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Par
Andrés CASANOVA

Patterns of nutrients and organic matter concentrations in temperate intermittent streams

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Rapporteurs avant soutenance :

Vicenç ACUÑA	Research Professor, Institut Català de Recerca de l'Aigua
Michael DANGER	Professeur, CNRS, Université de Lorraine

Composition du Jury :

Président :	Christophe CUDENNEC	Professeur, Institut Agro Rennes Angers
Examinatrices :	Marie-Claire PIERRET	Professeure, CNRS, Université de Strasbourg
	Camille VAUTIER	Enseignante-Chercheuse, École normale supérieure de Rennes
Dir. de thèse :	Anne JAFFREZIC	Professeure, Institut Agro Rennes Angers
Co-dir. de thèse :	Ophélie FOVET	Chargée de Recherche, INRAE
	Rémi DUPAS	Chargé de Recherche, INRAE

Foreword

This thesis results from a PhD conducted at the UMR SAS « Sol Agro et hydrosystème Spatialisation » at INRAE, Institut Agro Rennes Angers, from October 2022 to October 2025. The research was jointly supervised by Professor Anne Jaffrezic (Institut Agro Rennes-Angers) and co-supervised by Dr Ophélie Fovet and Dr Rémi Dupas (National Research Institute for Agriculture, Food and Environment — INRAE).

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Abstract

Intermittent and ephemeral streams are watercourses that cease to flow and/or dry at some period of the year along their course. They are estimated to be present in all biomes worldwide and experience the same impacts from human activities as perennial rivers. The temporal dynamics of these intermittent streams, comprising flowing, non-flowing and dry phases, support high biodiversity and influence biogeochemical cycles within the stream network. Therefore, understanding the biogeochemistry of intermittent streams is crucial, given the key role played by the presence of nutrients and organic matter in regulating the ecological functions of these ecosystems. The knowledge related to biogeochemical processes and patterns of intermittent streams is biased towards (semi–)arid and mountainous areas. **The aim of this thesis is to advance our understanding on the biogeochemical patterns and processes associated with hydrological fragmentation in a temperate oceanic context.** The particularities of this context expected to influence the biogeochemical response to stream fragmentation are the dominance of headwaters in streams affected by intermittence, the mild and lower variability of temperature compared to more documented contexts, and the high levels of nutrients and organic matter exported by these streams. The Brittany region, characterised by a wet climate and mild temperatures, intermittent headwater catchments dominated by subsurface flow and differences in topography, geology, hydrology and nutrient loadings, exhibits favourable conditions for studying these patterns and processes.

The thesis leverages interdisciplinary work on hydrology and biogeochemistry to address three main objectives across three chapters (2 to 4). Chapter 2 analyses the prevalence of intermittent streams in Brittany using discrete flow-state observations, comparing them with the French hydrographic reference map and a hydrographic network model to assess the relevance on mapping intermittence. The results revealed a gradient of intermittent streams consistent with the region's precipitation regime, indicating a higher presence of intermittent streams in the east than in the west. Predicting intermittence using a random forest classification model based on catchment spatial features revealed the existence of unmapped local controls (water abstraction, alteration of river morphology) that play a key role in controlling intermittence in streams. Field measurements

of stream geometry suggested that intermittent streams in the Brittany region had been significantly altered, potentially causing or exacerbating their intermittence.

Chapters 3 and 4 examine the biogeochemical patterns and processes during to stream fragmentation in the Naizin (5 km^2) and Etel (18 to 24 km^2) headwater catchments. Repeated synoptic sampling campaigns were conducted along the stream network in Naizin during spring, summer and autumn of 2023, and in Etel during spring, summer and winter of 2024/25. We analysed nutrients and dissolved organic matter in water samples focusing on four phases of hydrological fragmentation: stream recession, early and late stages of stream fragmentation and one date of stream reconnection in Naizin, as well as one high-flow date during winter in Etel. The results showed an increase in spatial variability of concentrations during hydrological fragmentation, i.e. when isolated pools were present. The isolated pools exhibited hypoxic conditions, leading to increased concentrations of reduced and organic forms of nitrogen (N) and phosphorus (P) (e.g. ammonium, dissolved organic nitrogen, , and other forms of P than dissolved reactive phosphorus), while nitrate concentrations decreased in both catchments. However, the concentrations of soluble reactive phosphorus differed between the two catchments: they increased in Naizin and decreased in Etel. Although both catchments experienced an increase in dissolved organic carbon in isolated pools, the fluorescence properties of the dissolved organic matter (DOM) also differed. In Naizin, the humic-like component of DOM increased in these pools, whereas it remained similar as those in the flowing reaches of Etel. We attribute these variations to redox processes occurring under anoxic conditions, such as denitrification, dissimilatory nitrate reduction to ammonium and the desorption and mobilisation of SRP and DOM, in the isolated pools of both catchments. We expect the observed biogeochemical patterns in nutrient and DOM concentrations to become more widespread in the future, as intermittent streams will become more frequent due to climate change. When monitoring intermittent agricultural streams, it is important to survey more nutrient species than are usually measured (e.g. nitrate and soluble reactive phosphorus), since forms of nutrients such as ammonium and organic phosphorus can become more significant. These nutrient forms present different degrees of bioavailability and toxicity to aquatic ecosystems.

Keywords:

intermittent stream, non-perennial, nutrient, DOM, temperate climate, intensive agriculture

Résumé

Les cours d'eau intermittents et éphémères sont des cours d'eau qui cessent de couler et/ou s'assèchent à certaines périodes de l'année le long de leur cours. On estime qu'ils sont présents dans tous les biomes du monde et qu'ils subissent les mêmes impacts des activités humaines que les rivières pérennes. La dynamique temporelle de ces cours d'eau intermittents, qui comprend des phases d'écoulement, d'absence d'écoulement et d'assèchement, favorise une grande biodiversité et influence les cycles biogéochimiques au sein du réseau hydrographique. Il est donc essentiel de comprendre la biogéochimie des cours d'eau intermittents, compte tenu du rôle clé joué par les nutriments et la matière organique dans la régulation des fonctions écologiques de ces écosystèmes. Les connaissances relatives aux processus biogéochimiques et aux motifs spatio-temporels des cours d'eau intermittents sont biaisées en faveur des zones (semi–)arides et montagneuses. **L'objectif de cette thèse est de faire progresser notre compréhension des motifs spatio-temporels et des processus biogéochimiques associés à la fragmentation hydrologique dans un contexte océanique tempéré.** Les particularités de ce contexte, que l'on suppose déterminants sur la réponse biogéochimique à la fragmentation, sont que l'intermittence a lieu dans les têtes de bassins versants, dans des conditions de température modérées et peu variables en comparaison aux contextes plus documentées, et des flux de nutriments et matières organiques élevés. La région Bretagne, caractérisée par un climat humide et des températures douces, des bassins versants intermittents dominés par les écoulements souterrains et des différences de topographie, de géologie, d'hydrologie et de flux de nutriments, présente des conditions favorables à l'étude de ces motifs et processus.

La thèse s'appuie sur des travaux interdisciplinaires en hydrologie et en biogéochimie pour aborder trois objectifs principaux répartis sur trois chapitres (2 à 4). Le chapitre 2 analyse la prévalence des cours d'eau intermittents en Bretagne à l'aide d'observations discrètes de l'état d'écoulement, en les comparant à la carte hydrographique de référence française et à un modèle de réseau hydrographique afin d'évaluer leur pertinence pour cartographier l'intermittence. Les résultats ont révélé un gradient d'intermittence lié au régime pluviométrique de la région, avec une présence plus importante de ces cours d'eau à l'est qu'à l'ouest. La prédiction de l'intermittence à l'aide d'un modèle de classification

aléatoire basé sur les caractéristiques spatiales des bassins versants intermittents a révélé l'existence d'attributs locaux non cartographiés qui jouent un rôle clé dans la prédiction de l'intermittence des cours d'eau (prélèvements en eau, modification du lit des rivières). Des mesures de la géométrie des rivières effectuées sur le terrain suggèrent que les cours d'eau intermittents en Bretagne ont été lourdement modifiés, ce qui a pu causer ou augmenter leur caractère intermittent.

Les chapitres 3 et 4 examinent les motifs et processus biogéochimiques liés à la fragmentation des cours d'eau dans les bassins versants de Naizin (5 km^2) et d'Etel (18 à 24 km^2). Des campagnes d'échantillonnage synoptique répétées ont été menées le long du réseau hydrographique à Naizin au printemps, en été et en automne de 2023, et à Etel au printemps, en été et en hiver de 2024/25. Nous avons analysé les nutriments et les matières organiques dissoutes dans des échantillons d'eau en nous concentrant sur quatre phases de fragmentation hydrologique : la récession du cours d'eau, les phases initiales et avancées de la fragmentation du cours d'eau et une date de reconnexion du cours d'eau à Naizin, ainsi qu'une date de débit élevé pendant l'hiver à Etel. Les résultats ont montré une augmentation de la variabilité spatiale des concentrations pendant la fragmentation hydrologique, c'est-à-dire la présence de mares isolées. Les mares isolées présentaient des conditions hypoxiques, entraînant une augmentation des concentrations de formes réduites et organiques d'azote et de phosphore (par exemple, l'ammonium, l'azote organique dissous et d'autres forme de phosphore que le réactif dissous), tandis que les concentrations de nitrate diminuait dans les deux bassins versants. Cependant, les concentrations de phosphore réactif dissous varient entre les deux bassins versants : elles ont augmenté à Naizin et ont diminué à Etel. Bien que les deux bassins versants aient connu une augmentation du carbone organique dissous dans les mares isolées, les propriétés de fluorescence de la matière organique dissoute (MOD) différent. À Naizin, la composante humique de la MOD a augmenté dans ces mares, tandis qu'elle est restée similaire à celle des tronçons en écoulement à Etel. Nous attribuons ces variations aux processus redox qui se produisent dans des conditions anoxiques, tels que la dénitrification, la réduction dissimilatoire des nitrates en ammonium et la désorption du phosphore réactif dissous et de la MOD, dans les mares isolées des deux bassins versants. Nous pensons que les variations spatio-temporelles observées des concentrations en nutriments et en MOD vont se généraliser à l'avenir, car les cours d'eau intermittents vont devenir plus fréquents en raison du changement climatique. La surveillance des cours d'eau agricoles intermittents devrait envisager d'étudier davantage d'espèces de nutriments que celles qui

sont habituellement mesurées (par exemple, le nitrate et le phosphore réactif dissous), car des formes telles que l'ammonium ou le phosphore organique peuvent devenir prédominantes. Ces formes présentent des degrés de biodisponibilité et de toxicité différents pour les écosystèmes aquatiques.

Mots-clés:

cours d'eau intermittent, non pérenne, nutriments, MOD, climat tempéré, agriculture intensive

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Chapter 1: General introduction

1.1 Alterations of river ecosystems by global change

1.1.1 The pivotal role of river in the water cycle

Rivers are watercourses that flow towards another body of water downstream, such as another river, a wetland, a lake or an ocean (Walther, 2014). In the water cycle, which describes the continuous movement of water between the atmosphere, the Earth's surface, groundwater stores and oceans, rivers rivers play a role in both the storage and transfer of water between land and sea. The main water input to the land surface comes from rainfall and snow, which run off towards streams and rivers, passing through vegetation, soils and bedrock along the way. These flows follow shallow and deep paths along the hillslope. Some of this water is stored as groundwater in aquifers within the cracks and pores of rock, potentially during several decades or centuries. Despite the significance of rivers for human development, the amount of water in rivers is small in comparison to other water pools (Fig. 1.1). The vast majority of water on the Earth's surface is saline water in oceans with over 96%, while freshwater represents 1.69% for groundwater and only 0.0002% for rivers (USGS, 2018).

Human activities have altered the water cycle in several ways: (i) water abstraction and storage for domestic uses, irrigation and industrial activities including energy production; (ii) alteration of the land surface through deforestation, agriculture and wetland destruction; and (iii) disruption the water flow and storage patterns through climate change (Abbott et al., 2019). These disturbances can alter the timing and amounts of precipitation, evapotranspiration, groundwater recharge and river discharge on a global scale. Therefore, water availability depends on how quickly water moves, how much is used, and how clean it is.

Rivers play an important role supporting biodiversity, biogeochemical cycles and human societies. As lotic systems (i.e. systems of flowing water, as opposed to lentic systems

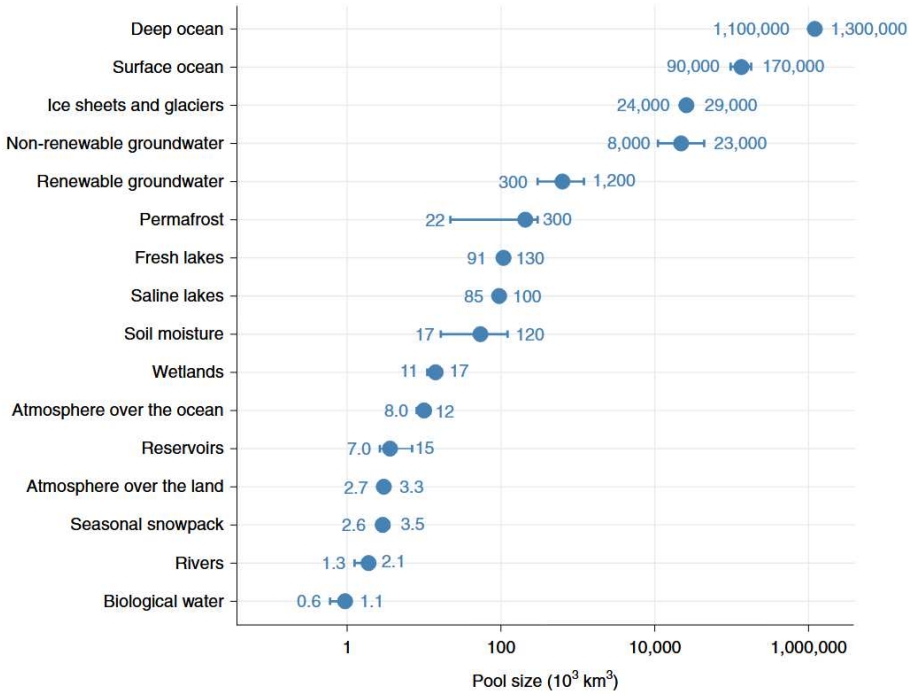

Figure 1.1 – Estimation of pool sizes in the global hydrological cycle, based on a synthesis of regional and global-scale studies. The central point represents the individual estimate, and error bars represent the range of reported uncertainties. The x axis is in log scale. Source: Abbott et al. (2019).

