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Spatio-temporal controls of C-N-P dynamics across headwater catchments of a temperate agricultural region from public data analysis

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Abstract. Characterizing and understanding spatial variability in water quality for a variety of chemical elements is an issue for present and future water resource management. However, most studies of spatial variability in water quality focus on a single element and rarely consider headwater catchments. Moreover, they assess few catchments and focus on annual means without considering seasonal variations. To overcome these limitations, we studied spatial variability and seasonal variation in dissolved C, N, and P concentrations at the scale of an intensively farmed region of France (Brittany). We analyzed 185 headwater catchments (from 5-179 km²) for which 10-year time series of monthly concentrations and daily stream flow were available from public databases. We calculated interannual loads, concentration percentiles, and seasonal metrics for each element to assess their spatial patterns and correlations. We then performed rank correlation analyses between water quality, human pressures, and soil and climate features. Results show that nitrate (NO_3) concentrations increased with increasing agricultural pressures and base flow contribution; dissolved organic carbon (DOC) concentrations decreased with increasing rainfall, base flow contribution, and topography; and soluble reactive phosphorus (SRP) concentrations showed weaker positive correlations with diffuse and point sources, rainfall and topography. An opposite pattern was found between DOC and NO_3: spatially, between their median concentrations, and temporally, according to their seasonal cycles. The annual maximum NO_3 concentration was in-phase with maximum flow when the base flow index was low, but this synchrony disappeared when flow flashiness was lower. The annual maximum SRP concentration occurred during the low-flow period in nearly all catchments. The approach shows that despite the relatively low frequency of public water quality data, such databases can provide consistent pictures of the spatio-temporal variability of water quality and of its drivers as soon as they contain a large number of catchments to compare and a sufficient length of concentration time series.

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1 Introduction

As a condition for human health, food production, and ecosystem functions, water quality is recognized as "one of the main challenges of the 21st century" (FAO and WWC, 2015; UNESCO, 2015), and potential impacts of climate change on water quality are even more challenging (Whitehead et al., 2009). To better estimate and reduce human impact on water quality, water scientists are expected to provide integrated understanding of multiple pollutants (Cosgrove and Loucks, 2015). Eutrophication risks (Dodds and Smith, 2016) are considered the main factors that decrease the quality of surface water, according to objectives set by the European Union Water Framework Directive. Mitigating the problem of eutrophication involves considering at least the three major elements: carbon (C), nitrogen (N), and phosphorus (P) (Le Moal et al., 2019).

Headwater catchments have been studied less than large rivers (Bishop et al., 2008), despite their influence on downstream water quality (Alexander et al., 2007; Barnes and Raymond, 2010; Bol et al., 2018) and higher spatial variability in their concentrations (Abbott et al., 2018a; Temnerud and Bishop, 2005). One reason for this is that most water quality monitoring networks coincide with the location of drinking-water production facilities, which explains why they focus on large rivers. Nonetheless, investigating spatial variability in upstream water quality is relevant for understanding what causes it to degrade, targeting locations with the greatest disturbances, and identifying which remediation policies would be most cost effective.

In non-agricultural headwater catchments, spatial variability in dissolved organic C (DOC) concentrations in streams has been related to topography, wetland coverage, and soil properties such as clay content or pH (Andersson and Nyberg, 2008; Brooks et al., 1999; Creed et al., 2008; Hytteborn et al., 2015; Temnerud and Bishop, 2005). Stream DOC concentrations and composition in agricultural and urbanized areas also generally differ greatly from those in semi-natural or pristine catchments (Graeber et al., 2012; Gücker et al., 2016). Over large gradients of human impact (e.g. from undisturbed to urban catchments), the cover of agricultural and urban land uses often appears as a key factor that explains differences in stream chemistry of C, N, and P species (e.g. Barnes and Raymond, 2010; Edwards et al., 2000; Mutema et al., 2015) and even silica (Onderka et al., 2012). Conversely, in more homogeneous catchments – e.g. mostly undisturbed (Mengistu et al., 2014) or mostly rural (Heppell et al., 2017; Lintern et al., 2018) – "natural" controls such as topography, geology, and flow paths are more frequently highlighted as the main factors that explain spatial variability in C, N and P.

Besides being spatially variable, C, N, and P concentrations also vary seasonally in streams and rivers (Aubert et al., 2013; Dawson et al., 2008; Duncan et al., 2015; Exner-Kittridge et al., 2016; Lambert et al., 2013), as does the composition of dissolved organic matter (Griffiths et al., 2011; Gücker et al., 2016). This seasonality can also be spatially structured. Several studies showed that the relative importance of catchment characteristics on water concentrations or loads varied by season because nutrient sources and biological and physico-chemical processes that influence nutrient mobilization and transfer in catchments (e.g. vegetation uptake, in-stream biomass production, denitrification) changed with the hydrological conditions (Ågren et al., 2007; Fasching et al., 2016; Gardner and McGlynn, 2009). Some variability in seasonal patterns of dissolved C, N, and/or P concentrations among headwater catchments has been reported (e.g. Van Meter et al., 2019; Abbott et al., 2018b;

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Duncan et al., 2015; Martin et al., 2004). Identifying these patterns is relevant from a management viewpoint as they may indicate changes in the locations of C, N, or P sources or their transfer pathways.

Thus, to date, analysis of spatial variability in water quality at the headwater scale:

1) is usually restricted to one element, although multi-element approaches are becoming more frequent (Edwards et al., 2000; Heppell et al., 2017; Lintern et al., 2018; Mengistu et al., 2014; Mutema et al., 2015),
2) is particularly rare for headwater catchments with similar human pressures (e.g. intensive farming), despite the high variability in water quality sometimes observed among them (e.g. Thomas et al. (2014)),
3) often uses mean annual values (concentration or load) to describe spatial variability in water quality among catchments, with little or no analysis of seasonal patterns (Ågren et al., 2007), and
4) is usually restricted to a few catchments: multiple-catchment studies are uncommon, despite their ability to identify dominant controlling factors better.

We studied the spatial variability and seasonal variation in water quality of 185 headwater catchments (from 5-179 km²) draining Brittany, an intensively farmed region of France. Our analysis focuses on dissolved C, N, and P concentrations as DOC, nitrate (NO_3), and soluble reactive P (SRP), respectively. We hypothesized that:

1) Human (i.e. rural and urban) pressures determine spatial variability in NO_3 and SRP concentrations, while soil and climate characteristics determine that in DOC and possibly SRP.
2) Seasonal variations in water quality provide information about spatial variability in biogeochemical sources and/or reactivity in catchments as a function of changes in water pathways and are correlated in part with spatial variability in concentrations and loads.

We selected headwater catchments for which relevant time series of DOC, NO_3, and SRP concentrations and stream flow were available (10 years of consecutive data measured at least monthly). In addition to estimating interannual loads, we calculated concentration metrics for each element to assess the spatial variability and temporal variation in water quality. Generalized Additive Models (GAMs) were applied to the time series to highlight average patterns of seasonal variation. Potential correlations between the water quality metrics and the geological, soil, climatic, hydrological, land cover, and human pressure characteristics of the corresponding headwater catchments were evaluated using rank correlation analyses.

2 Materials and Methods

2.1 Study area

Brittany is a 27,208 km² region in western France. Its bedrock is composed mainly of a crystalline substratum dominated by granite and schist (Supplement S1b). Its topography is moderate, with elevation ranging from 0-330 m a.s.l. Its climate is temperate oceanic, with precipitation ranging from 531 mm.yr^{-1} in the east to 1070 mm.yr^{-1} on the western coasts (regional

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median of 723.0 mm.yr^{-1}) (S1a), and a mean annual temperature of 12°C. The regional hydrographic network is dense, with a mean density of 1 km.km^{-2}. Its intensive agriculture has a strong influence on land use and agri-food production. Overall, 56.6% of the region was Utilized Agricultural Area (UAA) in 2017 (data from DREAL Bretagne, Brittany's Agency for Environment, Infrastructure, and Housing), which represented 6% of national UAA in 2016. Of total French production, Brittany produces 17.4% of milk and dairy products, 20% of pork products, and 17% of eggs and poultry (Brittany Chamber of Agriculture, 2016 data). At the canton (administrative district) scale, mean N and P surpluses are high and have high spatial variability (standard deviation (SD)): 50.01 ± 26.59 kg N.ha^{-1}.yr^{-1} and 22.52 ± 12.66 kg P.ha^{-1}.yr^{-1} (Supplement S1e,f). The region has a population of ca 3.3 million inhabitants (data 2017), some scattered throughout the region, and some concentrated in a few cities and near the coasts (Supplement S1c,d).

