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Phosphorus and nitrogen limitation and impairment of headwater streams relative to rivers in Great Britain: A national perspective on eutrophication

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HIGHLIGHTS

- National-scale assessment of headwater stream nutrient status, relative to rivers
- Greater potential for P limitation in rivers and N limitation in headwater streams
- Greater potential for P and N co-limitation in headwater streams than rivers
- Nutrient impairment of water quality was greatest in Lowland-High-Alkalinity rivers.
- Nutrient Limitation Assessment could help inform the prioritisation of remediation.

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ABSTRACT

This study provides a first national-scale assessment of the nutrient status of British headwater streams within the wider river network, by joint analysis of the national Countryside Survey Headwater Stream and Harmonised River Monitoring Scheme datasets. We apply a novel Nutrient Limitation Assessment methodology to explore the extent to which nutrients may potentially limit primary production in headwater streams and rivers, by coupling ternary assessment of nitrogen (N), phosphorus (P), and carbon (C) depletion, with N:P stoichiometry, and threshold P and N concentrations. P limitation was more commonly seen in the rivers, with greater prevalence of N limitation in the headwater streams. High levels of potential P and N co-limitation were found in the headwater streams, especially the Upland-Low-Alkalinity streams. This suggests that managing both P and N inputs may be needed to minimise risks of degradation of these sensitive headwater stream environments. Although localised nutrient impairment of headwater streams can occur, there were markedly lower rates of P and N impairment of headwater streams relative to downstream rivers at the national scale. Nutrient source contributions, relative to hydrological dilution, increased with catchment scale, corresponding with increases in the extent of agricultural and urban land-use. The estimated nutrient reductions needed to achieve compliance with Water Framework Directive standards, and to reach limiting concentrations, were greatest for the Lowland-High-Alkalinity rivers and streams. Preliminary assessments suggest that reducing P concentrations in the Lowland-High-Alkalinity headwater streams, and N concentrations in the Upland-Low-Alkalinity rivers, might offer greater overall benefits for water-quality remediation at the national scale, relative to the magnitude of nutrient reductions required. This approach could help inform the prioritisation of nutrient remediation, as part of a directional approach to water quality management based on closing the gaps between current and target nutrient concentrations.

1. Introduction

The macronutrients phosphorus (P), nitrogen (N) and carbon (C), along with light energy, underpin primary productivity, and are fundamental to sustaining freshwater ecosystems. There is growing interest

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in the coupled cycling of P, N and C in catchments; the limits imposed by varying availability of these three macronutrients on aquatic primary production; and how anthropogenic disturbance to these cycles and eutrophication impair river water quality and ecology (Crossman, 2016; Dupas et al., 2017; Jarvie et al., 2012a). Eutrophication is a global cause of water quality impairment, whereby excess nutrients promote the growth of nuisance phytoplankton (algal blooms) and macrophytes, and the associated loss of desirable plant and animal species (Smith, 2003). The main effects are on the ecological health of water bodies and water quality, however eutrophication can have wider societal impacts, including on the abstraction and treatment of drinking water, angling and fisheries, wildlife conservation and tourism. Eutrophication has been recognised as a significant environmental issue in Great Britain and across Europe since the late 1980s, and continues to present a long-term challenge for sustainable nutrient management (European Environment Agency, 2010; Leaf, 2017).

It is widely recognised that headwater streams (typically with Strahler order ≤3; and catchment area ≤10 km^2) play a key role in the biogeochemical connectivity between terrestrial and aquatic ecosystems, and control the routing and supply of macronutrients to the downstream river network (Alexander et al., 2007; Withers and Jarvie, 2008). Headwater streams account for >70% of the 389,000 km of streams and rivers in Britain (Smith and Lyle, 1979; UK National Ecosystem Assessment, 2011). It is increasingly recognised that headwater streams are critical for freshwater biodiversity and play a key role in ecosystem service delivery (Biggs et al., 2017; Kelly-Quinn et al., 2017), and that they contribute cumulatively and often disproportionately to downstream water quality and to the wider functional integrity of downstream aquatic ecosystems (Alexander et al., 2007; Nadeau and Rains, 2007; Neal et al., 2012; Triska et al., 2007). However, their large contributing drainage areas relative to water-body size and low dilution capacity also mean that headwater streams can be highly vulnerable to water–quality impairment (Dupas et al., 2015; Jarvie et al., 2010; Jarvie et al., 2008b; Withers et al., 2011). Despite this, compared with larger rivers, there is a relative paucity of large-scale strategic monitoring of headwater streams by national agencies, and they are largely excluded from water quality management planning, as there is no statutory obligation for monitoring headwater streams (Biggs et al., 2017; Lassaletta et al., 2010).

Here, we present and apply a novel Nutrient Limitation Assessment (NLA) methodology which couples ternary assessment of N, P and C depletion, with N:P stoichiometry, and threshold P and N concentrations. Using NLA we provided a first assessment of the nutrient status of British headwater streams at the national scale, relative to downstream larger rivers, by joint analysis of two national datasets: the Countryside Survey Headwater Stream and Harmonised River Monitoring Scheme water-quality datasets. We compared P, N and C concentrations and stoichiometry for headwater streams with larger rivers, for the major British catchment typologies, and evaluated compliance with European Union Water Framework Directive (WFD) nutrient criteria. We then evaluated the extent to which nutrient concentrations in headwater streams and rivers may limit eutrophication or impair water quality. This study is innovative in three key ways: (1) it presents a new framework for evaluating nutrient limitation and impairment in water bodies; (2) it provides a first national-scale assessment of the extent to which nutrient limitation of primary production and nutrient impairment occur in headwater streams, relative to larger rivers; (3) it quantifies the extent of reductions in nutrient concentrations which may be needed to curb eutrophication, and to achieve improvements in water quality of headwater streams, relative to larger rivers, according to catchment typology.

2. Methods

2.1. Headwater stream and river datasets

The Countryside Survey headwater stream and Harmonised River Monitoring datasets cover an extensive and representative range of streams and rivers across Great Britain (Fig. 1), along the continuum from headwater streams with catchments of less than 1 km^2 to the tidal limit of large river basins of several thousand km^2 (Table 1).

The Centre for Ecology & Hydrology's Countryside Survey (CS) is a sample-based study which assesses the state and change in the U.K. rural environment (Norton et al., 2012). 'Snapshot' spatial surveys of headwater stream chemistry were undertaken as part of the CS in 1990, 1998 and 2007, with sampling carried out from May to September (Dunbar et al., 2010). In this study, we used the 2007 CS stream chemistry dataset which, for the first time, analysed water samples for total oxidised nitrogen (TON), as well as reactive phosphorus (RP), and pH and alkalinity, which were used to calculate the dissolved inorganic carbon concentrations (DIC) using the THINCARB model (Jarvie et al., 2017). Details of the water quality measurements are provided in the Supplementary material S1. These measurements allowed an assessment of the dominant dissolved inorganic P, N and C fractions in headwater streams at the national scale. The CS covers 591 1 km × 1 km sample squares, which comprise a stratified random sample of England, Scotland and Wales (N.B. the CS does not cover Northern Ireland; see Norton et al., 2012). As a 'countryside' survey the CS does not include 1 km squares containing >75% of developed land or >90% of sea, but covers all other habitats found in Great Britain. For each CS square, where present, a single headwater stream site is surveyed, following a standard protocol which is detailed in Murphy and Weatherby (2008). Around 60% of the 591 squares surveyed in 2007 contained at least one linear water feature, which are defined here as "headwater streams". A total of 349 headwater streams were sampled in 2007, with a single water chemistry sample taken from each stream (Table 1).

The Environment Agency's Harmonised Monitoring Scheme (HMS) is a national-scale initiative to measure water quality in the major rivers draining to coastal areas in Great Britain (https://data.gov.uk/dataset/historic-uk-water-quality-sampling-harmonised-monitoring-scheme-summary-data). The monitoring scheme is designed to provide comprehensive spatial coverage of British rivers, from upland to lowland, rural and agricultural, to urban, and across the range of hydrogeological settings (Earl et al., 2014; Jarvie et al., 2017). In this study, the 2007 HMS river chemistry data were extracted for direct comparison with the 2007 CS headwater stream data (Table 1). In 2007, there were 249 HMS river monitoring sites and 2941 samples where data were available for RP, TON and pH and alkalinity for calculation of DIC, i.e., c.12 samples per site, typically collected at monthly intervals. For each of the HMS river monitoring sites, information on catchment areas, elevation, hydrogeology, and land use were extracted from the UK National River Flow Archive (NRFA) datasets (http://nrfa.ceh.ac.uk) (Jarvie et al., 2017).

Further details and evaluation of the nutrient measurements and sampling undertaken for the CS and HMS surveys are provided in the Supplementary material S1.