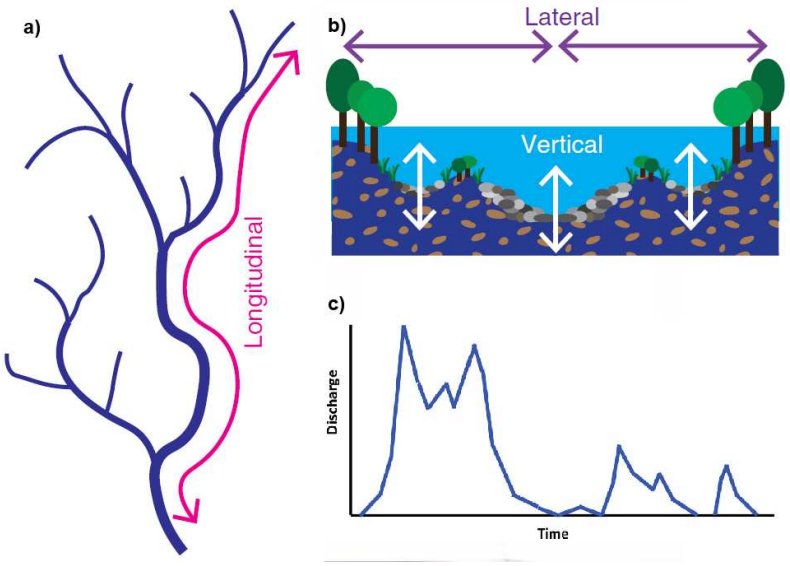

Figure 1.2 – River dimensions: (a) Longitudinal connection through the river network, (b) lateral and vertical connections across a river cross-section. (c) temporally, with discharge variation over time. Modified from: Allen et al. (2020) and Boulton et al. (2017).

of standing water), rivers are dynamic, four-dimensional systems, that are spatially connected (Fig. 1.2): longitudinally with upstream and downstream reaches; laterally, with the adjacent channels, riparian areas and floodplains; vertically, with groundwater and the atmosphere; and temporally (Allen et al., 2020; Boulton et al., 2017; Covino, 2017). From headwaters to mouth, stream networks receive large amounts of material from the surrounding terrestrial landscapes. This material is transported downstream by the flow of water and through the cycling of sediments, nutrients and energy. Rivers support the adjustment and adaptation of biotic communities by driving biogeochemical processes that cycle nutrients downstream (Covino, 2017; Vannote et al., 1980). Freshwater biodiversity depends on clean, natural water conditions, which are shaped by key ecological factors such as riparian structure, substrate composition, hydrological regime and the availability of trophic resources.

1.1.2 Water chemistry controls and catchment biogeochemical processes

The good ecological status of streams and rivers is influenced by physicochemical parameters such as dissolved oxygen (DO), light, temperature, pH, and concentrations. These parameters affect both the biotic structure (i.e. species richness and diversity) and the functions provided by the ecosystem (i.e. metabolism and biogeochemical processes). These physicochemical parameters are dynamic at different spatial and temporal scales in both small streams and large rivers (Gómez et al., 2017). Water concentrations in streams and rivers is determined by the surrounding landscape's climate, geology and land use. These factors control the inputs, outputs, storage and transformations of energy and matter from hillslopes and riparian zones towards the stream network (Fisher et al., 1998). The magnitude of the different biogeochemical processes vary in space (Fig. 1.3), therefore the variability in the catchment's characteristics along the three hydrological dimensions (Fig. 1.2), will result in heterogeneous chemical contributions to the downstream area (Zimmer et al., 2013).

The concept of connectivity assumes that stream solute concentration depends on the connection of hydrological compartments with different levels of solute richness, as emphasised by the spatial distribution of concentrations in groundwater. The connection and disconnection of these compartments is shown to be controlled by seasonal and multi-annual dynamics of the groundwater level along the hillslope (Dupas, Gruau, et

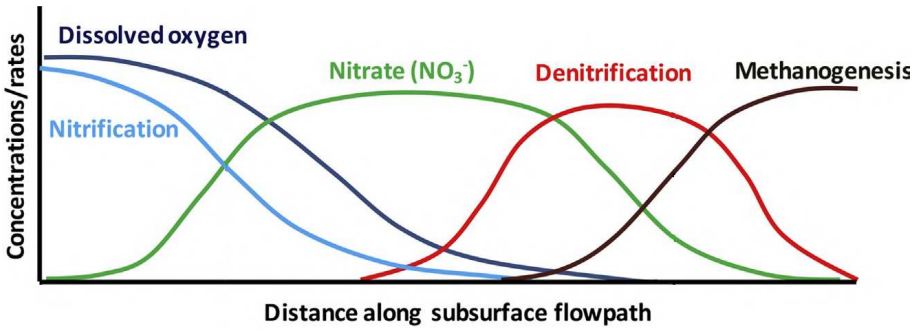

Figure 1.3 – Hypothetical trends of biogeochemical processes along a subsurface flow path and associated trends of O_2 and NO_3^-. Source: Boulton et al. (2017) and Malard et al. (2002).

al., 2015; Ocampo, Oldham, et al., 2006; Ocampo, Sivapalan, & Oldham, 2006). The event dynamics are associated to other compartments connection and disconnection with either dilution process from more surface flowpaths in the case of geogenic and anthropogenic solutes, or enrichment due to mobilization in the case of particulate elements (Moatar et al., 2017). The spatial heterogeneity of concentrations within the hydrological compartments is attributed to: i) the history of inputs (e.g. agricultural and other land use-associated pressures, changes in climate and/or atmospheric deposition) and ii) biogeochemical reactivity, which varies with space (e.g. biomass, biodiversity, nutrient availability, oxygenation and residence times) and time (e.g. light, temperature, moisture, oxygenation, and residence times). Most of the parameters such as water temperature, DO, pH and nutrient concentration in streams and rivers are also subject to diurnal variations controlled by the activity of living organisms via photosynthesis and respiration rates (Wetzel, 2001). These dynamics are highly influenced by riparian vegetation, which can limit solar radiation to the stream (Stanley et al., 1997; Vidal-Abarca et al., 2002). Therefore, mixing and biogeochemical reactivity are the two major types of processes controlling stream concentrations and its dynamics. Reactivity hot spots are typically identified in riparian zones (Dupas, Gruau, et al., 2015; Lupon et al., 2016; Montreuil et al., 2010)), and in-stream such as the hyporheic zone (Dent et al., 2007; Jones et al., 1995; Krause et al., 2022; Stanley & Boulton, 1995).

The biogeochemical processes that take place in the riparian and hyporheic zones are controlled by dissolved oxygen (DO) levels, which are regulated by the exchange between surface water and groundwater (Jones et al., 1995). Oxygen consumption occurs during the decomposition of organic matter in sediments. Once all consumed, anoxic processes



Figure 1.4 – Global trends in river surface water temperature for the period 1901-2010. Source: Intergovernmental Panel On Climate Change (Ipcc) (2023).

takes place such as denitrification, which leads to losses of NO_3^- as N_2 (Fig. 1.3), as well as other processes including sulfate, iron and manganese reduction, and methanogenesis (Jones et al., 1995; Malard et al., 2002). Under aerobic conditions, processes like nitrification, which leads to NO_3^- production occurs in soils and riverbed sediments (Stanley & Boulton, 1995).

1.1.3 Global change disrupts water and nutrient cycles

Apart from the natural processes that control water quality in rivers, human activities are also important drivers. For instance, irrigation and precipitation in agricultural and urban areas transport fertilisers and pesticides into rivers and groundwater. Climate change alters the water cycle, affecting water quality, quantity, timing, and use. Not only has the water temperature increased in rivers up to 1°per decade globally (Fig. 1.4), changes in stream flow have reduced the connectivity in rivers, but also a decline in DO concentrations and an increase in the frequency of cyanobacteria blooms with warming (Intergovernmental Panel On Climate Change (Ipcc), 2023). As global temperatures rise, the global water cycle will intensify, resulting in more variable precipitation and water availability over time and across different regions. Regions that previously benefited from high precipitation volumes could experience a warmer climate, leading to drier summers and potentially causing droughts (Tramblay et al., 2020).

In the scientific and international community, the Planetary Boundaries Framework, which aims to describe the limits to the impact of human activities on the Earth system (Richardson et al., 2023), includes changes to the availability of freshwater and biogeochemical flows among these boundaries. Based on quantitative assessments of the safe limits for human pressure on these processes, the use of both freshwater and green water has already surpassed the planetary boundary (Fig. 1.5). This includes both surface and groundwater flow, as well as plant–available water in root zone soil moisture (Richardson

et al., 2023). Moreover, anthropogenic perturbation also affects nutrient biogeochemical cycles. Nitrogen (N) and phosphorus (P) are two elements that have been identified as being significantly impacted by agriculture and industry on a global scale. These nutrients have drawn attention as their flow from land to freshwater systems and oceans causes eutrophication. An increase in the availability of these nutrients (Fig. 1.5) leads to a depletion of DO and harms biodiversity in aquatic ecosystems (Pinay et al., 2017). The estimated planetary boundaries for these nutrients are 62 Tg of N $year^{-1}$ and 11 Tg of P $year^{-1}$ from fresh water to the ocean. These boundaries are estimated as thresholds in order to avoid large-scale anoxia (Steffen et al., 2015). Currently, the application of industrially fixed N fertiliser is 112 Tg of N $year^{-1}$, and 22 Tg of P $year^{-1}$, so both boundaries for N and P are globally transgressed. Anthropogenic impacts on global carbon cycling are addressed as carbon dioxide levels of emissions mainly due to the emission of greenhouse gases and aerosols, but also land system change, such as deforestation and human overexploitation of biomass. According to the United Nations Paris Climate Agreement, the planetary boundary for atmospheric CO_2 concentrations is 350 ppm in order to not surpass the global temperature of $1.5°C$. However, the current estimated CO_2 emissions are 417 ppm (Richardson et al., 2023).

In France, the annual net withdrawal of freshwater averaged 4.2 km^3 over the 2008-2020 period. It accounts for 0.2% of the global net withdrawal estimated at 2,600 km^3 (General Commissariat for Sustainable Development, 2023). The "freshwater change" boundary is exceeded in one fourth of French catchments due to water abstraction, particularly in summer. The disruption of N and P cycles in France comes from intensive agriculture. Regions such as Brittany, with 59% of utilised agricultural area in 2020 (DRAAF, 2021), have mixed farming systems producing dairies, pork, poultry and eggs, as well as cereals and vegetables. This contributes to the disruption of N and P cycles through nutrient losses to groundwater and streams.

