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

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Abstract

Direct and indirect effects from human activity have dramatically increased nutrient loading to aquatic inland and estuarine ecosystems. Despite an abundance of studies investigating the impact of agricultural activity on water quality, our understanding of what determines the capacity of a watershed to remove or retain nutrients remains limited. The goal of this study was to identify proximate and ultimate controls on dissolved organic carbon and nutrient dynamics in small agricultural catchments by investigating the relationship between catchment characteristics, stream discharge, and water chemistry. We analyzed a five-year, high-frequency water chemistry dataset from 3 catchments ranging from 2.3 to 10.8 km² in western France. The relationship between hydrology and solute concentrations differed between the three catchments, associated with hedgerow density, agricultural activity, and geology. The catchment with thicker soil and higher surface roughness had relatively invariant carbon and nutrient chemistry across hydrologic conditions, indicating high resilience to human disturbance. Conversely, the catchments with smoother, thinner soils responded to both intra- and inter-annual hydrologic variation with high concentrations of PO_4^{3-} and NH_4^+ in streams during low flow conditions and strong increases in DOC, sediment, and particulate organic matter during high flows. Despite contrasting agricultural activity between catchments, the physical context (geology, topography, and land-use configuration) appeared to be the most important determinant of catchment solute dynamics based on principle components analysis. The influence of geology and accompanying topographic and geomorphological factors on water quality was both direct and indirect because the distribution of agricultural activity in these catchments is largely a consequence of the geologic and topographic context. This link between inherent catchment buffering capacity and probability of human disturbance provides a useful perspective for evaluating vulnerability of aquatic ecosystems and for managing systems to maintain agricultural production while minimizing leakage of nutrients.

1 Introduction

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

The capacity of a watershed to remove or retain nutrients is a function of biotic and abiotic conditions encountered as water flows through the soil, groundwater, riparian zone, hyporheic zone, and stream channel itself (Brookshire *et al.*, 2009; Seitzinger *et al.*, 2006; Sébilo et al., 2013; Pinay *et al.* 2015). For catchments larger than 100 km^2, riverine nutrient fluxes are tightly associated with percentage of agricultural cover (Jordan et al., 1997; Omernik et al., 1981; Strayer et al., 2003). However in drainage basins smaller than 10 km^2, nutrient fluxes vary widely despite similar land cover (Brookshire et al., 2009; Burt and Pinay, 2005; Lefebvre et al., 2007 Groffman et al., 2006; Sebilo, et al. 2013). This breakdown in the relationship between land cover and nutrient flux represents an important ecological uncertainty since 90% of global stream length occurs in catchments smaller than 15 km^2 (Bishop et al., 2008). It also highlights a practical problem, because though most water-quality monitoring takes place in large rivers, most land-management decisions are made at the parcel or small-catchment scale (Thenail et al., 2009). The diversity in headwater-catchment response to nutrient loading also represents an opportunity to identify the mechanistic controls regulating nutrient processing and removal.

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

2 Methods

2.1 Study area

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

2.2 Catchment characteristics and experimental design

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

We measured water flow and chemistry over 5 hydrologic years (from 10 April 1996 to 20 August 2000) at the outlets of the S-01 and GS-01 catchments with an automated sampler (Isco 3700™) controlled by a data logger (Campbell Scientific CR10™). Stage was continuously monitored using pressure transducers and discharge was calculated from rating curves determined by manual gauging with an impellor flow meter and by salt dilution (Day, 1976; Hongve, 1987). Additionally discharge was determined at the gaged station situated at the outlet of the Guyoult bassin (station J0323010) as a part of national environmental monitoring (DREAL).

2.3 Water quality analyses

Water samples were collected every 12 hours during baseflow for the first year, every 3 days for the following 2 years, and monthly for the last 2 years with automatic samplers. For catchments GS-01 and S-01, we programmed autosamplers to trigger more frequent sampling during discharge events, with samples taken every 30 minutes during the rising limb and every 3 hours during the falling limb. High-frequency sampling was triggered when the water level (h) changed more than 0.3 cm in one minute. h was measured every minute with a moving hourly mean (h_{mean}) calculated continuously. For each minute t, the trigger level $dh_{(t)}$ was determined as:

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

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

Water samples were filtered with 0.7 µm effective pore size glass fiber filters and stored at 4°C until analysis. Samples were analyzed for DOC, NO_3^-, NH_4^+, $P0_4^{3-}$, dissolved silica (DSi), particulate phosphorus (PP), dissolved organic phosphorus (DOP), dissolved organic nitrogen (DON), and chloride (Cl^-). DOC was analyzed with a Shimadzu TOC analyzer and nutrients were analyzed on a Lachat Quick Chem autoanalyser. NO_3^- was quantified with the modified Griess-Ilosvay method with copperized cadmium reduction, NH_4^+ by indophenol blue method, PO_4^{3-} by automatic ascorbic acid method, DSi by molybdosilicate colorimetric method, and Cl^- by colorimetric N-diethyl-p-phenylenediamine method. Total suspended sediment (TSS) was determined by filtering one liter to 0.7 µm and weighing the filter.

2.4 Spatial data and statistical analysis

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

$$R = \frac{\mathrm{Mean_{DEM}} - \mathrm{Min_{DEM}}}{\mathrm{Max_{DEM}} - \mathrm{Min_{DEM}}}, \quad 0<R<1$$

Land use was mapped annually from aerial imagery from 1996-2000, with ground validation. Forest and pastureland were distinguished from cultivated land, and corn was distinguished from other cereal crops (predominantly wheat but also barley; hereafter wheat) based on color and timing of planting and harvest. Total agricultural coverage was calculated as the sum of all corn, wheat, and other crops. The Web Map Service (WMS) of the *Bureau* *de Recherches Géologiques et Minières* (BRGM) was used for the geological map of the study area.

We performed a principle components analysis (PCA) to characterize correlations in the data and identify major sources of variability in water chemistry. We included morphological parameters (geology, topography, soil depth, density of hedgerows), land use, and solute concentrations. Specifically we included bedrock (% granite and schist), land use (wheat, corn, and pastureland), stream order (Strahler 1952), drainage area, difference in elevation between upstream and downstream (dZ), and concentrations of DOC, NO_3^-, PO_4^{3-}, Cl^-, and DSi. We also performed Spearman's rank correlations to test for individual correlations between water chemistry parameters. All analyses were performed in R 3.0.2 (R Core Team, 2014) with the FactoMineR package for PCA (Lê and Husson, 2008).

3 Results

3.1 Hydrological and land-use analysis

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

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

3.2 Effects of catchment characteristics on water chemistry

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

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

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

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

3.3 Solute dynamics during discharge events

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

3.4 Inter-annual solute dynamics

The three catchments showed distinct inter-annual dynamics for both hydrology and solute concentrations across the contrasting hydrologic years (Fig. 5). Specific discharge was consistently lowest for catchment GS-01, the steep transition catchment (Fig. 5a). DOC concentration in G-01 was invariant across the dry and wet years, whereas annual median DOC in GS-01 and S-01 generally tracked discharge (Fig. 5b). Highest median DOC concentration occurred in year 3 for all catchments, which was the year of transition from dry to wet conditions and the year with the most high-flow events. Contrary to the high-frequency trends, annual NO_3^- was positively associated with annual discharge for GS-01 and S-01 (Fig. 5c). Catchment G-01 was again relatively distinct in its behavior, with stable NO_3^- concentrations across years (Fig. 5d). Annual PO_4^{3-} concentration was negatively correlated with annual discharge across sites, with significantly higher concentrations in dry years (Fig. 5e). DSi was similar for catchments G-01 and S-01 but was consistently elevated for the steep catchment GS-01 (Fig. 5f).

4 Discussion

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

4.1 Proximate and ultimate controls on water quality

The relationship between agricultural practice and hydrologic nutrient flux is strong at the large-basin scale but breaks down at the small-basin scale with widely different water chemistry in catchments with similar land covers (Brookshire et al., 2009; Burt and Pinay, 2005; Lefebvre et al., 2007). In our study, this phenomenon is apparent for catchments G-01 and GS-01 which have very similar land-use but distinct carbon and nutrient signatures, and for catchments GS-01 and S-01 which have distinct land-use but similar chemical dynamics (Table 2). These differences in carbon and nutrient dynamics can be attributed to catchment characteristics, which modulate the effect of land use on carbon and nutrient dynamics. Granite parent material, such as in G-01, can give rise to thick but relatively acidic soils compared to schist substrate which produces thin and rich soils more conducive to row crop cultivation. Thicker soil and higher surface roughness in catchment G-01 (Fig. S13) increase transient storage and residence time (Kolbe et al., 2016), buffering the catchment to fluctuations in water chemistry. This is reflected in relatively invariant carbon and nutrient chemistry across hydrologic conditions. Conversely, catchments GS-01 and S-01, which are underlain primarily by schist, respond to both short- and long-term hydrologic changes with high concentrations of PO_4^{3-} and NH_4^+ during low flow conditions and strong increases in DOC, sediment, and particulate organic matter during high flows. This pattern held on inter-annual timescales as well, where the catchment on granitic substrate showed remarkable stability, while for the predominantly schist catchments, DOC concentration decreased with discharge in the wettest years.