2.1.1. Assessment of the representativeness the 2007 CS headwater stream survey

HMS rivers were sampled on a monthly basis during 2007, whereas the CS headwater streams were sampled on one occasion during 2007 as a "snapshot" survey, during the summer (between May and September). To explore how representative this snapshot survey in 2007 might be, a comparison was undertaken between the CS headwater stream data in 2007 and the same sites which were surveyed in 1998 using relative cumulative frequency distributions (Supplementary material Fig. S1). There was a strong coherence between the CS RP measurements in 1998 and 2007, indicating high reproducibility in results for both single-sample 'snapshot' surveys and that, overall, there has been little change in headwater stream RP concentrations over this time frame (note that TON was not measured in 1998, so an equivalent comparison between 2007 and 1998 cannot be made for TON).

2.1.2. Comparability of CS headwater stream and HMS river datasets

There was negligible difference between the RP and TON concentrations for HMS 2007 river samples collected between May and September

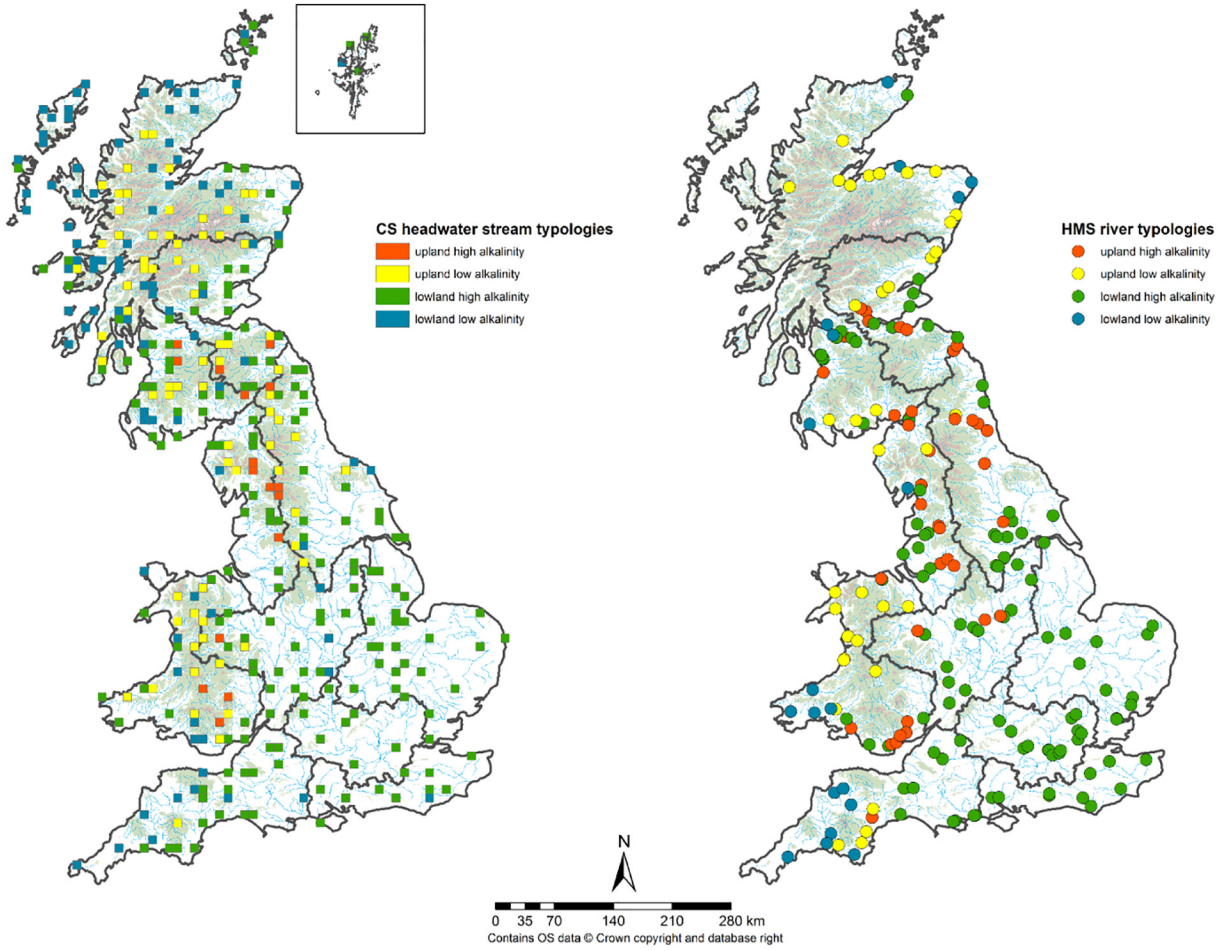


Fig. 1. Maps showing the distribution of the Countryside Survey squares containing headwater sampling streams, and the Harmonised River Monitoring Scheme sampling sites across Great Britain. Both the river and headwater stream sites are colour-coded according to their catchment typology.

(the period of the CS surveys) compared with the corresponding RP and TON concentrations for the full 2007 river dataset, with samples collected from January to December 2007 (Supplementary material Fig. S1). Therefore, for this study, the CS 2007 headwater stream data were compared with the full HMS 2007 rivers dataset. Moreover, the CS 2007 headwater stream RP and TON concentrations in 2007 were also markedly lower than the corresponding HMS 2007 river RP and TON concentrations, as shown by the divergence in the cumulative frequency curves (Supplementary material Fig. S1). The magnitude by which the HMS river RP and TON concentrations exceeded the CS headwater stream RP and TON concentrations (Fig. S1) exceeded the potential differences which could be attributed to differences in measurement methodologies between the CS and HMS surveys (see Supplementary Material S1).

2.1.3. Compliance with Water Framework Directive phosphorus standards

To assess compliance with WFD P standards, the measured CS headwater stream RP concentrations and the annual average HMS river RP concentrations were compared with the RP concentrations delineating "Good" P status for the EU WFD (UKTAG, 2013 see Supplementary material S2).

2.1.4. Typological Classification of headwater streams and rivers

A condition of use of the CS data is that the exact locations of the CS squares, and the headwater streams sampled therein, remain confidential, to protect the landowners who allow access for the survey, and to preserve the representativeness of sampling sites. Therefore, while land use and characteristics of the headwater catchments are available, and we know the typology and general location of the CS headwater streams, it was not possible to link the drainage of individual CS headwater streams into specific HMS rivers. Therefore, comparisons between headwater streams and rivers was based on established U.K. catchment typologies (UKTAG, 2003; see Supplementary material S3). The headwater streams and river catchments were classified according to typology, based on the altitude of the catchment and the river or

Table 1
Summary of the headwater stream and rivers datasets, showing the number of sampling sites, number of samples collected, and catchment area statistics.

Water body type	No. sites	No. samples	Catchment area (km^2)			
			Mean (SD)	Median	Min	Max
Headwater streams (CS)	349	349	10 (30)	1.73	0.02	265
Rivers (HMS)	249	2941	863 (1417)	385	27	9948

CS, Countryside Survey.
HMS, Harmonised Monitoring Scheme.
SD, Standard Deviation.

stream water alkalinity (Fig. 1). Of the 349 headwater streams, 169 were classified as Lowland-High-Alkalinity, 92 as Lowland-Low-Alkalinity, 72 as Upland-Low-Alkalinity, and 16 as Upland-High-Alkalinity. For the rivers, 197 sites had alkalinity and altitude data which allowed typological classification. Of these 197 rivers, 102 were classified as Lowland-High-Alkalinity, 19 as Lowland-Low-Alkalinity, 37 as Upland-Low-Alkalinity, and 39 as Upland-High-Alkalinity (Table 2).

2.2. Use of ternary plots for visualising the relationships between RP, TON and DIC concentrations

Ternary plots were used to visualise the relationships between RP, DIC and TON (Fig. 2), as described by Smith et al. (2017). Firstly, RP, TON and DIC concentrations from the headwater stream and river datasets were converted to molar units, and then transformed (as P_R, N_R, and C_R), so that the centre point of the ternary graphs ($P_R = 0.333$, $N_R = 0.333$, $C_R = 0.333$) corresponded with the Redfield ratio (1P:16N:106C) (Redfield, 1958). The Redfield ratio is widely used as a reference 'optimum' P:N:C ratio for primary production, and deviations from this optimum can indicate nutrient limitation. It is recognised that the Redfield ratio does not represent a universal chemical optimum, rather an average of species-specific P:N:C ratios (Kolzau et al., 2014). The headwater stream and river P_R, N_R and C_R data were then plotted in ternary space, with each sample colour-coded according to the RP concentration.