1.2 Intermittent rivers and streams

1.2.1 Non-perennial, ephemeral, intermittent or temporary rivers and streams

A considerable part of the hydrographic network ceases to flow at some point in time; Messager et al. (2021) have estimated that up to 60% of the global river network

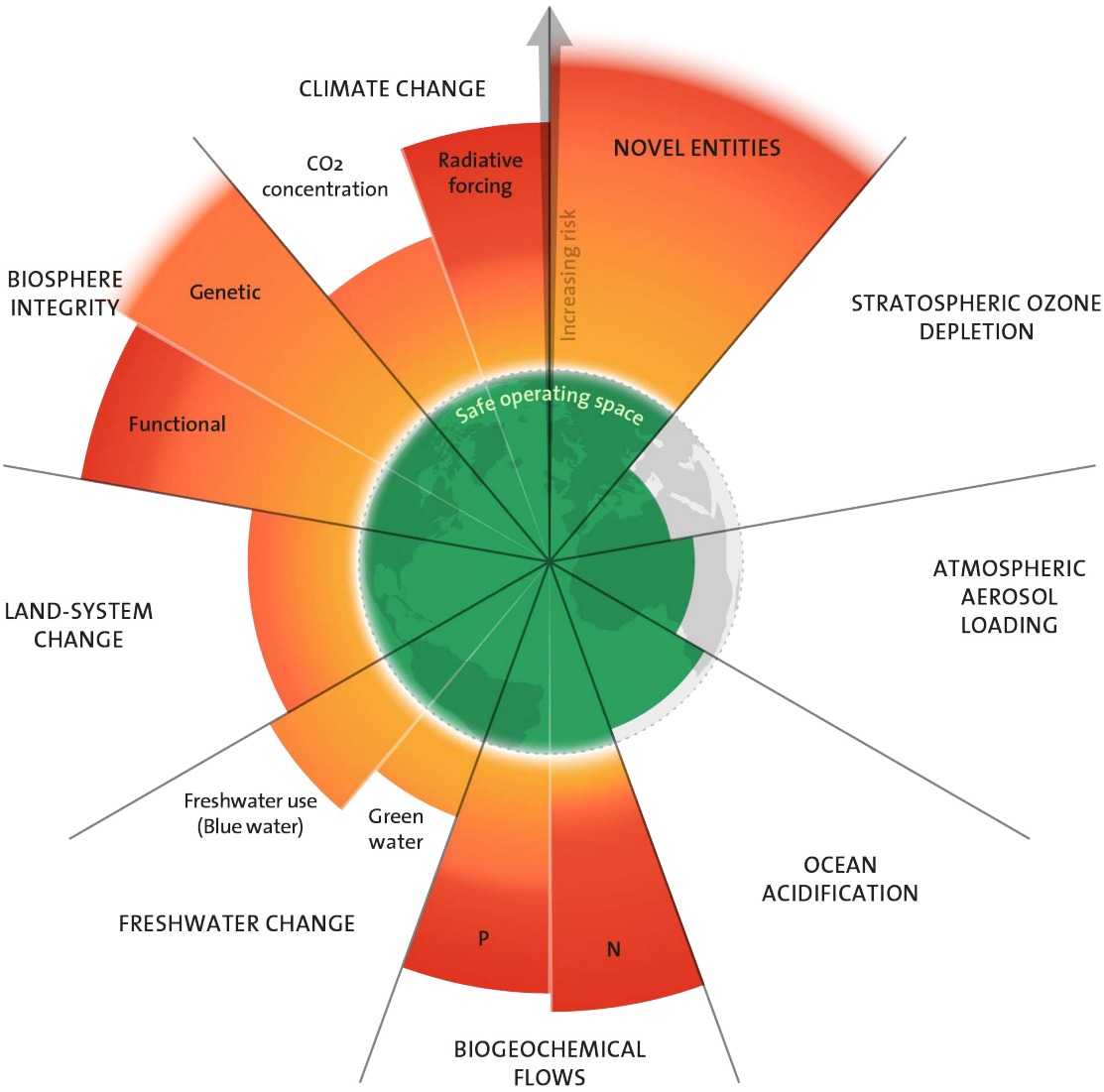

Figure 1.5 – Current status of control variables for all nine planetary boundaries. The green zone is the safe operating space (below the boundary). Yellow to red represents the zone of increasing risk. Source: Richardson et al. (2023).

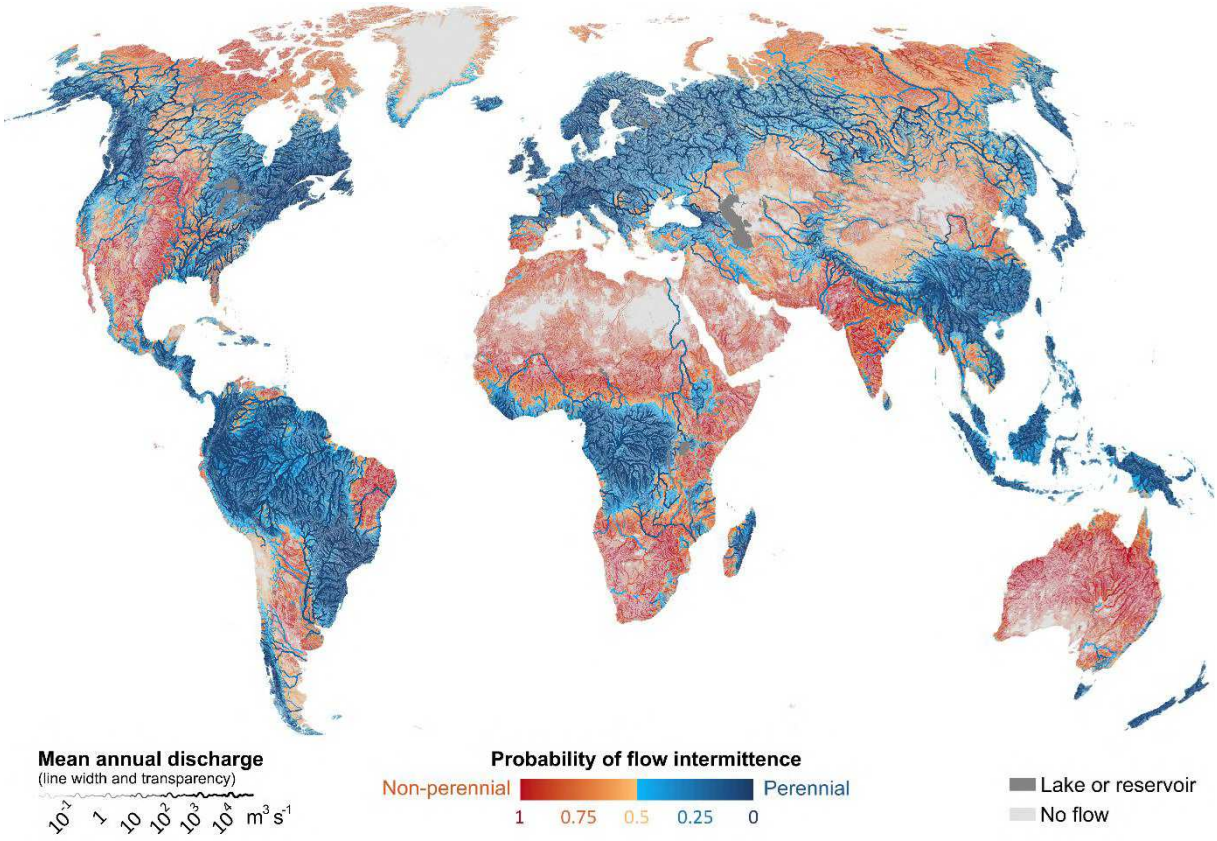

Figure 1.6 – Global distribution of intermittent rivers and streams Source: Messager et al. (2021).

is intermittent. Intermittent streams and rivers can be defined as watercourses that cease to flow and/or dry up at some period of the year along their course (Datry et al., 2017). These streams are sometimes called non-perennial or temporary, the term 'intermittent' is preferably used here, and it accounts for all cessation of flow, including stagnant water. Intermittent streams and rivers can be classified as ephemeral, when they only flow in response to rainfall events or seasonal, when they dry out in summer and rewet in winter. Intermittent streams often have the same uses as perennial rivers, they suffer the same impacts of human activities, and therefore are often less valued due to aesthetic, recreational and biological purposes (Cottet et al., 2023).

Rising temperatures and shifting precipitation regimes due to climate change may increase the occurrence of these intermittent streams around the world (Jaouen et al., 2025; Mimeau et al., 2025). However, intermittence is not dependent only on weather conditions: geology and geomorphology also plays an important role in the stream's response,

influencing flow patterns and the potential for water stagnation (Bonada et al., 2020). Intermittent streams are commonly associated with arid contexts with high temperatures and low precipitation, but they actually occur in all climates and biomes, and in every continent (Fig. 1.6) (Messager et al., 2021). Many of these intermittent streams are located in headwater areas where gauging stations are generally not available. Researchers and managers often ignore intermittent rivers, leaving a knowledge gap due to a lack of monitoring, as gauging stations are mainly located in downstream perennial reaches (Datry et al., 2014). In mountainous areas, low temperatures and freezing streams determine the intermittence. In flatlands and steppes, intermittence mainly occurs upstream or low order streams, when the groundwater-river connection is disrupted during the dry season.

1.2.2 Physical features and processes of intermittent rivers and streams

The three spatial dimensions of the hydrological connectivity of streams and rivers vary at different temporal scales (Allen et al., 2020). In intermittent streams, the flow regime disrupts hydrological connectivity along its three spatial dimensions. This phenomenon is largely governed by different interactions among rainfall regime (frequency, duration and magnitude), evaporation rates, fluvial geomorphology (channel and floodplain size, shape, gradient, riverbed composition and location in the network) and hydrogeological features (Boulton et al., 2017).

They hydrological cycle of an intermittent stream is commonly divided in four phases: contraction, fragmentation, desiccation and expansion. During a contraction phase (Fig. 1.7), the stream shrinks, reducing flow velocity and disconnecting it from the adjacent hillslopes (Costigan et al., 2015). During this phase, the reduction in groundwater input to the stream reduces the amount of water within the stream channel (Dahm et al., 2003), but also significantly increases the travel time of water flowing to the stream (van Meerveld et al., 2019). The contraction cycles of intermittent river networks can range across a complex, dynamic, spatial and temporal gradient of flow continuity (i.e. continuous flow at a specific location over time) and flow connectivity (i.e. continuous flow across time and space) (Costigan et al., 2015). After flow contraction, the discontinuation of flow in intermittent streams leads to fragmentation (Fig. 1.7), creating a heterogeneous landscape of isolated pools surrounded by dry streambeds (Fellman et al., 2011; von Schiller et al., 2011). These isolated pools can last several weeks and others only a few days, depending

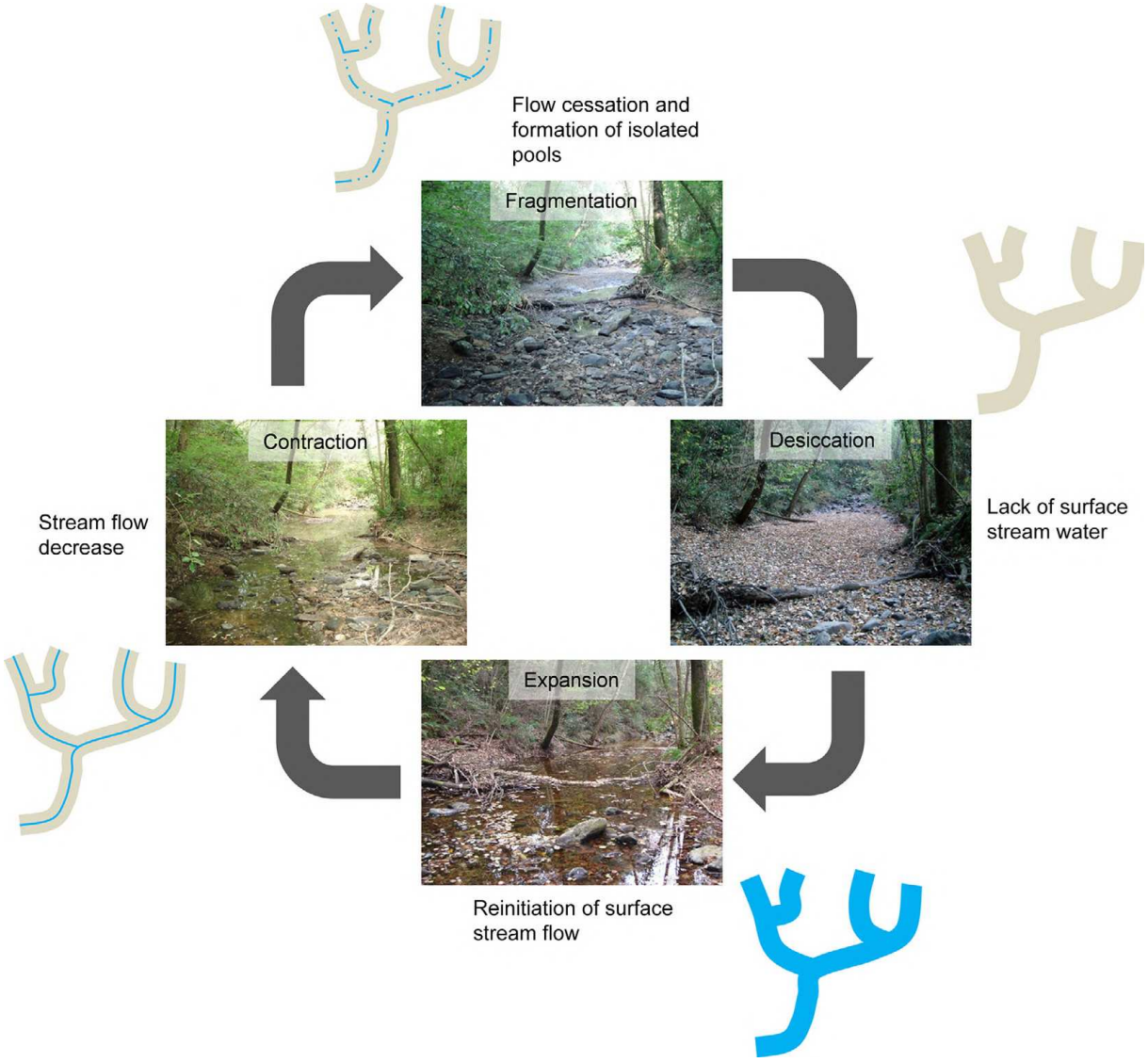

Figure 1.7 – Common hydrological phases driving high spatio-temporal variability in nutrient and organic matter dynamics. Photos and schema are from a reach in a Mediterranean intermittent stream (Catalonia, Spain). Source: von Schiller et al. (2017).

