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Unexpected spatial stability of water chemistry in headwater stream networks

Running title: Structure of water quality in stream networks

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Abstract

Understanding how water and solutes enter and propagate through freshwater landscapes in the Anthropocene is critical to protecting and restoring aquatic ecosystems and ensuring human water security. However, hydrochemical variability is believed to increase moving upstream, hindering modeling and management of headwaters where most carbon and nutrients enter stream networks. We developed an analytical framework informed by landscape ecology and catchment hydrology to quantify spatiotemporal variability across scales, which we tested in 56 headwater catchments, sampled periodically over 12 years in western France. Unexpectedly, temporal variability of dissolved carbon, nutrients, and major ions was preserved moving downstream and spatial patterns of water chemistry were stable on annual to decadal timescales, partly due to synchronous variation of solute concentrations. These findings suggest that while concentration and flux cannot be extrapolated among subcatchments, periodic sampling of headwaters provides valuable information about solute sources and subcatchment resilience to disturbance.

Introduction

How spatial and temporal variability change with scale is one of the fundamental problems of both ecology (Fisher *et al.* 1982; Horne & Schneider 1995; Altermatt 2013) and catchment hydrology (Blöschl *et al.* 1995; Shaman *et al.* 2004; McGuire *et al.* 2014). Because most ecological patterns change with spatiotemporal extent and grain of observation (Turner *et al.* 1989; Chapin *et al.* 1995; Kirchner & Neal 2013), an understanding of variance structure is necessary to scale predictions or implement effective interventions in dynamic landscapes (Haygarth *et al.* 2005; Lowe *et al.* 2006; Temnerud *et al.* 2010). For any ecosystem, variability in a biogeochemical stock or flux depends on on-site conditions and processes (e.g. temperature, redox state, biological activity, weathering) and lateral subsidies or debits from connected ecosystems (Chapin *et al.* 2006). Lateral fluxes are particularly influential in aquatic ecosystems such as stream networks, where delivery of carbon and nutrients from upstream and upslope environments is often orders of magnitude greater than production or removal at any given point in the stream (Lefebvre *et al.* 2007; Brookshire *et al.* 2009). Agriculture and urbanization have fundamentally altered lateral fluxes of carbon and nutrients, causing eutrophication, toxic cyanobacteria blooms, and expansive hypoxic dead zones that erode the capacity of ecosystems to feed and water human societies (Gruber & Galloway 2008; Vörösmarty *et al.* 2010; Sutton & UNEP 2013; Withers *et al.* 2014). Over the past 50 years, global fertilizer application has increased 5-fold (Foley *et al.* 2011), and anthropogenic pressures on aquatic ecosystems are expected to intensify due to population growth and increasing meat consumption through the middle of the century (Seitzinger *et al.* 2010).

Despite substantial investment to reduce carbon and nutrient pollution at local, national, and international levels, results remain mixed (Jarvie *et al.* 2013; Dupas *et al.* 2016;

Jenny *et al.* 2016), partly because of difficulty monitoring and predicting water quality in complex freshwater landscapes (Isaak *et al.* 2014; Abbott *et al.* 2016; Meter *et al.* 2016). Most regulatory frameworks, such as the U.S. Clean Water Act, the European Water Framework Directive, and the Chinese Water Law impose limits on annual loads or mean concentrations in medium to large rivers (Andreen 2004; Hering *et al.* 2010; Liu & Yang 2012). This is an appealing strategy because larger rivers integrate many small catchments, and from an estuarine or oceanic perspective, total nutrient load is the main metric of concern (Howarth 2008; Reed & Harrison 2016). However, there is growing evidence that to reduce these downstream nutrient fluxes, we need to understand sources and sinks in headwater catchments, where the vast majority of water and solutes enter aquatic ecosystems (Burt & Pinay 2005; Alexander *et al.* 2007; Bishop *et al.* 2008; Brookshire *et al.* 2009; McDonnell & Beven 2014).

It is generally held that the amplitude and frequency of chemical variation in stream networks decrease moving downstream (Burt & Pinay 2005; Lefebvre *et al.* 2007; Creed *et al.* 2015). For example, in catchments larger than 100 km^2, riverine nutrient loads are deterministically associated with percentage of agricultural cover and associated nutrient inputs (Omernik *et al.* 1981; Jordan *et al.* 1997; Howarth 2008), but nutrient loads vary widely despite similar land cover in drainage basins smaller than 20 km^2 (Burt & Pinay 2005; Lefebvre *et al.* 2007; Brookshire *et al.* 2009; Schilling *et al.* 2013). This breakdown of the relationship between land cover and nutrient load represents an important ecological unknown because 90% of global stream length occurs in catchments smaller than 15 km^2 (Burt & Pinay 2005; Bishop *et al.* 2008; Downing 2012). However, quantifying and improving water quality in headwater streams is easier said than done. New sensors of water chemistry produce high-frequency data (Kirchner *et al.* 2004; Dupas *et al.* 2016; Ruhala & Zarnetske 2017), but they are too expensive to equip headwater catchments, which are thousands of times more

92 abundant than the larger rivers where most monitoring currently occurs. This headwater
93 conundrum is particularly problematic for developing nations where the largest increases in
94 nutrient pollution are occurring (Seitzinger *et al.* 2010), and where water quality problems
95 most directly impact human health (Gundry *et al.* 2004).

96 Occasional, spatially extensive sampling of headwater streams has long been used to
97 complement high-frequency monitoring of downstream reaches (Kaufmann *et al.* 1991;
98 Wolock *et al.* 1997; Temnerud & Bishop 2005). Such synoptic sampling is often interpreted
99 to identify landscape parameters and ecosystem processes correlated with water chemistry,
100 but its utility in predicting longer-term water quality is questionable, given the high temporal
101 variability typical of small aquatic ecosystems (Kirchner & Neal 2013). In this context, we
102 developed a new approach for analyzing spatiotemporal variance in stream networks.
103 Specifically, building on theory from landscape ecology (Turner *et al.* 1989; Dent & Grimm
104 1999; Hammond & Kolasa 2014) and catchment hydrology (Blöschl *et al.* 1995; Rinaldo *et*
105 *al.* 1998; McGuire *et al.* 2014), we quantified the synchrony of hydrochemical changes, the
106 stability of spatial patterns, and the spatial scales of water chemistry drivers. We tested this
107 framework with a previously unpublished dataset from 56 catchments sampled periodically
108 over 12 years in western France. We found that while spatial variance of water chemistry
109 increased moving upstream, temporal variance was not systematically higher in the
110 headwaters, partially because solute concentrations (e.g. carbon and nutrients) varied
111 synchronously among sites. These dynamics created spatial patterns of water chemistry that
112 were relatively stable on seasonal to decadal timescales, suggesting that the spatiotemporal
113 variability of headwaters may not be as intractable as previously believed. Testing the
114 generality of these patterns in different climatic and socioecological conditions could provide
115 a pathway toward understanding terrestrial-aquatic connectivity and improving water quality
116 throughout the river network.

