Reply to Anonymous Referee #1

We appreciated that the Referee #1 found the study "*interesting for catchment scientists and water quality managers and suitable for HESS*".

He/she raised three major criticisms:

1) Methods: clarifying the choice of PCA and GAM, and analyzing the covariation among predicting variables

1a) *Statements made from the PCA could have been made from simple correlation analysis as well.*

And detailed comment on *L213ff: All these statements could have been made from a correlation analysis of C10, C50 and C90 (among and between the three nutrients) only. I do not see the added value of the PCA - from my point of view it may be taken out.*

We agree that correlation coefficients (see table below) led to the same conclusion. The PCA was chosen for graphical representation of the relationships between C10, C50 and C90. Figure S3a was already provided in supplemental rather than in the main text, therefore we suggest adding the correlation coefficients values in the main manuscript to clarify potential questions:

"First, percentiles (C10, C50, or C90) were grouped by solute, showing that the spatial organization remained the **same regardless of the concentration** percentile (**Spearman rank correlations between the three indices always greater than 0.56 for all elements**). […]. Second, there was a negative correlation between DOC and NO3 concentrations (rs= -0.58; Supplement S3b). Third, SRP concentrations had an orthogonal relation compared to DOC and NO3 concentrations **(rs close to zero)**."

Table R1: Spearman's rank correlations between the C10, C50 and C90 metrics for each element

	DOC		NO3		SRP	
	C50	C90	C50	C90	C50	C90
C10	0.89	0.56	0.87	0.56	0.9	0.78
C50		0.71		0.83		0.93

1b) *The GAM selects only catchments with a significant seasonality and discards chemostatic catchments. The basic findings could have maybe been also derived by simply describing seasonality indices and/ or a averaging of concentrations for each month of the year.*

And detailed comment on *L232f: Can you quantify that? Is mean SI lower for the cases where GAM could not be fitted?*

GAMs cannot be fitted with reasonable performance if there is no seasonal signal on the time series, thus it does allow for identifying “chemostatic” or - more consistently with the terminology proposed by Van Meter et al. (2019) that we are using in the text - “aseasonal” catchments. The seasonality metrics are then computed from the GAM outputs. For “aseasonal” catchments, amplitude and seasonal index are zero indeed, whereas PhaseMin and Phase Max cannot be identified (using GAM or not).

We agree that several methods can be used to characterize seasonality: averaging concentration (or discharge) of each month through the years is one of them. Here, we chose to smooth the data with a GAM model to limit the influence of outliers and to deal with data gaps: the results eventually look “smoother” than with a monthly aggregation method.

1c) *Finally, the correlation analysis with the catchment variables should touch and discuss covariation among the predicting variables. This often hinders interpretation towards underlying processes.*

There are indeed correlations among the predicting variables, which are expected, e.g. BFI and W2 are anti-correlated. We suggest adding the correlation matrix below in Supplemental.

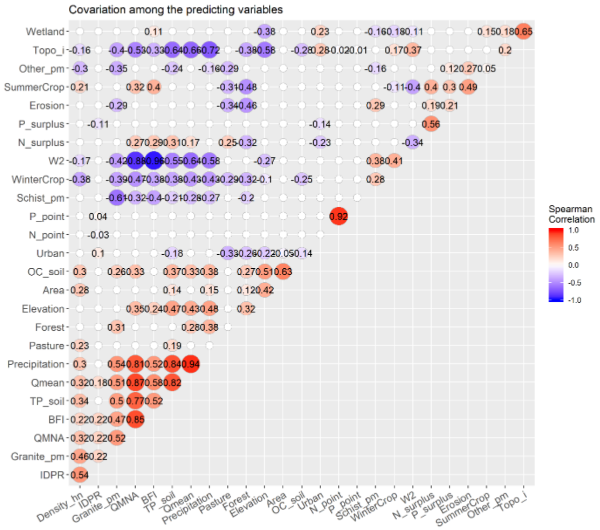


Figure R1: Correlation matrix between Headwater catchment descriptors, Spearman coefficients are visible when p-value > 0.05.

2) *Discussion: a synthesis that goes beyond the description is missing, in regards with previous literature on natural versus anthropogenic drivers*

And detailed comments in introduction:

L45-54: This exploration of human impacts on C, N and P concentration and spatial concentration variability is not totally convincing. I think some more words, a clear structure and a systematic evaluation of all three nutrients is needed. I miss a discussion on the spatial homogenization by agriculture that was discussed by Basu et al.(2010, 10.1029/2010gl045168) and Basu et al. (2011, 10.1029/2011wr010800)

The paragraph L45-54 aims at reviewing the reported factors of spatial variability in concentrations among various contexts. The following paragraph L. 55-65 aims at reviewing reported temporal variability in these C, N and P concentrations at the seasonal scale.

There is a considerable literature on the emergence of a chemostatic behavior in catchments due to management and agriculture (Basu et al., 2010; 2011; Thompson et al., 2011; Musolff et al., 2015; Moatar et al., 2017). Chemostaticity, or biogeochemical stationarity, is defined as the lower variability in water concentration relatively with flow variability (Thompson et al., 2011), so that solute mobilization rates only depends on water fluxes (Basu et al., 2011) and the transport of this solutes is qualified as “transport-limited” (Basu et al., 2010). This chemostaticity is supposed to be the typical behavior of catchments for geogenic solutes because of the geological legacy of “large, ubiquitous source mass distributed within the catchment”. In less impacted catchments, the export behavior is expected to be rather source limited as the contemporary sources are distributed within the catchment and because the biogeochemical processes (sorption, degradation) control the amount of solute available for export. These studies hypothesize that, in managed catchments, accumulation of nutrients lead to anthropogenic and spatially homogeneous legacy storages of nutrients within the catchment responsible for the emergence of a chemostatic behavior for these nutrients.

The chemostaticity is determined through the analysis of concentration-discharge or load-discharge relationships or of coefficient variation ratios of concentration versus discharge. It refers rather to the temporal variability of concentration in streams, and usually at inter-annual or long-term scales at which the legacy storages may be viewed as homogeneous within the catchment considering that every year these storages are connected at least during high flow periods (Moatar et al., 2017). Here, we focused on seasonal concentration patterns and they are sensitive to the source spatial distribution within the catchment because of the difference in their connectivity between high and low flow periods. Therefore, the spatial variability in those seasonal patterns does not depend on the management level but rather on the catchment intrinsic properties (topography, geology, climate…)

We suggest adding pieces of discussion to position our study in regards to these published results in the introduction:

“Besides being spatially variable, C, N, and P concentrations also vary **temporally. The variability of concentrations with flow has been described in several studies using concentration-flow relationships at event (Fasching et al., 2019) or inter-annual to long-term scales (Basu et al., 2010; 2011; Moatar et al., 2017). 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).”

and in the discussion subsection 4.4.:

“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. **Such dominance was found to increase with the level of human pressure in Thompson et al. (2011) for NO_3. In this study, such relationship was not visible as all the catchments exhibited a transport-limited behavior**. It may also suggest that the nutrient-surplus data at the local scale remained uncertain (Poisvert et al., 2017) ...”

Fasching, C., et al. (2019). "Natural Land Cover in Agricultural Catchments Alters Flood Effects on DOM Composition and Decreases Nutrient Levels in Streams." Ecosystems **22**(7): 1530-1545.

Moatar, F., et al. (2017). "Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions." Water Resources Research **53**(2): 1270-1287.

Thompson, S. E., et al. (2011). "Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients." Water Resources Research **47**(10).

Basu, N. B., et al. (2010). "Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity." Geophysical Research Letters **37**(23).

Basu, N. B., et al. (2011). "Hydrologic and biogeochemical functioning of intensively managed catchments: A synthesis of top-down analyses." Water Resources Research **47**(10).

3) Perspective: what are implications for ecological water quality and for management and potential future development of these catchments?

+ detailed comment on the “conclusion” : *The conclusions restate the major findings, which is ok for me, but miss implications (e.g. for management) and an overarching synthesis on catchments functioning (in concert with previous studies on e.g. denitrification or solute mobilization from the Brittany [Kolbe et al. 2019, 10.1073/pnas.1816892116], the above mentioned Fovet et al. 2018).*

We agree that adding perspectives on ecological and management implications would increase the impact of our article and we suggest adding the following subsection to the discussion section to enlarge these perspectives:

“5.4. Implications for headwater monitoring and management

The high regional and seasonal variations of nutrient concentrations in streams probably drive high variations of nutrient stoichiometry along the water year and over the region, and, as a consequence, high variations in time and space of eutrophication risks downstream (Westphal et al., 2020). Due to the combination of anthropogenic and hydrological drivers in explaining these stream concentrations, a better estimation on nutrient inputs and discharge in all headwater catchments, as a first step, is important to predict areas at risks.