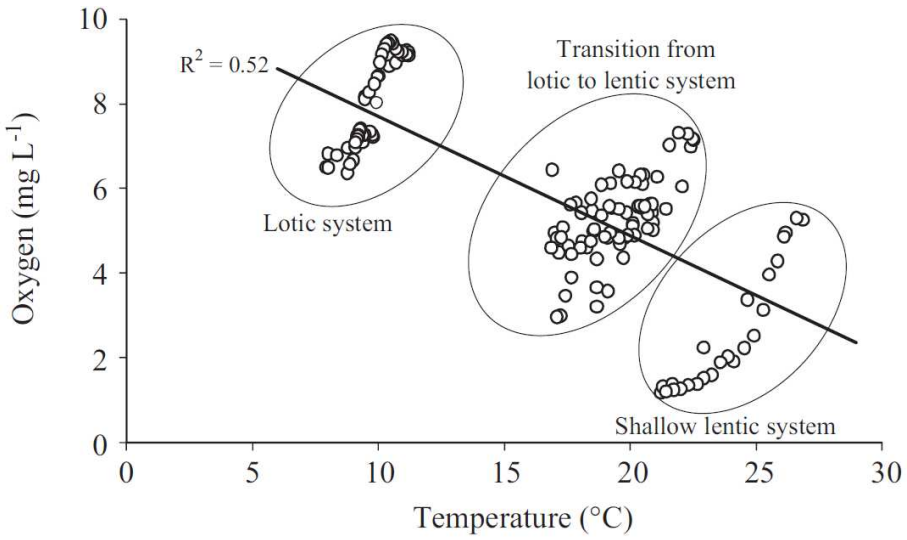

Figure 1.8 – Relationship between dissolved oxygen and temperature over a 24-hour cycle, illustrating the difference between lotic and lentic conditions in the Pardiela stream in Portugal. Source: Lillebø et al. (2007).

on the presence of groundwater inputs and evaporation rates (von Schiller et al., 2011), and create dynamic mosaics of aquatic and terrestrial habitats with their own physical, chemical and biological processes (Larned et al., 2010).

Stream fragmentation is often followed by the drying of the stream surface (Fig. 1.7). The drying of a stream starts with the fragmentation, followed by a loss of connectivity between the stream and groundwater (Bonada et al., 2020). At this stage, water remains in the subsurface, increasing vertical differences in biogeochemical processes (Merbt et al., 2016; Timoner et al., 2012). Drying can occur in both upstream and downstream directions, particularly in losing streams where the water table is fed by the stream (Boulton et al., 2017). Drying patterns are primarily influenced by regional geomorphology (Larned et al., 2011). They can occur over different spatial extents and with different degrees of asynchrony, which can be highly unpredictable (Datry et al., 2014; Stanley et al., 1997). The reinitiation of surface flow after a dry phase generally occurs after one or several significant rainfall events, which recharge groundwater stores that progressively reconnect with the stream channel (Jacobson & Jacobson, 2013; Stanley et al., 1997). Some intermittent streams have false starts of flow expansion in response to rainfall, before returning to a dry state, whereas others, the expansion is usually faster concomitant with resumption of surface flow (Boulton et al., 2017). Along with an increase in discharge during stream rewetting, the lateral, vertical and longitudinal hydrological connections along the

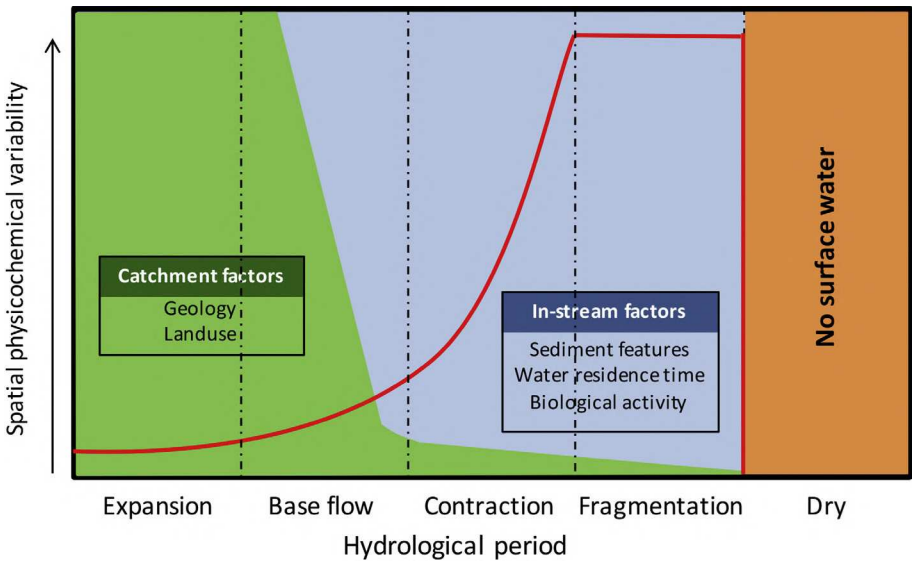

Figure 1.9 – Conceptual model of the physicochemical variability of surface water through the different phases of intermittence. Longitudinal heterogeneity (solid red line) is low during periods of high discharge and is governed by catchment factors, whereas it increases with fragmentation, whereby local in-stream factors become more important. Source: Gómez et al. (2017).

stream channel are restored (Fig. 1.7). Similar to drying, expansion patterns can occur at multiple spatial extents, largely governed by channel topography, as depressions fill and hold water for longer than surrounding areas (Costigan et al., 2016; Woodward et al., 2015).

1.3 Biogeochemical cycles in intermittent streams

Stream disconnection from the river network and from groundwater alters the physicochemical and biogeochemical properties of the stream (Allen et al., 2020; Gómez et al., 2017; von Schiller et al., 2017). Furthermore, the spatial heterogeneity among isolated pools in intermittent streams creates distinct individual ecosystems with differences in the biogeochemical processes that control nutrient and DOM concentrations (Dent & Grimm, 1999; Fellman et al., 2011; von Schiller et al., 2011). In Mediterranean climatic regions, where seasonal alternation between dry and wet periods is pronounced, there is a high variability in nutrient dynamics within the year (Bernal et al., 2012). During the fragmentation phase, the stream disconnection reduces nutrient supply from terrestrial ecosystems while increasing spatial variation in nutrient concentrations (Fig. 1.10). In

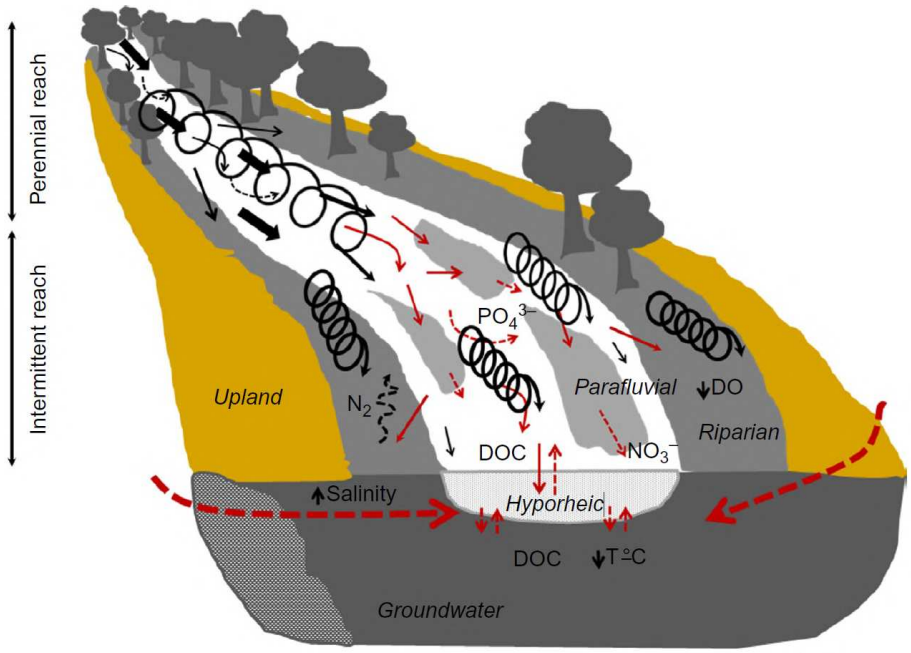

Figure 1.10 – Theoretical model showing differences in flow transport and processes between perennial and intermittent reaches. Black and red arrows indicate the flow paths of nutrient and OM cycles in the perennial and intermittent reaches, respectively. Larger arrows indicate dominant flow paths. In intermittent reaches, the fragmentation of the stream creates hotspots with a diversity of environmental conditions, such as organic matter content, water residence time and the structure and activity of biological communities. Interactions between the surface water and the hyporheic, parafluvial and riparian zone are present in perennial reaches and reinforced in intermittent reaches. The abbreviations shown here. DO: dissolved oxygen; DOC: dissolved organic carbon; N_2: nitrogen; NO_3^-: nitrate; PO_4^{3-}: phosphate; T: temperature. Source: Gómez et al. (2017).

this sense, the amount and form of nutrients transported in the stream varies depending on the spatial distribution of isolated pools (Dent et al., 2001; Fisher et al., 1998), water residence and surface-subsurface interactions through the flow path stream (Dent et al., 2007).

The literature on biogeochemistry of intermittent streams is dominated by Mediterranean and arid contexts (Dent & Grimm, 1999; von Schiller et al., 2011) and emphasizes that nutrient and OM dynamics are significantly impacted by each hydrological phase in intermittent streams (Fig. 1.9, Dahm et al., 2003; von Schiller et al., 2017). The hydrological contraction reduces their downstream export. This increases the influence

of in-stream sources of nutrients and OM compared to terrestrial sources (Bernal et al., 2012; Dahm et al., 2003; McKnight et al., 1999). The isolated pools created in the fragmentation phase are considered as isolated systems, and their biogeochemistry may differ from neighbouring perennial reaches due to differences in biotic and abiotic conditions (Bonada et al., 2020). In addition, the lack of water renewal and weak aeration rates in these isolated pools typically result in hypoxic or anaerobic environments (Fig. 1.8), resulting in changes in the concentration and forms of nutrients and OM, as well as enhancing ecosystem respiration rates upon expansion (Acuña et al., 2005; Lillebø et al., 2007; von Schiller et al., 2011). In the sediments of dry streambed, the biogeochemical processes are affected by the drying similarly to soils and if there is a developed riparian vegetation, it can drive the accumulation of leaf litter on the streambed (Acuña et al., 2007; Arce et al., 2019). Expansion phase is characterised by increasing hydrological connectivity and occurrence of high discharge events after heavy rainfall events causing large amounts of particulate and dissolved nutrients and OM to be mobilised downstream (Bernal et al., 2012; Datry et al., 2014; N. Skoulikidis & Amaxidis, 2009; Tzoraki et al., 2007; von Schiller et al., 2011). However, this rewetting pulse only has a limited contribution to annual DOM and nutrient loads, as concentrations quickly return to low levels after the initial pulse and subsequent floods (Bernal et al., 2005; Butturini et al., 2002; Jacobson & Jacobson, 2013). Consequently, it can stimulate respiration and mineralisation processes in downstream reaches (Corti & Datry, 2012).

1.3.1 Carbon cycle in intermittent streams

Carbon in the form of organic matter is an energy source for microbial communities in fluvial ecosystems. This organic matter can originate from allochthonous (inputs from the terrestrial part of the catchment) and autochthonous (in-stream production) sources, and exist in two forms: particulate organic matter (POM) and dissolved organic matter (DOM). DOM is generally estimated as dissolved organic carbon (DOC) and it comprises 50% of total carbon in rivers and more than 90% in oceans (Wetzel, 2001). DOC concentrations in rivers vary spatially according to the geomorphologic characteristics of the catchment, climate, vegetation, presence of wetlands and season of the year and low flow conditions.

In the context of intermittent rivers and streams, studies have reported an increase in DOC concentrations in isolated pools during stream fragmentation in a Mediterranean forested granitic catchment and an Australian subtropical dryland river (Fellman et al.,

2011; Vazquez et al., 2010). However, others have reported a decrease in DOC concentrations during periods of drying due to a reduction in the supply of nutrients and organic carbon from shallow groundwater in a forested catchment in the U.S. (Dahm et al., 2003). During these phases, the input of allochthonous DOM from the catchment is interrupted, leading to a decrease in the proportion of high-molecular-weight substances (e.g. polysaccharides), and an increased contribution of in-stream algal production and microbial processes to the total DOM pool (Dahm et al., 2003; Fellman et al., 2011; von Schiller et al., 2015). During dry conditions, abiotic processes such as photodegradation become more important for OM decomposition. The content and composition of OM can differ from adjacent terrestrial soils, probably due to differences in OM inputs, sediment texture, and transport (Abril et al., 2016; Jacobson & Jacobson, 2013).

Consequently, during the expansion phase, the contribution of allochthonous and autochthonous sources to the export of nutrients and OM in intermittent catchments may differ from that of perennial ones, as they depend on factors such as the type and timing of flushing or rewetting events, climate, and the catchment characteristics (von Schiller et al., 2017). The high hydrological connectivity during the expansion phase increases the importance of allochthonous terrestrial OM sources compared to those of in-stream origin (Bernal et al., 2012). The particulate matter that accumulated during the dry phase is mobilised downstream during flooding, resulting in significant OM mineralisation of the accumulated litter (Humphries & Baldwin, 2003; Merbt et al., 2016; Wilson & Baldwin, 2008). This expansion phase was also associated with intense biological activity, during which the high labile carbon could be rapidly metabolised by the majority of the heterotrophic microorganisms present in the litter (Datry et al., 2018). Another process that was not studied in this thesis is the high respiration rates and carbon dioxide (CO_2) emissions associated with metabolism in isolated pools. Low DO conditions and the time of hydrological disconnection of the isolated pools enhanced methane production and increased CO_2 emissions in dry riverbeds compared to running waters in intermittent Mediterranean fluvial networks in Spain (Gómez-Gener et al., 2015; Granados et al., 2020).

