



**HAL**  
open science

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

Benjamin W. Abbott, Florentina Moatar, Olivier Gauthier, Ophélie Fovet,  
Virginie Antoine, Olivier Ragueneau

### ► To cite this version:

Benjamin W. Abbott, Florentina Moatar, Olivier Gauthier, Ophélie Fovet, Virginie Antoine, et al.. Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France. *Science of the Total Environment*, 2018, 624, pp.845-858. 10.1016/j.scitotenv.2017.12.176 . hal-01686773

**HAL Id: hal-01686773**

**<https://univ-rennes.hal.science/hal-01686773>**

Submitted on 13 Jul 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

3 Benjamin W. Abbott<sup>1,2\*</sup>, Florentina Moatar<sup>3</sup>, Olivier Gauthier<sup>4,5</sup>, Ophélie Fovet<sup>6</sup>, Virginie  
4 Antoine<sup>4</sup>, Olivier Ragueneau<sup>4</sup>

5 <sup>1</sup>Brigham Young University, Department of Plant and Wildlife Sciences, Provo, USA

6 <sup>2</sup>ECOBIO, OSUR, CNRS, Université de Rennes 1, 35045 Rennes, France

7 <sup>3</sup>University François-Rabelais Tours, EA 6293 Géo-Hydrosystèmes Continentaux, Parc de Grandmont, 37 200 Tours, France

8 <sup>4</sup>Laboratoire des Sciences de l'Environnement Marin (LEMAR UMR 6539 CNRS UBO IRD IFREMER), Institut  
9 Universitaire Européen de la Mer, Université de Bretagne Occidentale, 29280 Plouzané, France

10 <sup>5</sup>Observatoire Marin (UMS 3113 CNRS), Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale,  
11 29280 Plouzané, France

12 <sup>6</sup>UMR SAS, AGROCAMPUS OUEST, INRA, 35000 Rennes, France

13 \*Corresponding author: benabbott@byu.edu

14 **Highlights:**

- 15 • High schools measured  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and silica weekly in 13 rivers for 18 years  
16 • Large decreases of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  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 ( $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ) 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  $\text{km}^2$ . Nutrient concentrations decreased substantially over the period of  
32 record (19 to 50% for  $\text{NO}_3^-$  and 14 to 80% for  $\text{PO}_4^{3-}$ ), 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 ( $\text{NO}_3^-$ )  
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  $\text{NO}_3^-$ , 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  $\text{NO}_3^-$ , phosphate ( $\text{PO}_4^{3-}$ ), 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  $\text{NO}_3^-$  in catchments with a legacy of groundwater pollution) and  
107 synchronously for those that decrease with depth (e.g.  $\text{NO}_3^-$  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  $\text{NO}_3^-$  fluxes vary from 9 to 89 kg N ha<sup>-1</sup> y<sup>-1</sup> among catchments (Gascuel-Oudoux et al.,  
127 2010), and phosphorus fluxes vary from 0.1 to 1.4 kg P ha<sup>-1</sup> yr<sup>-1</sup> (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<sup>-2</sup>, and pig density rapidly increased from 1960 to  
135 2005 when it reached 424 head km<sup>-2</sup> (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](http://www-iuem.univ-brest.fr/ecoflux)), which includes 12 small catchments of 26 to  
156 280 km<sup>2</sup>, and 1 medium catchment of 1490 km<sup>2</sup> (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/](http://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 NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>, 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, NO<sub>3</sub><sup>-</sup>  
172 and PO<sub>4</sub><sup>3-</sup> 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 PO<sub>4</sub><sup>3-</sup> and DSi samples, and LABOCEA-Idhesa, a certified,  
178 public laboratory, analyzed all NO<sub>3</sub><sup>-</sup> samples following international norms (ISO 15923-1).  
179 PO<sub>4</sub><sup>3-</sup> was quantified with a Shimadzu UV1700 spectrophotometer (SHIMADZU, Kyoto,  
180 Japan), and NO<sub>3</sub><sup>-</sup> and DSi with a Technicon Auto Analyser II (SEAL Analytical,  
181 Southampton, UK). Analytical precision was ± 5% for NO<sub>3</sub><sup>-</sup> and DSi (inline and automatic  
182 addition of reagents) and ± 6 to 10% for PO<sub>4</sub><sup>3-</sup> (manual addition of reagents). Though few

183 nutrient time series exist for comparison, Ecoflux NO<sub>3</sub><sup>-</sup> 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<sup>-1</sup> km<sup>-2</sup>), 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<sup>-1</sup>),  $Q_i$  is the corresponding  
204 instantaneous discharge value (m<sup>3</sup> s<sup>-1</sup>),  $\bar{Q}$  is the mean annual discharge computed from  
205 continuous flow records (m<sup>3</sup> s<sup>-1</sup>),  $A$  is the catchment area (m<sup>2</sup>), 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 ( $\text{adj-R}^2$ ) 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<sup>-1</sup> km<sup>-2</sup>; Table 1). Minimum  
272 monthly specific discharge was more variable (2.5 to 7.0 L s<sup>-1</sup> km<sup>-2</sup>), 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<sup>-1</sup> year<sup>-1</sup>, and 3 catchments exceeded 60 kg  
278 N ha<sup>-1</sup> year<sup>-1</sup> (rivers 8-10). P surplus was moderate to high, ranging from 19 to 32 kg P ha<sup>-1</sup>  
279 year<sup>-1</sup>. N surplus was not correlated with median NO<sub>3</sub><sup>-</sup> concentration (p > 0.05), but was  
280 correlated with median PO<sub>4</sub><sup>3-</sup> 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 ( $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$ ) and naturally-occurring (DSi) nutrients, with the median  
285 concentration over the period of record varying approximately 4-fold among rivers for  $\text{NO}_3^-$ ,  
286 3-fold for DSi, and 12-fold for  $\text{PO}_4^{3-}$  (Table 2). Median DSi and  $\text{NO}_3^-$  concentrations among  
287 rivers were positively correlated ( $r = 0.67$ ,  $p < 0.001$ ) as were median  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  ( $r =$   
288  $0.57$ ,  $p < 0.05$ ), but DSi and  $\text{PO}_4^{3-}$  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  $\text{NO}_3^-$  (0.92 and 0.82, respectively) but less than 1 for  $\text{PO}_4^{3-}$  (0.66), indicating that  
293 median concentration overestimated flow-weighted mean for  $\text{PO}_4^{3-}$ , due to systematic dilution  
294 during high flow events.  $C_{50}$  and  $C^*$  were good predictors of annual loads for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$   
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,  $\text{NO}_3^-$   
302 concentration decreased significantly ( $p < 0.05$ ) for all catchments,  $\text{PO}_4^{3-}$  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  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and DSi, respectively), but the Theil-Sen slopes  
306 were consistently shallower for  $\text{PO}_4^{3-}$  (Table S3), suggesting that changes in extreme values  
307 account for much of the long-term decreases. The regression slopes of scaled  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$   
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  $\text{NO}_3^-$  and 46 % (SD = 21) for  $\text{PO}_4^{3-}$  (Fig.  
310 4). For  $\text{PO}_4^{3-}$ , the greatest decreases occurred in rivers with highest initial  $\text{PO}_4^{3-}$  concentration  
311 ( $r = 0.70$ ,  $p < 0.01$ ), but changes in  $\text{NO}_3^-$  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  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ; 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  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , respectively, and minimum and maximum

317 trends were only correlated with each other for  $\text{PO}_4^{3-}$  ( $r = 0.58$ ,  $p < 0.05$ ; Fig. 5a). Low-flow  
318 concentrations (August) decreased faster than high-flow concentrations (December) for 62  
319 and 69 % of catchments for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , respectively, and low-flow and high-flow trends  
320 were only correlated with each other for  $\text{NO}_3^-$  ( $r = 0.63$ ,  $p < 0.05$ ; Fig. 5b). Furthermore,  
321 several catchments had extreme differences in long-term low-flow and high-flow trends of  
322 DSi and  $\text{PO}_4^{3-}$  (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  $\text{NO}_3^-$  concentration, 20 to 90 % for  
329  $\text{PO}_4^{3-}$ , 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  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and DSi, respectively) while river  
331 1 had the poorest fits (54, 28, and 59 % of overall variance explained for  $\text{NO}_3^-$ ,  $\text{PO}_4^{2-}$  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  $\text{NO}_3^-$ , 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  $\text{PO}_4^{3-}$ , 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  $\text{NO}_3^-$ , 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  $\text{NO}_3^-$   
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  $\text{PO}_4^{3-}$  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  $\text{PO}_4^{3-}$  (180-  
352 300 % of the C50) than for  $\text{NO}_3^-$  (100-170 %) and DSi (ca. 20 %), with the exception of river  
353 5, which had higher relative amplitude of seasonal fluctuations for both  $\text{NO}_3^-$  (380 %) and  
354 DSi (180 %) than  $\text{PO}_4^{3-}$  (70 %; Figs. 8 and 9). For most catchments, DSi maximum  
355 concentration occurred later in the season than  $\text{NO}_3^-$  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  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , primarily after  
360 2008 (Fig. 9a,c). Changes in the periodicity and timing of  $\text{PO}_4^{3-}$  fluctuations in rivers 7 and 13  
361 were particularly marked, with both rivers experiencing a shift in minimum  $\text{PO}_4^{3-}$   
362 concentration from winter to early spring, and a shift in  $\text{PO}_4^{3-}$  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 ( $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ) 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  $\text{NO}_3^-$ , 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  $\text{NO}_3^-$  (Figs. 8 and 9). The synchronous seasonal cycles  
388 observed in rivers 3, 5, and 6 could be explained by 1. top-loaded  $\text{NO}_3^-$  profiles (Fig. 1a)  
389 maintained by autotrophic denitrification deeper in the aquifer or sustained  $\text{NO}_3^-$  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  $\text{NO}_3^-$   
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- $\text{NO}_3^-$   
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  $\text{PO}_4^{3-}$ , 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  $\text{PO}_4^{3-}$  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  $\text{PO}_4^{3-}$ , which has primarily discrete sources, compared to  $\text{NO}_3^-$ , 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  $\text{PO}_4^{3-}$  seasonality (rivers 7 and 13) did not have the highest initial  $\text{PO}_4^{3-}$   
436 concentrations, they did have the highest P surplus and were among those that showed the  
437 greatest relative  $\text{PO}_4^{3-}$  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  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  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  $\text{NO}_3^-$  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  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  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  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  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  $\text{NO}_3^-$  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

## 502 **6. Acknowledgements**

503 We thank the regional government (Conseil Général du Finistère) and the European Institute  
504 for Marine Studies (IUEM) for supporting the Ecoflux program. We are grateful to the two  
505 anonymous reviewers, whose constructive critiques improved the manuscript. Abbott was  
506 supported by the European Union's Seventh Framework Program for research, technological  
507 development and demonstration under grant agreement no. 607150 (FP7-PEOPLE-2013-  
508 ITN-INTERFACES - Ecohydrologic interfaces as critical hotspots for transformations of  
509 ecosystem exchange fluxes and biogeochemical cycling). All nutrient data are freely available  
510 at <https://www-iuem.univ-brest.fr/ecoflux/observation/acces-aux-donnees>.

