Modeling the Ecological Impact of Phosphorus in Catchments with Multiple Environmental Stressors

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Abstract

The broken phosphorus (P) cycle has led to widespread eutrophication of freshwaters. Despite reductions in anthropogenic nutrient inputs that have led to improvement in the chemical status of running waters, corresponding improvements in their ecological status are often not observed. We tested a novel combination of complementary statistical modeling approaches, including random-effect regression trees and compositional and ordinary linear mixed models, to examine the potential reasons for this disparity, using low-frequency regulatory data available to catchment managers. A benthic Trophic Diatom Index (TDI) was linked to potential stressors, including nutrient concentrations, soluble reactive P (SRP) loads from different sources, land cover, and catchment hydrological characteristics. Modeling suggested that SRP, traditionally considered the bioavailable component, may not be the best indicator of ecological impacts of P, as shown by a stronger and spatially more variable negative relationship between total P (TP) concentrations and TDI. Nitrate-N ($p < 0.001$) and TP ($p = 0.002$) also showed negative relationship with TDI in models where land cover was not included. Land cover had the strongest influence on the ecological response. The positive effect of seminatural land cover ($p < 0.001$) and negative effect of urban land cover ($p = 0.030$) may be related to differentiated bioavailability of P fractions in catchments with different characteristics (e.g., P loads from point vs. diffuse sources) as well as resilience factors such as hydro-morphology and habitat condition, supporting the need for further research into factors affecting this stressor–response relationship in different catchment types. Advanced statistical modeling indicated that to achieve desired ecological status, future catchment-specific mitigation should target P impacts alongside multiple stressors.

Core Ideas

- Soluble reactive P (SRP) alone was not the best indicator of diatom response.
- Total P (TP) association with diatoms was more spatially variable than SRP.
- Nitrate-N and TP have a combined negative effect on the ecological response.
- Seminatural land use had the most important influence on ecological response.
- We recommend catchment-specific mitigation of multiple stressors.

THE BROKEN PHOSPHORUS (P) cycle leading to excess P inputs remains an important cause of freshwater eutrophication worldwide (Oliveira and Machado, 2013; Withers et al., 2014). Since the discovery of P in 1669, early agricultural revolutions primarily involved expansion of agricultural area and technological innovations (Pretty and Bharucha, 2014). Since the mid–20th century, the remarkable growth in food production during the Green Revolution, accompanied by increased use of inorganic fertilizers and rapid urbanization, led to a host of negative impacts, including widespread eutrophication of surface waters (Withers and Jarvie, 2008). While a significant proportion of the "first wave" of eutrophication in the 1970s and 1980s has been addressed through the management of point sources (Le Moal et al., 2019), current causes of eutrophication in the developed world are largely due to diffuse pollution (Le Moal et al., 2019), which is inherently much harder to identify and manage (Sharpley et al., 2015). Thus, the specialization of agricultural practices and the spatial disconnect between crop and livestock systems prevalent in modern agricultural systems led to a "broken P cycle" and P use inefficiencies, with negative impacts on aquatic ecosystems (Sharpley et al., 2018).

Over the past decades, significant effort has been made to control the anthropogenic input of excess nutrients to freshwater bodies from a variety of sources. However, despite observable reductions in nutrient concentrations that have led to an improvement in the chemical status of inland waters, a corresponding improvement in the ecological status in many catchments has not been observed (Bowes et al., 2012; Harris and Heathwaite, 2012; Sharpley et al., 2018). Understanding these links between P pollution and the ecological impact is often hampered by the disconnect between agricultural landscape-focused research and river science (Kreiling et al., 2017), limiting our understanding of the impact of multiple stressors on the aquatic environment and our ability to predict the effects of human activity (Nõges et al., 2016). Meanwhile, catchment managers are required to address

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Abbreviations: AIC, Akaike information criterion; CLMM, compositional linear mixed models; EQR, Environmental Quality Ratio; ICC, intraclass correlation coefficient; LMM, linear mixed models; PCA, principal component analysis; SRP, soluble reactive phosphorus; TDI, Trophic Diatom Index; TP, total phosphorus.

and mitigate the effect of multiple stressors in river catchments based on regulatory data, which are typically of low temporal and spatial resolution (i.e., monthly observations at catchment outlets). Understanding stressor interactions from these low-resolution data is difficult due to dynamic processes not captured by infrequent observations and a multitude of confounding factors where high "noise" may obscure the identification of a meaningful signal (Feld et al., 2016, Nõges et al., 2016).

While research on multiple stressors has increased over the past two decades (Meissner et al., 2019), experimental studies may struggle to fully resolve complex interactions as they are not able to completely account for what is observed in natural environments (Munn et al., 2018). Some studies have even suggested that each river basin represents a specific system, where stressor effects change along mixed climatic, hydrological, morphological and biotic gradients, thus necessitating catchment-specific understanding of stressor interactions to inform management interventions (Segurado et al., 2018). Therefore, novel statistical modeling approaches are needed to understand the relative importance of stressors and how they interact in complex real-world river systems (Gieswein et al., 2017) to inform better targeting of resources and maximize the use of a large amount of regulatory data that is now available thanks to a considerable investment of public funding.

Such advanced statistical approaches are increasingly applied to regulatory monitoring data to understand the interactions between multiple stressor gradients on ecological outcomes in real-world catchments (Feld et al., 2016; Gieswein et al., 2017; Segurado et al., 2018; Villeneuve et al., 2018; Gutiérrez-Cánovas et al., 2019; Meissner et al., 2019; Rankinen et al., 2019; Wu et al., 2019). While a range of statistical approaches are available, here we present a combined approach (i) to understand the potential associations between catchment-specific ecological responses and multiple stressors, while accounting for unmeasured sources of variability between locations, (ii) to derive overall relationships from available regulatory data that are generalizable to unmonitored locations, and (iii) to understand the importance of the absolute magnitude of individual stressors as well as the balances between them to maximize the complementary insights into these complex relationships based on low-resolution regulatory data.