1.3.2 Nitrogen cycle in intermittent streams

Similar to carbon, nitrogen (N) exists in various forms with different oxidation states. Inorganic reactive forms of N (NO_2^-, NO_3^-, NH_4^+, NH_3) and organic N fractions (dissolved organic nitrogen - DON, particulate organic nitrogen - PON) are present in fresh-

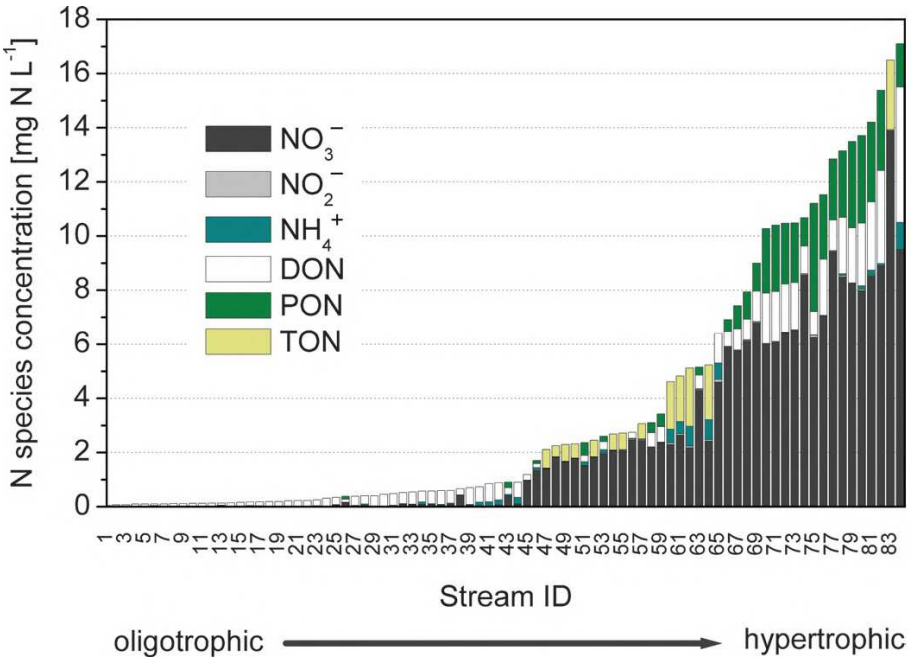

Figure 1.11 – Concentrations of different forms of nitrogen (NO_2^-: nitrite, NO_3^-: nitrate, NH_4^+: ammonium, DON: dissolved organic nitrogen, PON: particulate organic nitrogen, TON: total organic nitrogen) in 57 European rivers (some reported only TON as the organic form), arranged according to a total nitrogen gradient. Source: Durand et al. (2011).

water systems (Fig. 1.11). Water residence time is one factor shaping variations in N forms, which can be delivered to streams via atmospheric deposition, leaching from diffuse sources, sediment erosion and direct inputs from point sources (Durand et al., 2011). Nitrate (NO_3^-) is the most dominant form in highly enriched rivers and streams.

In intermittent rivers and streams the concentration of nitrate generally tends to decrease through denitrification processes enhanced in hypoxic environments (Kemp & Dodds, 2002; Stanley & Boulton, 1995; von Schiller et al., 2011). On the other hand, the concentration of other forms of N such as ammonium (NH_4^+), increases due to the mineralisation of accumulated organic detritus in the riverbed during stream fragmentation and during drying (Acuña et al., 2005; Lillebø et al., 2007; von Schiller et al., 2011). However, other studies have shown that processes such as dissimilatory nitrate reduction to ammonium (DNRA) in isolated pools with low redox potential (Arce et al., 2015), desorption from sediments (Baldwin & Mitchell, 2000) or photodegradation of DOM (Larson et al., 2007), may contribute to the increase in ammonium concentrations. Changes in the forms and concentrations of N during rewetting are related to denitrification and nitrification

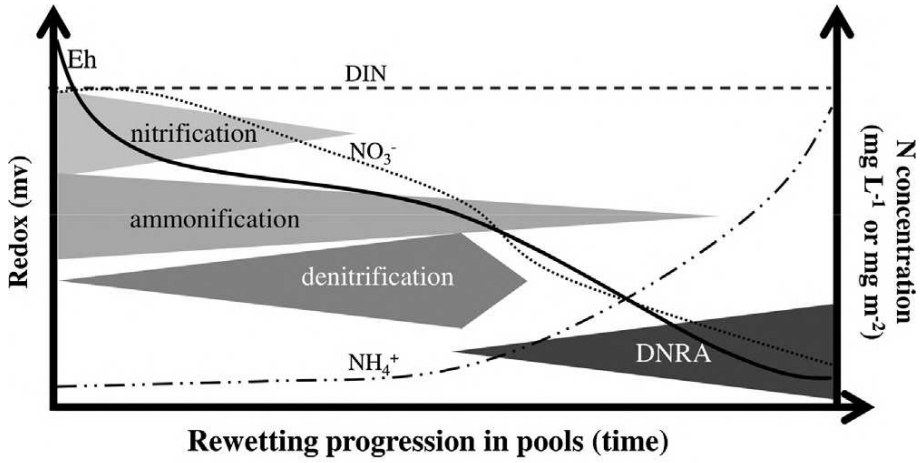

Figure 1.12 – Conceptual summary of major biogeochemical changes of N cycle proposed to occur during the rewetting/expansion phase. Direction of arrows indicates increasing values. Source: Arce et al. (2015).

processes (Fig. 1.12), which are activated during the first flow events (Arce et al., 2015). Consequently, the rates at which the mineralisation, nitrification and denitrification processes occur in the streambed sediments and adjacent riparian soils may influence the relative abundance of different nitrogen species (Bernal et al., 2005).

1.3.3 Phosphorus cycle in intermittent streams

Phosphorus (P) is less abundant in freshwater systems than other elements (carbon, hydrogen, nitrogen and oxygen), however it is one element that most commonly limits its biological productivity in freshwater ecosystems (Wetzel, 2001). Similar to nitrogen, phosphorus compounds can be separated into inorganic and organic forms, as well as into dissolved or particulate fractions. Soluble reactive phosphorus (SRP) is commonly associated with orthophosphate (PO_4^{3-}) which is the dominant ionic form of P in a solution, but also is the most widely studied form in freshwater because it is directly bioavailable.

In intermittent rivers and streams, SRP increases over time during the hydrological contraction, where anaerobic conditions favour solubilisation from sediments, changing the pH and reducing metals (Baldwin & Mitchell, 2000; Finn et al., 2009; von Schiller et al., 2011). The P content of sediments is affected by drying, due to a decrease in P binding capacity. Changes in the speciation of P towards a less available P were observed in two oligotrophic lakes in Spain and two Australian reservoirs, that were affected by

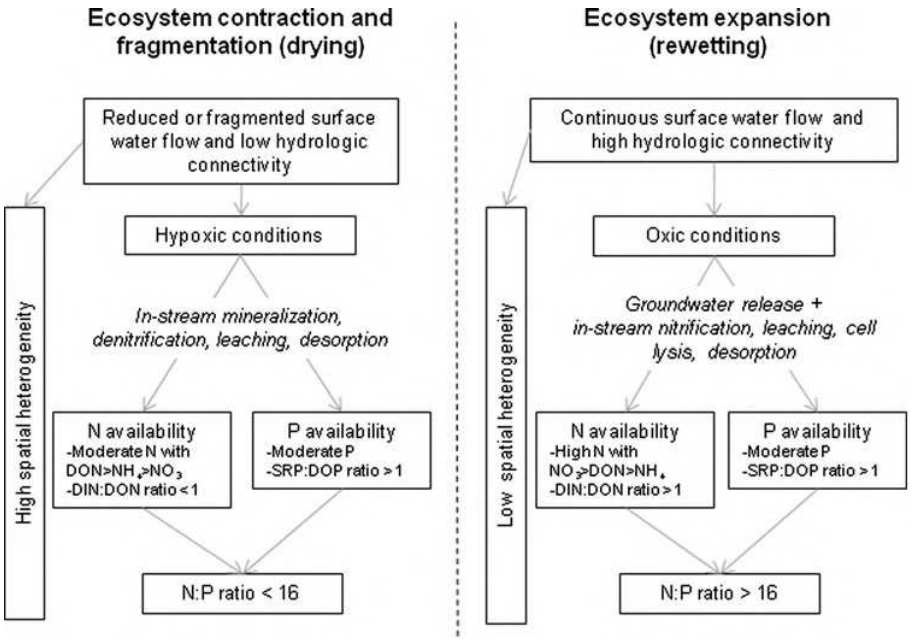

Figure 1.13 – Conceptual summary of the major processes involved in dissolved nitrogen and phosphorus in a Mediterranean intermittent stream. Dominant processes are in *italics*. Source: von Schiller et al. (2011).

drying and rewetting (de Vicente et al., 2010; Watts, 2000). Changes in P speciation are expected in streambed sediments, with a shift towards more reactive P, a decline in P adsorption capacity, and an increase in the proportion of labile soluble P. This is accompanied by stimulated mineralisation of organic P during stream fragmentation prior to desiccation (Dieter et al., 2015; Mitchell & Baldwin, 1998). Nevertheless, these results were established from experiments in laboratories, so in-situ investigation about the response of P dynamics to stream fragmentation is still needed. The lower amount of P exported compared to nitrogen N during rewetting is likely due to the greater release of N than P from streambed sediments (Fig. 1.13). However, a high proportion of particulate P may be released during the first flowing events (N. Skoulikidis & Amaxidis, 2009; Tzoraki et al., 2007; von Schiller et al., 2011).

1.4 Context of water resources in French Brittany

The Brittany region is a peninsula located in north-west France. This peninsula of approximately 27,000 km^2, bordered by the Atlantic Ocean and the English Channel, is exposed to oceanic climatic conditions. The climate is temperate and wet due to the

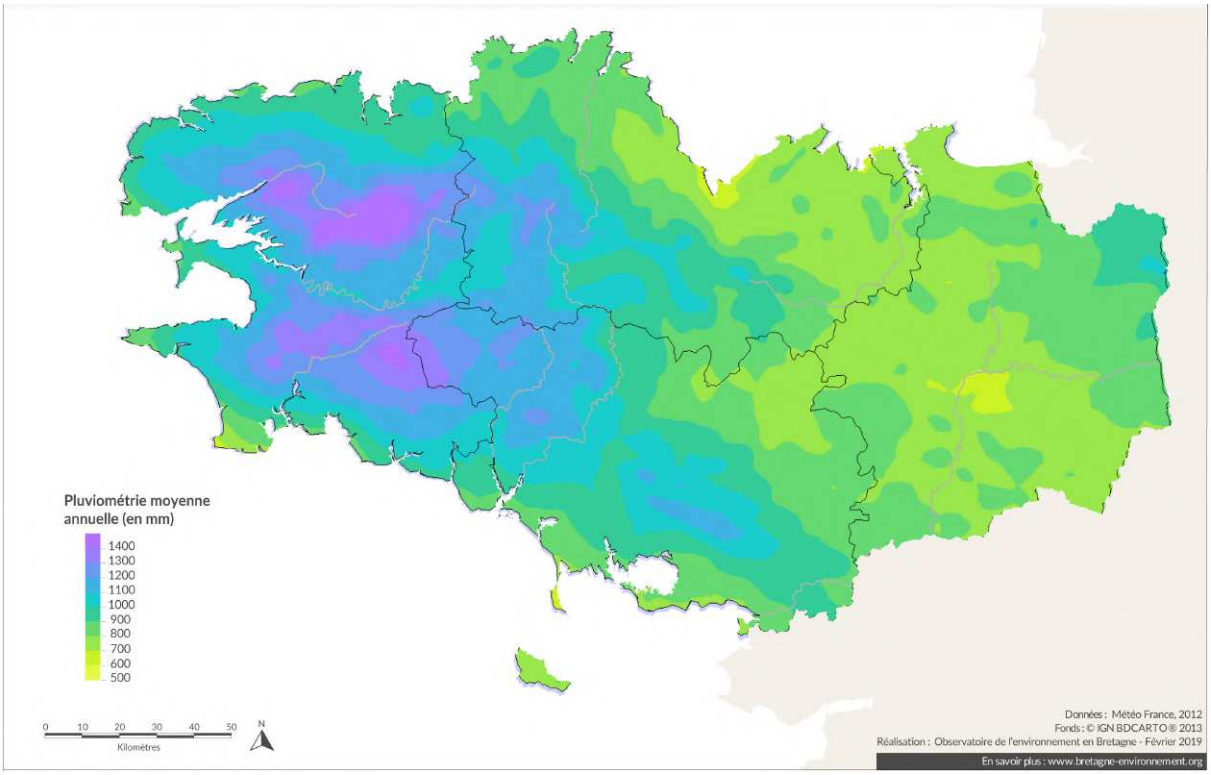

Figure 1.14 – Map of annual rainfall in Brittany in millimetres. Source: Brittany Environmental Observatory - OEB (2019) using data from Météo-France 2012.

dominant influence of ocean currents. The mean annual rainfall is approximately 860 mm for the region and it presents a gradient between western and eastern Brittany (Fig. 1.14). The rainfall gradient decreases from the Atlantic coast in the west to the north-eastern coast. Annual rainfall totals in the western part of the region are twice those in the Rennes basin in the eastern part. This rainfall determines the spatial and temporal distribution of water resources across the territory.

