Landscape spatial configuration influences phosphorus but not nitrate concentrations in agricultural headwater catchments

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Abstract

Landscape organized (or structured) heterogeneity influences hydrological and biogeochemical patterns across space and time. We developed landscape indices that describe the spatial configuration of nutrient sources and sinks as a function of their hydrological distance to the stream (lateral dimension) or to the outlet (longitudinal dimension) and their intersection with flow-accumulation areas. Using monthly nitrate, total phosphorus (TP), soluble reactive phosphorus (SRP) and daily discharge (Q) data from 221 rural catchments (1-300 km²) from 2010-2020, we observed higher variability in flow-weighted mean concentrations in smaller catchments than in larger ones. The variability in landscape configurations also decreased with increasing catchment size. A landscape configuration index, calculated as mean arable land use weighted by spatial data on hydrological distance and flow accumulation, improved prediction of TP and SRP, but not nitrate, compared to the unweighted mean arable land use. We conclude that landscape configuration influences phosphorus transfer more than nitrate transfer, and that flow-accumulation zones and riparian areas are critical source areas for TP and SRP, respectively. By contrast, landscape spatial configuration in the lateral (upslope-downslope) and longitudinal (upstream-downstream) dimensions did not have an identifiable influence on nutrients temporal dynamics. The indices developed in this study can help design landscapes that minimize diffuse phosphorus losses to streams and show that landscape management is not a first order control for nitrate losses.

Keywords: landscape; catchment; nutrient; agriculture; nitrate; phosphorus

1. Introduction

Landscape spatial organization is often assumed to influence hydrological and biogeochemical patterns across space and time. Topography drives the spatio-temporal dynamics of water flowpaths and residence times (Beven and Kirkby, 1979). Topography also influences the spatial arrangement of landscape elements (e.g. agricultural fields, buffer strips, hedgerows, ditches) that can act as sources or sinks for different forms of soluble and particulate nitrogen and phosphorus (P). The spatial arrangement of polygonal, linear or punctual landscape elements is called landscape spatial configuration. Interacting influences of topography on hydrological and landscape patterns thus result in spatially organized patterns in biogeochemical processes, including processes such as nutrient mobilization, retention or removal (Bernhardt et al., 2017; Covino et al., 2022; Krause et al., 2017).

Knowledge of topography-driven patterns in hydrological and biogeochemical hotspots at the catchment scale can help design landscapes that minimize nutrient losses to streams while maintaining an acceptable level of agricultural production (Casal et al., 2018; Doody et al., 2016; McDowell et al., 2014). This includes the use of techniques for mapping critical source areas (CSA) (i.e. areas where most diffuse pollution originates, and hence outside of which landscape elements considered as nutrient sources should be placed) and optimal placement of buffer zones (Dorioz et al., 2006; Schoumans et al., 2014).

Topographic indices derived from Digital Elevation Models (DEM) are often used to locate these areas (e.g. Djodjic and Villa (2015); Lane et al. (2009)). High uncertainties still exist in delineating CSAs, as validating them relies on walkover surveys of observable features such as erosion marks, which are tedious to perform (Reaney et al., 2019). Several studies have attempted to evaluate "expert-based" CSA delineation with water-quality data across contrasting catchments, but they often relied on few catchments (Djodjic and Markensten, 2019; McDowell and Srinivasan, 2009; Shore et al., 2014; Thomas et al., 2016). As an alternative, "data-driven" methods can assess the influence of landscape spatial configuration on nutrient export (Casquin et al., 2021; Peterson et al., 2011; Van Sickle and Johnson, 2008). These methods use one or several topographic indices as weighting functions of a land-use class considered as a nutrient source (typically agriculture or arable land use) to assess whether a topography-weighted land-use percentage predicts nutrient concentrations better than an unweighted land-use percentage. A significant improvement in predicting them for a large number of catchments is interpreted as landscape spatial configuration influencing nutrient losses, and the topography-weighted function can be used to delineate CSAs (Casquin et al., 2021). Such topographic indices typically combine flow-distance metrics, either to the stream or to the outlet, and flow-accumulation metrics (Peterson et al., 2011; Staponites et al., 2019, Zampella et al., 2007) and may involve one or more calibrated coefficients (Casquin et al., 2021; Van Sickle and Johnson, 2008; Walsh and Webb, 2014).

The influence of landscape structured heterogeneity on biogeochemical and hydrological processes may also influence the temporal dynamics of nutrient concentrations, which are important to consider when evaluating ecological impacts (Bol et al., 2018; Stamm et al., 2014). According to the concept of hydrological connectivity, different parts of catchments contribute differently depending on flow conditions: during the high-flow season or a runoff event, shallow flowpaths become active, while the contribution to flow of areas distant from the river network or located most upstream increases (Jencso et al., 2009; Zimmer and McGlynn, 2018). These three components of connectivity are termed vertical (shallow vs deep), lateral (upslope vs downslope) and longitudinal connectivity (upstream vs downstream). Using a physically-based parsimonious model, Musolff et al. (2017) showed that a major driver of dilution, enrichment and constant concentration-discharge patterns (a metric of concentration temporal dynamics) was structured heterogeneity of sources in relation to their hydrological distance to the outlet. Their virtual experiments, however, did not identify which dimension of structured heterogeneity (vertical, lateral or longitudinal) in source gradients were the most influential. Most studies interpreting concentration-discharge relationships as a function of structured heterogeneity of sources focus on the vertical dimension, and several of them support this hypothesis with data (e.g. Botter et al. (2020); Ebeling et al. (2021b); Stewart et al. (2022)). Others have assumed an influence of lateral gradients in sources on concentration temporal dynamics, such as when land use intensity in the riparian zone differs from that in the upslope part of the catchment (Musolff et al., 2021; Strohmenger et al., 2021), or an influence of longitudinal gradients, such as when land use and/or hydrology in upstream sub-catchments differ from those in the downstream part of the catchment (Dupas et al., 2021; Winter et al., 2021).

The research question of the present study was: Does the landscape spatial configuration influence nutrient concentrations and dynamics in headwater streams? To address this question, we i) characterized the landscape spatial configuration in 221 headwater catchments (i.e. the spatial configuration of arable land in the lateral and longitudinal dimension); ii) analysed correlations between a landscape configuration index and flow-weighted mean concentrations of nitrate, soluble reactive P (SRP) and total P (TP); and iii) explored relationships between indices of landscape spatial configuration and the slope of the concentration-discharge relationship.

Nitrate, SRP and TP are the nutrients most commonly monitored in regulatory surveillance programmes for the European Union Water Framework Directive, due to their role as factors that control eutrophication (Le Moal et al., 2019). The study area encompasses the Brittany region, western France, where a large number of small (<300 km²) and independent headwater catchments are monitored monthly using the same protocol (Guillemot et al., 2021). The study area spans large gradients in land use, topography, annual runoff (section 2.1.) and has high variability in nutrient concentration dynamics, but no large discontinuities in physiographic properties as would occur if using a national or continental database (Frei et al., 2020). Such discontinuities (e.g. contrasting geology) would influence nutrient concentration dynamics greatly and potentially mask the effect of the landscape spatial configuration that we wanted to distinguish (Dupas et al., 2020; Guillemot et al., 2021). Finally, the contribution of diffuse agricultural pollution to nutrient loads is particularly high in this region (Legeay and Gruau, 2014).

2. Material and methods

2.1. River monitoring data

The study area of Brittany (27,000km², Figure S1) is located in the Armorican Massif, which consists mainly of igneous and metamorphic rocks (schist, micaschist, granite, Fig S2), and has a relatively flat topography with elevation ranging from 0-385 m above sea level. The area has a temperate oceanic climatic, with mild temperatures (12°C on average) and a rainfall gradient of 700-1300 mm from east to west. Its hydrology is driven mainly by the dynamics of shallow groundwater that develops in the weathered rock aquifer. It has a marked seasonality, the hydrologically effective rainfall being the highest in winter. Overland flow is moderate and generated mainly in saturated areas. The wet conditions and relatively impervious bedrock lead to a high river density given the temperate oceanic climate (1 $km.km^{-1}$), and to the development of hydromorphic soils along the riparian zone that cover nearly 20% of the land area (Berthier et al., 2014). Agriculture represents 60% of the land use and is particularly intensive due to the regional specialization in mixed crop-livestock farming with high livestock densities. Previous studies have shown that diffuse agricultural sources represent >95% of nitrate and *ca.* 70% of P loads in rivers (Dupas et al., 2013; Legeay and Gruau, 2014).

We selected 221 independent headwater catchments (1-300 km^2, table S1) in which water quality was monitored as part of the EU Water Framework Directive, and made publically available via https://naiades.eaufrance.fr/. The water-quality parameters studied here were nitrate, SRP and TP. As water quality was typically monitored on a monthly basis, we calculated water-quality metrics when at least 40 concentration data points were available during the 2010-2020 study period. This selection criterion resulted in 221, 186 and 185 catchments for nitrate, SRP and TP, respectively. Because existing discharge monitoring stations in Brittany are not necessarily located at the water-quality monitoring points, we used the geomorphology-based SIMFEN model to estimate daily discharge at the outlet of each of our study catchments (de Lavenne and Cudennec, 2019). Developed for Brittany, SIMFEN predicts discharge in ungauged catchments by transposing hydrographs from neighbouring gauged 'donor' catchments by convoluting a "net rainfall" (i.e. the water flowing through the hillslope-river interface) through the river network of the ungauged catchments (de Lavenne and Cudennec, 2019).