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

In other contexts, this interaction between risk of human development and resilience to human disturbance can also mitigate impacts of agriculture (such as the preservation of forest in steep, erodible environments; Odgaard et al., 2013), but whether it has a net increase or decrease of human impacts on aquatic ecosystems at a global scale is largely unknown (Zabel et al., 2013; Ramankutty et al., 2008). We hypothesize that the preferential development of certain surfaces would decrease in areas of intense anthropogenic pressure where selectivity decreases as the system reaches saturation (Li et al., 2014), but could strongly influence the distribution of human activity in systems that are expanding or contracting such as the developing world or areas of rural exodus such as much of France. Quantifying the regional effects of the selective development of more or less resilient surfaces would be possible with existing data by intersecting water chemistry datasets with soil and geologic geographic information. This framework would provide guidance at multiple scales for land managers seeking to improve water quality while continuing agricultural production.

4.2 Controls on chemistry across scales

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

Different mechanisms can influence short- and long-term elemental fluxes (Moatar and Meybeck, 2012; Moatar et al., 2013), explaining the contrasting short- and long-term dynamics observed within individual catchments. For example, conditions that favor frequent flushing of soil may decrease short-term NO_3^- concentration but result in larger overall fluxes. In our study, NO_3^- concentration showed a non-linear decrease with discharge on short timescales but was higher in wetter years (Fig. 5), potentially due to changing NO_3^- sources. The convergence of NO_3^-, Cl^-, and DSi concentrations across catchments during high-flow periods (Figs. 2, 3 and Figs. S7, S8) implies a shift from catchment-scale controls on water chemistry during low flows to larger inter-catchment controls during high flows. The upper layer of the Brioverian schist substrate beneath these drainage basins is composed of unconsolidated weathered substrate of variable thickness that could provide an inter-basin solute source during storms. This shallow, unconfined aquifer has NO_3^- values that correspond to those measured at the catchment outlets during high-water periods (Clément et al., 2003) and in other regional aquifers (Molénat et al., 2008). The lack of significant dilution of NO_3^- and Cl^- during discharge events, and the increase in DOC concentrations, suggest that high flow is composed of both groundwater, presumably from the Brioverian schist, and shallow subsurface flow (Grimaldi et al., 2009; Grimaldi et al., 2012), including through the sub-soil weathered layer (Iwagami et al., 2010). The NO_3^- mobilized during storms may already be present or could result from mineralization and nitrification as the soils wet up. The lower, but also constant, concentration of NH_4^+ measured during high-water periods supports the hypothesis of high nitrogen mineralization from soil organic matter during these mild and humid periods and high NH_4^+ retention in soil. Nitrification of NH_4^+ to NO_3^- during these same periods could maintain NO_3^- supply, assuming that soils do not become water logged and anoxic. The relationship between NO_3^- and NH_4^+ concentrations with discharge during high water period (Fig. 3 and Fig. S8) follows a logarithmic or linear trend, underlining the importance of soil as an active nitrogen source during high-flow periods since the NH_4^+ concentration in groundwater is low. These differences in short- and long-term dynamics highlight the importance of considering management goals when designing water quality monitoring strategies, with high-frequency monitoring during extreme flows necessary to identify peak concentrations and lower-frequency, long-term monitoring more appropriate for evaluating annual loads.

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

4.3 Hedgerow density and vegetation effect on soil and shallow groundwater

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

5 Conclusions

Proximate and ultimate controls on carbon and nutrient concentrations differ across spatial and temporal scales, revealing distinct sources and transport dynamics for different elements. Thicker soils and higher surface roughness for catchments underlain by granite buffer fluctuations in water chemistry at both event and inter-annual scales, potentially due to increased transient storage and residence time from higher roughness and hedgerow density. Conversely, nutrient concentrations in catchments on schist substrates are highly sensitive to changes in hydrology. However, the convergence of water chemistry between catchments during discharge events suggests larger, regional influences independent of geology and topography.