The central zone within the triangle was delimited as the "Redfield Zone", where samples approach 'optimal' ratios of inorganic P, N and C for uptake by aquatic algae and where nutrient concentrations typically exceed limiting concentrations (Smith et al., 2017). Here, an operational boundary delineating the Redfield Zone ($P_R > 0.2$, $N_R > 0.2$, and $C_R > 0.2$) was chosen using the HMS river dataset. By applying a cut-off of >0.2, 96% of river samples in the Redfield Zone were above the upper P concentration threshold and 90% were above the upper N limitation thresholds; and all of the headwater streams within the Redfield Zone were above both P and N concentration thresholds. This confirms that the Redfield Zone is generally a zone of nutrient excess and that samples within the Redfield Zone are unlikely to be P or N limited.

The position of samples outside the Redfield Zone allows assessment of their relative depletion with respect to P, N or C. Accordingly, seven 'zones' of relative nutrient availability and depletion were defined by the following criteria (Fig. 2):

- Redfield Zone of nutrient availability ($P_R > 0.2$, $N_R > 0.2$, $C_R > 0.2$)
- P depletion, relative to N and/or C ($P_R < 0.2$);
- N depletion relative to P and/or C ($N_R < 0.2$);
- C depletion relative to P and/or N ($C_R < 0.2$).

The intersections of these zones of P, N and C depletion correspond with three zones of co-depletion (Fig. 2). The numbers and percentages of headwater and river samples which fell within each of these zones were then calculated.

2.3. Nutrient Limitation Assessment: combining nutrient stoichiometry and threshold P and N concentrations

The ternary visualisation of the relative availability and depletion of P, N and C provides a starting point for assessment of potential nutrient limitation. Here, we differentiate between *relative nutrient depletion* which is based on stoichiometry, and *nutrient limitation* where the absolute concentration of one or more nutrients falls below a limiting concentration threshold.

A Nutrient Limitation Assessment (NLA) framework is presented in Fig. 3. This provides a 3-tier sequential assessment: (i) the relative depletion of inorganic P and N derived from the ternary plot analysis (tier 1); (ii) a stoichiometric filter, based on the Redfield N:P ratio of 16 (tier 2); and (iii) an evaluation of absolute nutrient concentration relative to limiting thresholds, which determine whether nutrient limitation actually occurs (tier 3). Two threshold levels of limiting nutrient concentrations were applied: an upper concentration threshold of 0.05 mg-P L^{-1} and 0.4 mg-N L^{-1} (tier 3a), and a lower concentration threshold of 0.01 mg-P L^{-1} and 0.1 mg-N L^{-1} (tier 3b) The upper threshold represents concentrations at which P and N could become limiting (Mainstone and Parr, 2002), i.e., partial nutrient limitation. RP concentrations of c.0.05 mg-P L^{-1} have also been experimentally identified as a 'breakpoint' for P limitation (Bowes et al., 2012; McCall et al., 2014; McCall et al., 2017). Experimental results also indicate that the N breakpoint may be around 10 times higher than the P breakpoint (Keck and Lepori, 2012). The second lower threshold represents concentrations at which full nutrient limitation is likely to occur (Kolzau et al., 2014; Maberly et al., 2002).

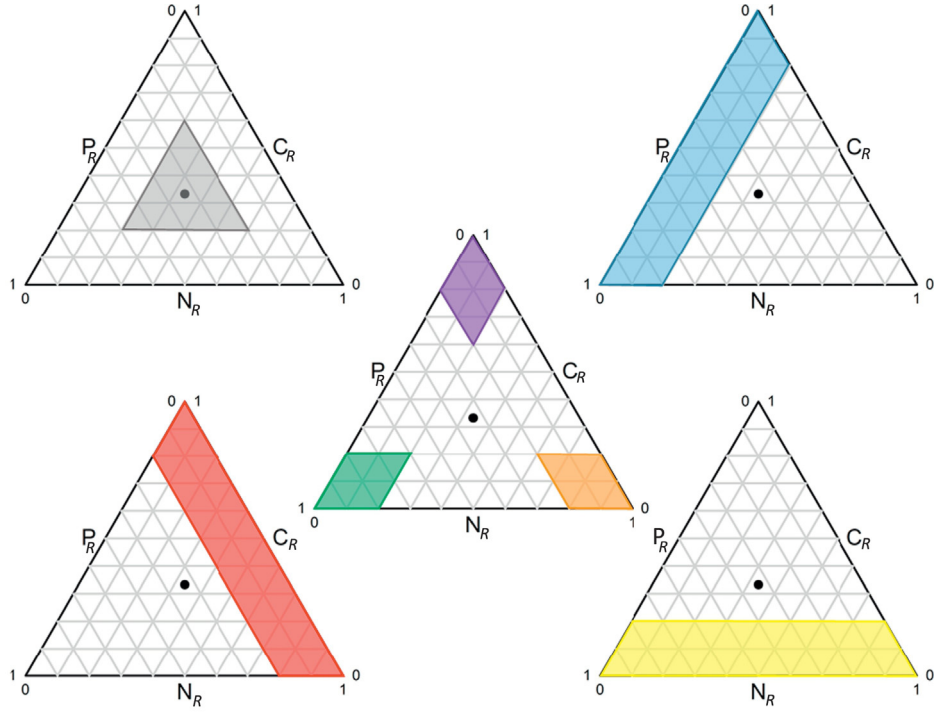
For simplicity, we refer to P, N and C "limitation", but highlight that in all cases, this is *potential* nutrient limitation, and, in this case, it is based on the inorganic nutrient fractions, as total nutrient concentrations were not measured. Although the inorganic nutrient fractions do not necessarily equate to the total nutrient pool, they do provide a measure of the immediately-bioavailable P, N and C fractions available for algal uptake and represent the dominant nutrient fractions contributing to the nutrient concentrations of U.K. rivers (Jarvie et al., 2008a; Jarvie et al., 2017; Neal et al., 2012). It is also recognised here that a range of other physico-chemical factors can also limit or co-limit aquatic algal growth, such as light, water temperature and hydromorphology (Bowes et al., 2016).

The three-tier NLA was firstly applied to the full headwater stream and river datasets, to derive the numbers and percentages of headwater stream and river samples meeting each of the nutrient criteria. The first and third tiers (without the stoichiometry filter) were used to examine the propensity for P and N co-limitation. The NLA was then applied to the four typologies for both headwater stream and river datasets.

Table 2
Summary of the number of headwater streams and rivers within each of the major catchment typologies, and their average altitude and alkalinity.

Water body type	Typology	No. sites	Altitude (m)		Alkalinity (mg-$CaCO_3$ L^{-1})	
			Median	Mean (SD)	Median	Mean (SD)
Headwater streams (CS)	Lowland-High-Alkalinity	169	50	62 (55)	181	185 (100)
	Lowland-Low-Alkalinity	92	75	91 (64)	17	18 (14)
	Upland-Low-Alkalinity	72	315	344 (134)	6	11 (12)
	Upland-High-Alkalinity	16	268	299 (92)	86	110 (64)
Rivers (HMS)	Lowland-High-Alkalinity	102	109	111 (41)	158	160 (58)
	Lowland-Low-Alkalinity	19	148	152 (34)	34	31 (11)
	Upland-Low-Alkalinity	37	287	302 (75)	17	21 (13)
	Upland-High-Alkalinity	39	248	250 (40)	88	93 (32)

CS, Countryside Survey.
HMS, Harmonised Monitoring Scheme.
SD, Standard Deviation.



Redfield Zone (approaching optimal C:N:P stoichiometry for primary production)
P-depleted relative to N and/or C
N-depleted relative to P and/or C
C-depleted relative to N and/or P
P and N co-depleted relative to C
N and C co-depleted relative to P
P and C co-depleted relative to N

Fig. 2. Conceptual diagram showing the use of ternary plots for visualising the relationships between P, N and C concentrations, and zones of P, N or C relative depletion and co-depletion (see text for explanation). The black circle symbol at the centre of the ternary diagram denotes the Redfield ratio (106C:16N:1P).

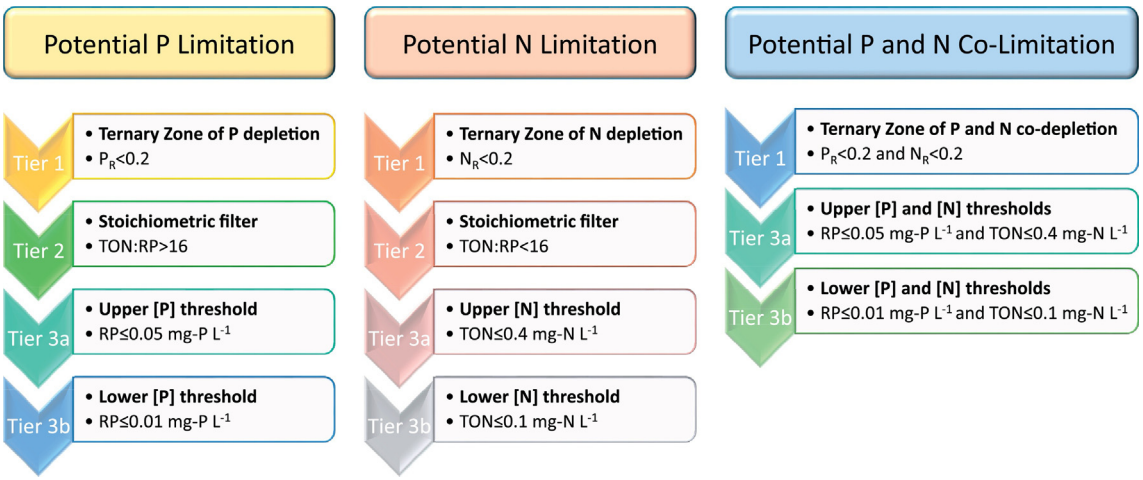


Fig. 3. Nutrient Limitation Assessment framework, showing the P and N criteria for the sequential tiers of assessment of potential P and N limitation and co-limitation.

