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Role of nitrogen and iron biogeochemical cycles on the production and export of dissolved organic matter in agricultural headwater catchments

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Abstract

To obtain better constraints on the control of the seasonal variations on dissolved organic carbon (DOC) export in lowland catchments, we combined monitoring of nitrates, iron, soluble phosphorus and dissolved organic matter concentration (as DOC) and composition (fluorescence) in soil and stream waters at a regular interval during one hydrological cycle. We installed 21 zero-tension lysimeters in in top soil organic-rich soil horizons (15 cm below the soil surface) in the riparian area of a well-monitored agricultural catchment in French Brittany and visited them with a weekly to biweekly frequency from October 2022 to June 2023. We observed a large increase in DOC concentrations in riparian soils during the high flow period, notably due to the establishment of Fe-reducing conditions and the subsequent release of organic molecules in soil waters. We also noted that the timing and the spatial variability of Fe(II) biodissolution in soils was regulated by nitrates from agricultural origin and the heterogeneity of water flow paths at the catchment scale. Contrary to our current understanding of DOC export in headwater catchment, our results lead us to consider the winter high flow period as an active phase of both DOC production and export in headwater catchments.

1. Introduction

Dissolved organic matter (DOM) is a key component of the ecological and biogeochemical functioning of aquatic ecosystems (Hanson et al., 2015), affecting for instance light penetration (Kelly et al., 2001), pollutant transport (Aiken et al., 2011), aquatic microbial metabolism (Wetzel, 1992), and the treatment of drinking waters (Chow et al., 2005). Aquatic DOM, which is mainly of terrestrial origin, represents a fundamental link between the terrestrial, oceanic, and atmospheric compartments of the global carbon cycle (Dean et al., 2020; Battin et al., 2008). Unravelling the sources and drivers of DOM export has become an urgent environmental issue in a context of long-term increasing concentrations of dissolved organic carbon (DOC, a proxy for DOM content) reported in numerous streams in the northern hemisphere (Monteith et al., 2007; De Wit et al., 2021).

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Headwater catchments are the main entry point of DOM into fluvial networks in temperate oceanic climate (Ågren et al., 2007) and riparian soils have been identified as the dominant sources of riverine DOM at the catchment scale owing to their location at the terrestrial-aquatic interface (Sanderman et al., 2009; Lambert et al., 2014). The flushing of shallow organic-rich soil layers during storm events represents the majority of annual DOC loads (Inamdar et al., 2006), and the DOC *versus* discharge relationships during storm events show that DOC export is transport-limited (Buffam et al., 2001; Zarnetske et al., 2018). At the annual scale, riparian soils act as a non-limited store (Hinton et al., 1998; Lambert et al., 2013), however the processes regulating the size of the pool of riparian DOM across seasons remain unclear.

DOC export at the annual scale is commonly conceptualized as a two-steps process in which DOM is produced and stored in the catchment during the hot and dry period, and then exported toward surface waters during the wet and cold period (Wen et al., 2020; Strohmenger et al., 2020; Tiwari et al., 2022; Ruckhaus et al., 2023; Deirmendjian et al., 2018). Antecedent soil conditions of wetness and temperature have been identified as a dominant control on stream DOC with concentrations typically increasing after dry events (Turgeon and Courchesne, 2008; Vázquez et al., 2007; Mehring et al., 2013). Periods of drought promote the production and accumulation of dissolved organic material in upper soil horizons through enhanced soil organic matter decomposition (Harrison et al., 2008; Fenner and Freeman, 2011; Xu and Saiers, 2010), resulting in high stream DOC concentrations during the subsequent rewetting phase of the catchment (Werner et al., 2019; Raymond and Saiers, 2010). In good agreement with this conceptual model is the observation based on long-term data that the mean annual DOC concentrations in streams can be related to the intensity and duration of preceding dry periods (Humbert et al., 2015; Tiwari et al., 2022).

However, the establishment of reducing conditions in riparian soils during the winter may have potential implications on our conceptualization of stream DOC export owing to the influence of redox conditions on the iron (Fe) cycle in soils. While particulate Fe-hydroxides absorb with a high affinity organic substances when oxidizing conditions prevail, the microbially-driven dissolution of Fe oxyhydroxides during reducing conditions led to the release of organic molecules previously bounded to surface minerals (Hagedorn et al., 2000; Blodau et al., 2008). The release of large amounts of DOM in riparian soils during the winter period – considered as passive (i.e., non-productive) in our current conceptualisation of stream DOC export – has been previously reported (Lambert et al., 2013; Lotfi-Kalahroodi et al., 2021), and several studies have suggested that iron redox cycles may play a major role on catchment DOM export (Knorr, 2013; Selle et al., 2019; Musolff et al., 2017). However, the impact of Fe reduction could be limited in terms of DOC export considering that reducing

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conditions are favoured by the hydrological confinement of soil horizons involved and by their isolation from the inflow of oxidizing species such as oxygen and nitrates from upslope that may prevent the reductive dissolution of iron (Mcmahon and Chapelle, 2008; Christensen et al., 2000).