Approach and methods

Spatial variance thresholds and subcatchment leverage

While pollutant sources have long been categorized dichotomously as point or non-point (Carpenter *et al.* 1998), landscape patches contributing or retaining solutes or particulates occur on a size continuum that can change on event, seasonal, and interannual timescales (Basu *et al.* 2010; Liu *et al.* 2016). Assuming that spatial variability in water chemistry in a stream network depends primarily on the extent and connectivity of upstream sources, we hypothesized that the size of source and sink patches could be assessed by the spatial scale of the collapse (i.e. reduction) in spatial variance (Fig. 1). For a given parameter, this spatial variance threshold is expected to occur where subcatchment size matches the size of patches controlling solute production or removal (Fig. 1b), with downstream reaches less likely to have extreme concentrations because they integrate multiple source and sink patches. The spatial variability of concentration depends on the strength and connectivity of both source and sink patches superimposed on the structure of the stream network (Fig. 1). This framework is analogous to the representative elementary area concept (Blöschl *et al.* 1995; Hoef *et al.* 2006; Zimmer *et al.* 2013), though we do not assume that variance thresholds remain the same through time or across solutes.

On an applied level, knowing the patch size and location of solute sources and sinks allows identification of subcatchments exerting a disproportionate influence on flux at the catchment outflow (Fig. 1c). Analogous to the concept of leverage in statistical regression, where a value's relative influence on model behavior depends on its position in factor space, the leverage of a subcatchment on outlet chemistry can be defined in terms of concentration difference from the catchment outlet, subcatchment size, and specific discharge:

$$\text{Subcatchment leverage} = (C_S - C_O) \times A_S/A_O \times Q_S/Q_O \quad [1]$$

where C is concentration, A is area, Q is specific discharge, S is subcatchment, and O is outflow. Subcatchment leverage has units of concentration, or percentage if normalized to outlet concentration, and can be interpreted as the contribution of the subcatchment to catchment-level mass flux. Alternatively stated, subcatchment leverage is the spatially distributed mass balance for each element. If specific discharge is similar between subcatchments, as is sometimes the case at the medium-catchment scale (Asano *et al.* 2009; Lyon *et al.* 2012; Karlsen *et al.* 2016), leverage can be estimated with only concentration and subcatchment area, which are easily measured even in remote or impoverished areas. Spatial variance thresholds tend to occur at the same spatial scales as the subcatchments with greatest leverage, where a large proportion of the subcatchment area is within a single source or sink patch (Fig. 1c).

Subcatchment synchrony and spatial stability

The usefulness of a synoptic assessment of variance thresholds and subcatchment leverage depends directly on the temporal persistence of the observed spatial patterns. Streams experience temporal variability in chemistry due to hydrologic pulses and fluctuations in biogeochemical activity (Rinaldo *et al.* 1998; Erlandsson *et al.* 2008; Raymond *et al.* 2016). As pulses move through stream networks, their downstream attenuation or preservation depends on the synchrony of pulse generation in subcatchments (Fig. 2a). If the chemistry of upstream subcatchments changes asynchronously, destructive interference reduces downstream temporal variance, but if change is synchronous, downstream temporal variance is preserved (Fig. 2b). Synchrony among subcatchments can be quantified by temporal covariance in water chemistry:

$$\text{Subcatchment synchrony} = \frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{n-1} \quad [2]$$

where x and y are the concentrations in the two subcatchments and n is number of repeat samplings.

Even when concentrations vary synchronously among subcatchments, the relative spatial structure in the stream network can change if amplitudes are different (Fig. 2a). Spatial stability of water chemistry patterns can be directly calculated with the rank correlation (r_s) between instantaneous and long-term subcatchment concentrations:

$$\text{Spatial stability} = \frac{\text{covariance}(\text{RC}_t, \text{RC}_{\bar{t}})}{\sigma_{\text{RC}_t}\sigma_{\text{RC}_{\bar{t}}}} \quad [3]$$

where spatial stability is the correlation coefficient between the rank concentrations of subcatchments at the time of synoptic sampling (RC_t) and the rank of the long-term flow-weighted concentrations or loads ($RC_{\bar{t}}$), and σ is the standard deviation. Subcatchment synchrony and spatial stability are complementary because synchrony quantifies similarity in response to hydrologic and biological changes, revealing prevalence of source, transport, and processing controls (Moatar *et al.* 2017), and spatial stability quantifies the temporal representativeness of an instantaneous sampling.

From an applied perspective, spatial stability in subcatchment water chemistry determines the sampling frequency necessarily to identify high-leverage subcatchments (Figs. 2a and 1c) and evaluate predicted critical source areas (White *et al.* 2009; Heathwaite 2010; Liu *et al.* 2016), while subcatchment synchrony determines the representativeness of high-frequency monitoring stations. In a synchronous catchment where pulses of pollutants are propagated in chorus (Fig. 2b), a single station anywhere in the network may capture the amplitude of water quality fluctuations. However, in an asynchronous catchment, destructive interference among subcatchments means downstream monitoring stations will underestimate extreme conditions in contributing subcatchments (Fig. 2b). Accurate quantification of

temporal variability is particularly important for aquatic organisms, because minimum and maximum concentrations or conditions (e.g. oxygen and temperature) are often more important to survival than mean values, and where shifts in extremes can indicate imminent state changes (Davis *et al.* 2010). Ultimately, these two indices are interrelated, because in more synchronous catchments the spatial stability is more resilient to temporal variability (Fig. 2c).

Site characteristics and sampling design

We quantified spatial variance thresholds, subcatchment leverage, subcatchment synchrony, and spatial stability in two sets of nested catchments in north-western France (Fig. S1). The Rance and Couesnon catchments are approximately 360 km^2 and have over 80% agricultural land use, primarily pastureland for dairy cows, corn, and wheat (Table S1). Nutrient concentrations in the area are very high, frequently triggering estuarine algal blooms (Gascuel-Odoux *et al.* 2010; Perrot *et al.* 2014). The climate is oceanic with average monthly temperature ranging from 18°C in July to 5°C in December, and mean annual precipitation averaging 970 mm, a third of which occurs from October to December (Thomas *et al.* 2016).

Starting in November 2004, repeat synoptic sampling occurred in 26 subcatchments of the Couesnon with an initial goal of identifying land use parameters driving differences in DOC and NO_3^- concentrations. Detailed land use was determined for the entirety of each subcatchment and for the area of potential wetlands closest to the stream network (Medde *et al.* 2014). The subcatchments were sampled 13 times (approximately every two weeks), but when no clear correlations emerged with catchment characteristics (Table S2), sampling was abandoned in 2005. After identifying 30 comparable locations in the Rance catchment, 50 km to the west, sampling resumed in both catchments from May 2006 to January 2007. Sampling spanned over 90% of the observed range of daily discharge for the Couesnon and over 70%

for the Rance. In November 2015 and March 2016, we resampled 21 of the original 56 subcatchments during the low- and high-flow periods, respectively. Because the outlet of the Rance is intermittently inundated by a small reservoir, we calculated outlet solute concentrations assuming conservative mixing of the three tributaries immediately upstream of the confluence with the reservoir. Calculated values agreed well with measured values for dates when the outlet was not inundated.

