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1 Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen
2 science in France

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14 **Highlights:**

- 15 • High schools measured NO₃⁻, PO₄³⁻, and silica weekly in 13 rivers for 18 years
16 • Large decreases of NO₃⁻ and PO₄³⁻ primarily due to elimination of point sources
17 • Despite decline, nutrient seasonality did not change for most catchments
18 • Concentrations remain high and future improvements may be slower than initial gains
19 • Citizen science can produce long-term, medium-frequency water quality data

20 **Keywords:** eutrophication, nitrogen, phosphorus, silica, time series analysis, citizen science

21 **Abstract**

22 Agriculture and urbanization have disturbed three-quarters of global ice-free land surface,
23 delivering huge amounts of nitrogen and phosphorus to freshwater ecosystems. These excess
24 nutrients degrade habitat and threaten human food and water security at a global scale.
25 Because most catchments are either currently subjected to, or recovering from anthropogenic
26 nutrient loading, understanding the short- and long-term responses of river nutrients to
27 changes in land use is essential for effective management. We analyzed a never-published,
28 18-year time series of anthropogenic (NO_3^- and PO_4^{3-}) and naturally derived (dissolved silica)
29 riverine nutrients in 13 catchments recovering from agricultural pollution in western France.
30 In a citizen science initiative, high-school students sampled catchments weekly, which ranged
31 from 26 to 1489 km^2 . Nutrient concentrations decreased substantially over the period of
32 record (19 to 50% for NO_3^- and 14 to 80% for PO_4^{3-}), attributable to regional, national, and
33 international investment and regulation, which started immediately prior to monitoring. For
34 the majority of catchments, water quality during the summer low-flow period improved faster
35 than during winter high-flow conditions, and annual minimum concentrations improved
36 relatively faster than annual maximum concentrations. These patterns suggest that water-
37 quality improvements were primarily due to elimination of discrete nutrient sources with
38 seasonally-constant discharge (e.g. human and livestock wastewater), agreeing with available
39 land-use and municipal records. Surprisingly, long-term nutrient decreases were not
40 accompanied by changes in nutrient seasonality in most catchments, attributable to persistent,
41 diffuse nutrient stocks. Despite decreases, nutrient concentrations in almost all catchments
42 remained well above eutrophication thresholds, and because additional improvements will
43 depend on decreasing diffuse nutrient sources, future gains may be much slower than initial
44 rate of recovery. These findings demonstrate the value of citizen science initiatives in
45 quantifying long-term and seasonal consequences of changes in land management, which are
46 necessary to identify sustainable limits and predict recovery timeframes.

47 **1. Introduction**

48 Nutrient pollution of freshwater and estuarine water bodies is degrading ecological
49 functioning and ecosystem services at a global scale. Economic damage from nitrate (NO_3^-)
50 contamination alone is estimated to cost 0.2 to 2.3 trillion USD annually—up to 3% of the
51 global gross domestic product (Bodirsky et al., 2014; Sutton and UNEP, 2013). In the past 50
52 years, global fertilizer use increased by over 500% (Foley et al., 2011), and nitrogen and
53 phosphorus pollution are expected to keep pace with population growth and meat
54 consumption, increasing until the middle of the century (Canfield et al., 2010; Seitzinger et
55 al., 2010). At the same time, human activity, primarily agriculture, has disturbed
56 approximately three-quarters of the Earth's ice-free land surface (Ellis et al., 2010), reducing
57 the capacity of ecosystems to buffer and process nutrient inputs (Pinay et al., 2015; Seitzinger
58 et al., 2006; Thomas et al., 2016a). The resulting nutrient excess has contaminated
59 groundwater aquifers (Aquilina et al., 2012; Ben Maamar et al., 2015; Jasechko et al., 2017)
60 and increased the flux of nutrients through river systems to the sea, creating eutrophic dead
61 zones in many lakes and estuaries, and altering biogeochemistry throughout the ocean (Diaz
62 and Rosenberg, 2008; Howarth, 2008; Reed and Harrison, 2016). In response to this
63 accelerating environmental crisis, governments have funded a broad range of programs to
64 monitor and improve water quality (Andreen, 2004; Hering et al., 2010; Liu and Yang, 2012;
65 Withers and Haygarth, 2007), but results of interventions have been mixed (Jarvie et al.,
66 2013; Jenny et al., 2016; Wilcock et al., 2013). In many developed countries, phosphorus
67 concentration and flux from large catchments have decreased over the last two decades,
68 mostly due to treatment of point sources (e.g. waste water treatment plants), but NO_3^- , which
69 is highly mobile and has many diffuse sources, has showed little change (Minaudo et al.,
70 2015; Moatar et al., 2017). Furthermore, in small to medium catchments, where the bulk of
71 terrestrial nutrient loading occurs (Abbott et al., 2017a; Alexander et al., 2007), trends are
72 even less clear, with nutrient fluxes differing substantially among apparently similar
73 catchments (Aubert et al., 2013b; Burt and Pinay, 2005; Stålnacke et al., 2003).

74 Two primary factors complicate the quantification of water-quality trends in small
75 catchments. First, nutrient concentrations and fluxes through river networks vary strongly at
76 event, seasonal, and interannual timescales (Gascuel-Oudoux et al., 2010; Moatar et al., 2013;
77 Thomas et al., 2016a), meaning that repeat measurements are necessary to characterize the
78 overall nutrient condition of a catchment. Second, because nutrient residence times can be on
79 the order of decades in soil, unsaturated zone, and groundwater (Howden et al., 2011; Kolbe
80 et al., 2016; Meter et al., 2016; Sebilo et al., 2013), substantial time lags can exist before

81 changes in management practice are reflected in water quality. Consequently, quantifying the
82 effectiveness of changes in land management requires both long-term (Abbott et al., 2017a;
83 Burt et al., 2011) and high-frequency monitoring (Abbott et al., 2016; Aubert et al., 2013a;
84 McDonald et al., 2016; Vilmin et al., 2016). One approach to achieving this ambitious goal is
85 to involve non-professional community members in sample collection (Bonney et al., 2014).
86 Citizen science has been used both as a tool to extend ecological observation and a
87 mechanism to improve the general public's engagement with science (Bonney et al., 2014;
88 Cohn, 2008; Silvertown, 2009). Though not without limitations in data reliability and
89 acceptance by researchers (Conrad and Hilchey, 2011), citizen science has successfully been
90 used for a variety of projects including mapping the distribution of species, quantifying
91 anthropogenic impacts, analyzing visual data, and monitoring water quality (Breuer et al.,
92 2015; Gardiner et al., 2012; Kyba et al., 2013; Savage, 2012).

93 In this context, we analyzed a never-published, 18-year time series of riverine nutrient
94 concentrations in 13 catchments recovering from agricultural pollution in western France.
95 Samples collected weekly from 1998 to 2016 by volunteer high school students were analyzed
96 for NO_3^- , phosphate (PO_4^{3-}), and dissolved silica (DSi). We analyzed long-term trends and
97 changes in seasonality, i.e. periodicity of cycles, timing of maximum and minimum
98 concentrations, and relationships between discharge and concentration. We hypothesized
99 generally that seasonal fluctuations in stream nutrient concentrations would depend on
100 interactions between three factors (Fig. 1): 1. vertical and horizontal location of nutrient
101 sources, which is a function of current and past land use and land cover, 2. seasonal changes
102 in water flowpath and associated residence time, and 3. seasonal and long-term changes in
103 biogeochemical nutrient retention and removal (e.g. denitrification or uptake by plants and
104 microorganisms). Based on this hypothesis, we predicted that discharge and concentration
105 would fluctuate asynchronously for nutrients that increase with depth (e.g. DSi, which is
106 primarily geogenic, or NO_3^- in catchments with a legacy of groundwater pollution) and
107 synchronously for those that decrease with depth (e.g. NO_3^- in a catchment with current
108 excess nitrogen input; Fig. 1a). We also hypothesized that decreases in diffuse-source
109 nutrients would more rapidly improve stream concentrations during the high-water period
110 when shallow flowpaths with shorter residence times contribute a larger portion of discharge,
111 but that elimination of seasonally-constant point sources (e.g. waste water effluents) would
112 result in relatively faster nutrient decreases during low flows (Fig. 1b). We tested these
113 predictions with a variance-partitioning approach, comparing the magnitude of seasonal,
114 annual, and interannual changes in nutrient concentrations.

115

116 **2. Methods**

117 **2.1 Land-use history in far western France**

118 The peninsula of Brittany is part of the Armorican Massif, which is underlain by
119 crystalline bedrock and overlain by Quaternary loess and alluvial and colluvial deposits
120 (Kolbe et al., 2016). Silty loam is the dominant soil texture. Brittany has a maritime climate
121 with monthly average temperatures ranging from 17.5 °C in July to 5 °C in December and
122 mean annual precipitation of around 1,000 mm, roughly evenly distributed through the year
123 (Thomas et al., 2016a). While the peninsula's many coastal catchments have relatively
124 homogeneous climate and lithology, there is a great diversity of current and past land use,
125 providing an ideal template to test the impact of agriculture on water quality. For example,
126 annual NO_3^- fluxes vary from 9 to 89 kg N ha⁻¹ y⁻¹ among catchments (Gascuel-Oudoux et al.,
127 2010), and phosphorus fluxes vary from 0.1 to 1.4 kg P ha⁻¹ yr⁻¹ (Delmas et al., 2015; Dupas
128 et al., 2015), covering most of the range observed throughout western Europe (Dupas et al.,
129 2013; Poisvert et al., 2017).

