

1 **Proximate and ultimate controls on carbon and nutrient dynamics**
2 **of small agricultural catchments**

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1 Abstract

2 Direct and indirect effects from human activity have dramatically increased nutrient loading
3 to aquatic inland and estuarine ecosystems. Despite an abundance of studies investigating the
4 impact of agricultural activity on water quality, our understanding of what determines the
5 capacity of a watershed to remove or retain nutrients remains limited. The goal of this study
6 was to identify proximate and ultimate controls on dissolved organic carbon and nutrient
7 dynamics in small agricultural catchments by investigating the relationship between
8 catchment characteristics, stream discharge, and water chemistry. We analyzed a five-year,
9 high-frequency water chemistry dataset from 3 catchments ranging from 2.3 to 10.8 km² in
10 western France. The relationship between hydrology and solute concentrations differed
11 between the three catchments, associated with hedgerow density, agricultural activity, and
12 geology. The catchment with thicker soil and higher surface roughness had relatively
13 invariant carbon and nutrient chemistry across hydrologic conditions, indicating high
14 resilience to human disturbance. Conversely, the catchments with smoother, thinner soils
15 responded to both intra- and inter-annual hydrologic variation with high concentrations of
16 PO₄³⁻ and NH₄⁺ in streams during low flow conditions and strong increases in DOC,
17 sediment, and particulate organic matter during high flows. Despite contrasting agricultural
18 activity between catchments, the physical context (geology, topography, and land-use
19 configuration) appeared to be the most important determinant of catchment solute dynamics
20 based on principle components analysis. The influence of geology and accompanying
21 topographic and geomorphological factors on water quality was both direct and indirect
22 because the distribution of agricultural activity in these catchments is largely a consequence
23 of the geologic and topographic context. This link between inherent catchment buffering
24 capacity and probability of human disturbance provides a useful perspective for evaluating
25 vulnerability of aquatic ecosystems and for managing systems to maintain agricultural
26 production while minimizing leakage of nutrients.

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1 1 Introduction

2 Direct and indirect effects from agriculture, urbanization, and resource extraction have
3 dramatically increased nutrient loading to aquatic inland and estuarine ecosystems. In the past
4 60 years, human activity has more than doubled global nitrogen fixation (Gruber and
5 Galloway, 2008) and quadrupled phosphorus loading (Elser and Bennett, 2011), primarily due
6 to agricultural activity and combustion of fossil fuels. At the same time human land-use has
7 directly disturbed approximately half of global land surface (Vitousek et al., 1997),
8 dramatically altering the capacity of ecosystems to buffer or process these nutrient inputs
9 (Seitzinger et al., 2006). These changes in land use and nutrient flux have also altered carbon
10 budgets, stimulating plant and algal growth in estuarine and marine ecosystems and
11 accelerating organic matter decomposition in inland waters (Gruber and Galloway, 2008;
12 Rosemond et al., 2015). Consequently, nitrogen and phosphorus pollution is considered to be
13 one of the most urgent environmental issues currently facing humanity along with loss of
14 biodiversity (Rockström et al., 2009).

15 The capacity of a watershed to remove or retain nutrients is a function of biotic and
16 abiotic conditions encountered as water flows through the soil, groundwater, riparian zone,
17 hyporheic zone, and stream channel itself (Brookshire et al., 2009; Seitzinger et al., 2006;
18 Sébilo et al., 2013; Pinay et al. 2015). For catchments larger than 100 km², riverine nutrient
19 fluxes are tightly associated with percentage of agricultural cover (Jordan et al., 1997;
20 Omernik et al., 1981; Strayer et al., 2003). However in drainage basins smaller than 10 km²,
21 nutrient fluxes vary widely despite similar land cover (Brookshire et al., 2009; Burt and
22 Pinay, 2005; Lefebvre et al., 2007 Groffman et al., 2006; Sebilo, et al. 2013). This breakdown
23 in the relationship between land cover and nutrient flux represents an important ecological
24 uncertainty since 90% of global stream length occurs in catchments smaller than 15 km²
25 (Bishop et al., 2008). It also highlights a practical problem, because though most water-
26 quality monitoring takes place in large rivers, most land-management decisions are made at
27 the parcel or small-catchment scale (Thenail et al., 2009). The diversity in headwater-
28 catchment response to nutrient loading also represents an opportunity to identify the
29 mechanistic controls regulating nutrient processing and removal.

30 Two non-exclusive mechanisms may account for the change in variability of nutrient
31 fluxes along stream networks. First, in-stream biogeochemical processes such as nutrient
32 uptake and spiraling vary longitudinally in stream ecosystems, typically decreasing in

1 importance as stream order or discharge increases (Ensign et al., 2006; Alexander et al., 2009;
2 Hall et al., 2013). Active in-stream removal or retention of nutrients in headwaters could
3 decouple land-use from nutrient flux (Trauth et al., 2013). Second, catchment characteristics
4 such as topography, stream network density, and surficial geology vary moving from uplands
5 to lowlands (Brookshire et al., 2007; Sidle, 2006; Strayer et al., 2003; Pinay et al., 2015)
6 potentially altering terrestrial-aquatic linkages, modulating transport and processing of carbon
7 and nutrients. To identify controls on carbon and nutrient dynamics in headwater catchments,
8 we used a multiannual, high-frequency dataset of water chemistry from three contrasting
9 catchments in western France. Based on observations of variability in headwater catchments
10 (Burt and Pinay, 2005), we hypothesized that landscape characteristics such as topography,
11 surficial geology, and location within stream network would modulate the impact of land use
12 on water quality. We hypothesized that carbon and nutrient concentrations would show
13 contrasting responses due to distinct sources and flowpaths across scales. We expected
14 phosphate (PO_4^{3-}) and ammonium (NH_4^+) to be associated with surface flow, dissolved
15 organic carbon (DOC) with surface and subsurface flow, nitrate (NO_3^-) to come primarily
16 from the unsaturated zone and groundwater, and dissolved silica (DSi) to come from
17 groundwater. To test these hypotheses, we investigated both high-frequency changes in solute
18 concentration during discharge events and overall catchment water quality.

19 2 Methods

20 2.1 Study area

21 We tested our hypotheses with a five-year dataset of water chemistry from three small
22 catchments located in the *Zone Atelier Armorique* long-term socio-ecological research
23 (LTSER) area in Brittany, France (Fig. 1). The research area is located on the French Massif
24 Armoricain ($48^\circ 36' \text{ N}$, $1^\circ 32' \text{ W}$) and is underlain by granite to the south and schist to the
25 north (Fig. 1c). 20 years of meteorological data were used to estimate mean temperature and
26 cumulative annual precipitation (Fig. S1). The climate is maritime with average monthly
27 temperature ranging from 17.5° C in July to 5° C in December, and mean annual precipitation
28 of 965 mm, a third of which occurs from October to December (Fig. S1). Since the 1950s, the
29 area has been subject to intense agriculture, with 90% of arable land occupied by corn, wheat,
30 and pastureland. The study area straddles the Couesnon and Guyoult River basins, which
31 discharge into the bay of Mont-Saint-Michel and the bay of Le Vivier sur Mer, respectively.