Samples were filtered in the field with pre-rinsed 0.2 µm cellulose acetate filters (Millipore Millex-GV), and analyzed within a week. Quantified analytes had a wide range of reactivities and sources, and included many common water quality parameters. Anions (NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, F^-, PO_4^{3-}, and Br^-) were quantified by ion chromatography (Dionex^{TM} DX 100; accuracy ± 2.5%) and dissolved organic and inorganic carbon (DOC and DIC) were quantified with a total carbon analyzer after coming to equilibrium with the atmosphere (Shimadzu TOC 5050; accuracy ± 5%). Specific ultra-violet absorbance at 254 nm ($SUVA_{254}$), an indicator of DOC aromaticity and source (Weishaar *et al.* 2003), was calculated from absorption (UVIKON XS, Bio-Tek). For concentrations below the detection limit, we assigned values of ½ the limit of quantification, which affected less than 5% of all measurements except PO_4^{3-}, NO_2^-, and Br^-, which had between 25 and 72% of sites below detection depending on the catchment and sampling. Despite these detection issues, which are common for these parameters, we retained them in the analysis because of their ecohydrologic relevance.

Statistical determination of spatial and temporal variance

We determined spatial variance thresholds among subcatchments using the pruned exact linear time (PELT) method (Killick *et al.* 2012), which compares differences among sequential data points (in this case ordered by subcatchment size) to partition the series into

clusters with statistically distinct variances (Jackson *et al.* 2005). PELT is computationally frugal and robust to unevenly spaced points (Jackson *et al.* 2005; Killick *et al.* 2012). We determined variance thresholds for each watershed independently using flow-weighted concentrations over the whole sampling period, and after binning the data into four groups separated by hydrologic quartiles to test how water discharge affected spatial variance (Table S2), using the "changepoint" package of R version 3.3.0 (R Core Team 2016). Following equations 1-3, we calculated subcatchment leverage, synchrony, and spatial stability with scaled data (subtracted catchment mean and divided by the standard deviation), which did not affect the statistical results, but facilitated comparison between parameters with different magnitudes. For subcatchment synchrony, we averaged the pairwise covariance between all subcatchments for each catchment and parameter. The resulting scaled covariance represents the joint variability across all subcatchments and sampling dates (i.e. the proportion of subcatchments and time steps where concentration changed in the same direction for a given parameter).

Results

Persistent thresholds of spatial variance and stable subcatchment structure

While subcatchments had diverse land use and land cover (Table S1), relationships between catchment characteristics and flow-weighted concentrations were typically weak (non-significant or low correlations), and differed by catchment (Table S2). Catchment characteristics in potential wetlands near the stream network were not systematically better at predicting water chemistry than whole-catchment values (Table S2). Spatial variance in concentration decreased with increasing subcatchment size for all parameters, with concentrations trending towards the overall catchment mean, suggesting conservative propagation of headwater signals with limited in-stream modification (Figs. 3A, S2). Spatial

variance thresholds occurred between 18 and 68 km^2 for most parameters, except for DIC in both catchments, and Cl^- and F^- in the Rance, which had thresholds from 113 to 216 km^2 (Figs. 3A, S2A). Variance thresholds were stable across flow conditions for 72 of the 80 parameter by flow quarter combinations (Table S3), suggesting that patch locations and stream network topology determined spatial patterns, rather than changes in hydrology and biogeochemical processing. The relative scale of variance thresholds for different parameters among the two catchments generally followed the same patterns (e.g. larger for DIC, smaller for PO_4^{3-}). Subcatchment leverage followed the expected pattern (Fig. 1c), with highest leverage at spatial scales just larger than variance thresholds (Fig. S3). Most parameters showed moderate to low leverage, with no single subcatchment accounting for more than 25% of outflow concentration. However, several subcatchments had extremely high leverage for PO_4^{3-} and NO_2^- (>1000%), indicating substantial retention or removal of these solutes before reaching the catchment outlet (Fig. S3).

Despite large changes in discharge and concentration (Figs. S4-S6), subcatchment water chemistry showed strong spatial stability for most parameters, meaning the relative rank of subcatchment concentrations changed little across flow conditions (Figs. 4, S7). Spatial stability of water quality among subcatchments was particularly strong for DOC, DIC, NO_3^-, and several anions (Fig. 5). The parameters with consistently low or variable spatial stability (PO_4^{3-}, NO_2^-, and Br^-) had a large number of samples at or below the detection limit, artificially decreasing estimates of spatial stability. During the first storm after the summer low-flow period in 2005, spatial stability dropped substantially for most parameters, indicating a spatial reorganization of water quality in the Couesnon catchment (Fig. 4).

Subcatchment synchrony (mean covariance among subcatchments), varied from less than 0.25 for some anions to 0.81 for DOC in the Couesnon (Fig. 5B), depending on the

consistency of concentration-discharge responses among subcatchments (Fig. S4). $SUVA_{254}$ was substantially less synchronous than DOC (Figs. 4-5), suggesting diversity in DOC sources despite synchronous fluctuations in bulk DOC concentration. Among parameters, spatial stability and synchrony were unrelated to temporal variance (Fig. 5), demonstrating that the overall magnitude of temporal variance did not determine spatial or temporal representativeness. Contrary to our hypotheses (Fig. 2), synchrony and spatial stability were unrelated (Fig. 5C), demonstrating that large differences in concentration among subcatchments can create spatial stability independent of synchrony.

Clearer temporal signals at smaller scales and decadal stability in structure

Temporal variance did not systematically decrease with increasing spatial scale (Figs. 3B, S2B). Instead, temporal variance followed the same pattern observed for spatial variance of subcatchments (Fig. 3a), with greater diversity left of the spatial variance threshold and a convergence towards the catchment mean at the outlet. Subcatchments smaller than the spatial variance threshold showed greater range in variances, but they were equally likely to be more or less dynamic than the catchment outlets. Catchment outlets had temporal variances near the overall catchment mean for most parameters (Figs. 3B, S2B), suggesting variance damping (mixing of strong and weak signals) rather than destructive interference of opposing signals. However, NO_3^-, SO_4^{2-}, and Br^- showed somewhat lower temporal variance at the catchment outlets, attributable to inconsistent or weak concentration-discharge responses among subcatchments (Fig. S4). Relationships between temporal variance and flow-weighted mean differed by parameter, with most biologically reactive parameters showing greater variance in subcatchments with low concentrations (Fig. S8).

The repeat samplings in 2015 and 2016 were strongly correlated with the flow-weighted mean concentration from 2004-2007 for most parameters, suggesting stability of the

spatial structure of water chemistry on decadal timescales (Fig. 6). The high-water sampling in the spring of 2016 was more representative of the 2004-2007 means for all parameters except NO_3^-. DOC, PO_4^{3-}, and NO_2^- concentrations were lower across most subcatchments in 2015 and 2016, but NO_3^-, Cl^-, $SUVA_{254}$, and SO_4^{2-} showed no systematic change (Fig. 6).