The spatial analysis shows high and poorly structured spatial variations of concentrations over the region. Nevertheless, the opposition between NO3 and DOC concentrations suggests that the C:N ratios will be even more variable:

1) In space: catchments with high DOC C50 and low NO3 C50 will exhibit very high C:N and vice versa
2) Over the season: as minimum of DOC and maximum of NO3 concentrations are in-phase: catchment where DOC-NO3 variations are in phase with Q will exhibit a low C:N ratio in winter high flow period and higher C:N ratio during low flow period. The N:P ratio in these catchments will be high during the low flow periods (high NO3 and low SRP concentrations). Catchments where DOC-NO3 variations are out-of-phase with discharge will exhibit probably less variation in their ratios (because of lower NO3 amplitude) with relatively higher winter C:N ratio than the previous type of catchments.“

Westphal, K., Musolff, A., Graeber, D., and Borchardt, D.: Controls of point and diffuse sources lowered riverine nutrient concentrations asynchronously, thereby warping molar N:P ratios, Environ. Res. Lett., 15, 104009, 2020.

Moreover, to make the link between the interpretations we propose in the discussion and the cited previous studies in similar sites (Kolbe et al., 2019 and Fovet et al., 2018) and following the detailed comment on *L350ff “The study may benefit from a conceptual sketch of the two general types of catchments, its N and C sources and seasonal changes.”*,

We suggest adding the following figure to illustrate section 4.2.

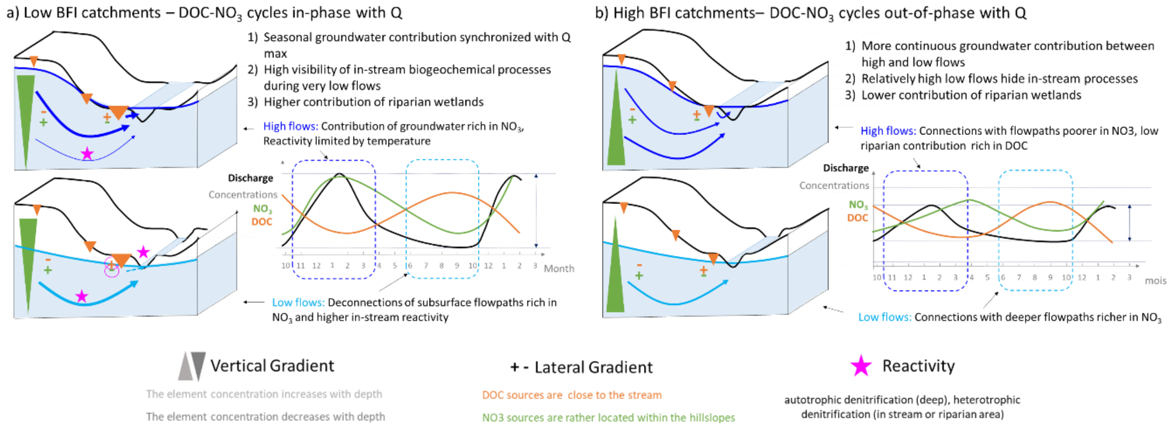


Figure R2 (new Figure 7) : Conceptual diagram of seasonal flowpaths involved in the DOC-NO$_3$ seasonal cycles leading to a) in-phase cycles with discharge or b) out-of-phase cycles with discharge.

Reply to specific comments

Abstract: I would have expected some discussion part on the underlying processes here. You describe patterns but you do not discuss these. Why?

We suggest adding two sentences for describing the discussed interpretations of these seasonal cycles in the abstract:

“The annual maximum NO3 concentration was in-phase with maximum flow when the base flow index was low, but this synchrony disappeared when flow flashiness was lower. **These DOC-NO3 seasonal cycle types were related to the mixing of flowpaths combined with the spatial variability of their respective sources and to local biogeochemical processes.** The annual maximum SRP concentration occurred during the low-flow period in nearly all catchments. **This likely resulted from the dominance of P point sources.** “

L23: "opposing pattern" would maybe fits better here.

The adjective “opposite” refers well here to “inverse” whereas the first sense of “opposing” would be “adverse”, while its second definition is indeed “opposite”. Then and after crosschecking with an American English native speaker, it seems that the initial formulation was correct.

Introduction

L39: Mentioning headwater catchments here seems to be disconnected from the line of argumentation. Why is it relevant to look at headwaters? You mention that later -maybe start with that argument here.

The paragraph from line 39 to line 44 describes why it is rare but relevant to look at headwaters quality. Because focusing on headwaters is a specificity of our study, we found important to explain this point as an element of context before the review and analysis of literature on spatial and seasonal variability of stream water C, N and P concentrations. However to better reconnect this paragraph with the previous we can rephrase as: “**In addition, the quality of** headwater catchments have been studied less than large rivers (Bishop et al., 2008), despite their influence on downstream water quality and higher spatial variability in their concentrations (Abbott et al., 2018a; Temnerud and Bishop, 2005).”

L49: Other studies such as Zarnetske et al. (2018, 10.1029/2018gl080005) or Musolff et al. (2018, 10.1016/j.jhydrol.2018.09.011) indicate a dominance of topography and connected wetlands in terms of concentrations (not DOC quality).

Indeed, and we describe this observation in the previous sentence (line 45-47): “DOC concentration 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).". We suggest adding these two suggested additional references to the citation list line 47.

L69: Why need the human pressure to be similar in headwater catchments to study them better?

Water chemistry in headwater catchments is influenced by human pressure and the catchments' intrinsic buffering capacity. It is easier to disentangle the effect of both factors when one is relatively constant while the other is spatially variable.

Several authors demonstrated that Human activities disturbed water quality using catchments depicting a gradient of human pressure. Along a gradient where the percentage of agricultural area varies from 0 to 50 or 60%, with an equilibrate distribution, it is likely that the main driver of spatial variability in water quality (e.g. in NO3 concentration) will be the percentage of agricultural area. Along a gradient where the percentage of agricultural area varies from 60 to 90%, it is likely that other drivers will play a major role in controlling spatial variability of the water quality.

L72: The reference (Agren) here has an unclear meaning. Does this study state the lack of seasonal analysis or also do not consider seasonality or consider as a rare case seasonality?

In Agren et al. (2007), the authors analyzed the importance of seasonality and small streams for regulation of DOC export studying 15 subcatchments (<30 km^2) over 3 years. They highlighted that the geographic controls of the spatial variation in DOC exports varied between seasons. We suggest to reformulate this point and change the reference for a list of citations that report seasonal patterns in C, N and/or P stream concentrations: "with little or no analysis of seasonal patterns **despite their frequent occurrence (Van Meter et al., 2019; Abbott et al., 2018b; Liu et al., 2014; Halliday et al., 2012; Mullholland et al. 1997)**".

L78f: This hypotheses needs to be better worked out above - see my comment above (referring to L45-54).

We suggest adding several references explaining where these hypotheses originate:

"We hypothesized that: 1) Human (i.e. rural and urban) pressures determine spatial variability in NO_3 and SRP concentrations **(Preston et al., 2011; Melland et al., 2012; Dupas et al., 2015; Kaushal et al., 2018)**, while soil and climate characteristics determine that in DOC and possibly SRP **(Lambert et al., 2011; Humbert et al., 2015; Gu et al., 2017)**."

Preston, S. D., et al. (2011). "Factors Affecting Stream Nutrient Loads: A Synthesis of Regional SPARROW Model Results for the Continental United States1." JAWRA Journal of the American Water Resources Association **47**(5): 891-915.

Melland, A. R., et al. (2012). "Stream water quality in intensive cereal cropping catchments with regulated nutrient management." Environmental Science & Policy **24**: 58-70.

Dupas, R., et al. (2015). "Assessing the impact of agricultural pressures on N and P loads and eutrophication risk." Ecological Indicators **48**: 396-407.

Kaushal, S. S., et al. (2018). "Watershed 'chemical cocktails': forming novel elemental combinations in Anthropocene fresh waters." Biogeochemistry **141**(3): 281-305.

Lambert, T., et al. (2013). "Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment." Water Resources Research **49**(9): 5792-5803.

Humbert, G., et al. (2015). "Dry-season length and runoff control annual variability in stream DOC dynamics in a small, shallowgroundwater-dominated agricultural watershed." Water Resources Research **51**(10): 7860-7877.