2.4. Nutrient impairment

Nitrogen and P can impair water quality when concentrations in the water column are sufficiently high to cause enhanced rates of primary production. Headwater streams or rivers are therefore likely to start to become P or N impaired when the measured nutrient concentrations exceed the upper P concentration limitation threshold of 0.05 mg-P L^{-1} and/or the upper N concentration limitation threshold of 0.4 mg-N L^{-1}, assuming that no other physico-chemical factors are simultaneously limiting primary production. Therefore, for assessment of nutrient impairment, we quantified the percentages of headwater and river samples which exceeded the upper P and N concentration thresholds.

2.5. Relationships between catchment characteristics, nutrient impairment and potential P and N limitation and co-limitation

Links between catchment characteristics and the extent to which headwater streams and rivers may be nutrient impaired or nutrient limited were explored using digital elevation and land cover data from the UK National River Flow Archive (see http://nrfa.ceh.ac.uk and Jarvie et al., 2017) and the Countryside Survey headwater stream database (see http://www.countrysidesurvey.org.uk/). Three sample classes were examined: (i) N or P impaired: streams or rivers with concentrations above the upper P or N concentration threshold, (ii) an "upper" nutrient limitation category: samples with concentrations above the lower P and/or N thresholds, but below the upper P and/or N thresholds (i.e. Tier 3a-3b of the NLA); (iii) a "lower" nutrient limitation category: samples with concentrations below the lower limitation P and/or N thresholds (i.e., Tier 3b of the NLA).

2.6. Nutrient compliance and limitation gaps

To provide a first approximation of the scale of nutrient reductions which may be needed to reduce eutrophication in headwater streams and rivers, an assessment was made of compliance and limitation gaps (Doody et al., 2014; Doody et al., 2016). The P compliance gap was defined here as the median concentration by which the measured RP exceeds the site-specific standards for Good P Status (see SI3). The P and N limitation gaps were defined as the median concentrations by which the measured RP or TON concentrations exceed the upper P and N concentration thresholds. Upper P and N concentration thresholds were used here, as these represent the concentrations at which at least partial P and/or N limitation would be expected. The P compliance and P and N limitation gaps therefore quantify the decrease in P or N concentration needed for 50% of samples, measured to be in exceedance, to reach the corresponding compliance or limitation threshold.

3. Results

3.1. Patterns in inorganic P, N and C concentrations

Higher RP and TON concentrations were observed in the major rivers compared with the headwater streams (Fig. SI1): median and mean (and standard deviation, SD, shown in parentheses) headwater stream RP concentrations were 0.01 mg-P L^{-1} and 0.124 (0.591) mg-P L^{-1} respectively, compared with 0.06 and 0.205 (0.390) mg-P L^{-1} for the rivers. Median and mean (and SD) headwater stream TON concentrations were 0.460 mg-N L^{-1} and 2.74 (4.65) mg-N L^{-1}, respectively, compared with 2.84 mg-N L^{-1} and 3.84 (3.42) mg-N L^{-1} for the rivers. There were comparatively small differences in DIC concentrations between the headwater streams and the rivers (Fig. SI1): median and mean (and SD) headwater stream DIC concentrations were 23.1 and 32.8 (18.8) mg-C L^{-1}, respectively, compared with 22.6 and 26.2 (36.9) mg-C L^{-1} for the rivers.

Comparing the four catchment typologies, RP and TON concentrations were highest in the lowland high-alkalinity headwater streams and rivers (Fig. 4). Despite the higher RP and TON concentrations in the rivers, the overall patterns in nutrient concentrations between the four major typologies were similar for both headwater streams and rivers, showing a gradation in TON concentration, where: Lowland-High-Alkalinity > Lowland-Low-Alkalinity > Upland-High-Alkalinity > Upland-Low-Alkalinity. In contrast, for both upland and lowland settings, and for both headwater streams and rivers, RP and DIC, concentrations were generally higher in the high-alkalinity catchments.

The relationships between P, N and C concentrations for the headwater streams and rivers are presented as ternary plots (Fig. 5). Table 3 shows the percentages of the headwater and river samples, and their component typologies, which fell within the Redfield Zone and zones of relative N, P and C depletion and co-depletion. The results of the ternary analysis showed:

- *Most headwater streams and rivers were P depleted relative to N and/or C.* A very high proportion of all headwater streams (93%) and rivers (85%) showed evidence of P depletion. Across all typologies for both rivers and headwater streams, there were high percentages of P depletion, ranging from 77% of Lowland-Low-Alkalinity rivers to 100% of Upland-High-Alkalinity headwater streams.
- *Headwater streams showed greater propensity for N depletion and PN co-depletion than rivers*: 58% of all headwater stream samples were depleted in N, and 54% were PN co-depleted, compared with c.12% of all rivers showing both N depletion and PN co-depletion. The highest incidence of N depletion and PN co-depletion was in the Upland-High-Alkalinity headwater streams, where 100% were both N-depleted and PN co-depleted.
- *Where N depletion occurs, P is usually also co-depleted:* The close correspondence between percentage of samples showing both N depletion and PN co-depletion suggest that, where N is depleted, P is usually also depleted. In contrast, there were much higher levels of P depletion relative to PN co-depletion across all headwater stream and river typologies.

A higher percentage of river samples (12%) plotted within the central Redfield Zone, compared with only c.1% of headwater streams. Lowland-High-Alkalinity rivers had the highest percentage of samples (19%) within the Redfield Zone.

The low-alkalinity typologies had the highest incidences of relative C depletion: c.7% of Upland-High-Alkalinity headwater streams and 14% of Lowland-Low-Alkalinity rivers were C depleted relative to P and N. However, all Lowland-Low-Alkalinity rivers which were C depleted were also NC or PC co-depleted. C depletion occurs relatively rarely compared with P and N depletion, and most often arises as a result of relative enrichment with P and/or N, rather than C limitation per se. Accordingly, the NLA in the following section focuses on N and P limitation.

3.2. Potential for P and/or N limitation

The NLA (Fig. 3) was applied to all the headwater stream and rivers and to their component typologies (Table 4). The percentage of samples complying with each tier of assessment, and the magnitude of the decreases in percentage between tiers provide key information about the extent and nature of nutrient limitation. For example, decreases in the percentage of samples complying with tier 2 (stoichiometric filter) compared with tier 1 (relative P or N depletion), reflect co-depletion effects. Moreover, large decreases between tier 2 and tier 3 (limitation thresholds) indicate that only a small proportion of the samples which were indicative of limitation according to the Redfield ratio (i.e., with N:P > 16 or N:P < 16) were actually P or N limited as determined by absolute P or N concentration. The results of the NLA (Table 4) showed:

- *Greater potential for PN co-limitation in the headwater streams:* Although 93% of all headwater streams were P depleted relative to N and/or C, only 45% of headwater streams had N:P > 16, reflecting extensive PN co-limitation: 35% of all headwater streams were at least partially PN