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

Author contribution

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

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		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 Guyoult	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

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

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

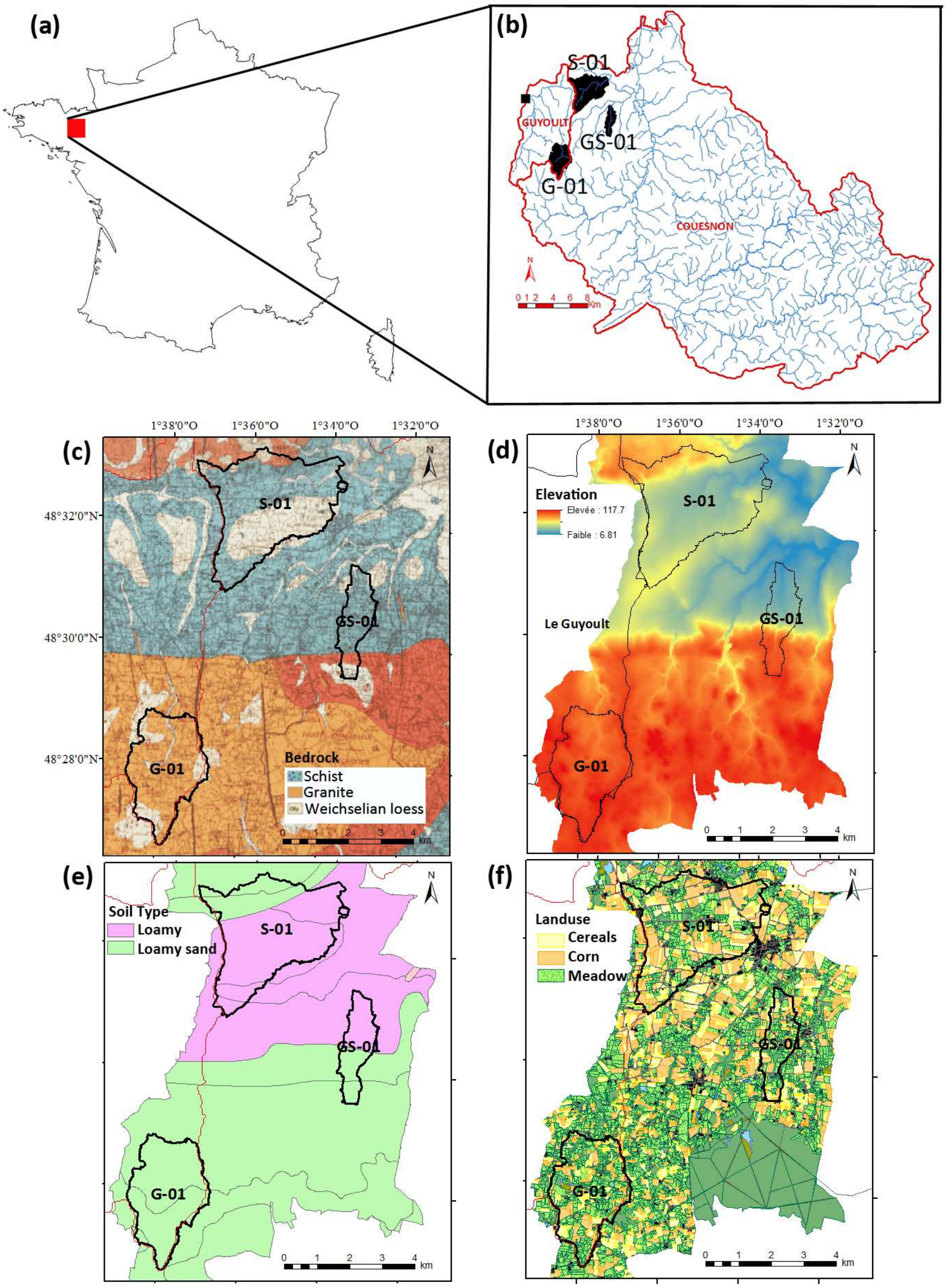

Figure 1. Location and physical characteristics of the three study catchments. (a) The red square delineates the *Zone Atelier Armorique* **LTSER on the map of France. (b) The catchment G-01 is a subcatchment of *Le Guyoult* basin (gauged outlet indicated by black square). The two catchments GS-01 and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