511

## 512 7. References

- 513 Abbott, B.W., Baranov, V., Mendoza-Lera, C., Nikolakopoulou, M., Harjung, A., Kolbe, T.,  
514 Balasubramanian, M.N., Vaessen, T.N., Ciocca, F., Campeau, A., Wallin, M.B., Romeijn, P.,  
515 Antonelli, M., Gonçalves, J., Datry, T., Laverman, A.M., de Dreuzy, J.-R., Hannah, D.M.,  
516 Krause, S., Oldham, C., Pinay, G., 2016. Using multi-tracer inference to move beyond single-  
517 catchment ecohydrology. *Earth-Sci. Rev.* 160, 19–42.  
518 <https://doi.org/10.1016/j.earscirev.2016.06.014>
- 519 Abbott, B.W., Gruau, G., Zarnetske, J.P., Moatar, F., Barbe, L., Thomas, Z., Fovet, O., Kolbe, T., Gu, S.,  
520 Pierson-Wickmann, A.-C., Davy, P., Pinay, G., 2017a. Unexpected stability and synchrony of  
521 water quality in stream networks. *Ecol. Lett.* Accepted. <https://doi.org/10.1111/ele.12897>
- 522 Abbott, B.W., Pinay, G., Burt, T.P., 2017b. Protecting Water Resources Through a Focus on  
523 Headwater Streams. *Eos Trans. Am. Geophys. Union* EO076897.  
524 <https://doi.org/10.1029/2017EO076897>
- 525 Aguilera, R., Marcé, R., Sabater, S., 2015. Detection and attribution of global change effects on river  
526 nutrient dynamics in a large Mediterranean basin. *Biogeosciences* 12, 4085–4098.  
527 <https://doi.org/10.5194/bg-12-4085-2015>
- 528 Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., Moore, R.B., 2007. The Role of Headwater  
529 Streams in Downstream Water Quality. *J. Am. Water Resour. Assoc.* 43, 41–59.  
530 <https://doi.org/10.1111/j.1752-1688.2007.00005.x>
- 531 Álvarez-Cabria, M., Barquín, J., Peñas, F.J., 2016. Modelling the spatial and seasonal variability of  
532 water quality for entire river networks: Relationships with natural and anthropogenic factors.  
533 *Sci. Total Environ.* 545–546, 152–162. <https://doi.org/10.1016/j.scitotenv.2015.12.109>
- 534 Andreen, W.L., 2004. Water Quality Today - Has the Clean Water Act Been a Success? (SSRN Scholarly  
535 Paper No. ID 554803). Social Science Research Network, Rochester, NY.
- 536 Aquilina, L., Vergnaud-Ayraud, V., Labasque, T., Bour, O., Molénat, J., Ruiz, L., de Montety, V., De  
537 Ridder, J., Roques, C., Longuevergne, L., 2012. Nitrate dynamics in agricultural catchments  
538 deduced from groundwater dating and long-term nitrate monitoring in surface- and  
539 groundwaters. *Sci. Total Environ.* 435–436, 167–178.  
540 <https://doi.org/10.1016/j.scitotenv.2012.06.028>
- 541 Aubert, A.H., Gascuel, C., Merot, P., 2013a. Annual hysteresis of water quality: A method to analyse  
542 the effect of intra- and inter-annual climatic conditions. *J. Hydrol.* 478, 29–39.  
543 <https://doi.org/10.1016/j.jhydrol.2012.11.027>
- 544 Aubert, A.H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., Grimaldi, C., Hamon,  
545 Y., Jaffrézic, A., Lecoz-Boutnik, M., Molénat, J., Petitjean, P., Ruiz, L., Merot, P., 2013b. Solute  
546 transport dynamics in small, shallow groundwater-dominated agricultural catchments:  
547 insights from a high-frequency, multisolute 10 yr-long monitoring study. *Hydrol. Earth Syst.*  
548 *Sci.* 17, 1379–1391. <https://doi.org/10.5194/hess-17-1379-2013>
- 549 Ben Maamar, S., Aquilina, L., Quaiser, A., Pauwels, H., Michon-Coudouel, S., Vergnaud-Ayraud, V.,  
550 Labasque, T., Roques, C., Abbott, B.W., Dufresne, A., 2015. Groundwater Isolation Governs  
551 Chemistry and Microbial Community Structure along Hydrologic Flowpaths. *Front. Microbiol.,*  
552 *Microbiological Chemistry and Geomicrobiology* 6, 1457.  
553 <https://doi.org/10.3389/fmicb.2015.01457>
- 554 Bodirsky, B.L., Popp, A., Lotze-Campen, H., Dietrich, J.P., Rolinski, S., Weindl, I., Schmitz, C., Müller, C.,  
555 Bonsch, M., Humpenöder, F., Biewald, A., Stevanovic, M., 2014. Reactive nitrogen  
556 requirements to feed the world in 2050 and potential to mitigate nitrogen pollution. *Nat.*  
557 *Commun.* 5. <https://doi.org/10.1038/ncomms4858>
- 558 Bonney, R., Shirk, J.L., Phillips, T.B., Wiggins, A., Ballard, H.L., Miller-Rushing, A.J., Parrish, J.K., 2014.  
559 Next Steps for Citizen Science. *Science* 343, 1436–1437.  
560 <https://doi.org/10.1126/science.1251554>
- 561 Borcard, D., Legendre, P., Drapeau, P., 1992. Partialling out the Spatial Component of Ecological  
562 Variation. *Ecology* 73, 1045–1055. <https://doi.org/10.2307/1940179>

563 Bouza-Deaño, R., Ternero-Rodríguez, M., Fernández-Espinosa, A.J., 2008. Trend study and  
564 assessment of surface water quality in the Ebro River (Spain). *J. Hydrol.* 361, 227–239.  
565 <https://doi.org/10.1016/j.jhydrol.2008.07.048>

566 Bowes, M.J., Smith, J.T., Neal, C., 2009. The value of high-resolution nutrient monitoring: A case  
567 study of the River Frome, Dorset, UK. *J. Hydrol.* 378, 82–96.  
568 <https://doi.org/10.1016/j.jhydrol.2009.09.015>

569 Breuer, L., Hiery, N., Kraft, P., Bach, M., Aubert, A.H., Frede, H.-G., 2015. HydroCrowd: a citizen  
570 science snapshot to assess the spatial control of nitrogen solutes in surface waters. *Sci. Rep.*  
571 5, 16503. <https://doi.org/10.1038/srep16503>

572 Burt, T.P., Howden, N.J.K., Worrall, F., McDonnell, J.J., 2011. On the value of long-term, low-  
573 frequency water quality sampling: avoiding throwing the baby out with the bathwater.  
574 *Hydrol. Process.* 25, 828–830. <https://doi.org/10.1002/hyp.7961>

575 Burt, T.P., Pinay, G., 2005. Linking hydrology and biogeochemistry in complex landscapes. *Prog. Phys.*  
576 *Geogr.* 29, 297–316. <https://doi.org/10.1191/0309133305pp450ra>

577 Canfield, D.E., Glazer, A.N., Falkowski, P.G., 2010. The Evolution and Future of Earth's Nitrogen Cycle.  
578 *Science* 330, 192–196. <https://doi.org/10.1126/science.1186120>

579 Cohn, J.P., 2008. Citizen Science: Can Volunteers Do Real Research? *BioScience* 58, 192–197.  
580 <https://doi.org/10.1641/B580303>

581 Conrad, C.C., Hilchey, K.G., 2011. A review of citizen science and community-based environmental  
582 monitoring: issues and opportunities. *Environ. Monit. Assess.* 176, 273–291.  
583 <https://doi.org/10.1007/s10661-010-1582-5>

584 Delmas, M., Saby, N., Arrouays, D., Dupas, R., Lemerrier, B., Pellerin, S., Gascuel-Oudou, C., 2015.  
585 Explaining and mapping total phosphorus content in French topsoils. *Soil Use Manag.* 31,  
586 259–269. <https://doi.org/10.1111/sum.12192>

587 Diaz, R.J., Rosenberg, R., 2008. Spreading Dead Zones and Consequences for Marine Ecosystems.  
588 *Science* 321, 926–929. <https://doi.org/10.1126/science.1156401>

589 Dodds, W.K., Jones, J.R., Welch, E.B., 1998. Suggested classification of stream trophic state:  
590 distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus.  
591 *Water Res.* 32, 1455–1462.

592 Dray, S., Blanchet, G., Borcard, D., Guenard, G., Jombart, T., Larocque, G., Legendre, P., Madi, N.,  
593 Wagner, H., 2017. Multivariate Multiscale Spatial Analysis. R package version 0.0-8.