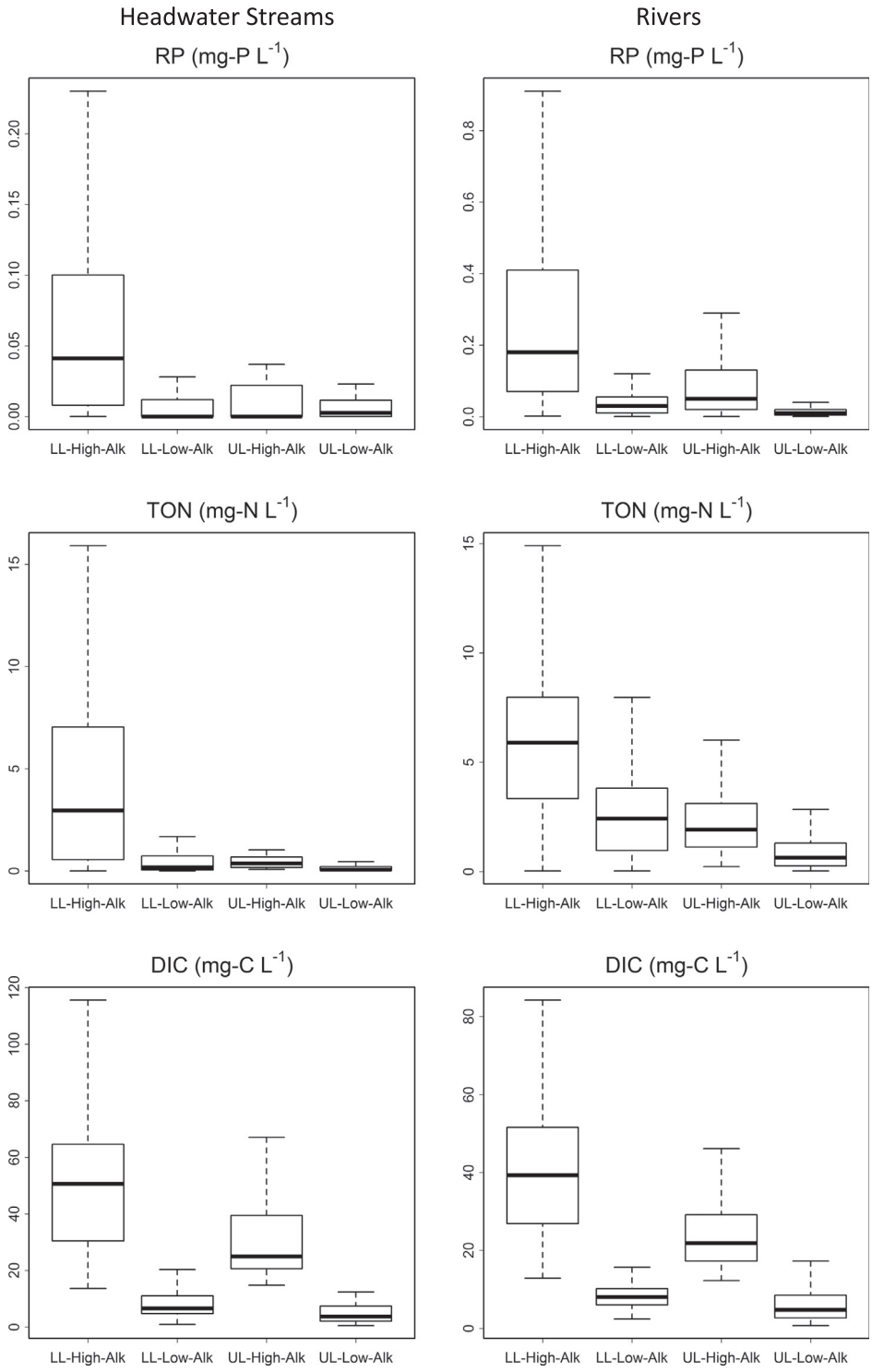


Fig. 4. Boxplots summarising the reactive phosphorus (RP), total oxidised nitrogen (TON), and dissolved inorganic carbon (DIC) concentrations for the four major typologies of British headwater streams and rivers. (Catchment typology classes: LL-High-Alk, Lowland-High-Alkalinity; LL-Low-Alk, Lowland-Low-Alkalinity; UL-High-Alk, Upland-High-Alkalinity; UL-Low-Alk, Upland-Low-Alkalinity).

co-limited and 16% were fully PN co-limited, compared with only 5% and 2% of all river samples. The incidence of PN co-limitation was greatest in the Upland-Low-Alkalinity headwater streams: 63% of Upland-Low-Alkalinity headwater streams were at least partially PN co-limited and 40% were fully PN co-limited, compared with 14% and 7% in Upland-Low-Alkalinity rivers.

- *Greater potential for single-element N limitation in the headwater streams:* The headwater streams showed consistently greater potential for single-element N limitation: 13% of all headwater streams were at least partially N-limited and 9% were fully N-limited, compared with only 1% of river samples. Very low instances of N limitation were seen in all four river typologies. Although 58% of all headwater streams were N depleted relative to P and/or C, only 16% had N:P < 16 and, while 13% of rivers were N depleted, only 2% had N:P < 16. There was greater propensity for PN co-depletion and co-limitation and, where N was limiting, P was usually also co-limiting. The Upland-Low-

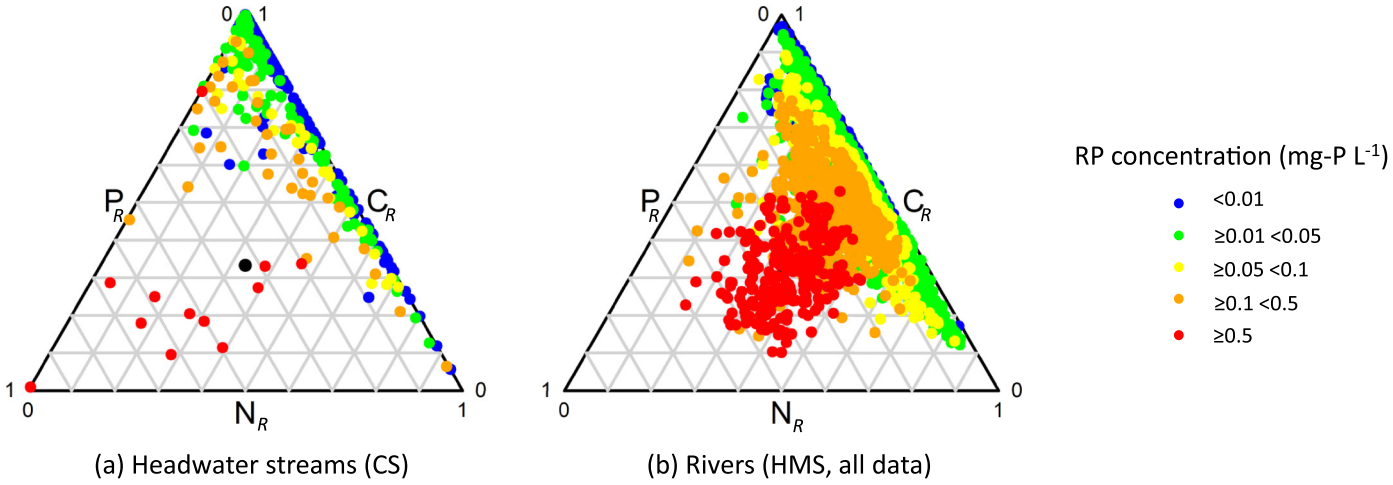


Fig. 5. Ternary plots showing the relationships between P, N and C concentrations in British headwater streams and rivers. Samples are colour-coded according to their RP (reactive phosphorus) concentration. The black circle symbol at the centre of the ternary diagram denotes the Redfield ratio (106C:16N:1P).

Alkalinity headwater streams showed greatest potential for N limitation, with 22% at least partially N-limited and 20% fully N-limited.

- *Greater potential for single-element P limitation in the rivers:* The rivers showed greater potential for single-element P limitation: 43% of all river samples were at least partially P-limited and 25% were fully P-limited. In contrast, 31% of headwater streams were at least partially P-limited and only 9% fully P-limited.
- *A greater proportion of rivers with N:P > 16 were not actually P-limited.* Although 84% of rivers had N:P > 16, only 43% of rivers had RP concentrations below the threshold of at least partial P limitation. Therefore, in 41% of river samples, N:P ratios of >16 did not result in P limitation, but arose from greater availability of N relative to P. In contrast, only 14% of headwater streams had N:P > 16 but no P limitation. The Lowland-High-Alkalinity rivers had the highest percentage of samples (62%) where N:P > 16, but with no P limitation.

3.3. Nutrient impairment

Conversely to the previous assessment of nutrient limitation, the assessment of nutrient impairment (Table 5) shows the percentages of headwater and river samples which exceed the upper P and N concentration thresholds. Three key patterns of nutrient impairment emerged:

- *Headwater streams showed a markedly lower degree of P and N impairment compared with the rivers*: 23% of all headwater samples exceeded the upper P concentration threshold, compared with 51% of river samples; and 52% of headwater streams exceeded the upper N concentration threshold, compared with 87% of river samples.
- *Nutrient impairment was generally greatest for Lowland-High-Alkalinity headwater streams and rivers*: 41% of Lowland-High-Alkalinity headwater streams and 81% of Lowland-High-Alkalinity river samples exceeded the upper P concentration threshold; and 78% of Lowland-High-Alkalinity headwater streams and 98% of Lowland-High-Alkalinity river samples exceeded the upper N concentration threshold.
- *Nutrient impairment was generally lowest in the Upland-Low-Alkalinity headwater streams and rivers*: <10% of Upland-Low-Alkalinity headwater stream and river samples were P impaired, while 15% of headwater streams and 61% of rivers were N impaired for the Upland-Low-Alkalinity typology.
- *Levels of N impairment were consistently higher than P impairment.* For all headwater stream and river typologies, a greater percentage of samples were N impaired than P impaired.

