis by Taylor and Townsend (2010) documented strong and consistent links between nitrate concentrations and OC and in freshwaters across scales and biomes that implicated controls by heterotrophic aquatic microbes. In fact, significant inorganic nutrient recycling and cumulative uptake through headwater streams to downstream river reaches has been widely reported (Mulholland, 2004; Mulholland et al., 2008; Ensign and Doyle, 2006; Rode et al., 2016), although the body of evidence is much stronger for N than for P. 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; Tanentzap et al., 2014). Meta-analysis by Taylor and Townsend (2010) strongly evidenced that heterotrophic microbes maintained low stream nitrate concentrations when $OC:NO_3$ ratios matched stoichiometric demands of microbial anabolism. 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).

The sources of aquatic OC are diverse. Heterotrophic microbial rates may be influenced by internal autotrophically-produced and catchment-derived OC. Studies suggest that both gross primary productivity (GPP; indicative of algal OC production) and DOC delivery exert controls on the microbial metabolism indicator of ecosystem respiration (Bernot et al., 2010; Fuß et al., 2017); with GPP influenced by N, P and light amongst other factors. However, Dodds (2007) suggested that allochthonous OC has the greatest impact on heterotrophic state in rivers. Our premise here is that, despite internal autotrophic OC sources, additional allochthonous OC benefits microbial nutrient processing when stoichiometric demands are met.

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 heterotrophic 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 "beneficial" OC, as agriculture and urbanisation intensifies. In this we aim to make connections between increases in N, P and changes in the nature, and role, of OC sources with landscape change. This recognises appropriate forms of allochthonous OC relative to highly labile effluent or autotrophic OC pulses that would likely cause side effects of oxygen depletion. Furthermore, we consider not only total or inorganic N, P 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 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.