Diatoms are used in environmental assessments of water bodies around the world (Kelly et al., 2012; Kelly, 2013; Stevenson, 2014; Poikane et al., 2016). In this study, we used the Trophic Diatom Index (TDI) and its Ecological Quality Ratio (EQR TDI) between the observed diatom status and that expected under reference conditions (Kelly et al., 2008) to understand the importance of P in ecological water quality impairment within the context of multiple stressors. The stressor–response relationship between diatoms, chemical stressors, soluble reactive P (SRP) loads, land cover, and catchment hydrological characteristics was examined using a novel combination of statistical modeling approaches, including random-effects regression trees and compositional and ordinary mixed models, all considering the clustered nature of the data according to catchment. In addition to ordinary linear mixed models applied in previous ecological studies (Segurado et al., 2018; Gutiérrez-Cánovas et al., 2019; Wu et al., 2019), we introduce novel compositional mixed models to understand the interplay

and relative influence of water chemistry and land cover stressors on the ecological response through trade-offs between them. Specifically, we address the following questions: (i) What is the association between P and diatom status in the context of multiple stressors in running waters? (ii) How do these stressor–response relationships vary between catchments? and (iii) What are the benefits of advanced statistical approaches to regulatory data analysis for catchment managers and how can they inform future P management strategies?

Materials and Methods
Data

In this work, we use the term *stressor* to mean an environmental factor (SI 1) that has an adverse impact on the ecological community (Kath et al., 2018) in terms of diatom response.

Ecological, water quality and hydrological data were obtained from the Scottish Environment Protection Agency (SI 1–2). Ecological monitoring data were provided for 88 locations across Scotland where continuous diatom sampling has taken place every 6 months in spring and autumn between January 2007 and September 2017. The data comprised observed and calculated TDIs and their EQR TDI (Kelly et al., 2008; UKTAG, 2014) for spring and autumn sampling.

Locations where diatom observations could be matched with water quality data at the nearest monitoring location within 200 m distance were retained, resulting in a dataset of 625 complete observations from 45 study catchments across Scotland (Fig. 1). Chemical parameters of interest included total P (TP), SRP, nitrate N (NO_3–N), nitrite-N (NO_2–N), ammonia-N (NH_3–N), suspended solids, and chloride (Cl). Total P was derived as a reduced phosphomolybdenum blue complex from a manual sulfuric acid–persulfate digest of unfiltered sample, while SRP represented the molybdate-reactive P determined from a <0.045-μm filtered sample. Analytical detection limits for TP were either 0.002 or 0.005 mg L^{-1} and for SRP either 0.008 or 0.009 mg L^{-1}, respectively. The different detection limits came from samples from different regions being handled by two laboratories. For 68 samples at the detection limit concentrations, this gave SRP/TP ratios >1. Since these apparent errors of SRP > TP occurred only with trace concentrations and in few observations, they did not adversely affect statistical models and were not further corrected.

For each monitoring location, the upstream contributing area was delineated using the ArcHydro tools in ArcGIS 10.2.1 and a 10-m or 50-m resolution digital elevation model, with topographic maps used to verify the results obtained through automatic delineation with digital elevation models. Proportion of arable, improved grassland, urban, woodland (including native and plantation) and seminatural (all types of unimproved grassland and dwarf shrub heath) land cover types were calculated for each catchment area in ArcGIS 10.2.1 based on the CEH Land Cover Map 2007 (Morton et al., 2011).

Hydrological characteristics of each study catchment were derived using dimensionless indices describing variability of streamflow in terms of distribution (ratio of high to low flows Q5:Q95; Jordan et al., 2005), seasonality (range of Pardé coefficients; Viglione et al., 2013), and oscillation (Richards–Baker Flashiness Index; Baker et al., 2004), as well as the base flow index.
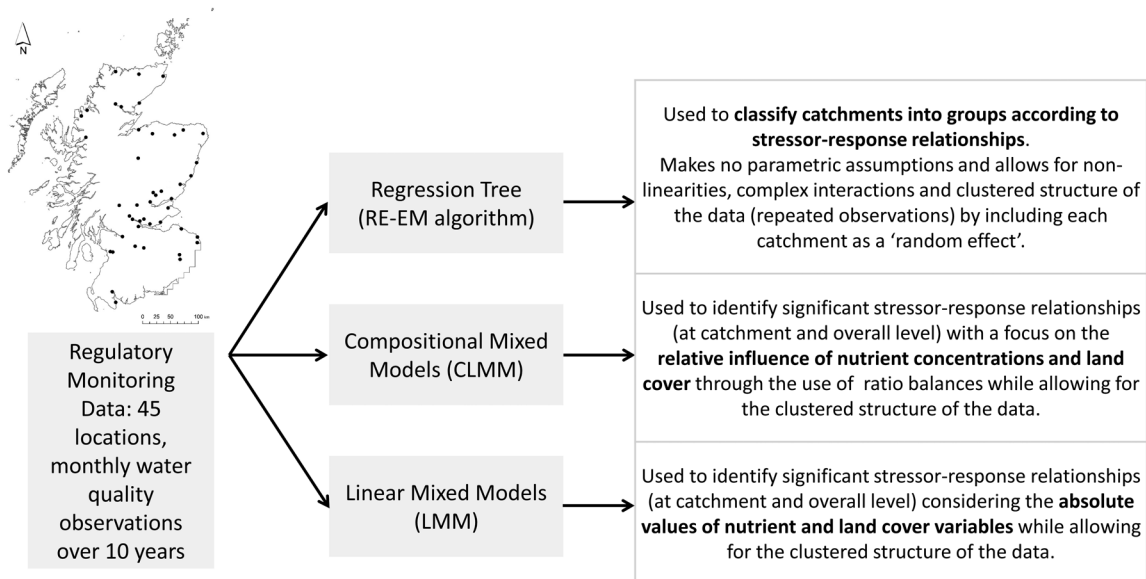
Fig. 1. Statistical modeling approaches applied to low-frequency regulatory data at 45 study sites in Scotland.