The metrics used to describe nutrient concentrations and dynamics were the flow-weighted mean concentration (FW-nitrate, FW-SRP, FW-TP), the slope of the linear log(concentration)-log(discharge) relationships and the ratio of the coefficient of variation of concentration to that of discharge (CVratio). Concentrations were calculated as flow-weighted means rather than ordinary arithmetic means to increase the contribution of data points during high-flows (when diffuse sources are dominant) and decrease the contribution of data points during low-flows (when point sources and in-stream processes may play a larger role). The slope of the linear log(concentration)-log(discharge) relationship and the CVratio are commonly used variables to characterize nutrient export regimes and export patterns (Musolff et al., 2015; Liu et al., 2022).

2.2.Landscape indices

We used two categories of landscape indices, to assess the influence of landscape spatial configuration on mean nutrient concentrations and seasonal dynamics. The first was the landscape configuration index (Casquin et al., 2021; Peterson et al., 2011), which aims to predict flow-weighted mean concentrations of nitrate, TP and SRP as a function of the distance of their sources to the stream and their intersection with flow-accumulation zones. The second category of landscape indices consisted of two metrics that describe the spatial configuration of nutrient sources in the lateral (upslope-downslope) and longitudinal (upstream-downstream) dimensions. The lateral and longitudinal configuration indices aim to test the hypothesis that the spatial arrangement of sources in those dimensions influences nutrient dynamics. For both categories of landscape indices, we considered the configuration of arable land as a nutrient source, as we selected study catchments in which diffuse agricultural contamination is the dominant source of contamination in rivers (Guillemot et al., 2021).

The landscape configuration index (LCI) was calculated as a single value for each catchment, as a weighted-mean percentage of arable land use. The weighting function is a topographic index that combines two variables derived from a DEM and two coefficients to optimize (a and b):

$$LCI(a,b) = \frac{\sum_i \left(\frac{Flowacc_i^a}{LatDistance_i^b} * arable_i\right)}{\sum_i \frac{Flowacc_i^a}{LatDistance_i^b}} \quad [1]$$

where, for each pixel "i" in a given catchment, "$flowacc_i$" is the flow accumulation (i.e. the drainage area of each grid cell), "$LatDistance_i$" is the hydrological distance to the stream and "$arable_i$" is 1 if the land-use type is arable or 0 if not. For (a=0, b=0), the index equals the percentage of arable land-use, while for (a=1, b=0) or (a=0, b=1) it equals the percentage of arable land-use weighted by "flowacc" alone or "1/LatDistance" alone, respectively.

We varied a and b to maximize the Spearman's rank correlation between LCI(a,b) and the flow-weighted mean nitrate, TP and SRP concentrations of the study headwaters. We varied a from 0-6 and b from 0-8, with an increment of 0.1. We restricted the exploration space for a and b so that the weight of the top 5% of pixels could not exceed 95% of the total weight in the region. This avoided finding optimal coefficient values that would correspond to an unrealistic situation in which only a few pixels would contribute nearly all the nutrient flux. This approach resulted in 4941 calculations of LCI(a, b), of which 2169 met the latter condition and whose correlations with the flow-weighted mean concentrations were analysed. We considered that landscape spatial configuration had an influence if it predicted flow-weighted mean concentrations better than the land use composition did (i.e. if at least one pair (a, b) resulted in LCI(a,b) > LCI(0,0) +0.1). We then examined the top 50 optimal (a, b) to assess the relative influence of flow accumulation and hydrological distance to the stream in determining CSAs. When successfully calibrated, the LCI weighting function $\sum_i \frac{Flowacc_i^a}{LatDistance_i^b}$ can be used as a nutrient export risk map and we considered pixels above the 90th percentile of this function to represent CSAs.

The lateral and longitudinal configuration indices were calculated as a single value for each catchment as follows:

$$LatIndex = \frac{\sum_i \left(\frac{1}{LatDistance_i} * arable_i\right)}{(\sum_i \frac{1}{LatDistance_i}) * mean(arable_i)} \quad [2]$$

$$LongIndex = \frac{\sum_i \left(\frac{1}{LongDistance_i} * arable_i\right)}{(\sum_i \frac{1}{LongDistance_i}) * mean(arable_i)} \quad [3]$$

where, for each pixel "i" in a given catchment, the variables "$LatDistance_i$" and "$arable_i$" are the same as in [1] and "$LongDistance_i$" is the longitudinal distance from the entry point to the stream to the catchment outlet. Because of the normalization by mean(arable), LatIndex >1 indicates that arable fields are located more downslope, i.e. near the stream network, while LatIndex <1 indicates that arable fields are located more upslope. Similarly, LongIndex >1 indicates that arable fields are located more downstream, i.e. near the catchment outlet, while LongIndex <1 indicates that arable fields are located more upstream. We analyzed correlations between LCI(a, b) and the flow-weighted mean concentrations of nitrate, SRP and TP to address research objective (ii), and we analyzed correlation between LatIndex, LongIndex and the log(concentration)-log(discharge) slopes to address research objective (iii).

2.3. GIS processing

Calculating the landscape indices requires a DEM raster, a map of arable land use and a river network. We generated the spatial data necessary to calculate the indices using ArcGis 10.8 (ESRI, 2021) and we performed the raster calculations in R (R Core Team, 2021).

We used a 25 m resolution DEM (BD ALTI, IGN 2018) that served as a reference layer for the rasterization and alignment of the river network and arable land-use data. The river network data came from the BD TOPAGE (IGN, 2021), while the reference spatial data for France and the arable land-use data came from the national Land Parcel Identification System (LPIS). In the LPIS, each parcel identified as arable at least once from 2010-2020 was assigned a value of arable = 1 and the rest arable = 0. Thus, agricultural land cover classes such as permanent grassland and orchards were not considered as sources, but temporary grassland in rotation with row crops was. This binary classification of land-use types may appear arbitrary, but attributing intermediate values to multiple land cover types would require strong assumptions about their respective influence on nutrient export or a computation-intensive calibration step. Furthermore, previous studies in the same region found a stronger correlation between nutrient concentrations and arable land use than total agricultural land use (Guillemot et al., 2021).

The DEM was hydrologically corrected by 'filling' depressions on hillslopes and 'burning' the river network. We used a multiple flow direction algorithm (Qin et al., 2007) to determine flow accumulation (log-transformed) and the flow distances. In the ArcGis 10.8 'Spatial analyst/Hydrology' toolbox, we used 'Flow Distance' to calculate LatDistance and the difference between the outputs of 'Flow Distance' and 'Flow Length' to calculate LongDistance. To calculate the landscape indices in R, we assigned the value 'NA' to pixels that intersected the river network.

3. Results and discussion

3.1. Variability in nutrient concentration dynamics and landscape spatial configuration

The 221 study catchments spanned a wide range of flow-weighted mean nutrient concentrations: nitrate ranged from 3.0-61.1 mg.l^{-1} (mean=29.5mg.l^{-1}), SRP ranged from 0.01-0.33 mg.l^{-1} (mean=0.05mg.l^{-1}) and TP ranged from 0.1-0.39 mg.l^{-1} (mean=0.13mg.l^{-1}). SRP represented 16-82% of TP (mean=37%).

Flow-weighted mean concentrations had a higher variability in smaller catchments than in larger ones (Figure 1). Previous studies have identified the same spatial trend in Brittany (Abbott et al., 2018a; Gu et al., 2021) as well as elsewhere (e.g. Shogren et al. (2019)). This could be because smaller catchments may capture the extreme conditions in the study area (related to nutrient source inputs, retention potential or landscape spatial arrangement), while larger catchments tend to be more representative of average conditions in the region. While the recent study of Guillemot et al. (2021) identified that land use (along with the climate, topography and soil type) could explain part of the variability observed, the present study specifically investigated the influence of landscape spatial configuration on concentrations (section 3.2) and concentration dynamics (section 3.3).

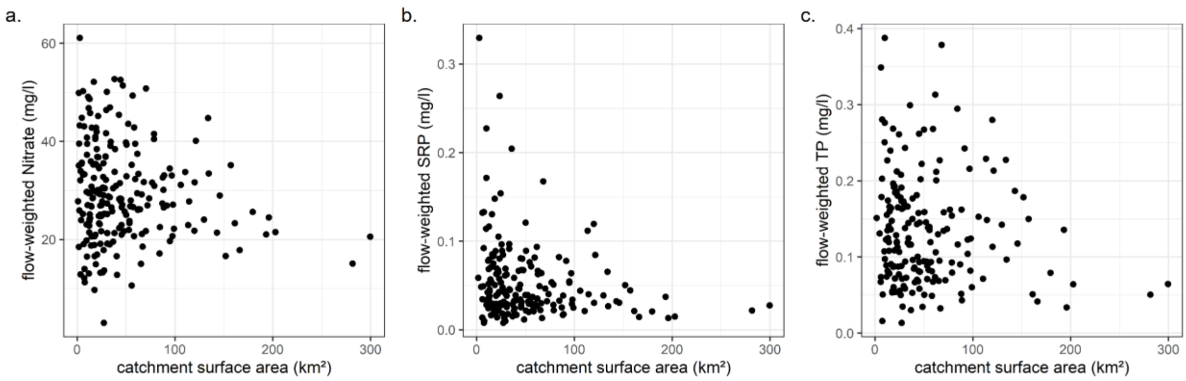

Figure 1. Relationships between catchment size and flow-weighted mean concentrations of (a) nitrate, (b) soluble reactive phosphorus (SRP) and (c) total phosphorus (TP) in 221 headwater catchments in Brittany (2010-2020).