Discussion

Ecohydrologic explanations for observed patterns in variability

While it is widely held that temporal variability is greater in headwater streams due to their size and reactivity (Vannote *et al.* 1980; Creed *et al.* 2015), we found that temporal variance did not systematically decrease with catchment size for most parameters, though the range of temporal variances did diminish. Three, non-exclusive phenomena could be contributing to this unexpected preservation of variability: 1. synchronous hydrologic variation among subcatchments, 2. source-patch homogeneity in small subcatchments, and 3. increasing variance from in-stream biogeochemical processes in larger subcatchments. First, water flow determines connectivity between stream and catchment, mediating what landscape components contribute particulate materials and solutes to the stream network at what times. Subsequently, hydrology controls the residence time of those particulates and solutes in different components of the stream network, determining exposure to biogeochemical transformation (Pinay *et al.* 2015; Abbott *et al.* 2016; Raymond *et al.* 2016). Hydrology is also the predominant mode of disturbance in most stream ecosystems (e.g. flood and drought), structuring the ecological community and its capacity to remove or retain carbon and nutrients (Widder *et al.* 2014; Dong *et al.* 2017). Consequently, some degree of synchrony is expected in a river system where storm events and changes in evapotranspiration are likely to affect multiple subcatchments near the same time. Moving upstream, the synchrony of hydrologic variability among nearby subcatchments is likely to increase (Hammond & Kolasa 2014;

Isaak *et al.* 2014), potentially counteracting the expected downstream decrease in temporal variance. Second, temporal variability could become more distinct upstream of spatial variance thresholds because of larger relative coverage of source or sink patches with distinct ecohydrologic characteristics. Differences in persistence and connectivity of the dominant patch could cause higher or lower temporal variability in small subcatchments. Several ecohydrologic characteristics have been identified that could mediate temporal variance at the spatial scales observed here, including variability in groundwater contribution and specific discharge (Burns *et al.* 1998; Sivapalan 2003; Lyon *et al.* 2012) and changes in subsurface contact time (Wolock *et al.* 1997). Third, in-stream biogeochemical uptake or mineralization of carbon and nutrients could create variability unassociated with source fluctuations, particularly for elements that limit biological activity (Mulholland 2004; McGuire *et al.* 2014; Dong *et al.* 2017). Diversity and activity of biological processes become more variable in smaller subcatchments (Alexander *et al.* 2007; Altermatt 2013; Widder *et al.* 2014), though the causality of links between biota and water chemistry is not clear. Regardless of the cause, the divergence of temporal variability regimes in small catchments has implications for developing statistical or mechanistic models of ecohydrologic behavior. Models parameterized with data from a single headwater catchment may be misleading given the diversity of the spatial and temporal dynamics even among adjacent headwater streams. Repeat synoptic sampling of nearby subcatchments should be routine at long-term or high-frequency monitoring sites to assure representativeness of time series used in model calibration or scaling.

The spatial patterns of most parameters were stable on decadal timescales, despite large changes in nutrient inputs to these catchments over the 12 years of sampling (Aquilina *et al.* 2012; Kolbe *et al.* 2016; Poisvert *et al.* 2017). One explanation for this unexpected spatial stability could be that subcatchments differ substantially in their resilience to solute

loading and disturbance. There are myriad characteristics that can alter retention or removal capacity of a subcatchment (Pinay *et al.* 2015; Kolbe *et al.* 2016), most of which are not measured or measureable at catchment scales. Ecological parameters that could influence subcatchment resilience include the distribution of preferential flowpaths in soils and aquifers, which determines residence times in different catchment components; the vertical and horizontal distribution of soil properties; differences in biogeochemical activity in the non-saturated zone or groundwater; land-use history; and heterogeneity in near-surface geology. Because agricultural activity is not randomly distributed across the landscape, some of these same inherent characteristics indirectly control land use and associated nutrient loading and disturbance (Odgaard *et al.* 2013; Zabel *et al.* 2014; Thomas *et al.* 2016). For example, in our study area, differences in soil fertility and surface roughness have resulted in the preferential cultivation of subcatchments underlain by schist, which are also more prone to nutrient export than granitic catchments with thicker soils (Thomas *et al.* 2016). The combined effect of differences in resilience to nutrient loading and associated differences in disturbance regime could explain the observed spatial stability of water chemistry, and more generally, the breakdown in the relationship between nutrient inputs and outputs at the small catchment scale (Burt & Pinay 2005; Lefebvre *et al.* 2007; Brookshire *et al.* 2009; Schilling *et al.* 2013).

Implications for monitoring and intervention

While our methods cannot and do not attempt to quantify annual loads or high-frequency dynamics (Kirchner & Neal 2013), the high spatial variability observed among small subcatchments coupled with the persistent spatial stability of water quality suggests that occasional synoptic sampling of subcatchments can provide valuable information for catchment characterization and management. Specifically, knowing the spatial structure of water quality and the typical grain size of source and sink patches in the landscape could

improve site selection for monitoring, restoration, and conservation efforts. Interventions applied at spatial scales larger than the variance threshold for the parameter of concern, where subcatchment size is much larger than the grain size of the pollutant drivers and sinks, would be suboptimal at best (treating non-offending areas) and at worst could unnecessarily disturb ecosystems or human activity.

For parameters with high spatial stability, synoptic sampling can allow targeted intervention in the subcatchments with highest leverage, potentially yielding catchment-level improvements (Heathwaite 2010; Liu *et al.* 2016; Roley *et al.* 2016). Conversely, efforts to quantify loads with high-frequency monitoring would be most effective downstream of variance thresholds, where the channel integrates multiple patches. While these locations will underestimate the amplitude of temporal variability compared to the most dynamic smaller subcatchments (Temnerud *et al.* 2010), this bias is not necessarily greater than randomly selecting a subcatchment upstream of the variance threshold, where temporal variability could be much lower than at the catchment outflow (Figs. 3, S2).

In catchments where water quality shows little correlation with observed land use (as is the case here), redistribution of agricultural activity based on subcatchment leverage could improve outflow water chemistry without decreasing agricultural yields. Aligning agricultural activity with subcatchment resilience could improve water quality even in the absence of mechanistic understanding of the proximate causes of that resilience (Musolff *et al.* 2015; Thomas *et al.* 2016). While this approach is not socioeconomically feasible in areas where agricultural activity is at capacity (Li *et al.* 2014), it could optimize land management choices where the extent or intensity of agricultural activity are changing, such as much of the developing world or areas of rural exodus (Thomas *et al.* 2016). We emphasize that when differences in subcatchment water quality are due to unmeasured differences in land use (e.g.

nutrient loading or disturbance) rather than subcatchment resilience to nutrient loading, blind redistribution of agricultural activity could have unforeseen consequences, degrading water quality in previously pristine subcatchments with no net improvement in catchment-level water quality.