The ratio of high to low flows (Q5:Q95 ratio) relates the streamflow that is exceeded 5% of the days to streamflow with an exceedance frequency of 95%. Streamflow quantiles were calculated using the function fdc in the R-package hydroTSM (Zambrano-Bigiarini, 2015).

The Pardé coefficient (Pardé, 1947) relates long-term mean monthly streamflow to long-term mean annual streamflow. To convert the Pardé coefficient into one single value expressing seasonality (rather than 12 values, 1 for each month), Viglione et al. (2013) introduced the range of the Pardé coefficients, which is the difference between the maximum Pardé coefficient and the minimum Pardé coefficient.

The Richards–Baker Flashiness Index relates the difference between the streamflow of the current to the previous day as

$$ RBI = \frac{\sum_{i=1}^{n} |Q_i - Q_{i-1}|}{\sum_{i=1}^{n} Q_i} $$

where Q_i is the streamflow of the current day, Q_{i-1} is the streamflow of the previous day, and n is the number of observations.

The base flow index was derived from streamflow records using the function base flows implemented in the R package *hydrostats* (Bond, 2015).

All hydrological indices were calculated based on daily observed streamflow for the time period 2007 to 2016. Stream discharge was determined to regulatory standards, using a combination of stage-discharge relationships with stilling wells in the banks of natural channels as wells as control structures in other locations.

Modeled P source apportionment load estimates (kg yr⁻¹) from sewage treatment works (SWLOAD), septic tanks (STLOAD), combined storm overflows (CSOLOAD), urban (URLOAD), livestock (LSLOAD) and arable (ARLOAD) land cover types were obtained from the Scottish Environment Protection Agency as the output from the SAGIS source apportionment tool (Daldorph, 2017). These P source variables were

included as complementary to land cover variables, serving as a proxy for potentially differing bioavailability of P between the sources inherent within the broad land cover types (Stutter et al., 2014; Glendell et al., 2019).

Statistical Analysis
Data Preprocessing and Exploration

Data were visually screened for outliers and checked for normality. Chemistry data were log-transformed and standardized (*z*-scores), and EQR TDI data (originally defined in the [0, 1] interval) were arcsin transformed to better accommodate linearity and model residuals assumptions for principal component analysis (PCA) and ordinary linear mixed modeling. The regression tree was invariant to monotonic transformation of explanatory variables, and chemistry data in original units were considered to facilitate interpretation of values at the tree nodes. However, this was not the case for the response variable, and the tree was fitted to arcsine-transformed EQR TDI for consistency across methods (note that the endpoint values shown in Fig. 3 are back transformations, which approximate the corresponding average values on the original scale). Chemistry and land cover data received specific treatment for compositional mixed modeling as detailed below. Cases with EQR TDI = 1 (equating to 29 observations) were excluded to achieve homoscedasticity of model residuals. We applied PCA on *z*-transformed variables to the potential stressors to investigate the presence of main environmental gradients and correlations in the multivariate dataset.

Statistical Modeling

Formal statistical modeling was undertaken using three different modeling approaches (Fig. 1): regression trees for clustered data (RE-EM algorithm allowing for random effects), compositional linear mixed models (CLMM), and ordinary linear mixed models (LMM). For the linear mixed models, either compositional or ordinary, we considered two scenarios of alternative model structures to account for model structural uncertainty: one with all water chemistry variables, P source apportionment, hydrological variables, and land cover type distribution (Scenario

A) and another with only chemistry, P source apportionment, and hydrological variables (Scenario B). Statistical analyses and modeling were undertaken in the R system for statistical computing v3.4 (R Core Team, 2018).

A regression tree was fitted using the RE-EM algorithm as implemented in the *REEMtree* package in R (Sela and Simonoff, 2012) to understand potential differences in relevant stressors of diatom response between different catchment types, with sites included as a random effect to account for the repeated measurements within the 45 study catchments. Regression trees make no parametric assumptions and accommodate nonlinear relationships and complex interactions between variables (e.g., the same variable can intervene several times at different levels), which are represented as a hierarchical tree of optimal binary splits (nodes) according to values of the most relevant variable at each point. The RE-EM algorithm alternates iteratively the estimates of an ordinary regression tree and a linear mixed model. The splitting algorithm aims to maximize the reduction of the sum of squares at each node (Breiman et al., 1984). The linear mixed model part is fitted by restricted maximum likelihood. Tenfold cross-validation was used to prevent overfitting and prune the tree at each iteration. Splitting continued until the difference between the likelihoods of the linear models of two consecutive iterations was less than 0.001. The performance of the RE-EM regression tree model was assessed by computing R^2 and root mean square error (RMSE) from the actual and fitted values.

Compositional linear mixed models considered the nutrient concentrations and land cover proportions synergistically as compositional variables representing fractions or parts of a whole according to their units (mg L^{-1} and percentage land cover respectively). This concept implies that their values are not free to vary independently of each other and the total amounts are disregarded, with relevant information carried in the ratios between variables. Thus, instead of treating these variables separately, we used a compositional statistical approach (Aitchison, 1986; Pawlowsky-Glahn et al., 2015) to focus on their relative importance by working with log-ratios. This guarantees that the results are the same regardless of the scale of measurement of the variables. Following the procedure described in Palarea-Albaladejo et al. (2017) to define a compositional mixed model, a particular type of log-ratios, so-called balances (representing trade-offs between subsets of variables), were built according to the strength of the association or co-dependence between variables. These co-dependences were computed as the variance of their pairwise log-ratios as suggested by Aitchison (1986) and were graphically represented using compositional PCA biplots (Aitchison and Greenacre, 2002; Supplemental Fig. S4.1). They were used as input to perform R-mode Ward's clustering, which determined subsets of closely co-dependent compositional variables going into numerator and denominator of the log-ratio term of each balance (Supplemental Fig. S4.2 and S4.3). These balances were then used in place of the original nutrient and land cover variables as fixed effects in ordinary mixed models (Palarea-Albaladejo et al., 2017) and fitted as described below, along with the hydrological and P source apportionment covariates. Analytical tools from the R package *compositions* (van den Boogaart et al., 2018) were used to derive the balances.