The CV ratio was <1 for 100%, 98% and 96% of the catchments for nitrate, SRP and TP respectively. It was <0.5 for 98%, 53% and 43% of the catchments for nitrate, SRP and TP respectively. The lower variability in concentrations compared to that of discharge, often called chemostasis, is commonly observed for many solutes and catchment types (Godsey et al., 2019; Musolff et al., 2015; Thompson et al., 2011), especially in intensive agricultural catchments with large amounts of legacy nutrients in the soil and groundwater (Basu et al., 2010).

For the statistically significant (p-value<0.05) C-Q relationships, the slope was positive for nitrate in most of the catchments (73%), negative for SRP in all catchments and negative for TP in most of the catchments (86%). Slopes were non-significant in 48%, 47% and 76% of the catchments for nitrate, SRP and TP, respectively. There were strong correlations between the C-Q slope and CV ratio for nitrate (positive for positive C-Q slopes and negative for negative C-Q slopes), while relationships between the C-Q slope and CV ratio were less clear for SRP and TP (Figure 2).

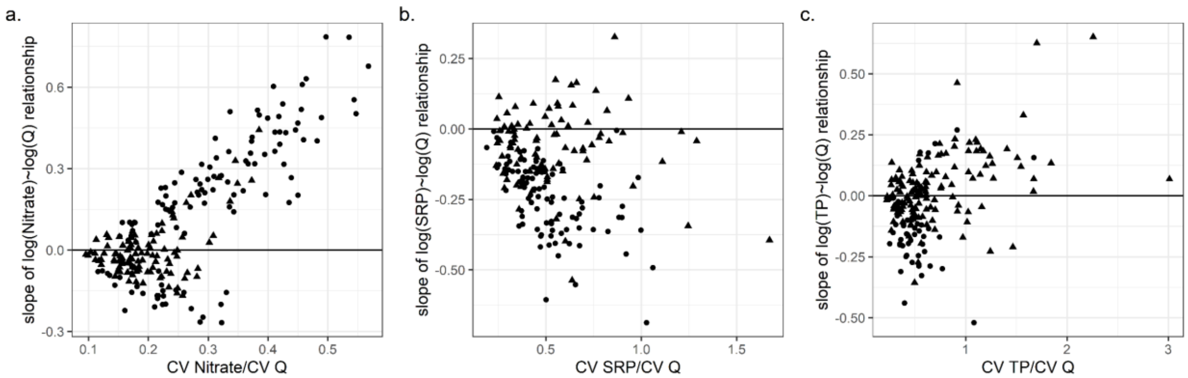

Figure 2. Relationships between the coefficient of variation (CV) ratio and concentration-discharge (C-Q)-slope for (a) nitrate, (b) soluble reactive phosphorus (SRP) and (c) total phosphorus (TP) in 221 headwater catchments in Brittany (2010-2020). Round dots indicate significant C-Q slope (p<0.05) and triangular dots non-significant C-Q slopes (p>0.05).

The most common pattern identified in temperate catchments is a dominance of positive C-Q slopes for nitrate and negative slopes for SRP and TP (Betton et al., 1991; Ebeling et al., 2021a). Minaudo et al. (2019) and Musolff et al. (2021) showed that seasonal variations predominantly influenced these patterns captured with low frequency data. Analysis of high-frequency data in Brittany showed that nitrate is higher and P lower during the winter high-flow season, despite the prevalence of dilution patterns for nitrate and accretion patterns at the scale of storm events (Fovet et al., 2018). The large percentage of non-significant slopes may have been due to this contrasting influence of flow at seasonal and event time scales (Minaudo et al., 2019; Moatar et al., 2017). The existence of negative C-Q patterns for nitrate in contexts of a dominant diffuse source was previously documented in Brittany, but the factors that control them remain unclear (Guillemot et al., 2021; Martin et al., 2004; Ruiz et al., 2002). In the literature, C-Q patterns are generally interpreted in terms of i) dominance of point versus diffuse sources (Abbott et al., 2018b; Ehrhardt et al., 2021; Van Meter et al., 2020); ii) heterogeneity in nutrient sources and temporally variable hydrological connectivity, especially in the vertical dimension (Botter et al., 2020; Ruiz et al., 2002; Zarnetske et al., 2018) and iii) biogeochemical processes in- and near-stream, which may remove nitrate and retain/remobilize P forms (Casquin et al., 2020; Lutz et al., 2020).

Like for flow-weighted mean concentrations, we observed higher variability in LatIndex and LongIndex in smaller catchments than in larger ones (Figure 3). Most LatIndex values were <1, indicating that arable fields were preferentially located upslope. This spatial distribution of arable fields was expected, as valley bottoms typically consist of less productive hydromorphic soils in Brittany, while hillslopes are more suitable for arable crops and intensive temporary grassland (Frei et al., 2020). LongIndex values were equally distributed on both sides of the y=1 line, indicating no general trend in the distribution of arable land in the longitudinal dimension, but a high variability in situations, especially in the smaller catchments. This confirms observations made in other studies (e.g. Bishop et al. (2008); Bol et al. (2018); Gu et al. (2021)) that studying small headwaters is key to increasing the variability in catchment conditions when statistically analysing water-quality and catchment attributes such as landscape indices. For this reason, we limited the analysis of correlations between water-quality metrics and landscape indices to sub-catchments smaller than 50 km², leaving 148 of the 221 catchments for subsequent analyses. Using a threshold of *ca.* 50 km² to study relationships between water-quality metrics and landscape indices is also justified by the increasing influence of in-stream processes in larger catchments, which may significantly alter nutrient concentrations and dynamics (Casquin et al., 2020). Finally, a threshold of *ca.* 50 km² to analyze headwater variability is consistent with previous work throughout Europe (Bol et al., 2018; Djodjic et al., 2021).

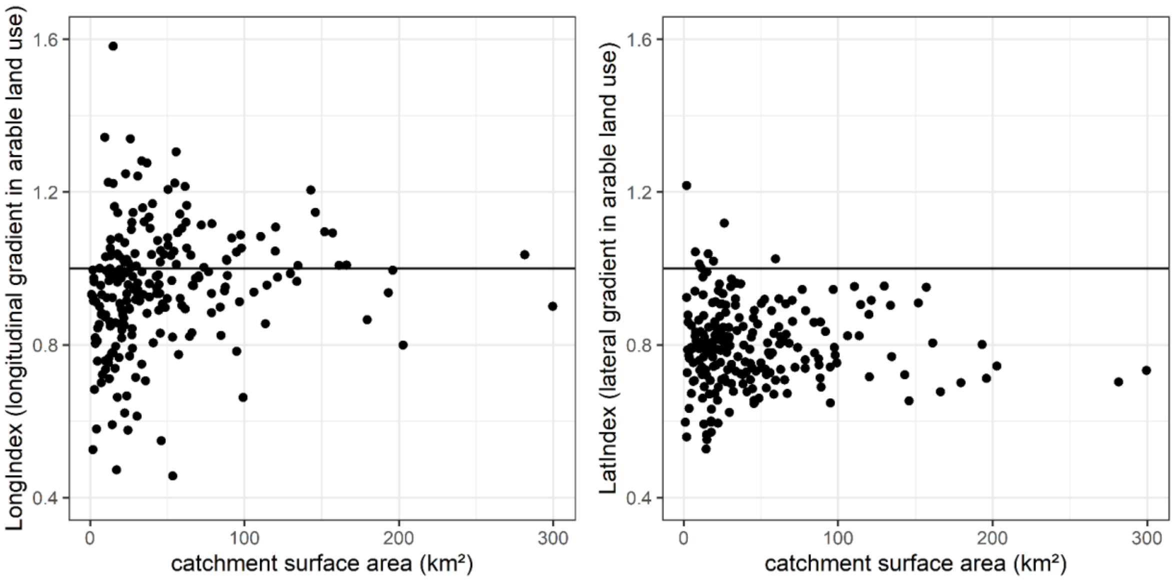

Figure 3. Relationships between catchment size and LatIndex and LongIndex. LatIndex >1 indicates arable fields preferentially located downslope (i.e. near the stream network), while LatIndex <1 indicates arable fields preferentially located upslope. LongIndex >1 indicate arable fields preferentially located downstream (i.e. near the catchment outlet), while LongIndex <1 indicates arable fields preferentially located upstream.

3.2. Relationships between the Landscape configuration index and flow-weighted mean nutrient concentrations

The percentage of arable land use (i.e. the value of LCI(0,0)) had a stronger rank correlation with flow-weighted mean nitrate concentration (r=0.74) than with SRP (r=0.27) and TP (r=0.40). A stronger correlation between land-use composition metrics and nitrate concentrations compared to P forms is common in statistical analyses of catchment data (Guillemot et al., 2021; Minaudo et al., 2019). Several potential reasons have been suggested: i) estimated mean P concentrations have a higher uncertainty than those of nitrate concentrations, hence mean P concentrations are more difficult to predict with catchment descriptors than mean nitrate concentrations; ii) point sources of pollution represent a larger percentage of P export than nitrate export, hence a proxy of diffuse agricultural sources alone cannot accurately predict P; iii) P is subjected to more complex and spatially variable retention processes than N, and landscape spatial configuration is one of the factors that control landscape P retention. The LCI aimed to test the latter hypothesis by identifying whether (a,b) pairs exist for which LCI(a,b)>LCI(0,0)+0.1.