2.2 Stream data selection and headwater characteristics

Water quality data consisted of time series of DOC, NO_3, and SRP concentrations, extracted from two public monitoring networks – OSUR (Loire-Brittany Water Agency, 554 sites) and HYDRE/BEA (DREAL Bretagne, ca. 1964 sites), measured for regulatory monitoring, regional contracts, or specific programs. Concentrations were measured from grab samples. Headwater catchments were selected according to the following two criteria: (i) independence, with no overlap of the drained areas of the water-quality stations selected, and (ii) availability of at least 80 measurements of DOC, NO_3, and SRP concentrations at the same station (after removing outliers, i.e. values > 200 mg N.L^{-1} or 5 g P.L^{-1}) over 10 calendar years (2007-2016). We selected 185 stations (83% and 17% from OSUR and HYDRE/BEA, respectively) (hereafter, "concentration (C) stations"), which had mean frequencies of 12, 14, and 11 analyses per year for DOC, NO_3, and SRP, respectively.

Each C station was paired with a hydrometric station (Q). Observed daily streamflow data from the national hydrometric network (http://hydro.eaufrance.fr/) were used when draining headwater catchments for C and Q stations shared at least 80% of their areas (25% of cases). When observed Q data were not available, or at a frequency less than 320 measurements per year from 2007-2016 (75% of cases), discharge data were simulated using the GR4J model (Perrin et al., 2003). The headwater catchments selected and their associated C and Q stations were distributed throughout Brittany (Fig. 1).

The 185 headwater catchments selected cover ca. 32% of Brittany's area. Despite having a similar hydrographic context dominated by subsurface flow, the catchments have large differences in topography, geology, hydrology, and diffuse and point-source pressures of N and P. We used a set of catchment descriptors to quantify this variability (Table 1) (see Supplemental S2 for their statistical distribution). The descriptors selected included a set of spatial metrics for element sources (e.g. land use, pressure, soil contents) and for mobilization and retention processes (e.g. hydrology, climate, topography, geology, and soil properties).

The headwater catchments range in area from 5-179 km² (median of 38 km²), and the density of each one's hydrographic network ranges from 0.47-1.49 km.km^{-2} (median of 0.90 km.km^{-2}). Strahler stream order is 3 for 36% of the catchments, 2 for 18%, 4 for 17%, and 1 for 11%. Substrate composition is dominated by schists/micaschists (44%) or granites/gneisses (31%).

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In the topsoil horizon (0-30 cm), the soil organic C content varies greatly from 18.6-565.4 $g.kg^{-1}$ (median of 126.9 $g.kg^{-1}$), while the total P (Dyer method) content varies from 0.6-1.4 $g.kg^{-1}$ (median of 0.9 $g.kg^{-1}$). Land use is largely agricultural, although some catchments have high percentages of forested and urbanized areas. Riparian wetlands cover 12.3-36.3% of catchment area (median of 22.4%), forest covers 1.3-55.7% (median of 13.2%), pasture covers 10.3-46.7% (median of 25.6%), summer crops cover 6.5-50.3% (median of 27.8%), and winter crops cover 7.0-51.0% (median of 22.7%). The N and P surplus (potential diffuse agricultural sources) vary from 12.9-96.0 kg $N.ha^{-1}.yr^{-1}$ (median of 47.7) and 2.8-63.2 kg $P.ha^{-1}.yr^{-1}$ (median of 18.9), respectively. Urban areas cover 1.3-31.8% of the headwater catchments (median of 6%), with point-source input estimates ranging from 0-6.2 kg N. $ha^{-1}.yr^{-1}$ and 0-0.626 kg P. $ha^{-1}.yr^{-1}$. These data illustrate relative diversity in human pressures among the catchments despite a regional context of intensive agriculture. The daily mean flow (Qmean) varies from 4.8-24.5 $l.s^{-1}.km^{-2}$ (median of 10.8 $l.s^{-1}.km^{-2}$), the median of annual minimum of monthly flows (QMNA) varies from 0.2-5.9 $l.s^{-1}.km^{-2}$, and the flow flashiness index (W2), defined as the percentage of total discharge that occurs during the highest 2% of flows (Moatar et al., 2020), ranges from 10-28%.

2.3 Data analysis

2.3.1 Concentration and load metrics

To analyze spatial variability in DOC, NO_3, and SRP concentrations in streams, we calculated their 10th, 50th, and 90th percentiles of concentration (C10, C50, and C90, respectively) for each headwater catchment from 2007-2016. We also calculated the ratio of the coefficient of variation (CV) of mean concentration (CVc_{mean}) and to that of mean flow (CVq_{mean}) to compare spatial variabilities in concentrations and stream flow. We estimated interannual loads for a 10-year period (2007-2016), with 8-12 C-Q values per year. However, a 5-year period (2010-2014) was considered to analyze the spatial variability because it minimized data gaps (in C and Q time series) among all stations simultaneously.

To calculate interannual DOC, NO_3, and SRP loads for each headwater catchment, we tested different methods and selected the most suitable, depending on the reactivity of the element with flow. When C-Q relationships were relatively flat or diluted (NO_3) or slowly mobilized (DOC) during high flow (Q>Q50) , we used the discharge weighted concentration (DWC) method (Eq. 1), which estimates loads with lower uncertainties (Moatar and Meybeck, 2007; Raymond et al., 2013):

$$\mathrm{DWC} = \frac{k}{A} \times \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \overline{Q} \qquad (1)$$

where DWC is the mean of annual loads ($kg.y^{-1}.ha^{-1}$), C_i is the instantaneous concentration ($mg.l^{-1}$), Q_i is the corresponding flow rate ($m^3.s^{-1}$), $\overline{Q}$ is the mean annual flow rate calculated from daily data ($m^3.s^{-1}$), A is the area of the headwater catchment (m^2), k is a conversion factor (31557.6), and n is the number of C-Q pairs per year.

The loads estimated by the DWC method were corrected for bias. Precisions were calculated from the number of samples (n), number of years, export regime exponent (b_{50high}), and W2 (Moatar et al., 2020).

To calculate SRP loads, regression methods were more suitable (because of strong concentration patterns when stream flow increases). We averaged the loads estimated by two regression methods developed by Raymond et al. (2013) – Integral Regression Curve (IRC) and Segmented Regression Curve (SRC) – both based on a regression between concentration and flow:

$$\mathrm{IRC} = \frac{k'}{A} \times \sum_{i=1}^{n} C_i Q_i \quad (2)$$

$$\mathrm{SRC} = \frac{k'}{A} \times \left(\sum_{i=1}^{n} C_{inf} Q_i + \sum_{i=1}^{n} C_{sup} Q_i\right) \quad (3)$$

where IRC and SRC are the mean of annual loads (kg.$^{y-1}$.ha^{-1}); C_i, C_{sup}, and C_{inf} are instantaneous concentrations estimated by the regression curves (mg.l^{-1}); C_{sup} and C_{inf} are concentrations of flows above and below the median flow, respectively; and k' is a conversion factor (86.4).

2.3.2 Seasonal signal

Seasonal dynamics of discharge and solute concentrations were modeled using GAMs (Wood, 2017), which can estimate smoothed seasonal dynamics from time series (Musolff et al., 2017). The smoothing function was a cyclic cubic spline fitted to the month of the year (1-12); thus, the ends of the spline were forced to be equal, using the R package mgcv. We did not consider a long-term trend in the time series over the 10 years, for two reasons. First, significant long-term trends (according to Man-Kendall tests) had low amplitudes: mean Theil-Sen slopes ranged from -3% to 0% of the median concentration (while mean seasonal relative amplitudes exceeded 50%). Second, performance of the GAMs did not increase significantly when a long-term trend was added: the mean adjusted coefficient of determination (Rsq) increased from 0.16 to 0.18 for DOC and from 0.30 to 0.40 for NO_3. We considered a seasonal dynamic to exist at Rsq $\geq$ 0.10.

Seasonal dynamics of the concentrations of the three solutes (DOC, NO_3, and SRP) and river discharge were then analyzed using five metrics calculated from the daily simulations of the GAMs. The first three were the annual amplitude (Ampli; i.e. annual maximum minus annual minimum), and the mean time in which annual maximum and minimum concentrations occurred (MaxPhase and MinPhase, respectively; in months from 1 January). The next was Ampli standardized by the corresponding mean concentration to compare the three solutes. The last metric was a seasonality index (SI), which measures the relative importance of summer (1 June to 31 July) concentrations compared to winter (15 January to 15 March) concentrations of an element, as follows (Eq. 4):

$$\mathrm{SI} = \frac{C_{winter} - C_{summer}}{C_{winter} + C_{summer}} \quad (4)$$

where C_{winter} and C_{summer} are the mean of the GAM fitted at daily time step for winter and summer, respectively. Positive values of SI (near 1) indicate that $C_{winter} > C_{summer}$, while negative values (near -1) indicate that $C_{winter} < C_{summer}$. We

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considered that SI values close to 0 (from -0.1 to 0.1) indicated that $\mathrm{C_{winter}}$ equaled $\mathrm{C_{summer}}$. The SI integrates both amplitude and phasing features of the seasonal signal.