594 Dray, S., Legendre, P., Peres-Neto, P.R., 2006. Spatial modelling: a comprehensive framework for  
595 principal coordinate analysis of neighbour matrices (PCNM). *Ecol. Model.* 196, 483–493.  
596 <https://doi.org/10.1016/j.ecolmodel.2006.02.015>

597 Duan, S., Kaushal, S.S., Groffman, P.M., Band, L.E., Belt, K.T., 2012. Phosphorus export across an  
598 urban to rural gradient in the Chesapeake Bay watershed. *J. Geophys. Res. Biogeosciences*  
599 117, G01025. <https://doi.org/10.1029/2011JG001782>

600 Dupas, R., Curie, F., Gascuel-Oudou, C., Moatar, F., Delmas, M., Parnaudeau, V., Durand, P., 2013.  
601 Assessing N emissions in surface water at the national level: Comparison of country-wide vs.  
602 regionalized models. *Sci. Total Environ.* 443, 152–162.  
603 <https://doi.org/10.1016/j.scitotenv.2012.10.011>

604 Dupas, R., Delmas, M., Dorioz, J.-M., Garnier, J., Moatar, F., Gascuel-Oudou, C., 2015. Assessing the  
605 impact of agricultural pressures on N and P loads and eutrophication risk. *Ecol. Indic.* 48,  
606 396–407. <https://doi.org/10.1016/j.ecolind.2014.08.007>

607 Dupas, R., Jomaa, S., Musolff, A., Borchardt, D., Rode, M., 2016. Disentangling the influence of  
608 hydroclimatic patterns and agricultural management on river nitrate dynamics from sub-  
609 hourly to decadal time scales. *Sci. Total Environ.* 571, 791–800.  
610 <https://doi.org/10.1016/j.scitotenv.2016.07.053>

611 Dupas, R., Musolff, A., Jawitz, J.W., Rao, P.S.C., Jäger, C.G., Fleckenstein, J.H., Rode, M., Borchardt, D.,  
612 2017. Carbon and nutrient export regimes from headwater catchments to downstream  
613 reaches. *Biogeosciences* 14, 4391–4407. <https://doi.org/10.5194/bg-14-4391-2017>

614 Ellis, E.C., Klein Goldewijk, K., Siebert, S., Lightman, D., Ramankutty, N., 2010. Anthropogenic  
615 transformation of the biomes, 1700 to 2000: Anthropogenic transformation of the biomes.  
616 *Glob. Ecol. Biogeogr.* 586–606. <https://doi.org/10.1111/j.1466-8238.2010.00540.x>

617 Exner-Kittridge, M., Strauss, P., Blöschl, G., Eder, A., Saracevic, E., Zessner, M., 2016. The seasonal  
618 dynamics of the stream sources and input flow paths of water and nitrogen of an Austrian  
619 headwater agricultural catchment. *Sci. Total Environ.* 542, Part A, 935–945.  
620 <https://doi.org/10.1016/j.scitotenv.2015.10.151>

621 Foley, J.A., Ramankutty, N., Brauman, K.A., Cassidy, E.S., Gerber, J.S., Johnston, M., Mueller, N.D.,  
622 O’Connell, C., Ray, D.K., West, P.C., Balzer, C., Bennett, E.M., Carpenter, S.R., Hill, J.,  
623 Monfreda, C., Polasky, S., Rockström, J., Sheehan, J., Siebert, S., Tilman, D., Zaks, D.P.M.,  
624 2011. Solutions for a cultivated planet. *Nature* 478, 337–342.  
625 <https://doi.org/10.1038/nature10452>

626 Fovet, O., Ruiz, L., Faucheux, M., Molénat, J., Sekhar, M., Vertès, F., Aquilina, L., Gascuel-Oudou, C.,  
627 Durand, P., 2015. Using long time series of agricultural-derived nitrates for estimating  
628 catchment transit times. *J. Hydrol.* 522, 603–617.  
629 <https://doi.org/10.1016/j.jhydrol.2015.01.030>

630 Gardiner, M.M., Allee, L.L., Brown, P.M., Losey, J.E., Roy, H.E., Smyth, R.R., 2012. Lessons from lady  
631 beetles: accuracy of monitoring data from US and UK citizen-science programs. *Front. Ecol.*  
632 *Environ.* 10, 471–476. <https://doi.org/10.1890/110185>

633 Gascuel-Oudou, C., Arousseau, P., Durand, P., Ruiz, L., Molenat, J., 2010. The role of climate on  
634 inter-annual variation in stream nitrate fluxes and concentrations. *Sci. Total Environ.*, Special  
635 Section: Integrating Water and Agricultural Management Under Climate Change 408, 5657–  
636 5666. <https://doi.org/10.1016/j.scitotenv.2009.05.003>

637 Gu, S., Gruau, G., Dupas, R., Rumpel, C., Crème, A., Fovet, O., Gascuel-Oudou, C., Jeanneau, L.,  
638 Humbert, G., Petitjean, P., 2017. Release of dissolved phosphorus from riparian wetlands:  
639 Evidence for complex interactions among hydroclimate variability, topography and soil  
640 properties. *Sci. Total Environ.* 598, 421–431. <https://doi.org/10.1016/j.scitotenv.2017.04.028>

641 Hering, D., Borja, A., Carstensen, J., Carvalho, L., Elliott, M., Feld, C.K., Heiskanen, A.-S., Johnson, R.K.,  
642 Moe, J., Pont, D., Solheim, A.L., de Bund, W. van, 2010. The European Water Framework  
643 Directive at the age of 10: A critical review of the achievements with recommendations for  
644 the future. *Sci. Total Environ.* 408, 4007–4019.  
645 <https://doi.org/10.1016/j.scitotenv.2010.05.031>

646 House, W.A., Leach, D.V., Armitage, P.D., 2001. Study of dissolved silicon, and nitrate dynamics in a  
647 fresh water stream. *Water Res.* 35, 2749–2757. [https://doi.org/10.1016/S0043-1354\(00\)00548-0](https://doi.org/10.1016/S0043-1354(00)00548-0)

649 Howarth, R.W., 2008. Coastal nitrogen pollution: A review of sources and trends globally and  
650 regionally. *Harmful Algae, HABs and Eutrophication* 8, 14–20.  
651 <https://doi.org/10.1016/j.hal.2008.08.015>

652 Howden, N.J.K., Burt, T.P., Worrall, F., Mathias, S., Whelan, M.J., 2011. Nitrate pollution in intensively  
653 farmed regions: What are the prospects for sustaining high-quality groundwater? *Water*  
654 *Resour. Res.* 47, W00L02. <https://doi.org/10.1029/2011WR010843>

655 Jarvie, H.P., Sharpley, A.N., Withers, P.J.A., Scott, J.T., Haggard, B.E., Neal, C., 2013. Phosphorus  
656 Mitigation to Control River Eutrophication: Murky Waters, Inconvenient Truths, and  
657 “Postnormal” Science. *J. Environ. Qual.* 42, 295–304. <https://doi.org/10.2134/jeq2012.0085>

658 Jasechko, S., Perrone, D., Befus, K.M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., Luijendijk, E.,  
659 McDonnell, J.J., Taylor, R.G., Wada, Y., Kirchner, J.W., 2017. Global aquifers dominated by  
660 fossil groundwaters but wells vulnerable to modern contamination. *Nat. Geosci.* 10, 425–  
661 429. <https://doi.org/10.1038/ngeo2943>

662 Jenny, J.-P., Normandeau, A., Francus, P., Taranu, Z.E., Gregory-Eaves, I., Lapointe, F., Jautzy, J., Ojala,  
663 A.E.K., Dorioz, J.-M., Schimmelmann, A., Zolitschka, B., 2016. Urban point sources of  
664 nutrients were the leading cause for the historical spread of hypoxia across European lakes.  
665 *Proc. Natl. Acad. Sci.* 201605480. <https://doi.org/10.1073/pnas.1605480113>

666 Kolbe, T., Marçais, J., Thomas, Z., Abbott, B.W., de Dreuzy, J.-R., Rousseau-Gueutin, P., Aquilina, L.,  
667 Labasque, T., Pinay, G., 2016. Coupling 3D groundwater modeling with CFC-based age dating  
668 to classify local groundwater circulation in an unconfined crystalline aquifer. *J. Hydrol.* 543,  
669 Part A, 31–46. <https://doi.org/10.1016/j.jhydrol.2016.05.020>

670 Komsta, L., 2005. Median-Based Linear Models. R Package Version.

671 Kyba, C.C.M., Wagner, J.M., Kuechly, H.U., Walker, C.E., Elvidge, C.D., Falchi, F., Ruhtz, T., Fischer, J.,  
672 Hölker, F., 2013. Citizen Science Provides Valuable Data for Monitoring Global Night Sky  
673 Luminance. *Sci. Rep.* 3, 1835. <https://doi.org/10.1038/srep01835>

674 Legendre, P., Borcard, D., Roberts, D.W., 2012. Variation partitioning involving orthogonal spatial  
675 eigenfunction submodels. *Ecology* 93, 1234–1240. <https://doi.org/10.1890/11-2028.1>

676 Legendre, P., Gauthier, O., 2014. Statistical methods for temporal and space-time analysis of  
677 community composition data. *Proc. R. Soc. B Biol. Sci.* 281, 20132728–20132728.  
678 <https://doi.org/10.1098/rspb.2013.2728>

679 Linton, J., 2014. Modern water and its discontents: a history of hydrosocial renewal. *Wiley*  
680 *Interdiscip. Rev. Water* 1, 111–120. <https://doi.org/10.1002/wat2.1009>

681 Liu, J., Yang, W., 2012. Water sustainability for China and beyond. *Science* 337, 649–650.

682 Martin, C., Aquilina, L., Gascuel-Oudou, C., Molénat, J., Faucheux, M., Ruiz, L., 2004. Seasonal and  
683 interannual variations of nitrate and chloride in stream waters related to spatial and  
684 temporal patterns of groundwater concentrations in agricultural catchments. *Hydrol.*  
685 *Process.* 18, 1237–1254. <https://doi.org/10.1002/hyp.1395>

686 McDonald, R.I., Weber, K.F., Padowski, J., Boucher, T., Shemie, D., 2016. Estimating watershed  
687 degradation over the last century and its impact on water-treatment costs for the world's  
688 large cities. *Proc. Natl. Acad. Sci.* 113, 9117–9122. <https://doi.org/10.1073/pnas.1605354113>

689 MEDD & Agences de l'eau, 2003. Système d'évaluation de la qualité de l'eau des cours d'eau.

690 Mellander, P.-E., Melland, A.R., Murphy, P.N.C., Wall, D.P., Shortle, G., Jordan, P., 2014. Coupling of  
691 surface water and groundwater nitrate-N dynamics in two permeable agricultural  
692 catchments. *J. Agric. Sci.* 152, S107–S124.