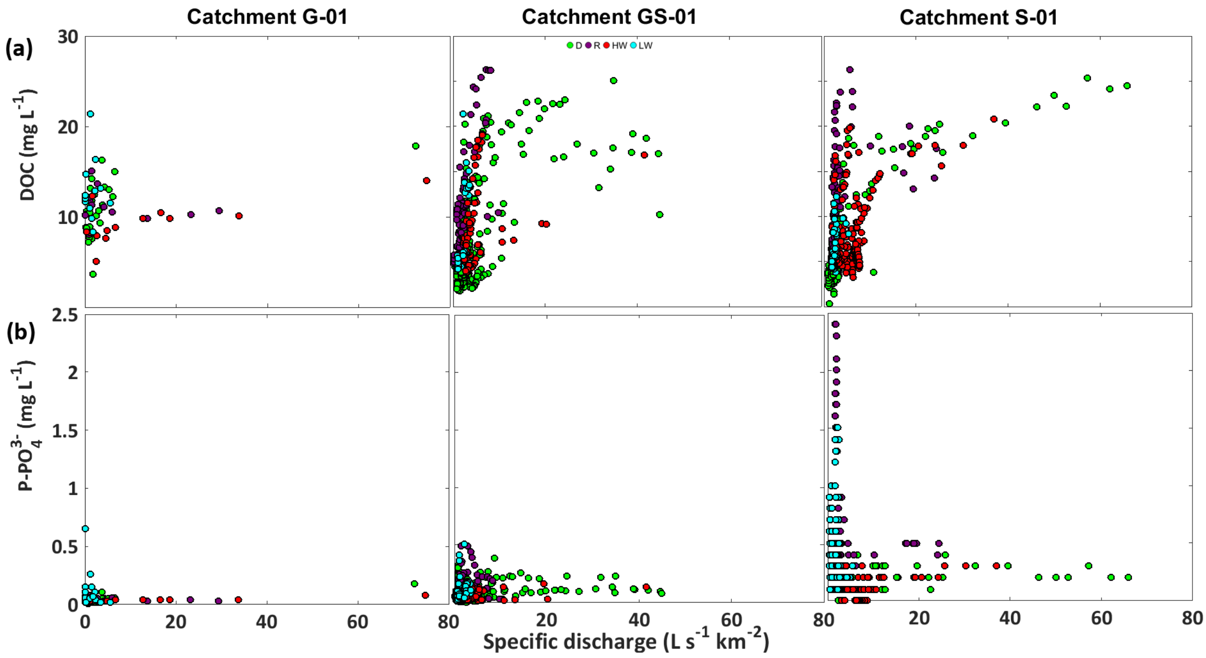

Figure 2. Relationship between specific discharge and (a) dissolved organic carbon, and (b) phosphate, for three headwater catchments G-01, GS-01, and S-01, in Brittany France. Chemistry data from daily automatic sampling supplemented by sub-daily sampling for catchments GS-01 and S-01 during discharge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