Because most of the studies investigating DOC export in headwater catchments rely on data collected in stream waters, the processes regulating the size of the mobile DOM pool in riparian soils and the interaction with other biogeochemical cycles remain largely unseen and we still lack studies investigating how processes occurring in soil waters reflect our conceptualization of solutes dynamics based on observations made in surface waters. In this study, we investigated the potential influence of Fe redox cycles on stream DOC dynamics in an agricultural headwater catchment. More specifically, we tested the hypothese that the controls of Fe reduction in riparian soils could affect significantly the export of DOC a the annual scale. Among these controls, we intended to pay particular attention to the dynamics of NO3 inflow from upslope. To this end, zero-tension lysimeters were installed in the riparian area of a well-instrumented agricultural catchment located in Brittany (France) that shows a low but significant increase in stream DOC concentrations over the last decades (Strohmenger et al., 2020). The variations of soil solution chemistry during the 2022-2023 hydrological cycle was tracked. We measured DOC, Fe(II) and NO_3^- concentrations but also DOM composition (absorbance and fluorescence properties coupled with parallel factor analysis) and soluble reactive phosphorus (SRP) as an additional tracer of Fe reductive dissolution (Gu et al., 2017; Smith et al., 2021). The results allowed us to decipher complex interactions across C, N, and Fe cycles in agricultural catchments and to highlight the occurrence of several processes sustaining DOM export during the winter period.

2. Material and method

2.1. Study site

The Kervidy-Naizin research observatory is a 4.9-km^2 agricultural headwater catchment located in Brittany (western France, Fig. 1). It belongs to the French Critical Zone Observatories (OZCAR) network and is instrumented since the 1970s for the long-term monitoring of the soil-atmosphere-hydrosphere continuum in a context of intensive agriculture (see Fovet et al., 2018 for a complete presentation of the study site).

The site is characterized by gentles slopes (<5%) and low elevation that ranges from 98–140 m above sea level. The bedrock is composed of impermeable Brioverian schists above which a locally fractured layer of schists is underlaid by 1 – 30 m of weathered material and silty loam soils. Soils are well drained except in riparian zones, where water excess leads to hydromorphic, poorly drained soil. The land use is intensive mixed farming, with 91% of the

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watershed area under agriculture that grows crops to feed a high density of dairy cattle, pigs and poultry.. The watershed area is dominated by maize (38%), straw cereals (30%), and grasslands (15%), and wooded areas are mainly confined to valley bottoms along the stream channel or to some hedgerows along fields (Fig. 1).

The climate is temperate oceanic, with mean annual temperature of 11.2 ± 0.6°C and mean annual precipitation of 810 ± 180 mm. Precipitation varies seasonally throughout the year, with higher precipitation from October to February (mean monthly precipitation of 92 ± 31 mm) and lower precipitation from March to July (mean monthly precipitation of 50 ± 14 mm). The dynamics of the draining stream, called the Coët Dan, reflects the seasonal pattern of rainfall and evapotranspiration with high discharge periods from November to April and completely dry periods from July to October depending on hydrological years.

Groundwater level fluctuations are recorded every 15 min along the Kerolland (K) transect, rainfall is monitored at hourly intervals using a weather station located ~ 1400 m from the catchment outlet, and stream discharge is recorded every minute with an automatic gauge station at the outlet of the catchment. A S::SCAN probe is installed at the outlet of the catchment for the measurement of DOC and other variables at high-frequency (Fovet et al., 2018).

2.2. Monitoring and manual sampling

We investigated the seasonal variability of the riparian DOM pool using zero-tension lysimeters installed in September 2022 in topsoil organic horizons (15 cm depth) in the Kerroland riparian zone, an area known to be a major contributor of stream DOC export in this catchment (Lambert et al., 2014). Lysimeters were randomly installed at different distances from the stream channel with the aim to capture different water flowpaths with different degrees of nitrate concentrations. In total, 29 zero-tension lysimeters were installed, but some were lost during the study period because of degradation by rodents. We retained lysimeters for which at least seven consecutive dates of data were available, resulting in 17 lysimeters used for the study. We collected soil waters from November 2022 to June 2023 at a frequency ranging from 2 to 4 visits per month depending on the hydro-climatic conditions (Fig. 1). The end of sampling was imposed by the lack of water in lysimeters owing to the gradual drawdown of the water table in the riparian zone during the spring. Soil waters were collected with a vacuum pump and filtered at 0.2 µm with acetate cellulose syringe encapsulated filters directly on site for all analyses including DOC, NO_3^-, SRP, Fe(II), and DOM composition. Unfiltered water was used to measure basic physico-chemistry variables including temperature and pH with an ODEON probe (XXX). In addition, surface waters were

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collected right next to the riparian area where lysimeters were installed and at the outlet of the catchment. The laboratory analyses were identical for soil and surface waters.

2.3. Analytical procedures

With the exception of Fe(II) measurements that were performed the same day as sampling, all analyses were done within two weeks after sampling. Samples were stored in a 4°C cold room in the dark. Fe(II) analyses were determined using the 1.10-phenanthroline colorimetric method (Lambert et al., 2013): dissolved iron was trapped on site and the optical density of the complex formed with phenanthroline was measured the same day once back to the laboratory at 510 nm with an UV-vis spectrophotometer (XXX). DOC concentrations were measured using a total carbon analyzer (SHIMADZU TOC-V) with a precision estimated at ± 5% using a standard potassium hydrogen phthalate solution (SIGMA ALDRICH). NO_3^- and SRP were determined by spectrometry with an automatic sequential analyzer (SmartChem 200, AMS Alliance, France).