The higher percentages of rivers showing P impairment, compared with headwater streams, correspond with the higher river WFD P compliance failures (Table 5). For both the headwater stream and river typologies, there was close agreement between the percentages of samples which exceeded both Good P Status and the upper P concentration threshold. 53% of all rivers failed to comply with Good P Status, compared with 20% of all headwater streams. WFD P compliance failures were highest in the Lowland-High-Alkalinity typology, where 77% of rivers and 34% of headwater streams failed to achieve Good P Status.

Moreover, 3% of headwater streams and 11% of rivers had RP concentrations well above nutrient impairment thresholds at >0.5 mg-P L^{-1}, and 2% of headwater streams and 4% of rivers had RP concentrations >1 mg-P L^{-1} (see Supplementary material Table S1). For the Lowland-High-Alkalinity typology, 6% of headwater streams and 20% of rivers had RP concentrations >0.5 mg-P L^{-1}, and 4% of headwater streams and 8% of rivers had RP concentrations >1 mg-P L^{-1}.

3.4. Links between catchment characteristics, nutrient limitation and nutrient impairment

The relationships between catchment characteristics, nutrient availability and potential P and N limitation and co-limitation for headwater streams and rivers are shown in Fig. 6. There were clear transitions from nutrient impairment to limitation with land use, altitude and alkalinity for both headwater streams and rivers. For example, samples which were nutrient impaired had higher percentages of arable/horticulture and urban land, as well as higher alkalinity, lower altitude, and low percentages of mountain/heathland/bog vegetation, compared with samples which were P limited, N limited and PN co-limited. For the rivers, the transition from nutrient impairment, via the lower P limitation, N limitation and PN co-limitation classes corresponded with a reduction in median alkalinity of 128 > 37 > 6 > 5 mg-$CaCO_3$ L^{-1}, an increase in altitude of 115 < 231 < 345 < 351 m, and a reduction in percentage arable land area of 20 > 5.2 > 0.5 > 0%. Moreover, the lower nutrient limitation categories for both headwater streams and rivers were generally characterised by higher altitude, higher percentages of mountain/heathland/bog vegetation, but lower alkalinity and arable/horticultural, grassland, and urban land area, than the corresponding upper limitation categories.

3.5. Water Framework Directive P compliance and P and N limitation gaps

As a first approximation of the scale of nutrient reductions needed to reduce eutrophication in headwater streams and rivers, an assessment was made of the WFD P compliance and P and N limitation gaps (Table 6). These provide an estimate of the decrease in nutrient concentrations needed for 50% of the samples, which currently exceed the target concentration, to reach the corresponding compliance or limitation thresholds. Table 6 also shows the increase in the percentage of samples

Table 3
Percentages of headwater streams, rivers, and their respective typologies, within the Redfield Zone and in the zones of relative nutrient depletion according to ternary stoichiometric analysis (see text and Fig. 2).

	Headwater streams					Rivers				
	All	Lowland-High-Alk	Lowland-Low-Alk	Upland-Low-Alk	Upland-High-Alk	All	Lowland-High-Alk	Lowland-Low-Alk	Upland-Low-Alk	Upland-High-Alk
Redfield Zone	1.2	2.5	0	0	0	12	19	5.5	2.9	9.4
Redfield Zone where RP > 0.05 mg-L^{-1} & TON > 0.4 mg-N L^{-1}	1.2	2.5	0	0	0	12	19	5.5	0.6	9.4
Zone of P depletion	93	93	99	87	100	85	77	92	95	88
Zone of N depletion	58	45	64	77	100	13	7.2	14	16	23
Zone of C depletion	3.4	3.1	2.4	6.7	0	3.3	2.4	14	1.8	2.7
Zone of P and N co-depletion	54	41	63	65	100	12	6.3	11	15	23
Zone of N and C co-depletion	1.9	1.2	2.4	3.3	0	1.4	0	14	0.4	0
Zone of P and C co-depletion	1.9	1.2	2.4	3.3	0	1.4	0	14	0.4	0

Table 4
Nutrient Limitation Assessment for all headwater streams and rivers and their component typologies, showing the percentage of headwater streams and rivers complying with each tier of the Nutrient Limitation Assessment (see Fig. 3).

	Tier	P and/or N criteria	Headwater streams					Rivers				
			All	Lowland-High-Alk	Lowland-Low-Alk	Upland-Low-Alk	Upland-High-Alk	All	Lowland-High-Alk	Lowland-Low-Alk	Upland-Low-Alk	Upland-High-Alk
Potential P limitation	1	Zone of relative P depletion	93	93	99	87	100	85	77	92	95	88
	2	& N:P > 16	45	64	25	23	38	84	77	90	90	87
	3 (a)	& N:P > 16 & P ≤ 0.05 (partial P limitation)	31	38	23	23	38	43	15	69	85	48
	3 (b)	& N:P > 16 & P ≤ 0.01 (full P limitation)	9	9	8	8	13	25	5	28	68	22
Potential N limitation	1	Zone of relative N depletion	58	45	64	77	100	13	7	14	16	23
	2	& NP < 16	16	15	16	22	6	2	1	4	5	1
	3 (a)	& NP < 16 & N ≤ 0.4 mg L^{-1} (partial N limitation)	13	10	16	22	6	1	0	2	5	0
	3 (b)	& NP < 16 & N ≤ 0.1 mg L^{-1} (full N limitation)	9	4	12	20	0	1	0	0	5	0
Potential N & P co-limitation	1	Zone of P and N co-depletion	54	41	63	65	100	12	6	11	15	23
	3 (a)	P < 0.05 & N ≤ 0.4 (partial PN co-limitation)	35	13	58	63	44	5	1	9	14	2
	3 (b)	P ≤ 0.01 & N ≤ 0.1 (full PN co-limitation)	16	3	27	40	6	2	0	0	7	0

Table 5
Nutrient impairment of headwater streams, rivers, and their component typologies: the percentage of samples which exceed the upper P and N limitation thresholds, and which fail to comply with Good P Status.

Water body type	Typology	Threshold exceedance		Failure to comply with Good P Status
		Upper P threshold	Upper N threshold	
Headwater streams	All	23	52	20
	Lowland-High-Alkalinity	41	78	34
	Lowland-Low-Alkalinity	4	33	4
	Upland-Low-Alkalinity	8	15	11
	Upland-High-Alkalinity	6	50	6
Rivers - annual means	All	51	87	53
	Lowland-High-Alkalinity	81	98	77
	Lowland-Low-Alkalinity	25	81	32
	Upland-Low-Alkalinity	8	61	5
	Upland-High-Alkalinity	44	96	42

which would be expected to achieve P or N targets if the corresponding compliance or limitation targets were achieved (i.e., if concentrations were reduced by the corresponding compliance or limitation gap), and the overall percentage of samples expected to achieve P or N targets if the compliance or limitation gap was closed.

For example, for the 34% Lowland-High-Alkalinity headwater streams which are currently non-compliant with Good P Status (Table 5), a reduction in RP concentration by the P compliance gap of 0.102 mg-P L^{-1} (Table 6) would be expected to achieve a 50% reduction in samples currently exceeding the P compliance targets, thus bringing about a 17% increase in overall P compliance. This would therefore increase the percentage of samples currently meeting the P compliance targets from 66% to 83%. However for Lowland-High-Alkalinity headwater streams currently failing P compliance targets, an average reduction in RP concentrations of 55% would be needed. Closing the P limitation gap of 0.09 mg L^{-1} is expected to yield similar results: an increase in the percentage of samples meeting P limitation targets by 21%, from 59% to 80%, for an average reduction in RP concentration of 64%.

For both headwater stream and river typologies, by closing the P compliance and limitation gaps, the greatest expected percentage gains in meeting the P targets were for the Lowland-High-Alkalinity typology. Greater percentage gains were expected in the Lowland-High-Alkalinity rivers compared with headwater streams. An approximate 40% increase in Lowland-High-Alkalinity river samples achieving the P compliance and limitation targets (from c. 20–60%) was expected, but this would require a 70–80% reduction in RP concentrations in those rivers currently exceeding these P targets.

For the Upland-Low-Alkalinity rivers, the P compliance and limitation gaps were much lower (c. 0.03 mg-P L^{-1}) but, given the already high rates of compliance with P targets, reducing the RP concentration by the compliance and limitation gaps would likely result in only marginal improvements in achieving the P compliance and limitation standards. For example, for the Upland-Low-Alkalinity rivers, reducing RP concentrations by the P compliance and limitation gap of c.0.03 mg L^{-1} would be expected to increase the percentage of samples achieving the P compliance and P limitation targets by c.3%, i.e., from c.95% to 98%. Similarly, for Upland-Low-Alkalinity headwater streams, by reducing RP concentrations by the P compliance and limitation gap of c.0.08 mg-P L^{-1}, only an additional 5% of samples would meet these P targets, i.e., raising compliance from 90% to 95%.