Testing the generality of subcatchment leverage, synchrony, and spatial stability

We do not propose that the specific patterns of spatiotemporal variability observed here are general, and we recognize that our conceptual framework needs to be tested with more complete spatial time series of both chemistry and discharge in diverse environments. Spatial stability and synchrony of water chemistry likely differ by biome (Krause *et al.* 2014; Jantze *et al.* 2015), though evidence from relatively pristine catchments in temperate (Asano *et al.* 2009; Zimmer *et al.* 2013), boreal (Temnerud & Bishop 2005), and desert (Fisher *et al.* 1982; Dong *et al.* 2017) regions suggest that the patterns observed here are not unique to agricultural ecosystems. Generally, we predict that ecosystems with less hydrologic variability will show greater chemical stability, while ecosystems with more pronounced seasonal or event-level hydrologic shifts will experience more reorganizations of subcatchment chemistry due to changes in source area, residence time, and flowpath (Godsey & Kirchner 2014). Likewise, because topography systematically influences vegetation, soil conditions, hydrology, and human activity (Duncan *et al.* 2013; Thomas *et al.* 2016), we expect topographic heterogeneity to reduce spatial variance thresholds, creating smaller but more distinct source and sink patches, and less stable spatial patterns. We also predict that limiting nutrients will have less spatial stability than non-limiting nutrients (Mulholland 2004; Doyle 2005; Dong *et al.* 2017), which are more evenly distributed in the landscape and less influenced by in-stream processes (Basu *et al.* 2010). However, there are plausible mechanisms that could counteract some of these predicted patterns. For example, synchrony

may be higher in ecosystems with greater hydrologic variability, and spatial stability could be greater in heterogeneous landscapes where absolute differences in concentration among subcatchments are larger. Indeed, the lack of correlation between spatial stability and synchrony observed here suggests that the magnitude of concentration differences between subcatchments strongly influences the representativeness of synoptic sampling. On a basic level, quantifying variance thresholds, spatial stability, and synchrony in contrasting ecosystems could elucidate links between spatial and temporal variability (Hammond & Kolasa 2014) to generate general understanding of how water, carbon, and nutrients move through freshwater landscapes (Ward *et al.* 2017) and cost-effectively inform management decisions in developing and developed countries.

As a final note, we point out that this variance-partitioning approach in no way supplants the need for detailed, high-frequency investigation of concentration and flux dynamics at multiple scales (Isaak *et al.* 2014; Blaen *et al.* 2016; Ruhala & Zarnetske 2017). Such studies identify mechanisms ultimately responsible for the temporal and spatial variability revealed by periodic synoptic sampling. The growing number of tools for interpreting and predicting water chemistry in stream networks (Hirsch *et al.* 2010; McGuire *et al.* 2014) together with increasingly accessible historical datasets (Burt *et al.* 2011; Kirchner & Neal 2013) are laying the foundation for inter-catchment comparisons of spatiotemporal dynamics, potentially moving ecohydrology beyond descriptions of site-specific heterogeneity (McDonnell *et al.* 2007; Krause *et al.* 2014; Abbott *et al.* 2016). To this end, the simple analyses presented here could be widely tested with existing high, medium, or low frequency datasets, including those unsuitable for other network-scale analyses (Hoef *et al.* 2006; Isaak *et al.* 2014; McGuire *et al.* 2014). The interpretation of periodic synoptic sampling in a framework of subcatchment leverage, synchrony, and spatial stability could complement high-frequency studies to improve management of socioecological systems and

address problems that do not respect disciplinary boundaries between ecology, hydrology, and sociology.

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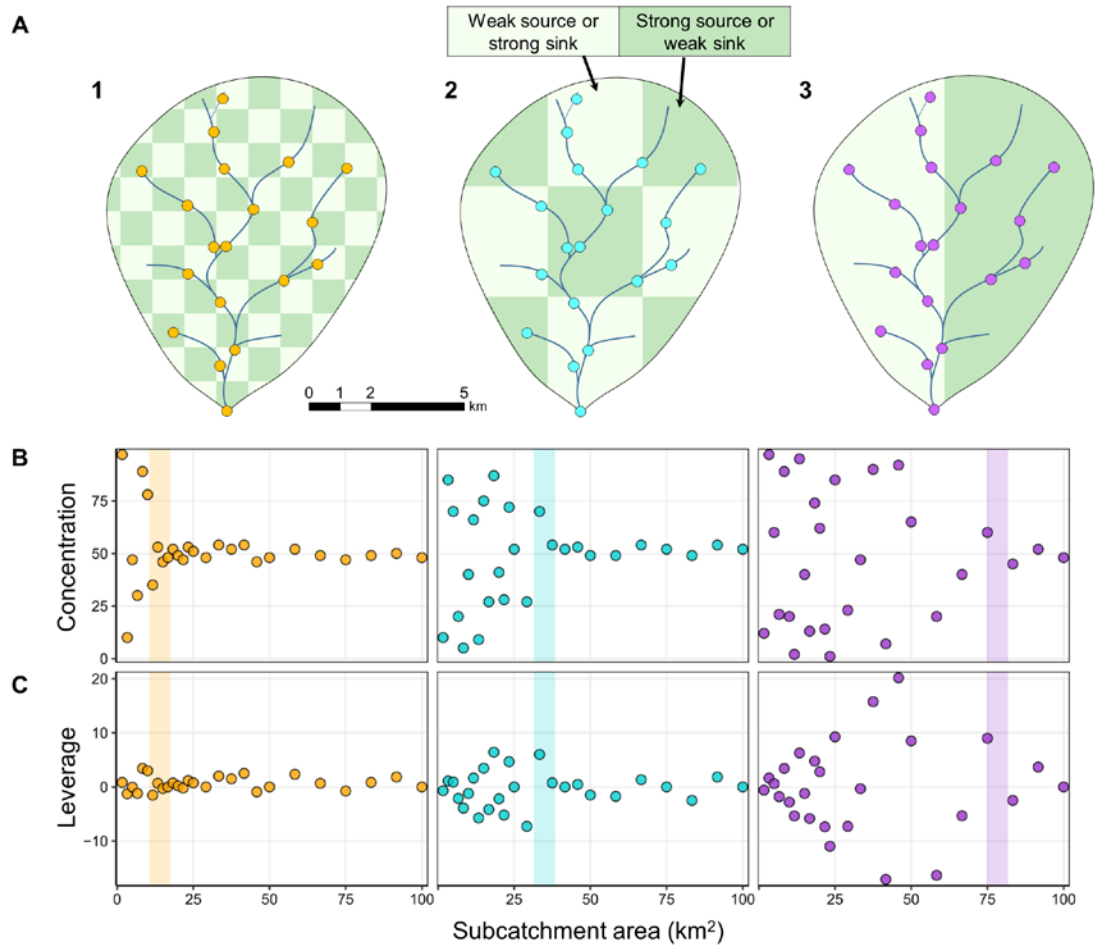
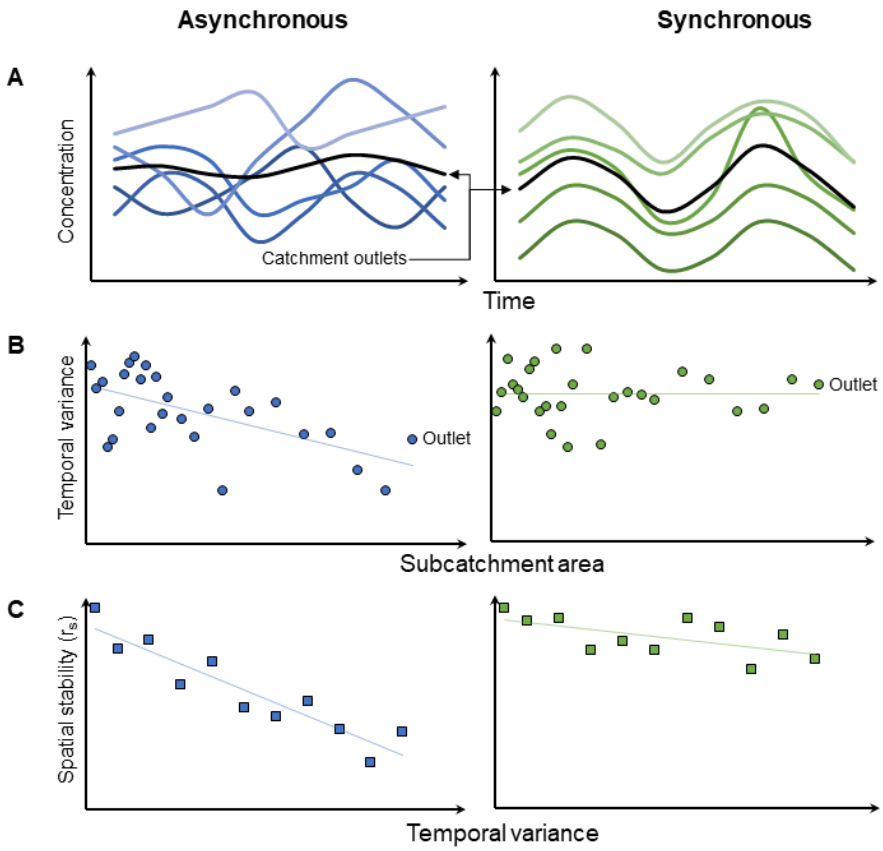