693 Meter, K.J.V., Basu, N.B., 2015. Catchment Legacies and Time Lags: A Parsimonious Watershed Model  
694 to Predict the Effects of Legacy Storage on Nitrogen Export. *PLOS ONE* 10, e0125971.  
695 <https://doi.org/10.1371/journal.pone.0125971>

696 Meter, K.J.V., Basu, N.B., Veenstra, J.J., Burras, C.L., 2016. The nitrogen legacy: emerging evidence of  
697 nitrogen accumulation in anthropogenic landscapes. *Environ. Res. Lett.* 11, 035014.  
698 <https://doi.org/10.1088/1748-9326/11/3/035014>

699 Meybeck, M., Moatar, F., 2012. Daily variability of river concentrations and fluxes: indicators based  
700 on the segmentation of the rating curve. *Hydrol. Process.* 26, 1188–1207.  
701 <https://doi.org/10.1002/hyp.8211>

702 Minaudo, C., Meybeck, M., Moatar, F., Gassama, N., Curie, F., 2015. Eutrophication mitigation in  
703 rivers: 30 years of trends in spatial and seasonal patterns of biogeochemistry of the Loire  
704 River (1980–2012). *Biogeosciences* 12, 2549–2563. <https://doi.org/10.5194/bg-12-2549-2015>

705 Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G., 2017. Elemental properties, hydrology, and  
706 biology interact to shape concentration-discharge curves for carbon, nutrients, sediment,  
707 and major ions. *Water Resour. Res.* 53, 1270–1287. <https://doi.org/10.1002/2016WR019635>

708 Moatar, F., Meybeck, M., Raymond, S., Birgand, F., Curie, F., 2013. River flux uncertainties predicted  
709 by hydrological variability and riverine material behaviour. *Hydrol. Process.* 27, 3535–3546.  
710 <https://doi.org/10.1002/hyp.9464>

711 Musolff, A., Schmidt, C., Rode, M., Lischeid, G., Weise, S.M., Fleckenstein, J.H., 2016. Groundwater  
712 head controls nitrate export from an agricultural lowland catchment. *Adv. Water Resour.* 96,  
713 95–107. <https://doi.org/10.1016/j.advwatres.2016.07.003>

714 Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H., 2015. Catchment controls on solute export. *Adv.*  
715 *Water Resour.* 86, 133–146. <https://doi.org/10.1016/j.advwatres.2015.09.026>

716 Neal, C., Neal, M., Wickham, H., Harrow, M., 2000. The water quality of a tributary of the Thames,  
717 the Pang, southern England. *Sci. Total Environ.* 251–252, 459–475.  
718 [https://doi.org/10.1016/S0048-9697\(00\)00399-5](https://doi.org/10.1016/S0048-9697(00)00399-5)

719 Ohtani, K., 2004. Sampling Properties of R-squared When an Inequality. *Kobe Univ. Econ. Rev.* 50, 1–  
720 12.

721 Oksanen, J., Kindt, R., Legendre, P., O’Hara, B., Stevens, M.H.H., Oksanen, M.J., Suggests, M., 2007.  
722 The vegan package. *Community Ecol. Package* 10, 631–637.

723 Oulehle, F., Cosby, B.J., Austnes, K., Evans, C.D., Hruška, J., Kopáček, J., Moldan, F., Wright, R.F., 2015.  
724 Modelling inorganic nitrogen in runoff: Seasonal dynamics at four European catchments as  
725 simulated by the MAGIC model. *Sci. Total Environ.* 536, 1019–1028.  
726 <https://doi.org/10.1016/j.scitotenv.2015.05.047>

727 Perrot, T., Rossi, N., Ménesguen, A., Dumas, F., 2014. Modelling green macroalgal blooms on the  
728 coasts of Brittany, France to enhance water quality management. *J. Mar. Syst.* 132, 38–53.  
729 <https://doi.org/10.1016/j.jmarsys.2013.12.010>

730 Pinay, G., Peiffer, S., De Dreuzy, J.-R., Krause, S., Hannah, D.M., Fleckenstein, J.H., Sebiló, M., Bishop,  
731 K., Hubert-Moy, L., 2015. Upscaling Nitrogen Removal Capacity from Local Hotspots to Low  
732 Stream Orders’ Drainage Basins. *Ecosystems* 18, 1101–1120.  
733 <https://doi.org/10.1007/s10021-015-9878-5>

734 Piot-Lepetit, I., Moing, M.L., 2007. Productivity and environmental regulation: the effect of the  
735 nitrates directive in the French pig sector. *Environ. Resour. Econ.* 38, 433–446.  
736 <https://doi.org/10.1007/s10640-007-9086-7>

737 Poisvert, C., Curie, F., Moatar, F., 2017. Annual agricultural N surplus in France over a 70-year period.  
738 *Nutr. Cycl. Agroecosystems* 107, 63–78. <https://doi.org/10.1007/s10705-016-9814-x>

739 R Core Team, 2016. R: A language and environment for statistical computing. R Foundation for  
740 Statistical Computing, Vienna, Austria.

741 Raymond, S., Moatar, F., Meybeck, M., Bustillo, V., 2013. Choosing methods for estimating dissolved  
742 and particulate riverine fluxes from monthly sampling. *Hydrol. Sci. J.* 58, 1326–1339.  
743 <https://doi.org/10.1080/02626667.2013.814915>

744 Reed, D.C., Harrison, J.A., 2016. Linking nutrient loading and oxygen in the coastal ocean: A new  
745 global scale model. *Glob. Biogeochem. Cycles* 30, 2015GB005303.  
746 <https://doi.org/10.1002/2015GB005303>

747 Regional Algal Bloom Plans, 2015. Plan gouvernemental de lutte contre les algues vertes 2010-2015.

748 Regional Counsel, 2013. Région\_Bretagne - mise en oeuvre de la strategie regionale de lutte contre  
749 les mares vertes.

750 Ruhala, S.S., Zarnetske, J.P., 2017. Using in-situ optical sensors to study dissolved organic carbon  
751 dynamics of streams and watersheds: A review. *Sci. Total Environ.* 575, 713–723.  
752 <https://doi.org/10.1016/j.scitotenv.2016.09.113>

753 Savage, N., 2012. Gaining Wisdom from Crowds. *Commun ACM* 55, 13–15.  
754 <https://doi.org/10.1145/2093548.2093553>

755 Schmidt, J.J., 2014. Historicizing the hydrosocial cycle. *Water Altern.* 7.

756 Schoumans, O.F., Silgram, M., Groenendijk, P., Bouraoui, F., Andersen, H.E., Kronvang, B., Behrendt,  
757 H., Arheimer, B., Johnsson, H., Panagopoulos, Y., Mimikou, M., Porto, A.L., Reisser, H., Gall,  
758 G.L., Barr, A., Anthony, S.G., 2009. Description of nine nutrient loss models: capabilities and  
759 suitability based on their characteristics. *J. Environ. Monit.* 11, 506–514.  
760 <https://doi.org/10.1039/B823239C>

761 Sebiló, M., Mayer, B., Nicolardot, B., Pinay, G., Mariotti, A., 2013. Long-term fate of nitrate fertilizer  
762 in agricultural soils. *Proc. Natl. Acad. Sci.* 110, 18185–18189.  
763 <https://doi.org/10.1073/pnas.1305372110>

764 Seitzinger, S., Harrison, J.A., Böhlke, J.K., Bouwman, A.F., Lowrance, R., Peterson, B., Tobias, C.,  
765 Drecht, G.V., 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecol. Appl.*  
766 16, 2064–2090. [https://doi.org/10.1890/1051-0761\(2006\)016\[2064:DALAWA\]2.0.CO;2](https://doi.org/10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2)

767 Seitzinger, S.P., Mayorga, E., Bouwman, A.F., Kroeze, C., Beusen, A.H.W., Billen, G., Van Drecht, G.,  
768 Dumont, E., Fekete, B.M., Garnier, J., Harrison, J.A., 2010. Global river nutrient export: A  
769 scenario analysis of past and future trends. *Glob. Biogeochem. Cycles* 24, GB0A08.  
770 <https://doi.org/10.1029/2009GB003587>

771 Silvertown, J., 2009. A new dawn for citizen science. *Trends Ecol. Evol.* 24, 467–471.  
772 <https://doi.org/10.1016/j.tree.2009.03.017>

773 Stålnacke, P., Grimvall, A., Libiseller, C., Laznik, M., Kokorite, I., 2003. Trends in nutrient  
774 concentrations in Latvian rivers and the response to the dramatic change in agriculture. *J.*  
775 *Hydrol.* 283, 184–205. [https://doi.org/10.1016/S0022-1694\(03\)00266-X](https://doi.org/10.1016/S0022-1694(03)00266-X)

776 Sutton, M.A., UNEP (Eds.), 2013. Our nutrient world: the challenge to produce more food and energy  
777 with less pollution ; [global overview on nutrient management]. Centre for Ecology &  
778 Hydrology, Edinburgh.