Varying the coefficients a and b did not substantially (>0.1) improve the correlation between LCI(a,b) and flow-weighted mean nitrate concentration, but did improve its correlation with flow-weighted mean SRP and TP, by +0.29 and +0.21, respectively. We interpret this result as indicating that landscape spatial configuration influences the export of P more than that of nitrate. This does not mean that landscape management is irrelevant for reducing nitrate transfer, as other studies have demonstrated an effect (Casal et al., 2018; McDowell et al., 2014). Instead, it could mean that the effect is too small to be detected with our method or that relevant landscape configurations that maximize N retention should consider factors besides those included in the LCI. Our method also may not have detected an influence of landscape configuration on nitrate because the landscape configurations that actually minimize N losses did not occur in the study catchments, or the binary classification of land-use types into sources or sinks was too simplistic. We think, however, that using intermediate source/sink values instead of the binary approach would result in indetermination problems and obscure the influence of landscape configuration in the LCI. The lack of a significant influence of landscape spatial configuration on nitrate transfer is consistent with knowledge on its main transfer pathway via groundwater, which frequently bypasses landscape buffers that may be present on the surface (Guillemot et al., 2021; Ruiz et al., 2002).

The optimal (a,b) pairs for predicting flow-weighted mean SRP and TP were (1.9, 3.6) and (5.7, 0.3), respectively, and the top 50 pairs were located in the same area of parameter space for each parameter (Figure 4). These optimal values differed from (a=0, b=0), (a=0, b=1), (a=1, b=0) or (a=1, b=1), which shows that, compared to previous landscape indices calculated as arable land weighted by flow accumulation alone, inverse distance to the stream alone or their ratio (Peterson et al., 2011; Staponites et al., 2019, Zampella et al., 2007), the addition of calibrated coefficients (a, b) as power-law coefficients improved prediction of TP and SRP. Both distance to the stream and flow-accumulation influenced SRP and TP, as also determined by Casquin et al. (2021) in 19 headwaters in Brittany. Thus, current regulations that consider only the distance to river networks to restrict certain agricultural practices or encourage the establishment of buffer zones (e.g. the European Nitrate directive and Water Framework directive) could be refined by considering flow-accumulation information as well. The optimal (a,b) pairs for predicting TP and SRP showed greater influence of flow accumulation or distance to the stream, respectively. The combined effect of both types of topographic data, but a different predominant type for TP and SRP, was clearly visible in a CSA map created from the >90th percentile of the LCI weighting function (Figure 5). Greater influence of distance to the stream for SRP and flow-accumulation for TP, which comprises a majority of particulate P (Dupas et al., 2015), is consistent with current knowledge on their respective transfer mechanisms. Soluble reactive P is transferred mainly via subsurface groundwater pathways or runoff on water-saturated soils (i.e. in the riparian zone where the shallow groundwater can intersect the soil surface during wet periods) (Bol et al., 2018; Dupas et al., 2017; Gu et al., 2017; Mellander et al., 2015). Particulate P, on the other hand, is more susceptible to transfer via concentrated erosion processes, which is more likely to occur in flow-accumulation areas (Pionke et al., 1999; Reaney et al., 2019). The two P forms, however, are not independent, because particulate forms can transform into to soluble forms (and vice-versa) along the transport continuum from soils to streams and rivers (Bol et al., 2018; Casquin et al., 2020; Gu et al., 2017). Fig S3 shows an optimization of the LCI for particulate P, approximated as TP-SRP: as expected, the optimal (a,b) pairs lie in the same area of parameter space as for TP (Fig 4).

Statistical approaches in catchment research often risk finding spurious correlations (Casquin et al., 2021; Guillemot et al., 2021). Here, the fact that optimal (a, b) pairs for nitrate, SRP and TP agreed with knowledge on their transfer pathways increases our confidence that the correlation represent mechanistic associations and the CSA map derived from these correlations (Figure 5) could be used for management purposes. Of course, correlations between the optimized LCI and flow-weighted mean P concentrations remain modest (r=0.56 and 0.61 for SRP and TP, respectively), as several factors not included in the LCI have an influence: point sources, characteristics of cropping systems, soil properties, etc. (Frei et al., 2020; Guillemot et al., 2021).

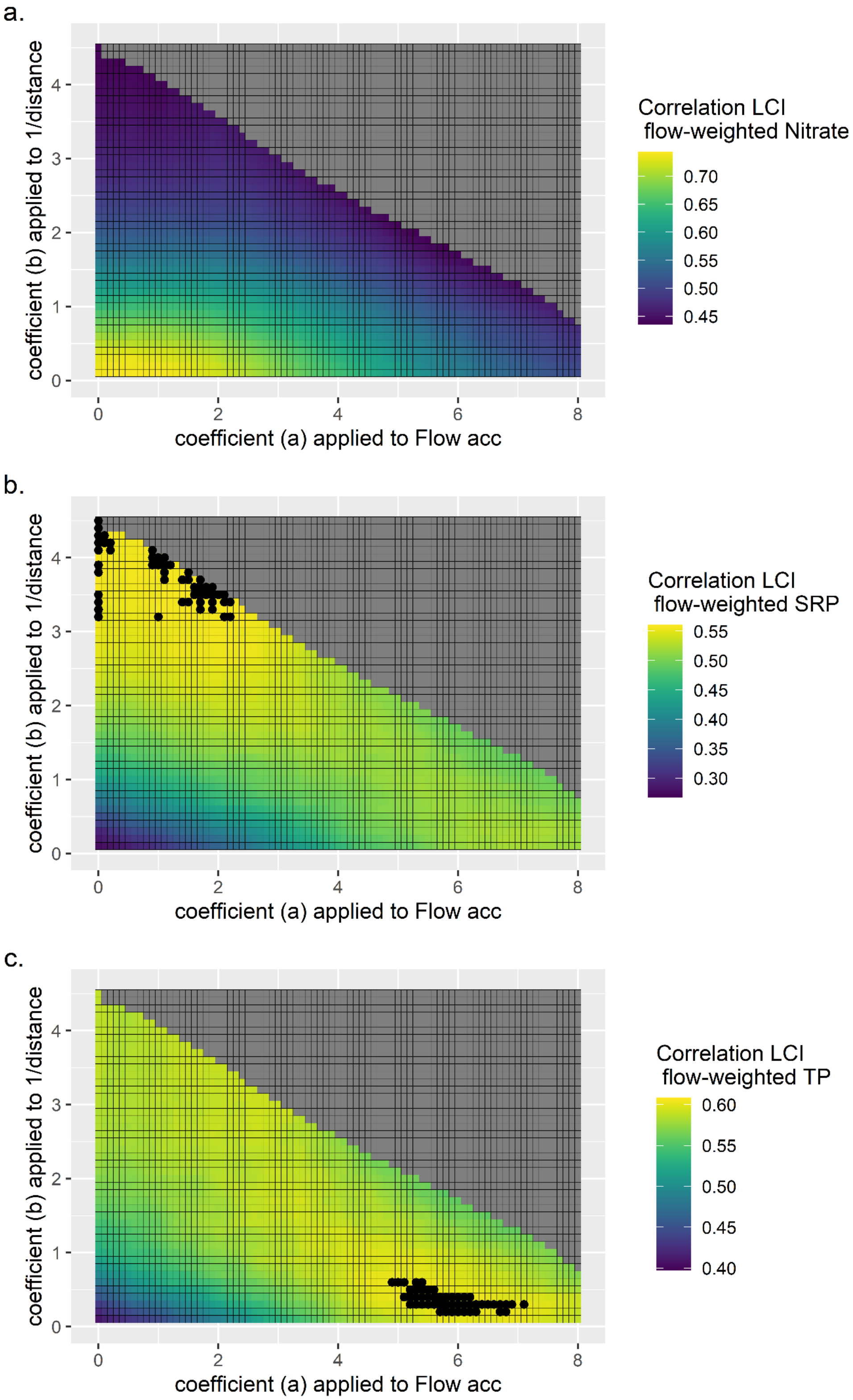

Figure 4. Optimization of the landscape configuration index (LCI) for (a) flow-weighted mean nitrate, (b) SRP and (c) TP. Black dots represent the top 50 optimal (a, b) pairs to examine uncertainty in parameter estimation.

