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1 **Unexpected spatial stability of water chemistry in headwater stream networks**

2 **Running title:** Structure of water quality in stream networks

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28 **Abstract**

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

42

43 **Introduction**

44 How spatial and temporal variability change with scale is one of the fundamental
45 problems of both ecology (Fisher *et al.* 1982; Horne & Schneider 1995; Altermatt 2013) and
46 catchment hydrology (Blöschl *et al.* 1995; Shaman *et al.* 2004; McGuire *et al.* 2014). Because
47 most ecological patterns change with spatiotemporal extent and grain of observation (Turner
48 *et al.* 1989; Chapin *et al.* 1995; Kirchner & Neal 2013), an understanding of variance
49 structure is necessary to scale predictions or implement effective interventions in dynamic
50 landscapes (Haygarth *et al.* 2005; Lowe *et al.* 2006; Temnerud *et al.* 2010). For any
51 ecosystem, variability in a biogeochemical stock or flux depends on on-site conditions and
52 processes (e.g. temperature, redox state, biological activity, weathering) and lateral subsidies
53 or debits from connected ecosystems (Chapin *et al.* 2006). Lateral fluxes are particularly
54 influential in aquatic ecosystems such as stream networks, where delivery of carbon and
55 nutrients from upstream and upslope environments is often orders of magnitude greater than
56 production or removal at any given point in the stream (Lefebvre *et al.* 2007; Brookshire *et al.*
57 2009). Agriculture and urbanization have fundamentally altered lateral fluxes of carbon and
58 nutrients, causing eutrophication, toxic cyanobacteria blooms, and expansive hypoxic dead
59 zones that erode the capacity of ecosystems to feed and water human societies (Gruber &
60 Galloway 2008; Vörösmarty *et al.* 2010; Sutton & UNEP 2013; Withers *et al.* 2014). Over the
61 past 50 years, global fertilizer application has increased 5-fold (Foley *et al.* 2011), and
62 anthropogenic pressures on aquatic ecosystems are expected to intensify due to population
63 growth and increasing meat consumption through the middle of the century (Seitzinger *et al.*
64 2010).

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

67 Jenny *et al.* 2016), partly because of difficulty monitoring and predicting water quality in
68 complex freshwater landscapes (Isaak *et al.* 2014; Abbott *et al.* 2016; Meter *et al.* 2016).
69 Most regulatory frameworks, such as the U.S. Clean Water Act, the European Water
70 Framework Directive, and the Chinese Water Law impose limits on annual loads or mean
71 concentrations in medium to large rivers (Andreen 2004; Hering *et al.* 2010; Liu & Yang
72 2012). This is an appealing strategy because larger rivers integrate many small catchments,
73 and from an estuarine or oceanic perspective, total nutrient load is the main metric of concern
74 (Howarth 2008; Reed & Harrison 2016). However, there is growing evidence that to reduce
75 these downstream nutrient fluxes, we need to understand sources and sinks in headwater
76 catchments, where the vast majority of water and solutes enter aquatic ecosystems (Burt &
77 Pinay 2005; Alexander *et al.* 2007; Bishop *et al.* 2008; Brookshire *et al.* 2009; McDonnell &
78 Beven 2014).

79 It is generally held that the amplitude and frequency of chemical variation in stream
80 networks decrease moving downstream (Burt & Pinay 2005; Lefebvre *et al.* 2007; Creed *et al.*
81 2015). For example, in catchments larger than 100 km^2 , riverine nutrient loads are
82 deterministically associated with percentage of agricultural cover and associated nutrient
83 inputs (Omernik *et al.* 1981; Jordan *et al.* 1997; Howarth 2008), but nutrient loads vary
84 widely despite similar land cover in drainage basins smaller than 20 km^2 (Burt & Pinay 2005;
85 Lefebvre *et al.* 2007; Brookshire *et al.* 2009; Schilling *et al.* 2013). This breakdown of the
86 relationship between land cover and nutrient load represents an important ecological unknown
87 because 90% of global stream length occurs in catchments smaller than 15 km^2 (Burt & Pinay
88 2005; Bishop *et al.* 2008; Downing 2012). However, quantifying and improving water quality
89 in headwater streams is easier said than done. New sensors of water chemistry produce high-
90 frequency data (Kirchner *et al.* 2004; Dupas *et al.* 2016; Ruhala & Zarnetske 2017), but they
91 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.