2.3.2 Statistical analyses

To compare the concentration metrics of the elements, a multivariate analytical approach, principal component analysis (PCA), was performed for the 9 variables of concentration percentiles (C10, C50, and C90) of DOC, NO_3, and SRP for the dataset of 185 headwater catchments. To identify dominant drivers of spatial variability in concentration percentiles, seasonality, and loads of DOC, NO_3, and SRP, we calculated Spearman's rank correlation (r_s) between these water-quality metrics and the descriptors of the headwater catchments. We considered a rank correlation to be significant if the corresponding p-value was ≤ 0.05. All analyses were performed using R software (v. 3.6.1) with packages mgcv, hydroGOF, hydrostats, FactoMineR, tidyverse, lubridate, reshape2, plyr, ggcorrplot, and ggplot2 (Grolemund and Wickham, 2011; Le et al., 2008; Wickham, 2016, 2011; Wood, 2017; Zambrano-Bigiarini, 2020).

3 Results

3.1 Spatial variability in concentrations and loads

The C50 of the 185 headwater catchments ranged from 2-14.6 mg C.l^{-1} for DOC, 0.9-15.8 mg N.l^{-1} for NO_3, and 8-241 µg P.l^{-1} for SRP (with 75% of the SRP C50 < 64 µg P.l^{-1}). The C50 displayed spatial gradients: rivers with DOC concentrations > 5 mg C.l^{-1} were located in eastern Brittany, while the highest NO_3 concentrations were located on the west coast (Fig. 2). In contrast, the highest concentrations of SRP (C50 > 68 µg P.l^{-1}) were located in northern Brittany.

The two first axes of the PCA (Supplemental S3a) performed on the percentiles of DOC, NO_3, and SRP concentrations of the 185 headwater catchments explained 58% of the variance and revealed three important points. First, percentiles (C10, C50, or C90) were grouped by solute, showing that the spatial organization remained the same statistically regardless of the percentile. This illustrated the stability of spatial patterns, which were demonstrated by Abbott et al. (2018a) in Brittany, and confirmed by Dupas et al. (2019) in whole France. Second, there was a negative correlation between DOC and NO_3 concentrations (r_s = -0.58; Supplement S3b). Third, SRP concentrations had an orthogonal relation compared to DOC and NO_3 concentrations.

The ratios of mean concentration (CVc_{mean}) to mean flow (CVq_{mean}) were < 1 for DOC and NO_3 (Table 2), indicating that concentrations varied less in space than in flow, and vice-versa for SRP.

For DOC and NO_3, Ampli was not correlated significantly with C50, but it was with C90 (Fig. 3). For SRP, correlations between Ampli and the percentiles were high, with r_s > 0.85 for C50 and C90 (Fig. 3). The SI and phases were correlated more with C10 for DOC and NO_3 (negatively for SI and positively for the phases), and more with C90 for SRP (negatively, for SI only).

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Mean (± 1 SD) interannual loads had high spatial variabilities – 20.71 ± 10.52 kg $C.ha^{-1}.yr^{-1}$ for DOC, 27.48 ± 18.51 kg $N.ha^{-1}.yr^{-1}$ for NO_3, and 0.315 ± 0.11 kg $P.ha^{-1}.yr^{-1}$ for SRP – which differed from those observed for concentrations (Fig. 2). Unsurprisingly, interannual loads of the three solutes were significantly ($p<0.001$) and strongly correlated with annual water fluxes (Pearson r = 0.88 for DOC, 0.90 for NO_3, and 0.75 for SRP). There were weak but significant positive correlations between mean interannual loads and seasonality indices (Ampli, SI) or C90 for DOC (Fig. 3). Mean interannual loads of NO_3 were significantly and positively correlated with C10 and C50, and negatively with its seasonality indices. The strongest significant correlation was found between mean interannual loads and concentration percentiles for SRP.

3.2 Characterization of concentrations seasonality

3.2.1 Performance of GAMS

Of the 185 catchments, GAMs were fitted for 159 for DOC concentrations, 168 for NO_3 concentrations, 162 for SRP concentrations, and 185 for discharge. The cases for which fitting was not possible corresponded to those with no seasonal cyclicity or with excessive interannual variability. The percentage of variance explained by the GAM varied by site and solute. Fitting performed best for NO_3, followed by SRP and then DOC: the means and SDs of the adjusted Rsq were 0.30 ± 0.18, 0.16 ± 0.11, and 0.22 ± 0.15 for NO_3, DOC, and SRP, respectively (Supplemental S4 and S5), and the percentages of catchment for which the fitted model had Rsq > 0.20 were 67%, 52% and 38%, respectively. Metrics calculated from monthly data differed only moderately from those calculated from sub-monthly data (Supplemental S6), which tended to validate the approach of using monthly data.

3.2.2 Types of seasonal cyclicity in DOC, NO_3, and SRP

Most of the catchments had a seasonal concentration cycle: 85%, 71%, 78%, and 100% for NO_3, DOC, SRP and discharge, respectively (Fig. 4). Means and SDs of the standardized Ampli were 0.59 ± 0.46 for NO_3, 0.53 ± 0.30 for DOC, 0.79 ± 0.14 for SRP, and 1.99 ± 0.38 for discharge. The distribution of the calculated seasonality indices is provided in Supplemental S7. For all catchments, the annual phases for discharge were more stable than those for concentrations. The highest discharge period was centered on mid-February (winter) and the lowest discharge period on September. A strong gradient of hydrological dynamics was observed among catchments (Fig. 4). The highest W2 was associated with both severe low-flow discharge and many high discharge events. Values of Q_{mean}, BFI, W2, and QMNA clearly followed an east-west gradient (not shown). Because of similar seasonal discharge dynamics in all catchments, SI can be used to describe the seasonal dynamics of a concentration relative to those of discharge. When SI was positive, the concentration seasonality was in-phase with discharge; when negative, the concentration seasonality was out-of-phase with discharge (Fig. 4).

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Most of the catchments had opposite dynamics for DOC and NO_3. For 90% of them, Pearson correlation between the daily GAM estimates of DOC and NO_3 was negative, and for 50% of the catchments, less than -0.79. The remaining 10% of catchments (15) had low Ampli of DOC and NO_3. The DOC and NO_3 concentrations had out-of-phase seasonal cycles, as shown by the negative correlation between SI and DOC or NO_3 for all catchments that had a significant seasonality in these concentrations (Fig. 5; $R^2 = 0.62$). We classified two types of catchments according to their seasonality in both DOC (MinPhase) and NO_3 (MaxPhase) concentrations and consistent with the SI (Fig. 5, Supplemental S7). NO_3 MaxPhase and DOC MinPhase that occurred before 1 May were classified as "in-phase" with discharge (Q), while those that occurred after were "out-of-phase" with Q. All catchments experienced high stability of the DOC MaxPhase and NO_3 MinPhase, which always occurred between July and December (Fig. 4, Supplemental S7).

The first type, "in-phase" (68% of the catchments with seasonality), had a NO_3 MaxPhase between October and May (Fig. 4, Supplemental S7) (i.e. high-flow period, in-phase with maximum discharge and usually with DOC MinPhase). For these catchments, the mean SI was positive for NO_3 (0.22 ± 0.19) and usually negative or null for DOC (0.00 ± 0.13). They tended to be located toward central Brittany and be associated with mesoscale catchments (mean of 52.6 ± 38.8 km²). They had large Ampli for NO_3 and low Ampli for DOC (mean relative Ampli of 0.83 ± 0.46, and 0.44 ± 0.23 for DOC) and relatively low C50 of NO_3 (means of 5.74 ± 2.46 mg $N.l^{-1}$ and 5.92 ± 2.00 mg $C.l^{-1}$).

The second type, "out-of-phase" (32% of the catchments with seasonality), had a DOC MinPhase and NO_3 MaxPhase between May and September (Fig. 4; Supplemental S7) (i.e. low-flow period, out-of-phase with maximum discharge). For most catchments, maximum NO_3 and minimum DOC concentrations occurred a mean of 1.85 months before minimum discharge or 5.5 months after maximum discharge, respectively. For these catchments, the mean SI was negative or null for NO_3 (-0.08 ± 0.06) and weakly positive for DOC (0.21 ± 0.10). These catchments were close to the coast and relatively small (mean of 31.4 ± 21.7 km²). The had smaller Ampli than "in-phase" catchments for NO_3, and higher Ampli for DOC (mean relative Ampli of 0.13 ± 0.13, and 0.74 ± 0.30 for DOC) and relatively high C50 of NO_3 (means of 8.27 ± 2.90 mg $N.l^{-1}$ and 5.00 ± 1.62 mg $C.l^{-1}$).