Ordinary LMM (see, e.g., Zuur et al., 2009) fitted by restricted maximum likelihood allowed investigation of the relationship between explanatory variables specified as fixed effects and the ecological response, with sites specified as a random effect to allow for the clustered structure of the data (i.e., repeated observations) in each study catchment, using the *lme4* package in R (Bates et al., 2015). Unlike ordinary linear regression modeling, LMM accounted for random variability between sites and enabled estimates to be made at the individual catchment level as well as averaged over all catchments. All continuous variables were *z*-transformed to homogenize the scales of variation and to facilitate comparison of effect sizes between them.

Selection between alternative mixed models (CLMM and LMM) to explain EQR TDI was based on the Akaike information criterion (AIC) using maximum likelihood estimation (Burnham and Anderson, 2002). Relative variable importance (Supplemental Table S6) was determined by summing Akaike weights over all candidate models with up to three explanatory variables where the variable was included. Models were screened for collinearity, and only models with correlations between stressors lower than 0.6 were retained. Top models with delta AIC (AIC difference) < 2 and *r* < 0.6 were selected and then refitted using restricted maximum likelihood and averaged to obtain final model estimates. Model performance was evaluated using conditional R^2, intraclass correlation coefficients (ICCs) for mixed models (Nakagawa et al., 2017), and RMSE. The ICC measured the proportion of the variance explained by the site random effects and, hence, contributed to determine the adequacy of using random-effects models.

Results

What Is the Association between Phosphorus and Diatom Status in the Context of Multiple Stressors in Running Waters?

The first three principal components accounted for 67.70% of the total variance in the explanatory variables (Supplemental Table S3.1). All chemical parameters were positively correlated with PC1, which accounted for 33.89% of the variation. Arable, improved grassland and urban land cover types, as well as P loads from all sources, were positively correlated with PC1, while seminatural land cover was negatively correlated with PC1. Thus, PC1 represented a land cover and hydro-chemical gradient, with sites in good ecological status related more closely (but not exclusively) to a higher proportion of seminatural land cover, while sites in poor ecological status related more closely (but not exclusively) to higher concentrations of all constituent and P loads from all sources (Supplemental Fig S3.1). Nutrient concentrations were more strongly positively correlated with PC1 than loads, especially TP, which was more strongly correlated (0.834) than SRP (0.771) or N species (0.743 and 0.763). Conversely, seminatural land cover type was strongly negatively correlated with PC1 (−0.775).

Phosphorus loads from all sources other than arable were strongly positively correlated with PC2. Principal component PC3 represented a gradient of differentiated hydrological response, with the Richards–Baker Flashiness Index and Q5:Q95 correlated positively and baseflow index correlated negatively with this axis (Supplemental Table S3.1).

A ranking of explanatory variables obtained from compositional and ordinary mixed models according to variable importance in Supplemental Table S6 showed the overriding importance of seminatural land cover on the ecological response in Scenario A and the importance of P as the main chemical stressor of ecological response in Scenario B. These ranks are not necessarily consistent with the stressors selected in the best approximating CLMM and LMM below, as they take into account a large number of models with different combinations of variables (Segurado et al., 2018).

Compositional PCA biplots represent visually the structure of co-dependence within the nutrient and land cover compositions (Supplemental Fig. S4.1). For the nutrient concentrations (70.68% total variance explained by PC1 and PC2), NO_3–N concentrations were the least associated to the others, whereas NH_3–N and NO_2^-–N concentrations, as well as TP and SRP concentrations, were highly proportional (indicated by the proximity of the corresponding arrowheads in Supplemental Fig. S4.1a). Regarding land cover proportions (91.62% total variance explained by PC1 and PC2), arable and urban types were the most independent, whereas seminatural and woodland land cover were more related (Supplemental Fig. S4.1b). A CLMM considering all stressors (Scenario A) showed that the diatom response was significantly negatively associated with the trade-off between TP and SRP on the one hand and NH_3, NO_2^-, Cl^-, and suspended solids on the other hand (represented by balance b_2; Supplemental Table S4.1; Supplemental Fig. S4.2; $p = 0.034$), as well as to that between NH_3–N and NO_2^--N (balance b_6; Supplemental Table S4.1; Supplemental Fig. S4.2; $p = 0.017$). Diatom response was also positively associated with the land cover balance l_1 related to the contrast of seminatural and woodland versus arable, grassland, and urban land cover types (Supplemental Table S4.1; Supplemental Fig. S4.3; $p < 0.001$). In Scenario B, the nutrient balances b_2 and b_6 were the only statistically significant terms related to the ecological response ($p = 0.022$ and $p = 0.026$ respectively).

Using ordinary LMM in Scenario B (where land cover was not included in the analysis), concentration of TP and NO_3–N were significantly negatively associated to EQR TDI with a comparable effect size, along with season (Supplemental Table S5.3) ($R^2 = 0.60$, ICC = 0.42, RMSE = 0.14). To explore the temporal aspect of the impact of TP and NO_3–N on EQR TDI, an extended model that included interactions between TP and season and NO_3–N and season was fitted (Supplemental Table S5.4; Fig. 2c–d) ($R^2 = 0.60$, ICC = 0.42, RMSE = 0.14). It showed that the negative effect of TP on EQR TDI did not vary statistically significantly by season ($p = 0.49$; Fig. 2c) but that the negative effect of NO_3–N concentration did ($p <$ 0.001; Fig. 2d), being significantly greater in the autumn than in the spring (estimated slope −0.08 vs. −0.02).