779 Thomas, Z., Abbott, B.W., Troccaz, O., Baudry, J., Pinay, G., 2016a. Proximate and ultimate controls  
780 on carbon and nutrient dynamics of small agricultural catchments. *Biogeosciences* 13, 1863–  
781 1875. <https://doi.org/10.5194/bg-13-1863-2016>

782 Thomas, Z., Rousseau-Gueutin, P., Kolbe, T., Abbott, B.W., Marçais, J., Peiffer, S., Frei, S., Bishop, K.,  
783 Pichelin, P., Pinay, G., de Dreuzy, J.-R., 2016b. Constitution of a catchment virtual observatory  
784 for sharing flow and transport models outputs. *J. Hydrol., RESIDENCE TIMES IN SUBSURFACE*  
785 *HYDROLOGICAL SYSTEMS: Signature of hydrological processes and impact on environmental*  
786 *applications* 543, 59–66. <https://doi.org/10.1016/j.jhydrol.2016.04.067>

787 Tunaley, C., Tetzlaff, D., Lessels, J., Soulsby, C., 2016. Linking high-frequency DOC dynamics to the age  
788 of connected water sources. *Water Resour. Res.* 52, 5232–5247.  
789 <https://doi.org/10.1002/2015WR018419>

790 Vilmin, L., Flipo, N., Escoffier, N., Groleau, A., 2016. Estimation of the water quality of a large  
791 urbanized river as defined by the European WFD: what is the optimal sampling frequency?  
792 *Environ. Sci. Pollut. Res.* 1–17. <https://doi.org/10.1007/s11356-016-7109-z>

793 Wickham, H., 2009. *ggplot2: Elegant Graphics for Data Analysis*. Springer New York, New York, NY.  
794 <https://doi.org/10.1007/978-0-387-98141-3>

795 Wilcock, R.J., Monaghan, R.M., Quinn, J.M., Srinivasan, M.S., Houlbrooke, D.J., Duncan, M.J., Wright-  
796 Stow, A.E., Scarsbrook, M.R., 2013. Trends in water quality of five dairy farming streams in  
797 response to adoption of best practice and benefits of long-term monitoring at the catchment  
798 scale. *Mar. Freshw. Res.* 64, 401–412. <https://doi.org/10.1071/MF12155>

799 Withers, P.J.A., Haygarth, P.M., 2007. Agriculture, phosphorus and eutrophication: a European  
800 perspective. *Soil Use Manag.* 23, 1–4. <https://doi.org/10.1111/j.1475-2743.2007.00116.x>

801 Worrall, F., Howden, N.J.K., Burt, T.P., 2015. Time series analysis of the world’s longest fluvial nitrate  
802 record: evidence for changing states of catchment saturation. *Hydrol. Process.* 29, 434–444.  
803 <https://doi.org/10.1002/hyp.10164>

804 Zhang, Q., Brady, D.C., Boynton, W.R., Ball, W.P., 2015. Long-Term Trends of Nutrients and Sediment  
805 from the Nontidal Chesapeake Watershed: An Assessment of Progress by River and Season.  
806 *JAWRA J. Am. Water Resour. Assoc.* 51, 1534–1555. [https://doi.org/10.1111/1752-  
807 1688.12327](https://doi.org/10.1111/1752-1688.12327)

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 <sup>2</sup>	Population hab km <sup>2</sup>	Altitude (mean) m	Relief m	Rainfall mm	Q specific l s <sup>-1</sup> km <sup>-2</sup>	Q specific min l s <sup>-1</sup> km <sup>-2</sup>	W2 %	Pasture %	Crops %	Hedgerow %	Forest %	Wetland %	Urban %	Granite gneiss %	Schist %	Other %	N Surplus (2007) kg N ha <sup>-1</sup>	P Surplus (2010) kg P ha <sup>-1</sup>
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  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and dissolved silica (DSi; 1998-2016)

River (ID)	$\text{NO}_3^-$			$\text{PO}_4^{3-}$			DSi		
	C50 $\text{mg L}^{-1}$	C* $\text{mg L}^{-1}$	Load $\text{kg N ha}^{-1} \text{y}^{-1}$	C50 $\text{mg L}^{-1}$	C* $\text{mg L}^{-1}$	Load $\text{kg P ha}^{-1} \text{y}^{-1}$	C50 $\text{mg L}^{-1}$	C* $\text{mg L}^{-1}$	Load $\text{kg Si ha}^{-1} \text{y}^{-1}$
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 ( $\pm 12\%$ )	0.054	0.061	0.12 ( $\pm 12\%$ )	7.6	7.8	47 ( $\pm 9\%$ )
Douffine (6)	19.0	20.4	36 ( $\pm 13\%$ )	0.212	0.139	0.34 ( $\pm 3\%$ )	5.7	5.4	42 ( $\pm 10\%$ )
Elorn (7)	34.1	32.3	48 ( $\pm 5\%$ )	0.212	0.139	0.28 ( $\pm 7\%$ )	9.2	8.5	57 ( $\pm 5\%$ )
Quillimadec (8)	50.9			0.418			16.1		
Fleche (9)	61.1			0.272			14.4		
Guillec (10)	77.5	69.5	81 ( $\pm 3\%$ )	0.394	0.318	0.54 ( $\pm 5\%$ )	14.0	13.2	68 ( $\pm 4\%$ )
Penze (11)	45.2	45.2	68 ( $\pm 10\%$ )	0.397	0.230	0.50 ( $\pm 4\%$ )	11.8	11.1	73 ( $\pm 8\%$ )
Dossen (12)	27.0	26.1	30.4 ( $\pm 7\%$ )	0.285	0.239	0.39 ( $\pm 2\%$ )	12.4	11.6	59 ( $\pm 5\%$ )
Dourduff (13)	35.9	33.6	30 ( $\pm 7\%$ )	0.224	0.154	0.20 ( $\pm 12\%$ )	13.0	12.5	47 ( $\pm 5\%$ )

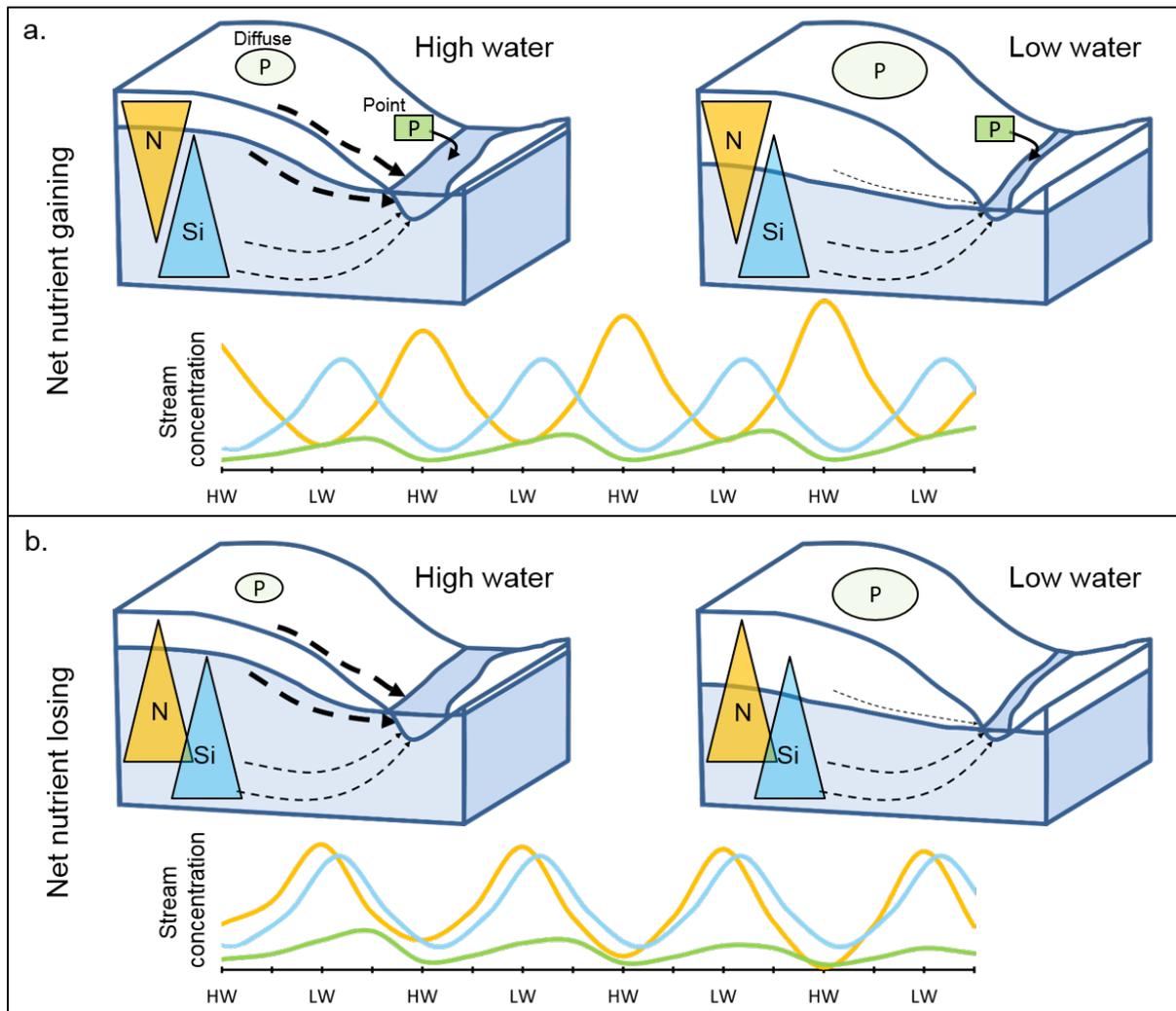
2 C\* and load were computed for rivers where flow data were available.