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.

L84: What are "relevant" time series?

The relevance of the time series refers here to the end of the sentence, i.e. the availability of the four parameters (Q, DOC, NO3, SRP) over a long-term period (10 years) and at medium frequency (monthly).

L87: I suggest to leave out "potential" here. The causality of the correlation may be potentially hint to an underlying process.

We agree with the suggestion.

Material and Methods

Table 1: Catchment descriptors are not always self-explaining: What is the topographic index? Is elevation referring to the mean elevation? What is the "class" of dominant soil thickness?

- The downstream topographic index (Topo_i) is a steady state wetness index commonly used to quantify topographic control on hydrological processes and developed by (Beven and Kirkby, 1979) :

  $$Topo\_i = log\,\frac{\alpha}{\tan\beta}$$

  Where α is the drainage area (ha) and β is the downstream slope (%) (Merot et al., 2003). It can be used to predict the spatial distribution of soil wetness: a low Topo_i indicates potentially wet area while a high Topo_i indicates well-drained area.

Beven, K. J. and Kirkby, M. J. (1979) A physically based, variable contributing area model of basin hydrology, Hydrological Sciences Bulletin, 24:1, 43-69, DOI: 10.1080/02626667909491834.

Merot, P., Squividant, H., Aurousseau, P., Hefting, M., Burt, T., Maitre, V., Kruk, M., Butturini, A., Thenail, C., and Viaud, V.: Testing a climato-topographic index for predicting wetlands distribution along an European climate gradient, Ecological Modelling, 163, 51-71, 2003.

- Elevation is the mean elevation of the catchment indeed
- The “dominant soil thickness” classes are 40-60 cm, 60-80 cm, 80-100cm and >100cm.

We agree the information has to be added to Table 1 for the sake of clarity.

eq 1: Did you considered the offset when the discharge gauge was not at the same position as the water quality station?

Yes, we considered the offset when the discharge gauge was not at the same position as the water quality station. When the discharge gauge was not at the same position as the water quality station, the daily flows were extrapolated to the water quality station by multiplying the flow rate by the ratio between the drained areas of the water quality station and the discharge gauge.

L172ff: Did I rightly understood that GAM considered month of the year as only variable? This is not fully clear from the text. Later on it looks like day of the year was the predicting variable.

All GAM for concentrations are obtained by fitting smooth spline functions of month of the year to observed monthly time series. Then, we extracted the values of the fitted GAM at a daily time step. These allowed us to calculate the C_{winter} and C_{summer}, and the SI.

We agree with referee #1 that sentence **line 189** introduces some confusion then we suggest rephrasing as: **“where C_{winter} and C_{summer} are the averages of winter and summer concentrations, (calculated from daily values from fitted GAM) ».**

L177: "Amplitude" of a trend is maybe not the right wording. "Slope" is totally fine.

“Amplitude” line 177 refers well to the seasonal amplitude but indeed to avoid th confusion we should modify “amplitude” by “slope” line 176: “First, significant long-term trends (according175to Man-Kendall tests) had low **slopes**: mean Theil-Sen slopes ranged from -3%to 0% of the median concentration (while mean seasonal relative amplitudes exceeded 50%). “

L179: I don’t understand this last sentence.

We suggest rephrasing as “we considered a seasonal dynamic to exist **when the GAM adjusted coefficient of determination was greater than 0.10**” for more clarity.

Results

L212f: This is already a discussion of your result and should thus be part of the discussion section.

We agree the sentence should be moved to the discussion in section 4.1.

L231f: Check this sentence. Better "fitted to XX DOC concentration time series"?

We agree with the suggestion to modify the sentence as : “Of the 185 catchments, GAMs were fitted for 159 **to** DOC concentrations **time series**, 168 **to** NO3 concentrations **time series,** 162 **to** SRP concentrations **time series**, and 185 **to** discharge **time series**”.

L241: Check this sentence. Discharge cannot have a seasonal concentration cycle.

We suggest rephrasing the sentence as: “Most of the catchments had a seasonal concentration cycle: 85%, 71%, 78%, for NO3, DOC, SRP concentration respectively **and 100% of them had a seasonal discharge cycle**”.

L244: Does that refer to the comparison between all catchments? That is not clear here.

Yes it does. We suggest rephrasing as: “The annual phases for discharge were more stable among all catchments than those for concentrations”.

L245f: I am not sure were to see this gradient in Fig. 4. Is that referring to the right figure?

Yes, we should specify that this is referring to Fig. 4d (and Supplemental S7) which shows that the relative amplitude of discharge seasonal variations are more or less important depending on the catchments.

L257f: What does that stability means? That the pattern does not change between the years? This cannot be seen from the GAM averaging over all years. I am a bit lost here.

It means that these two metrics are stable between all catchments. Indeed, we suggest clarifying by rephrasing: “The DOC MaxPhase and NO3MinPhase **were the same for all catchments** as they always occurred between July and December (Fig.4, Supplemental S7).

L288: You may give direction of the correlation with the hydrologic variables as well.

We suggest rephrasing as: “It correlated most strongly with soil P stock (r_s=-0.40), climate and hydrology (**r_s=-0.43 to -0.34 with** effective rainfall, Qmean, QMNA), elevation, and hydrographic network density”.

Discussion

L304ff: Rather than directly with the interaction of N and C wouldn’t it be better to first explain the individual spatial patterns?

Because the individual patterns of NO3 and DOC are opposite, we think that it makes sense to explain them together. We argue that the quality of this discussion section was highlighted by referee #2 and that individual interpretations of DOC and NO3 would lead to redundant paragraphs. Therefore, we think this is worth to keep this structure for the discussion section.

L313ff: But this argument would lead to high concentrations of both, C and N?

If high SOC content in such soils are associated to higher N leaching this lead to a reservoir rich in organic Carbon but poor in Nitrogen.

L324ff: Wouldn't Fovet et al. (2018, 10.1016/j.jhydrol.2018.02.040) provide a good mechanistical backup for the processes described here?

Indeed, similar mechanisms of mixing lateral (along the hillslopes) and vertical (with depth) gradients of elements sources are discussed in Fovet et al. (2018) but for interpreting temporal patterns observed during rainfall-discharge events. We agree with the recommendation of referee#1 to illustrate the interpretation of temporal patterns using a conceptual diagram (see reply to major comment 3 above).

L334ff: You need some references for these statements.

We suggest adding the following references: Davidson et al., (2006); Hénault and Germon, (2000); Luo and Zhou, (2006)

Davidson, E. A., Janssens, I. A., and Luo, Y.: On the variability of respiration in terrestrial ecosystems: moving beyond Q10, Global Change Biology, 12, 154-164, 2006.

Hénault, C. and Germon, J. C.: NEMIS, a predictive model of denitrification on the field scale, European Journal of Soil Science, 51, 257-270, 2000.