117 **Approach and methods**

118 *Spatial variance thresholds and subcatchment leverage*

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

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

140
$$\text{Subcatchment leverage} = (C_S - C_O) \times A_S/A_O \times Q_S/Q_O \quad [1]$$

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

152 *Subcatchment synchrony and spatial stability*

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

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

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

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

170
$$\text{Spatial stability} = \frac{\text{covariance}(\text{RC}_t, \text{RC}_{\bar{t}})}{\sigma_{\text{RC}_t} \sigma_{\text{RC}_{\bar{t}}}} \quad [3]$$

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

178 From an applied perspective, spatial stability in subcatchment water chemistry
179 determines the sampling frequency necessarily to identify high-leverage subcatchments (Figs.
180 2a and 1c) and evaluate predicted critical source areas (White *et al.* 2009; Heathwaite 2010;
181 Liu *et al.* 2016), while subcatchment synchrony determines the representativeness of high-
182 frequency monitoring stations. In a synchronous catchment where pulses of pollutants are
183 propagated in chorus (Fig. 2b), a single station anywhere in the network may capture the
184 amplitude of water quality fluctuations. However, in an asynchronous catchment, destructive
185 interference among subcatchments means downstream monitoring stations will underestimate
186 extreme conditions in contributing subcatchments (Fig. 2b). Accurate quantification of

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

193 *Site characteristics and sampling design*

194 We quantified spatial variance thresholds, subcatchment leverage, subcatchment
195 synchrony, and spatial stability in two sets of nested catchments in north-western France (Fig.
196 S1). The Rance and Couesnon catchments are approximately 360 km² and have over 80%
197 agricultural land use, primarily pastureland for dairy cows, corn, and wheat (Table S1).
198 Nutrient concentrations in the area are very high, frequently triggering estuarine algal blooms
199 (Gascuel-Odoux *et al.* 2010; Perrot *et al.* 2014). The climate is oceanic with average monthly
200 temperature ranging from 18°C in July to 5°C in December, and mean annual precipitation
201 averaging 970 mm, a third of which occurs from October to December (Thomas *et al.* 2016).

202 Starting in November 2004, repeat synoptic sampling occurred in 26 subcatchments of
203 the Couesnon with an initial goal of identifying land use parameters driving differences in
204 DOC and NO₃⁻ concentrations. Detailed land use was determined for the entirety of each
205 subcatchment and for the area of potential wetlands closest to the stream network (Medde *et*
206 *al.* 2014). The subcatchments were sampled 13 times (approximately every two weeks), but
207 when no clear correlations emerged with catchment characteristics (Table S2), sampling was
208 abandoned in 2005. After identifying 30 comparable locations in the Rance catchment, 50 km
209 to the west, sampling resumed in both catchments from May 2006 to January 2007. Sampling
210 spanned over 90% of the observed range of daily discharge for the Couesnon and over 70%

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

217 Samples were filtered in the field with pre-rinsed 0.2 μm cellulose acetate filters
218 (Millipore Millex-GV), and analyzed within a week. Quantified analytes had a wide range of
219 reactivities and sources, and included many common water quality parameters. Anions (NO_3^- ,
220 NO_2^- , SO_4^{2-} , Cl^- , F^- , PO_4^{3-} , and Br^-) were quantified by ion chromatography (DionexTM DX
221 100; accuracy $\pm 2.5\%$) and dissolved organic and inorganic carbon (DOC and DIC) were
222 quantified with a total carbon analyzer after coming to equilibrium with the atmosphere
223 (Shimadzu TOC 5050; accuracy $\pm 5\%$). Specific ultra-violet absorbance at 254 nm
224 (SUVA₂₅₄), an indicator of DOC aromaticity and source (Weishaar *et al.* 2003), was
225 calculated from absorption (UVIKON XS, Bio-Tek). For concentrations below the detection
226 limit, we assigned values of $\frac{1}{2}$ the limit of quantification, which affected less than 5% of all
227 measurements except PO_4^{3-} , NO_2^- , and Br^- , which had between 25 and 72% of sites below
228 detection depending on the catchment and sampling. Despite these detection issues, which are
229 common for these parameters, we retained them in the analysis because of their ecohydrologic
230 relevance.

231 *Statistical determination of spatial and temporal variance*

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

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

249 **Results**

250 *Persistent thresholds of spatial variance and stable subcatchment structure*

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

259 variance thresholds occurred between 18 and 68 km² for most parameters, except for DIC in
260 both catchments, and Cl⁻ and F⁻ in the Rance, which had thresholds from 113 to 216 km²
261 (Figs. 3A, S2A). Variance thresholds were stable across flow conditions for 72 of the 80
262 parameter by flow quarter combinations (Table S3), suggesting that patch locations and
263 stream network topology determined spatial patterns, rather than changes in hydrology and
264 biogeochemical processing. The relative scale of variance thresholds for different parameters
265 among the two catchments generally followed the same patterns (e.g. larger for DIC, smaller
266 for PO₄³⁻). Subcatchment leverage followed the expected pattern (Fig. 1c), with highest
267 leverage at spatial scales just larger than variance thresholds (Fig. S3). Most parameters
268 showed moderate to low leverage, with no single subcatchment accounting for more than 25%
269 of outflow concentration. However, several subcatchments had extremely high leverage for
270 PO₄³⁻ and NO₂⁻ (>1000%), indicating substantial retention or removal of these solutes before
271 reaching the catchment outlet (Fig. S3).