3

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

River (ID)	$\text{NO}_3^-$				$\text{PO}_4^{3-}$				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	<b>0.24</b>	0.54	0.02	0.03	<b>0.22</b>	0.28	<b>0.22</b>	0.19	0.15	0.59
Ris (2)	<b>0.21</b>	0.03	<b>0.24</b>	0.52	0.07	0.07	0.06	0.20	<b>0.31</b>	<b>0.33</b>	0.16	0.83
Lapic (3)	0.29	<b>0.31</b>	0.11	0.78	0.13	<u>0.41</u>	<b>0.24</b>	0.78	<b>0.22</b>	0.10	<b>0.21</b>	0.61
Aulne (5)	0.12	<u>0.52</u>	0.12	0.85	0.10	0.09	<b>0.29</b>	0.50	0.13	<b>0.38</b>	<b>0.22</b>	0.87
Douffine (6)	0.19	0.18	0.18	0.62	<b>0.21</b>	<u>0.42</u>	0.17	0.82	0.13	<b>0.22</b>	<b>0.27</b>	0.63
Elorn (7)	0.17	0.15	<b>0.22</b>	0.58	0.16	<b>0.27</b>	0.18	0.60	0.09	0.18	<b>0.35</b>	0.69
Quillimadec (8)	0.18	0.15	0.19	0.57	0.14	0.14	<b>0.21</b>	0.52	0.06	<b>0.32</b>	<b>0.24</b>	0.60
Fleche (9)	0.19	0.20	0.16	0.57	0.16	0.14	<b>0.27</b>	0.64	0.11	<b>0.25</b>	0.20	0.61
Guillec (10)	<b>0.32</b>	0.14	0.11	0.63	<b>0.28</b>	<b>0.25</b>	0.18	0.73	0.12	<b>0.21</b>	<b>0.26</b>	0.65
Penze (11)	<u>0.46</u>	0.04	0.13	0.68	<b>0.34</b>	<u>0.43</u>	0.07	0.90	<b>0.21</b>	<b>0.24</b>	<b>0.24</b>	0.75
Dossen (12)	<b>0.29</b>	0.07	<b>0.21</b>	0.61	0.20	<b>0.32</b>	0.13	0.71	0.15	0.17	<b>0.38</b>	0.71
Dourduff (13)	<b>0.30</b>	0.10	0.13	0.55	<b>0.38</b>	0.33	0.08	0.81	0.07	<b>0.32</b>	0.15	0.57

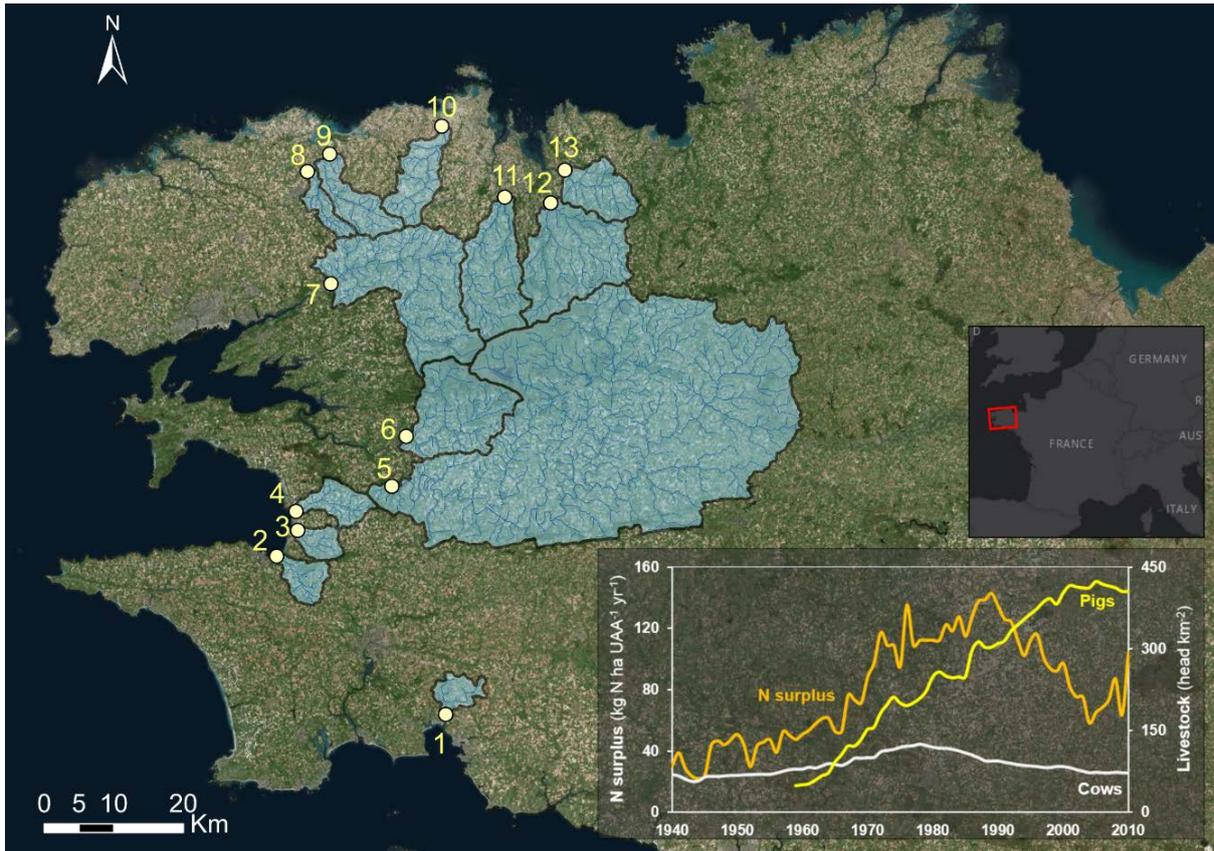
5 Reported values are adjusted- $R^2$  between observed nutrient concentrations and predicted values from one or more sets of  
6 explanatory variables in the dbMEM (see Section 2.3.2). All values are significant at  $\alpha = 0.05$ . To facilitate interpretation,  
7 we bolded values with  $R^2 > 0.2$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



8

9 **Figure 1.** Hypothesized seasonal and interannual changes stream concentrations of nitrate  
 10 ( $\text{NO}_3^-$ ), dissolved silica (DSi), and phosphate ( $\text{PO}_4^{3-}$ ) 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.  $\text{NO}_3^-$  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.  $\text{PO}_4^{3-}$ ), 4. no interannual change in DSi but later arrival of the DSi peak relative  
 19 to  $\text{NO}_3^-$ , 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

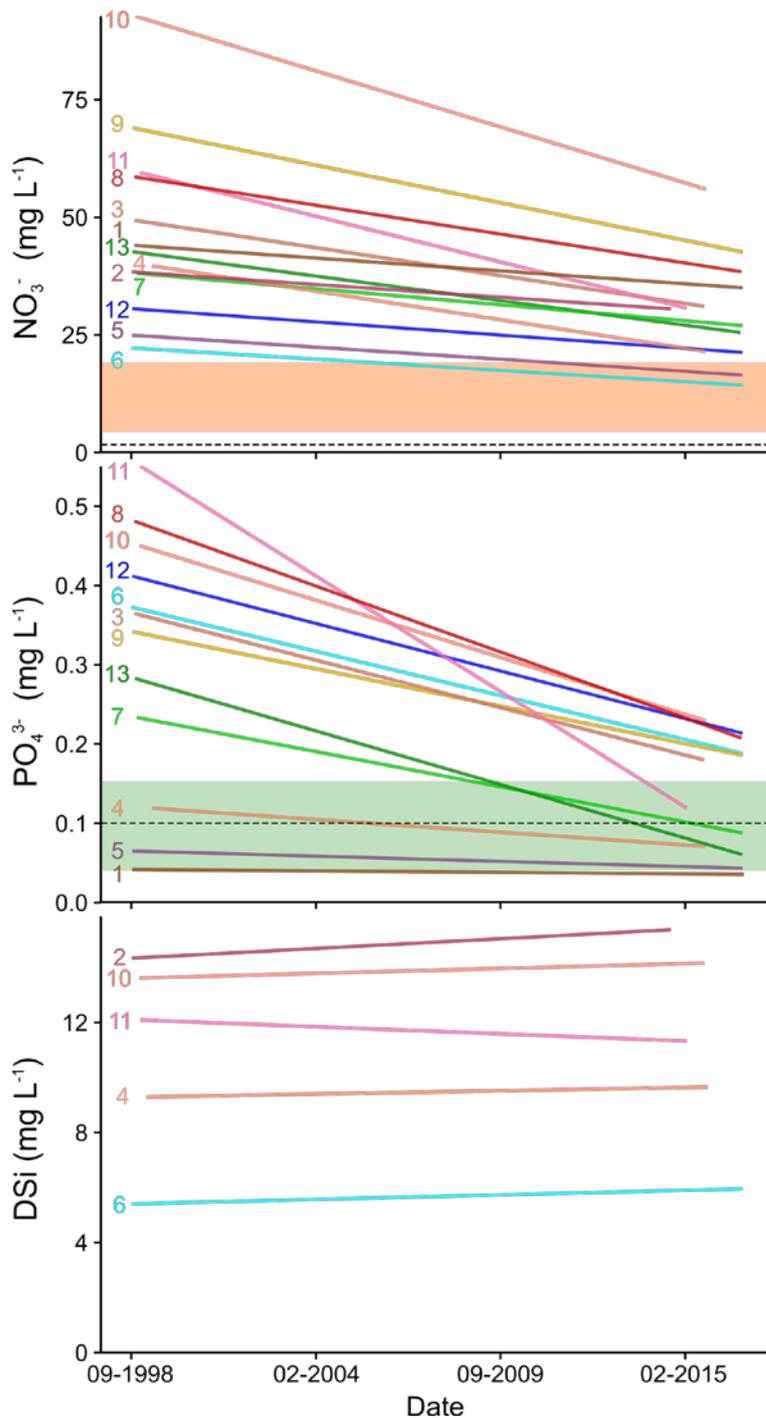


24

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.