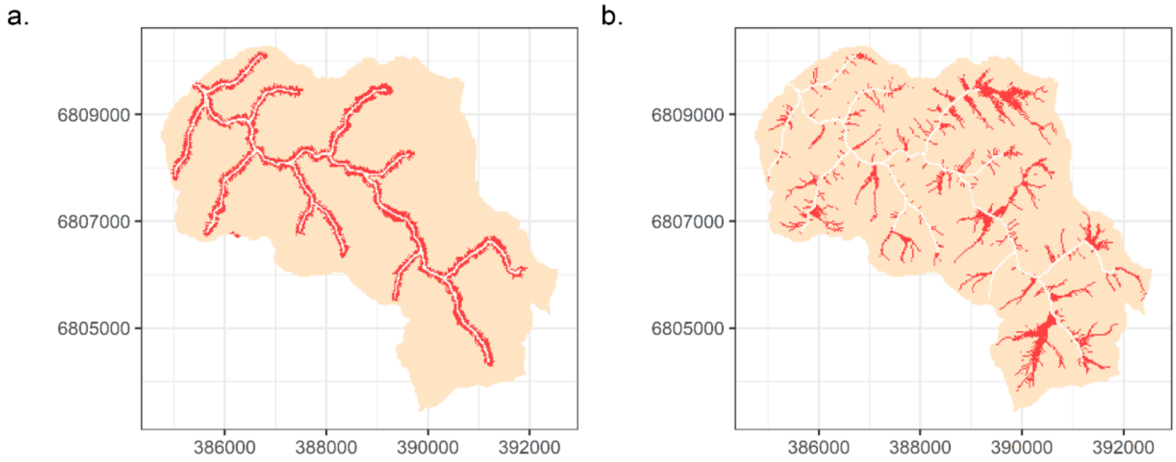

Figure 5. Example of mapping critical source area (red) for (a) soluble reactive phosphorus and (b) total phosphorus (b) for one subcatchment in the study area.

3.3. Relationships between longitudinal and lateral distribution of arable land and concentration dynamics

We investigated the influence of landscape spatial configuration on nitrate, SRP and TP concentration dynamics by examining correlations between indices of longitudinal and lateral distributions of arable land and the slope of the log(concentration)-log(discharge) relationship. Contrary to our hypothesis, none of the six relationships was significantly negative ($p>0.05$), suggesting that the spatial distribution of nutrient sources in the longitudinal and lateral dimensions did not significantly influence concentration dynamics (Figure 6). This contradicts recent modelling (Musolff et al., 2017) or observational studies based on a few catchments (Dupas et al., 2021; Knapp et al., 2022) that suggested that lateral and longitudinal distributions of sources influenced concentration dynamics. It does support, however, most studies, which assume that vertical concentration gradients are the main factors that control concentration-discharge relationships (Botter et al., 2020; Ebeling et al., 2021b; Stewart et al., 2022). Although the vertical dimension showed higher nitrate concentrations in the subsurface in most situations (e.g. Stewart et al. (2022)), higher concentrations in deeper groundwater were also observed in research catchments in Brittany, resulting in negative nitrate concentration-discharge relationships (Martin et al., 2004; Ruiz et al., 2002). According to these studies, these “reverse” gradients can occur when the catchments are on a path of recovery, as the deeper groundwater is more contaminated than the younger shallow groundwater. In addition to spatial gradients of nutrient sources, in- and near-stream processes can alter land-to-stream temporal dynamics via retention and remobilization processes, which may mask effects of landscape spatial configuration (Casquin et al., 2020; Jarvie et al., 2011).

Relationships between the C-Q slope, lithology and the 10^{th} percentile of discharge (Fig S4), suggest that the supply of water during low flow and biogeochemical transformations has a key influence on the seasonal dynamics of nitrates as captured by the log(concentration)-log(discharge) slope. Previous research shows that the P concentration dynamics captured with low-resolution data were controlled mainly by in-stream retention/remobilization processes and the degree of dilution of point sources, even when the point sources represent a small fraction of annual loads (Abbott et al., 2018b; Casquin et al., 2020; Dupas et al., 2018). Therefore, we conclude that landscape spatial configuration does not control riverine nutrient dynamics more than the other factors previously identified in the literature.

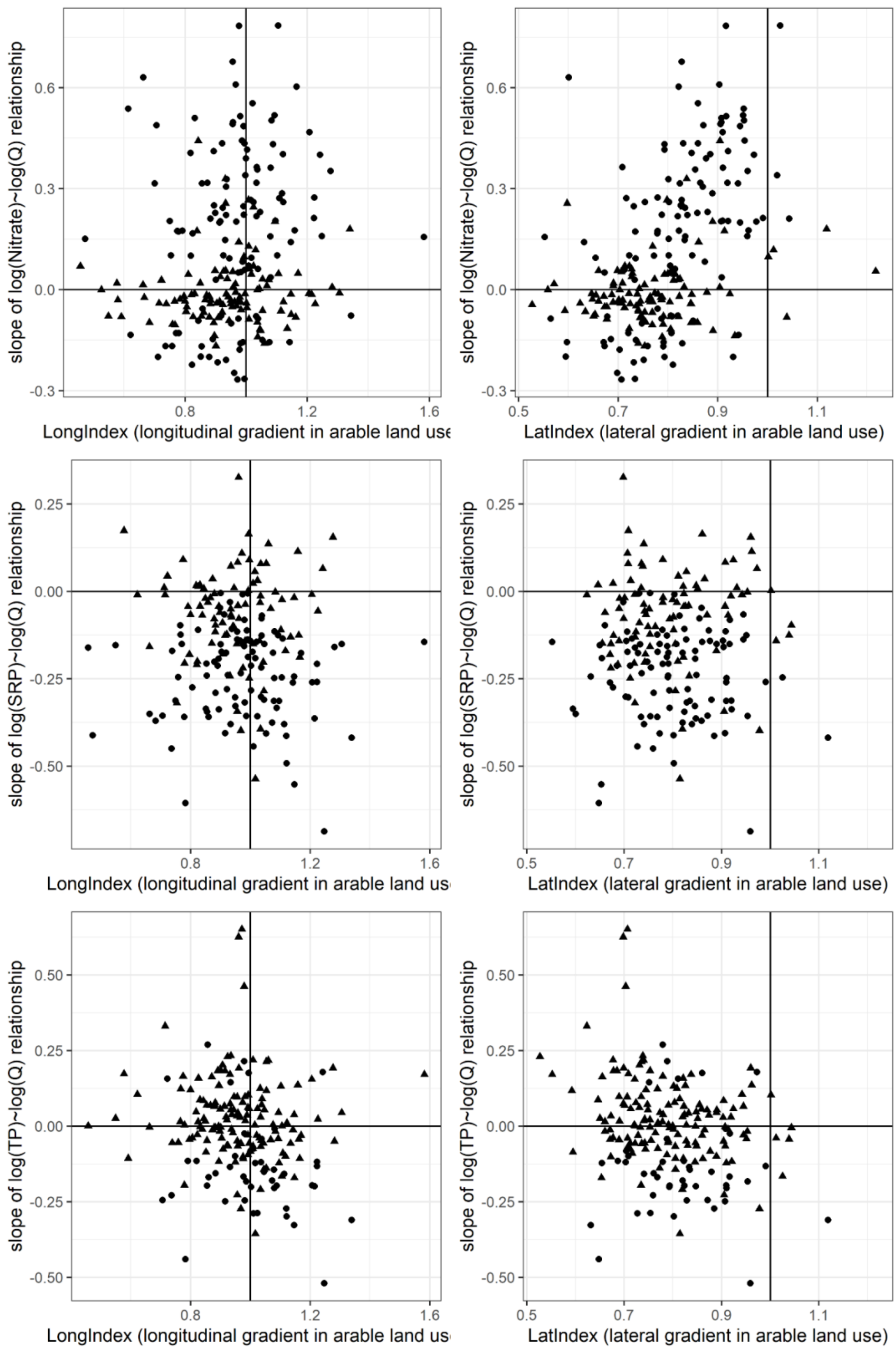

Figure 6. Relationships between the longitudinal and lateral distribution of arable land and nitrate, soluble reactive phosphorus (SRP) and total phosphorus (TP) concentration dynamics. Round dots indicate significant C-Q slope (p<0.05) and triangular dots non-significant C-Q slopes (p>0.05).

4. Conclusion

This study investigated the influence of the landscape spatial configuration on nitrate, SRP and TP mean flow-weighted mean concentrations and seasonal dynamics. We used public water quality and discharge data from >200 small headwaters located within a relatively homogeneous region to limit the influence of confounding factors besides landscape configuration. We found that studying small (<50 km²) headwater catchments led to inclusion of high variability in concentrations, landscape composition and landscape organization. A landscape configuration index that included information on flow distance to the stream and flow accumulation identified of critical source areas for SRP and TP, but not nitrate. The predominant influence of flow distance on SRP and flow accumulation on TP, and the lack of influence of the landscape configuration on nitrate, is consistent with knowledge on the dominant transfer pathways of these three nutrient forms. This increased our confidence that the correlation represents mechanistic associations. The CSA maps created from this statistical analysis may thus help design landscapes that minimize nutrient losses while maintaining arable land for crop production. For example, one could relocate arable fields outside the CSAs, and widen the buffer strips or increase the density of hedgerows within the CSAs. By contrast, the lateral and longitudinal distributions of arable land did not seem to influence nutrient dynamics, which supports results of most previous studies, which indicate that other factors such as vertical concentration gradients and the degree of dilution of point sources have more influence. Future research on landscape and nutrient transfers should include a wider variety of landscape elements, including linear elements such as ditches, hedgerows or other land uses, while maintaining the simplicity of the parsimonious modelling framework used in this study.

DATA AVAILABILITY

The data and R scripts used in this paper are provided in the supplementary information.

5. References

Abbott, B.W. et al., 2018a. Unexpected spatial stability of water chemistry in headwater stream networks. Ecology Letters, 21(2): 296-308.