The mean annual temperature in the Brittany region is 11.3 °C. Within the region, there is also a gradient in temperature, with a fairly mild winter in the eastern part of the region and summers warmer than in the west of the region (Fig. 1.15). The rainiest months are from October to February during autumn and winter, and the driest months are from March to September during spring and summer. This particular weather affects the evapotranspiration and groundwater recharge. The bedrock in the Brittany region is mainly composed of a crystalline substratum dominated by granite and schist. The topography is moderate, with elevations ranging from 0 to 330 metres above sea level. Overall, agricultural crops account for 59% of the region's total area. Of the farms in

Brittany, 63% of farms specialise in dairy or pig production, while 10% engage in mixed crop and multi-livestock farming systems (DRAAF, 2021).

Most headwater catchments in the Brittany region are dominated by subsurface flow (i.e. shallow groundwater inputs). However, they present differences in their topography, geology, hydrology, and diffuse and point-source nutrient pressures. Nutrient surpluses are high and spatially variable within the region with mean ± standard deviation of 50.0 ± 26.6 $kgNha^{-1}yr^{-1}$ and 22.5 ± 12.7 $kgPha^{-1}yr^{-1}$ (Guillemot et al., 2021). The behaviour of nutrients within the catchment is related to hydrological variability, which can affect the spatial distribution of concentrations at seasonal or event scales (Dupas et al., 2016; Ebeling et al., 2021). For instance, during the low-flow season, biological processes in the benthic and hyporheic zones can strongly influence water chemistry due to high residence times and temperatures. However, during the high-flow season, the larger nutrient flux could reduce the biological influence on water chemistry (Ebeling et al., 2021; Moatar et al., 2017). These observed biogeochemical patterns in the relationship between concentration and discharge across diverse catchments are attributed to the legacy of anthropogenic nutrient sources (Basu et al., 2010; Godsey et al., 2009; Musolff et al., 2015).

1.5 Research questions and thesis structure

Understanding the biogeochemistry of intermittent streams is crucial, as the presence of nutrients and organic matter influences biodiversity within these ecosystems (Foulquier et al., 2024; Zimmer et al., 2022). Most studies of the biogeochemistry in intermittent streams have been conducted in arid and Mediterranean climates (Gómez-Gener et al., 2021; N. T. Skoulikidis, Sabater, et al., 2017), these studies have shown that the high spatial heterogeneity in solute concentrations is result of isolated pools formed during stream fragmentation (Dent & Grimm, 1999; Fellman et al., 2011; von Schiller et al., 2011). While other studies of Alpine glacial catchments have evaluated the physicochemistry and function of headwater streams, showing mixed water source inputs (Robinson et al., 2015), they have also shown no variation in standing stocks of organic matter. However, they have also shown an increase in the assimilation of periphyton by aquatic macroinvertebrates (Siebers et al., 2020, 2022). However, intermittent streams are also prevalent in temperate oceanic climates (Messager et al., 2021; Snelder et al., 2013), where intermittent flow is usually limited to headwaters catchments (Fovet et al., 2021;

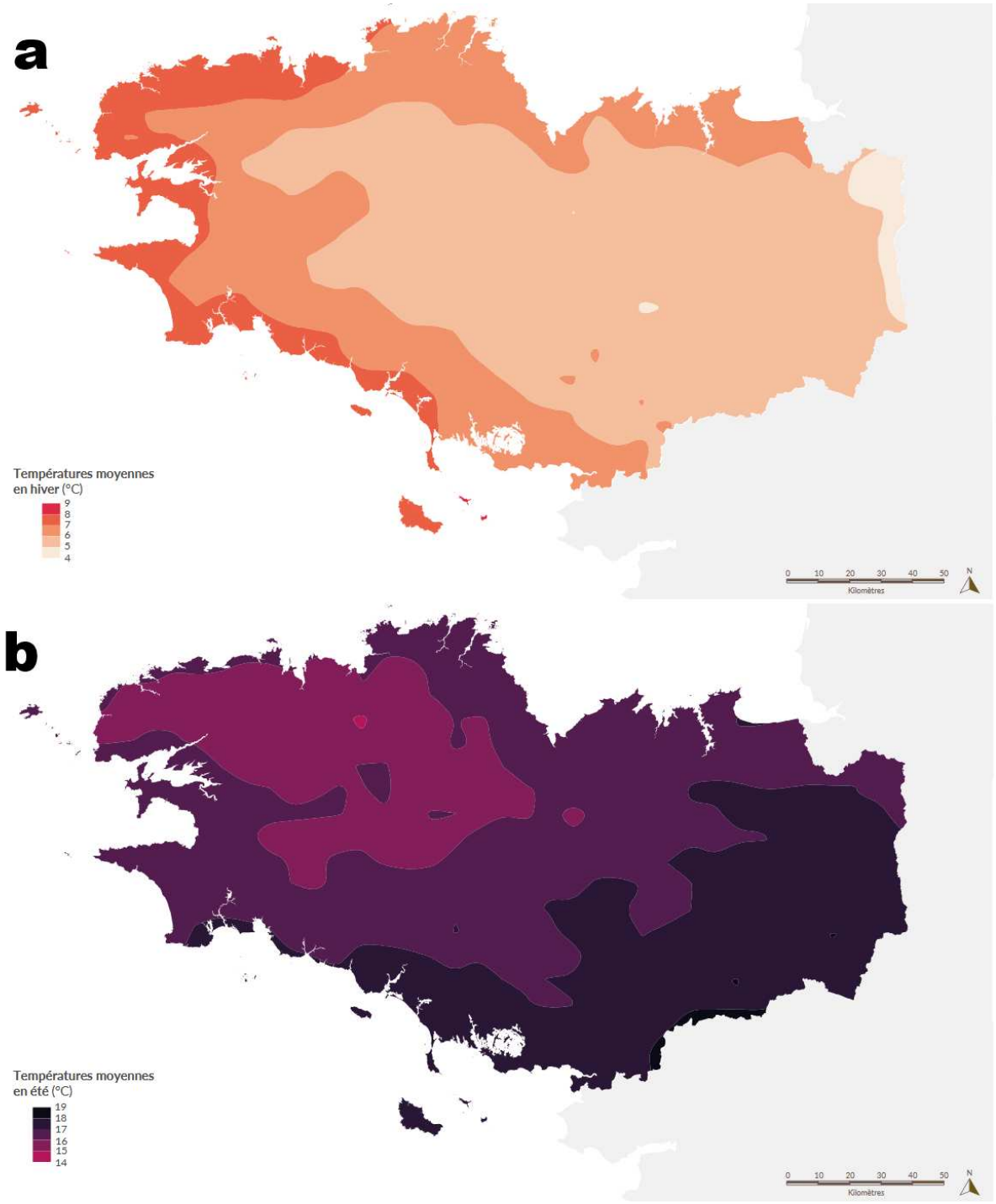

Figure 1.15 – Maps of mean annual temperatures (a) in winter and (b) in summer in the Brittany region, from the period of 1976-2005. Data source Météo-France (SAFRAN/SIM2). Source: Brittany Environmental Observatory - OEB (2025).

Kaplan et al., 2020; Stubbington et al., 2017). These temperate headwater catchments are mainly subjected to high nutrient loads from agricultural land use (Guillemot et al., 2021; Stubbington et al., 2017), resulting in elevated concentrations compared to more pristine environments. However, the concentrations of these nutrients exhibit less variations over time and space (Basu et al., 2010; Godsey et al., 2009; Musolff et al., 2015). Although, research into these intermittent streams in temperate-oceanic landscapes impacted by agriculture is lacking. The response to stream fragmentation in Brittany is likely to differ from that of Mediterranean, arid or mountainous streams due to: *(i)* their size; as the relative importance of in-stream biogeochemical processes is expected to be small in headwaters and to increase in downstream waters (Creed et al., 2015; Vannote et al., 1980). *(ii)* their historical nutrient legacies from agricultural activities, which buffer the temporal and spatial variability of water concentrations and which influence the dominant forms and nature of C, N and P elements in the streams (Arheimer & Lidén, 2000; Heathwaite & Johnes, 1996; Heinz et al., 2015). *(iii)* their mild temperatures, which are likely to enhance biogeochemical reactivity compared to warmer (or cooler) conditions, or to reduce seasonal variations in reactivity due to reduced thermal amplitude (Acuña et al., 2008; Enquist et al., 2003; Friberg et al., 2009).

1.5.1 Objectives

This thesis aims to expand the knowledge of biogeochemical cycles in intermittent rivers and streams within an oceanic temperate context. The study focuses on the Brittany region of France, an area with high agricultural nutrient inputs and diffuse pollution, abundant rainfall and mild temperatures. Consequently, there is a particular interest in the future of nutrient loading in dynamic stream networks, especially in intermittent headwaters catchments. The thesis addresses the following main research question: **What are the biogeochemical patterns and processes associated with hydrological intermittence in a temperate oceanic context?** This research question has led to three specific questions emerging:

1. **What are the drivers of intermittence in the Brittany region?** We conduct the identification of intermittent rivers and streams in the Brittany region using discrete flow state observations and the available information regarding intermittence. We expect the following: *(i)* the spatial distribution of intermittent rivers and streams in Brittany is structured, and *(ii)* the controls of this spatial

structure of hydrological intermittence can be predicted based in local geographical characteristics at the catchment scale.

2. **How does hydrological fragmentation alter the spatial variability of dissolved nutrients and organic matter concentrations along the stream in an agricultural catchment?** We investigated this question by conducting repeated synoptic sampling of nutrient and organic matter concentrations at a high spatial resolution during the fragmentation of a headwater stream network. We can hypothesise the following: *(i)* the increase of spatial variability of nutrient and OM concentrations observed during the fragmentation of Mediterranean and arid streams could also be observed in a temperate-oceanic catchment subject to intensive agricultural practices. *(ii)* the direction of change in nutrient and organic matter concentrations during the fragmentation of an intermittent stream could be predicted based on observations of perennial streams in the same region during the low-flow season.
3. **How do the speciation of nutrients and the composition of dissolved organic matter change during the stream fragmentation in an agricultural catchment?** We investigate this question by analysing repeated synoptic characterisation of N forms, dissolved reactive versus total P, and DOM optical properties during the fragmentation of three headwater coastal streams. During stream fragmentation, stagnant water in the channel typically exhibits hypoxic conditions. We therefore expect the following: *(i)* the reduced and organic forms of N and P will increase while the more oxidised and inorganic forms will decrease. *(ii)* the microbial and protein forms of dissolved organic matter will tend to increase due to the increased residence time and temperature in isolated pools during hydrological fragmentation.

1.5.2 Thesis structure

The **Chapter 2: Characterisation of intermittent streams in a temperate oceanic region**, provides an overview of intermittent streams in Brittany by examining public databases of flow state recordings. Unlike the following chapters, this one is not intended to be published as a research article. It rather provides contextual information before addressing the main research question related to the biogeochemistry of intermittent temperate streams (Chapters 3 and 4). Chapter 2 evaluates the accuracy of spatial

public data on intermittence in the region's stream networks. The chapter explores the spatial, climatic, and environmental controls on river intermittence using random forest modelling. Furthermore, the chapter discusses the geomorphological controls of intermittence, comparing field measurements with regional data on stream channel structure. Finally, the chapter seeks to estimate the rewetting date and the role of groundwater in controlling intermittent flow of a headwater agricultural catchment.

The **Chapter 3: Spatial variability in nutrient and organic matter concentrations during hydrological fragmentation of an intermittent temperate catchment**, investigates changes in the spatial configuration of nutrient and organic matter concentrations during the hydrological fragmentation of an intermittent stream network in a temperate-oceanic agricultural catchment. Using repeated synoptic sampling at a high spatial resolution, the analysis assessed dissolved organic carbon concentrations and fluorescence properties, as well as dissolved inorganic nitrogen and soluble reactive phosphorus concentrations, during four different phases of intermittence in one hydrological year. This includes stream recession, as well as two stages of stream fragmentation and reconnection of the stream. This chapter has been written in the form of a scientific article.

The **Chapter 4: Hydrological fragmentation alters nutrients and organic matter speciation in intermittent agricultural catchments**, examines changes in the speciation of nutrients and organic matter in three intermittent sub-catchments within a temperate-oceanic catchment that drains into an inner sea. The repeated synoptic sampling method was employed to capture subcatchments with various land uses. The organic and inorganic forms of nitrogen and phosphorus were analysed, as well as optical properties of dissolved organic matter and dissolved organic carbon concentrations. The intended sampling covers four stages of the stream network's hydrology, including stream recession, two phases of fragmentation and a winter sampling date to capture high flow conditions. This chapter has been written in the form of a scientific article.

The **Chapter 5: General discussion**, considers the results and arguments of the previous three chapters, connecting them and responding to the research questions. It then proposes some perspectives and conclusions on the thesis as a whole.

Chapter 2

Characterisation of intermittent streams in an temperate oceanic region

2.1 Abstract

Intermittent rivers and streams are those who cease to flow at some point during the year. They are estimated to be present in all biomes worldwide, including temperate regions in France. Here, we analyse the prevalence of intermittent streams in Brittany, a region characterised by a wet climate and mild temperatures. The headwater catchments are also dominated by subsurface flow, and the region exhibits spatial differences in topography, geology, and hydrology. First, we analysed the discrete flow-state observation data from 129 monitoring sites in the region, collected by the National Drought Observatory (ONDE), and compared it to the French hydrographic reference system (TOPAGE), and the theoretical hydrographic network (RHT), which is based on a digital elevation model for France. The results revealed a gradient of intermittent streams, indicating higher presence of intermittent streams in the eastern part of the region than in the western part. Comparisons revealed an underestimation of intermittent reaches on the TOPAGE reference map and greater accuracy in the probability of intermittence from the RHT model. Secondly, we attempted to predict intermittence using a random forest classification model and spatial data from the 129 selected catchments. The results of the model showed that climatic variables and catchment properties, such as slope, were important factors. Consequently, we evaluate the role of the geomorphology of watercourses in determining the intermittent nature of headwater streams. To do this, we analyse the depth-to-width ratio of two such catchments and compare the results with publicly available data on the geomorphology of watercourses in the region. The results showed that our study sites were more incised than the regional reference data, but unfortunately this

does not prove that geomorphological alterations to rivers cause intermittency. Finally, an analysis of the influence of the water table on the flow dynamics of the surface stream in an intermittent headwater catchment, showed that the lower the water table, the more precipitation is needed for the stream to flow again. These results showed a hydrological overview of intermittent streams in Brittany at regional and local scale.