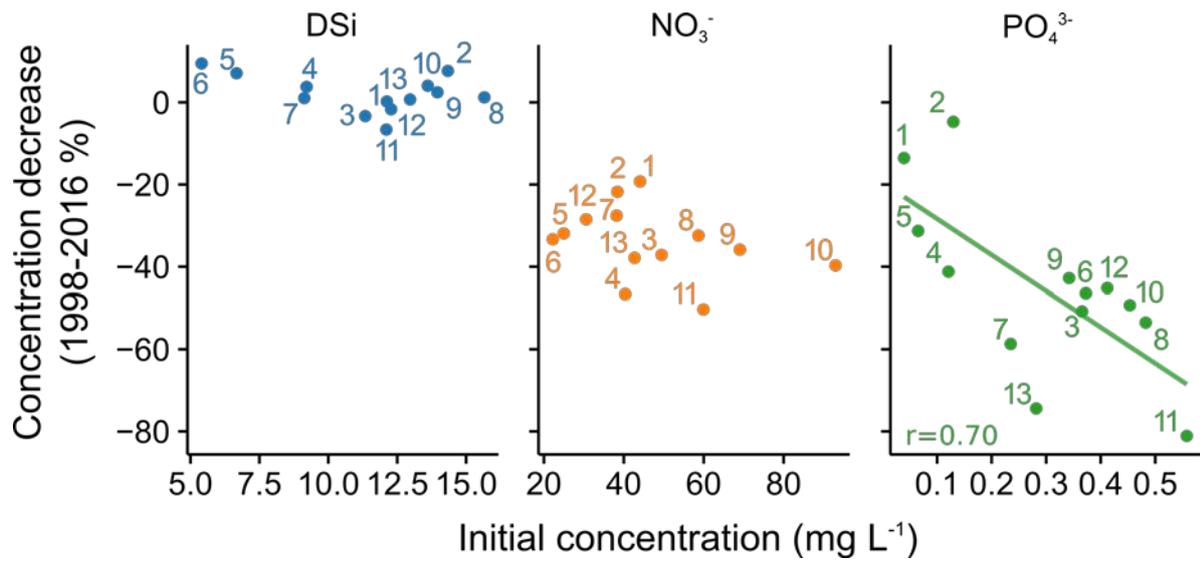
30

31



32

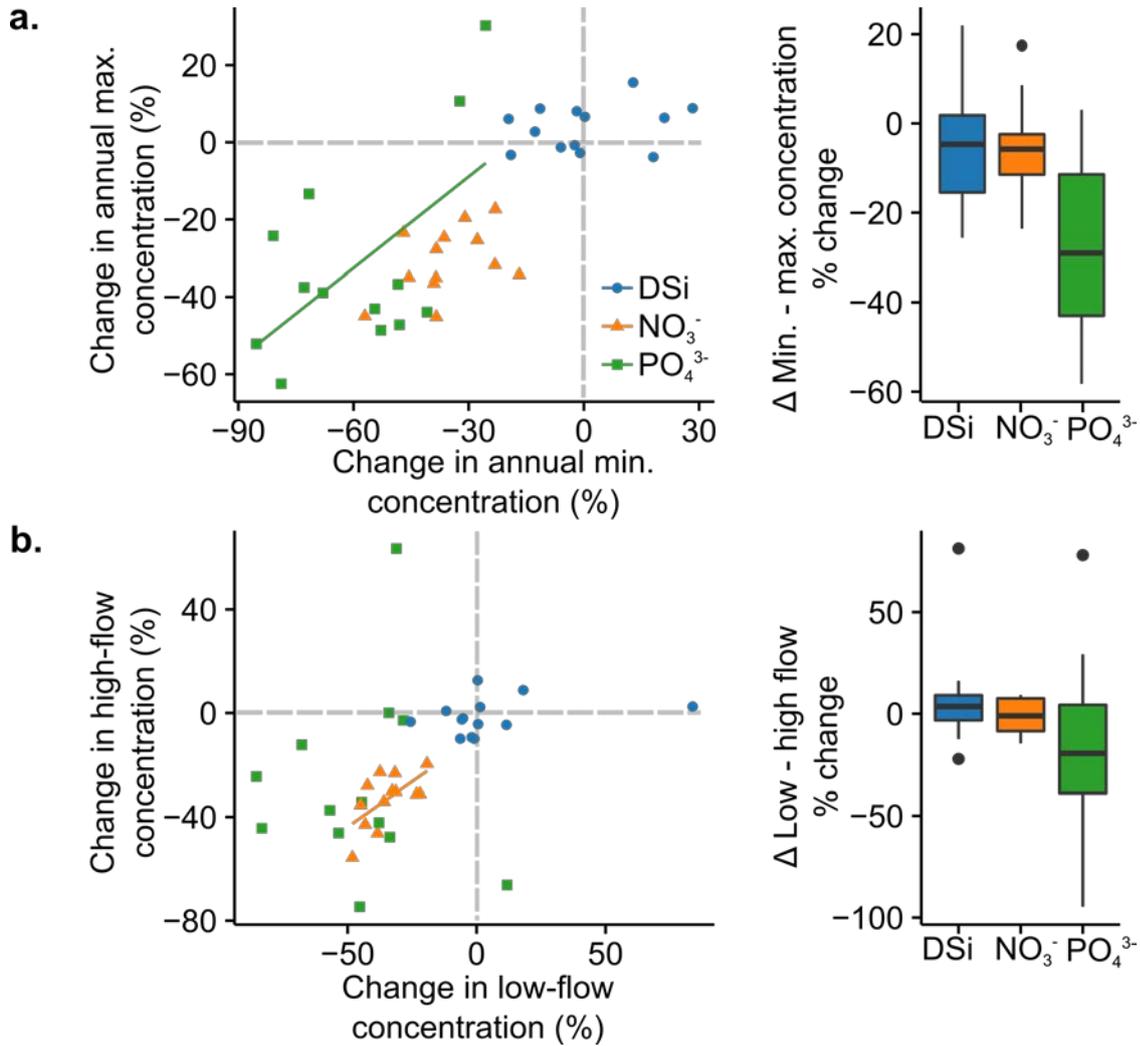
33 **Figure 3.** Statistically significant long-term trends in nutrient concentrations (Mann-Kendall  
 34 test  $\alpha = 0.05$ ). The shaded rectangles for the  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  plots represent the estimated  
 35 concentrations necessary to substantially reduce inland and 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  $\text{NO}_3^-$  concentration, 1 to 23  
 39 % (median = 10 %) for  $\text{PO}_4^{3-}$ , 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).