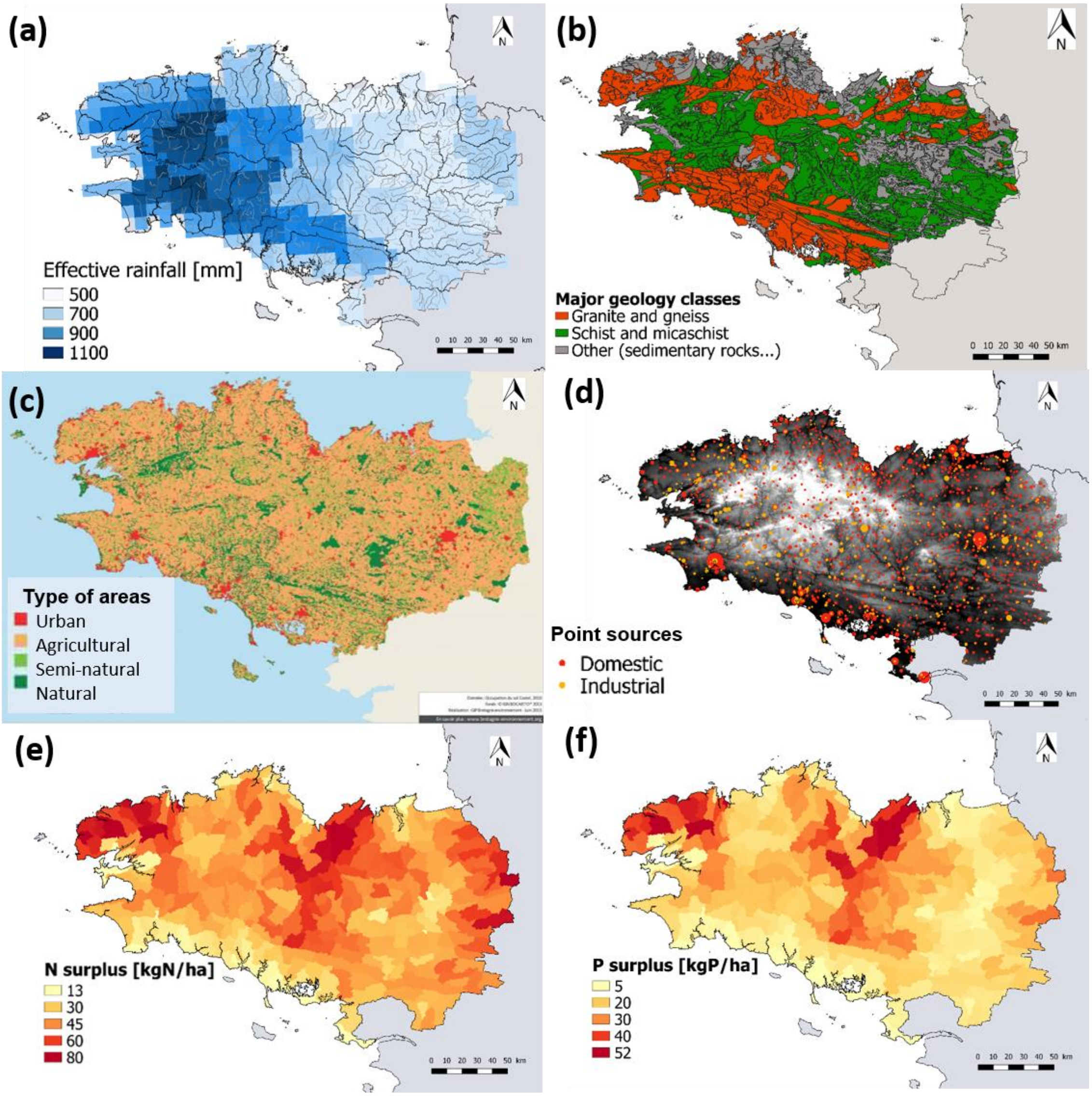
Luo, Y. and Zhou, X.: CHAPTER 5 - Controlling Factors. In: Soil Respiration and the Environment, Luo, Y. and Zhou, X. (Eds.), Academic Press, Burlington, 2006.

L400f: You may show and quantify this earlier on by the ratio of CVc and CVq as done in Thompson et al. (2011, 10.1029/2010wr009605).

Many recent papers on the temporal variability in C and Q have used the CV ratio as a descriptive metrics. We decided to use different metrics here, specifically focusing on seasonality is an originality of our analysis compared to published work of others.

SI Fig. S1: Panel b does not make sense without a legend. Typo in panel d legend name.

Figure S1 has been corrected:


(a)
N
Effective rainfall [mm]
500
700
900
1100
0 10 20 30 40 50 km
(b)
N
Major geology classes
Granite and gneiss
Schist and micaschist
Other (sedimentary rocks...)
0 10 20 30 40 50 km
(c)
N
Type of areas
Urban
Agricultural
Semi-natural
Natural
(d)
N
Point sources
Domestic
Industrial
0 10 20 30 40 50 km
(e)
N
N surplus [kgN/ha]
13
30
45
60
80
0 10 20 30 40 50 km
(f)
N
P surplus [kgP/ha]
5
20
30
40
52
0 10 20 30 40 50 km

Reply to Anonymous Referee #2

We thank Referee #2 for his/her positive evaluation of the study. "*The multi-element, many sight approach utilized does provide interesting insight into the potential influences of changing seasonal hydrology/ flowpath and landscape characteristics on the biogeochemistry of the study region.".*

He/she raised two major comments:

1) *"The paucity of other studies focusing on multi-element patterns, in headwater streams, that examine seasonal patterns, or that focus on multiple catchments is somewhat overemphasized in the framing of the research though and further cross comparison with studies that include all or only some of those criteria would benefit the introduction and discussion*."

And specific comment on *Lines 65-75- I understand the point that the authors are making here, but there are actually a number of studies meeting most of these criteria that could be helpful in interpretation of results and in understanding the generality of the patterns observed across regions. A couple of ideas that came to mind when reading this section were:*

- *Fasching et al. 2019 in Ecosystems also use GAM models and the approach used to explore multiple drivers may be helpful, Natural land cover in agricultural catchments alters flood effects on DOM composition and decreases nutrient levels in streams -https://doi.org/10.1007/s10021-019-00354-0*
- *Although larger watersheds in the region are also included in the analysis I would suggest that some comparison should be made with Moatar et al. 2017, WRR, Elemental properties, hydrology, and biology interact to shape concentration- discharge curves for carbon, nutrients, sediment, and major ions https://doi.org/10.1002/2016WR019635*
- *The review and conceptual paper presented by Kaushal et al. 2018 in Biogeochemistry may also be helpful in evaluating the role of season and land use on multi-element water chemistry.*

Indeed, and in the Introduction paragraph L45-54, factors of spatial variability in concentrations are reviewed from various contexts (headwaters or not) and from studies that analyzed at least one of the three elements. Similarly, the following paragraph L. 55-65 reviews seasonal variations in at least of the three element concentrations but without filter on catchment size or number of catchments included in the analysis. Therefore, we highlighted the scarcity of studies dealing with multi-element and multiple catchments, in headwater streams and including analysis of seasonal pattern in the introduction section only to describe the need for more investigation, which our work aims to contribute to (Lines 66-74).

We thank referee # 2 for the relevant additional references, and according recommendations from referee # 1 too, we suggest the following modifications in order to position our study in regards to these published results in the introduction:

"Besides being spatially variable, C, N, and P concentrations also vary **temporally. The variability of concentrations with flow has been described in several studies using concentration-flow relationships at event (Fasching et al., 2019) or inter-annual to long-term scales (Basu et al., 2010; 2011; Moatar et al., 2017). Concentrations also vary seasonally** in streams and rivers ..."

"We hypothesized that: 1) Human (i.e. rural and urban) pressures determine spatial variability in NO_3 and SRP concentrations **(Preston et al., 2011; Melland et al., 2012; Dupas et al., 2015; Kaushal et al., 2018)**, while soil and climate characteristics determine that in DOC and possibly SRP **(Lambert et al., 2011; Humbert et al., 2015; Gu et al., 2017)**."

Please see also the reply to referee # 1, major comment 2.

2) "*Regarding the GAM model used to describe seasonality, this is a useful approach, but I also wonder if there may be opportunity to modify the presentation and possibly the models slightly to explore interactions between multiple drivers (e.g. season x land use or flow x soil).*"

We thanks referee #2 for the suggested reference of Fasching et al., 2019, which is indeed very relevant here. In the presented study, we used GAM to described the seasonal patterns from concentration measurements. We used then correlation analyses with Land uses, flow and soils to see if they had a relationship or not with those seasonal patterns. The approach suggested by referee # 2 to fit the GAM according to time but also land use, flow and soils could be another way to explore these relationships indeed but the possible interpretation of the GAM should not be different from the one we could have using the correlation analysis.

Note also that, we tested a GAM fitting using both the month and the year in order to extract a long-term component (lines 175-179). The model sometimes failed in converging, and then it seems reasonable to limit the GAM complexity and to keep a two-steps analysis: 1) extracting seasonality using GAM and 2) analyzing the relationships between the extracted seasonality and the geographical variables.

Reply to specific comments

Lines 45-50 – “There have been a number of studies in Canada and United States to evaluate the influence of agricultural land use on DOC concentration and DOM composition. Although the statement that composition is usually quite altered is true, often concentration is more a function of the same factors as in non-agricultural catchments, in particular the presence of wetlands and soil drainage properties.”

Indeed, DOC concentration has been primarily linked to topography and presence of wetlands and saturated areas which is true both in forested and agricultural catchments. As also suggested by referee #1, we suggest adding more references (lines 45-47):

“DOC concentration 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; **Zarnetske et al., 2018; Musolff et al., 2018**).”

Line 68 - This is true, but there is a lot of study that goes on further upstream in even smaller catchments where land management can be linked directly to impact.

Indeed, we did not state that there were no literature at the scale of headwater catchments: several studies at such scales in agricultural or impacted contexts focused on the link between specific land management practices and water quality. However, such studies rarely compare more than 100 catchments like we did in the present study in order explore the spatial variability of this link between land management and impacts.

Line 73- maybe also ad “multi-element” to this statement because there are many studies that examine multi-catchment patterns for a single element.