130 The western tip of Brittany, where our 13 study catchments are located, has a long
131 history of intensive animal husbandry and row-crop agriculture (Fig. 2). Brittany represents
132 only 7 % of French agricultural area, but produces 55 %, 40 %, and 25 % of the nation's pigs,
133 poultry, and milk, respectively (Gascuel-Oudoux et al., 2010). Cow density gradually grew
134 until 1978 when it peaked at 125 head km⁻², and pig density rapidly increased from 1960 to
135 2005 when it reached 424 head km⁻² (Poisvert et al., 2017). Total nitrogen (N) surplus, an
136 integrative estimate of nutrient inputs and outputs at the soil level, peaked in 1989 at 143 kg
137 per ha of used agricultural area (UAA) per year (Fig. 2; Poisvert et al., 2017). In the 1970s,
138 point and non-point nutrient sources started causing frequent harmful algal blooms in
139 estuaries and bays around the peninsula, triggered by a combination of high nutrient loading
140 from coastal rivers, semi-enclosed bays that limit oceanic flushing of estuaries, and clear
141 ocean water that favors rapid algal growth (Perrot et al., 2014). In response to this widespread
142 eutrophication of inland and coastal ecosystems, a coordinated and multi-faceted series of
143 mitigation actions and regulation measures were implemented starting in 1992 (MEDD &
144 Agences de l'eau, 2003). Reinforced by international and national regulation in 1998 and
145 2000 (Hering et al., 2010; Piot-Lepetit and Moing, 2007), millions of Euros have been
146 invested to fund local and regional remediation projects (Regional Algal Bloom Plans, 2015;
147 Regional Counsel, 2013). Livestock facilities have been systematically improved to reduce
148 seepage of animal waste, application of chemical and organic fertilizer has been regulated,

149 and some landscape restoration programs have been conducted to replant hedgerows and
150 preserve wetlands (*e.g.* Breizh Bocage). Considerable efforts have also been made to decrease
151 urban pollution, with installation or improvement of sewage treatment plants in many towns
152 and cities since 2000.

153 **2.2 Citizen-science program and chemical analysis**

154 We analyzed data from 13 stations in the Ecoflux river monitoring program (data are
155 available at www-iuem.univ-brest.fr/ecoflux), which includes 12 small catchments of 26 to
156 280 km², and 1 medium catchment of 1490 km² (Fig. 1; Table 1). Climate and topography are
157 relatively similar among the catchments, with annual rainfall ranging from 990 to 1395 mm
158 and mean altitude from 70 to 164 m. Long-term, continuous discharge was available for 7 of
159 the 13 catchments, as part of regional environmental monitoring (DREAL;
160 www.hydro.eaufrance.fr/, Table S1).

161 The Ecoflux program was founded in 1998 by the regional government (Conseil
162 Général du Finistère) and the European Institute for Marine Studies (IUEM) to monitor
163 nutrient concentrations in agricultural catchments and improve awareness of the importance
164 of water quality for agricultural students who will be the next generation of farmers and land
165 managers. Starting in their second year of high school, students from agricultural, natural
166 science, and general academic tracks participated in the sampling. Following a standardized
167 protocol, volunteer students and teachers from primarily rural high schools collected weekly
168 water samples from the 13 stations from September 1998 to December 2015 (5 rivers) or
169 November 2016 (8 rivers; Table 1). Students filled two acid-washed, 100 mL, glass bottles for
170 NO₃⁻ and PO₄³⁻, and one 100 mL plastic bottle for DSi. Students filtered samples in the field
171 to 200 µm with glass fiber filters to remove particulates, and upon returning to the lab, NO₃⁻
172 and PO₄³⁻ samples were frozen and DSi samples were stored at 4°C until analysis in one of
173 two professional labs (details below). Volunteers from the community collected samples
174 during school vacations. Since the program started, approximately 18 researchers, 10 graduate
175 students, 21 adult volunteers, and 5,000 high-school students from 6 educational institutions
176 have participated in sampling and analysis.

177 The IUEM analyzed all PO₄³⁻ and DSi samples, and LABOCEA-Idhesa, a certified,
178 public laboratory, analyzed all NO₃⁻ samples following international norms (ISO 15923-1).
179 PO₄³⁻ was quantified with a Shimadzu UV1700 spectrophotometer (SHIMADZU, Kyoto,
180 Japan), and NO₃⁻ and DSi with a Technicon Auto Analyser II (SEAL Analytical,
181 Southampton, UK). Analytical precision was ± 5% for NO₃⁻ and DSi (inline and automatic
182 addition of reagents) and ± 6 to 10% for PO₄³⁻ (manual addition of reagents). Though few

183 nutrient time series exist for comparison, Ecoflux NO₃⁻ concentration in river 7 showed
184 excellent short- and long-term agreement with a professionally operated monitoring station
185 located 4 km upstream (Fig. S1). The overall sampling success rate was 79% over the
186 monitoring period (i.e. 21% of the week by river combinations were not sampled or
187 analyzed), constituting 8,929 sets of nutrient samples. The only major gap in data occurred for
188 river 4, which was not sampled from 2004 to 2013, due to budget and personnel constraints.

189 **2.3. Data analysis**

190 **2.3.1. Metrics of annual and interannual concentrations and loads**

191 For rivers with discharge data (Tables 1 and S1), we calculated monthly and annual
192 specific discharge (L s⁻¹ km⁻²), and the percentage of total discharge that occurs during the
193 highest 2% of flows (W2), a metric of flow variability (Moatar et al., 2013). To characterize
194 annual concentrations and loads, we calculated the median concentration (C50), the flow-
195 weighted mean concentration based on discharge at the time of sampling (C*), and the annual
196 load using the following protocol. For each catchment and nutrient combination, we assessed
197 the optimal method for estimating load based on the flux variability matrix, which combines
198 hydrologic variability (i.e. W2) and concentration-discharge relationships (Meybeck and
199 Moatar, 2012; Raymond et al., 2013). According to this matrix, the *discharge-weighted*
200 *concentration method* was the most appropriate for the majority of the rivers and nutrients,
201 thus the specific annual load (F_s) was estimated as:

$$202 \quad F_s = \frac{k \sum_{i=1}^n C_i Q_i}{A \sum_{i=1}^n Q_i} \bar{Q} \quad \text{Equation 1}$$

203 where C_i is the instantaneous measured concentration (mg L⁻¹), Q_i is the corresponding
204 instantaneous discharge value (m³ s⁻¹), \bar{Q} is the mean annual discharge computed from
205 continuous flow records (m³ s⁻¹), A is the catchment area (m²), and k is a conversion factor
206 that accounts for the sampling period (1 week in this case). An advantage of this approach is
207 that uncertainty intervals can be calculated based on the discharge and concentration
208 variabilities for a given sampling frequency, and estimates can be corrected according to the
209 associated bias (Moatar et al., 2013). We calculated Pearson correlations (r) to test for
210 relationships between median stream nutrient concentrations and modeled nitrogen (N) and
211 phosphorus (P) surplus from agriculture, estimated with land use data and a wide range of N
212 and P processes (Dupas et al., 2013; Schoumans et al., 2009). For example, the N module of
213 the model included symbiotic fixation, atmospheric deposition, application of synthetic and
214 organic fertilizers, volatilization, and hydrologic N export (Dupas et al., 2013). For the rivers

215 with discharge data, pairwise linear regressions between C50, C*, and annual load were used
216 to assess whether median concentrations were good predictors of annual loads.

217 **2.3.2. Time series analysis of nutrient concentrations**

218 We modeled the amplitude, frequency, and phase of nutrient concentrations for all
219 catchments except river 4 (excluded because a gap in measurements from 2004 to 2013).
220 First, we calculated long-term trends with simple linear regression to detrend time series with
221 significant interannual slopes, creating stationary series for all subsequent analyses (Legendre
222 and Gauthier, 2014). We then used distance-based Moran's Eigenvector Maps (dbMEMs;
223 Borcard et al., 1992; Dray et al., 2006) to model frequency and amplitude of fluctuations for
224 nutrient concentrations. This method yields sine wave variables at multiple frequencies,
225 similar to those obtained from Fourier transformation, allowing partitioning of overall
226 variance between multiple timescales. The time variables are the result of a principal
227 coordinates analysis (PCoA) of the temporal distance matrix. We computed dbMEMs from
228 the oldest to the most recent sampling date for each river-nutrient combination. We analyzed
229 the positive temporal structures of the dataset using a lag of 1 week as the threshold for
230 determining neighbors, and performed multiple linear regressions with all positive dbMEMs
231 and the associated nutrient concentrations. We used forward selection of explanatory
232 variables to thin significant models. Reduced models were then split in 3 sub-models relating
233 to different timescales: long-term (longer than 64 weeks), seasonal (40 to 64 weeks), and
234 short-term (less than 40 weeks), by grouping and re-computing selected dbMEMs according
235 to their wavelength. We then determined the portion of overall variance explained by each
236 sub-model with hierarchical partitioning of variance, which ranks sub-models according to
237 goodness of fit with temporal structure, and in case of overlap in explained variance, gives
238 precedence to the longer timescale (Legendre et al., 2012). We used the adjusted coefficient
239 of determination (adj-R^2) as an unbiased measure of goodness of fit for all models (Ohtani,
240 2004).

241 To test if rate of recovery was associated with initial anthropogenic pressure, we
242 correlated initial concentration (intercept of the linear model) with percent change (based on
243 linear slopes) for each nutrient, using the regressions calculated during the detrending
244 procedure described at the beginning of this section. To allow comparison among nutrients,
245 we calculated linear slopes for both raw and scaled data (after subtracting the mean and
246 dividing by the standard deviation; SD). To test our prediction that elimination of point
247 sources would cause relatively larger nutrient decreases during low flow, while decreases in
248 diffuse sources would result in larger high-flow nutrient decreases (Fig. 1), we compared

249 slopes of interannual trends for mean August concentrations (low flow) and December
250 concentrations (high flow). Additionally, to assess whether annual maximum or minimum
251 concentrations changed faster, we compared slopes of interannual trends for the mean of the
252 five highest and lowest values from each year for each nutrient. We evaluated the significance
253 of long-term trends with Mann Kendall tests and compared parametric detrended slopes with
254 Theil-Sen slope estimates determined following the Siegel method (Komsta, 2005). While
255 uniform land-use and nutrient input data did not exist at these spatial and temporal scales, we
256 re-extracted annual N surplus for each catchment from Poisvert et al., (2017), and analyzed all
257 available departmental data on phosphorus loading from livestock to assess changes in non-
258 point nutrient sources prior and during the study period (i.e. 1988, 2000, and 2010). To
259 quantify changes in point sources, we compiled records from wastewater treatment plants and
260 industrial sites (e.g. slaughterhouses and food processing plants) for 1998, 2001-2006, and
261 2015. The compiled data represented 52 to 100 % (mean = 80 %) of the area for 11 out of the
262 13 catchments, providing a robust estimate of relative changes in point and non-point nutrient
263 inputs.

264 All analyses were conducted in R (R Core Team, 2016) with the `vegan`, `adespatial`, and
265 `ggplot2` packages (Dray et al., 2017; Oksanen et al., 2007; Wickham, 2009), with additional
266 functions from Legendre and Gauthier (2014).