1 2.2 Catchment characteristics and experimental design

2 To compare the influence of catchment characteristics on carbon and nutrient
3 concentrations we monitored water chemistry at three headwater catchments ranging from 2.3
4 to 10.8 km² with distinct topography, geology, soil characteristics, and land-use (Fig. 1; Table
5 1). For the purposes of this study we named catchments by near-surface geology, with the
6 catchment G-01 occurring on granite, catchment S-01 occurring on schist, and catchment GS-
7 01 straddling the boundary between the two geologies (detailed catchment characteristics
8 presented in Fig. 1, Table 1, and supplementary tables S1 and S2). Soil depth, elevation, and
9 land-use vary systematically between the surficial geologies, with the granite portion
10 characterized by thicker soils (≥ 0.8 m), higher elevation (85 to 110 m), loamy sand soil type,
11 and more permanent or semi-permanent pastureland (Table 1 and Fig. 1). The portion of the
12 research area underlain by schist has shallower soils (0.45 to 0.7 m), a thinner weathered
13 layer, lower elevation (14.5 to 60 m), loamy soils, and a larger proportion of arable land
14 occupied by corn and wheat cultivation (Fig. 1f and Table 1). The catchment situated in the
15 transition zone between granite and schist (catchment GS-01) has contrasted topography
16 (from 105 m upstream to 12.5 m at the outlet) and a mix of pasture and cultivated land.

17 We measured water flow and chemistry over 5 hydrologic years (from 10 April 1996
18 to 20 August 2000) at the outlets of the S-01 and GS-01 catchments with an automated
19 sampler (Isco 3700TM) controlled by a data logger (Campbell Scientific CR10TM). Stage was
20 continuously monitored using pressure transducers and discharge was calculated from rating
21 curves determined by manual gauging with an impellor flow meter and by salt dilution (Day,
22 1976; Hongve, 1987). Additionally discharge was determined at the gaged station situated at
23 the outlet of the Guyoult bassin (station J0323010) as a part of national environmental
24 monitoring (DREAL).

25 2.3 Water quality analyses

26 Water samples were collected every 12 hours during baseflow for the first year,
27 every 3 days for the following 2 years, and monthly for the last 2 years with automatic
28 samplers. For catchments GS-01 and S-01, we programmed autosamplers to trigger more
29 frequent sampling during discharge events, with samples taken every 30 minutes during the
30 rising limb and every 3 hours during the falling limb. High-frequency sampling was triggered
31 when the water level (h) changed more than 0.3 cm in one minute. h was measured every

1 minute with a moving hourly mean (h_{mean}) calculated continuously. For each minute t , the
2 trigger level $dh_{(t)}$ was determined as:

$$dh_{(t)} = h_{mean} - h_{(t)}$$

3 There were six discharge events captured by the automated samplers at GS-01 and S-
4 01 from June 1997 to April 1998. For some of the longer events sampling frequency slowed
5 during the falling limb and for the largest event (April 1998) only the rising limb was sampled
6 because the high water level **incapacitated** the autosampler.

7 Water samples were filtered **with 0.7** μm effective pore size glass fiber filters and
8 stored at 4°C until analysis. Samples were analyzed for DOC, NO_3^- , NH_4^+ , PO_4^{3-} , dissolved
9 silica (DSi), particulate phosphorus (PP), dissolved organic phosphorus (DOP), dissolved
10 organic nitrogen (DON), and chloride (Cl). DOC was analyzed with a Shimadzu TOC
11 analyzer and nutrients were analyzed on a Lachat Quick Chem autoanalyser. NO_3^- was
12 quantified with the modified Griess-Ilosvay method with copperized cadmium reduction,
13 NH_4^+ by indophenol blue method, PO_4^{3-} by automatic ascorbic acid method, DSi by
14 molybdosilicate colorimetric method, and Cl by colorimetric N-diethyl-p-phenylenediamine
15 method. Total suspended sediment (TSS) was determined by filtering one liter to **0.7** μm and
16 weighing the filter.

17 2.4 Spatial data and statistical analysis

18 A 2-m digital elevation model (DEM) based on airborne LiDAR data was used to
19 extract morphological data used in the statistical analysis (Fig. 1d). **We characterized surface**
20 **roughness, a predictor of catchment transient storage and runoff response (Kirkby et al., 2002;**
21 **Candela et al., 2005) with the mean, maximum, and minimum elevations for a grid of**
22 **10x10m. The roughness index was calculated as:**

$$23 \quad R = \frac{\text{Mean}_{\text{DEM}} - \text{Min}_{\text{DEM}}}{\text{Max}_{\text{DEM}} - \text{Min}_{\text{DEM}}}, \quad 0 < R < 1$$

24 Land use was mapped annually from aerial imagery from 1996-2000, with ground
25 validation. Forest and pastureland were distinguished from cultivated land, and corn was
26 distinguished from other cereal crops (predominantly wheat but also barley; hereafter wheat)
27 based on color and timing of planting and harvest. Total agricultural coverage was calculated
28 as the sum of all corn, wheat, and other crops. The Web Map Service (WMS) of the **Bureau**

1 *de Recherches Géologiques et Minières* (BRGM) was used for the geological map of the
2 study area.

3 We performed a principle components analysis (PCA) to **characterize** correlations in the
4 data and identify major sources of variability in water chemistry. We included morphological
5 parameters (geology, topography, soil depth, density of hedgerows), land use, and solute
6 concentrations. Specifically we included bedrock (**%** granite and schist), land use (wheat,
7 corn, and pastureland), stream order (Strahler 1952), drainage area, difference in elevation
8 between upstream and downstream (dZ), and concentrations of DOC, NO₃⁻, PO₄³⁻, Cl⁻, and
9 DSi. We also performed Spearman's rank correlations to **test for** individual correlations
10 between water chemistry parameters. All analyses were performed in R 3.0.2 (R Core Team,
11 2014) with the FactoMineR package for PCA (Lê and Husson, 2008).

12 **3 Results**

13 **3.1 Hydrological and land-use analysis**

14 Hydrologic conditions varied widely across the five years (Table S1). The first three
15 hydrological years (September, 1 1995 to August, 31 1998) were 145 to 180 mm below the
16 20-year average of 965 mm, while the last two years were 170 **and** 330 mm above average
17 (Table S1, Fig. S1 in the Supplement). Discharge from the three catchments was in good
18 agreement with the *Le Guyoult* basin station though there were occasional phase shifts and
19 departures, likely due to localized precipitation and differences in transient storage (Figs. S2,
20 S3, S4 and S5 in the Supplement).

21 The distribution of agricultural land was associated with soil and topographical
22 parameters with 55% agricultural coverage of the total land surface in catchment S-01 in the
23 northwest part of the study area, which has flat topography and thin soils **overlying** schist
24 bedrock. Conversely, catchments G-01 and GS-01 were dominated by pastureland and forest,
25 with less than 38% agricultural coverage (Fig. 1b, Table 1). The density of hedgerows also
26 varied by a factor of two between catchments; with 105 m ha⁻¹ of hedgerows in catchment G-
27 01 and 50 m ha⁻¹ in catchment S-01. **Though there was some rotation of individual parcels**
28 **between corn, wheat, and pastureland, catchment-level** land-use changed little over the study
29 period, with consistent differences between the 3 catchments. For the catchment S-01,
30 variability in land use was highest for corn and wheat (SD 6.6 and 5%, respectively, Table 1).