Absorbance for colored DOM (CDOM) was measured with a Lambda 365 UV/vis spectrophotometer (Perkin Elmer) from 200 to 700 nm (1 nm increment) using a 1 cm quartz cuvette. CDOM spectra were used to correct excitation-emission matrices (EEMs) for inner filter effects (Ohno, 2002). Fluorescence DOM (FDOM) was collected as EEMs with a Lambda LS45 (Perkin Elmer) using a 1 cm quartz cuvette across excitation wavelengths of 270 – 450 nm (5 nm increment) and emission wavelengths of 290 – 600 nm (0.5 nm increment). Samples were diluted in most case to reduce inner filter effects and iron quenching. Usual DOM absorbance and fluorescence indices such as specific UV absorbance or slope ratio were not calculated because of they are sensitive to the presence of iron (Logozzo et al., 2022) while the deconvolution of EMMs through parallel factor analysis (PARAFAC) is not (Poulin et al., 2014).

2.4. PARAFAC modelling

EEMs preprocessing (Raman scattering removal and standardization to Raman units) was performed prior to the PARAFAC modeling. Normalization was done using a Milli-Q water sample run the same day as the sample. A five-component PARAFAC model was obtained using the drEEM 0.3.0 Toolbox (Murphy et al., 2013) for MATLAB (MathWorks, Natick, MA, USA). Split-half analysis, random initialization, and visualization of residuals EEMs were used to test and validate the model. The positions of maximum peaks of the PARAFAC components were compared to previous studies carried out in similar context of human-impacted catchments with the open fluorescence database OpenFluor using the OpenFluor add-on for the open-source chromatography software OpenChrom (Murphy et al., 2014). The maximum fluorescence F_{Max} values of each component for a particular sample provided by

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the model were summed to calculate the total fluorescence signal F_{Tot} of the sample in Raman units. The relative abundance of any particular PARAFAC component X was then calculated as $\%C_X = F_{Max}(X)/F_{Tot}$.

2.5. Statistical analyses

A principal component analysis (PCA) coupled with a cluster analysis was performed to identify and group lysimeters having similar patterns. Data used included the mineral composition of soil waters (i.e. DOC, NO_3^-, SRP and Fe(II) concentrations) as well as the composition of DOM based on PARAFAC results (i.e. PARAFAC components). Data for each lysimeters were first averaged and then normalized. The PCA was performed using the *prcomp* function in the R software, and the *factoextra* package was used to identify the variables that contribute the most to the first two dimensions of the PCA. The cluster analysis, based on the results from the PCA and called Hierarchical Clustering on Principal Components (Josse, 2010), was performed with the *FactoMineR* package for R (Lê et al., 2008).

3. Results

3.1. Hydro-climatic context

The hydrological regime of small temperate catchments developed above fractured substrate such as Kervidy-Naizin is characterized by several three distinct successive periods determined by groundwater fluctuations (Fig. 2A-B). The first period (01/09/2022 – 17/12/2022) corresponds to the rewetting phase of the catchment after the dry summer season: moderate precipitations (5.1±5.3 mm d^{-1}, cumulated precipitation = 338.5 mm) progressively lead to the rise of groundwater first in the riparian zone and then in upland domain but stream discharge remains low owing to a low groundwater table. The second period (18/12/2022 – 15/05/2023) corresponds to the high flow period initialized by the rise of the water table in upland soils. Frequent and intense rainfall events maintained a high stream flow, except during several weeks without significant precipitations (17/01/2023 – 06/03/2023, 2.1±4.5 mm d^{-1}, cumulated precipitation = 23 mm). Although stream flow declined significantly, the water table remained close to the surface and riparian soils remained waterlogged. Finally, the third period (16/05/2023 – 01/07/2023) corresponds to the gradual drawdown of the water table in the catchment owing to rarer and scattered precipitations associated with higher temperature and evapotranspiration rates. Air temperature (Fig. 2C) showed a smoothed seasonal variability with decreasing values from September to December (from ~20°C to -2°C) followed by a rise in temperature from 0°C to 20°C from February to July. This pattern was only interrupted by a relatively short episode of

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temperature close to 10°C during the winter, higher than usual temperature at this period, coinciding with the first intense rainfall period of the year.

3.2. Fluorescence properties of DOM

Five PARAFAC components were identified in soil solutions (Supplementary Fig. S1), all of which already described in previous studies. All five components had humic-like fluorescence properties (Fellman et al., 2010). Components C1 (excitation/emission peaks = 350 nm /444 nm), C2 (<270/450), and C5 (410/488) predominantly cover the regions of EEMs associated with peaks A and C and are common tracers of terrestrially-derived DOM in surface waters (Kothawala et al., 2015; Stedmon and Markager, 2005; Logozzo et al., 2023; Lambert et al., 2017) while C3 (330/406) and C4 (295/410) are both located near the classical peak M, indicating a microbial transformation of terrestrial DOM (Williams et al., 2010; Lambert et al., 2022; Yamashita et al., 2010). The maximum fluorescence intensity of all components were strongly related to DOC concentrations (not shown) and the relative contribution of each component decreased from as C1 (29.7±3.1%) > C2 (28.3±3.6%) > C3 (19.5±2.5%) > C4 (12.9±6.6%) > C5 (9.7±2.1%).