272 Despite large changes in discharge and concentration (Figs. S4-S6), subcatchment
273 water chemistry showed strong spatial stability for most parameters, meaning the relative rank
274 of subcatchment concentrations changed little across flow conditions (Figs. 4, S7). Spatial
275 stability of water quality among subcatchments was particularly strong for DOC, DIC, NO₃⁻,
276 and several anions (Fig. 5). The parameters with consistently low or variable spatial stability
277 (PO₄³⁻, NO₂⁻, and Br⁻) had a large number of samples at or below the detection limit,
278 artificially decreasing estimates of spatial stability. During the first storm after the summer
279 low-flow period in 2005, spatial stability dropped substantially for most parameters,
280 indicating a spatial reorganization of water quality in the Couesnon catchment (Fig. 4).

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

283 consistency of concentration-discharge responses among subcatchments (Fig. S4). SUVA₂₅₄
284 was substantially less synchronous than DOC (Figs. 4-5), suggesting diversity in DOC
285 sources despite synchronous fluctuations in bulk DOC concentration. Among parameters,
286 spatial stability and synchrony were unrelated to temporal variance (Fig. 5), demonstrating
287 that the overall magnitude of temporal variance did not determine spatial or temporal
288 representativeness. Contrary to our hypotheses (Fig. 2), synchrony and spatial stability were
289 unrelated (Fig. 5C), demonstrating that large differences in concentration among
290 subcatchments can create spatial stability independent of synchrony.

291 *Clearer temporal signals at smaller scales and decadal stability in structure*

292 Temporal variance did not systematically decrease with increasing spatial scale (Figs.
293 3B, S2B). Instead, temporal variance followed the same pattern observed for spatial variance
294 of subcatchments (Fig. 3a), with greater diversity left of the spatial variance threshold and a
295 convergence towards the catchment mean at the outlet. Subcatchments smaller than the spatial
296 variance threshold showed greater range in variances, but they were equally likely to be more
297 or less dynamic than the catchment outlets. Catchment outlets had temporal variances near the
298 overall catchment mean for most parameters (Figs. 3B, S2B), suggesting variance damping
299 (mixing of strong and weak signals) rather than destructive interference of opposing signals.
300 However, NO₃⁻, SO₄²⁻, and Br⁻ showed somewhat lower temporal variance at the catchment
301 outlets, attributable to inconsistent or weak concentration-discharge responses among
302 subcatchments (Fig. S4). Relationships between temporal variance and flow-weighted mean
303 differed by parameter, with most biologically reactive parameters showing greater variance in
304 subcatchments with low concentrations (Fig. S8).

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

307 spatial structure of water chemistry on decadal timescales (Fig. 6). The high-water sampling
308 in the spring of 2016 was more representative of the 2004-2007 means for all parameters
309 except NO_3^- . DOC, PO_4^{3-} , and NO_2^- concentrations were lower across most subcatchments in
310 2015 and 2016, but NO_3^- , Cl^- , SUVA₂₅₄, and SO_4^{2-} showed no systematic change (Fig. 6).

311 **Discussion**

312 *Ecohydrologic explanations for observed patterns in variability*

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

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

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

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

373 *Implications for monitoring and intervention*

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

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

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

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

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

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

409 We do not propose that the specific patterns of spatiotemporal variability observed
410 here are general, and we recognize that our conceptual framework needs to be tested with
411 more complete spatial time series of both chemistry and discharge in diverse environments.
412 Spatial stability and synchrony of water chemistry likely differ by biome (Krause *et al.* 2014;
413 Jantze *et al.* 2015), though evidence from relatively pristine catchments in temperate (Asano
414 *et al.* 2009; Zimmer *et al.* 2013), boreal (Temnerud & Bishop 2005), and desert (Fisher *et al.*
415 1982; Dong *et al.* 2017) regions suggest that the patterns observed here are not unique to
416 agricultural ecosystems. Generally, we predict that ecosystems with less hydrologic
417 variability will show greater chemical stability, while ecosystems with more pronounced
418 seasonal or event-level hydrologic shifts will experience more reorganizations of
419 subcatchment chemistry due to changes in source area, residence time, and flowpath (Godsey
420 & Kirchner 2014). Likewise, because topography systematically influences vegetation, soil
421 conditions, hydrology, and human activity (Duncan *et al.* 2013; Thomas *et al.* 2016), we
422 expect topographic heterogeneity to reduce spatial variance thresholds, creating smaller but
423 more distinct source and sink patches, and less stable spatial patterns. We also predict that
424 limiting nutrients will have less spatial stability than non-limiting nutrients (Mulholland 2004;
425 Doyle 2005; Dong *et al.* 2017), which are more evenly distributed in the landscape and less
426 influenced by in-stream processes (Basu *et al.* 2010). However, there are plausible
427 mechanisms that could counteract some of these predicted patterns. For example, synchrony