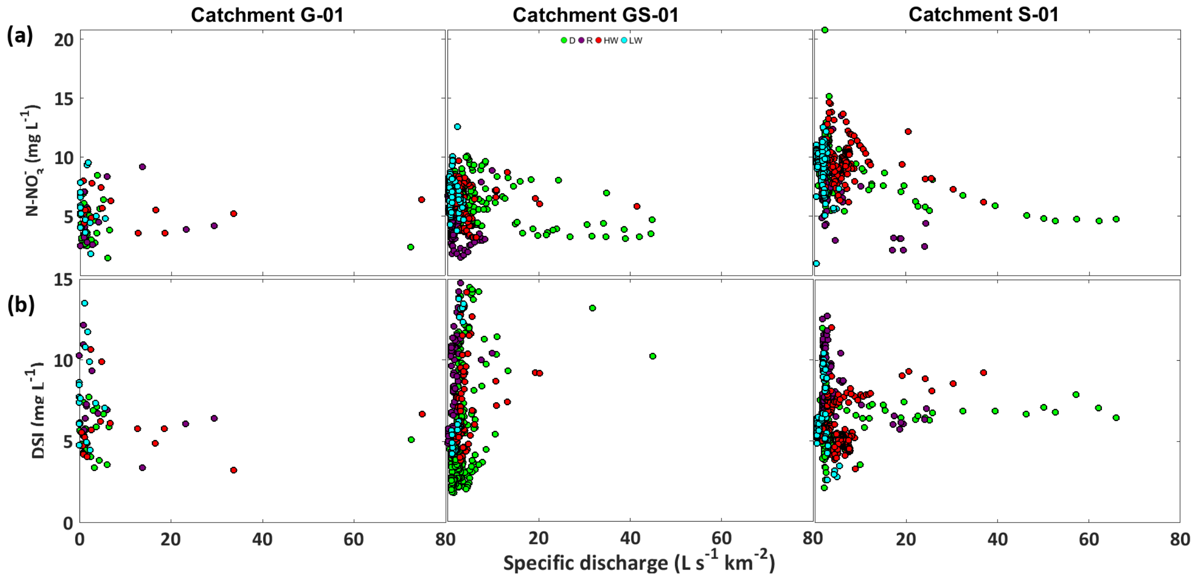

Figure 3. Relationship between specific discharge and (a) nitrate, and (b) dissolved silica for three headwater catchments G-01, GS-01, and S-01, in Brittany France. Chemistry data from daily automatic sampling supplemented by sub-daily sampling for catchments GS-01 and S-01 during discharge events (see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