267

268 **3. Results**

269 **3.1. Hydrologic and stoichiometric differences among rivers**

270 For the 7 rivers with long-term hydrologic monitoring, mean annual specific discharge
271 (1966-2016) varied less than a factor of 2 (12.2 to 23.5 L s⁻¹ km⁻²; Table 1). Minimum
272 monthly specific discharge was more variable (2.5 to 7.0 L s⁻¹ km⁻²), with some catchments
273 showing influence from groundwater (e.g. river 10) or reservoirs (e.g. river 7) during low
274 flows (Table 1). Hydrologic variability was highest for rivers 6 and 5, which had flashy
275 hydrographs (W2 > 10%), and lowest for the four northeastern rivers 10-13 (W2 between 7.2
276 and 8.4 %), which showed more buffered discharge during floods. All but 1 catchment (river
277 1) had modeled N-surplus greater than 30 kg N ha⁻¹ year⁻¹, and 3 catchments exceeded 60 kg
278 N ha⁻¹ year⁻¹ (rivers 8-10). P surplus was moderate to high, ranging from 19 to 32 kg P ha⁻¹
279 year⁻¹. N surplus was not correlated with median NO₃⁻ concentration (p > 0.05), but was
280 correlated with median PO₄³⁻ concentration (r = 0.69, p < 0.05), potentially due to differences
281 in nutrient retention and removal capacity among the catchments. Modeled P surplus was not
282 correlated with any median nutrient concentrations (p > 0.05).

283 There was substantial variation in concentration among the rivers for both
284 anthropogenic (PO_4^{3-} and NO_3^-) and naturally-occurring (DSi) nutrients, with the median
285 concentration over the period of record varying approximately 4-fold among rivers for NO_3^- ,
286 3-fold for DSi, and 12-fold for PO_4^{3-} (Table 2). Median DSi and NO_3^- concentrations among
287 rivers were positively correlated ($r = 0.67$, $p < 0.001$) as were median NO_3^- and PO_4^{3-} ($r =$
288 0.57 , $p < 0.05$), but DSi and PO_4^{3-} were not correlated ($p > 0.05$), and N:P and DSi:P ratios
289 varied widely (Fig. S2). The pairwise linear regressions between concentration and load
290 parameters showed that flow-weighted means (C^*) were strongly associated with median
291 concentrations (C_{50} ; $R^2 > 0.86$, $p < 0.01$ for all parameters; Table 2). Slopes were near 1 for
292 DSi and NO_3^- (0.92 and 0.82, respectively) but less than 1 for PO_4^{3-} (0.66), indicating that
293 median concentration overestimated flow-weighted mean for PO_4^{3-} , due to systematic dilution
294 during high flow events. C_{50} and C^* were good predictors of annual loads for NO_3^- and PO_4^{3-}
295 (R^2 between 0.77 and 0.89) but not for DSi ($R^2 = 0.43$ and 0.38 for C_{50} and C^* , respectively).

296 **3.2. Long-term trends in nutrient concentrations**

297 Between 1998 and 2015, point-source nutrient inputs at the departmental level
298 decreased 91 % for N and 86 % for P due to construction of wastewater treatment plants and
299 regulation of industrial discharge (Table S2). Non-point nutrient inputs peaked in 1987 and
300 then decreased an average of 59 % (SD = 8.7) for N by 2015 and 65 % (SD = 6.1) for P by
301 2010 for the catchments with available data (Fig. S3). Between 1999 and 2016, NO_3^-
302 concentration decreased significantly ($p < 0.05$) for all catchments, PO_4^{3-} decreased for all but
303 1 catchment, and DSi showed little or no change (Figs. 3 and 4; Table S3). The parametric
304 regression slopes and the Theil-Sen slope estimates were strongly correlated for all nutrients
305 ($r = 0.97$, 0.95, and 0.89, for NO_3^- , PO_4^{3-} , and DSi, respectively), but the Theil-Sen slopes
306 were consistently shallower for PO_4^{3-} (Table S3), suggesting that changes in extreme values
307 account for much of the long-term decreases. The regression slopes of scaled PO_4^{3-} and NO_3^-
308 time series were similar, ranging from $-0.3 \cdot 10^{-4}$ to $-2.4 \cdot 10^{-4}$ (Fig. S4; Table S3), representing
309 mean 1998 to 2016 decreases of 34 % (SD = 8.8) for NO_3^- and 46 % (SD = 21) for PO_4^{3-} (Fig.
310 4). For PO_4^{3-} , the greatest decreases occurred in rivers with highest initial PO_4^{3-} concentration
311 ($r = 0.70$, $p < 0.01$), but changes in NO_3^- and DSi were not correlated with initial
312 concentrations ($p > 0.1$; Fig. 4). For the 7 rivers with discharge data, annual nutrient fluxes
313 followed the same general pattern as concentrations (decreasing for NO_3^- and PO_4^{3-} ; no trend
314 for DSi), but were more variable due to inter-annual differences in river discharge (Fig. 6).

315 Annual minimum concentrations decreased faster than maximum concentrations for
316 77 and 92 % of catchments for NO_3^- and PO_4^{3-} , respectively, and minimum and maximum

317 trends were only correlated with each other for PO_4^{3-} ($r = 0.58$, $p < 0.05$; Fig. 5a). Low-flow
318 concentrations (August) decreased faster than high-flow concentrations (December) for 62
319 and 69 % of catchments for NO_3^- and PO_4^{3-} , respectively, and low-flow and high-flow trends
320 were only correlated with each other for NO_3^- ($r = 0.63$, $p < 0.05$; Fig. 5b). Furthermore,
321 several catchments had extreme differences in long-term low-flow and high-flow trends of
322 DSi and PO_4^{3-} (e.g. in river 5 there was a strongly increasing trend for DSi during low flows,
323 driven by extreme low-flow conditions in 2011, but there was no trend for high flows; Fig.
324 5b).

325 **3.3. Partitioning variance between timescales**

326 Modeled fluctuations in nutrients showed good agreement with measured values (Fig.
327 7), though the proportion of explained variance varied by nutrient and river (Table 3). Final
328 models explained 52 to 85 % of the temporal variation in NO_3^- concentration, 20 to 90 % for
329 PO_4^{3-} , and 57 to 87 % for DSi (Table 3). River 11 was particularly well explained by temporal
330 variables for all nutrients (68, 90, and 75 % for NO_3^- , PO_4^{3-} , and DSi, respectively) while river
331 1 had the poorest fits (54, 28, and 59 % of overall variance explained for NO_3^- , PO_4^{2-} and DSi,
332 respectively; Table 3).

333 Short-term timescales (< 40 weeks) tended to account for the smallest portion of
334 variance across nutrients, explaining less than 30 % of the variation in concentrations
335 excepted for DSi in rivers 7 and 12 (38 %). For NO_3^- , the long-term component (> 64 weeks)
336 explained the largest portion of variance for all rivers except river 5, where 52% of variation
337 was explained by seasonal fluctuations. For PO_4^{3-} , the relative importance of seasonal and
338 long-term fluctuations depended on the river (Table 3). For DSi, which showed little to no
339 long-term trend, seasonal fluctuation (40 to 64 weeks) explained the largest proportion of
340 variation for most rivers.

341 **3.4. Contrasting seasonal cycles**

342 For the rivers where seasonal variation accounted for at least 10 % of overall variance,
343 synchrony between concentration and discharge differed by river and nutrient (Fig. 8). For
344 NO_3^- , 3 rivers showed synchronous fluctuations (positive concentration-discharge
345 relationship) and 4 rivers showed asynchronous fluctuations (Fig. 9a,b). Contrary to our
346 hypothesis (Fig. 1), the synchronous catchments tended to have lower initial and median NO_3^-
347 concentrations compared to asynchronous catchments, and there was no apparent relationship
348 with magnitude of long-term decrease and fluctuation type (Figs. 4 and 9). For PO_4^{3-} and DSi,
349 all the fluctuations were asynchronous except for river 5, which had a hydrologically
350 synchronous cycle for DSi (Fig. 9c-e).

351 The relative amplitude of seasonal fluctuations was generally higher for PO_4^{3-} (180-
352 300 % of the C50) than for NO_3^- (100-170 %) and DSi (ca. 20 %), with the exception of river
353 5, which had higher relative amplitude of seasonal fluctuations for both NO_3^- (380 %) and
354 DSi (180 %) than PO_4^{3-} (70 %; Figs. 8 and 9). For most catchments, DSi maximum
355 concentration occurred later in the season than NO_3^- maximum (Fig. 8).

356 Most catchments showed the same concentration-discharge relationship for each
357 nutrient over the period of record (i.e. each catchment remained either asynchronous or
358 synchronous), but there was an increase through time in variance among asynchronous
359 catchments in the periodicity of seasonal fluctuations for both NO_3^- and PO_4^{3-} , primarily after
360 2008 (Fig. 9a,c). Changes in the periodicity and timing of PO_4^{3-} fluctuations in rivers 7 and 13
361 were particularly marked, with both rivers experiencing a shift in minimum PO_4^{3-}
362 concentration from winter to early spring, and a shift in PO_4^{3-} maximum from summer to fall
363 or winter (Figs. S5 and S6).

364

365 **4. Discussion**

366 **4.1. Using seasonality and interannual trends to infer nutrient legacies**

367 Because river flow integrates water from multiple flowpaths with a distribution of
368 residence times, river chemistry is the product of overlapping historical inputs and reaction
369 rates, which are spatially distributed and temporally weighted within the catchment (Abbott et
370 al., 2016; Gu et al., 2017; Meter and Basu, 2015). We hypothesized that the seasonality of
371 nutrient concentrations could reveal net nutrient balance at the catchment scale and that
372 differences in interannual trajectories of low- and high-water nutrient concentrations could
373 indicate whether changes in point or diffuse nutrient sources accounted for improvements
374 (Fig. 1). All of the catchments in our study showed decreasing trends for anthropogenic
375 nutrients (NO_3^- and PO_4^{3-}) starting from the beginning of the record in 1998. These water
376 quality improvements can be attributed to better land management rather than less intensive
377 agricultural land use, because the number of livestock continued to increase through 2005
378 (Fig. 2; Poisvert et al., 2017). In line with our predictions for net nutrient losing catchments
379 with bottom-loaded nutrients (Fig. 1b), most catchments showed asynchronous nutrient-
380 discharge fluctuations and delayed arrival of DSi peaks compared to NO_3^- , though we
381 recognize that both pre- and post-intervention monitoring is necessary to more definitively
382 test the link between nutrient seasonality and catchment-scale net nutrient balance.