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

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

453 address problems that do not respect disciplinary boundaries between ecology, hydrology, and
454 sociology.
455

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464

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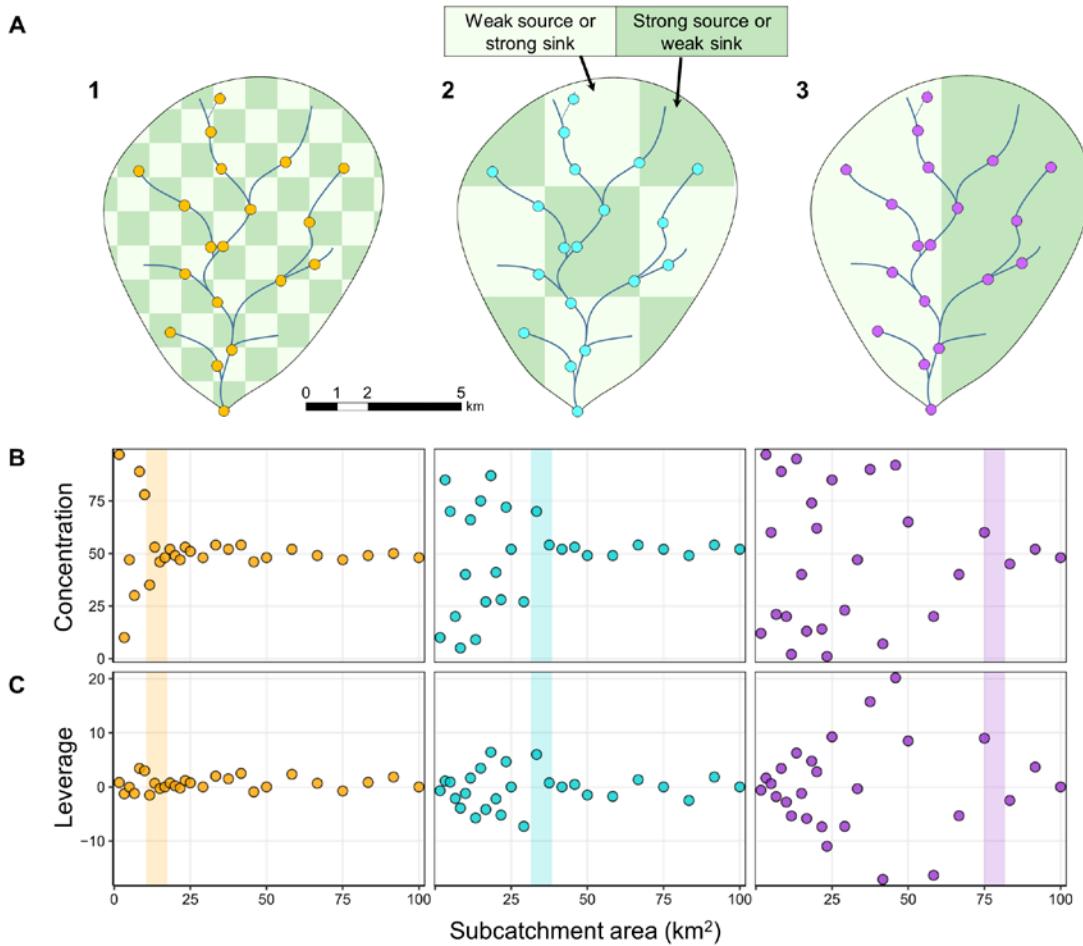
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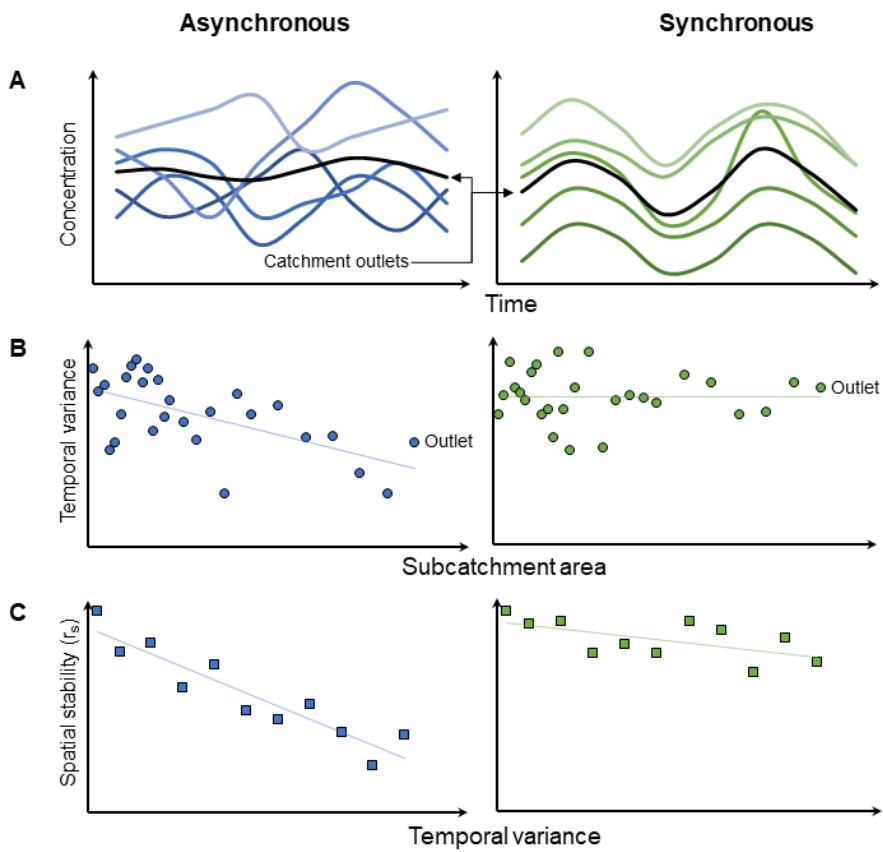