Abbott, B.W. et al., 2018b. Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France. Science of the Total Environment, 624: 845-858.

Basu, N.B. et al., 2010. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophysical Research Letters, 37.

Bernhardt, E.S. et al., 2017. Control Points in Ecosystems: Moving Beyond the Hot Spot Hot Moment Concept. Ecosystems, 20(4): 665-682.

Berthier, L. et al., 2014. Enveloppes des milieux potentiellement humides de la France métropolitaine. . Ministère d’Ecologie, du Développement Durable et de l’Energie.: 50.
Betton, C., Webb, B.W., Walling, D.E., 1991. RECENT TRENDS IN NO3-N CONCENTRATION AND LOADS IN BRITISH RIVERS, Symp at the 20th General Assembly of the International Union of Geodesy and Geophysics - Sediment and Stream Water Quality in a Changing Environment. Iahs Publication, Vienna, Austria, pp. 169-180
Beven, K.J., Kirkby, M.J., 1979. A physically based, variable contributing area model of basin hydrology / Un modèle à base physique de zone d'appel variable de l'hydrologie du bassin versant. Hydrological Sciences Bulletin, 24(1): 43-69.
Bishop, K. et al., 2008. Aqua Incognita: the unknown headwaters. Hydrol. Process., 22(8): 1239-1242.
Bol, R. et al., 2018. Challenges of Reducing Phosphorus Based Water Eutrophication in the Agricultural Landscapes of Northwest Europe. Frontiers in marine science, 5(276).
Botter, M., Li, L., Hartmann, J., Burlando, P., Fatichi, S., 2020. Depth of Solute Generation Is a Dominant Control on Concentration-Discharge Relations. Water Resour. Res., 56(8).
Casal, L. et al., 2018. Optimal location of set-aside areas to reduce nitrogen pollution: a modelling study. Journal of Agricultural Science, 156(9): 1090-1102.
Casquin, A. et al., 2021. The influence of landscape spatial configuration on nitrogen and phosphorus exports in agricultural catchments. Landsc. Ecol., 36(12): 3383-3399.
Casquin, A. et al., 2020. River network alteration of C-N-P dynamics in a mesoscale agricultural catchment. Science of the Total Environment, 749.
Covino, T., Riveros-Iregui, D.A., Schneider, C.L., 2022. 6.04 - Geomorphology Imparts Spatial Organization on Hydrological and Biogeochemical Fluxes. In: Shroder, J.F. (Ed.), Treatise on Geomorphology (Second Edition). Academic Press, Oxford, pp. 53-67.
de Lavenne, A., Cudennec, C., 2019. Assessment of freshwater discharge into a coastal bay through multi-basin ensemble hydrological modelling. Science of the Total Environment, 669: 812-820.
Djodjic, F., Bieroza, M., Bergstrom, L., 2021. Land use, geology and soil properties control nutrient concentrations in headwater streams. Science of the Total Environment, 772.
Djodjic, F., Markensten, H., 2019. From single fields to river basins: Identification of critical source areas for erosion and phosphorus losses at high resolution. Ambio, 48(10): 1129-1142.
Djodjic, F., Villa, A., 2015. Distributed, high-resolution modelling of critical source areas for erosion and phosphorus losses. Ambio, 44: S241-S251.
Doody, D.G. et al., 2016. Optimizing land use for the delivery of catchment ecosystem services. Frontiers in Ecology and the Environment, 14(6): 325-332.
Dorioz, J.M., Wang, D., Poulenard, J., Trevisan, D., 2006. The effect of grass buffer strips on phosphorus dynamics - A critical review and synthesis as a basis for application in agricultural landscapes in France. Agriculture Ecosystems & Environment, 117(1): 4-21.
Dupas, R., Causse, J., Jaffrezic, A., Aquilina, L., Durand, P., 2021. Flowpath controls on high-spatial-resolution water-chemistry profiles in headwater streams. Hydrol. Process., 35(6).
Dupas, R. et al., 2013. Assessing N emissions in surface water at the national level: comparison of country-wide vs. regionalized models. Sci Total Environ, 443: 152-62.
Dupas, R., Ehrhardt, S., Musolff, A., Fovet, O., Durand, P., 2020. Long-term nitrogen retention and transit time distribution in agricultural catchments in western France. Environmental Research Letters.
Dupas, R., Gascuel-Odoux, C., Gilliet, N., Grimaldi, C., Gruau, G., 2015. Distinct export dynamics for dissolved and particulate phosphorus reveal independent transport mechanisms in an arable headwater catchment. Hydrol. Process., 29(14): 3162-3178.
Dupas, R. et al., 2017. The role of mobilisation and delivery processes on contrasting dissolved nitrogen and phosphorus exports in groundwater fed catchments. Science of the Total Environment(599-600): 1275–1287.
Dupas, R., Minaudo, C., Gruau, G., Ruiz, L., Gascuel-Odoux, C., 2018. Multidecadal trajectory of riverine nitrogen and phosphorus dynamics in rural catchments. Water Resour. Res., 54: 5327–5340.
Ebeling, P. et al., 2021a. Long-Term Nitrate Trajectories Vary by Season in Western European Catchments. Global Biogeochemical Cycles, 35(9).

Ebeling, P. et al., 2021b. Archetypes and Controls of Riverine Nutrient Export Across German Catchments. Water Resour. Res., 57(4).

Ehrhardt, S. et al., 2021. Nitrate Transport and Retention in Western European Catchments Are Shaped by Hydroclimate and Subsurface Properties. Water Resour. Res., 57(10).

Fovet, O. et al., 2018. Seasonal variability of stream water quality response to storm events captured using high-frequency and multi-parameter data. Journal of Hydrology, 559: 282-293.

Frei, R.J. et al., 2020. Predicting Nutrient Incontinence in the Anthropocene at Watershed Scales. Frontiers in Environmental Sciences, 7: 200.

Godsey, S.E., Hartmann, J., Kirchner, J.W., 2019. Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate. Hydrol. Process., 33(24): 3056-3069.

Gu, S. et al., 2021. Spatial Persistence of Water Chemistry Patterns Across Flow Conditions in a Mesoscale Agricultural Catchment. Water Resour. Res., 57(7).

Gu, S. et al., 2017. Release of dissolved phosphorus from riparian wetlands: evidence for complex interactions among hydroclimate variability, topography and soil properties. Science of the Total Environment(598): 421–431.

Guillemot, S. et al., 2021. Spatio-temporal controls of C-N-P dynamics across headwater catchments of a temperate agricultural region from public data analysis. HESSD.

Jarvie, H.P. et al., 2011. Quantifying Phosphorus Retention and Release in Rivers and Watersheds Using Extended End-Member Mixing Analysis (E-EMMA). Journal of Environmental Quality, 40(2): 492-504.

Jencso, K.G. et al., 2009. Hydrologic connectivity between landscapes and streams: Transferring reach- and plot-scale understanding to the catchment scale. Water Resour. Res., 45.

Knapp, J.L.A., Li, L., Musolff, A., 2022. Hydrologic connectivity and source heterogeneity control concentration-discharge relationships. Hydrol. Process., 36(9).

Krause, S. et al., 2017. Ecohydrological interfaces as hot spots of ecosystem processes. Water Resour. Res., 53(8): 6359-6376.

Lane, S.N., Reaney, S.M., Heathwaite, A.L., 2009. Representation of landscape hydrological connectivity using a topographically driven surface flow index. Water Resour. Res., 45(8): n/a-n/a.

Le Moal, M. et al., 2019. Eutrophication: A new wine in an old bottle. Science of The Total Environment, 651: 1-11.

Legeay, P.-L., Gruau, G., 2014. Spatio-temporal analysis of phosphorus fluxes and sources in Breton rivers. Trans-P project.

Liu, S. et al., 2022. Controls on Spatial Variability in Mean Concentrations and Export Patterns of River Chemistry Across the Australian Continent. Water Resour. Res., 58(e2022WR032365).

Lutz, S.R. et al., 2020. How Important is Denitrification in Riparian Zones? Combining End-Member Mixing and Isotope Modeling to Quantify Nitrate Removal from Riparian Groundwater. Water Resour. Res., 56(1).

Martin, C. et al., 2004. Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments. Hydrol. Process., 18(7): 1237-1254.

McDowell, R.W. et al., 2014. Contrasting the spatial management of nitrogen and phosphorus for improved water quality: Modelling studies in New Zealand and France. European Journal of Agronomy, 57: 52-61.

McDowell, R.W., Srinivasan, M.S., 2009. Identifying critical source areas for water quality: 2. Validating the approach for phosphorus and sediment losses in grazed headwater catchments. Journal of Hydrology, 379(1-2): 68-80.

Mellander, P.E., Jordan, P., Shore, M., Melland, A.R., Shortle, G., 2015. Flow paths and phosphorus transfer pathways in two agricultural streams with contrasting flow controls. Hydrol. Process.

Minaudo, C. et al., 2019. Seasonal and event-based concentration-discharge relationships to identify catchment controls on nutrient export regimes. Advances in Water Resources.

Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G., 2017. Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resour. Res., 53(2): 1270-1287.

Musolff, A., Fleckenstein, J.H., Rao, P.S.C., Jawitz, J.W., 2017. Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. Geophysical Research Letters, 44(9): 4143-4151.

Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H., 2015. Catchment controls on solute export. Advances in Water Resources, 86: 133-146.