The hydrological catchment characteristics were not statistically significant predictors of the ecological response in any of the scenarios.

How Do the Stressor–Response Relationships Vary between Catchments?

The RE-EM regression tree ($R^2 = 0.64$, RMSE = 0.15) indicated a strong negative relationship between TP and diatom response. Low EQR TDI (average EQR TDI = 0.58) can be expected in catchments with TP concentrations >0.035 mg L^{-1} and urban land cover <5% (Group A in Fig. 3). Values of ~0.67 on average for EQR TDI can be expected where TP concentrations are >0.035 mg L^{-1} and arable land cover exceeds 27% (Group B), whereas EQR TDI values of ~0.76 can be expected where arable land cover is <27% (Group C). In catchments with TP concentrations <0.035 mg L^{-1} and >12% woodland cover, the average EQR TDI value was 0.74 (Group D). The highest EQR TDI (average value = 0.82) can be expected in catchments with TP concentrations <0.035 mg L^{-1} and woodland cover <12% (Group E).

Ordinary LMMs were used to characterize the relationship between EQR TDI and absolute nutrient concentrations, SRP loads, hydrological indices, and land cover (Scenario A) in individual catchments, as well as an overall relationship across all catchments. Averaged top-five LMMs in Scenario A showed that SRP, TP, and urban land cover were negatively related to the diatom response, whereas seminatural land cover was instead positively related. However, only land cover variables together with season were statistically significant (Supplemental Table
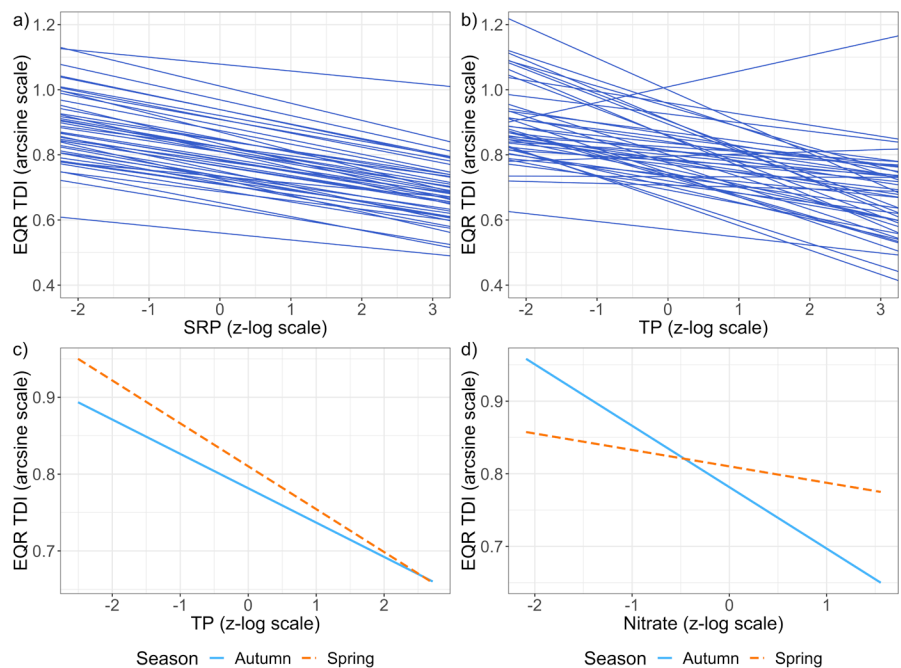