383 Contrary to observational and modeling studies that concluded increasing agricultural
384 pressure results in chemostatic nutrient behavior due to homogenization of nutrient sources

385 and saturation of removal capacity (Dupas et al., 2016; Moatar et al., 2017; Musolff et al.,
386 2016), we found that catchments with lower nutrients tended to show less temporal variability
387 and synchronous fluctuation of NO_3^- (Figs. 8 and 9). The synchronous seasonal cycles
388 observed in rivers 3, 5, and 6 could be explained by 1. top-loaded NO_3^- profiles (Fig. 1a)
389 maintained by autotrophic denitrification deeper in the aquifer or sustained NO_3^- loading
390 (Fovet et al., 2015), or 2. enhanced biological uptake in the catchment or river during summer
391 low flows. Both denitrification and uptake are more likely to affect bulk fluxes when
392 concentrations are low due to mass balance and stoichiometric constraints (Abbott et al.,
393 2017a; Pinay et al., 2015), supporting the hypothesis of biological regulation of NO_3^-
394 concentration during low flows in the less eutrophic catchments (Moatar et al., 2017).

395 In addition to land-use legacy, hydrologic or biogeochemical differences among
396 catchments can influence nutrient-discharge synchrony. In agricultural catchments, both
397 synchronous (Álvarez-Cabria et al., 2016; Aubert et al., 2013b; Bowes et al., 2009; Dupas et
398 al., 2016; Exner-Kittridge et al., 2016; Mellander et al., 2014; Minaudo et al., 2015) and
399 asynchronous (Fovet et al., 2015; Martin et al., 2004; Oulehle et al., 2015) discharge- NO_3^-
400 relationships have been observed. However, it remains unclear how much of these patterns are
401 due to current and past nitrogen loading versus differences in hydrologic characteristics and
402 inherent resilience to nutrient loading. For PO_4^{3-} , asynchronous fluctuations appear to be the
403 rule in disturbed ecosystems, likely associated with dilution of point sources during high
404 flows and enhanced release of reactive phosphorus during warm periods (Aguilera et al.,
405 2015; Bowes et al., 2009; Duan et al., 2012; Minaudo et al., 2015). DSi seasonality also
406 appears to be consistently asynchronous with discharge, due to dilution and seasonal
407 differences in uptake by diatoms (Bowes et al., 2009; House et al., 2001; Moatar et al., 2017;
408 Neal et al., 2000). DSi concentration in the sole synchronous river in our study (river 5) is
409 likely due to its large artificial reservoir, which could increase summer uptake or delay
410 delivery of dilute winter water. Ultimately, the utility of nutrient seasonality as a proxy of net
411 nutrient balance needs to be tested in a broader set of anthropogenic, topographic, and
412 climatic contexts where land use and land management can be better constrained (Dupas et
413 al., 2017; Meter and Basu, 2015; Musolff et al., 2016; Worrall et al., 2015). While such
414 datasets are currently rare, increased efforts to compare catchments and synthesize land use
415 and water chemistry are critical to teasing apart the role of loading legacies, hydrology, and
416 biological dynamics (Abbott et al., 2017b; Dupas et al., 2016; Thomas et al., 2016b).

417 **4.2. Stable seasonality despite deep decreases**

418 Despite large decreases in point and diffuse nutrient inputs and annual river
419 concentrations, seasonality of nutrient fluctuations remained stable across the time series,
420 except for PO_4^{3-} in two catchments. One reason for this stability in seasonality may be that the
421 relatively smaller decreases in diffuse nutrient inputs may not have fully propagated
422 through soils and aquifers to alter concentration-discharge relationships (Dupas et al., 2016;
423 Meter et al., 2016; Musolff et al., 2015). Groundwater residence time in similar catchments in
424 the region varies from 35 to 74 years (Kolbe et al., 2016), meaning that elimination of diffuse
425 nutrient sources could take decades before influencing river chemistry. Conversely, the large
426 decrease of discrete nutrient sources immediately affected nutrient concentrations, resulting in
427 relatively larger low-flow improvements in water quality as predicted. The greater relative
428 decreases in PO_4^{3-} , which has primarily discrete sources, compared to NO_3^- , which is mobile
429 and often diffuse, was also in line with large point-source reductions (Bouza-Deaño et al.,
430 2008; Minaudo et al., 2015; Moatar et al., 2017). In contrast to changes in diffuse sources,
431 which could flip the catchment-scale vertical distribution of nutrients and concentration-
432 discharge relationships (Dupas et al., 2016), point-source reduction is expected to decrease
433 low-flow peak concentrations but not fundamentally change seasonality (Fig. 1), explaining
434 the observed stability in seasonal patterns. While the two catchments that showed evidence of
435 shifting PO_4^{3-} seasonality (rivers 7 and 13) did not have the highest initial PO_4^{3-}
436 concentrations, they did have the highest P surplus and were among those that showed the
437 greatest relative PO_4^{3-} decrease (Fig. 4; Table 1). In these two catchments, decreases in both
438 point and diffuse phosphorus sources could have delayed peak concentrations from summer to
439 fall or winter, when the soils are first hydrologically connected to the stream network after the
440 dry period (Dupas et al., 2015; Gu et al., 2017; Thomas et al., 2016a).

441 Changes in NO_3^- and PO_4^{3-} seasonality have been observed in long time series, due to
442 both anthropogenic and environmental trends (Minaudo et al., 2015; Worrall et al., 2015;
443 Zhang et al., 2015). For example, from 1868-2009, peak concentration of NO_3^- concentration
444 in the Thames River (U.K.) shifted several times from late winter to early or late spring,
445 independent of interannual changes in concentration, while the timing of annual minimum
446 concentration followed timing of minimum stream flow (Worrall et al., 2015). Additionally,
447 the amplitude of PO_4^{3-} and NO_3^- seasonal fluctuations have generally decreased over the last
448 30 years in the Loire River (France) as nutrient concentrations have fallen (Minaudo et al.,
449 2015). Finally, timing of seasonal maximum and minimum nutrient concentrations has
450 remained relatively stable for most tributaries of the Chesapeake Bay (U.S.A.) since 1980,
451 except the Susquehanna River, which has experienced major shifts in the timing and

452 magnitude of nutrient seasonality due to dam removal (Zhang et al., 2015). Together these
453 examples suggest that new metrics of nutrient seasonality should be integrated into analyses
454 of water quality time series.

455 **4.3. Citizen science as a means and an end**

456 The Ecoflux program is an example of how citizen science can sustain long-term,
457 medium-frequency water quality monitoring, allowing the quantification of seasonal nutrient
458 trajectories on decadal timescales. While less obvious than the quantitative data products
459 generated by this program, a secondary benefit is the personal impact on awareness and
460 mentality of the thousands of students and volunteers who have participated over the years.
461 How the general public perceives and values aquatic ecosystems directly influences how they
462 are managed by political and administrative entities (Linton, 2014; Schmidt, 2014). In this
463 sense, participatory water quality monitoring is not only a means of generating understanding
464 of how water and nutrients propagate through catchments; it is a mechanism to improve water
465 quality itself.

466 Because water quality recovery trajectories are typically far slower than ambitious
467 improvement programs (Hering et al., 2010), maintaining interest and morale of stakeholders
468 is central to successful protection and rehabilitation of aquatic ecosystems. Even when water
469 quality does not immediately respond to substantial investment and change in land
470 management, citizen science efforts such as the Ecoflux program are one way to deliver a
471 tangible reward for these efforts by providing quality educational experiences for the children
472 of involved land managers and users (e.g. farmers, politicians, special interest groups etc.).
473 New sensors now allow high-frequency monitoring of water quality, opening up new horizons
474 for detailed, mechanistic study of in-stream and catchment processes (Ruhala and Zarnetske,
475 2017; Tunaley et al., 2016). However, these sensors are expensive and difficult to maintain.
476 Though technological solutions are always in vogue, we believe there are substantial ancillary
477 benefits of low-tech, participatory monitoring approaches. Ultimately, high-frequency and
478 citizen science approaches are extremely complimentary, but when budget constraints put
479 them in competition, the built-in engagement and education associated with citizen science, as
480 well as its low cost, are strong reasons to advocate for wider implementation of this strategy.

481

482 **5. Conclusions**

483 We used 18 years of weekly nutrient data collected by high-school students and
484 community volunteers to assess how improvements in land management affect interannual
485 trends and seasonality of nutrient concentrations. Decreases in nutrient concentrations were

486 apparent from the beginning of the monitoring period, demonstrating that changes in land
487 management can initially improve riverine nutrient concentrations at the catchments scale.
488 There were substantial decreases in annual and seasonal NO_3^- and PO_4^{3-} concentrations, with
489 more pronounced decreases in annual minimum nutrient concentrations and during low flows,
490 in line with historical observations that improvements are primarily due to the elimination of
491 point sources. However, nutrient concentrations in nearly all rivers remained well above
492 regulatory limits (Hering et al., 2010; MEDD & Agences de l'eau, 2003) and thresholds
493 needed to reduce inland and coastal eutrophication (Dodds et al., 1998; Perrot et al., 2014),
494 suggesting that future gains in water quality will depend on addressing diffuse nutrient
495 sources, which remains challenging. Seasonal covariation of discharge and nutrient
496 concentrations was largely asynchronous across the time series, indicating that dilution
497 dynamics are dominant and that biological activity only affects NO_3^- flux in the least polluted
498 catchments. This project demonstrates that when institutional support and funding are
499 available, citizen science initiatives can produce high quality data on decadal timescales and
500 improve public engagement with socioecological issues.