We suggest to rephrase as “multiple-catchment studies” **on multiple element**s are uncommon”.

Line 109- This is good. Often selecting sites in a stream network without spatial independence is a pitfall for many site studies in a region, particularly when working with data where the authors did not chose the original sampling locations.

Yes, it was for us an important criterion to focus the analysis on the spatial variability and not on the “longitudinal” variability within nested catchments.

Line 111- Please explain why these criteria were used for outlier selection and how commonly extremely high concentrations were observed.

The concentration databases initially included some extremely high maximum NO3, PO4 and Ptot values. We could clearly interpret these as outliers. Our thresholds for the selection of outliers (values > 200 mg $N.L^{-1}$ or 5 g $P.L^{-1}$) were chosen: 1) by expert advice (producer of the data) and 2) after verification on the data (in terms of proportions of values eliminated on each time series and number of time series concerned).
Among the 185 NO3 time series, 3 were concerned and for Phosphorus 5 were concerned. Only one value was removed by time series.

109-112 – Were data examined to ensure that there were not seasonal biases in the timing of missing data and that certain sites were not heavily sampled only in one season (summer samples only for example)

We have imposed a criterion for selecting the time series according to the sampling frequency (at least 6 years of data with at least 8 values per year). We also looked at the data to see which months were least sampled and in the OSUR database no bias was observed as it is based on fixed and regular frequencies while in the HYDRE / BEA we noticed a few time series where summer periods were actually less sampled but for some years only(over the 10 years). We suggest adding this information in the main text.

Line 185- The seasonality metric is interesting, but doesn't really separate the flow condition or discharge from other factors like temperature that vary seasonally. Calculation of a similar metric for high flow vs low flow for comparison to the SI might be quite revealing. An example of that method is in Fasching et al. 2019.

Indeed, but in the studied catchments, high flows are well in phase for all the catchments with maximum of discharge in winter (colder season) and low flows are all occurring at the end of summer (warmer season). Therefore, the suggested metric is relevant but it would lead to the same results as our seasonal index with this data set of catchments. However, a seasonal index based on season only has the advantage of being applicable even if there is no stream flow data, and in such case, the interpretation of the index should be adapted of course.

Figure 4 – I think the information displayed here is valuable, but I wonder if a visual with additional information might be possible with the GAM results if the influence of 2 different drivers were displayed in a 3d version of the figure similar to Figure 7 in Fasching et al. 2019. It could be discharge or land use on the other axis.-

We think that the use of the GAM proposed by Fasching et al., 2019 is fully valuable and interesting. However, in the way we used the GAM here, we first smooth the observations to compute metrics on the average seasonal pattern of concentrations, and then, we investigated potential drivers within a correlation analysis between catchment descriptors and concentration metrics. Again, given the relative moderate number of concentration points in each station, fitting the GAM on both temporal (month) and spatial (geographic variables such as discharge or land uses) variables could be difficult (see also reply to major comment 2).

The discussion on DOC/NO3 patterns is well written and I agree with the authors general interpretation of the results.

Thank you.

For the SRP discussion it may be worthwhile to reference the strong correlations that have been observed in small agricultural catchments between soil P and runoff concentrations. There are metrics included in the predictor dataset for TP_soil and P surplus which appear to be model outputs. It may help with interpretation of results if it can be noted whether these follow anticipated patterns of buildup where more intensive livestock or fertilizer input is occurring.

We suggest adding such discussion to subsection 4.3., line 376:

“Nonpoint sources of P in agricultural runoff, historical inputs of fertilizer and manure in excess of crop requirements have led to a build-up of soil P levels, particularly in areas of intensive crop and livestock production (Sharpley et al., 1994). This led to correlations between soil P and runoff concentrations in agricultural catchments (Cooper et al., 2015; Sandström et al., 2020), as found here.”

Sharpley, A. N., et al. (1994). "Managing Agricultural Phosphorus for Protection of Surface Waters: Issues and Options." Journal of Environmental Quality **23**(3): 437-451.

Sandström, S., et al. (2020). "Particulate phosphorus and suspended solids losses from small agricultural catchments: Links to stream and catchment characteristics." Science of The Total Environment **711**: 134616.

Line 380 – In the context of the observed seasonal pattern can you comment on the timing of nutrient applications and whether there is potential for depletion of soluble sources over time or not.

As explained in reply to previous comment, the inputs of fertilizer and manure in excess of crop requirements have led to a build-up of soil P legacy storage (Sharpley et al., 1994), which gradually leaches into the water for decades (Sandström et al., 2020). Therefore, the timing of current nutrient applications is likely to be invisible in the stream concentrations due to such time lags. Therefore, the correlations found between SRP C50 and variables related to P sources (TP_soil, domestic point sources, P surplus…) are significant but weaker (Line 287).

Table 1 – Presumably some fields are used for both summer and winter crops. A total % cropland variable might be useful if not already considered

The "Winter crop" variable corresponds to crops with a winter plant cover and a phenological maximum in April, thus relating to three major crops: wheat, barley and rapeseed. The "Summer crop" variable corresponds to crops with bare winter soil and a phenological maximum in early summer (July), thus relating to two major crops: corn (and sunflower but it is not cultivated in the studied region). We distinguished these two types in order to refine the proxy of pressures regarding potential NO_3 leaching (higher for summer crops because of potentially bare winter soils). Adding the total percentage of cropland would not add more information than the percentages of grassland and forest.

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. In addition, the quality of ~~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. These DOC-NO_3 seasonal cycle types were related to the mixing of flowpaths combined with the spatial variability of their respective sources and to local biogeochemical processes. The annual maximum SRP concentration occurred during the low-flow period in nearly all catchments. This likely resulted from the dominance of P point sources. 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.

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).

In addition, the quality of ~~H~~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; Musolff et al., 2018; Temnerud and Bishop, 2005; Zarnetske et al., 2018). 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 temporally. The variability of concentrations with flow has been described in several studies using concentration-flow relationships at event (Fasching et al., 2019) or inter-annual to long-term scales (Basu et al., 2010; 2011; Moatar et al., 2017). 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; 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 despite their frequent occurrence (Van Meter et al., 2019; Abbott et al., 2018b; Liu et al., 2014; Halliday et al., 2012; Mullholland et al. 1997)~~(Ågren et al., 2007)~~, and
4) is usually restricted to a few catchments: multiple-catchment studies on multiple elements 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 km^2) 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 (Preston et al., 2011; Melland et al., 2012; Dupas et al., 2015a; Kaushal et al., 2018), while soil and climate characteristics determine that in DOC and possibly SRP (Lambert et al., 2013~~1~~; Humbert et al., 2015; Gu et al., 2017).
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. C~~Potential c~~orrelations 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 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 based on expert knowledge, 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. We checked that there was no bias in the timing of concentration data: OSUR database has fixed and regular sampling frequencies while we noticed a few time series where summer periods were less sampled in the HYDRE/BEA data for some years only.

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 and S3 for their correlations). 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%). 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):

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

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:

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

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

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~~slopes: 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 when the GAM adjusted coefficient of determination was greater than 0.10~~at Rsq ≥ 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):