3.3. Overview of the seasonal variations in soil and stream waters

Temperature in soil waters (Fig. 3A) followed the same pattern as air temperature: values oscillated from 5°C to 15°C during November – January, reached minimums between 4 and 7 °C in January – March and then increased gradually during the rest of the study period up to 18 – 20 °C in June. pH varied from 6.2 to 7.4 (mean 6.9 ± 0.3) across lysimeters and didn't exhibit significant trends over the study period (Fig. 3B). Solutes, however, exhibited complex patterns with a high variability across lysimeters and time, especially during the high flow period (Fig. 3C-F). Overall, these elements were strongly linked to each other (Fig. 4). DOC concentrations ranged from 2.3 to 87.4 mg L^{-1} (mean = 30.2±12.8 mg L^{-1}) over the study period and were linearly and positively associated with Fe(II) that ranged from 0 to 45.8 mg L^{-1} (mean = 9.8±7.6 mg L^{-1}). Fe(II) was negatively correlated with NO_3 (from 0 to 16.4 mg L^{-1}, mean = 0.9±1.1 mg L^{-1}), and SRP (from 0 to 0.5 mg L^{-1}, mean = 0.1±0.1 mg L^{-1}) was also positively related to Fe(II), but not as strongly as for DOC. Some lysimeters, however, did not followed these relationships and showed some variations in DOC and SRP concentrations but no significant Fe(II) concentrations.

Stream DOC was highly variable, ranging from 2.9 to 36.8 mg L^{-1} (Fig. 7), and reached its maximum concentrations during rainfall events as subsurface flows flush DOM-rich waters from the riparian area (Lambert et al., 2011). Maximum and minimum concentrations trended downwards from December to March but concentrations at peak discharge showed an

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increasing pattern from March to May, a feature resembling that displayed by soil waters from the riparian area.

3.4. PCA and cluster analysis

Overall, the two first components of the PCA explained 69.4 % of the variance and discriminated lysimeters depending on the degree of Fe(II) biodissolution in soil waters occurring in the riparian zone of the Kervidy-Naizin catchment (Fig. 5). The first principal component (PC1, 54% of the total variance) mainly related to NO_3 concentrations and terrestrial humic-like components (C1, C2, and C5) on positive scores, and to DOC and Fe(II) concentrations and the microbial humic-like component C4 on negative scores. The second component (PC2, 15.4% of the total variance) was related to SRP (positive score) and the component C3 (negative score). In other words, lysimeters capturing Fe(II) biodissolution in the riparian area were associated with high DOC and a greater proportion of C4 component compared to lysimeters enriched in nitrates where no Fe(II) was measured.

The hierarchical clustering based on the PCA results grouped the lysimeters in two distinct clusters based on the presence (cluster 1) or absence (cluster 2) of Fe(II) (Fig. 5). This approach allowed us to gain more precise insights into the temporal evolution of solutes in soil solutions since clear patterns appeared once the data were grouped by cluster (Fig. 6). Hence, soil solutions grouped in cluster 1 showed an initial flushing dynamic for all elements except Fe(II) that was almost absent from soil solutions during the rewetting phase of the catchment. Iron reductive biodissolution was triggered during the high flow period in January, at a moment when soil solutions were depleted in nitrate. Then, Fe(II) concentrations showed a gradual increase up to 26.3±10.3 mg L^{-1} until the drawdown of the water table and the consecutive aeration of riparian soils in June led Fe(II) to quickly decrease below 10 mg L^{-1}. This increasing pattern was interrupted during a short period in February – March, *i.e.* during the 'dry' period of the winter, during which Fe(II) dropped from 16.6±9.6 mg L^{-1} to 9.1±4.5 mg L^{-1} before starting again to rise. DOC and SRP both followed a similar trend as Fe(II): concentrations gradually raised from January to the end of March up to 54.9±25.0 mg L^{-1} and 0.18±0.11 mg L^{-1}, respectively, and then dropped to 17.5±10.9 mg L^{-1} and 0.02±0.02 mg L^{-1} in June, respectively.

Soil solutions from the second cluster also showed a flushing pattern, however it lasted longer than soil solutions form the first cluster and concerned only DOC and SRP. Indeed, while NO_3 concentrations decreased in lysimeters from cluster 1, it increased in lysimeters from cluster 2. These patterns of decreasing DOC (from 34.5±7.1 mg L^{-1} to < 10 mg L^{-1}) and SRP (from 0.19±0.08 mg L^{-1} to < 0.02 mg L^{-1}) but increasing NO_3 (from 0.57±0.81 mg L^{-1} to ~ 8 mg L^{-1}) lasted until the middle of February/beginning of March. After that, DOC and SRP

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increased up to > 20 mg L^{-1} and 0.16 mg L^{-1} (but note that SRP dropped close to depletion at the end of the monitoring), respectively, while NO_3 decreased until a complete depletion at the beginning of the recession period of the water table. In these lysimeters, Fe(II) was not measured at significant concentrations (*i.e.* remained below 0.5 mg L^{-1}) except in March, during which Fe(II) increased from 1.2±1.9 to 4.1±0.2 mg L^{-1}.