1 3.2 Effects of catchment characteristics on water chemistry

2 The relationship between specific discharge and solute concentration differed by solute
3 and catchment (Figs. 2, 3 and Figs. S7, S8). Solutes typically expressed one of three responses
4 to increases in discharge: an asymptotic increase (TSS, DOC), an asymptotic decrease (DON,
5 DOP, and PO_4^{3-}), or a decrease in variability and a convergence to a moderate concentration
6 (NO_3^- , NH_4^+ , DSi, and Cl). Solutes with similar response patterns were more tightly
7 correlated, though significance and sometimes sign of individual relationships varied
8 somewhat by catchment (Table 2). The catchment G-01, which had low gradient, high
9 roughness, and relatively less agriculture, had more stable chemistry during both baseflow
10 and highflow conditions, particularly for DOC, TSS, Cl, NO_3^- , and all phosphorus species
11 (Figs. 2, 3 and Figs. S7, S8). This lower amplitude of variation in water chemistry in
12 catchment G-01 resulted in fewer significant correlations between water chemistry
13 parameters, and notably discharge was not significantly correlated with any solute
14 concentrations ($p > 0.05$, Spearman's rank correlation; Table 2). The steep and small
15 catchment GS-01 and the highly agricultural catchment S-01 showed similar patterns of solute
16 response to discharge, though nitrogen and phosphorus concentrations were generally lower
17 in GS-01 than S-01 (Fig. 3 and Fig. S8). GS-01 had lower maximum specific discharge (47 L
18 $\text{s}^{-1} \text{ km}^{-2}$) than catchments S-01 ($66 \text{ L s}^{-1} \text{ km}^{-2}$, respectively; Figs. 2 and 3).

19 Mean DOC concentration was highest in catchment G-01, but did not differ between
20 catchments GS-01 and S, despite a 20% difference in agricultural coverage (Table 1). Mean
21 NO_3^- concentration increased linearly with agricultural coverage from an average of 5 mg N
22 L^{-1} in G-01 to an average of 10 mg N L^{-1} in S-01 (Fig. S9). The highest concentration and
23 variability in PO_4^{3-} occurred in S-01 where mean PO_4^{3-} concentration was nearly three-times
24 higher than in the less agricultural catchments (Fig. S9).

25 The PCA exploring the structure of the water chemistry data and catchment characteristics
26 explained 80% of the variability in the data with the first three axes (Figs. 4 and S6). The first
27 axis explained 50% of the overall variability and was most strongly correlated with hedgerow
28 density ($r = 0.98$), land use ($r = -0.94, 0.92, \text{ and } 0.78$ for meadows, corn, and wheat,
29 respectively), geology ($r = -0.70$ for percent of catchment underlain by granite), and NO_3^- ($r =$
30 0.66). The second axis explained 19% of total variability and was positively associated with
31 DOC ($r = 0.88$) and discharge ($R^2 = 0.69$) and negatively associated with NO_3^- ($R^2 = -0.46$).
32 The third axis explained 11 % of total variability and was associated primarily with PO_4^{3-} (R^2

1 = 0.79). Overall, the first axis was determined by physical context (geology and topography
2 represented by the differences in elevation and land use) and the second axis was determined
3 by factors strongly associated with hydrology (discharge, TSS, and DOC). The three
4 catchments showed clear separation along the first axis and varied along the second axis
5 largely within their discrete, first-dimensional boundaries. The main departures along axis
6 three (in the upper right corner of Fig. 4) are from PO_4^{3-} flushing events during dry years
7 (year 1 and year 3).

8 **3.3 Solute dynamics during discharge events**

9 The high-frequency samples collected during six discharge events at S-01 and GS-01
10 revealed a primarily counterclockwise hysteresis for DOC (higher concentration during the
11 falling limb than at the equivalent discharge on the rising limb), a clockwise hysteresis for
12 NO_3^- and PO_4^{3-} , and no clear pattern in NH_4^+ except for large variations during the rising limb
13 of the discharge events (Fig. S10). DOC and NO_3^- concentrations during discharge events
14 were strongly negatively correlated (Figs. S11 and S12), with the elements showing nearly
15 mirror-image responses to changes in discharge. NO_3^- concentration was highest and DOC
16 was lowest at or immediately after the start of the discharge event, except for GS-01 during
17 the largest two discharge events that were sampled in April 1998 when NO_3^- was higher and
18 DOC was lower after the event (Figs. S9, S10). DOC concentration was higher during the
19 second storm pulse than the first for that compound event. Maximum PO_4^{3-} concentration
20 typically occurred after the NO_3^- peak, but before the maximum discharge, except for S-01 in
21 November 1997. Maximum ammonium concentration occurred during the rising limb. DOC
22 was more strongly correlated with discharge for S-01, though DOC increased for both
23 catchments during the rising limb of the hydrograph (Fig. S10). PO_4^{3-} concentration increased
24 strongly at both sites at the onset of the rising limb, with similar peaks for the two subsequent
25 discharge events in S-01 (Fig. S10).

26 **3.4 Inter-annual solute dynamics**

27 The three catchments showed distinct inter-annual dynamics for both hydrology and
28 solute concentrations across the contrasting hydrologic years (Fig. 5). Specific discharge was
29 consistently lowest for catchment GS-01, the steep transition catchment (Fig. 5a). DOC
30 concentration in G-01 was invariant across the dry and wet years, whereas annual median
31 DOC in GS-01 and S-01 generally tracked discharge (Fig. 5b). Highest median DOC

1 concentration occurred in year 3 for all catchments, which was the year of transition from dry
2 to wet conditions and the year with the most high-flow events. Contrary to the high-frequency
3 trends, annual NO_3^- was positively associated with annual discharge for GS-01 and S-01 (Fig.
4 5c). Catchment G-01 was again relatively distinct in its behavior, with stable NO_3^-
5 concentrations across years (Fig. 5d). Annual PO_4^{3-} concentration was negatively correlated
6 with annual discharge across sites, with significantly higher concentrations in dry years (Fig.
7 5e). DSi was similar for catchments G-01 and S-01 but was consistently elevated for the steep
8 catchment GS-01 (Fig. 5f).

9 **4 Discussion**

10 To quantify the influence of physical, hydrologic, and anthropogenic controls on surface
11 water quality, we monitored discharge and water chemistry from three agricultural catchments
12 in western France for five years. We hypothesized that carbon and nutrient concentrations
13 would show contrasting responses to topographic and land-use differences due to both distinct
14 sources and transport dynamics across scales. We found that carbon and nutrient dynamics
15 differed between the three study catchments both on event and inter-annual temporal scales.
16 However, spatially, the effect of hydrology on solute concentration was strongly modulated
17 by catchment characteristics such as hedgerow density, agricultural activity, and geology.
18 Because the distribution of agricultural activity in these catchments is largely a consequence
19 of the geologic and topographic context, these factors are the ultimate controls on the
20 retention and release of carbon and nutrients, potentially explaining the decoupling of
21 agricultural activity and water quality observed in small catchments (Burt and Pinay, 2005).

