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Hydrology and Earth System Sciences Discussions

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Interactive comment on "Spatio-temporal controls of C-N-P dynamics across headwater catchments of a temperate agricultural region from public data analysis" *by* Stella Guillemot et al.

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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).”

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

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 Fig R1 in Supplemental.

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 NO3, 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 NO3. 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:

âĂć In space: catchments with high DOC C50 and low NO3 C50 will exhibit very high C:N and vice versa

âĂć Over the season: as minimum of DOC and maximum of NO3 concentrations are

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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 Figure R2 to illustrate section 4.2.

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.

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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 km2) 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 NO3 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).

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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 α/tanâĄąβ

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 Cwinter and Csummer, and the SI.

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

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.

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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 (rs=-0.40), climate and hydrology (rs=-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.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2020-257, 2020.

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

Fig. 1. Table R1: Spearman's rank correlations between the C10, C50 and C90 metrics for each element

Fig. 2. Figure R1 :Correlation matrix between Headwater catchment descriptors, Spearman coefficients are visible when p-value > 0.05.

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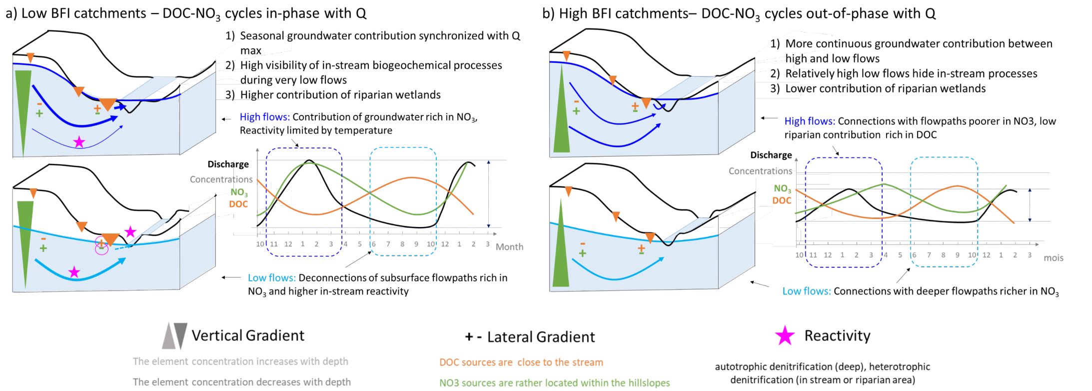

Fig. 3. Figure R2 (new Figure 8) : Conceptual diagram of seasonal flowpaths involved in the DOC-NO3 seasonal cycles leading to a) in-phase cycles with discharge or b) out-of-phase cycles with discharge.

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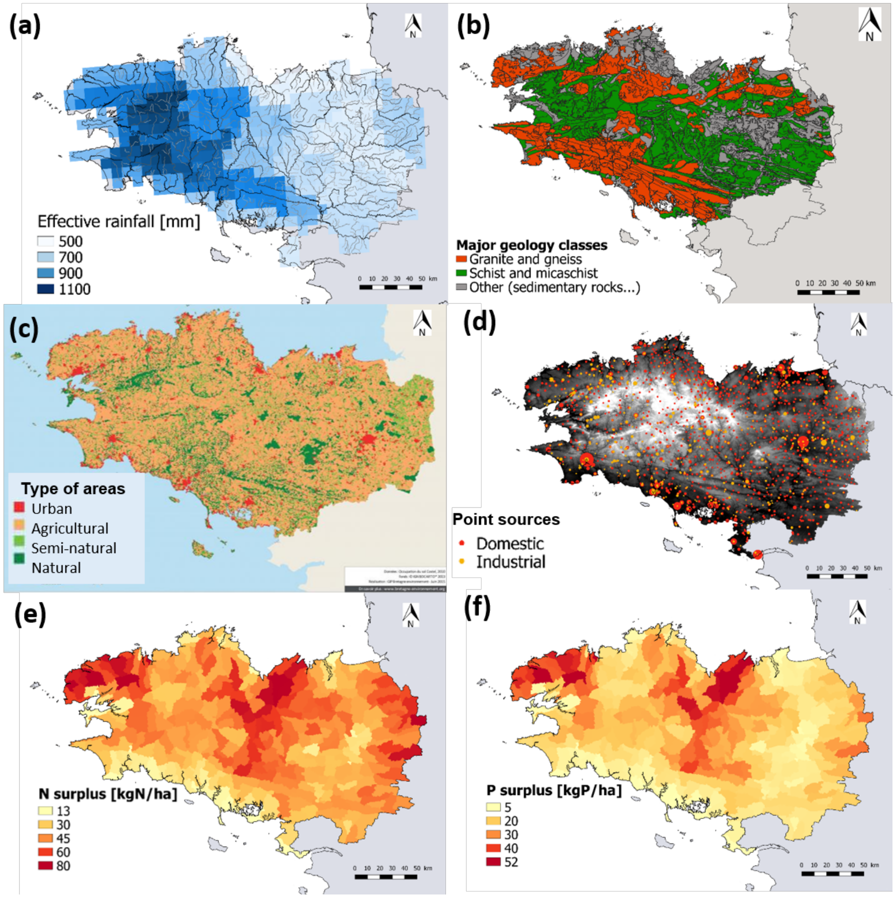

Fig. 4. Figure S1 corrected