4. Discussion

4.1. The buffering effect of nitrates on iron reductive dissolution

The reductive biodissolution of iron during the high-water winter period is a recurrent process in riparian soils of headwater catchments (Škerlep et al., 2023; Smolders et al., 2017) and the amplitudes of variations in Fe(II) and associated DOC and SRP dynamics reported in this study are in line with previous works conducted in the same research catchment (Lambert et al., 2013; Lotfi-Kalahroodi et al., 2021; Gu et al., 2017). Our results, however, clearly evidenced a marked variability in the intensity of iron dissolution across lysimeters that we attributed to the spatial distribution of NO_3-rich water flow paths that can inhibit and delay the apparition of Fe(II) (and DOC) in soil solutions.

A fundamental condition for the establishment of reductive conditions is the prolonged waterlogging of riparian soils. As shown earlier for this and other lowland catchments on impervious bedrock, the higher hydraulic gradient induced by the rise of the upland groundwater level during winter maintains a strong hydrologic connection between upland and riparian domains (Pacific et al., 2010; Molenat et al., 2008). Under these conditions, riparian soils remained waterlogged even during low-precipitation moments as long as the water table level remained elevated in upland areas (Fig. 2). Soil horizons may therefore remain waterlogged, leading to the establishment of reductive conditions as long as inputs of oxidizing species remained limited and/or counterbalanced by higher rate of consumption through microbial activity. This pattern was well illustrated by records from lysimeters grouped in the first cluster (Fig. 6). After a quick depletion of an initial stock of nitrate accumulated during the previous summer, reductive conditions were rapidly established during the winter period and Fe-biodissolution was triggered. The increase in Fe(II) concentrations during January implies that precipitation events were not intense enough to provide oxygen to soil waters while the slight decrease observed during the February/March period illustrates the influence of the hydraulic gradient in regulating reductive conditions in riparian soils. As a direct consequence, DOC and SRP showed an increasing pattern in soil waters from December to May but abruptly decreased in June as riparian soils became aerated. The restoration of aerobic conditions owing to the drawdown of the water table in

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the bottomland domain led to the formation of Fe-minerals and the subsequent retention of DOC and SRP (Gu et al., 2017).

Lysimeters included in the second cluster showed a very different pattern. Although some of them were located close (< 1m) to lysimeters in which reducing conditions prevailed, there was no evidence of Fe(II) release owing to the presence of nitrate in soil waters. Indeed, and in agreement with studies carried out in wetland (Lucassen et al., 2004) and lacustrine (Andersen, 1982) sediments, we argued that the Fe-biodissolution biodissolution was inhibited as long as long as NO_3 remained in sufficient quantity in soil waters. In the absence of such mobilization or regeneration process, both DOC and SRP showed a net depletion pattern from November to March. The influence of nitrate as a buffer of Fe-biodissolution was furthermore supported by the observation of a slight release of Fe(II) in May, at a moment when nitrate became depleted from soil waters, probably because of plant uptake. Interestingly, we found that the threshold value of nitrates above which the process is activated (based on the nitrates *versus* Fe(II) relationship (Fig. 4) as well as timing of Fe-biodissolution identified in cluster 1 and cluster 2) ranged between 1.2 and 1.8 N-NO_3 (4.1 – 6.2 mg L^{-1}), which is close to the threshold value of 6 mg L^{-1} reported by Musolff et al., 2017 in German streams.

Our study evidences a strong spatial heterogeneity of the establishment of reducing conditions in the riparian area of the Kervidy-Naizin catchment, associated with differences in the composition of DOM released in soil solutions. The PARAFAC components identified in the model pointed to a dominance of highly aromatic and conjugated molecules, typical of DOM derived from soil organic matter and found in poorly drained soils in riparian or wetland areas (Sanderman et al., 2009; Lambert et al., 2013; Yamashita et al., 2010). A greater proportion of the C4 component within the DOM pool was found in soil waters under reducing conditions, indicating a greater proportion of microbially-derived DOM that we associated with the microbial reduction of Fe oxyhydroxides. It remain to be determined, however, the reason for such variability in biogeochemical processes occurring in riparian soils. A first explanation can be related to the water circulation in soils. In intensive agricultural catchments such as our study site, inflow of NO_3-rich water may arise from the rise of contaminated groundwater in valley bottom s and/or from subsurface flow paths that connect upland soils to riparian soils (Molenat et al., 2008). It is likely that lysimeters from the second cluster captured preferential flow paths of NO_3-rich waters while lysimeters from the first cluster were disconnected from those preferential water circulations. Alternatively, the absence of nitrates in soil waters may arise from a higher rate of denitrification that counterbalanced NO_3 inputs. Research based on field observation remained limited to decipher the respective role of hydrology *versus* biogeochemistry in controlling Fe(II)

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biodissolution in riparian soils, and experimental studies would be required to provide more quantitative values on these potential drivers and their interactions.