22 **4.1 Proximate and ultimate controls on water quality**

23 The relationship between agricultural practice and hydrologic nutrient flux is strong at the
24 large-basin scale but breaks down at the small-basin scale with widely different water
25 chemistry in catchments with similar land covers (Brookshire et al., 2009; Burt and Pinay,
26 2005; Lefebvre et al., 2007). In our study, this phenomenon is apparent for catchments G-01
27 and GS-01 which have very similar land-use but distinct carbon and nutrient signatures, and
28 for catchments GS-01 and S-01 which have distinct land-use but similar chemical dynamics
29 (Table 2). These differences in carbon and nutrient dynamics can be attributed to catchment
30 characteristics, which modulate the effect of land use on carbon and nutrient dynamics.
31 Granite parent material, such as in G-01, can give rise to thick but relatively acidic soils

1 compared to schist substrate which produces thin and rich soils more conducive to row crop
2 cultivation. Thicker soil and higher surface roughness in catchment G-01 (Fig. S13) increase
3 transient storage and residence time (Kolbe et al., 2016), buffering the catchment to
4 fluctuations in water chemistry. This is reflected in relatively invariant carbon and nutrient
5 chemistry across hydrologic conditions. Conversely, catchments GS-01 and S-01, which are
6 underlain primarily by schist, respond to both short- and long-term hydrologic changes with
7 high concentrations of PO_4^{3-} and NH_4^+ during low flow conditions and strong increases in
8 DOC, sediment, and particulate organic matter during high flows. This pattern held on inter-
9 annual timescales as well, where the catchment on granitic substrate showed remarkable
10 stability, while for the predominantly schist catchments, DOC concentration decreased with
11 discharge in the wettest years.

12 In addition to directly influencing catchment hydrology and nutrient retention, geology
13 and accompanying topographic and geomorphological factors exert a strong control on the
14 distribution of human agriculture, indirectly influencing nutrient loading and disturbance
15 regime. Because farmers and land managers do not randomly select surfaces for cultivation,
16 land use in Brittany and throughout the world closely follows geologic and soil
17 characteristics. Soil fertility is a function of natural weathering processes and land use (Tye et
18 al., 2013). Spatial variability of soil moisture, which is often controlled by topography and
19 soil properties (Yeakley et al., 1998) play important roles in land use distribution and
20 organization. In our study area, the interactions between catchment context and human use
21 have resulted in preferential agricultural development of schist catchments, which
22 unfortunately appear to be more prone to nutrient export.

23 In other contexts, this interaction between risk of human development and resilience to
24 human disturbance can also mitigate impacts of agriculture (such as the preservation of forest
25 in steep, erodible environments; Odgaard et al., 2013), but whether it has a net increase or
26 decrease of human impacts on aquatic ecosystems at a global scale is largely unknown (Zabel
27 et al., 2013; Ramankutty et al., 2008). We hypothesize that the preferential development of
28 certain surfaces would decrease in areas of intense anthropogenic pressure where selectivity
29 decreases as the system reaches saturation (Li et al., 2014), but could strongly influence the
30 distribution of human activity in systems that are expanding or contracting such as the
31 developing world or areas of rural exodus such as much of France. Quantifying the regional
32 effects of the selective development of more or less resilient surfaces would be possible with

1 existing data by intersecting water chemistry datasets with soil and geologic geographic
2 information. This framework would provide guidance at multiple scales for land managers
3 seeking to improve water quality while continuing agricultural production.

4 4.2 Controls on chemistry across scales

5 We present a synthesis of our understanding of carbon and nutrient dynamics in
6 different catchment components in Fig. 6. Based on discharge deconvolution, the connectivity
7 between unsaturated and saturated zones depends on water input to the soil and weathered
8 zone. Organic carbon is consumed by microorganisms and phosphorus is sorbed to soil
9 particles as water moves downward. Conversely, the relative abundance of inorganic nitrogen
10 (particularly NO_3^-) increases due to mineralization and nitrification, shifting the nutrient
11 stoichiometry. Consequently, nutrient concentration in streams depends on the connectivity
12 and thickness of those layers, which determine stoichiometry, and typical water velocity,
13 which determines solute flux. By modulating the connectivity between the hydrologic
14 compartments, discharge regime controls nutrient export (DOC and PO_4^{3-} increasing with
15 discharge and NO_3^- decreasing). On shorter timescales, sinusoidal nutrient fluctuations result
16 from discrete storm events. Various pathways and interaction between hillslope and stream
17 are affected to a lesser extent by discharge regime (Fig. 6). Groundwater fluxes toward the
18 stream may also control nutrient concentration especially for NO_3^- which is relatively highest
19 in this compartment (Fig. 6).

20 Different mechanisms can influence short- and long-term elemental fluxes (Moatar and
21 Meybeck, 2012; Moatar et al., 2013), explaining the contrasting short- and long-term
22 dynamics observed within individual catchments. For example, conditions that favor frequent
23 flushing of soil may decrease short-term NO_3^- concentration but result in larger overall fluxes.
24 In our study, NO_3^- concentration showed a non-linear decrease with discharge on short
25 timescales but was higher in wetter years (Fig. 5), potentially due to changing NO_3^- sources.
26 The convergence of NO_3^- , Cl^- , and DSi concentrations across catchments during high-flow
27 periods (Figs. 2, 3 and Figs. S7, S8) implies a shift from catchment-scale controls on water
28 chemistry during low flows to larger inter-catchment controls during high flows. The upper
29 layer of the Brioverian schist substrate beneath these drainage basins is composed of
30 unconsolidated weathered substrate of variable thickness that could provide an inter-basin
31 solute source during storms. This shallow, unconfined aquifer has NO_3^- values that
32 correspond to those measured at the catchment outlets during high-water periods (Clément et

1 al., 2003) and in other regional aquifers (Molénat et al., 2008). The lack of significant dilution
2 of NO_3^- and Cl^- during discharge events, and the increase in DOC concentrations, suggest that
3 high flow is composed of both groundwater, presumably from the Brioverian schist, and
4 shallow subsurface flow (Grimaldi et al., 2009; Grimaldi et al., 2012), including through the
5 sub-soil weathered layer (Iwagami et al., 2010). The NO_3^- mobilized during storms may
6 already be present or could result from mineralization and nitrification as the soils wet up.
7 The lower, but also constant, concentration of NH_4^+ measured during high-water periods
8 supports the hypothesis of high nitrogen mineralization from soil organic matter during these
9 mild and humid periods and high NH_4^+ retention in soil. Nitrification of NH_4^+ to NO_3^- during
10 these same periods could maintain NO_3^- supply, assuming that soils do not become water
11 logged and anoxic. The relationship between NO_3^- and NH_4^+ concentrations with discharge
12 during high water period (Fig. 3 and Fig. S8) follows a logarithmic or linear trend,
13 underlining the importance of soil as an active nitrogen source during high-flow periods since
14 the NH_4^+ concentration in groundwater is low. These differences in short- and long-term
15 dynamics highlight the importance of considering management goals when designing water
16 quality monitoring strategies, with high-frequency monitoring during extreme flows necessary
17 to identify peak concentrations and lower-frequency, long-term monitoring more appropriate
18 for evaluating annual loads.

19 The divergent response of chemistry across temporal scales can give insight into
20 sources and pathways of carbon and nutrients. For catchments GS-01 and S-01, DOC
21 increased strongly with discharge at both event and inter-annual scales (Figs. 2 and 5).
22 However, high concentrations of DON and DOP were only observed at low-flows (Fig. S7).
23 This shift in dissolved organic matter (DOM) stoichiometry indicates a change in DOC
24 sources, with stormflow dominated by plant-derived DOM from surface soils and baseflow
25 dominated by microbial DOM from deeper soils and shallow groundwater (Inamdar et al.,
26 2012; Yang et al., 2015). The rapid increase of DOC concentration early in discharge events,
27 followed by a plateau at high discharge indicates source-limitation of DOC, potentially due to
28 changes in contributing area. In colluvial soils such as our study area, riparian wetlands are
29 the major source of DOC to the stream, based on ^{13}C and molecular analysis of DOC
30 (Jeanneau et al., 2014; Lambert et al., 2014). At the beginning of a storm event, this riparian
31 DOC is readily transported to the stream, but increased discharge connects upslope soils,
32 which tend to be poorer in organic carbon, resulting in a plateau (Walter and Mérot, 2007;
33 Laudon et al., 2011). High DOC concentration in these headwater agricultural streams

1 highlights the importance of understanding carbon production and transport dynamics in
2 small freshwater systems (Agren et al., 2007; Cole et al., 2007).