501

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511

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808

Table 1. Catchment characteristics for the 13 studied rivers in western France

River (ID)	General					Hydrologic**			Land cover						Geologic substrate			Nutrient loading	
	Area km ²	Population hab km ²	Altitude (mean) m	Relief m	Rainfall mm	Q specific l s ⁻¹ km ⁻²	Q specific min l s ⁻¹ km ⁻²	W2 %	Pasture %	Crops %	Hedgerow %	Forest %	Wetland %	Urban %	Granite gneiss %	Schist %	Other %	N Surplus (2007) kg N ha ⁻¹	P Surplus (2010) kg P ha ⁻¹
St-Laurent (1)	30	223	90	152	1151	-	-	-	9	28	55	2	3	2	100	0	0	19	19
Ris (2)*	36	92	82	224	1242	-	-	-	3	32	60	1	0	3	90	10	0	-	-
Lapic (3)*	26	64	91	276	1251	-	-	-	5	39	50	0	1	5	18	82	0	46	23
Kerharo (4)*	45	51	85	378	1202	-	-	-	2	32	60	0	0	6	0	84	16	34	24
Aulne (5)	1489	36	164	376	1237	18.2	2.5	10.3	29	28	32	2	0	8	10	81	3	40	21
Douffine (6)	159	27	156	363	1395	23.5	4.1	11.4	18	24	39	7	0	12	0	89	11	51	31
Elorn (7)	279	100	126	380	1277	21.8	7	9.6	10	44	36	1	0	9	35	55	3	60	31
Quillimadec (8)	29	141	70	89	1184	-	-	-	1	33	63	0	0	3	88	0	12	65	21
Fleche (9)	65	64	75	115	1158	-	-	-	0	53	42	0	0	5	88	0	8	75	27
Guillec (10)*	73	77	73	117	1055	16.1	6.2	7.2	0	82	16	0	0	2	15	0	85	65	27
Penze (11)*	142	50	149	373	1167	20.3	4.9	7.7	26	40	29	0	0	5	57	35	0	54	23
Dossen (12)	191	83	153	364	1139	16.7	4.7	7.6	28	31	27	4	0	10	45	49	0	37	29
Dourduff (13)	69	133	94	172	990	12.2	2.8	8.4	6	50	40	0	1	4	0	62	38	39	32

*Monitoring of these rivers stopped at the end of 2015 due to limited budget.

**Interannual mean and interannual monthly minimum of specific discharge were calculated from the nearest hydrologic station (details on hydrologic monitoring in Table S1). Altitudes were derived from a 25 m digital elevation model and lithology was extracted from maps created by the French National Institute for Agricultural Research (INRA).

1

Table 2. Medians, flow-weighted concentrations, and nutrient yields for NO_3^- , PO_4^{3-} and dissolved silica (DSi; 1998-2016)

River (ID)	NO_3^-			PO_4^{3-}			DSi		
	C50 mg L ⁻¹	C* mg L ⁻¹	Load kg N ha ⁻¹ y ⁻¹	C50 mg L ⁻¹	C* mg L ⁻¹	Load kg P ha ⁻¹ y ⁻¹	C50 mg L ⁻¹	C* mg L ⁻¹	Load kg Si ha ⁻¹ y ⁻¹
St-Laurent (1)	41.2			0.033			12.2		
Ris (2)	35.0			0.097			14.9		
Lapic (3)	41.2			0.209			11.3		
Kerharo (4)	35.0			0.086			9.18		
Aulne (5)	22.1	26.6	37 (± 12%)	0.054	0.061	0.12 (± 12%)	7.6	7.8	47 (± 9%)
Douffine (6)	19.0	20.4	36 (± 13%)	0.212	0.139	0.34 (± 3%)	5.7	5.4	42 (± 10%)
Elorn (7)	34.1	32.3	48 (± 5%)	0.212	0.139	0.28 (± 7%)	9.2	8.5	57 (± 5%)
Quillimadec (8)	50.9			0.418			16.1		
Fleche (9)	61.1			0.272			14.4		
Guillec (10)	77.5	69.5	81 (± 3%)	0.394	0.318	0.54 (± 5%)	14.0	13.2	68 (± 4%)
Penze (11)	45.2	45.2	68 (± 10%)	0.397	0.230	0.50 (± 4%)	11.8	11.1	73 (± 8%)
Dossen (12)	27.0	26.1	30.4 (± 7%)	0.285	0.239	0.39 (± 2%)	12.4	11.6	59 (± 5%)
Dourduff (13)	35.9	33.6	30 (± 7%)	0.224	0.154	0.20 (± 12%)	13.0	12.5	47 (± 5%)

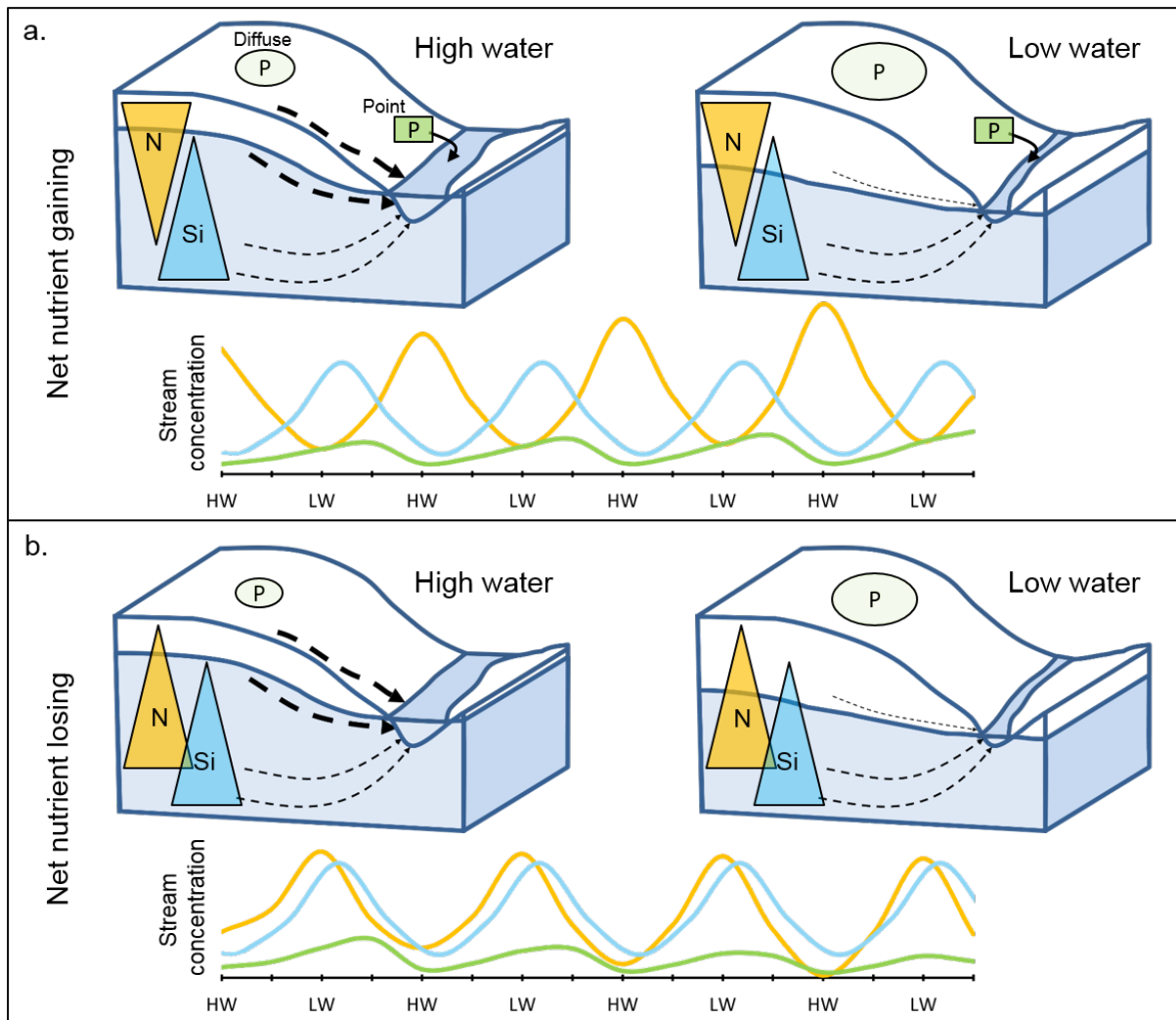
2 C* and load were computed for rivers where flow data were available.

3

Table 3. Variance explained by the long-term, seasonal, and short-term components of the nutrient fluctuation models

River (ID)	NO_3^-				PO_4^{3-}				DSi			
	Long-term	Seasonal	Short-term	Total	Long-term	Seasonal	Short-term	Total	Long-term	Seasonal	Short-term	Total
St-Laurent (1)	0.17	0.10	0.24	0.54	0.02	0.03	0.22	0.28	0.22	0.19	0.15	0.59
Ris (2)	0.21	0.03	0.24	0.52	0.07	0.07	0.06	0.20	0.31	0.33	0.16	0.83
Lapic (3)	0.29	0.31	0.11	0.78	0.13	<u>0.41</u>	0.24	0.78	0.22	0.10	0.21	0.61
Aulne (5)	0.12	<u>0.52</u>	0.12	0.85	0.10	0.09	0.29	0.50	0.13	0.38	0.22	0.87
Douffine (6)	0.19	0.18	0.18	0.62	0.21	<u>0.42</u>	0.17	0.82	0.13	0.22	0.27	0.63
Elorn (7)	0.17	0.15	0.22	0.58	0.16	0.27	0.18	0.60	0.09	0.18	0.35	0.69
Quillimadec (8)	0.18	0.15	0.19	0.57	0.14	0.14	0.21	0.52	0.06	0.32	0.24	0.60
Fleche (9)	0.19	0.20	0.16	0.57	0.16	0.14	0.27	0.64	0.11	0.25	0.20	0.61
Guillec (10)	0.32	0.14	0.11	0.63	0.28	0.25	0.18	0.73	0.12	0.21	0.26	0.65
Penze (11)	<u>0.46</u>	0.04	0.13	0.68	0.34	<u>0.43</u>	0.07	0.90	0.21	0.24	0.24	0.75
Dossen (12)	0.29	0.07	0.21	0.61	0.20	0.32	0.13	0.71	0.15	0.17	0.38	0.71
Dourduff (13)	0.30	0.10	0.13	0.55	0.38	0.33	0.08	0.81	0.07	0.32	0.15	0.57