4.2. Implication on stream DOM export at the catchment scale

The current understanding of DOM export in lowland headwater catchments is based on a two-steps conceptual model according to which the pool of DOM is built in soils during a low hydrological connectivity period and then flushed toward surface waters during the following high flow period (e.g. Tiwari et al., 2022; Ruckhaus et al., 2023; Strohmenger et al., 2020; Raymond and Saiers, 2010). Although the decline in DOC concentrations in soil waters from cluster 2 between November and mid-February and to a lesser extent in soil waters in cluster 1 from November to mid-December are in good agreement with this view, the general increase in DOC in all lysimeters between March and May now leads us to consider the high flow period as an active phase of both production and export.

We know from isotopic studies that riparian soils where we installed our lysimeters are the dominant source of DOM at the catchment scale (Lambert et al., 2014). The contribution of uppermost soil horizons of riparian areas has been estimated between 80-90% of stream DOC fluxes due to the formation of shallow flow paths that connect soil and stream waters during storm events (Lambert et al., 2014). This previous knowledge is consistent with the observation that stream DOC variability closely reflected the temporal dynamics of DOC measured in soil waters (Fig.s 6 and 7). The general decrease of stream DOC during base flow and at peak discharge from November to February illustrated well the mobilisation and exhaustion of an initial supply-limited pool of DOM built during the summer period (Humbert et al., 2015). The general flushing behaviour of the catchment at this moment was illustrated by the strong decrease of DOC and SRP observed in soils from cluster 2 that became almost depleted in February-March (Fig. 6). On the other hand, the rapid onset of Fe biodissolution in some areas of the riparian domain (cluster 1) sustained DOM export and likely explained why stream DOC concentrations at peak discharge remained stable across successive storms in January (Fig. 7).

Conversely, the increase in DOC in soil solutions in the valley bottoms during the second high flow period have two important implications regarding our conceptualisation of DOM export in headwater catchments. First, it challenges the idea that the wet period acts mainly as a passive exportation period for DOC, with no or little DOC production (Strohmenger et al., 2020; Ruckhaus et al., 2023; Wen et al., 2020). The large two to three fold increase in DOC concentrations in riparian soils (in cluster 1 and 2, respectively) denotes a large mobilisation of DOM despite wet and low temperature conditions with significant consequences on stream DOC fluxes. Indeed, the gradual regeneration of the riparian DOM

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pool was well reflected in stream DOC, whose concentrations at peak discharge showed an increasing trend across successive storm events from March to May (Fig. 7). Secondly, the release of large amount of DOM in lysimeters of cluster 2 where Fe(II) did not increase implies that several production mechanisms other than iron biodissolution can produce or regenerate the pool of riparian DOM. It is unlikely that agricultural inputs (crop residues, manure application, etc) main may explain the increases in the riparian area, as these sources are episodic and/or size-limited (Lambert et al., 2014; Humbert et al., 2015; Pacific et al., 2010). The highly aromatic nature of DOM strongly supports our assessment that the rise of DOM is due to a "local" production rather than external inputs.This observation echoes previous works on the Kervidy-Naizin catchment showing effective interannual regeneration mechanisms of the pool of soluble phosphorus in soils unrelated to iron dynamics (Gu et al., 2017), a statement supported here by the fact that SRP concentrations followed a similar pattern as DOC in soils grouped in the second cluster (Fig. 6). Unfortunately, we do not have the necessary data such as isotopes or molecular markers to elucidate the precise origin and DOM (and SRP) release in soils unrelated to iron biodissolution, and this should be the focus of future work combining experimental and field studies.

Conclusion

The combined monitoring of soil and stream waters in a lowland headwater catchment allowed us to evidence the dual role of high flow period as both an active phase of DOC production and export. The establishment of Fe-reducing conditions in riparian areas was identified as a major mechanism for stream DOC export, but our study also highlighted the buffering role of nitrates that could delay the release of large amount of DOM in soils, spatially and temporally.

The interactions between N and Fe biogeochemical cycles may have potential implications regarding the reasons for long-term increases in DOC in streams of Brittany. Indeed, stream DOC in the Kervidy-Naizin catchment has been slowly but significantly increasing in the last two decades, and this trend is mirrored by a decline in NO_3 concentrations (Strohmenger et al., 2020). While part of the DOC trend can be related to changes in climatic conditions as winters tend to wetter over the years, the long-term decline in N inputs from agriculture may have favoured the increase in stream DOC by enhancing Fe(II) biodissolution in riparian soils. If this was verified, it could partly explain why catchments having similar geomorphological and climatic properties present contrasting long-term trends at the scale of the Brittany region (Supplementary Fig. S2). Indeed, nitrate concentrations have largely decreased during the last decades, but the rate of recovery is not uniform across the region (Abbott et al., 2018). Studies carried out at the regional scale aiming to decipher the

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interactions between local (agricultural practices) and global (climatic conditions) and the consequences on stream DOC export would be critical considering the influence of DOM on water quality and on the ecological and biogeochemical functioning of surface waters.