2.2 Introduction

Most of the river networks around the world periodically cease to flow, or only flow after intense rainfall (Datry et al., 2017; Messager et al., 2021). In many cases, these intermittent streams are located in headwaters, i.e. in the upstream part of river networks and they feed downstream perennial streams. They play an important role in the functioning of rivers and provision of ecosystem services such as supporting biodiversity and regulating water quality (Bieroza et al., 2024; Křeček et al., 2017). Intermittent headwater streams are particularly sensitive to climate change and other human impacts such as water abstraction, channelisation and pollution (Van Meerveld et al., 2020).

Recent studies underline the importance of better characterising the hydrological functioning of headwater intermittent streams, but highlight that the availability of hydrological information regarding these systems is currently scarce (Acuña et al., 2017; Beaufort et al., 2019). Moreover, most gauging stations are located in perennial downstream rivers, therefore intermittent headwater streams are underrepresented in hydrological studies (Godsey & Kirchner, 2014; Snelder et al., 2013). Nevertheless, recent initiatives should help in filling this lack of data in the future. For example, the use of citizen-participatory science initiatives can help overcome the lack of hydrological data on such intermittent streams (Gallart et al., 2016; Truchy et al., 2023; Van Meerveld et al., 2017). In France, a network of flow-state observations called ONDE (Observatoire National des Etiages) has been developed for the long-term monitoring of low-flow states in headwater streams during the summer (Nowak Céline, 2016).

The spatial variability of intermittent rivers is driven by climate, specially aridity at global, continental and national scales but it results from a combination of geological (porosity, permeability) and geomorphological properties at the regional or local scale (Hammond et al., 2021; Messager et al., 2021; Sauquet et al., 2021; Snelder et al., 2013). This combination of controls tends to be unique depending on the region (Boulton et al.,

2017; Hammond et al., 2021; Snelder et al., 2013). In this chapter, we aim at informing the occurrence and controls of intermittent stream in the region of Brittany, western France.

While the core of this PhD thesis is about the biogeochemistry of intermittent streams, this requires knowledge on the prevalence of these intermittent streams in the study region from a hydrological perspective. This is because, contrary to Mediterranean or Alpine regions of France, no peer-reviewed studies exist on flow intermittence in Brittany. The literature on intermittent streams in temperate regions is beginning to grow but mainly in sedimentary catchments (Kaplan et al., 2020; Stubbington et al., 2017). French Brittany is dominated by impervious bedrock geology (granite, schists) leading to stream networks mainly supplied by relatively shallow groundwater flow paths and relatively low water storage capacity. Then, groundwater fluctuations are expected to be a major driver of intermittence in its headwater streams (e.g. Abhervé et al. (2024)). As in many other temperate regions, intermittent headwater streams in French Brittany often flow through agricultural landscapes, where disturbances to the river channel are likely to occur through tile drainage and the channelisation of watercourses (Bieroza et al., 2024). Changes in fluvial geomorphology (e.g. changes in the shape, longitudinal profile and cross-section geometry of the channel, changes in the channel-bed substrate, and changes in the extent of the floodplain) affect the hydrological and sediment regimes by altering the timing, frequency, magnitude and duration of the water discharge (Jaeger et al., 2017).

The interaction between the catchment-scale drivers can result in diverse flow cessation, drying and rewetting processes. To characterise the spatial and temporal variability in flow intermittence, and identify their controlling factors in the study region, is an important contextual information before addressing the main research questions for the PhD work on their biogeochemistry (Chapters 3 and 4). Section 2 first examines the spatial distribution of the intermittent streams within Brittany and evaluates the consistency of available information regarding intermittence including the data on low flows that are more recently available (ONDE). Section 3 then investigates the drivers of intermittence. We use geographic information to identify the spatial drivers of intermittence, and temporal records from a local research observatory to determine the influence of interactions between groundwater and surface water on controlling intermittence in the study area.

2.3 Spatial distribution of intermittent streams in the Brittany region

This section introduces the Brittany region, and then uses a dataset of discrete flow-state observations to analyse stream fragmentation in low-order rivers. The aim is to: (*i*) describe the spatial variability of intermittent streams in an oceanic temperate climate region; (*ii*) evaluate the relevance of a hydrographic reference map (e.g. TOPAGE) for classifying intermittence; and (*iii*) estimate the accuracy with which a topographic-hydrological model (e.g. RHT) can predict intermittence.

2.3.1 Spatial distribution of intermittent streams according to a national program of discrete flow-state observations

The ONDE network (Observatoire National des Étiages), is a national program of discrete flow-state observations created in 2012 by the French Biodiversity Agency (AFB, now OFB, https://ofb.gouv.fr). It aims to establish a long-term monitoring dataset of discrete flow-state observations in headwater streams during summer, in order to anticipate and manage water crises during severe droughts (Beaufort et al., 2019; Nowak Céline, 2016). This network comprises 3220 stations in metropolitan France, including 129 stations in the Brittany region. The network provides discrete field observations at a monthly frequency (around the 25th from May to September), with additional observations sometimes taking place outside this period in order to monitor droughts. The observation sites are mainly located in catchments with a drainage area of less than 50 km^2 (Fig. 2.1).

The field observations for each station are classified into three classes: visible flow; continuous flow, permanent and visible to the naked eye, non-visible flow; the riverbed contains water but the flow rate is zero (e.g. presence of isolated pools), and dry; water has completely evaporated or infiltrated over more than 50% of the station (Nowak Céline, 2016). Here we consider two intermittence states: "Flowing" when there is visible flow across the channel and "Non-flowing", when there is non-visible flow or the channel is dry. The relative frequency of non-flow was estimated by calculating the proportion of non-visible flow and dry observations out of the total number of observations per site. For the study period of 2012–2024, the relative frequency of non-flow was calculated for the 129 ONDE sites in the region (Fig. 2.2).

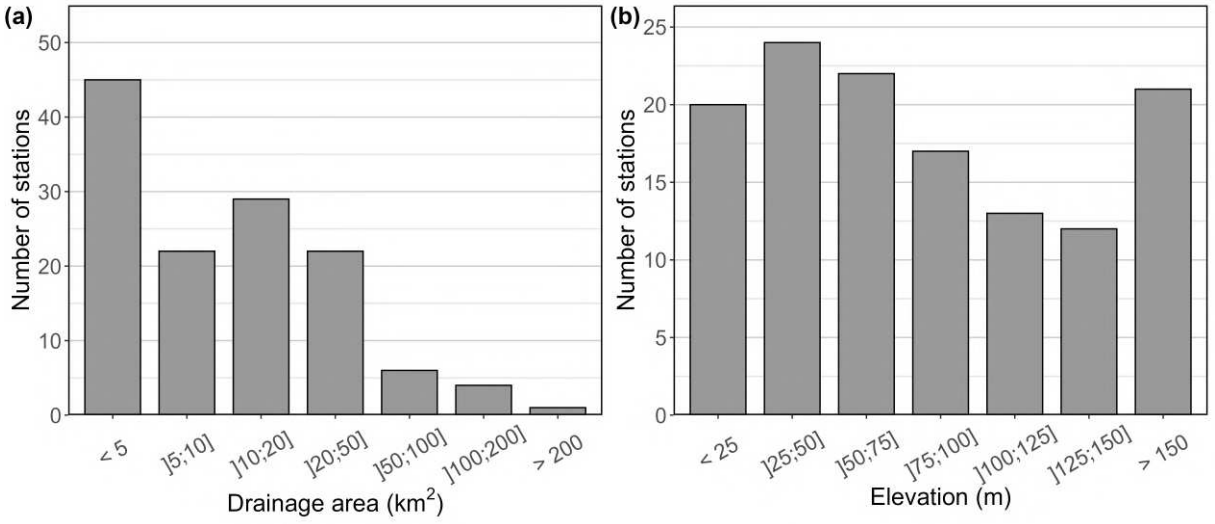

Figure 2.1 – Distribution of (a) drainage area and (b) elevation for the 129 ONDE sites in the Britany region.

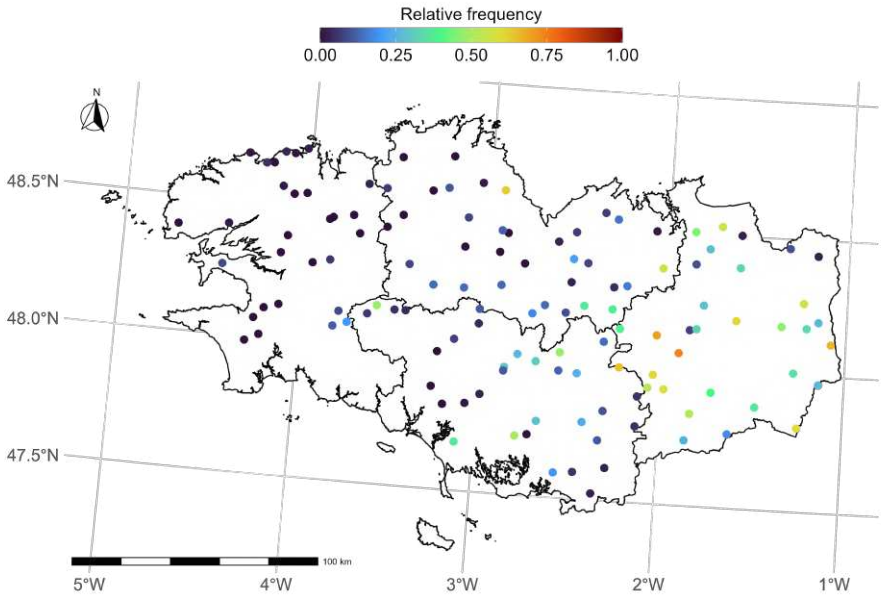

Figure 2.2 – Relative frequency of intermittence of the 129 ONDE sites in the Brittany region. The data is from 2012-2024 and the frequency is calculated as the non-visible flow and dry observations over the total observations.

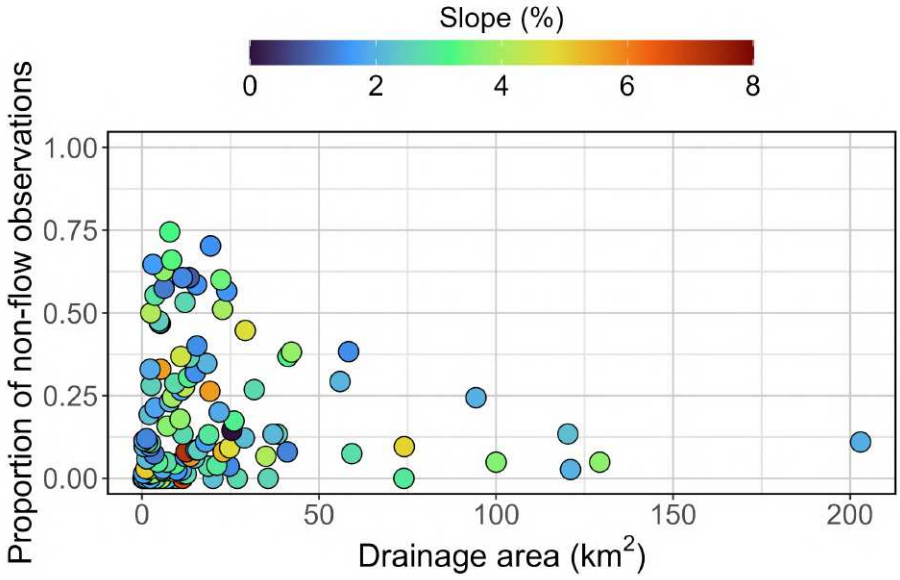

Figure 2.3 – Relative frequency of non-flow observations compared to the drainage area and elevation of the 129 ONDE sites in the Brittany region.

The proportion of non-flow observations ranged from 0 (where all observations showed continuous and permanent flow state) to 0.74 (where there was a higher number of observations of non-visible flow and dry states). Higher proportions of non-flow observations intermittence were found in sites with small drainage areas (Fig. 2.3). The estimated proportions need to be taken into account carefully as they may be biased due the regular period of observations (May to September) and to a greater number of observations during periods of high dryness (i.e. complementary observations per site) outside the regular period. The results show a gradient, with a higher density of intermittent watercourses in the eastern part of the region (Fig. 2.2), where catchments are flatter and drier the in the west (more detailed analysis of spatial attributes are presented in section 3). The discrete observations of ONDE provide a precise monitoring of intermittence in low-order streams.

However, this information is only available at a few (129) monitoring locations, whereas managers would require more extensive information along the entire river network. In Brittany, there are two extensive maps of the river network that provide information on the intermittent versus perennial status of river sections. The first of these are TOPAGE maps, which describe France's hydrographic features on a national scale. The second are RHT maps, for which the hydrological features are estimated using a topographic model.

The ONDE observations provide a unique opportunity to evaluate these maps, which is crucial for assessing the proportion of intermittent streams in the Brittany region and for managing the ecological status of local rivers. The following subsections assess how accurately these maps identify intermittent streams in Brittany using discrete flow-state observations from ONDE.