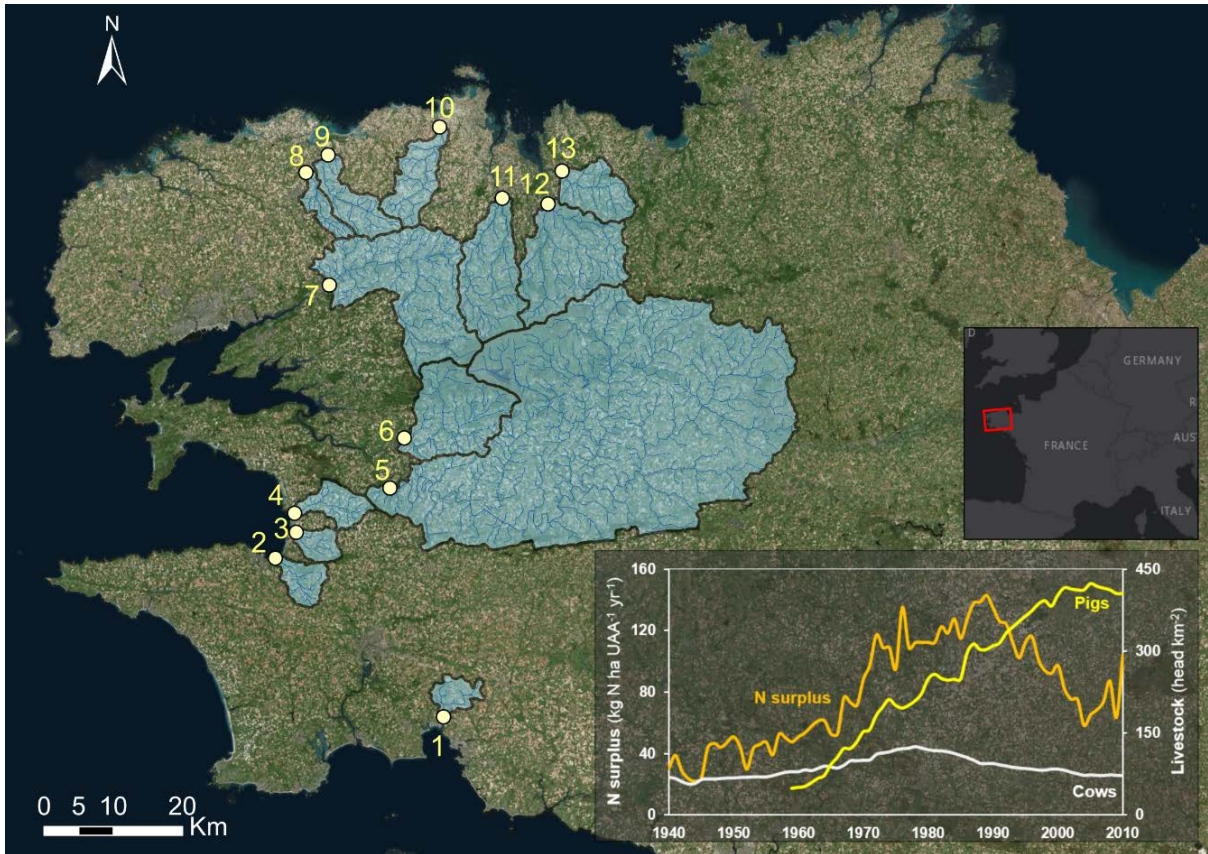
5 Reported values are adjusted- R^2 between observed nutrient concentrations and predicted values from one or more sets of
6 explanatory variables in the dbMEM (see Section 2.3.2). All values are significant at $\alpha = 0.05$. To facilitate interpretation,
7 we bolded values with $R^2 > 0.2$ and underlined values with $R^2 > 0.4$.



8

9 **Figure 1.** Hypothesized seasonal and interannual changes stream concentrations of nitrate
 10 (NO_3^-), dissolved silica (DSi), and phosphate (PO_4^{3-}) in (a) a catchment experiencing net
 11 nutrient gain of N and P, and (b) a catchment experiencing net nutrient loss of N and P.
 12 Concentrations were simulated with a simple mixing model based on water flow and nutrient
 13 availability, assuming conservative transport. Key predictions include: 1. opposite seasonal
 14 signals for top-loaded and bottom-loaded nutrients with diffuse sources (e.g. NO_3^- in a
 15 gaining and losing catchment, respectively), 2. greater interannual change for high-water
 16 (HW) relative to low-water (LW) concentrations for nutrients with diffuse sources, 3. greater
 17 interannual change for LW concentrations for nutrients with seasonally constant point
 18 sources (e.g. PO_4^{3-}), 4. no interannual change in DSi but later arrival of the DSi peak relative
 19 to NO_3^- , due to deeper DSi sources that are not affected by human activity. In a real
 20 catchment, the outflow concentration would be further modified by biogeochemical activity,
 21 which varies seasonally. However, these predictions are not unrealistic since nutrients are
 22 often transported relatively conservatively in highly saturated systems.

23

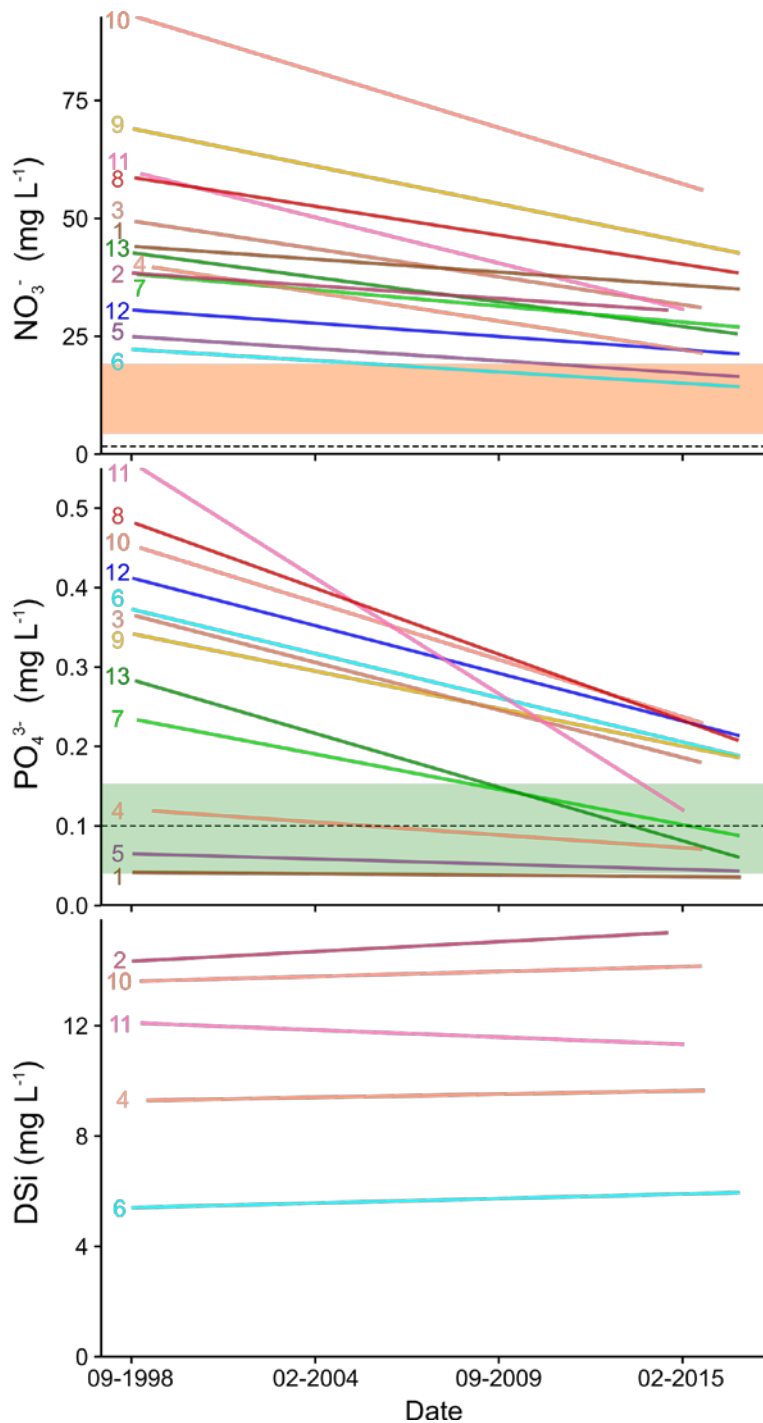


24

25 **Figure 2.** Location of 13 agricultural catchments that were sampled weekly from 1998 to
 26 2016 as a part of a citizen science initiative in Brittany, France. Inset figure shows historical
 27 agricultural activity for the Department of Finistère where the catchments are located,
 28 including nitrogen surplus, determined by soil surface balance, and density of pigs and cows
 29 (Poisvert et al., 2017). Catchment names are listed in Table 1.