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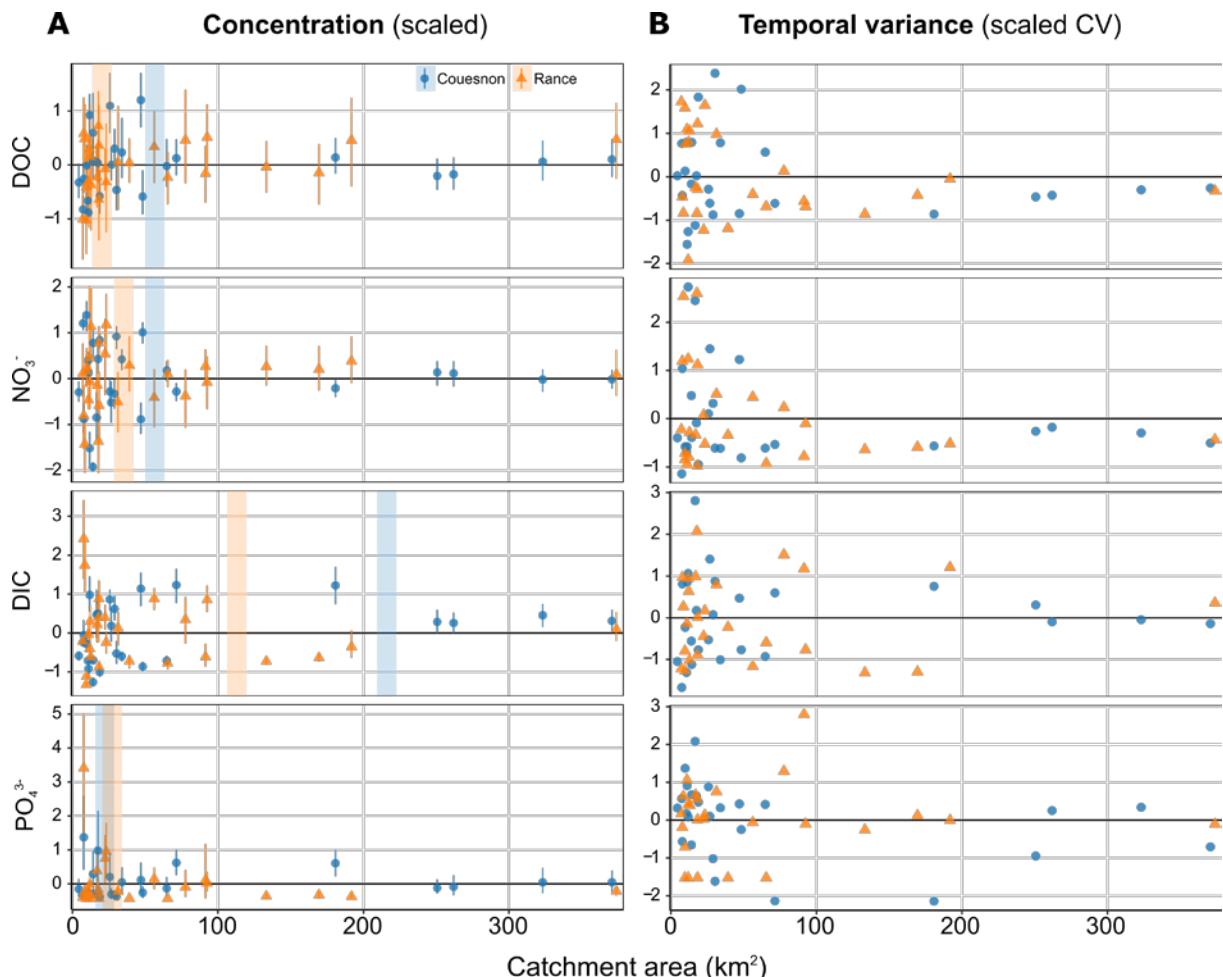
730 **Figure 1.** Example patterns of stream network chemistry for three hypothetical solutes
 731 distributed in equal quantity to the same 100 km^2 catchment. **A)** The distribution of solute
 732 sources is represented by shading, where darker patches are strong net sources (100) and
 733 lighter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