Figure 1. Example patterns of stream network chemistry for three hypothetical solutes distributed in equal quantity to the same 100 km^2 catchment. **A)** The distribution of solute sources is represented by shading, where darker patches are strong net sources (100) and lighter patches make no net contribution (0). **B)** Simulated solute concentrations at the subcatchment sampling points based on the upstream distribution of solute sources. Though the three solutes have the same concentration at the catchment outlet, differences in source patch size alter the location of the collapse of spatial variance, represented by the vertical colored bars. **C)** The leverage of each subcatchment on catchment outflow concentration (Equation 1). Influence or leverage of a subcatchment on outlet chemistry depends on subcatchment discharge and difference from the outlet concentration. Note that in a real catchment the variance threshold for a given solute depends on the interaction between patch size, location, and strength, and the temporally dynamic extent of the hydrologic network including subsurface flowpaths. Quantifying the variance threshold could just as well reveal the grain size of retention or removal patches as source patches, since the same pattern would be expected for a system with a homogeneous solute source (e.g. atmospheric deposition or large-scale geologic source) but non-homogeneous retention capacity.



747

748 **Figure 2.** Synchrony among subcatchments determines expected patterns of spatial and
749 temporal variability in water chemistry. **A)** Temporal change in concentration of a solute for
750 five subcatchments of an asynchronous and synchronous catchment. Asynchronous
751 subcatchments show little temporal covariance, while the synchronous subcatchments show
752 complete covariance. **B)** The temporal coefficient of variation (CV) for a larger set of nested
753 subcatchments in the two catchments. For the asynchronous catchment, temporal variance
754 decreases moving downstream due to destructive interference of chemical signals, while there
755 is no change in variance in the synchronous catchment. **C)** The predicted relationship between
756 temporal variability (CV) and spatial stability (the rank correlation (r_s) between an individual
757 sampling and the long-term flow-weighted mean or flux) for multiple asynchronous and
758 synchronous catchments. In the asynchronous catchments, the representativeness of a
759 snapshot sampling (spatial stability) decreases strongly with temporal variability (CV) due to
760 reshuffling of subcatchment rank. In highly synchronous catchments, spatial stability is more
761 resilient to temporal variation.
762