Some catchments had intermediate behavior between these two types (Figs. 4 and 5). Some had a plateau with maximum NO_3 and minimum DOC concentrations from winter to summer, while others showed two maxima for NO_3 or two minima for DOC (one synchronous with maximum discharge and another with minimum discharge). Other catchments also had maximum NO_3 synchronous with discharge, but minimum DOC after maximum discharge.

The seasonal dynamics of SRP were more stable than those of DOC and NO_3, but less stable than those of discharge. Thus, there was only one type of seasonality for SRP, which was out-of-phase with flow: MaxPhase SRP dominated in summer (mid-August ± 1.4 months), and MinPhase SRP dominated in late winter (March ± 1.2 months) (Fig. 4, Supplement S7), except for two catchments with maximum SRP in January-February.

3.3 Controlling factors of concentration percentiles and seasonality

The C50 of DOC was correlated significantly with 15 spatial variables and most strongly ($|r_s|\geq0.4$) with topographic index, QMNA, and the other hydrological indices. The C50 of NO_3 was correlated significantly with 12 spatial variables, in particular diffuse agricultural sources (r_s=0.68 for the percentage of summer crops, r_s>0.39 for N and P surplus, and r_s=0.48 for soil erosion rate) and hydrological indices, through the base flow index (BFI) (positively) and W2 (negatively), (Table 3). The C50 of SRP was correlated significantly with more variables (18), but the correlations were slightly weaker. It correlated most strongly with soil P stock (r_s=-0.40), climate and hydrology (effective rainfall, Qmean, QMNA), elevation, and hydrographic network density. It had weaker positive correlations (r_s<0.3) with the soil erosion rate and domestic and agricultural pressures (urban percentage and P surplus).

Ampli and SI for DOC and NO_3 were correlated most with the hydrodynamic properties, followed by agricultural pressures (Fig. 6, Table 3). The catchments "in-phase" with discharge (i.e. positive SI-NO_3 and negative SI-DOC correlations) were associated with high hydrological reactivity (low BFI and high W2) and a low percentage of summer crops (Table 3). Conversely, catchments "out-of-phase" with discharge (i.e. negative SI-NO_3 and positive SI-DOC correlations) were associated with low hydrological reactivity (high BFI and QMNA, low W2) and a high percentage of summer crops.

Correlations of SI with catchment descriptors were weaker ($|r_s| \leq 0.4$) for SRP than for DOC and NO_3 because most catchments had the same seasonal pattern, with maximum SRP concentration during low flow. Catchments with the highest amplitudes of SRP concentration were associated with low QMNA and Q_{mean}, high W2, low effective rainfall, and low soil P stock. Interannual loads were correlated mainly with hydrological descriptors (positively with Qmean and QMNA, and negatively with W2) (Table 3). Interannual NO_3 loads were also correlated with the percentage of summer crops and soil TP content, while interannual SRP loads were correlated weakly with the percentage of summer crops, agricultural surplus, erosion, and point sources.

4 Discussion

4.1 Interpretation of the spatial opposition between DOC and NO_3

Spatial opposition between DOC and NO_3 concentrations has been reported for a wide range of ecosystems. Taylor and Townsend (2010) found a non-linear negative relationship between them for soils, groundwater, surface freshwater, and oceans, from global to local scales, and highlighted that this negative correlation prevails in disturbed ecosystems. Goodale et al. (2005) reported a similar negative correlation among 100 streams in the northeastern USA. Heppell et al. (2017) found that DOC and NO_3 concentrations were inversely correlated with the BFI in six reaches of the Hampshire Avon catchment (UK). Our contribution brings an original focus on this relationship in headwater catchments with high domestic and agricultural pressures. Taylor and Townsend (2010) interpreted this spatial opposition as a response of microbial processes (i.e. biomass production, nitrification, and denitrification) to the ratio of ambient DOC:NO_3, which controls NO_3 export/retention in

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catchments (see also Goodale et al. (2005)). In semi-natural ecosystems, high but poorly labile soil organic C pools were associated with lower N retention capacity and thus higher N leaching (Evans et al., 2006). Similarly, several studies (e.g. Hedin et al. (1998), Hill et al. (2000)) suggested that DOC supply limits in- and near-stream denitrification. In contrast, other studies claimed that N can influence loss of DOC from soils by altering substrate availability or/and microbial processing of soil organic matter (Findlay, 2005; Pregitzer et al., 2004). In our study, C50 were correlated with both BFI and QMNA, positively for NO_3 and negatively for DOC, which suggests that catchments strongly sustained by groundwater flow produced higher NO_3 and lower DOC concentrations, as reported in other rural catchments (e.g. Heppell et al., 2017). The C50 of NO_3 increased with agricultural pressures (percentage of summer crop, N surplus), as observed by Lintern et al. (2018), while that of DOC increased in flatter catchments, which is consistent with results of Mengistu et al. (2014) and Musolff et al. (2018). This suggests that this spatial opposition between DOC and NO_3 results from the combination of heterogeneous human inputs, heterogeneous natural pools, and different physical and biogeochemical connections between C and N pools. In surface water, these heterogeneous sources are expressed to differing degrees depending on the catchment's hydrological behavior. When deep or slow flowpaths dominate, they store and release N via groundwater and mobilize little the sources rich in organic matter. When shallower and faster flowpaths dominate, they transport some of the N via compartments rich in organic matter, which causes N depletion and release of more DOC to the streams. The initial amounts of NO_3 along these flowpaths are a function of human pressures.

4.2 Interpretation of the temporal opposition between DOC and NO_3

The seasonal opposition between DOC and NO_3 concentration dynamics could be another manifestation of the spatial opposition between DOC and NO_3 sources, because the strength of the hydrological connection between sources and streams varies seasonally (e.g. Mulholland and Hill (1997), Weigand et al. (2017)). The direct contribution of biogeochemical reactions that connect DOC and NO_3 cycles may also vary seasonally (Mulholland and Hill, 1997; Plont et al., 2020). Indeed, temperature, wetness condition, and light availability influence rates of these organic matter reactions. In addition, the relative importance of the fluxes produced or consumed via these reactions appears clearer during the low-flow period, when the fluxes exported from the terrestrial ecosystem and delivered to the stream decrease. These reactions consume NO_3 (e.g. denitrification, biological uptake) and release (reductive dissolution) or produce (autotrophic production) DOC. Of the two seasonal NO_3-DOC cycles, the most common in our datasets is thus maximum NO_3 in-phase with maximum discharge and minimum DOC, which has been reported in Brittany (Abbott et al., 2018b; Dupas et al., 2018) and elsewhere (Van Meter et al., 2019; Dupas et al., 2017; Halliday et al., 2012; Minaudo et al., 2015; Weigand et al., 2017). The main control of seasonal DOC-NO_3 cycles appears to be related to hydrological indices (expressed as BFI and W2). Hydrological flashiness reflects the relative importance of subsurface flow compared to deep base flow (Heppell et al., 2017); thus, low BFI (or high W2) would indicate higher connectivity with subsurface riparian sources and shorter transit times. This is consistent with results of

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Weigand et al. (2017), who observed higher seasonal amplitudes in DOC and NO_3 concentrations and stronger temporal anti-correlation between DOC and NO_3 concentrations in stream water dominated by subsurface runoff.

Our results are consistent with these previous results, while the correlations with catchment characteristics can provide some explanation. Catchments with low BFI have larger shallow flows and experience seasonal DOC-NO_3 cycles that are in-phase with flow and have higher NO_3 amplitudes. These cycles can be interpreted as the combination of several mechanisms:

1) Synchronization of NO_3-rich and DOC-poor groundwater contribution with maximum flow.
2) Large contribution of near-/in-stream biogeochemical processes at reduced low flows that decreases NO_3 concentration (e.g. NO_3 consumption by aquatic microorganisms, biofilms, and macrophytes).
3) Large DOC-rich riparian contribution throughout the year, but larger in autumn, when flow starts to increase, as described in detail in previous AgrHys Observatory studies (Aubert et al., 2013; Humbert et al., 2015).

In contrast, catchments with higher BFI have smaller shallow flows and experience mainly DOC and NO_3 cycles that are out-of-phase with flow and have lower amplitudes. These cycles can be attributed to the following:

1) More continuous groundwater contribution, combined with a decrease in agricultural pressures over time, which could increase NO_3 concentrations more in deeper groundwater than in shallower groundwater (Abbott et al., 2018b; Martin et al., 2004; Martin et al., 2006). This vertical gradient in groundwater supply could explain why NO_3 concentrations peaked during the annual discharge recession, which is sustained mainly by deep groundwater inputs.
2) Little contribution of near-/in-stream biogeochemical processes at reduced low flows due to larger inputs from groundwater, which maintains a relatively high minimum NO_3 concentration.
3) Contribution of DOC-rich riparian sources, mainly in autumn, that are smaller than those in in-phase catchments, again due to a predominantly deeper geometry of water circulation.