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

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

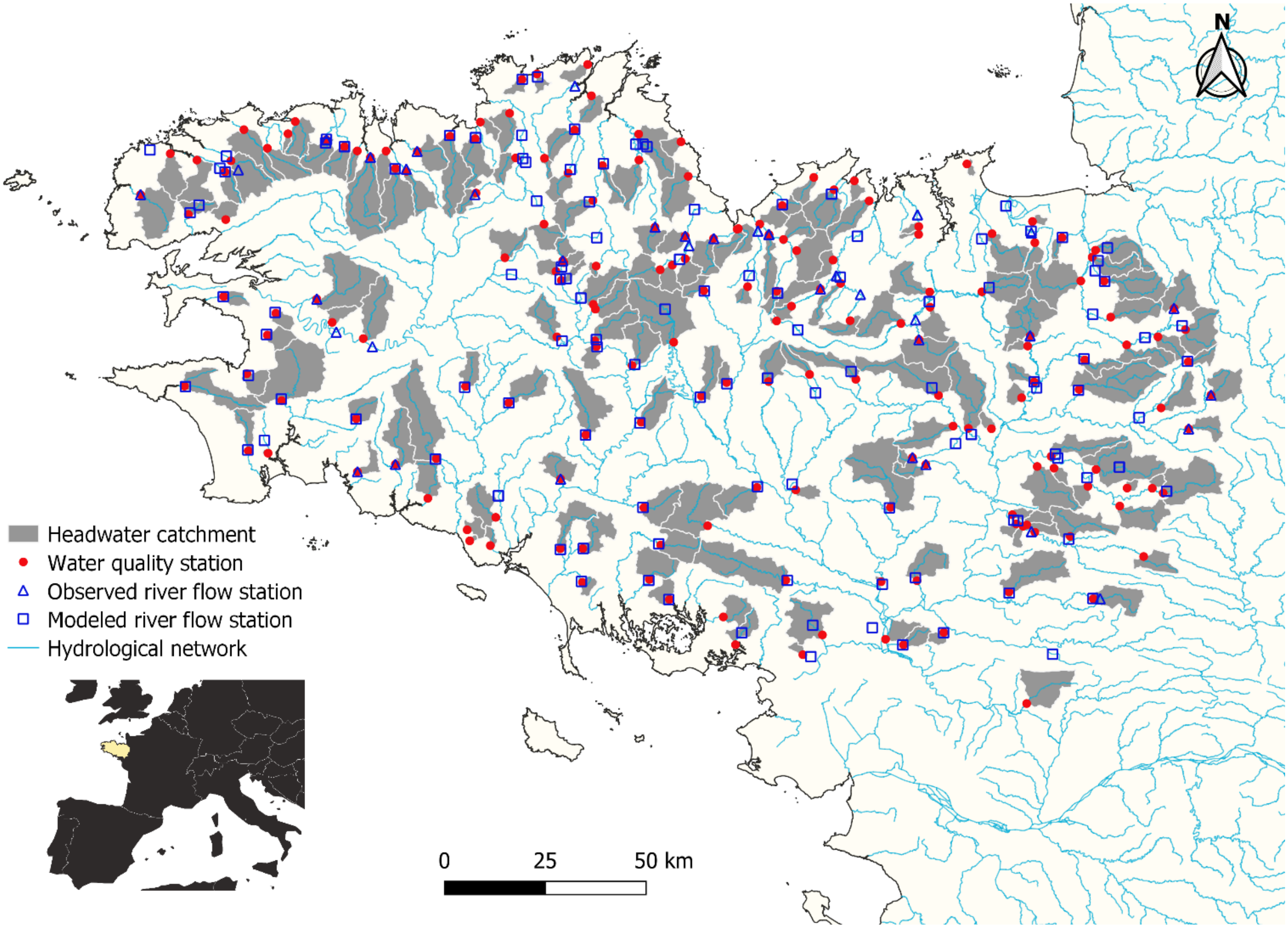

Figure 1. Locations of the 185 study headwater catchments where dissolved organic carbon, nitrate, and soluble reactive phosphorus concentrations were monitored monthly at the outlet from 2007-2016, and paired discharge stations where daily records of stream flow were available from observations or modeling.

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. $\mathbf{Topo\_i} = \boldsymbol{log}\frac{\boldsymbol{\alpha}}{\tan\boldsymbol{\beta}}$, (Beven and Kirkby, 1979), where $\boldsymbol{\alpha}$ is the drainage area (ha) and $\boldsymbol{\beta}$ is the downstream slope (%), (Merot et al., 2003). [a] there are 3 classes of soil thickness: 40-60 cm, 60-80 cm, 80-100 cm and >100 cm. [b] Winter crops have a winter plant cover and a phenological maximum in April (wheat, barley, rapeseed). [c] Summer crops correspond to bare winter soils and a phenological maximum in early summer (corn).

Type	**Descriptor name**	**Unit**	**Definition**	**Source**
Topography	Area	km^2	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	Mean 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)	Downstream 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	Classes of dominant soil thickness[a]	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[b] land	OSO database, CESBIO, land-cover map 2016 (1 ha) from http://osr-cesbio.ups-tlse.fr/~oso/
	WinterCrop	%	Percentage of winter crop[c] 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
Diffuse and point N and P sources	N_surplus	$kg.ha^{-1}.yr^{-1}$	Nitrogen surplus (= the maximum quantity on a given agricultural area that is likely to be transferred to the stream network)	CASSIS-N estimates by (Poisvert et al., 2017) from https://geosciences.univ-tours.fr/cassis/login
	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

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~~S4a) 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 concentration percentile (Spearman rank correlations between the three indices always greater than 0.56 for all elements). ~~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; Supplemental ~~S3b~~S4b). Third, SRP concentrations had an orthogonal relation compared to DOC and NO_3 concentrations (r_S close to zero).

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).

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.

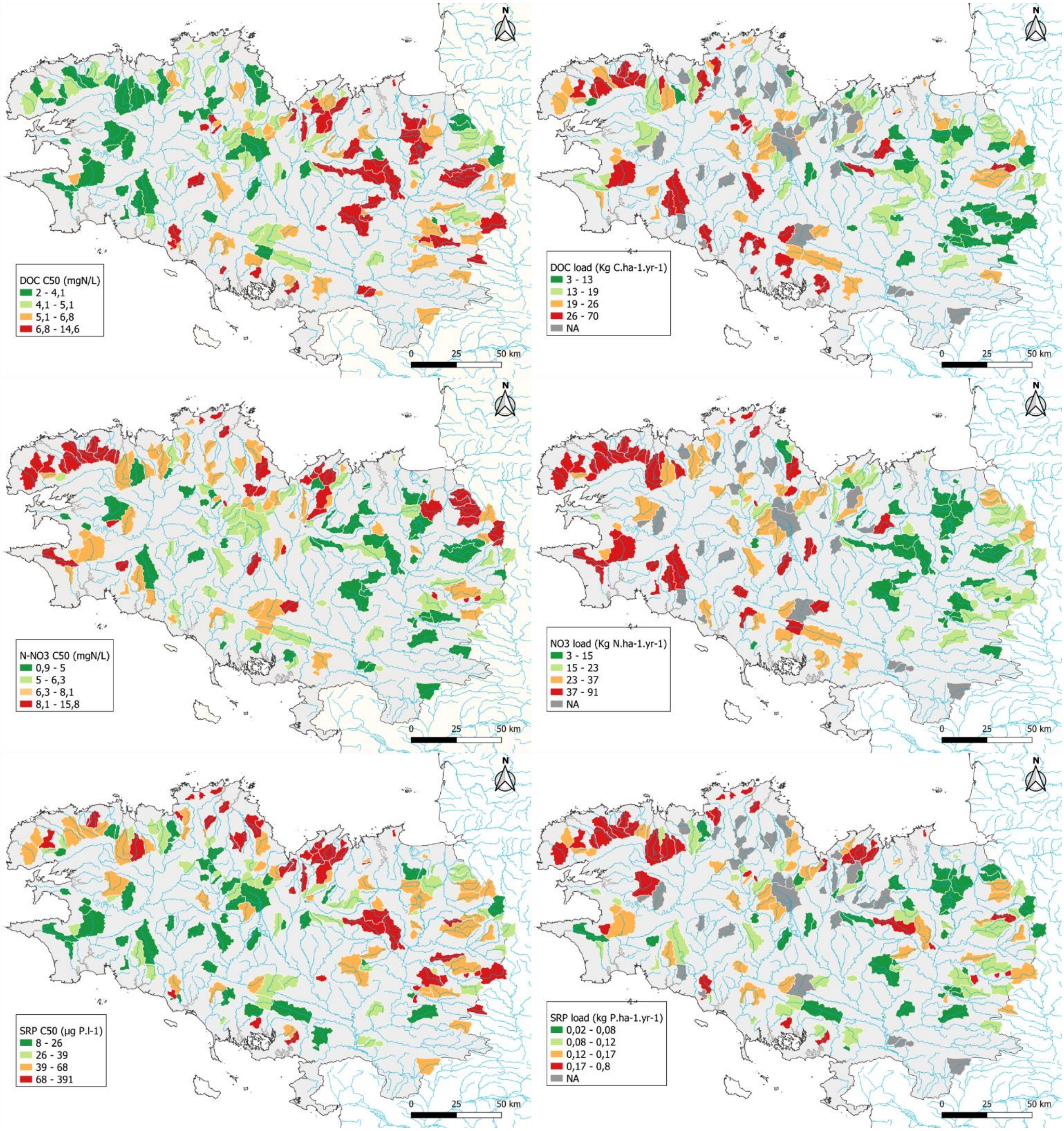

Figure 2. Map of median (left) concentrations C50 and (right) loads of dissolved organic carbon (DOC), nitrate N (N-NO$_3$), and soluble reactive phosphorus (SRP) for the 185 streams. The catchments in gray did not meet the criteria to estimate a mean average interannual load. Classes in the legends have equal numbers of catchments.