Data availability

Data on soil solutions will be published on Zenodo.org upon the reservation that the paper will be accepted for publication. Hydrological and climatic data from the Kervidy-Naizin site are available here: https://geosas.fr/web/?page_id=103.

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Author contribution

TL conceived the study, collected field samples and made laboratory analysis. TL drafted the manuscript with inputs from RD. All authors contributed to the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Figure Caption

Figure 1 – Location map of the Kervidy-Naizin experimental catchment. Grey areas located along the stream channel network indicate the extent of hydromorphic soils commonly waterlogged during the winter period. Soil waters were located downslope the piezometer PK1.

Figure 2 – A) Record of hourly discharge and daily rainfall, B) record of hourly piezometric levels in wetland (PK1) and upland (PK3) domains, and C) record of daily air temperature. Black triangles in panel A indicate fieldwork for manual sampling of soil and stream waters.

Figure 3 – Evolution of (A) temperature, (B) pH, (C) DOC, (D) nitrates, (E) iron, and (F) SRP in soil waters during the study period.

Figure 4 – Relationships between (A) DOC and iron, (B) iron and nitrates, ad (C) SRP and iron in soil waters during the study period.

Figure 5 – PCA biplot, including loadings plot for the input variables and scores plot for lysimeters. One point represents one lysimeters, PCA being based on average values calculated over the study period. Markers are coloured according to the cluster identified by the Hierarchical Clustering on Principal Components (see material and methods).

Figure 6 – Evolution of (A) DOC, (B) iron, (C) nitrates, and (D) SRP in soil waters. Lysimeters are grouped according the Hierarchical Clustering on Principal Components (Fig. 5).

Figure 7 – Evolution of stream DOC measured at the outlet of the catchment. Variations in soil DOC concentrations grouped by cluster are also plotted for comparison.

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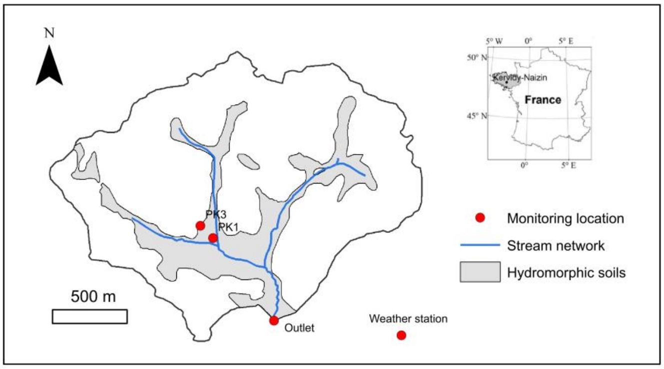
Figure 1