Fig. 2. Estimated linear mixed model (LMM) slopes in scenario A for (a) soluble reactive P (SRP) and (b) total P (TP) showing greater variability in the stressor–response relationship between TP and Trophic Diatom Index Environmental Quality Ratio (EQR TDI) than between SRP and EQR TDI in studied catchments. Estimated interaction effects between (c) TP and season and (d) NO_3–N and season on the EQR TDI from averaged linear mixed models (LMM) in Scenario B.
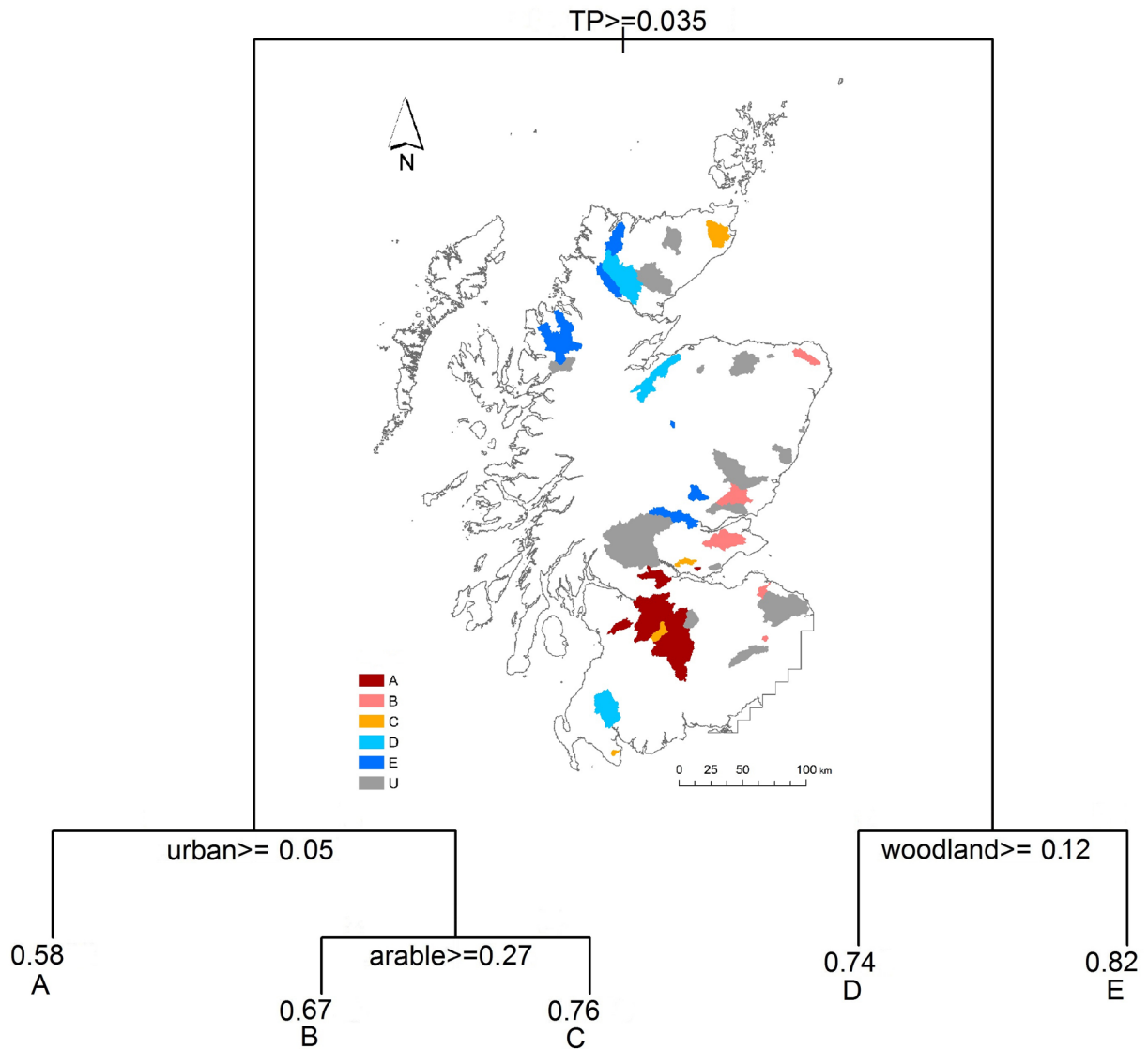
Fig. 3. Regression tree from 596 observations of water quality, discharge, land cover, and P apportionment loads. The endpoints of the tree (leaves) show average Trophic Diatom Index Environmental Quality Ratio (EQR TDI) according to splits (tree branches) of the variables at optimal threshold values. If condition is satisfied, the split follows the tree branch to the left; if condition is false, the split follow the tree branch to the right. The map shows the spatial distribution of the predicted groups. Note that a U group was added to refer to an undefined catchment group where the observations from the study catchment fell into two possible end points. TP, total P.

S5.1), likely because SRP and TP were closely correlated (R^2 = 0.62, ICC = 0.22, RMSE = 0.15).

As SRP and TP measurements were highly correlated, the top-five models were also examined separately (Supplemental Table S5.2). The five models (indicated below using numbers 1–5) produced statistically significant results for the following stressors:

1. SRP, seminatural and urban land cover (R^2 = 0.62, ICC = 0.22, RMSE = 0.15).
2. SRP, season, and seminatural land cover (R^2 = 0.61, ICC = 0.25, RMSE = 0.15).
3. TP, seminatural and urban land cover (R^2 = 0.65, ICC = 0.24, RMSE = 0.14).
4. TP, season, and seminatural land cover (R^2 = 0.64, ICC = 0.27, RMSE = 0.14).
5. Season, seminatural and urban land cover (R^2 = 0.64, ICC = 0.24, RMSE = 0.14).

These models accounted for a similar amount of EQR TDI variation (R^2 = 0.61–0.65). Urban land cover, SRP, and TP had negative associations with EQR TDI, while seminatural land cover had a positive association with EQR TDI. In most models, seminatural land cover had the greatest effect size on the diatom response, as indicated by the standardized model coefficients (Supplemental Table S5.2). Note that the relationship between TP and EQR TDI was estimated to be more variable between study catchments than the relationship between SRP and EQR TDI (see regression slope estimates by catchment from the fitted linear mixed models in Fig. 2a, b). The slopes for TP indicate potentially stronger but variable control of TP on the ecological status, affected by site-specific catchment characteristics; whereas the response to SRP was more homogenous between locations and less affected by site-specific effects. The median ratio of SRP/TP concentrations for individual observations was 0.58 (min. = 0.06, max. = 3.63, including the 11% of values with ratios >1 associated with trace concentrations at or

near the detection limits) (see Supplemental Tables S2.1–S2.3 for all stressor gradient lengths).

Discussion

What Is the Association between Phosphorus and Diatom Status in the Context of Multiple Stressors in Running Waters?

Principal component analysis was a first step in the process of disentangling the association between nutrients, SRP loads, hydrological variables, land cover type, and the ecological response. All chemicals were positively correlated with the first PCA axis. Thus, compositional analysis was useful to understand which pollutant ratios were most influential on EQR TDI. From the CLMM approach, we concluded that the combined ratio of TP and SRP to other nutrients (balance b_2) and the trade-off between NH_3–N and NO_2^--N (balance b_6) were the main chemical stressors negatively influencing EQR TDI in both scenarios considered, with the latter having a stronger association (Supplemental Tables S4.1 and S4.2). Balance b_6 may be indicative of point-source pollution, including domestic effluent discharges from septic tanks (Richards et al., 2016), suggesting that these P sources may be particularly important in affecting ecological status. When land cover was included (Scenario A), the influence of the combined ratio of seminatural and woodland land cover types versus arable, grassland, and urban land cover types (balance l_1) was also highly statistically significant ($p < 0.001$), with the size of the association being comparable to balance b_6 but in a positive direction. These results suggest that while P species are significantly negatively linked to ecological status, the anoxic conditions indicated by the NH_3–N to NO_2^--N balance (likely linked to organic pollution) have an equally important negative relationship, ameliorated by the presence of seminatural habitats (balance l_1). Therefore, these combined relationships should be considered when setting mitigation targets.