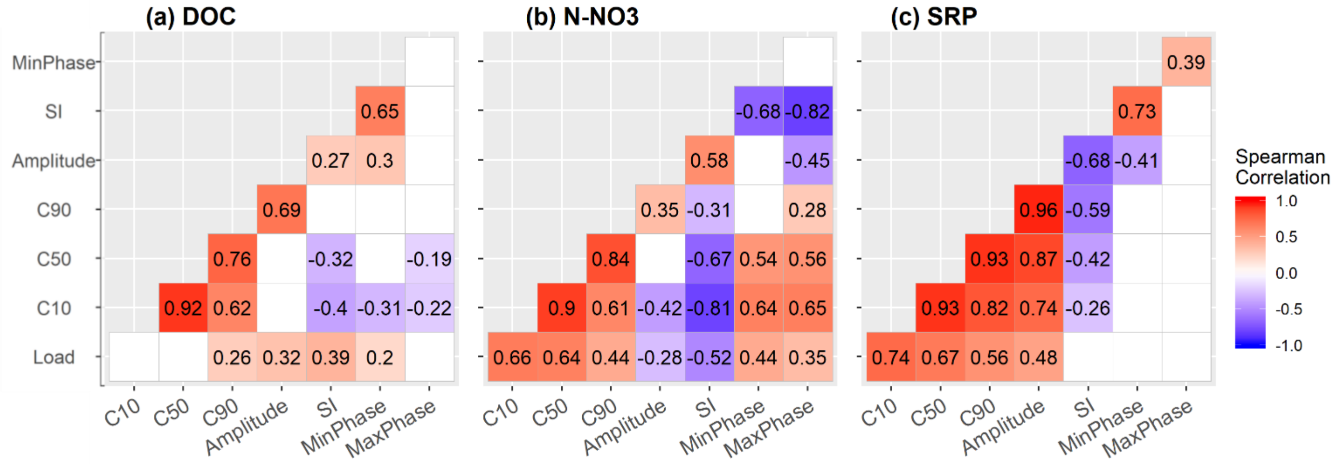

Figure 3. Matrices of Spearman's rank correlations of water quality (load, concentration percentiles (10th (C10), 50th (C50), and 90th (C90)), and seasonality metrics) for (a) dissolved organic carbon (DOC), (b) nitrate N (N-NO_3), and (c) soluble reactive phosphorus (SRP) (c). Only significant ($p \leq 0.05$) values are shown.

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

3.2 Characterization of concentrations seasonality

3.2.1 Performance of GAMS

Of the 185 catchments, GAMs were fitted for 159 t~~f~~o~~r~~ DOC concentrations time series, 168 t~~f~~o~~r~~ NO_3 concentrations time series, 162 t~~f~~o~~r~~ SRP concentrations time series, and 185 t~~f~~o~~r~~ discharge time series. 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~~ S5 and ~~S5~~S6), 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~~S7), 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 concentration respectively and 100% of them had a seasonal discharge cycle~~,~~ ~~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~~S8.

~~For all catchments, t~~The annual phases for discharge were more stable among all catchments 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. 4d and Supplemental S~~7~~8). 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).

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~~S8). 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 NO3 MinPhase~~,~~ were the same for all catchments ~~which~~ as they always occurred between July and December (Fig. 4, Supplemental ~~S7~~S8).

The first type, “in-phase” (68% of the catchments with seasonality), had a NO$_3$ MaxPhase between October and May (Fig. 4, Supplemental ~~S7~~S8) (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~~S8) (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.

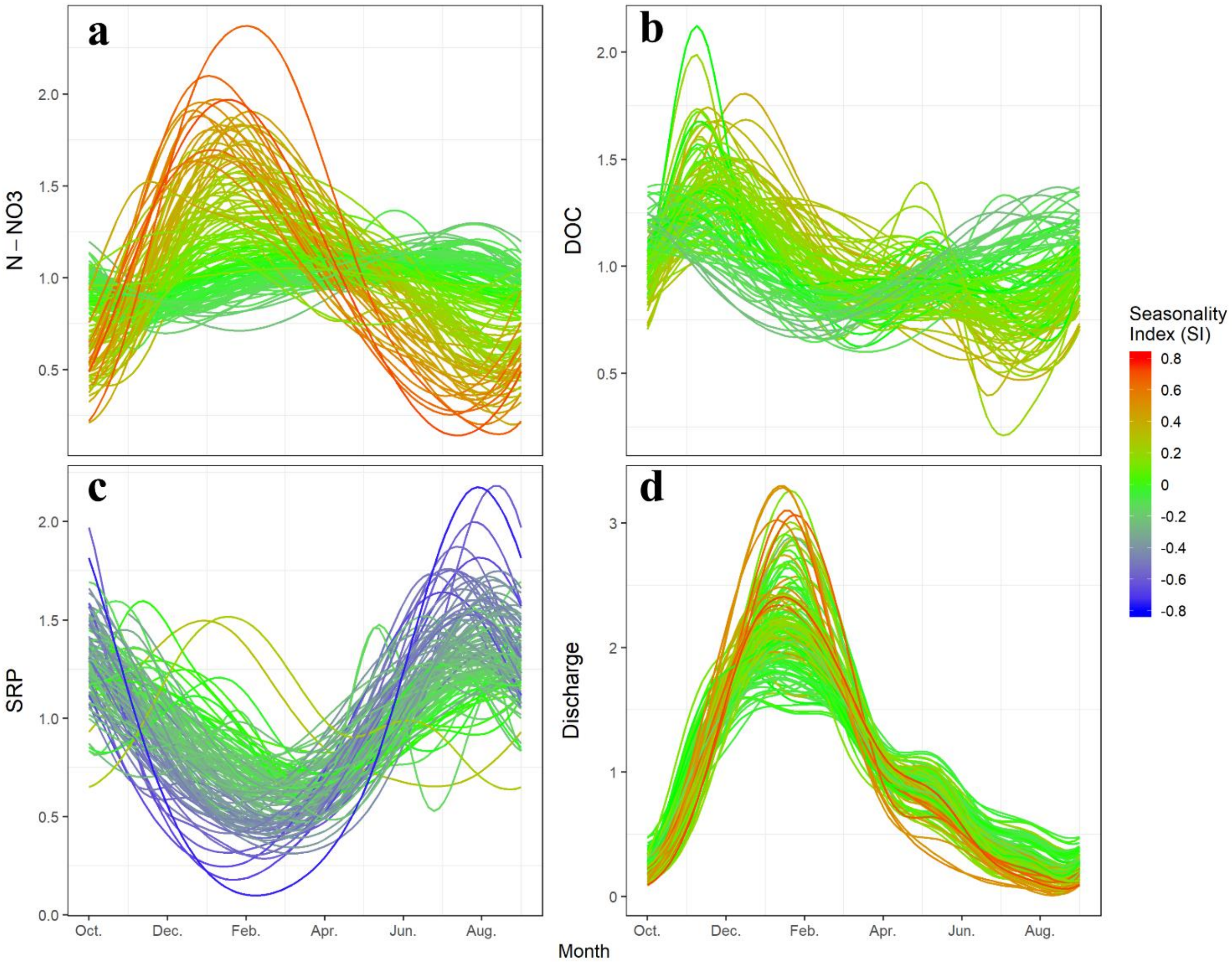

Figure 4. Seasonal dynamics of nitrate N ($N\text{-}NO_3$), dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), and daily discharge modeled by Generalized Additive Models for 185 headwater catchments. To compare concentrations, they are standardized by their mean interannual concentration.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