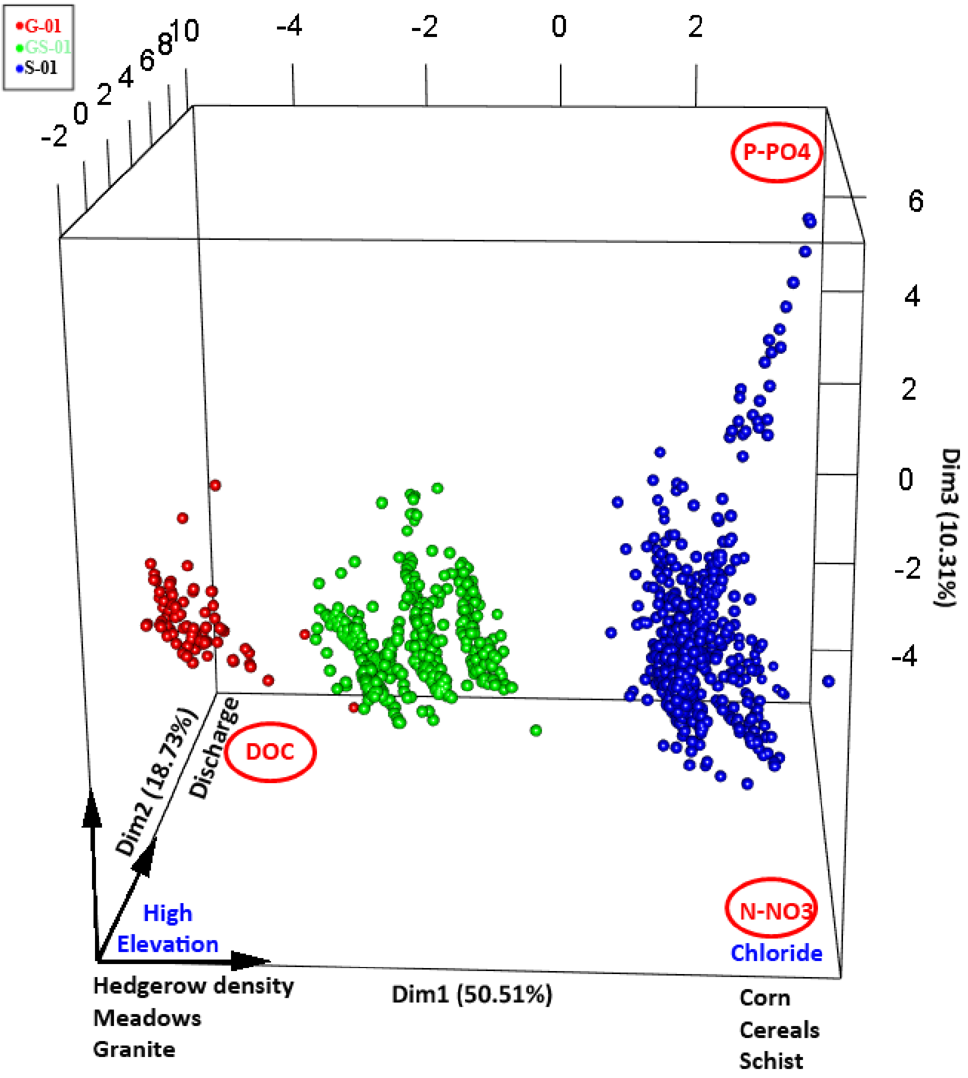

Figure 4. Principle components analysis of the major sources of variability in water chemistry. Together, the first-three axes explain 80% of the total variability of the data. Principal and supplementary variables are indicated respectively in black and blue. Red circles indicate the poles of carbon, nitrogen, and phosphorus associated with cereals and corn for N-NO$_3^-$, high discharge on granite bedrock for DOC, and both discharge and agricultural land use for P-PO$_4^{3-}$. PCA scores are indicated in the supplemental table S3.

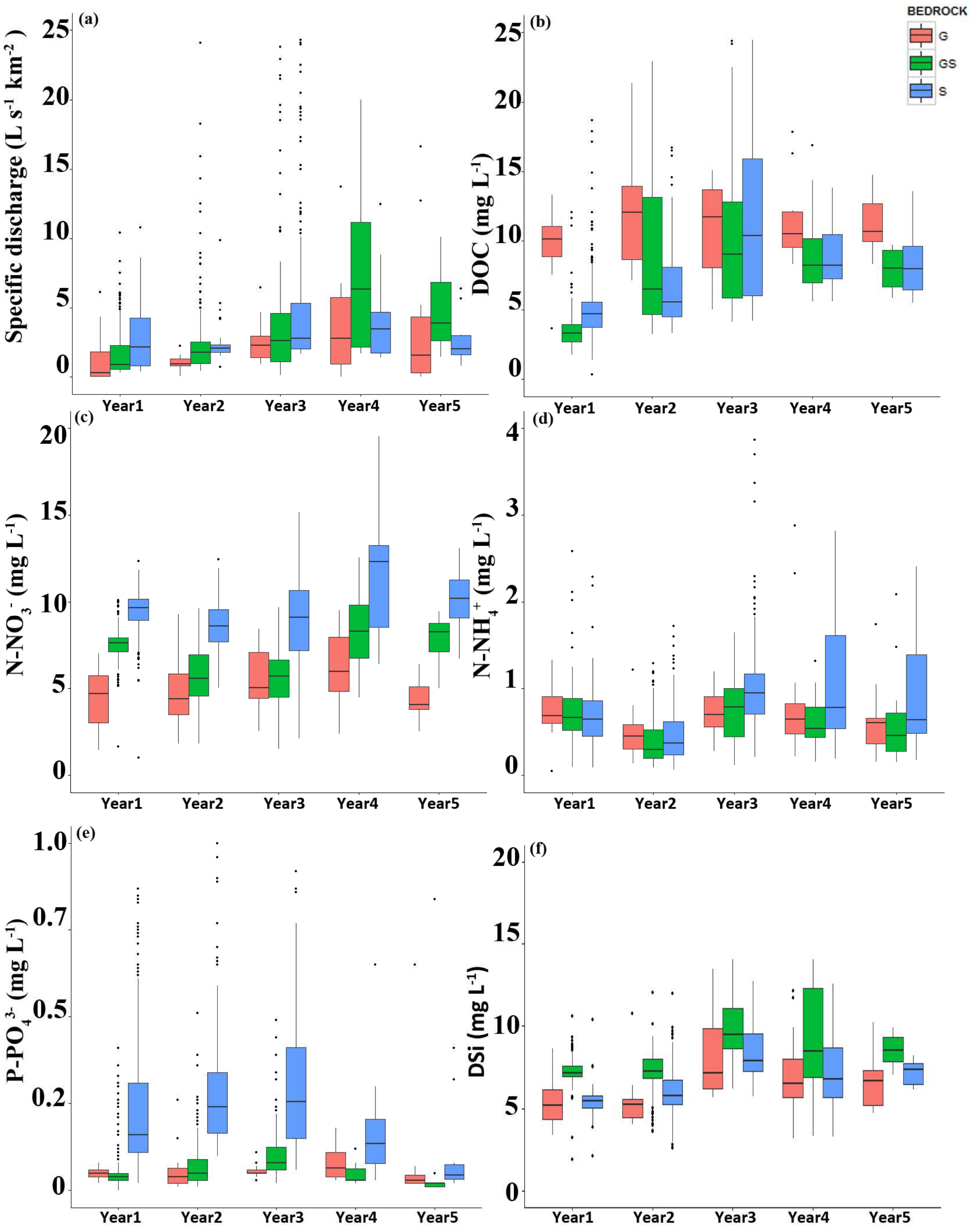

Figure 5. Discharge and carbon and nutrient concentrations during 5 contrasting hydrological years. Boxplots of (a) Specific discharge, (b) dissolved organic carbon, (c) nitrate$^-$, (d) ammonium, (e) phosphate, and (f) dissolved silica for the catchments G-01 (red box), GS-01 (green box), and S-01 (blue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