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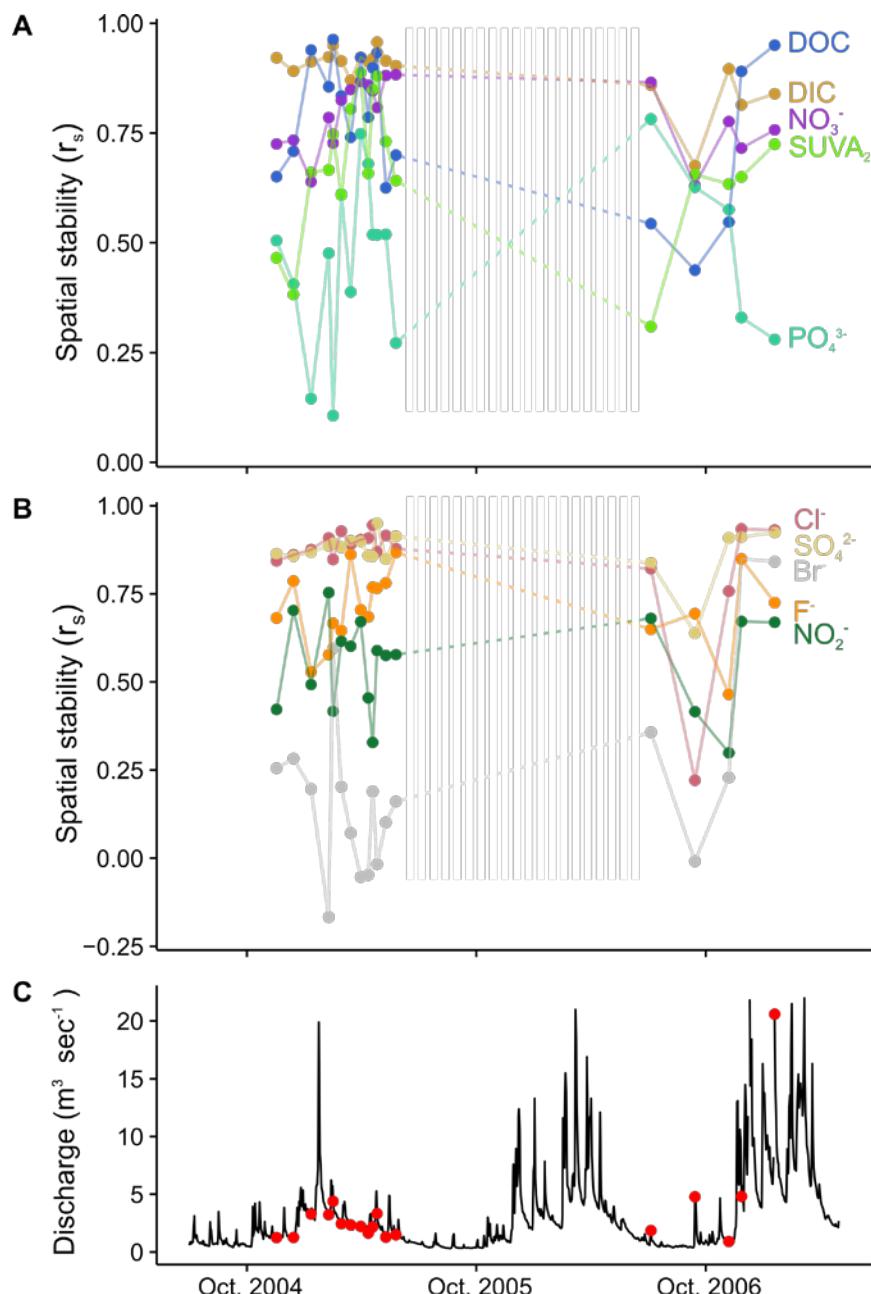
748 **Figure 2.** Synchrony among subcatchments determines expected patterns of spatial and
749 temporal variability in water chemistry. **A)** Temporal change in concentration of a solute for
750 five subcatchments of an asynchronous and synchronous catchment. Asynchronous
751 subcatchments show little 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.