Linear mixed models with nutrients, source apportionment, and land cover type (Scenario A) identified concentration of TP and SRP as the main chemical stressors negatively influencing the diatom status, although seminatural and urban land cover types had the strongest positive and negative relationship, respectively. These models accounted for up to 65% of the variability in EQR TDI.

Identifying which operationally defined P fraction best represents bioavailable P, and is more closely related to the ecological response, is still subject to debate in the scientific literature (Li and Brett, 2015). While annual mean SRP concentration is used for setting water quality targets in running waters in the United Kingdom, in the United States TP is used to link P to the ecological response (Jarvie et al., 2013; Stevenson, 2014). In this study, the combined evidence from different modeling approaches showed that TP was potentially more closely related to EQR TDI than SRP (see Fig. 3, Supplemental Table S5.2), consistent with other studies that found TP to be the main predictor of diatom responses (Herrero et al., 2018; Munn et al., 2018). This may be because TP accounts for additional P fractions such as particulate P attached to sediment particles as well as soluble unreactive P, both of which can contribute to the pool of bioavailable P (Baker et al., 2014; Stutter et al., 2014). In addition,

TP may also be associated with other fine sediment-bound contaminants that could affect ecological status, such as through physical effects or as a vector for metals and herbicides (Munn et al., 2018). However, the dual role of SRP and TP apparent from CLMM indicates that neither fraction, typically quantified in regulatory water quality monitoring schemes, fully accounts for bioavailable P (Ellison and Brett, 2006; Ekholm et al., 2009) and may either over- or underestimate the ecological response.

Formal modeling in the present study did not find a statistically significant link between loads of SRP from different sources and the ecological response in running waters, supporting the finding that in running waters, loads are indeed less relevant to ecological status than are nutrient concentrations (Stamm et al., 2014). However, it has to be noted that these loads were derived from a source apportionment model. They might then be subject to some error that might have some influence on our results.

In linear mixed models without land cover (Scenario B), NO_3–N concentration had the strongest negative relationship with EQR TDI alongside TP (Supplemental Table S5.3). The importance of both P and N in management of eutrophication in running waters was highlighted previously (Cha et al., 2016; Dodds and Smith, 2016) as both N and P can enhance the rates of primary production and lead to impairment of water quality (Stevenson, 2014; Paerl et al., 2016; Wagenhoff et al., 2017a, 2017b; Crnkovic et al., 2018; Jarvie et al., 2018). Targeting of both of these nutrients may be particularly important in upland low alkalinity rivers that are naturally both N and P limited (Jarvie et al., 2018). This study found that NO_3–N had a stronger negative relationship with EQR TDI in autumn than in spring, likely due to N limitation on primary production during summer months. Therefore, minimizing NO_3–N losses during the growing season should be a key part of mitigation strategies.

Seminatural land cover was estimated to be have a stronger positive influence on EQR TDI than the negative influence of either TP or SRP (Supplemental Tables S4.1, S5.1, S5.2, S6), and combined evidence from different modeling approaches shows that land cover had an overriding influence on the ecological response, which is in line with other studies that also found a hierarchy of stressors from land cover, followed by physicochemical (e.g., sediment and nutrient concentrations) and hydromorphological (e.g., river bed and riparian corridor characteristics) variables (Villeneuve et al., 2018). Here, seminatural land cover is likely acting as a proxy for other factors (Segurado et al., 2018), such as varying bioavailability of P fractions (Ellison and Brett, 2006; Prestigiacomo et al., 2016; Stutter et al., 2018), river morphology, riparian and/or aquatic habitat structure, and absence of toxic contaminants (e.g., herbicides). In addition, the bioavailability of P forms has been shown to vary between 12 and 73% for TP and between 6 and 81% for particulate P in catchments dominated by different land cover types (Ellison and Brett, 2006; Egemose and Jensen, 2009; Poirier et al., 2012; Baker et al., 2014). Some land cover types, such as agriculture and urban land use, make TP more bioavailable (Ellison and Brett, 2006; Prestigiacomo et al., 2016), while TP from seminatural land cover is likely to be less bioavailable (Stutter et al., 2018).

Woodland was not directly related to the water pollution gradient in PCA (Supplemental Fig S3.1, Supplemental Table S3.1) and did not appear to have a significant association with EQR TDI according to the fitted linear mixed model. However,

the RE-EM regression tree indicated a potential negative impact of woodland on the ecological outcome. These contrasting findings may reflect confounding relationships that could not be discerned from the available data in the present study, such as those from native versus plantation woodland, specific woodland management practices, and the spatial arrangement (riparian vs. catchment, distance to stream) at which positive or negative influence of woodland may become apparent (Soulsby et al., 2002; King et al., 2005; Roberts et al., 2016).

How Do Stressor–Response Relationships Vary between Catchments?

The linear mixed model regression slopes for TP varied more between study catchments than for SRP (Fig. 2a, b), pointing toward a differentiated stressor–response relationship between TP, SRP, and river ecology in different catchment types. This may be related to a number of complex interactions and "catchment resilience" factors such as river morphology, aquatic habitat structure, and riparian shading, as well as different bioavailability of P fractions, pointing toward a need for different prioritization of management interventions in catchments with different characteristics (Doody et al., 2016).