3 **4.3 Hedgerow density and vegetation effect on soil and shallow groundwater**

4 We found that the effect of hydrology on solute concentration was strongly modulated by
5 hedgerow density, which was the strongest predictor of stream chemistry in the PCA. There
6 was less variation in carbon and nutrient concentrations for the highest hedgerow density
7 catchment G-01. Hedgerows exert multiple controls on hydrology and biology (Mérot and
8 Bruneau, 1993). Because vegetation is one of the major controls on water and energy balance,
9 the removal or redistribution of vegetation with land use alters albedo and evapotranspiration
10 (Davin et al., 2007). Vegetation plays a central role in the interface between the atmosphere
11 and groundwater via water uptake by roots and redistribution of water in the soil column,
12 affecting soil moisture and groundwater recharge. Increased transpiration (Thomas et al.
13 2012) and interception (Ghazavi et al., 2008) by hedgerows can decrease soil moisture at a
14 local scale, potentially reducing the transfer of carbon and nutrients from soils to groundwater
15 or surface waters. Indeed, the relatively dry soil beneath hedgerows (Caubel et al., 2001;
16 Thomas et al., 2008) corresponds with lower soil and groundwater NO_3^- concentration
17 (Grimaldi et al., 2012). Enhanced NO_3^- removal and retention by hedgerows could be due to
18 both increased variability in soil moisture and longer residence time, which create local
19 microsites for denitrification (Parkin, 1987) and increase likelihood of uptake. In our study
20 area, hedgerow density is also associated with geologic and topographic parameters. In
21 catchments S-01 and GS-01, where soils are more suitable for intensive agriculture,
22 hedgerows were removed to consolidate fields during the post-war period. While our study
23 cannot untangle the relative impacts of hedgerow density and geology, it does suggest that
24 hedgerow density can impact NO_3^- mass balance at larger scales.

25 **5 Conclusions**

26 Proximate and ultimate controls on carbon and nutrient concentrations differ across
27 spatial and temporal scales, revealing distinct sources and transport dynamics for different
28 elements. Thicker soils and higher surface roughness for catchments underlain by granite
29 buffer fluctuations in water chemistry at both event and inter-annual scales, potentially due to
30 increased transient storage and residence time from higher roughness and hedgerow density.
31 Conversely, nutrient concentrations in catchments on schist substrates are highly sensitive to

1 changes in hydrology. However, the convergence of water chemistry between catchments
2 during discharge events suggests larger, regional influences independent of geology and
3 topography.

4 Direct human impact on a catchment (fertilizer input, soil disturbance, urbanization) is
5 asymmetrically linked with inherent catchment properties (geology, soil, topography), which
6 together determine catchment resilience or vulnerability to human activity. The effect of
7 hydrology on solute concentration is proximately controlled by catchment characteristics such
8 as hedgerow density and agricultural activity, but because the distribution of agricultural land
9 use in these catchments is largely a consequence of the geologic and topographic context,
10 these are the ultimate controls on retention and release of carbon and nutrients. This link
11 between inherent catchment buffering capacity and probability of human disturbance provides
12 a useful perspective for evaluating vulnerability of aquatic ecosystems and for managing
13 systems to **maintain** production while minimizing leakage of nutrients.

14 **Author contribution**

15 Pinay and Baudry designed the experiments. Troccaz carried them out. Thomas and
16 Abbott analyzed the data and prepared the manuscript with contributions from all co-authors.

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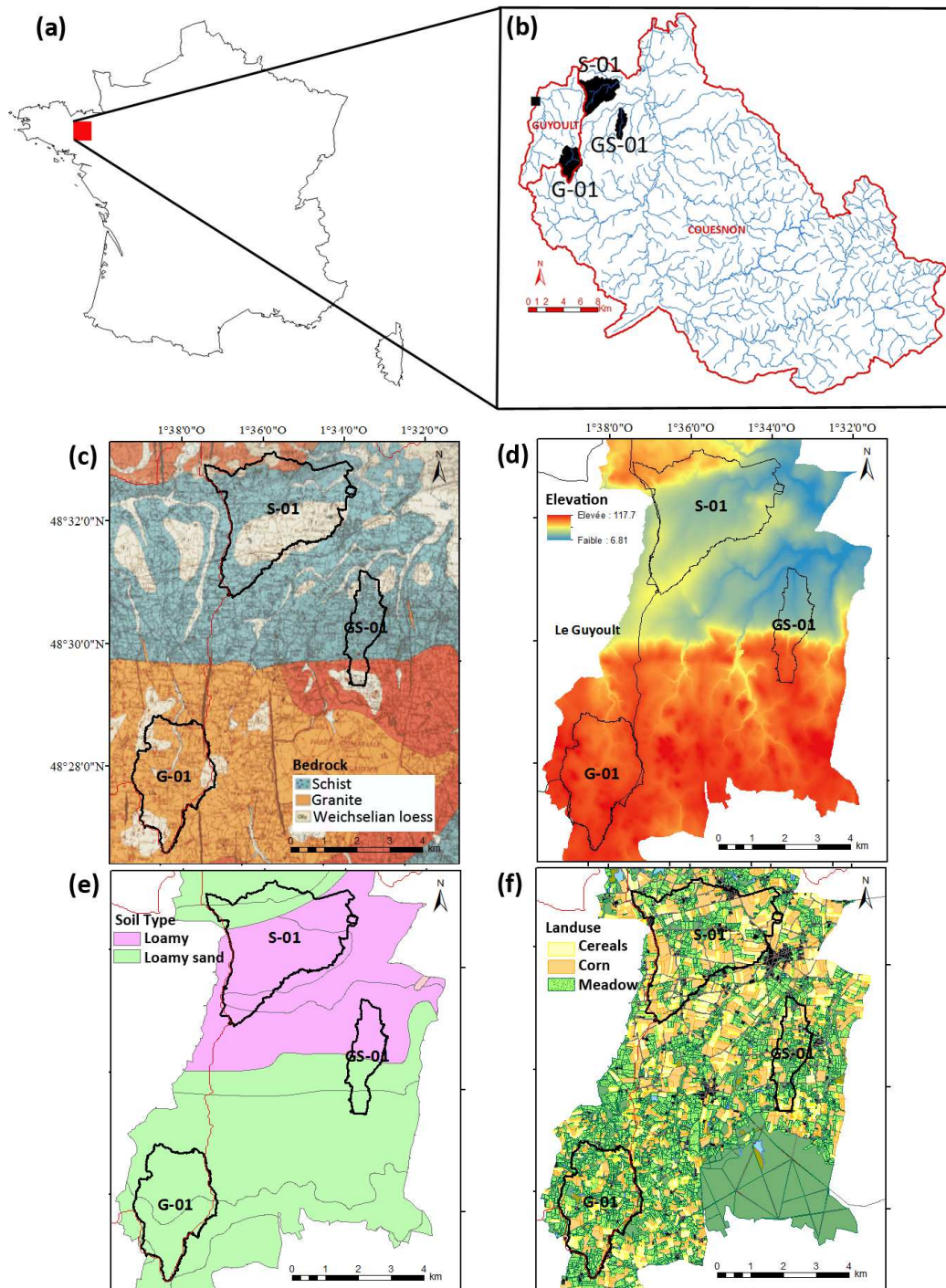
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22
23