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635 **Figure 2**

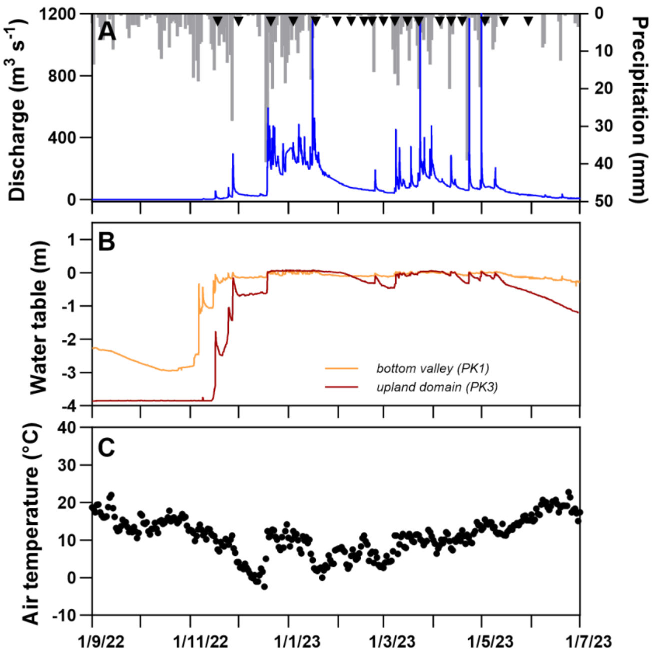

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Figure 3

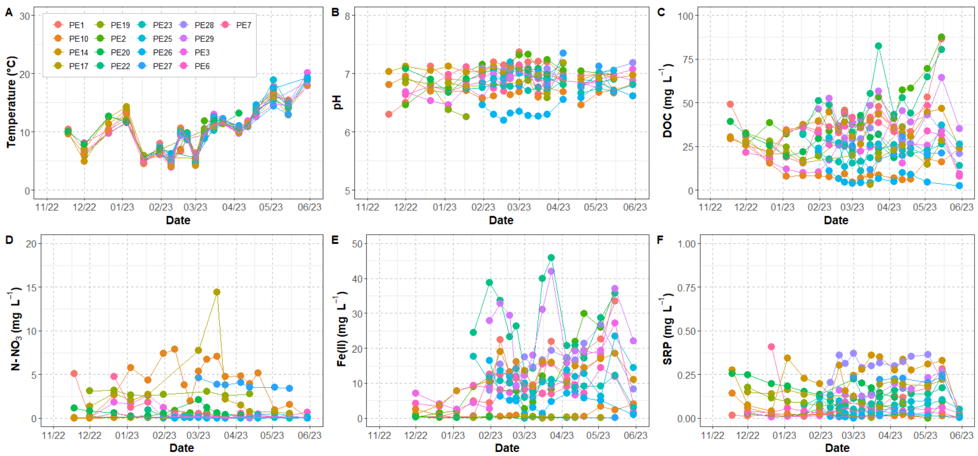

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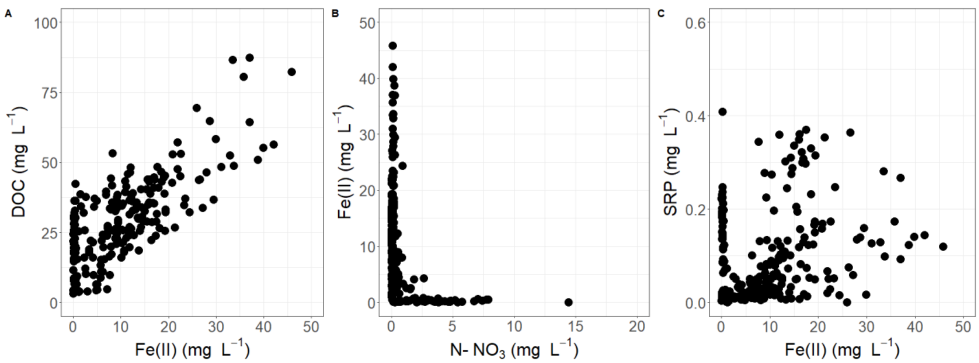
Figure 4



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644 **Figure 5**

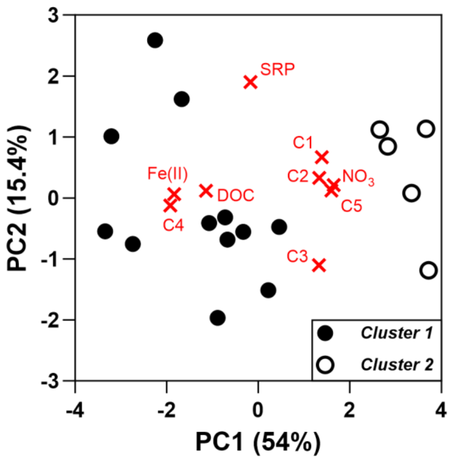

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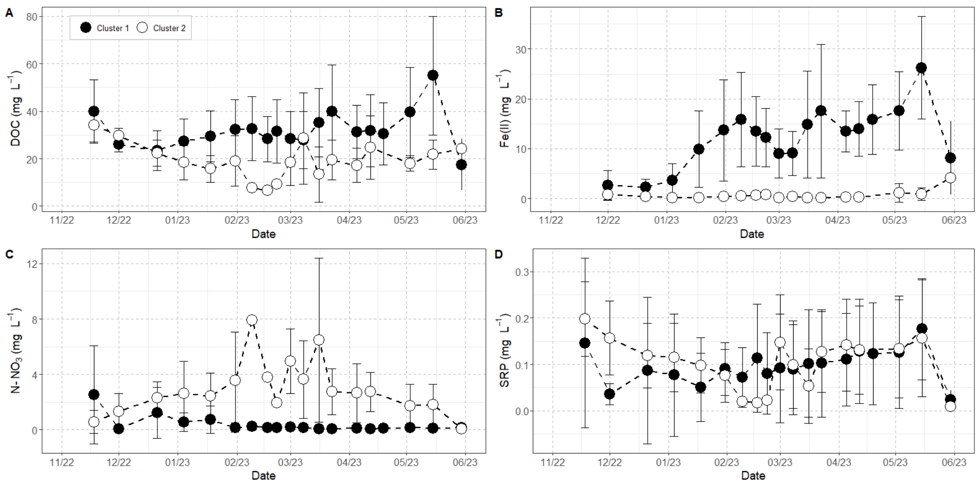
Figure 6



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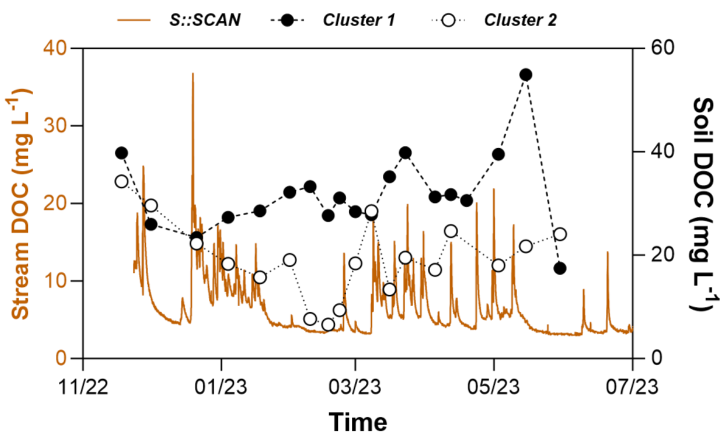
650 **Figure 7**



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