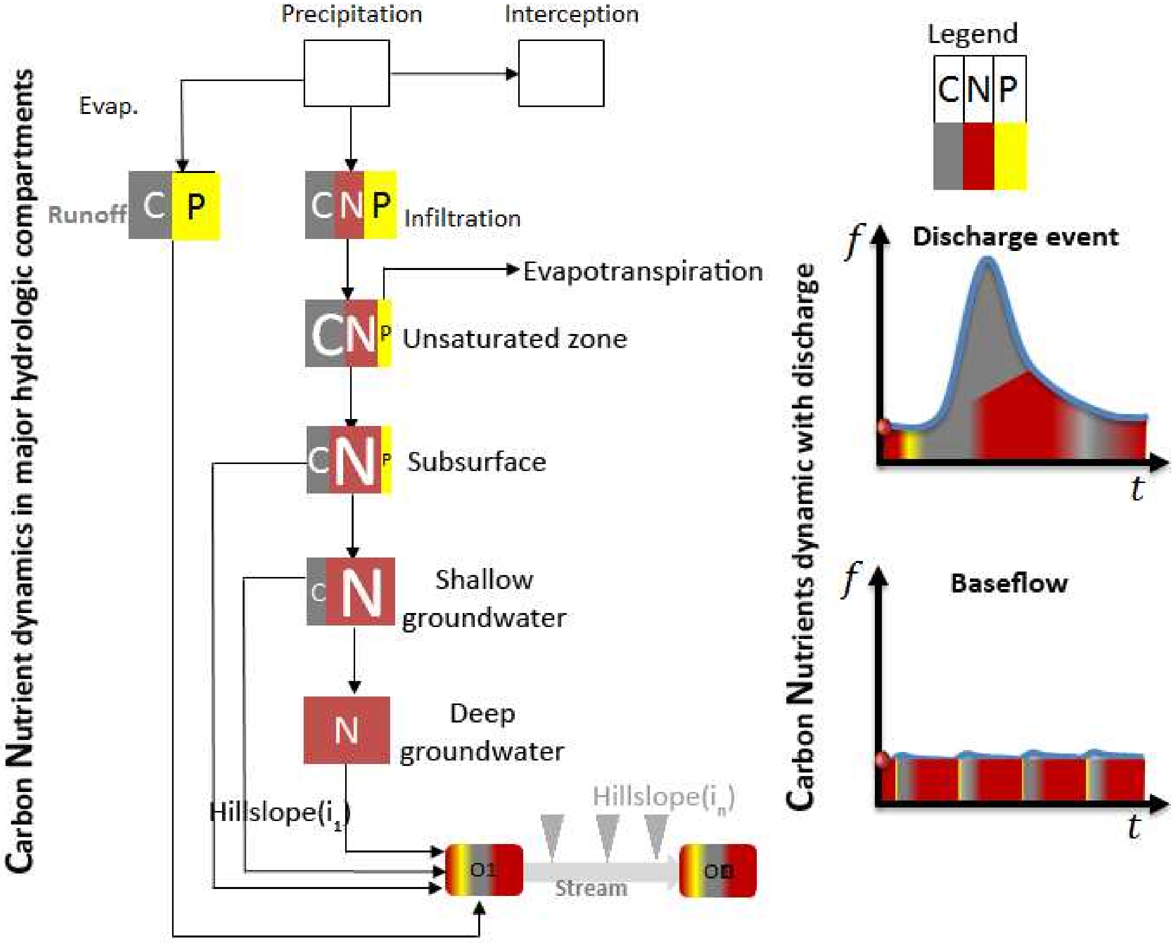

Figure 6. Conceptual model of carbon and nutrient dynamics in major hydrologic compartments during transient (discharge events) and steady state (baseflow) discharge regimes. On the left side, we represent the relative abundance of carbon, nitrogen, and phosphate during vertical transport through soil,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