4.3 Interpretation of the spatial and temporal signature of SRP

The correlations between the C50 of SRP and geographic variables highlighted the importance of P sources (soil P stocks, followed by domestic and agricultural pressures) and surface flowpaths (e.g. hydrological indices, elevation, erosion risk). Similarly, analysis of regression models that predicted spatial variability in total P concentration of 102 rural catchments in Australia also indicated positive effects of human-modified land uses, natural land uses prone to soil erosion, mean P content of soils, and to a lesser extent, topography (Lintern et al., 2018). They always included the percentage of urban area, which suggests a considerable effect of sewage discharge, even at low levels of urbanization. The catchments analyzed in the present study have a homogeneous and relatively dense distribution of small villages but no large city, which seems to support this last hypothesis. Sobota et al. (2011) studied spatial relationships among P inputs, land cover and mean annual concentrations of different forms of P in 24 catchments in California, USA. They found that P concentrations were significantly correlated with agricultural inputs and, to a lesser extent, agricultural land cover but not with estimates of sewage discharge.

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The seasonality of SRP was generally the same in the region studied, and C50 and amplitudes were significantly correlated. A peak in seasonal SRP concentrations at low flow has been reported previously (Abbott et al., 2018b; Bowes et al., 2015; Dupas et al., 2018; Melland et al., 2012). It is interpreted as the result of a dominance of point sources diluted during high flow (Minaudo et al., 2019, 2015; Bowes et al., 2011) or of stream-bed sediment sources for which P release increases with temperature (Duan et al., 2012).

Correlation between spatial patterns of NO_3 and SRP was expected given the dominant agricultural origin of N and substantial agricultural origin of P, but it was not observed in all catchments. The C50 of NO_3 and SRP were high mainly on the northwestern coast, perhaps due to intensive vegetable production associated with a dominance of mineral fertilization (Lemercier et al., 2008). Elsewhere, a high proportion of allochthonous P in the topsoil results from livestock farming and manure application (Delmas et al., 2015). The P-retention capacity of soils (related to their Al, Ca, Fe, and clay contents) is also likely to increase spatial variability in the release of P from catchments (Delmas et al., 2015). Synchronous variations in SRP and DOC, such as those observed in small, completely agricultural headwater catchments without villages (Cooper et al., 2015; Dupas et al., 2015b; Gu et al., 2017), were not observed in the present set of catchments. We assume that synchronicity of SRP and DOC in small catchments depends on soil processes, such as reduction of soil Fe-oxyhydroxides in wetland zones (Gu et al., 2019), which are hidden by in-stream processes (P adsorption on streambed sediments) and downstream point-source inputs (especially P inputs) in the set of larger catchments studied.

Regarding the geographic data used as spatial descriptors, the region studied did not have a few dense urban centers but rather smaller domestic points scattered across the region, which is harder to characterize finely. Moreover, Brittany's coastlines may have higher population densities in spring and summer due to tourism. Refined estimates of domestic point sources and their seasonal variations would be useful in future analyses.

4.4 Hydrological vs. anthropogenic controls of spatial variability in water quality

Among the headwater catchments selected, the human pressures (agriculture for NO_3 and sewage water discharge for SRP) influenced the C50 and loads of NO_3 and SRP. However, the influence of hydrological descriptors on the spatial variability in their loads suggested a transport-limited behavior of these catchments (Basu et al., 2010). Nutrient load estimates had high uncertainties due to i) using modeled flow data when measurements were not available and ii) the frequency of concentration data (monthly), which is low for estimating nutrient loads (especially of P) (Raymond et al., 2013). Thus, these load estimates allowed only their relative spatial variation to be analyzed. Although land-use or agricultural pressure variables, in combination with rainfall and discharge variables, are good predictors of nutrient loads at larger scales (Dupas et al., 2015a; Grizzetti et al., 2005; Preston et al., 2011), the correlations with loads were lower in the set of headwater catchments selected. For NO_3, this can be explained by higher spatial variability (CVs) in water fluxes than in concentrations (Table 2), which can explain the dominance of hydrological fluxes in the spatial organization of nutrient loads. It may also suggest that the nutrient-surplus data

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at the local scale remained uncertain (Poisvert et al., 2017) or that at this scale, data on agricultural practices would be more relevant, and that variability in concentration depends less on the magnitude of nutrient inputs than on their locations.

The catchments studied have clear seasonal dynamics in concentration, which is consist with previous observations (Minaudo et al., 2019; Abbott et al., 2018a). The seasonal pattern is controlled mainly by hydrological variables. It partly reflects the mixing of contrasting sources that are connected to streams by seasonally varying flowpaths with nutrients that are transferred vs. nutrients that are processed locally in hotspots (e.g. riparian buffer, stream water, stream sediments) or delivered over point sources. The seasonal NO_3-DOC pattern seemed to become somewhat homogenous among catchments larger than 100 km^2, where seasonal cycles with maximum NO_3 in-phase with flow seemed less common. This may be related to an increase in in-stream biological activity during summer as catchment size increases, enhanced by a lower stream water level and slower discharge (Minaudo et al., 2015). Therefore, the potential relationship between seasonal cycle type and catchment size should be studied over a wider range of catchment sizes and nested catchments to include variations along the hydrographic network.

5 Conclusion

To analyze spatial variability in water quality at a regional scale, we used an original dataset from public databases, little used by the scientific community, for the French region of Brittany with monthly measurements of water quality. The dataset selected covers 185 headwater and agricultural catchments monitored over a period sufficiently long (10 years) to allow the spatial (regional) variability and temporal (seasonal) variation in DOC, NO_3, and SRP concentrations to be analyzed. We described spatio-temporal variations in concentrations, loads, and seasonal patterns and analyzed their correlations with geographic variables (related to topography, hydro-climate, geology, soils, land uses, and human pressures). Our study showed the following:

1) Seasonal cycles of DOC and NO_3 concentrations are usually opposite from each other. Catchments with a low base-flow index exhibit maximum NO_3 in-phase with maximum flow, while those with a higher base-flow index exhibit maximum NO_3 after maximum flow. Both types exhibited maximum DOC in autumn, at the beginning of the annual increase in flow.
2) NO_3 concentrations increased as human pressures and base flow contribution increased. DOC concentrations decreased as rainfall, base flow contribution, and elevation increased. SRP concentrations showed weaker correlations with human pressures, rainfall, and hydrological and topographic variables.
3) Seasonal SRP cycles are synchronized in nearly all catchments that have a clear seasonal amplitude, with maximum SRP concentrations that occur during the summer low-flow period due to a decreased dilution capacity of point sources.

The spatial and temporal opposition between DOC and NO_3 concentrations likely results from a combination of heterogeneous human inputs and biogeochemical connection between these pools. The seasonal cycles in stream concentrations result from the mixing of water parcels that followed contrasting flowpaths, combined with high spatial variability in nutrient sources, local-scale biogeochemical processes, and point sources. As a perspective, we recommend further studies of multiple elements that are likely to show contrasting responses to diverse human pressures and to the retention/removal capacities of hydrosystems.

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Table 1. Headwater catchment descriptors identified as potential explanatory variables of spatial variability and temporal variation in dissolved organic carbon (DOC), nitrate (NO_3), and soluble reactive phosphorus (SRP) in stream and river water.

Type	Descriptor name	Unit	Definition	Source
Topography	Area	km²	Drainage area of the monitoring station	Web Processing Service "Service de Traitement de Modèles Numériques de Terrain" and DEM 50 m by IGN
	Elevation	m	Elevation of headwater catchment	DEM 25 m by IGN
	Density_hn	$km.km^{-2}$	Density of the hydrographic network	BD Carthage by IGN
	Topo_i	$log(m^3)$	Topographic index of the headwater	
	IDPR	-	Hydrographic Network Development and Persistence Index	http://infoterre.brgm.fr/ BRGM data and geoservices portal (Mardhel and Gravier, 2004)
Geology	Granite_pm	%	Percentage of granite and gneiss area	Web Mapping Service "Carte des Sols de Bretagne" by UMR 1069 SAS INRAE - Agrocampus Ouest http://www.sols-de-bretagne.fr/
	Schist_pm	%	Percentage of schist and micaschist area	
	Other_pm	%	Percentage of various geological substrata	
Soil	Erosion	%	Percentage of area with high to very high erosion risk (derived from land use, topography and soil properties)	Erosion risk map estimated from MESALES by GIS Sol, INRAE from Colmar et al. (2010)
	OC_soil	$g.kg^{-1}$	Organic carbon content in the topsoil horizon (0-30 cm)	Web Mapping Service from BDAT database, Saby et al. (2015) by GIS Sol
	Thick_soil	cm	Class of dominant soil thickness	Web Mapping Service "Carte des Sols de Bretagne" by UMR 1069 SAS INRAE - Agrocampus Ouest
	TP_soil	$g.kg^{-1}$	Total phosphorus content in the topsoil horizon (0-30 cm)	Web Mapping Service from BDAT database by GIS Sol
Land use	SummerCrop	%	Percentage of summer crop land	OSO database, CESBIO, land-cover map 2016 (1 ha) from http://osr-cesbio.ups-tlse.fr/~oso/
	WinterCrop	%	Percentage of winter crop land	
	Forest	%	Percentage of forest land	
	Pasture	%	Percentage of pasture land	
	Urban	%	Percentage of urban land	
	Wetland	%	Percentage of potential wetlands	Web Mapping Service "Enveloppe des milieux potentiellement humides de France réalisée par les laboratoires Infosol et UMR SAS" by UMR 1069 SAS INRAE - Agrocampus Ouest / US 1106 InfoSol INRAE
	N_surplus	$kg.ha^{-1}.yr^{-1}$	Nitrogen surplus (= the maximum quantity on a given agricultural area that	CASSIS-N estimates by (Poisvert et al., 2017) from