Musolff, A. et al., 2021. Spatial and Temporal Variability in Concentration-Discharge Relationships at the Event Scale. Water Resour. Res., 57(10).

Peterson, E.E., Sheldon, F., Darnell, R., Bunn, S.E., Harch, B.D., 2011. A comparison of spatially explicit landscape representation methods and their relationship to stream condition. Freshw. Biol., 56(3): 590-610.

Pionke, H.B., Gburek, W.J., Schnabel, R.R., Sharpley, A.N., Elwinger, G.F., 1999. Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed. Journal of Hydrology, 220(1-2): 62-73.

Qin, C. et al., 2007. An adaptive approach to selecting a flow-partition exponent for a multiple-flow-direction algorithm. International Journal of Geographical Information Science, 21(4): 443-458.

Reaney, S.M. et al., 2019. Identifying critical source areas using multiple methods for effective diffuse pollution mitigation. Journal of Environmental Management, 250.

R Core Team (202). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/

Ruiz, L. et al., 2002. Effect on nitrate concentration in stream water of agricultural practices in small catchments in Brittany : II. Temporal variations and mixing processes. Hydrology and Earth System Sciences, 6(3): 507-513.

Schoumans, O.F. et al., 2014. Mitigation options to reduce phosphorus losses from the agricultural sector and improve surface water quality: A review. Science of the Total Environment, 468: 1255-1266.

Shogren, A.J. et al., 2019. Revealing biogeochemical signatures of Arctic landscapes with river chemistry. Scientific Reports, 9.

Shore, M. et al., 2014. Evaluating the critical source area concept of phosphorus loss from soils to water-bodies in agricultural catchments. Science of the Total Environment, 490: 405-415.

Stamm, C., Jarvie, H.P., Scott, T., 2014. What's More Important for Managing Phosphorus: Loads, Concentrations or Both? Environmental Science & Technology, 48(1): 23-24.

Staponites, L.R., Bartak, V., Bily, M., Simon, O.P., 2019. Performance of landscape composition metrics for predicting water quality in headwater catchments. Scientific Reports, 9.

Stewart, B. et al., 2022. Streams as Mirrors: Reading Subsurface Water Chemistry From Stream Chemistry. Water Resour. Res., 58(1).

Strohmenger, L., Fovet, O., Hrachowitz, M., Salmon-Monviola, J., Gascuel-Odoux, C., 2021. Is a simple model based on two mixing reservoirs able to reproduce the intra-annual dynamics of DOC and NO3 stream concentrations in an agricultural headwater catchment? Science of the Total Environment, 794.

Team, R.C., 2021. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Thomas, I.A. et al., 2016. A sub-field scale critical source area index for legacy phosphorus management using high resolution data. Agriculture Ecosystems & Environment, 233: 238-252.

Thompson, S.E., Basu, N.B., Lascurain, J., Jr., Aubeneau, A., Rao, P.S.C., 2011. Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. Water Resour. Res., 47.

Van Meter, K.J., Chowdhury, S., Byrnes, D.K., Basu, N.B., 2020. Biogeochemical asynchrony: Ecosystem drivers of seasonal concentration regimes across the Great Lakes Basin. Limnology and Oceanography, 65(4): 848-862.

Van Sickle, J., Johnson, C.B., 2008. Parametric distance weighting of landscape influence on streams. Landsc. Ecol., 23(4): 427-438.

Walsh, C.J., Webb, J.A., 2014. Spatial weighting of land use and temporal weighting of antecedent discharge improves prediction of stream condition. Landsc. Ecol., 29(7): 1171-1185.

Winter, C. et al., 2021. Disentangling the Impact of Catchment Heterogeneity on Nitrate Export Dynamics From Event to Long-Term Time Scales. Water Resour. Res., 57(1).

Zampella, R.A., Procopio, N.A., Lathrop, R.G., Dow, C.L., 2007. Relationship of land-use/land-cover patterns and surface-water quality in the Mullica River basin. Journal of the American Water Resources Association, 43(3): 594-604.

Zarnetske, J.P., Bouda, M., Abbott, B.W., Saiers, J., Raymond, P.A., 2018. Generality of Hydrologic Transport Limitation of Watershed Organic Carbon Flux Across Ecoregions of the United States Geophysical Research Letters.

Zimmer, M.A., McGlynn, B.L., 2018. Lateral, Vertical, and Longitudinal Source Area Connectivity Drive Runoff and Carbon Export Across Watershed Scales. Water Resour. Res., 54(3): 1576-1598.

SUPPORTING INFORMATION: Landscape spatial configuration influences phosphorus but not nitrate concentrations in agricultural headwater catchments

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The R code to compute the Landscape Configuration Index is provided in a .zip file.

Table S1. Catchment properties

	surface area (km^2)	annual runoff (mm)	10% percentile of discharge (mm/day)	%arable land use
minimum	1	163	0	3
1st quartile	16	263	0.05	44
median	30	403	0.13	53
mean	47	436	0.17	51
3rd quartile	60	593	0.25	59
max	300	878	0.62	76

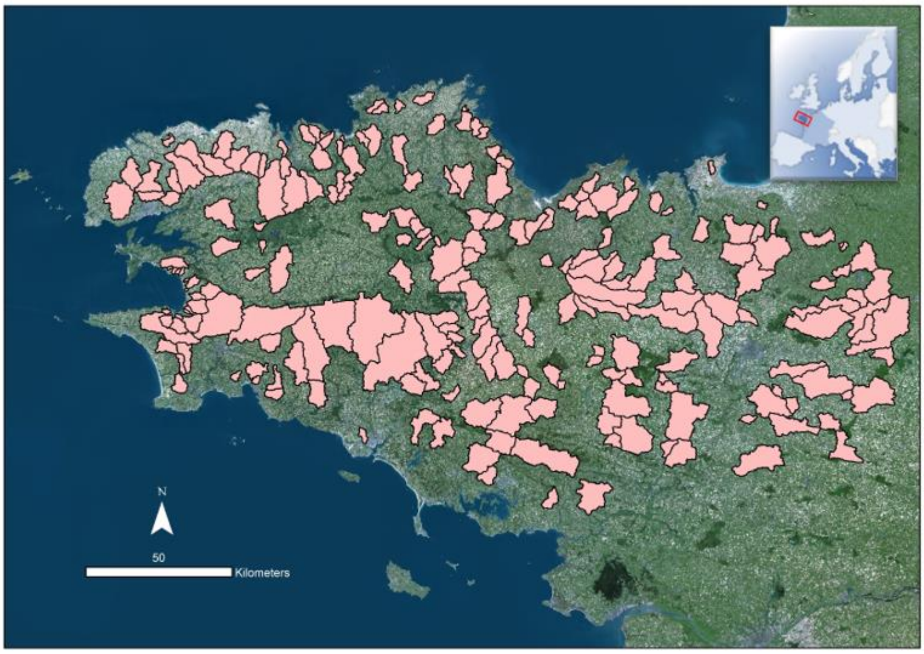

Figure S1. Location of the 221 study catchments in the Brittany region (western France).