Reducing TON concentrations in the Lowland-High-Alkalinity headwater streams and rivers which currently exceed the N limitation target N limitation gaps (4.25 mg-N L^{-1} and 5.5 mg-N L^{-1}, respectively), would be expected to increase the percentage of samples meeting the N limitation targets by c.40–50%, and achieve overall compliance rates of c.50–60%. However, this would require a >90% reduction in the current TON concentrations. For the Upland-Low-Alkalinity headwater streams and rivers, N limitation gaps were markedly lower than for the Lowland-High-Alkalinity typology, both in terms of absolute concentrations (0.22 and 0.69 mg-N L^{-1}, respectively) and also as a percentage of TON concentrations (35 and 63%, respectively). However, reducing TON concentrations by the N limitation gap in headwater streams would only increase the percentage of samples achieving N limitation targets by 8%. In contrast, there were greater benefits of closing the N limitation gap for the Upland-Low-Alkalinity rivers, where the percentage increase in samples achieving N limitation targets was expected to increase by 31%, i.e., from 39% to 70%.

4. Discussion

Although there was localised nutrient impairment of headwater streams, particularly in the Lowland-High-Alkalinity agricultural and urban catchments, at the national scale, headwater streams had markedly lower P and N concentrations, and were subject to a lower degree of P and N and impairment than rivers. 23% of all headwater streams were P-impaired, compared with 51% of all rivers; and 52% of headwater streams were N-impaired compared with 87% of rivers. Failure to comply with WFD standards for Good P Status was closely linked with levels of P impairment and there was also a close convergence between the upper P concentration threshold and the site-specific P standards required to support good ecological status. This indicates that the thresholds used here to denote partial P limitation broadly equate with the site-specific standards for Good P status.

Only 20% of all headwater streams failed to achieve Good P Status, compared with 53% of all rivers. For both headwater stream and rivers, the Upland-Low-Alkalinity typology had the lowest levels of P and N impairment, with the Lowland-High-Alkalinity typology recording the highest levels of P and N impairment. The net effect was a cumulative anthropogenic nutrient enrichment along the river continuum, with increases in N and P pressures with catchment scale, linked to increases in the range and complexity of urban and agricultural source types (Jarvie et al., 2008a, 2008b; Neal et al., 2012; Neal et al., 2008; Neal et al., 2010).

Headwater streams also showed greater potential for PN co-limitation and single-element N-limitation (35% and 13%, respectively) compared with the rivers (5% and 1% respectively). This suggests that managing and controlling *both* P and N inputs to headwater streams will be needed to minimise the risks of degradation of these sensitive headwater environments. For both headwater streams and rivers, where N is limiting, P is usually also co-limiting, however the reverse does not hold, with widespread P limitation without N co-limitation. The majority (>60%) of Lowland-High-Alkalinity rivers had N:P > 16, but no P limitation. The relative abundance of N may reflect: the greater availability of N from groundwater in the lowland agricultural areas underlain by permeable calcareous geology; the effects of P removal at sewage treatment works; and greater rates of in-stream P retention, compared with more conservative transport of nitrate (Jarvie et al., 2005; Neal et al., 2006; Neal et al., 2002). This also highlights the drawbacks of relying solely on nutrient ratios to infer nutrient limitation. C

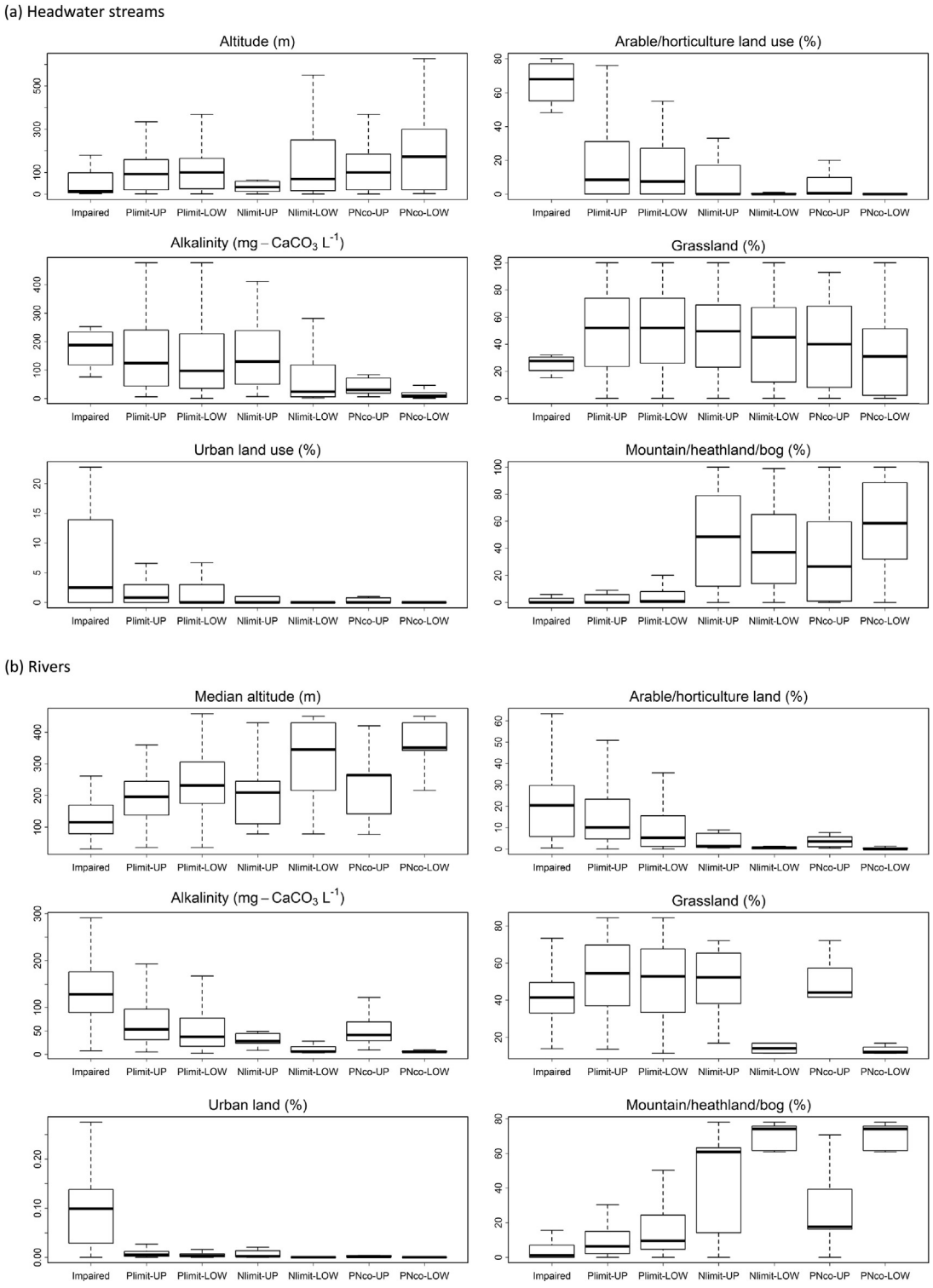


Fig. 6. Boxplots summarising the catchment characteristics of sites which are nutrient impaired and nutrient limited for (a) headwater streams, and (b) rivers. (Key: 'Impaired': samples within the Redfield Zone, with concentrations above the upper P and N concentration threshold; 'Plimit-UP': the upper P limitation category, i.e., samples with concentrations ≤0.05 mg-P L^{-1} and >0.01 mg-P L^{-1}; 'Plimit-LOW' a lower P limitation category: samples with concentrations ≤0.01 mg-P L^{-1}; 'Nlimit-UP': the upper N limitation category, i.e., samples with concentrations ≤0.4 mg-N L^{-1} and >0.1 mg-N L^{-1}; 'Nlimit-LOW' a lower N limitation category: samples with concentrations ≤0.1 mg-N L^{-1}; 'PNco-UP': the upper P and N co-limitation category, i.e., samples with concentrations ≤0.05 mg-P L^{-1} and >0.01 mg-P L^{-1}, and ≤0.4 mg-N L^{-1} and >0.1 mg-N L^{-1}; 'PNco-LOW' a lower P and N co-limitation category: samples with concentrations ≤0.01 mg-P L^{-1} and ≤0.1 mg-N L^{-1}).

limitation rarely limits primary production in rivers or streams, as a result of an abundant DIC source (as HCO_3^-) from weathering of carbonate rocks and soils (Jarvie et al., 2017). Indeed, C limitation tends to occur only occasionally, in low-alkalinity waters during major algal bloom events (Jarvie et al., 1997, 2017).