			is likely to be transferred to the stream network)	https://geosciences.univ-tours.fr/cassis/login
Diffuse and point N and P sources	P_surplus	kg.ha^{-1}.yr^{-1}	Phosphorous surplus	NOPOLU estimates by (SoeS, 2013)
	N_point	kg.ha^{-1}.yr^{-1}	Sum of nitrogen loads from domestic and industrial point sources	Data from Loire-Bretagne Water Agency data (2008-2012)
	P_point	kg.ha^{-1}.yr^{-1}	Sum of phosphorus loads from domestic and industrial point sources	Data from Loire-Bretagne Water Agency (2008-2012)
Hydrology	Qmean	l.s^{-1}.km^{-2}	Interannual mean flow	Calculated from flow data observations: HYDRO regional database by DREAL Bretagne & GR4J simulations (Perrin et al., 2003)
	QMNA	l.s^{-1}.km^{-2}	Median of annual minimum monthly specific discharge	
	BFI	%	Base flow index (Lyne et Hollick, 1979)	
	W2	%	Percentage of total discharge that occurs during the highest 2% of flows (Moatar *et al.*, 2013)	
	Rainfall	mm.yr^{-1}	Mean effective rainfall from 2008-2012	SAFRAN database (8 km²) by Météo France

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Table 2. Coefficients of variation (spatial variability among catchments) of flow-weighted mean concentration (CVcmean) and mean stream flow (CVqmean), and the value of their ratio, for dissolved organic carbon (DOC), nitrate (NO_3), and soluble reactive phosphorus (SRP).

Parameter	CVcmean	CVqmean	CVcmean:CVqmean
DOC	0.2954	0.4614	0.6403
NO_3	0.3285	0.4709	0.6976
SRP	0.9207	0.4743	1.9412

Table 3. Spearman rank correlations between water quality indices and geographical descriptors for dissolved organic carbon (DOC), nitrate (NO_3), and soluble reactive phosphorus (SRP). Only significant correlations (p≤0.05) are shown, and bold text indicates |r| ≥ 0.40.

		DOC				NO_3				SRP			
Spatial variable		C50	Ampli	SI	Load	C50	Ampli	SI	Load	C50	Ampli	SI	Load
Topography	Area	-	-0.24	-	-	-	-	-	-	-	-	-	-
	Elevation	**-0.46**	-0.18	-	-	-	-0.31	-0.20	0.19	-0.20	-	-	-
	Density_hn	-	-	-	-	-	-0.22	-	0.16	-0.30	-0.27	0.19	-
	Topo_i	**0.54**	-	-	-	-	**0.41**	0.25	-0.33	0.39	0.25	-	0.18
	IDPR	-	-	-	-	-	-	-	-	-0.21	-0.19	-	-
Geology	Granite_pm	-	-	0.21	**0.41**	-	**-0.43**	-0.31	0.27	-0.26	-0.24	-	-
	Schist_pm	-	-0.21	-0.37	-0.29	-0.16	0.25	0.22	-0.23	-	-	-	-0.20
	Other_pm	-	0.32	0.35	-	0.28	-	-	-	0.28	0.16	-	0.35
Soil	Erosion	-0.36	0.24	-	-	**0.48**	0.16	-0.26	0.39	0.24	0.17	-	0.33
	OC_soil	-0.27	-0.21	-	-	-	-0.29	-	0.18	-0.20	-0.19	-	-
	TP_soil	**-0.44**	-	-	0.38	-	**-0.51**	-0.34	**0.49**	**-0.40**	-0.32	-	-
Land use	SummerCrop	-0.30	0.28	**0.54**	-	**0.68**	-	**-0.47**	**0.54**	-	-	0.29	0.36
	WinterCrop	0.19	-	-0.20	-0.29	-	**0.48**	0.21	-0.23	0.17	-	-0.18	-
	Forest	-	-0.17	-0.30	0.23	-0.37	**-0.47**	-	-	-0.29	-0.19	-	-0.27
	Pasture	-	-	-	-	-0.30	-	0.26	-0.20	-	-	-	-
	Urban	-	-	-	-	-	-	-	-	0.23	-	-	-
N and P diffuse and point sources	N_surplus	-0.21	0.20	-	-	0.39	-	-	0.38	-	-	0.29	0.29
	P_surplus	-0.24	0.33	-	-0.22	**0.49**	-	-0.32	0.37	0.20	-0.19	-	0.35
	N_point	-	-0.17	-	-	-	-	-	-	-	-	-	-
	P_point	-	-0.16	-	-	-	-	-	0.21	-	-	-	0.21
Hydrology	Qmean	**-0.49**	0.19	-	**0.53**	0.16	**-0.58**	**-0.42**	**0.67**	-0.39	-0.31	0.21	0.18
	QMNA	**-0.52**	0.25	**0.41**	**0.48**	**0.42**	**-0.54**	**-0.56**	**0.76**	-0.34	-0.32	0.35	0.27
	BFI	**-0.41**	-0.27	**0.64**	0.38	**0.54**	**-0.52**	**-0.69**	**0.57**	-0.20	-0.23	0.32	0.23
	W2	**0.43**	-	**-0.61**	**-0.46**	**-0.49**	**0.54**	**0.68**	**-0.59**	0.20	0.20	-0.26	-0.24
	Precipitation	**-0.50**	-	-	**0.47**	-	**-0.60**	-0.39	**0.60**	**-0.43**	-0.33	0.18	-
	Wetland	0.16	-	0.31	0.38	-	-	-	-	-	-	-	0.35

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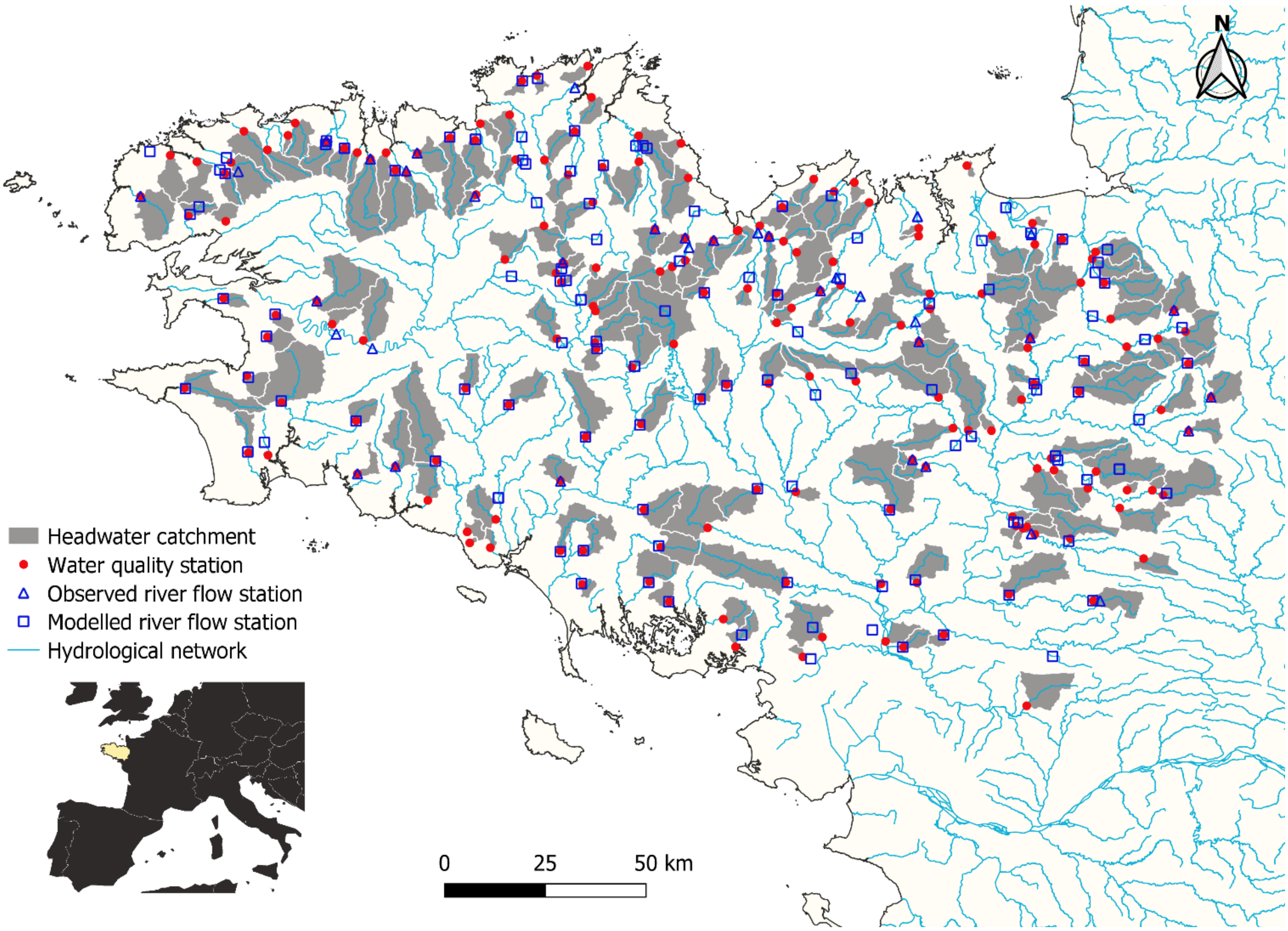