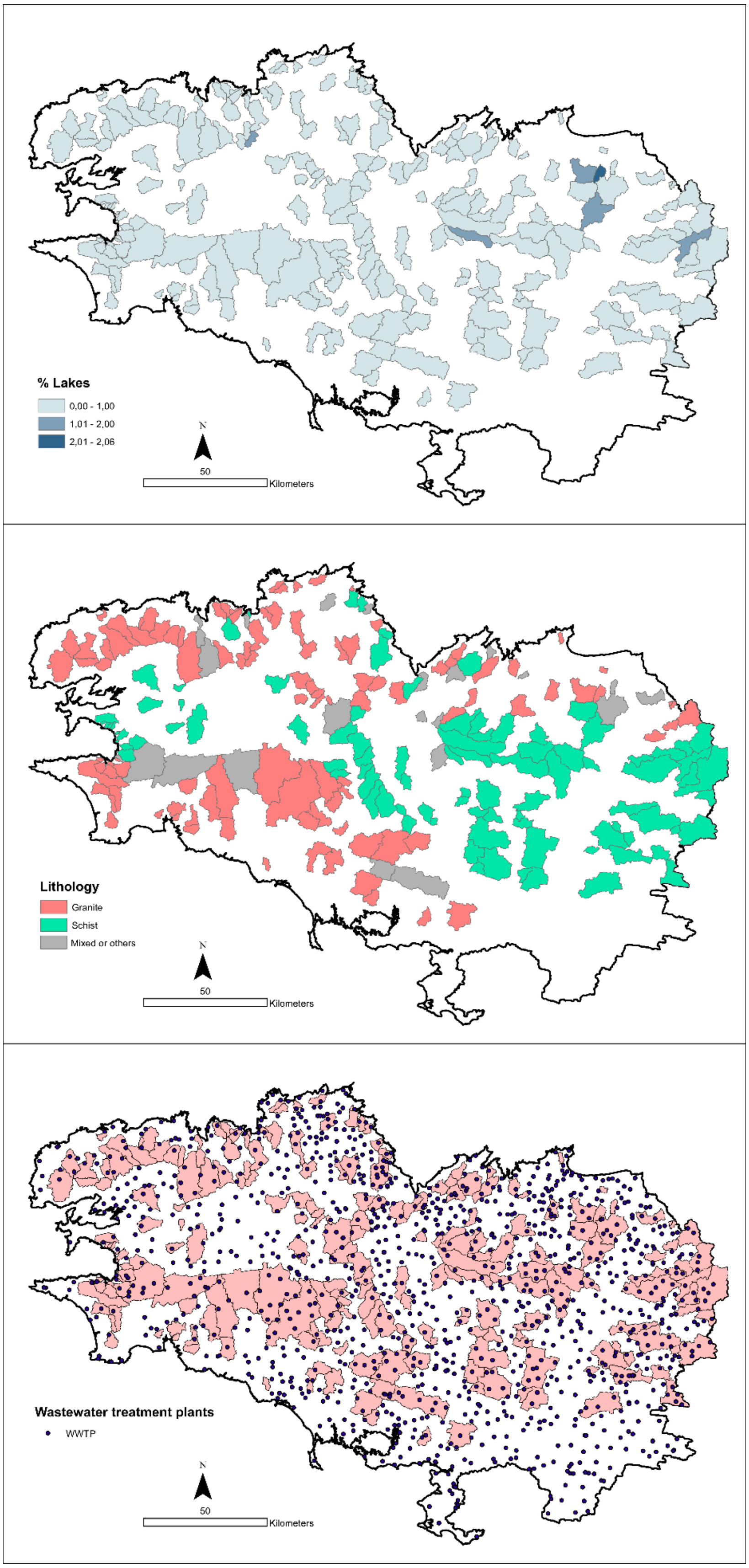

Figure S2. Additional catchments properties: percentage of the catchment area covered by lakes, main lithology and location of wastewater treatment plants.

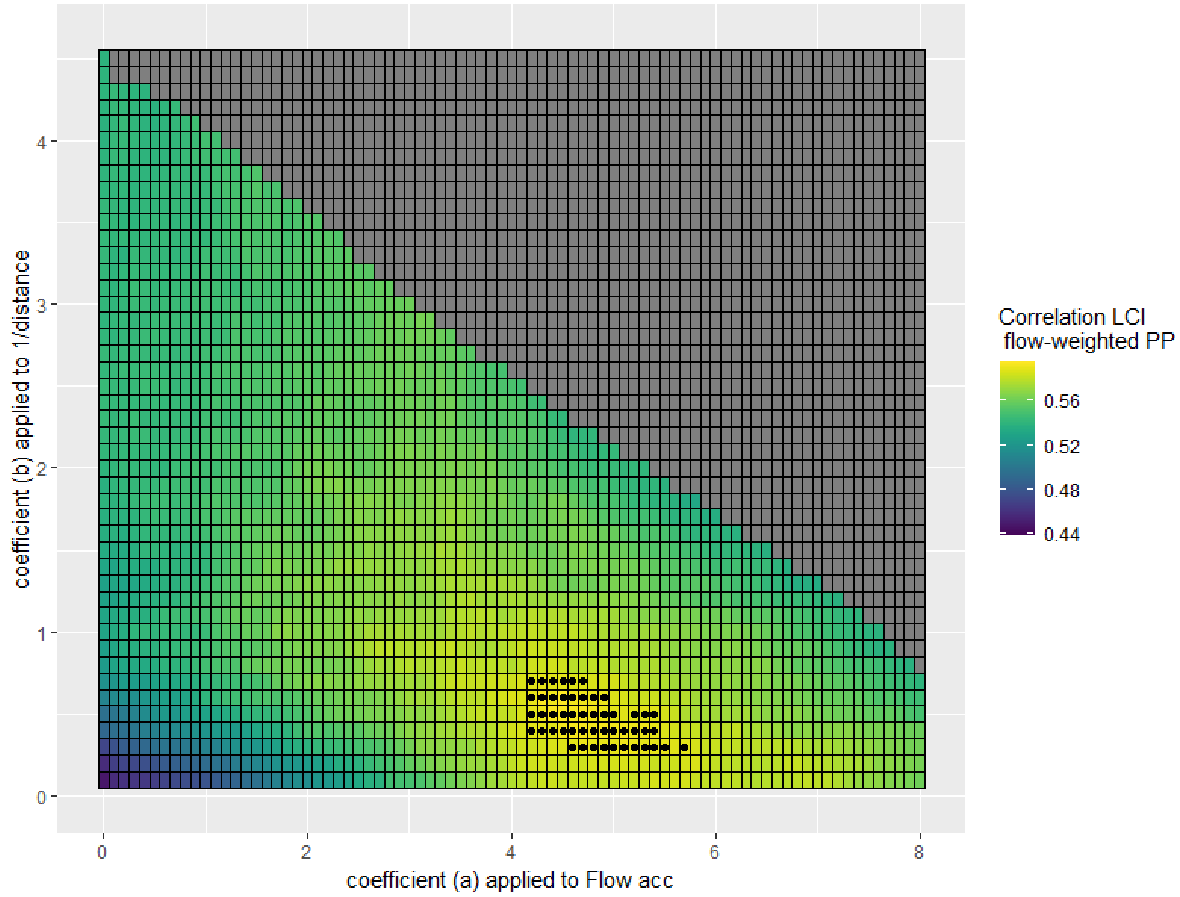

Figure S3. Optimization of the landscape configuration index (LCI) for particulate phosphorus PP, estimated as TP-SRP. Black dots represent the top 50 optimal (a, b) pairs to examine uncertainty in parameter estimation.

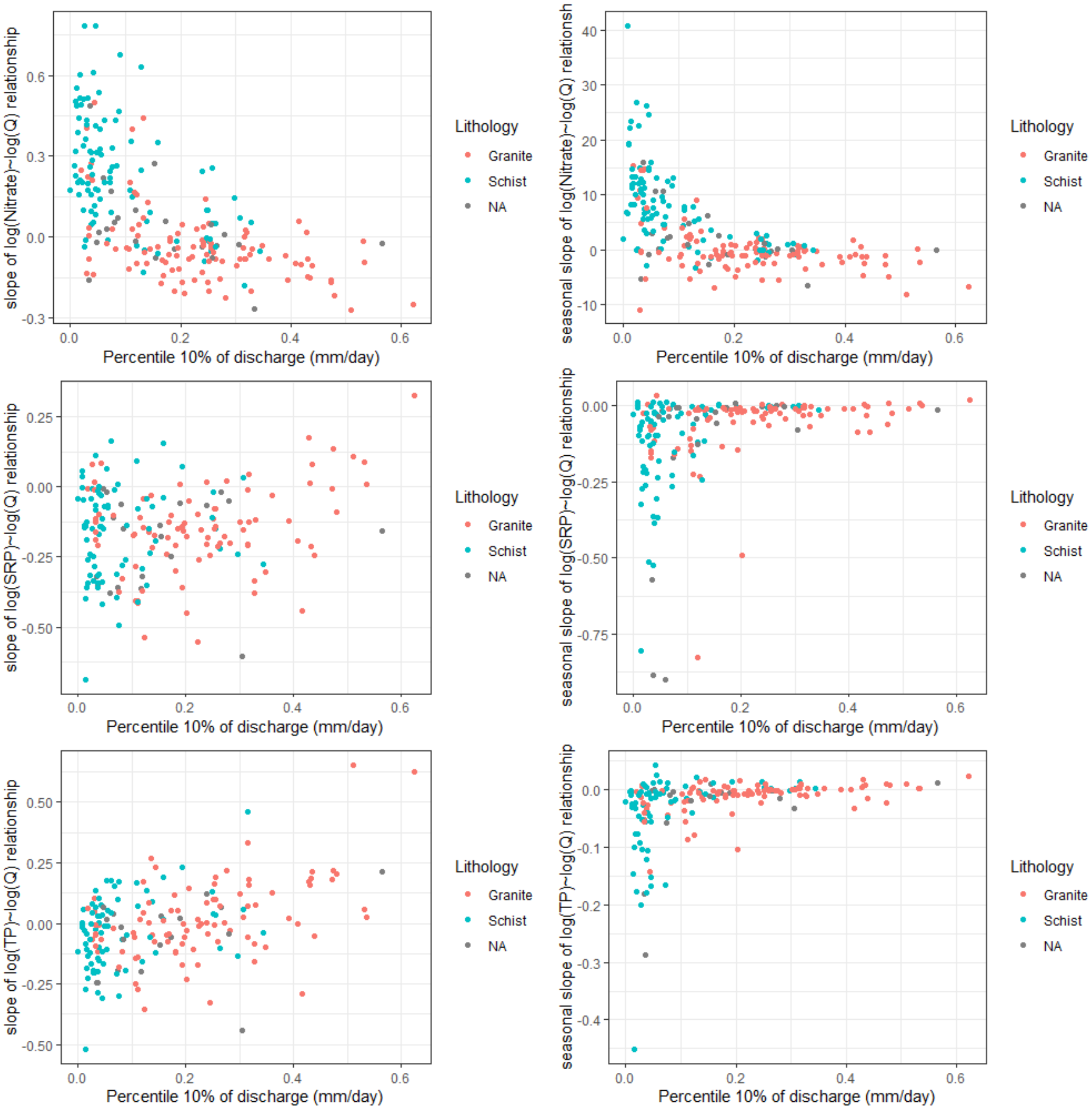

Figure S4. Relationships between the slope of the log(concentration)-log(discharge) slope and catchments variables: dominant lithology class and percentile 10% of discharge.