The lower P and N concentrations in the headwater streams may also reflect a greater capacity for nutrient-limited streams to retain and process P and N inputs under stable low-flow conditions (Jarvie et al., 2012b; Weigelhofer, 2017; Withers and Jarvie, 2008). Compared with the larger cross-sectional area of rivers, headwater streams are

Table 6
Compliance and limitation gap assessment for headwater stream and river typologies (see text for details).

Target		Headwater streams				Rivers			
		Lowland-High-Alk	Lowland-Low-Alk	Upland-Low-Alk	Upland-High-Alk	Lowland-High-Alk	Lowland-Low-Alk	Upland-Low-Alk	Upland-High-Alk
Good P Status	P compliance gap (mg-P L^{-1})	0.102	0.036	0.087	0.063	0.193	0.028	0.028	0.104
	P compliance gap as a % of stream/river RP conc.	55	47	76	69	70	37	39	61
	Expected % increase in samples achieving P compliance targets if gap is closed	17	2	6	3	39	16	3	21
	Expected percentage of samples achieving P compliance targets if gap is closed	83	98	95	97	62	84	98	79
Upper P limitation threshold (0.05 mg L^{-1})	P limitation gap (mg-P L^{-1})	0.090	0.060	0.070	0.041	0.190	0.030	0.030	0.100
	P limitation gap as a % of stream/river RP conc.	64	50	58	45	79	38	38	67
	Expected % increase samples in achieving P limitation targets if gap is closed	21	2	4	3	41	13	4	22
	Expected percentage of samples achieving P limitation targets if gap is closed	80	98	96	97	60	88	96	78
Upper N limitation threshold (0.4 mg-N L^{-1})	N limitation gap (mg-N L^{-1})	4.25	0.91	0.22	0.28	5.50	2.38	0.69	1.54
	N limitation gap as a % of stream/river TON conc.	91	69	35	38	93	86	63	79
	Expected % increase in samples achieving N limitation targets if gap is closed	39	17	8	25	49	41	31	48
	Expected percentage of samples achieving N limitation targets if gap is closed	61	84	93	75	51	60	70	52

characterised by large benthic surface areas relative to water volume, and a high degree of connectivity within riparian and hyporheic zones. This promotes nutrient uptake by periphyton and biofilms attached to benthic surfaces and microbial cycling of P and N in benthic, hyporheic and riparian sediments (Bernal et al., 2015; Triska et al., 2007). There may also be a progressive saturation of the in-stream nutrient retention capacity along the river continuum, arising from higher nutrient loadings, and a shift from nutrient subsidy to nutrient stress (Withers and Jarvie, 2008).

P compliance and P and N limitation gaps were used to explore the scale of P and N reductions in headwater streams and rivers needed to curb eutrophication and to bring about a transition from nutrient impairment to nutrient limitation. However, the relative benefits of closing the P and N compliance gaps varied greatly across the catchment typologies. The smallest P compliance and limitation gaps, i.e., the smallest reductions in P concentrations needed to achieve a 50% increase in samples meeting target P concentrations, were in the Upland-Low-Alkalinity headwater streams and rivers (c.0.08 mg-P L^{-1} and c.0.03 mg-P L^{-1}, respectively). However, given the already high levels of compliance with P targets, management measures to reduce P concentrations in Upland-Low-Alkalinity headwater streams and rivers would likely only result in marginal (5%) improvements in overall P compliance rates for this typology. Preliminary indications are that N reductions in the Upland-Low-Alkalinity rivers could have greater overall benefits (>30%) in N target compliance, bringing compliance rates up to 70%, for an approximate 60% reduction in average N concentrations in currently impaired rivers. Further, for impaired Lowland-High-Alkalinity headwater streams, a 60% reduction in average P concentration could increase P target compliance rates by 20%, to 80% compliance. By focusing mitigation in headwater catchments, there could also be a cumulative downstream improvement in river water quality (Jarvie et al., 2002).

A major challenge and limitation, however, is the relative paucity of information about headwater stream quality and ecology, and we highlight the pressing need for national water-quality monitoring to be extended to surveillance monitoring of representative headwater stream typologies. To a large degree, headwater streams are not monitored because of their small size and the vast numbers of sites involved. This leaves a major information gap in our understanding of catchments. It has been estimated that there are around 62,000 headwater streams in England (from estimates made in Wright and Symes, 1997) and headwaters account for >70% of the river network (Smith and Lyle, 1979) but form only ~17% of the chemical monitoring network (Mainstone et al., 2016). Headwater streams tend to be highly variable in condition, implying that a greater proportion of sites may need to be monitored than for larger rivers, rather than a smaller proportion. With limited resources available for monitoring, we need to make best use of information that is collected for other purposes, particularly representative sampling that can be used to make inferences about the status of habitats at national scale. We demonstrate in this paper how routine monitoring datasets may be enhanced by ad hoc surveys to investigate detailed, specific, questions, and inform future monitoring and/or field manipulations. Despite the lack of temporal resolution compared to WFD monitoring, the Countryside Survey yielded a valuable dataset because it was focused on under-monitored headwater habitats, the sampling sites were not biased towards detecting stressors and were representative of their catchments, and the spatial coverage was extensive, and included a wide spectrum of environmental conditions and headwater typologies. Thus, Countryside Survey provided us with a unique insight into the nutrient status of headwater streams that far outweighed the difficulties of marrying a statutory monitoring programme with a separate survey in our analytical framework. Moreover, knowledge gained from the Countryside Survey provides new insight about how monitoring, as well as scientific research, could be expanded and prioritised to provide a more holistic understanding of the water quality and ecological dynamics of headwater streams.

The NLA presented here provides a broad-scale screening tool to identify where P and/or N limitation may occur or where there is

nutrient impairment and risk of eutrophication. In terms of future work, the NLA has wide-ranging international applicability; for example, to explore nutrient limitation and impairment relative to WFD nutrient standards across the EU, and nutrient criteria in North America. Further, the NLA could be used alongside ecological indicators of water quality and biological status (e.g. Norton et al., 2016). For nutrient impaired rivers and streams, the evaluation of gaps between measured and target nutrient concentrations provides a first approximation of the scale of nutrient remediation which may be required to reverse eutrophication, by reducing concentrations to target limiting levels. These approaches could help to inform the prioritisation of catchments for nutrient remediation. Here, we provide an overview at the national scale but, for water-quality management purposes, local field "ground-truthing" will be needed to establish the actual compliance and limitation gaps for individual water bodies. And, given the potential disconnects between the macroscale and the local social, economic, environmental realities and constraints of water quality management at the field to catchment scale (Sharpley et al., 2016), local assessment will be also be needed to evaluate the extent to which reductions in P and/or N concentrations could be realistically achieved, based on best management practices which address the site-specific nutrient sources, and the characteristics of the land, climate and farming systems. It is probably unrealistic, in the short term, to expect to reduce P and N concentrations to compliance and limitation target concentrations, especially in highly impaired catchments with multiple complex sources and with long-term legacy nutrient source contributions (Haygarth et al., 2014; Jarvie et al., 2013a; Jarvie et al., 2013b; Sharpley et al., 2013). However, combining Nutrient Limitation Assessment with an evaluation of compliance and limitation gaps provides a basis for developing a directional approach to nutrient water quality compliance, which focuses on closing the gaps between current and target concentrations (Jarvie and Jenkins, 2014).

5. Conclusions

This study shows that there were markedly higher rates of P and N impairment of rivers relative to headwater streams at the national scale. The net effect was a cumulative anthropogenic nutrient enrichment with increasing catchment scale. This pattern was replicated in all four major catchment typologies with the greatest degree of impairment of rivers relative to headwater streams in the Lowland-High-Alkalinity typology, which have higher agricultural and urban influence than other typologies. Lowest levels of nutrient impairment were observed in the Upland-Low-Alkalinity typology, where there was also greater convergence in the degree of P and N impairment between headwater streams and rivers.

The Nutrient Limitation Assessment revealed high levels of P and N co-limitation in headwater streams, especially in the Upland-Low-Alkalinity headwater streams. This suggests that managing and controlling both P and N inputs to headwater streams may be needed to minimise risks of eutrophication and water-quality degradation of these sensitive headwater stream environments, which play a key role in freshwater biodiversity and ecosystem services (Biggs et al., 2017). P and N reductions needed to reach target WFD and limiting concentrations were greatest for the Lowland-High-Alkalinity catchments and lowest in the Upland-Low-Alkalinity catchments. Our preliminary assessments suggested that, at the national scale, management measures to reduce N concentrations in the Upland-Low-Alkalinity rivers and measures to reduce P concentrations in the Lowland-High-Alkalinity headwater streams might offer greater overall benefits for improving compliance with WFD targets and reducing nutrient concentrations to limiting levels. This macro-scale approach might also help inform the prioritisation of nutrient remediation to reduce eutrophication, as part of a directional approach to water quality management which focuses on closing the gaps between current and target nutrient concentrations.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.128.

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