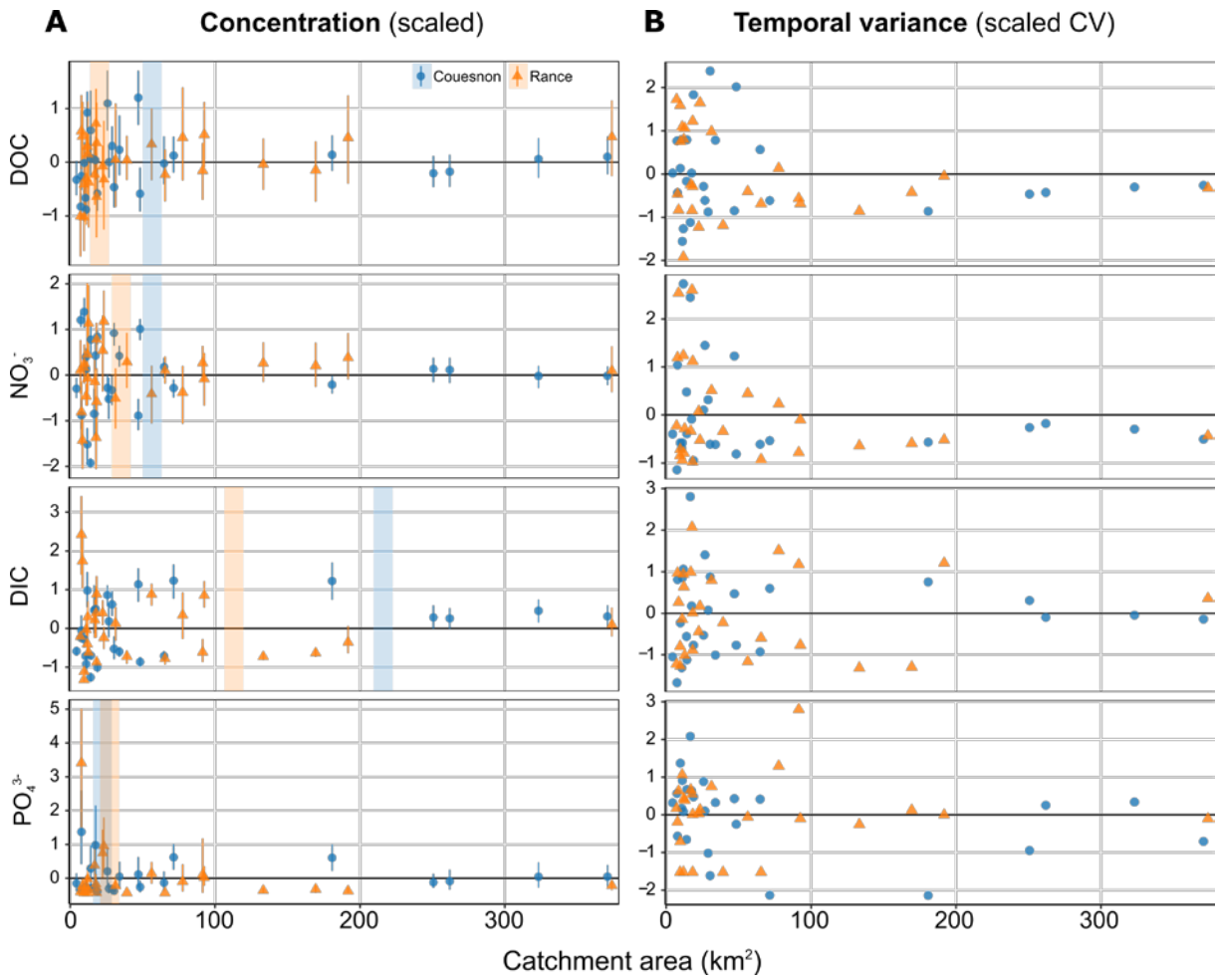


Figure 3. Variability in concentration and temporal variance for subcatchments of differing sizes in the Couesnon (blue) and Rance (orange) catchments. **A)** Scaled, flow-weighted mean values for dissolved organic carbon (DOC), nitrate (NO_3^-), dissolved inorganic carbon (DIC), and phosphate (PO_4^{3-}) from 26 Couesnon subcatchments and 30 Rance subcatchments (Fig. S1). Error bars represent bootstrapped non-parametric 95% confidence intervals of the scaled, flow-weighted mean for repeat samples from each subcatchment (n=6 for Rance, n=18 for Couesnon). The vertical colored bands represent statistical changes in spatial variance among subcatchments based on change point analysis implemented for each catchment separately. **B)** The relationship between temporal variability (scaled CV of repeat samplings for each subcatchment) and catchment size. Concentrations and CVs for each catchment were scaled by subtracting the mean and dividing by the standard deviation to facilitate comparison of changes in variance and evaluate convergence towards the catchment mean (0 on the Y-axis).

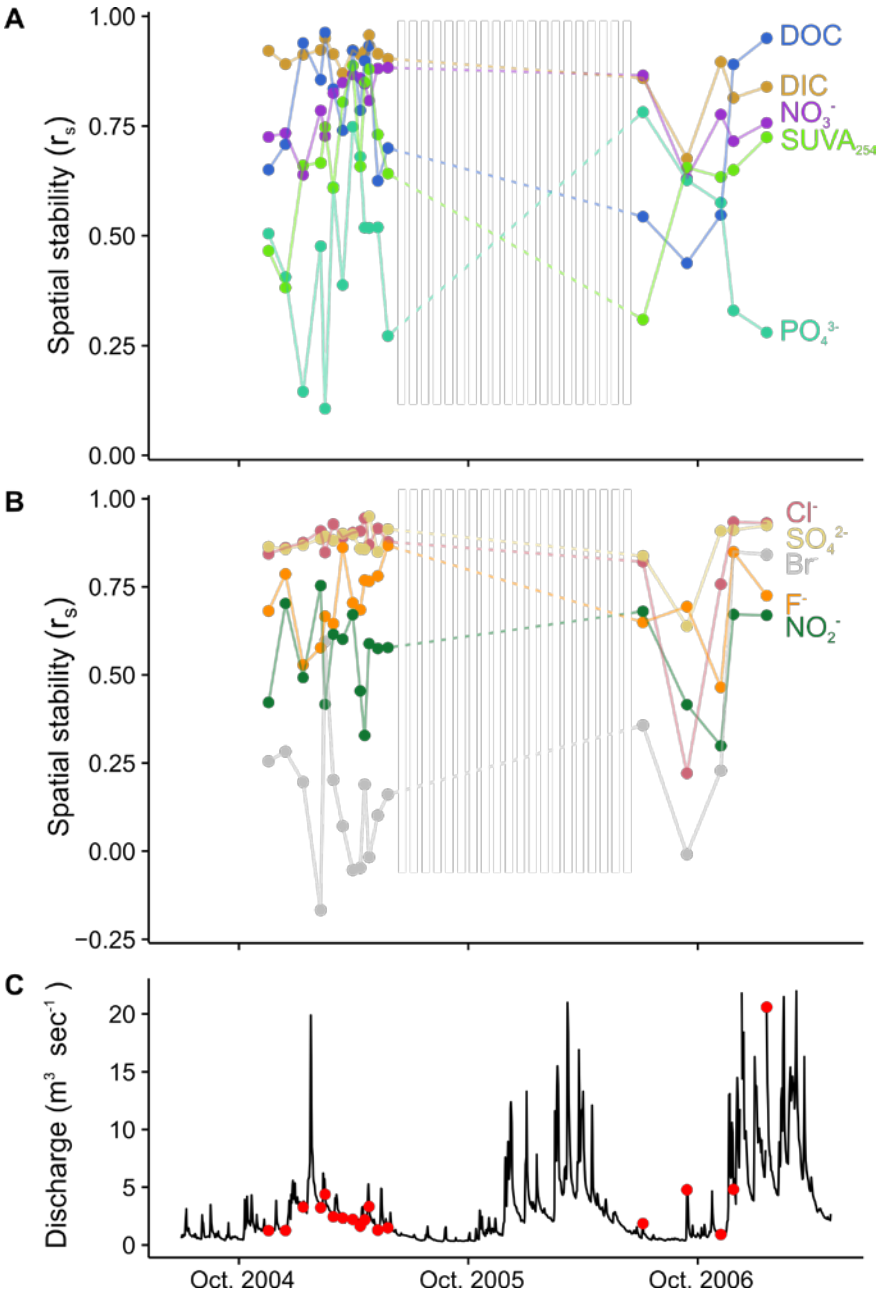
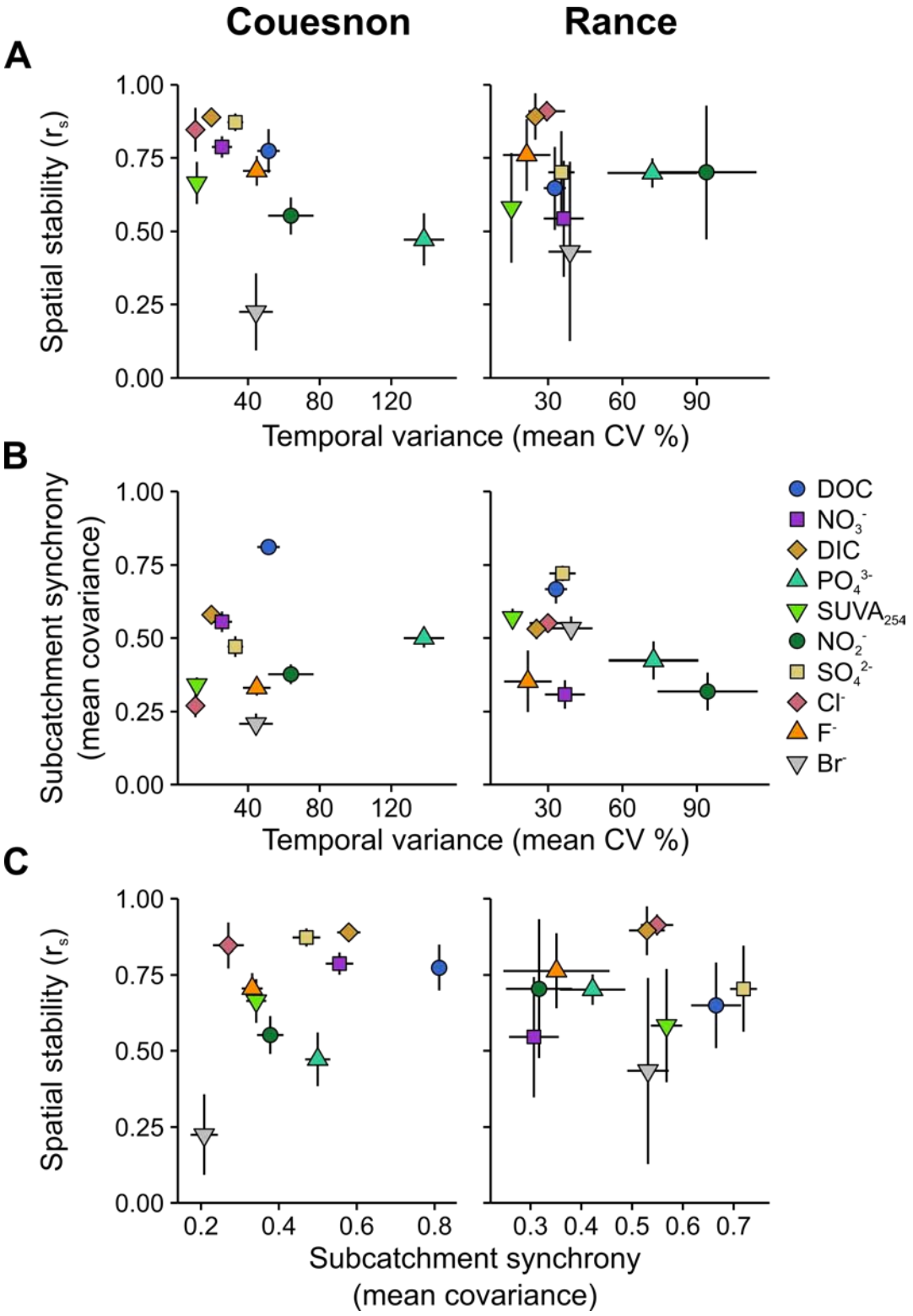