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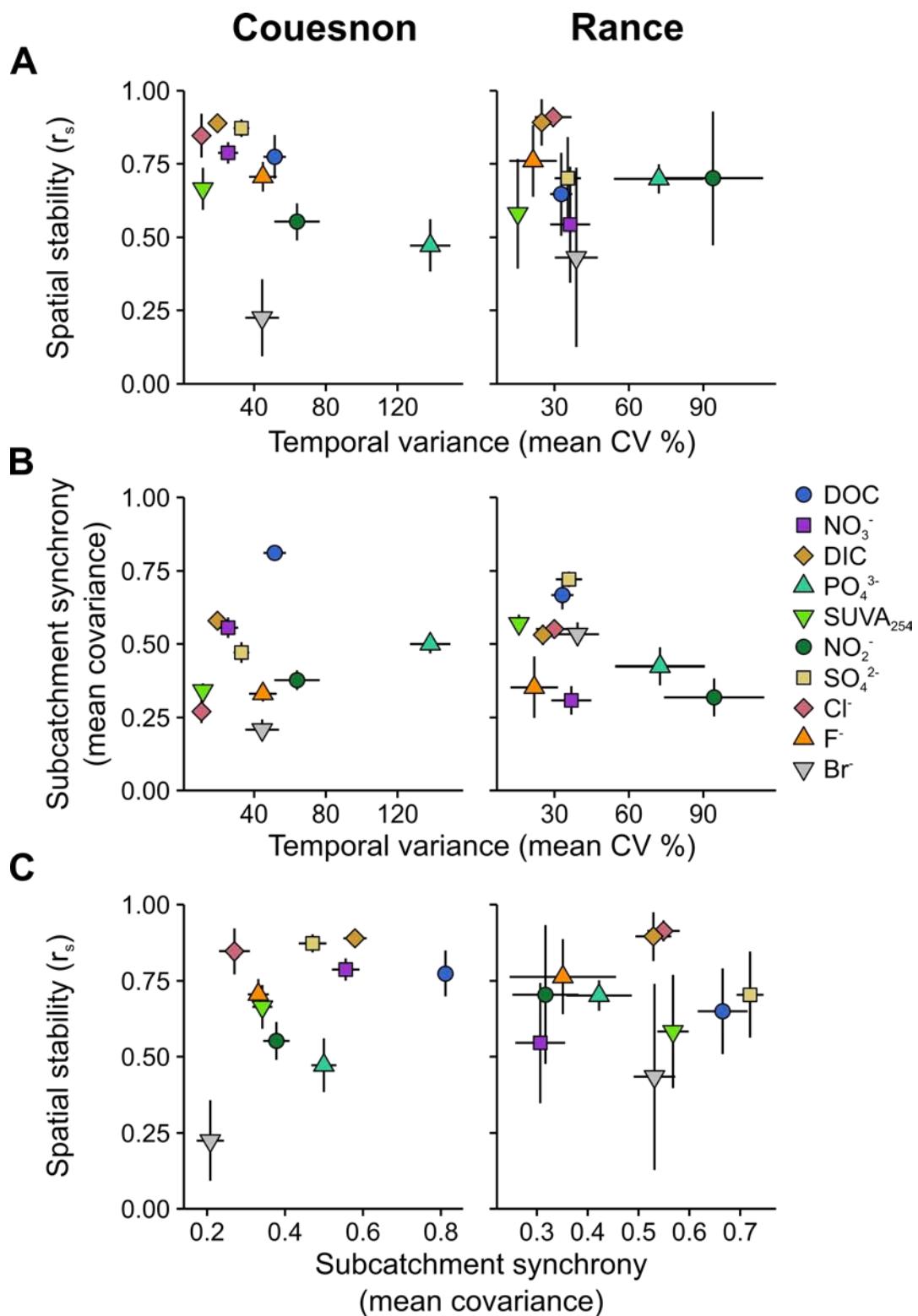