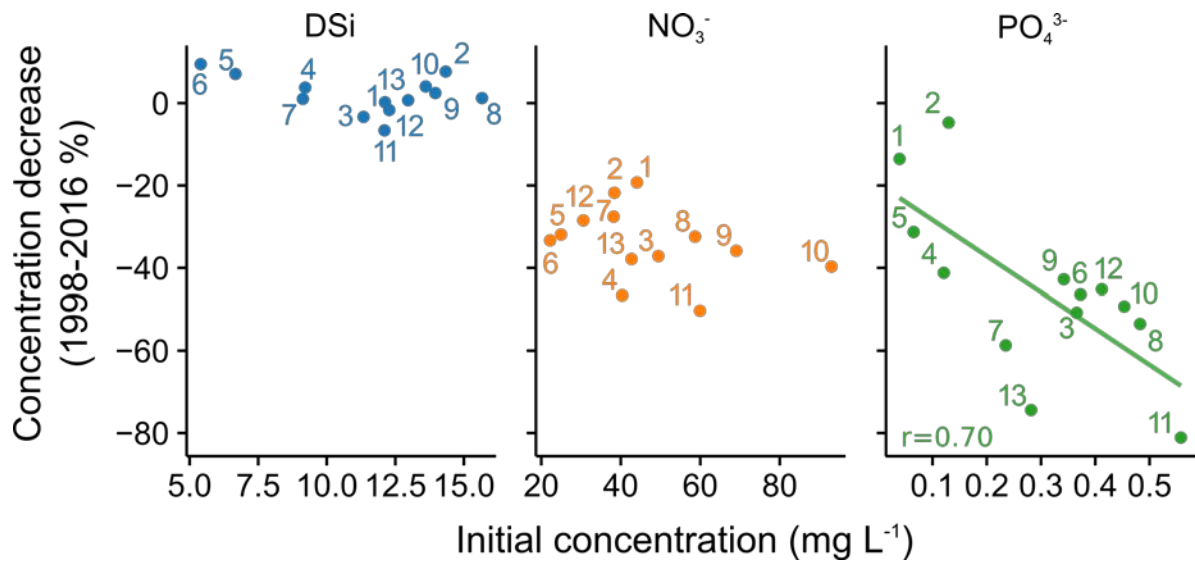
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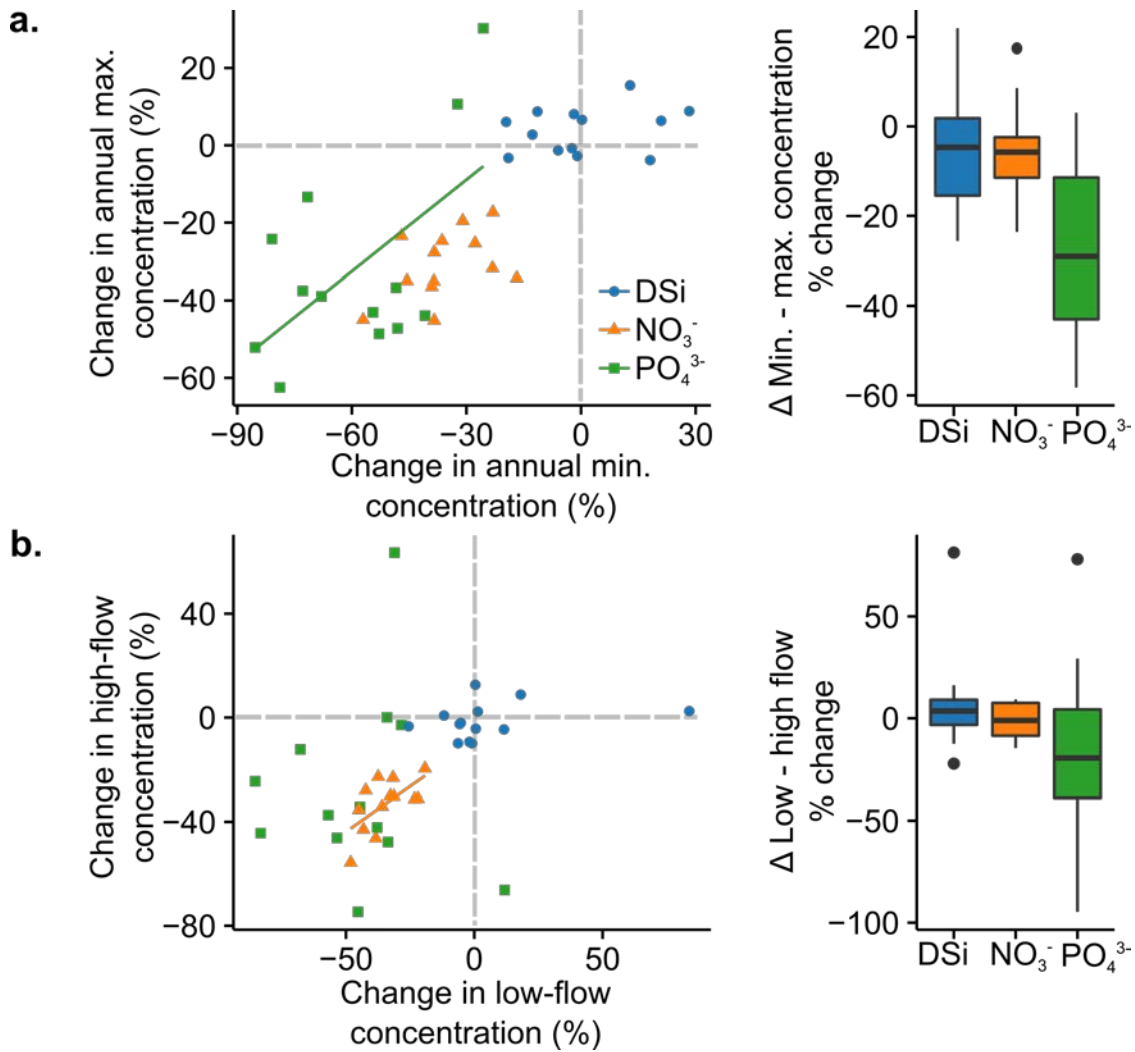
33 **Figure 3.** Statistically significant long-term trends in nutrient concentrations (Mann-Kendall
 34 test $\alpha = 0.05$). The shaded rectangles for the NO_3^- and PO_4^{3-} plots represent the estimated
 35 concentrations necessary to substantially reduce inland and coastal eutrophication (Dodds et
 36 al., 1998; Perrot et al., 2014) and the dotted lines represent the nationally standardized "Blue-
 37 Green" targets used by all water agencies in France (MEDD & Agences de l'eau, 2003).
 38 Trends explained 5 to 37 % (median = 17 %) of total variance of NO_3^- concentration, 1 to 23
 39 % (median = 10 %) for PO_4^{3-} , and 1 to 3 % (median = 2 %) for DSi. Detailed summary of
 40 linear models is provided in Table S3.



41

42 **Figure 4.** Percent change in nutrient concentrations from 1998 to 2016 plotted against initial
 43 concentration based on the slope and intercept of the linear models (Fig. 3).

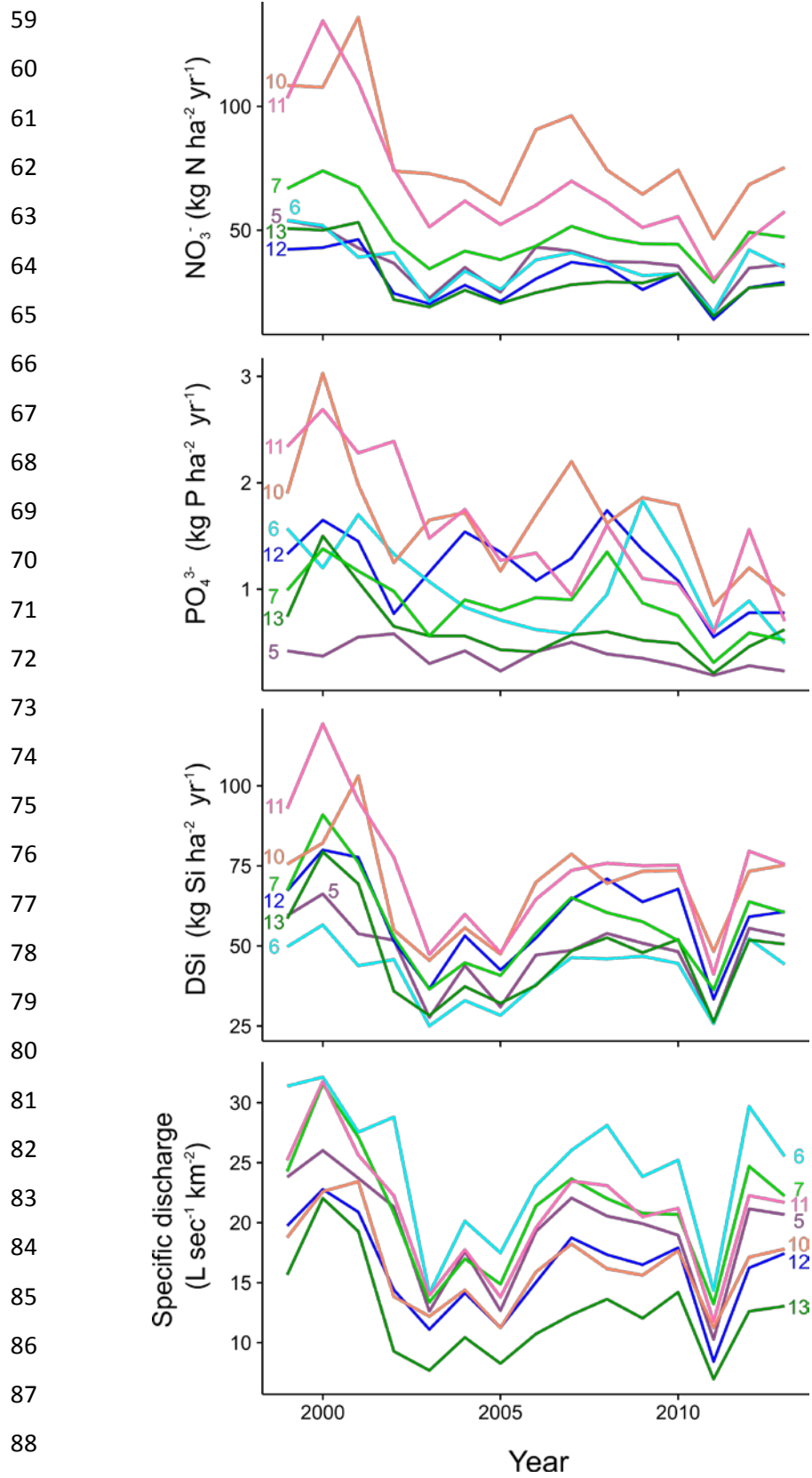
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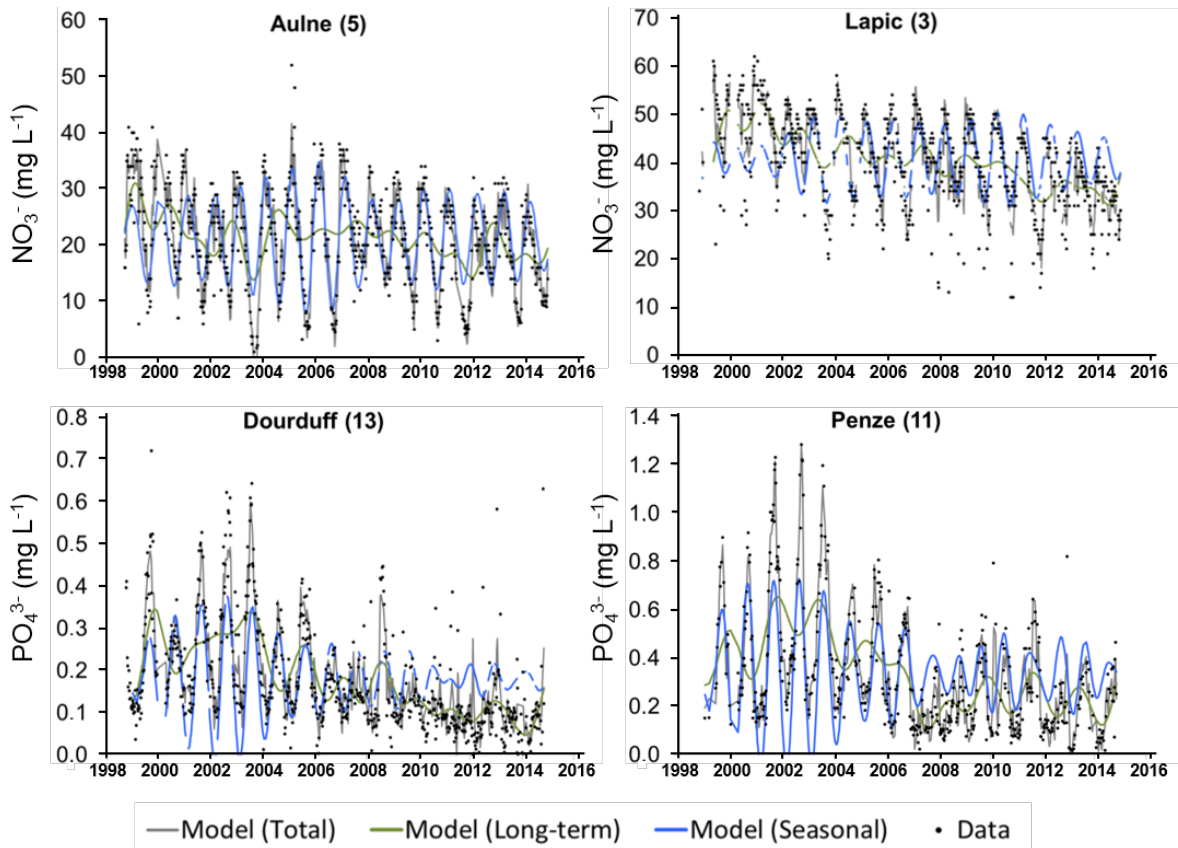
47 **Figure 5.** Comparison between trends in (a) annual maximum and minimum concentrations,
 48 and (b) annual low-flow and high-flow concentrations. Trends are presented in % change for
 49 each solute from 1998 to 2016. Mean values of the five highest and lowest concentrations
 50 annually were used to calculate trends in (a), and mean August concentrations (low-flow
 51 period) and mean December concentrations (high-flow) were used to calculate trends in (b).
 52 Boxplots represent the difference between trends in min. and max. concentrations and low-
 53 flow and high-flow concentrations, with the median, quartiles, minimum and maximum
 54 values within the interquartile range, and points beyond 1.5 times the interquartile
 55 range. Values above 0 indicate greater change (usually decrease) in max. concentration (a) or high-
 56 flow concentration (b), while those below the 0 line experienced larger relative change of
 57 min. concentrations (a) or during low flows.