Figure 4. A) and **B)** Spatial representativeness of individual synoptic samplings in the Couesnon River as quantified by spatial stability: the rank correlation (r_s) between the snapshot subcatchment concentrations and flow-weighted means. A value of 1 means that the sampling date perfectly predicts the relative flow-weighted mean concentration of the whole observation period. **C)** Daily discharge of the Couesnon River and timing of samplings. See Fig. S6 for the same information for the Rance watershed.



785

786 **Figure 5.** Relationships among mean spatial stability (rank correlation coefficient (r_s) of
787 individual sampling concentrations and the flow-weighted mean), coefficient of variation
788 (CV) as a metric of temporal variability, and subcatchment synchrony (covariance) among
789 subcatchments for all measured parameters. Error bars represent the 95% confidence intervals
790 of the mean.
791

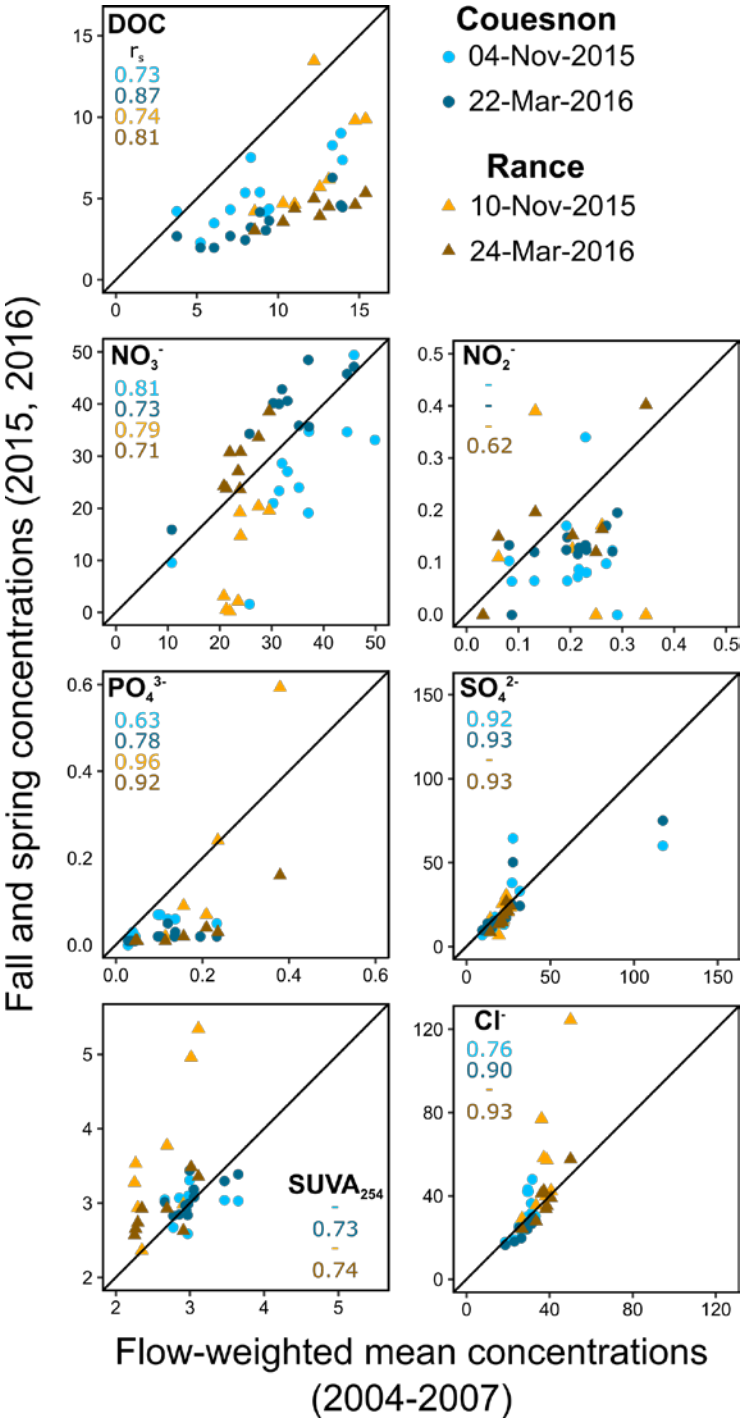


Figure 6. Correlations between the flow-weighted mean concentration for 2004 to 2007 and individual samplings in 2015 and 2016 for the 21 resampled subcatchments. Significant rank correlations ($\alpha = 0.05$) are reported in each panel. Points falling above the 1:1 line were higher in 2015 and 2016 than from 2004 to 2007 and points below the line decreased in the time between.