		Catchment		
		G-01	GS-01	S-01
Soil	Depth (m)	≥0.8	0.7-0.8	0.45-0.7
Topography	Upstream Elevation (m)	110.0	105.0	60.0
	Downstream Elevation (m)	85.0	12.5	14.5
	Difference in elevation (m)	25.0	92.5	45.5
Bedrock	Granite (% of area)	100.0	17.0	6.0
	Schist (% of area)	0.0	83.0	94.0
Hydrology	Drainage area (km ²)	6.4	2.3	10.8
	Basin	Le Guyout	Couesnon	
Land use	% Corn	21.3 (3.2)	26.4 (1.4)	32.8 (6.6)
	% Wheat	11.5 (2.0)	11.5 (3.5)	23.0 (5.1)
	% Pasture or forest	65.9 (6.8)	61.5 (11.5)	41.8 (4.6)
	Hedgerow density (m ha ⁻¹)	104.72	82.76	49.77

1 Table 1. Catchment characteristics for the catchments on granite (G-01), schist (S-01), and
2 mixed (GS-01) substrate. Mean (standard deviation) of the % of corn, cereals, meadows and
3 woods on arable land use were determined from annual aerial photographs taken during the 5-
4 year study period.

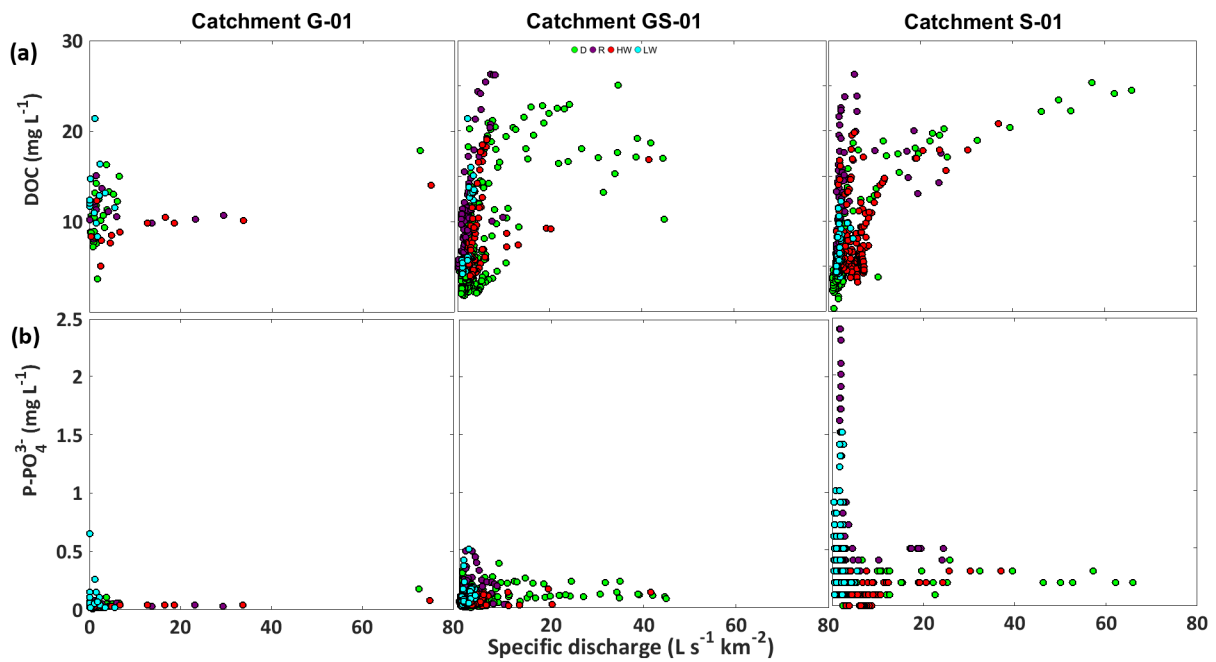
Catchment G-01	Q	NO ₃ ⁻	NH ₄ ⁺	PO ₄ ³⁻	DSi	DOC
NO ₃ ⁻	-0.06					
NH ₄ ⁺	0.14	-0.08				
PO ₄ ³⁻	-0.1	-0.09	0.1			
DSi	-0.11	0.23	0.18	0.28		
DOC	0.1	-0.33	-0.12	0.48	0.14	
TSS	-0.04	-0.16	-0.01	0.37	0.22	0.46
Catchment GS-01	Q	NO ₃ ⁻	NH ₄ ⁺	PO ₄ ³⁻	DSi	DOC
NO ₃	-0.24					
NH ₄	-0.1	0.01				
PO ₄	0.18	-0.30	0.1			
DSi	-0.08	-0.13	0.04	0.05		
DOC	0.49	-0.62	0.02	0.62	0.13	
TSS	0.23	-0.08	0.12	0.59	-0.16	0.42
Catchment S-01	Q	NO ₃ ⁻	NH ₄ ⁺	PO ₄ ³⁻	DSi	DOC
NO ₃	-0.14					
NH ₄	-0.07	-0.16				
PO ₄	-0.48	-0.31	0.23			
DSi	-0.16	-0.11	0.25	0.43		
DOC	0.51	-0.28	0.28	0.22	0.31	
TSS	0.22	-0.17	0.13	0.18	0.23	0.48

1 Table 2. Spearman's rank correlations for water chemistry parameters. Significant
2 correlations ($p < 0.05$, Bonferroni-corrected) are in bold.