58



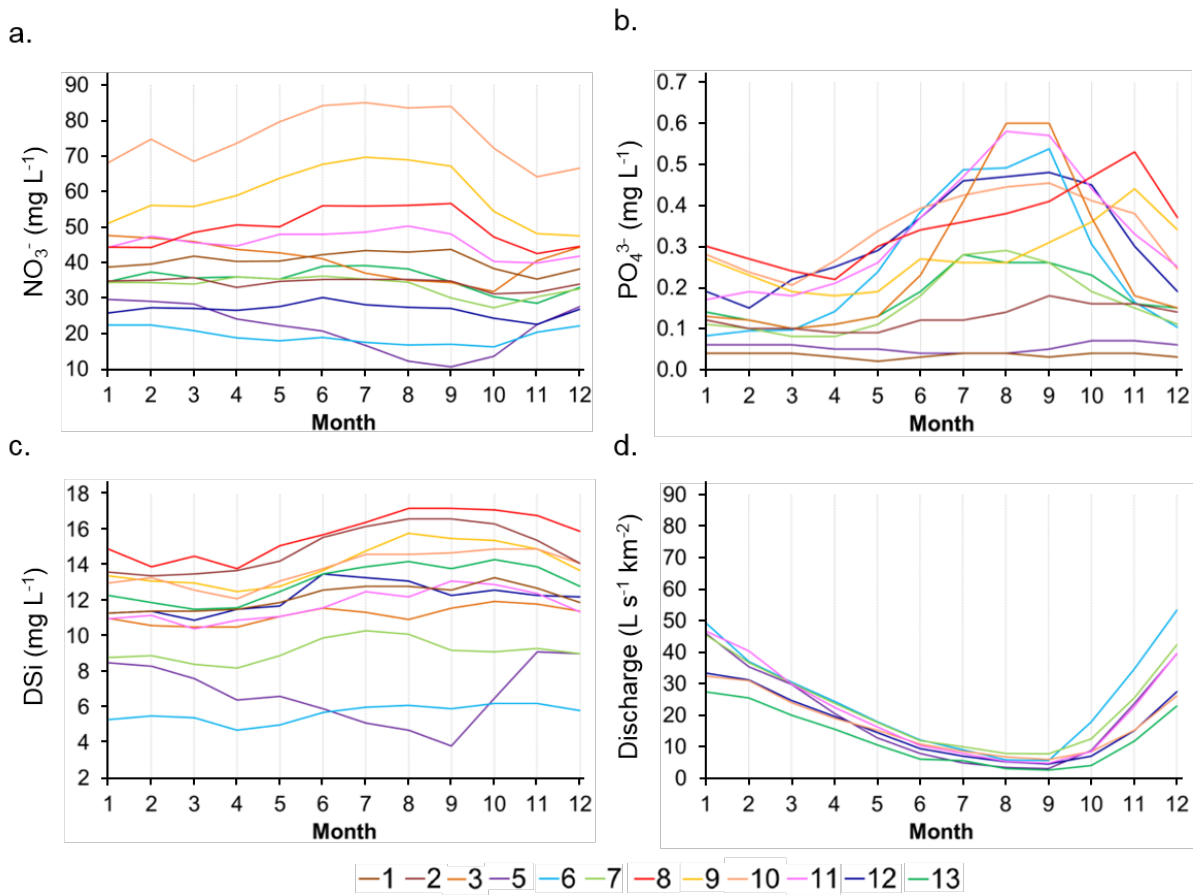
89 **Figure 6.** Trends in nutrient and water fluxes for the 7 rivers where long-term discharge data
 90 were available. We calculated fluxes with the discharge-weighted concentration method,
 91 which was the most robust for these catchments and nutrients (see methods).

92



93

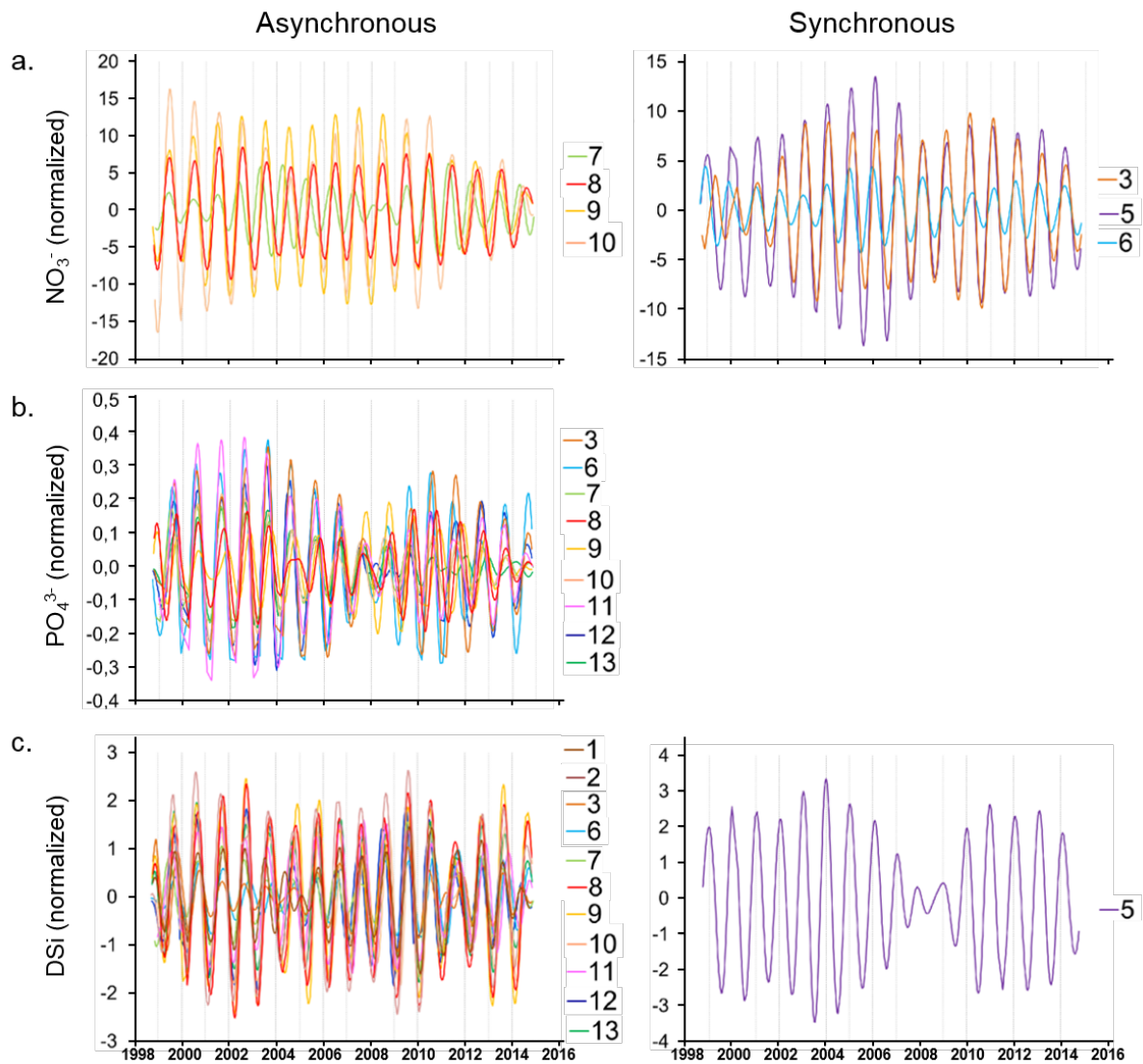
94 **Figure 7.** Example modeled and observed time series, and modeled long-term and seasonal
 95 subcomponents from four catchments. See Table 3 for overall model performance and
 96 breakdown of timescales.



98

99 **Figure 8:** Monthly mean observed concentrations of (a) NO_3^- , (b) PO_4^{3-} , (c) DSi, and (d)
 100 monthly specific discharge. We observed two types of seasonal fluctuations: synchronous,
 101 where hydrology and nutrient concentration were in phase (annual peak concentration during
 102 high flow), and asynchronous, where hydrology and concentration are out of sync (annual
 103 minimum concentration during high flow).

104



106

107 **Figure 9.** Long-term changes in seasonal nutrient fluctuations. Curves are the seasonal
 108 component of the variance partitioning models for NO_3^- (**a**), PO_4^{3-} (**b**), and DSi (**c**). Time
 109 series were detrended and centered to facilitate comparison of changes in periodicity through
 110 time. Only rivers where at least 10 % of the total variance was explained by the seasonal
 111 component are shown (Table 3).

112