Figure 1. Locations of the 185 study headwater catchments where dissolved organic carbon, nitrate, and soluble reactive phosphorus concentrations were monitored monthly at the outlet from 2007-2016, and paired discharge stations where daily records of stream flow were available from observations or modeling.

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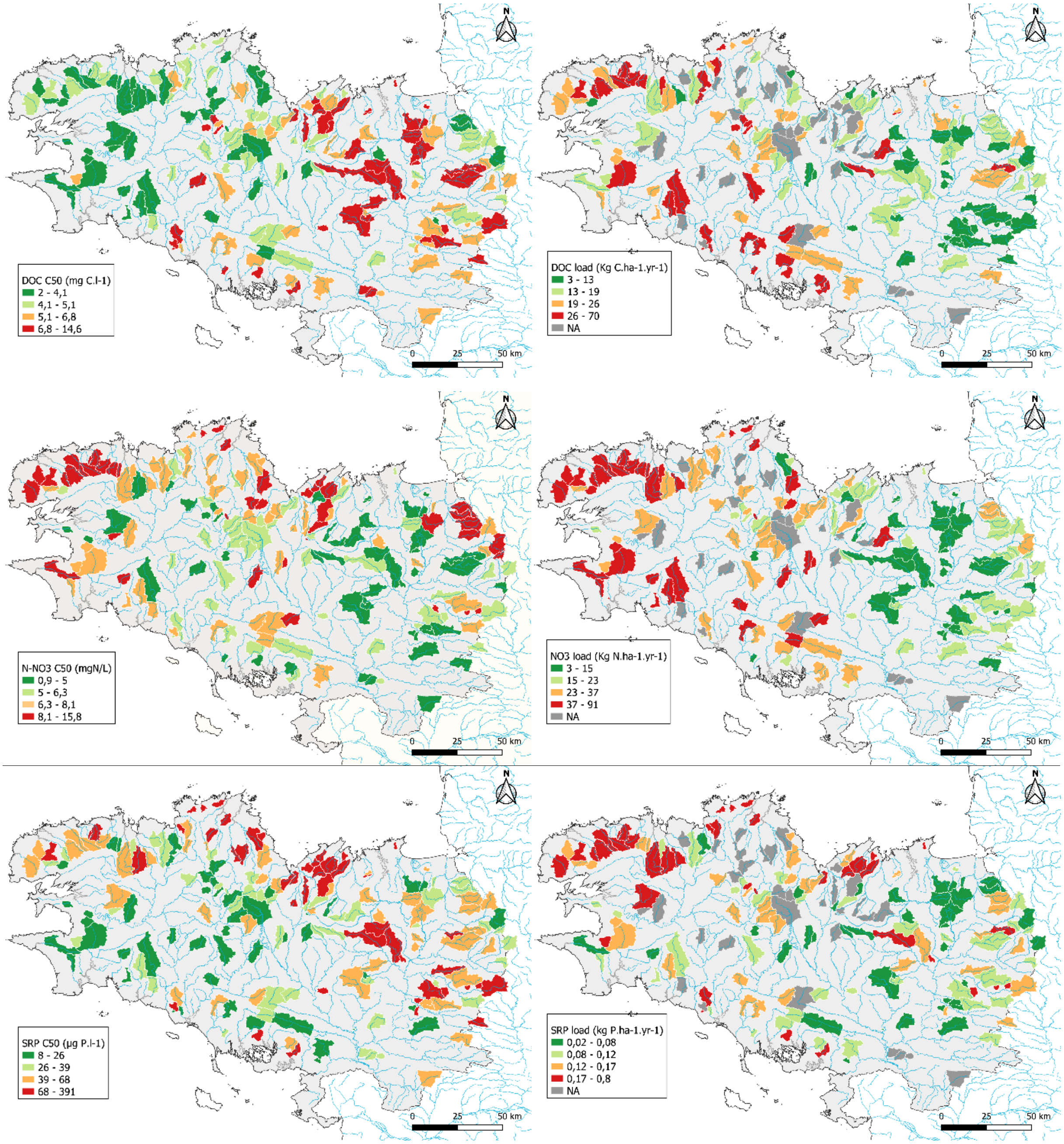

705 **Figure 2. Map of median (left) concentrations C50 and (right) loads of dissolved organic carbon (DOC), nitrate N (N-NO₃), and soluble reactive phosphorus (SRP) for the 185 streams. The catchments in gray did not meet the criteria to estimate a mean average interannual load. Classes in the legends have equal numbers of catchments.**

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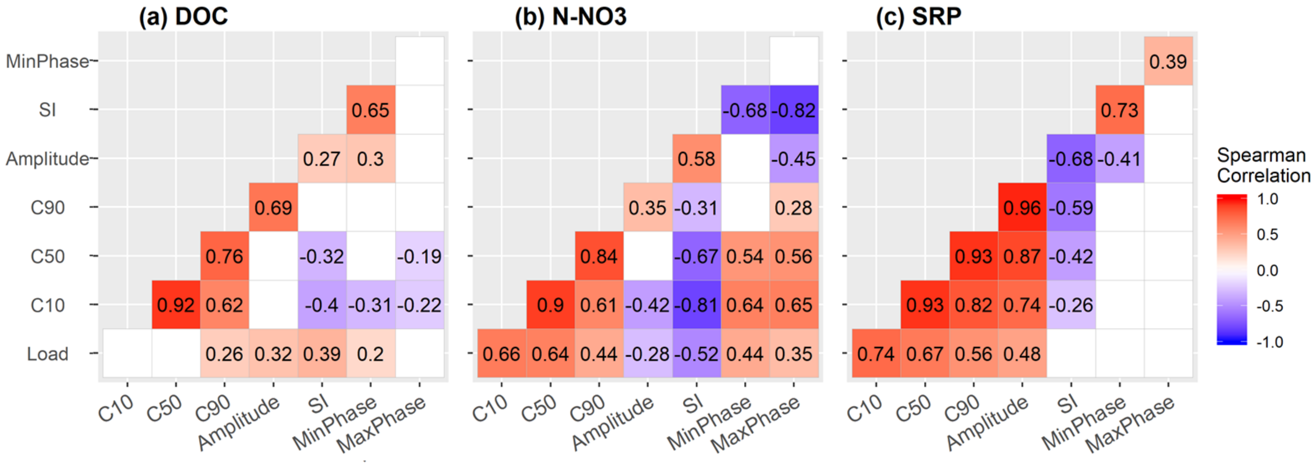

Figure 3. Matrices of Spearman's rank correlations of water quality (load, concentration percentiles (10th (C10), 50th (C50), and 90th (C90)), and seasonality metrics) for (a) dissolved organic carbon (DOC), (b) nitrate N (N-NO$_3$), and (c) soluble reactive phosphorus (SRP) (c). Only significant ($p \leq 0.05$) values are shown.