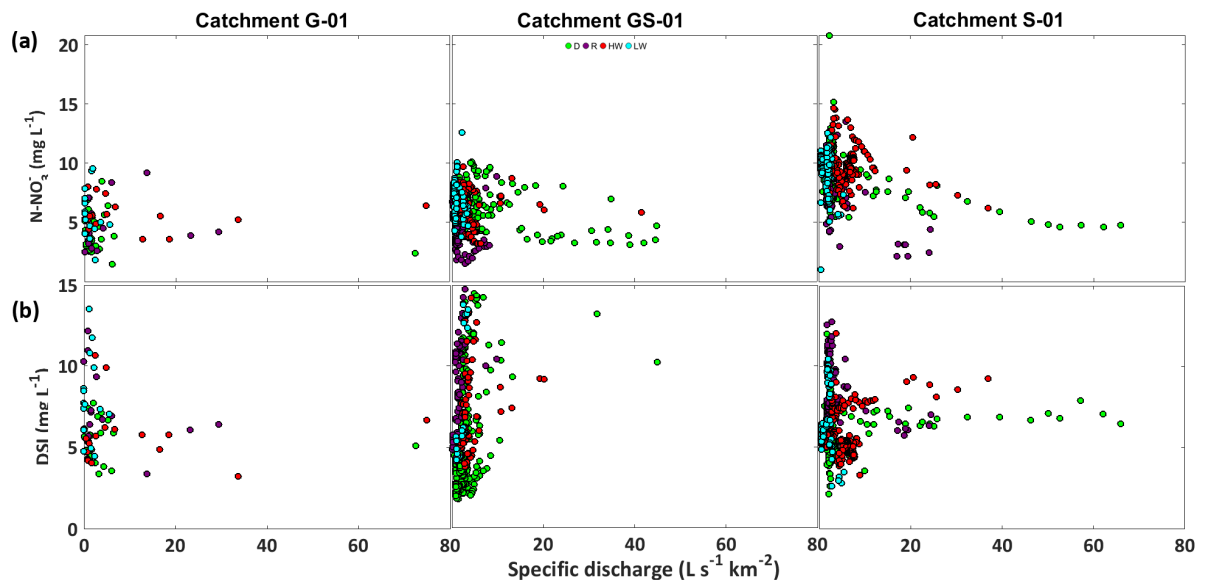


1

2 **Figure 1. Location and physical characteristics of the three study catchments. (a) The**
 3 **red square delineates the *Zone Atelier Armorique LTSEr* on the map of France. (b) The**
 4 **catchment G-01 is a subcatchment of *Le Guyoult* basin (gauged outlet indicated by black**
 5 **square). The two catchments GS-01 and S-01 are subcatchments of the *Couesnon* basin.**
 6 **(c) Geological overview showing granite in the south and schist in the north. (d) Digital**
 7 **Elevation Model from LIDAR with a 2m resolution. (e) Land use from the last year of**
 8 **studied period (*i.e.* 2000). (f) Map of soil type.**



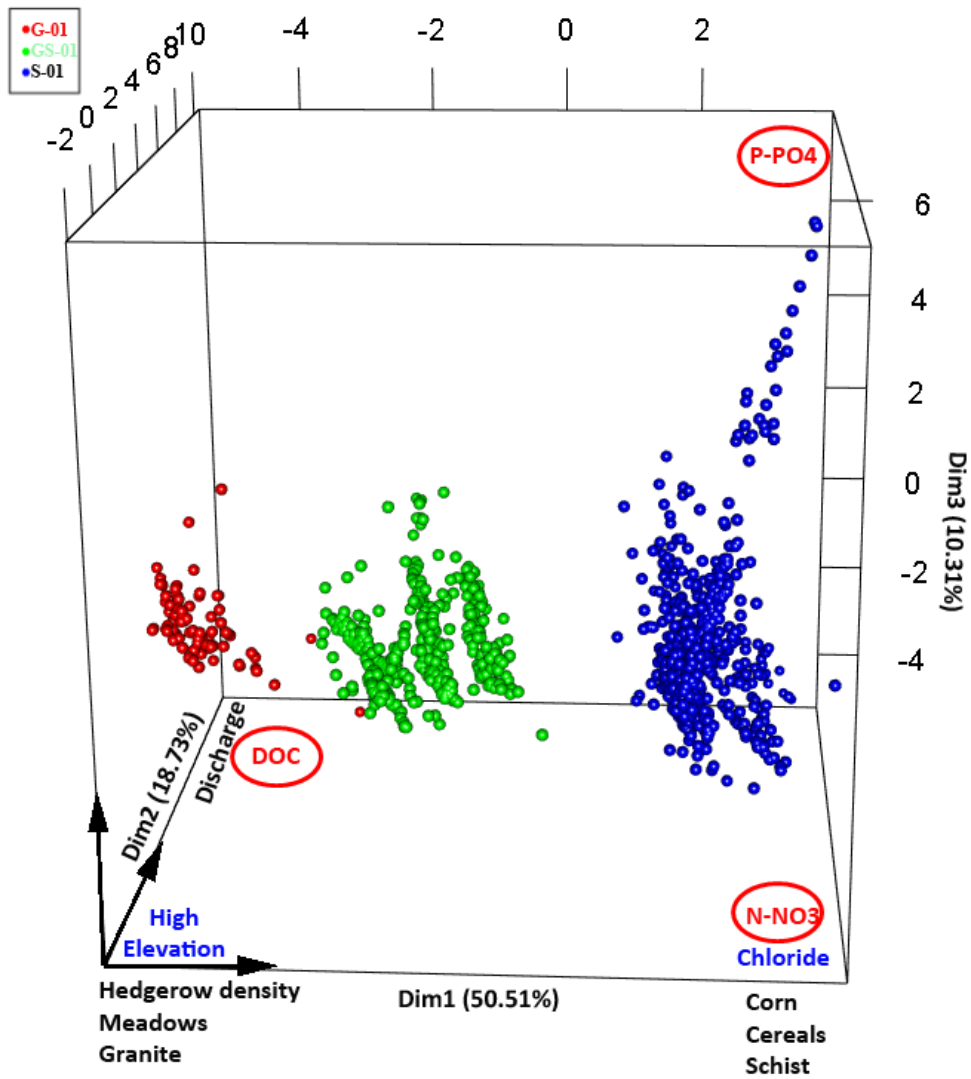
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 2 Figure 2. Relationship between **specific** discharge and (a) dissolved organic carbon, and (b)
 3 phosphate, for three headwater catchments G-01, GS-01, and S-01, in Brittany France.
 4 Chemistry data from daily automatic sampling supplemented by sub-daily sampling for
 5 catchments GS-01 and S-01 during discharge events (see methods for detailed sampling
 6 description). **Data are colored by hydrologic period: D=discharge (April-June), LW=low**
 7 **water (July-September), R=recharge (October-December), HW=high water (January-March).**
 8



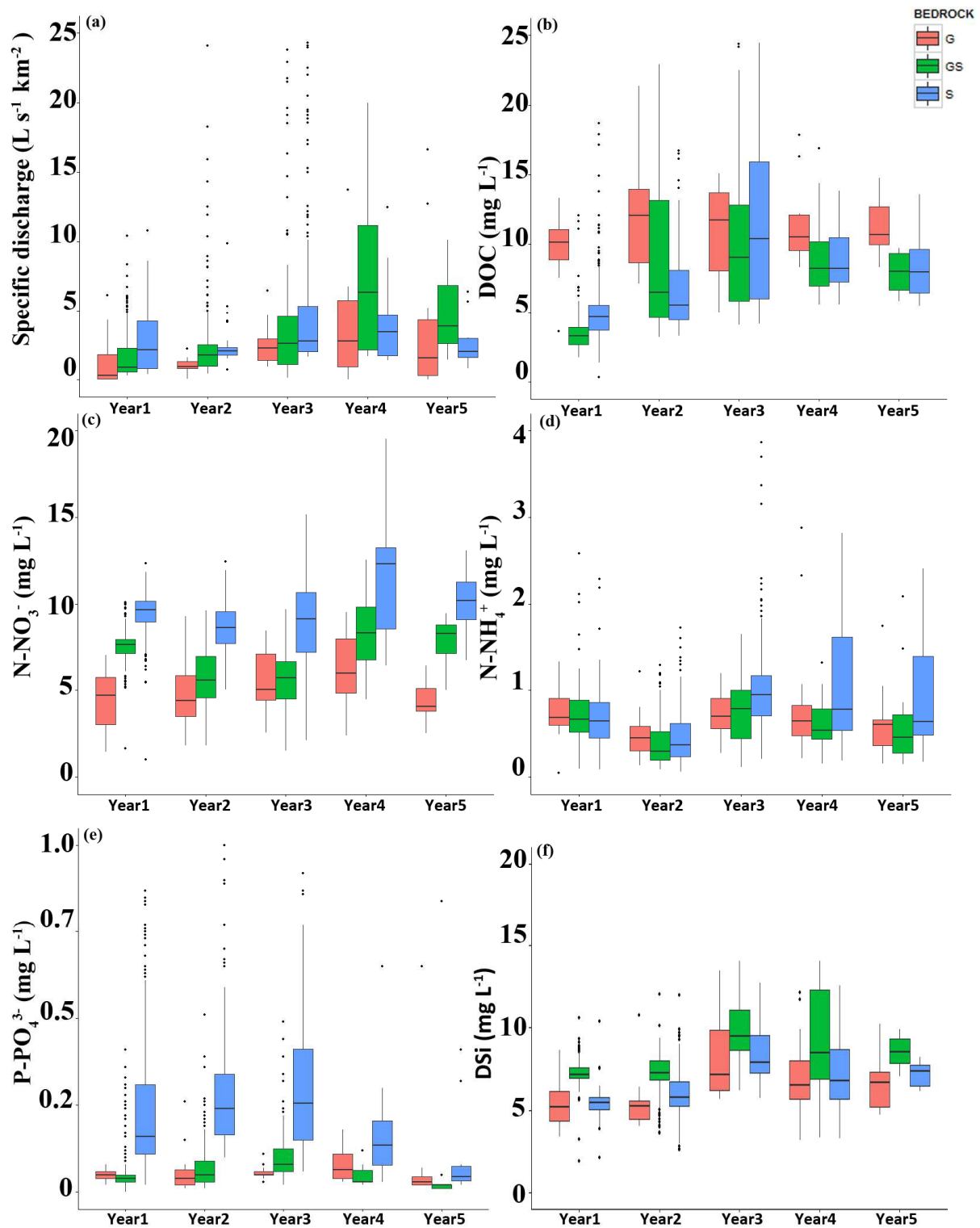
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2 Figure 3. Relationship between **specific** discharge and (a) nitrate, and (b) dissolved silica for
 3 three headwater catchments G-01, GS-01, and S-01, in Brittany France. Chemistry data from
 4 daily automatic sampling supplemented by sub-daily sampling for catchments GS-01 and S-
 5 01 during discharge events (see methods for detailed sampling description). **Data points are**
 6 **colored by hydrologic period** (see Fig. 2 for definitions).