In this study, both nutrients and catchment land cover were significantly associated with ecological status. The RE-EM regression tree identified TP concentration of 0.035 mg L^{-1} as the primary breakpoint in the dataset, distinguishing between catchments in good and mixed ecological status (Fig. 3). This breakpoint appears plausible, as it lies within the range of previously reported limiting P concentrations in British streams between 0.01 and 0.05 mg L^{-1} (Jarvie et al., 2018) and coincides with a threshold of 0.03 mg L^{-1} at which significant change in diatom assemblage was observed in mesocosm experiments (Bowes et al., 2012; McCall et al., 2017).

However, the RE-EM regression tree analysis also indicated that urban land cover >5% and arable land cover >27% had a detrimental association with the ecological response, with the lowest EQR TDI scores likely to be expected in catchments with a higher proportion of urban land cover (Fig. 3). The negative association with urban land cover was greater than either TP, SRP, or season (Supplemental Tables S5.1, S5.2). Other studies also found urbanization to be strongly negatively linked to aquatic ecology (King et al., 2011; Teittinen et al., 2015; Golden et al., 2016; Herrero et al., 2018). This negative association with urban land cover may be linked to additional pollutants associated with surface runoff as well as more bioavailable nutrients from point sources (Ekholm and Krogerus, 2003; Ekholm et al., 2009; Richards et al., 2016; Stutter et al., 2018) likely to have a greater impact on river ecology (Shore et al., 2017).

What Are the Benefits of Advanced Statistical Approaches to Regulatory Data Analysis for Catchment Managers, and How Can They Inform Future Phosphorus Management Strategies?

Recent studies applying advanced statistical approaches to understand the interactions between multiple stressor gradients on ecological outcomes in real-world catchments (e.g., Feld et al., 2016; Gieswein et al., 2017; Villeneuve et al., 2018; Segurado et al., 2018; Gutiérrez-Cánovas et al., 2019; Wu et al., 2019; Rankinen et al., 2019; Meissner et al., 2019) typically evaluated the hierarchy and compared the weight and effect size of individual stressors and stressor interactions (Segurado et al., 2018). As models are imperfect representation of reality based on limited observational data, different modeling approaches commonly result in different answers. Furthermore, ecological recovery trajectories from poor condition are subject to many interactions and confounding factors that are difficult to detect (Jarvie et al., 2013). Thus, a combined modeling approach, such as the one presented in this study, offers insight into the data available from different perspectives and facilitates prioritization of stressors and mitigation strategies based on the strength of combined evidence.

Segurado et al. (2018) suggested that each catchment needs to be understood as a specific system, with specific stressor interactions along environmental gradients. Advanced statistical modeling approaches, such as those used in this study, allow for this kind of catchment-specific analysis. Here, the regression tree model allowed understanding the stressor hierarchy that leads to different ecological states in groups of catchments, while the mixed effect models enabled understanding how the association with TP varies between catchments. We therefore recommend that regulatory agencies periodically commission a reanalysis of the growing body of standardized regulatory data using a portfolio of advanced statistical tools to understand how multiple stressors change along environmental gradients in their respective catchments and thus allow catchment-specific targeting of mitigation measures. To optimize catchment interventions, we recommend that future P mitigation should be addressed in concert with other stressors, not just P in isolation, with catchment-specific targets. In addition, application of these advanced statistical approaches to high temporal-resolution data from catchment observatories across multiple regions may offer further insights by allowing testing of the influence of temporal data resolution on the modeled results (Hipsey et al., 2015).

The additive nature of the stressor–response relationships found in linear mixed model analysis implies that the chemical and land cover stressors could be addressed separately (Herrero et al., 2018). However, while management that addresses the stressor with the largest estimated association will likely have the greatest immediate benefit (Nõges et al., 2016), targeting all of the stressors in a concerted way would be the most meaningful strategy (Jarvie et al., 2013), an approach supported by the CLMM analysis, which recognizes that the chemicals and the land cover variables are intrinsically interrelated. In this context, seminatural land cover consistently had the greatest positive association with ecological status. While it is unrealistic to aim to increase the extent of seminatural land cover in catchments where other ecosystem services, especially food production, are a priority (Doody et al., 2016), it may be possible to strategically increase this type of land cover in specific landscape locations in a cost-effective way. To date, analyses of the influence of spatial targeting of land cover change interventions on water quality in river catchments are scarce (Hashemi et al., 2016; Dupas et al., 2019). Therefore, further research is needed to inform the optimal spatial arrangement of land cover change interventions and

their link to river ecology (McCluney et al., 2014) in different catchment typologies across scales.

It has been suggested that current mitigation policies may not be sufficient to achieve good ecological status of inland waters and that targeted land cover change may need to be considered (McDowell et al., 2016), especially in vulnerable landscapes where some production systems may be inherently unsustainable, regardless of the mitigation measures that can be adopted (Sharpley et al., 2018; Le Moal et al., 2019). While land cover change may appear to be a radical proposition in intensively farmed productive landscapes, targeting of measures based on catchment vulnerability may increase the efficiency of mitigation measures in a cost-effective way (Bol et al., 2018; Hashemi et al., 2016). Such landscape redesign could include a shift to heterogeneous landscape mosaics (Stutter et al., 2012) and mixed land use farming (McDowell et al., 2016), perhaps as part of climate-change adaptation, redistribution of polluting land uses away from critical source areas (Hashemi et al., 2016) or targeting of interventions to headwater catchments with lowest resilience and highest source properties (Bol et al., 2018). Thus, to repair this aspect of the broken P cycle, this work shows that for optimal future mitigation, future regulatory efforts should target P impacts alongside multiple chemical and land use stressors, tailored to catchment-specific responses.

Supplemental Material

The supplemental material includes S1, summary of data used in the study; S2, summary statistics; S3, PCA results; S4, CLMM results; S5 LMM results; and S6, comparison of relative stressor importance hierarchy.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgments

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