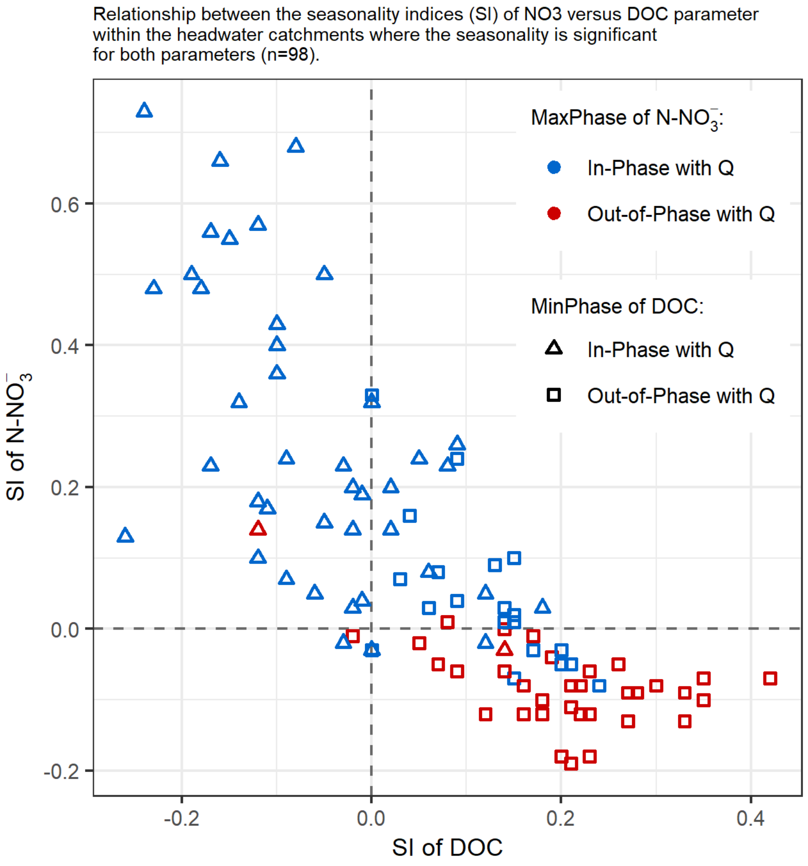

Figure 5. Relationship between the seasonality indices (SI) of nitrate N (N-NO$_3$) vs. dissolved organic carbon (DOC) in the headwater catchments for which seasonality was significant for both parameters (n=98). The color and shape of symbols identify the seasonality types based on the NO$_3$ MaxPhase 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.

3.3 Controlling factors of concentration percentiles and seasonality

The C50 of DOC was correlated significantly with 15 spatial variables and most strongly ($|r_s|\geq 0.4$) 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 (r_s=-0.43 to -0.34 with 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 Qmean, 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.

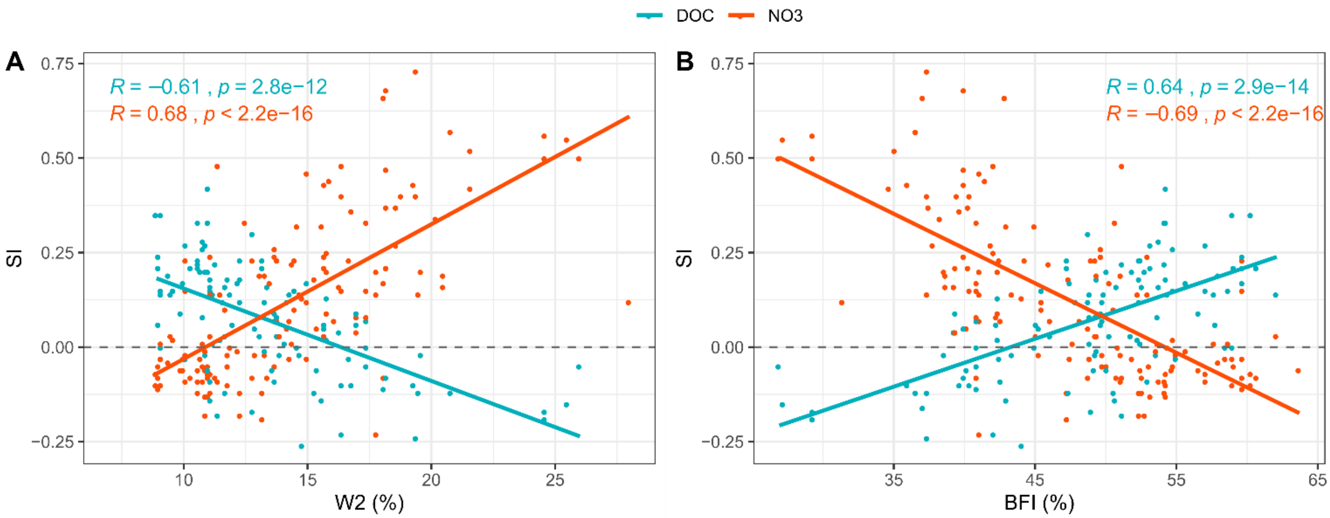

Figure 6. Relationship between the seasonality index (SI) of dissolved organic carbon (DOC) and nitrate (NO_3) and the hydrological reactivity descriptors (A) flow flashiness index (W2) and (B) base-flow index (BFI) for 124 headwater catchments.

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 ($p \leq 0.05$) are shown, and bold text indicates $|r| \geq 0.40$.

		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

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 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 (Davidson et al., 2006; Hénault and Germon, 2000; Luo and Zhou, 2006). 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 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 (Fig. 7):

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.

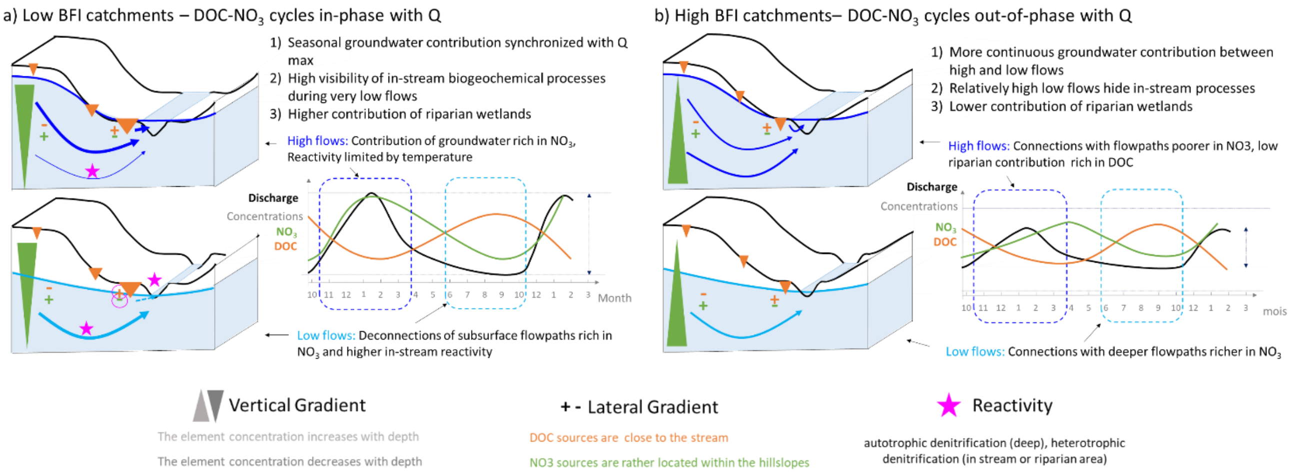

Figure 7. Conceptual diagram of seasonal flowpaths involved in the DOC-NO$_3$ seasonal cycles leading to a) in-phase cycles with discharge or b) out-of-phase cycles with discharge.

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. Nonpoint sources of P in agricultural runoff, historical inputs of fertilizer and manure in excess of crop requirements have led to a build-up of soil P levels, particularly in areas of intensive crop and livestock production (Sharpley et al., 1994). This led to correlations between soil P and runoff concentrations in agricultural catchments (Cooper et al., 2015; Sandström et al., 2020), as found here.

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. Such dominance was found to increase with the level of human pressure in Thompson et al. (2011) for NO_3. In this study, such relationship was not visible as all the catchments exhibited a transport-limited behavior. It may also suggest that the nutrient-surplus data 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.

4.5 Implications for headwater monitoring and management

The high regional and seasonal variations of nutrient concentrations in streams probably drive high variations of nutrient stoichiometry along the water year and over the region, and, consequently, high variations in time and space of eutrophication risks downstream (Westphal et al., 2020). Due to the combination of anthropogenic and hydrological drivers in explaining these stream concentrations, a better estimation on nutrient inputs and discharge in all headwater catchments, as a first step, is important to predict areas at risks. The spatial analysis shows high and poorly structured spatial variations of concentrations over the region. Nevertheless, the opposition between NO_3 and DOC concentrations suggests that the C:N ratios will be even more variable:

3) In space: catchments with high DOC C50 and low NO_3 C50 will exhibit very high C:N and vice versa
4) Over the seasons: as minimum of DOC and maximum of NO_3 concentrations are in-phase: catchment where DOC-NO_3 variations are in phase with Q will exhibit a low C:N ratio in winter high flow period and higher C:N ratio during low flow period. The N:P ratio in these catchments will be high during the low flow periods (high NO_3 and low SRP concentrations). Catchments where DOC-NO_3 variations are out-of-phase with discharge will exhibit probably less variation in their ratios (because of lower NO_3 amplitude) with relatively higher winter C:N ratio than the previous type of catchments.

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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