7

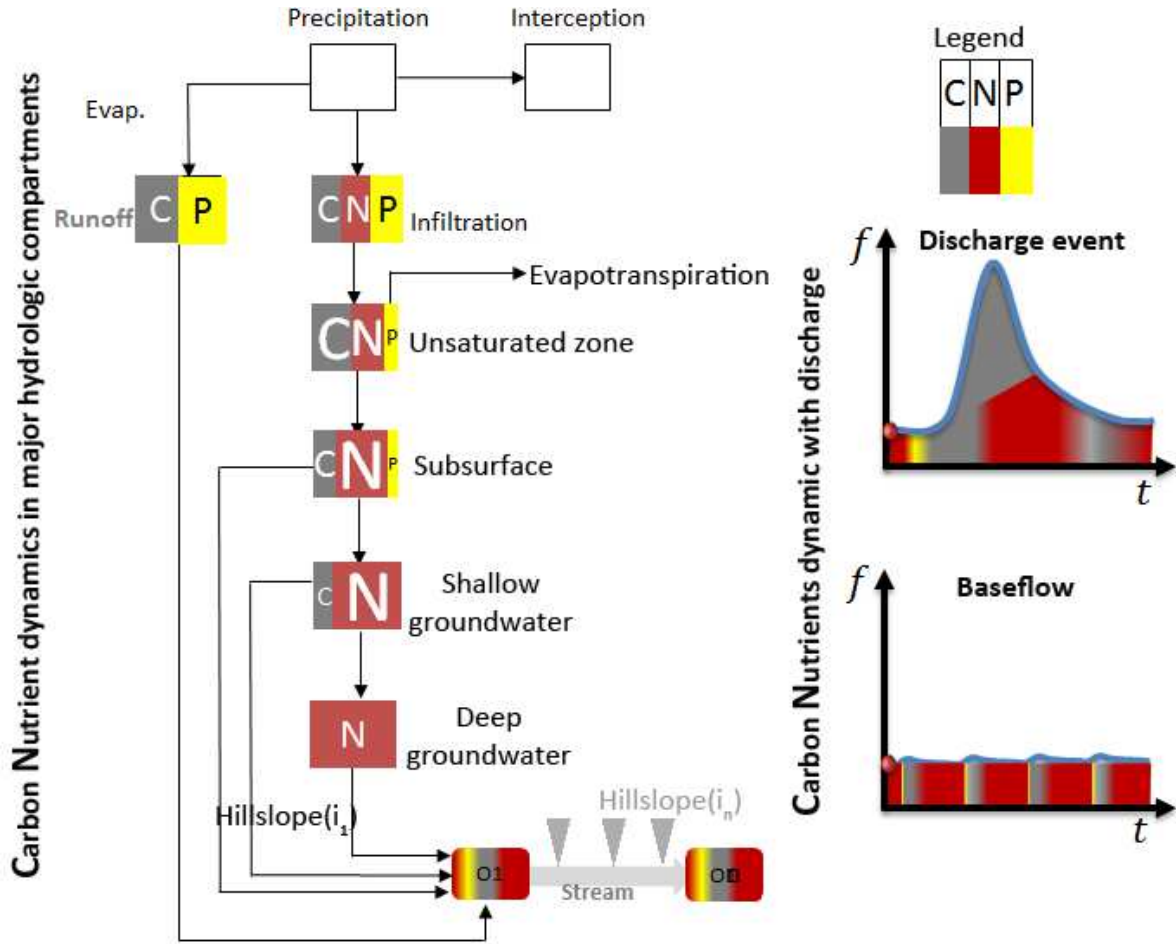


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 2 Figure 4. Principle components analysis of the major sources of variability in water
 3 chemistry. Together, the first-three axes explain 80% of the total variability of the data.
 4 Principal and supplementary variables are indicated respectively in black and blue. Red
 5 circles indicate the poles of carbon, nitrogen, and phosphorus associated with cereals and corn
 6 for N-NO_3^- , high discharge on granite bedrock for DOC, and both discharge and agricultural
 7 land use for P-PO_4^{3-} . PCA scores are indicated in the supplemental table S3.



1
 2 Figure 5. Discharge and carbon and nutrient concentrations during 5 contrasting hydrological
 3 years. Boxplots of (a) Specific discharge, (b) dissolved organic carbon, (c) nitrate⁻, (d)
 4 ammonium, (e) phosphate, and (f) dissolved silica for the catchments G-01 (red box), GS-01
 5 (green box), and S-01 (blue box). Box plots represent median, quartiles, minimum and
 6 maximum within 1.5 times the interquartile range, and outliers beyond 1.5 interquartile range.

1



2

3 Figure 6. **Conceptual model** of carbon and nutrient dynamics in major hydrologic
 4 compartments during transient (discharge events) and steady state (baseflow) discharge
 5 regimes. **On the left side, we represent the relative abundance of carbon, nitrogen, and**
 6 **phosphate during vertical transport through soil, unsaturated zone, and groundwater. Arrows**
 7 **represent flowpaths, which can either descend through the soil column or lead directly to the**
 8 **stream (represented at the bottom of the figure), which experiences fluctuations in water**
 9 **chemistry based on the relative contribution of these flowpaths from multiple hillslopes. On**
 10 **the right side of the figure, schematic representations of stream chemistry during stormflow**
 11 **and baseflow. The colors represent carbon, nitrogen, and phosphorus concentration which**
 12 **vary depending on hydrologic conditions. See section 4.2 in the discussion for more detailed**
 13 **interpretation.**