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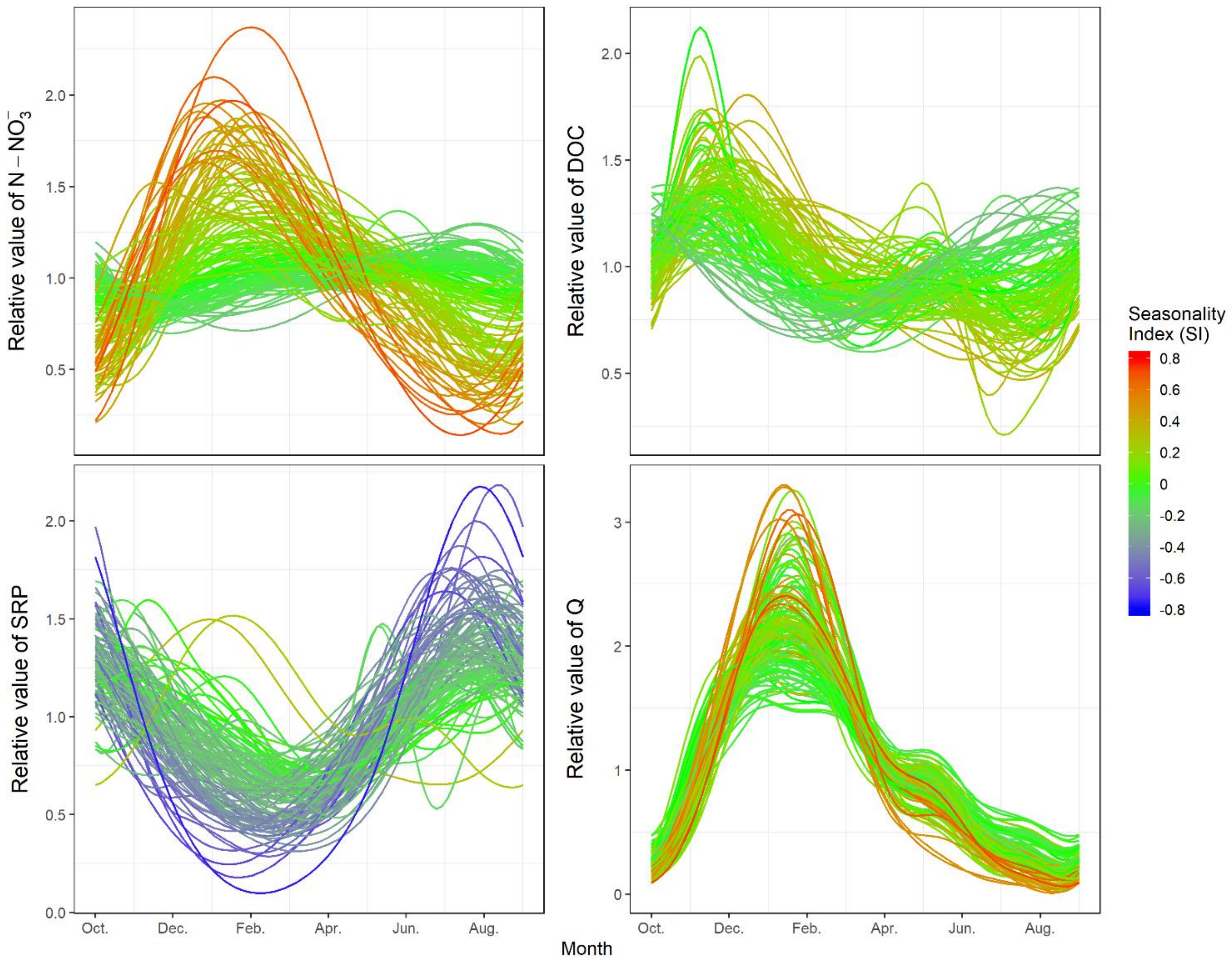
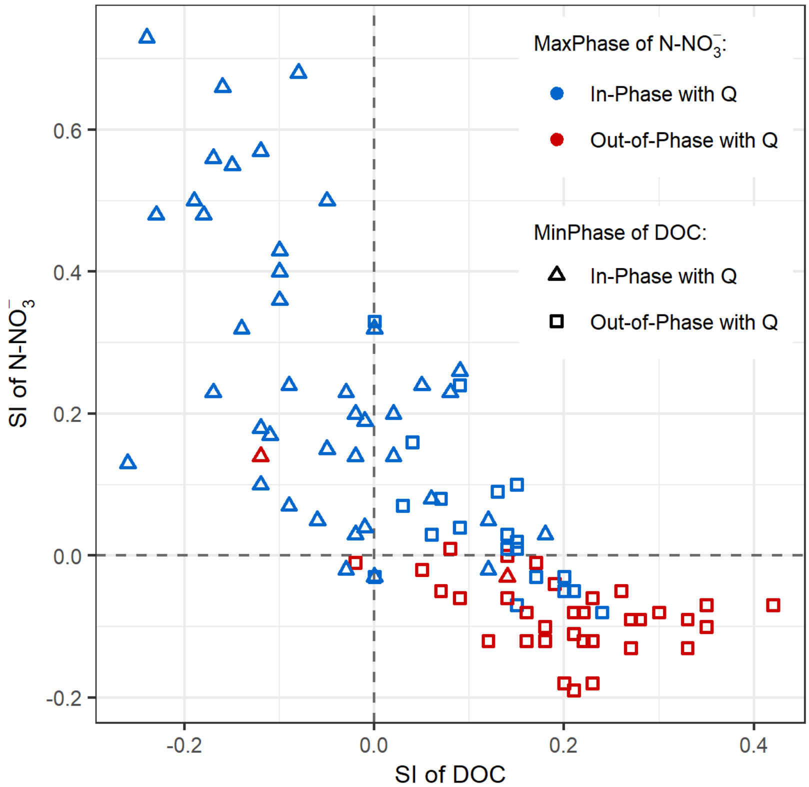
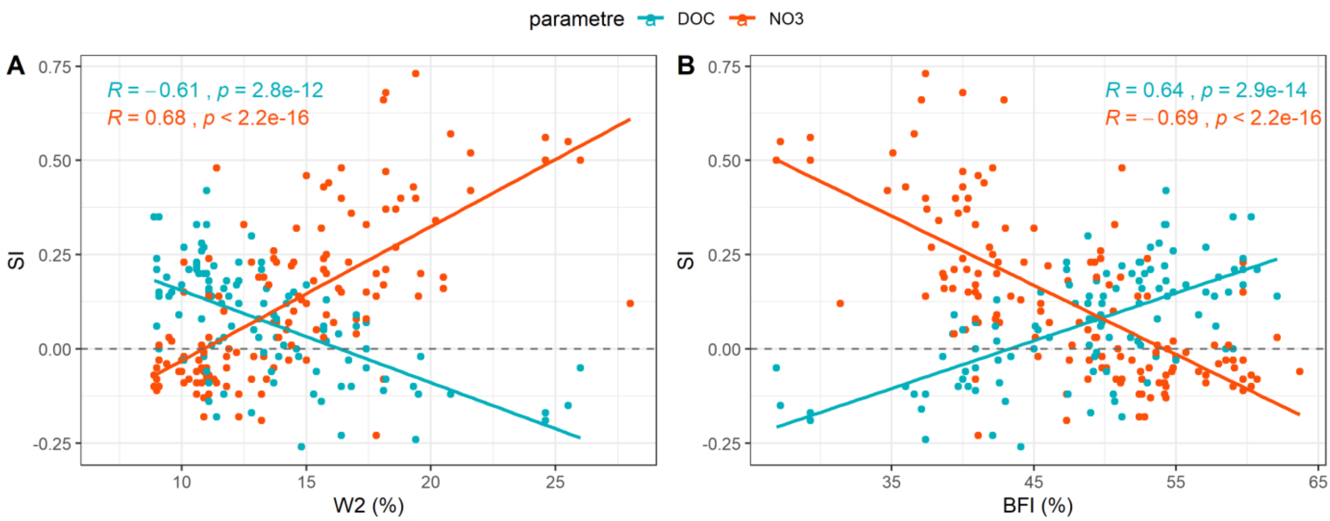


Figure 4. Seasonal dynamics of nitrate N (N-NO_3), dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), and daily discharge modeled by Generalized Additive Models for 185 headwater catchments. To compare concentrations, they are standardized by their mean interannual concentration. The color gradient represents the seasonality index of each parameter; thus, a headwater catchment's color can vary among panels.



725 **Figure 5. Relationship between the seasonality indices (SI) of nitrate N (N-NO$_3$) vs. dissolved organic carbon (DOC) in the headwater catchments for which seasonality was significant for both parameters (n=98). The color and shape of symbols identify the seasonality types based on the NO$_3$ MaxPhase and DOC MinPhase metrics. The threshold date was 1 May: MaxPhase that occurred before were classified as "in-phase" with discharge (Q), while those that occurred after were "out-of-phase" with Q. The DOC MinPhase metric is shown to highlight the synchrony between minimum DOC and maximum N-NO$_3$ concentrations.**



730 **Figure 6. Relationship between the seasonality index (SI) of dissolved organic carbon (DOC) and nitrate (NO_3) and the hydrological reactivity descriptors (A) flow flashiness index (W2) and (B) base-flow index (BFI) for 124 headwater catchments.**