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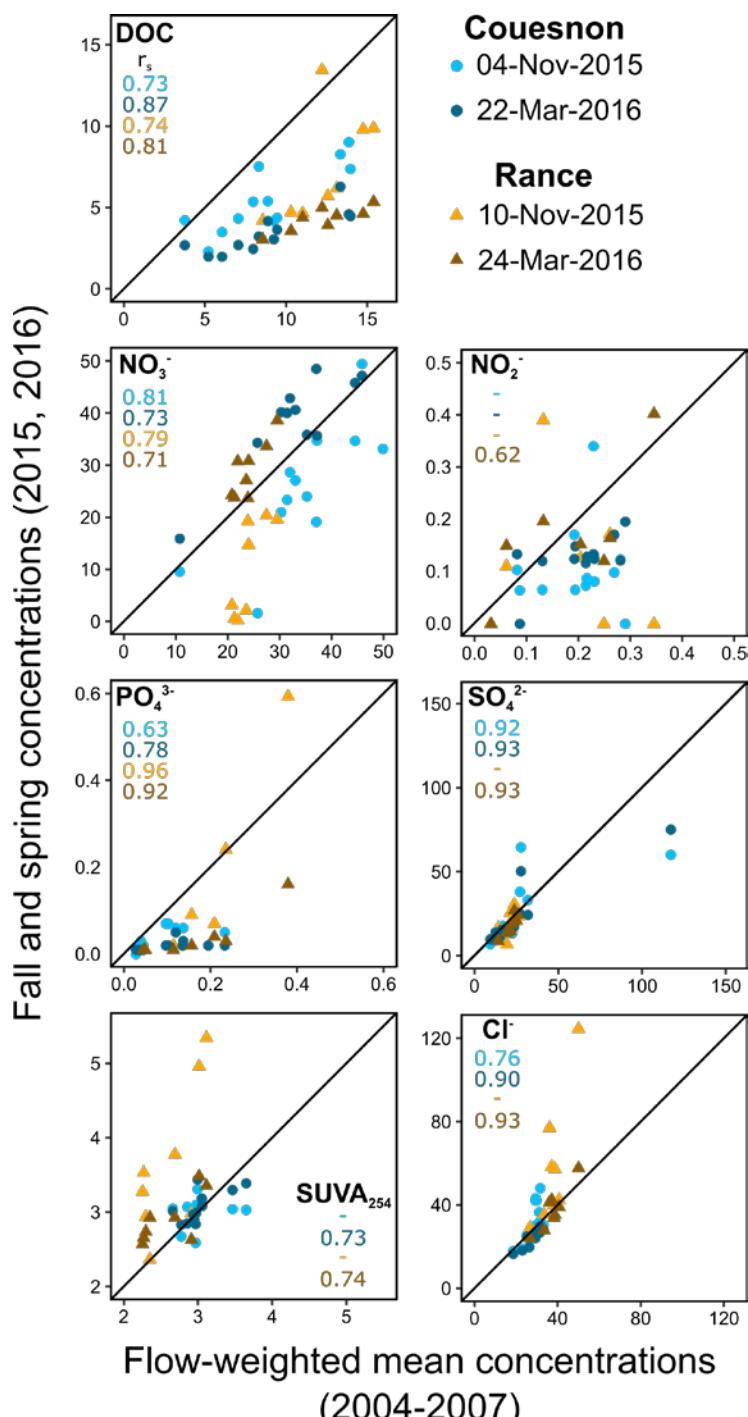
Figure 3. Variability in concentration and temporal variance for subcatchments of differing sizes in the Couesnon (blue) and Rance (orange) catchments. **A)** Scaled, flow-weighted mean values for dissolved organic carbon (DOC), nitrate (NO₃⁻), dissolved inorganic carbon (DIC), and phosphate (PO₄³⁻) 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).



778 **Figure 4. A) and B)** Spatial representativeness of individual synoptic samplings in the
779 Couesnon River as quantified by spatial stability: the rank correlation (r_s) between the
780 snapshot subcatchment concentrations and flow-weighted means. A value of 1 means that the
781 sampling date perfectly predicts the relative flow-weighted mean concentration of the whole
782 observation period. **C)** Daily discharge of the Couesnon River and timing of samplings. See
783 Fig. S6 for the same information for the Rance watershed.
784



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



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