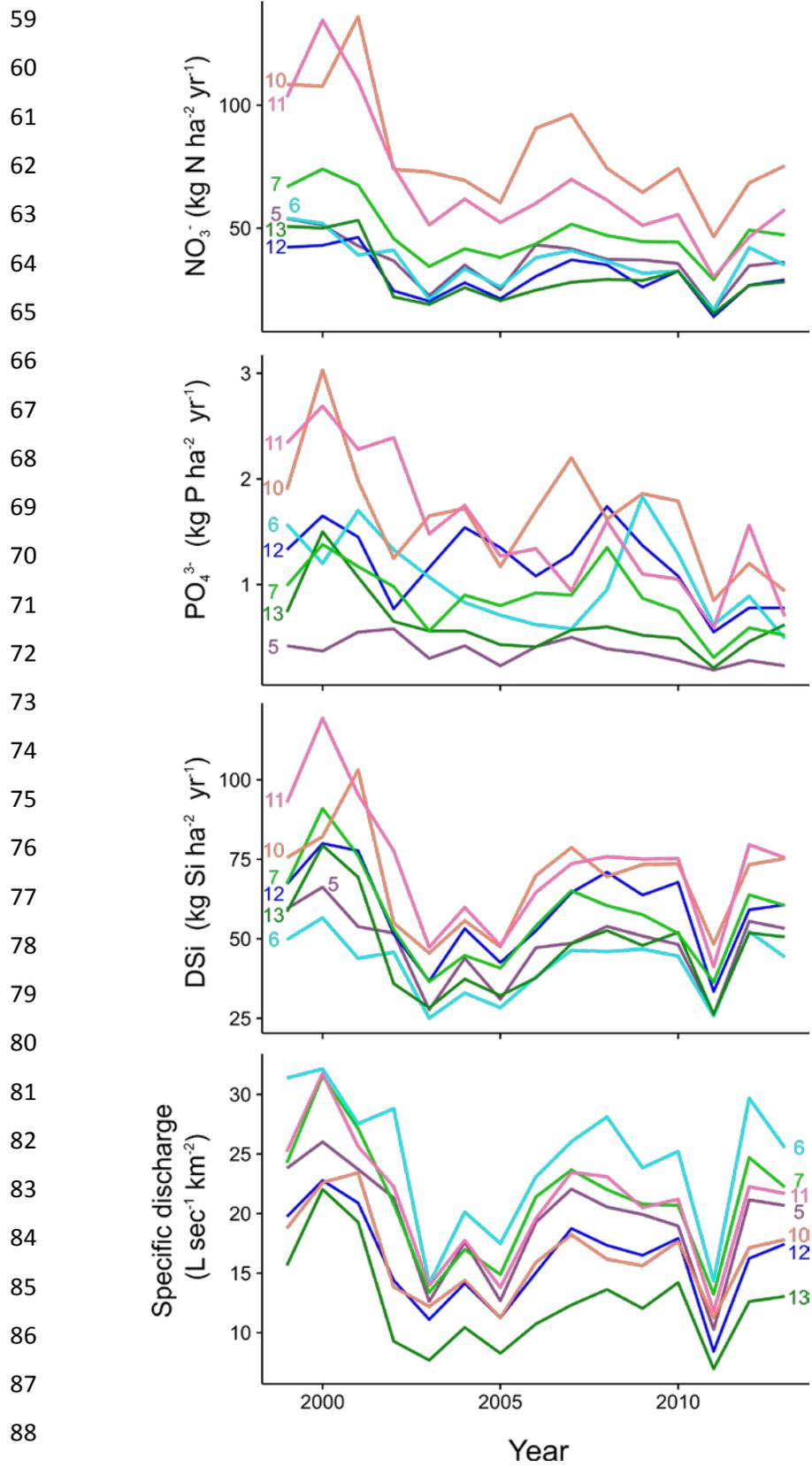
44



46

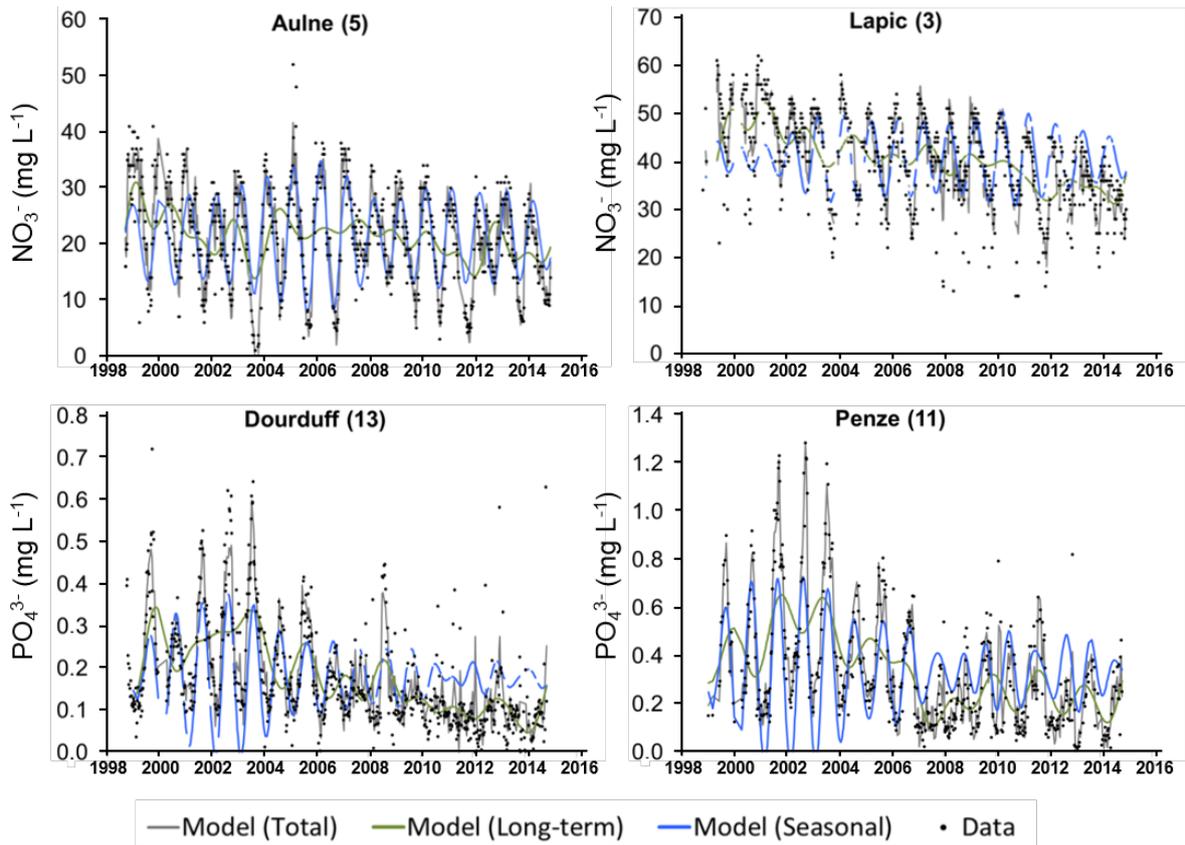
47 **Figure 5.** Comparison between trends in (a) annual maximum and minimum concentrations,  
 48 and (b) annual low-flow and high-flow concentrations. Trends are presented in % change for  
 49 each solute from 1998 to 2016. Mean values of the five highest and lowest concentrations  
 50 annually were 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



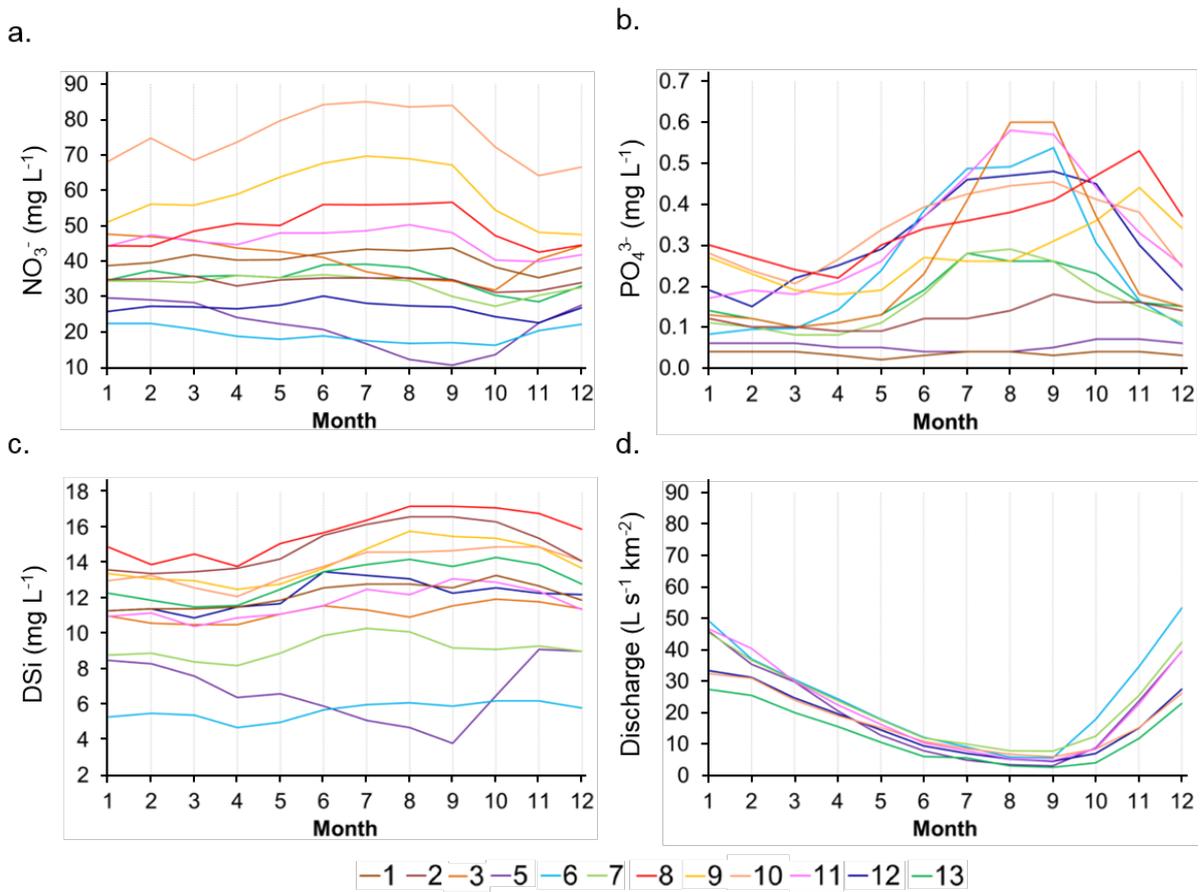
89 **Figure 6.** Trends in nutrient and water fluxes for the 7 rivers where long-term discharge data  
 90 were available. We calculated fluxes with the discharge-weighted concentration method,  
 91 which was the most robust for these catchments and nutrients (see methods).

92



93

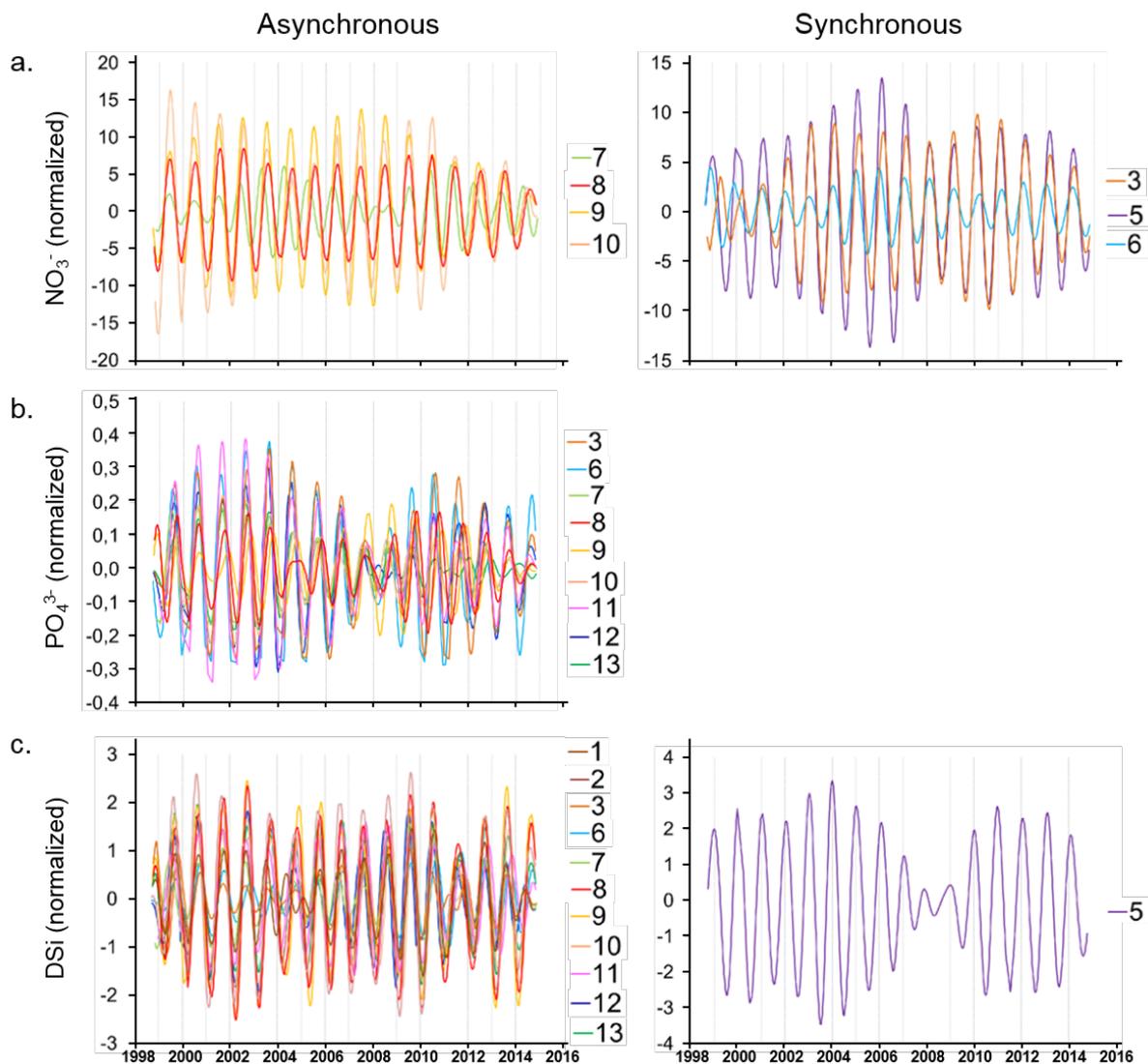
94 **Figure 7.** Example modeled and observed time series, and modeled long-term and seasonal  
 95 subcomponents from four catchments. See Table 3 for overall model performance and  
 96 breakdown of timescales.



98

99 **Figure 8:** Monthly mean observed concentrations of (a)  $\text{NO}_3^-$ , (b)  $\text{PO}_4^{3-}$ , (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  $\text{NO}_3^-$  (**a**),  $\text{PO}_4^{3-}$  (**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