2.3.2 Low accuracy of the French hydrographic reference system in predicting intermittence

The French hydrographic reference system (TOPAGE) aims to describe the hydrographic features in France, in order to create a national reference system for locating water-related data (SANDRE, 2020). The TOPAGE database contains publicly available data in vector format, such as watercourses, water bodies, hydrographic sections, hydrographic basins, topographic catchment areas, and land-sea boundaries. The classification used to categorise watercourses as intermittent originates from the Infrastructure of Spatial Information in Europe (INSPIRE) (INSPIRE, 2024). According to INSPIRE, river segments are classified as follows: perennial (flowing continuously throughout the year), intermittent (flowing during part of the year), ephemeral (flowing during and immediately after rainfall), dry (flowing rarely, usually only during or immediately after heavy rainfall), or of unknown status. In the Brittany region there are three classes identified; perennial, intermittent and unknown (Fig. 2.4). The data used in this chapter was extracted from the 2025 database for the Brittany region, which presented three categories of water flow persistence: perennial, intermittent, and unknown. Intermittent segments from the database represented 55% of the total stream network. As expected from out knowledge of intermittence in Brittany, the intermittent segments of the network are located mainly on headwaters catchments, and a weak east-wet gradients appears on the TOPAGE map (Fig. 2.4).

The objective of this subsection is to use discrete (in space and time) flow-state observation data from ONDE to compare them with the data of the French hydrographic reference system TOPAGE to asses if the TOPAGE segments accurately represent intermittence. Using the sf package (Pebesma, 2018), the spatial information of TOPAGE segments containing ONDE sites was selected based on the closest distance from the ONDE station to the nearest TOPAGE segment. This was done in R (Team, 2024). The comparison between actual (i.e. ONDE) and predicted (i.e. TOPAGE) classifications are

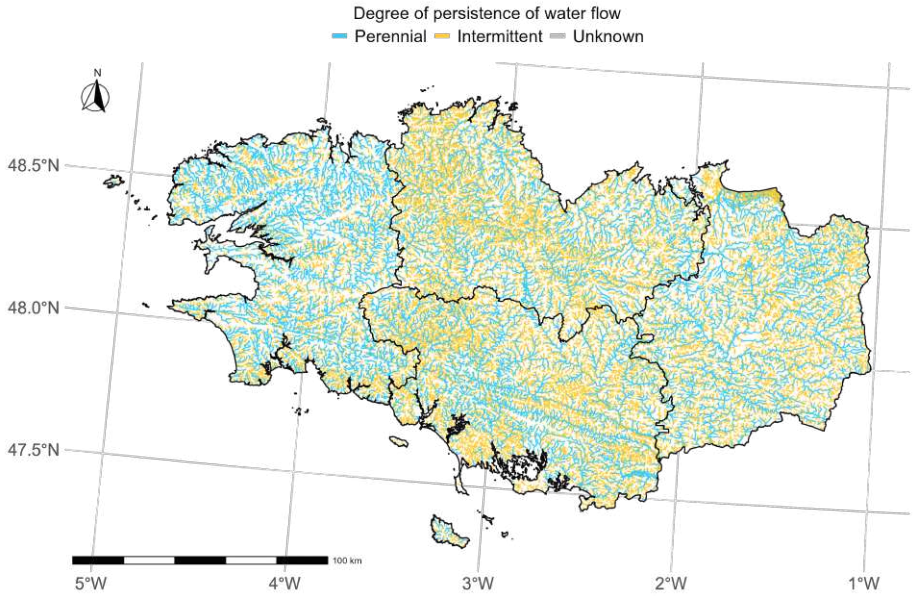

Figure 2.4 – French hydrographic reference system (TOPAGE) zoomed in on the Brittany region. The colours of the lines represent the degree of persistence of water flow in the segments of the hydrographic network.

summarised using a contingency table. From the discrete variables from ONDE categories of hydrological state, the site is considered intermittent if it has at least 1 dry observation of at least one year of the full dataset, and perennial if 100% of dates are classified as visible flow. These values were compared to the segment classification of persistence (i.e. Persistence of water flow: Perennial or intermittent) that has the same ONDE site. The total number of comparisons was 129. Additionally, the Cohen's Kappa coefficient was estimated to measure the agreement between the two categorical variables (Cohen, 1960). Values closer to $k = 1$ mean a complete agreement between the two categories, while values closer to $k = 0$ mean there is no agreement among the categories other than what would be expected randomly.

The proportions of intermittent reaches (in TOPAGE) and intermittent points (in ONDE) at the same catchment location were also compared. A Wilcoxon signed-rank test was performed on two matched samples of categorical TOPAGE data in order to compare the relative frequency of intermittence at the ONDE sites. If the result of this test was significant ($p < 0.05$), a post hoc Dunn test was performed with Bonferroni correction in order to adjust the significance level.

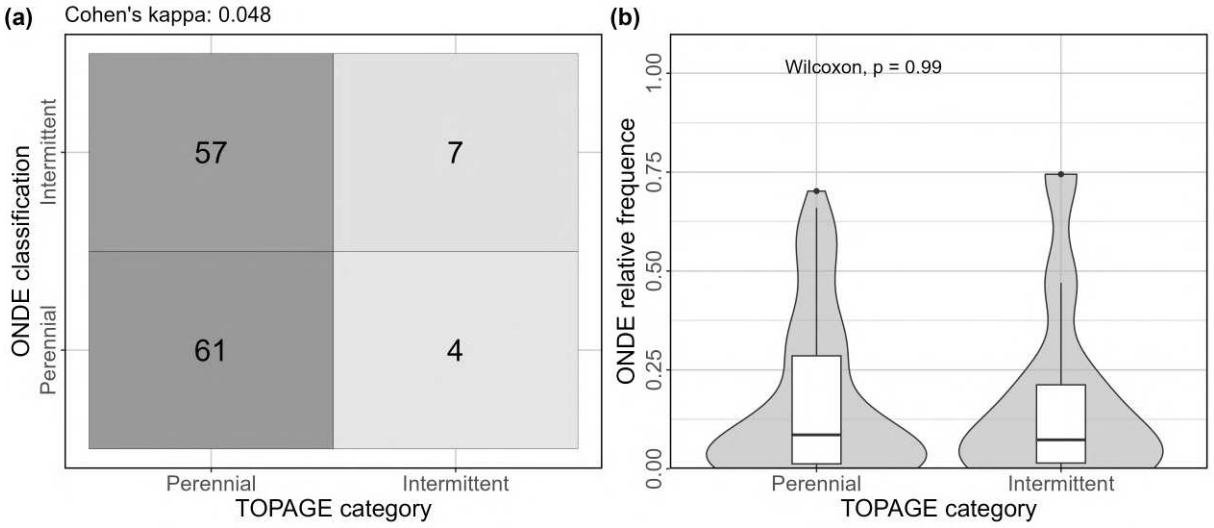

Figure 2.5 – Comparison between (a) ONDE discrete data and TOPAGE categories of persistence of water flow, (b) ONDE relative frequency of intermittence and TOPAGE categories of persistence of water flow. Statistical analysis used: (a) Contingency table with Cohen's Kappa coefficient, (b) Wilcoxon non-parametric test.

The Cohen's Kappa coefficient is lower than 0.05, indicating no agreement between the two datasets. The contingency table shows 61 true negative sites that were classified as perennial in both datasets, and only 7 true positives that were classified as intermittent in both datasets. (Fig. 2.5a). On the other hand, 57 out of 129 sites are intermittent in ONDE but perennial for TOPAGE; this is classified as false negative indicating that the condition of intermittence does not hold. In addition, the TOPAGE category of perennial and intermittent does not explain any effect on the ONDE relative frequency of intermittence (Fig. 2.5b). The difference of means between the two groups is negligible ($p > 0.05$), suggesting that the TOPAGE category does not account for the variation in proportions of the ONDE sites. In conclusion, we found TOPAGE's segments attribute (intermittent or perennial) to be not reliable with a general underestimation of intermittence occurrence in TOPAGE map. Furthermore, we explore in the next subsection if the spatial distribution of intermittent rivers can be better estimated with the RHT hydrographic network model.

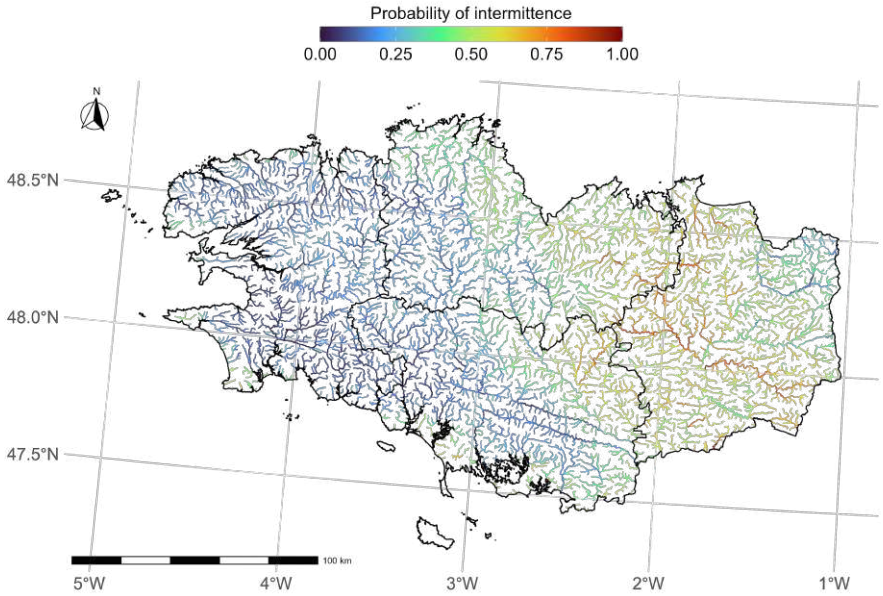

Figure 2.6 – Theoretical hydrographic network (RHT, acronym in French) in the Brittany region, showing the probability of intermittence from the final model (Snelder et al., 2013).

2.3.3 Better, but unsatisfactory accuracy of a national model at predicting the intermittence of watercourses

The theoretical hydrographic network (RHT) is an oriented network along which a number of reach-scale and catchment-scale environmental attributes are provided. The network is a digital hydrographical network derived from the BD Alti® digital elevation model of the French Geographic National Institute (IGN) (Pella et al., 2012). It enables a precise identification of catchments and simulations of flows, including other modelled environmental attributes (topologic, hydrologic and climatic features). Modelling the distribution of intermittent watercourses in France is based on catchment characteristics derived from the RHT (geology, climate, geography, etc.) (Pella et al., 2012; Snelder et al., 2013). The intermittent model was calibrated using data from 628 gauging stations in the French hydrological database, in order to predict the frequency of drying throughout the river network. This was achieved with a statistical model to assess flow regimes related to environmental variables (Fig. 2.6).

The RHT modelling results show the probability of intermittence for each segment of the hydrographic network (Fig. 2.6). The map shows an east-west gradient of intermittence with a high density of intermittence in the eastern part of the region, and, a

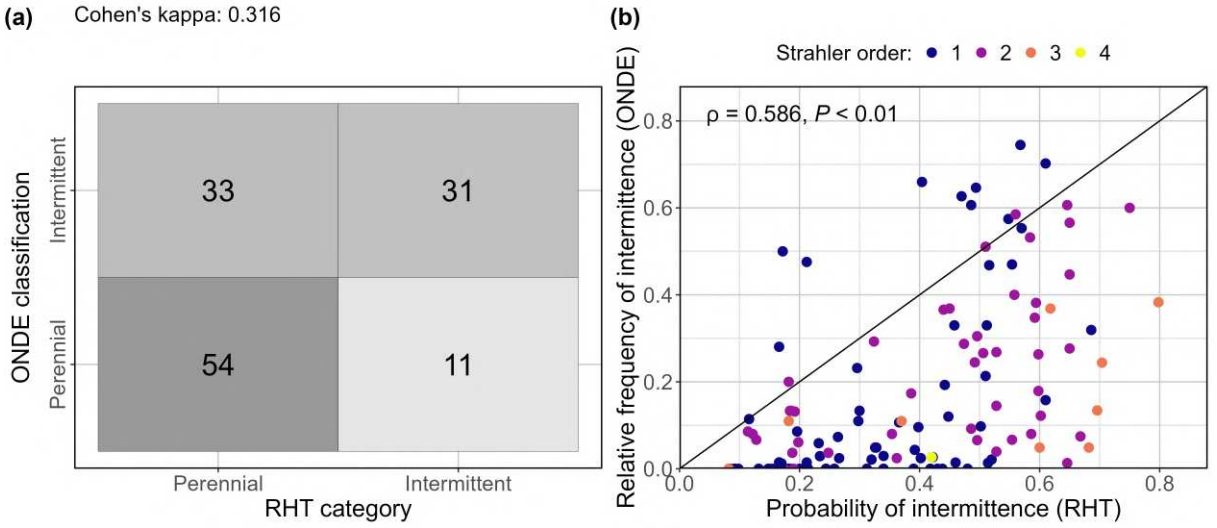

Figure 2.7 – Comparison between (a) ONDE discrete data and RHT categories of probability of intermittence ≥ 0.5 for intermittent, (b) Scatter plot the relative frequency of intermittence observed at ONDE sites from 2012 to 2024 (n = 129) in x axis, and the probability of intermittence of the segment where the ONDE site is placed, estimated by the hydrological model RHT. Colors represent the Strahler order for each segment. Statistics shown are (a) Contingency table with Cohen's Kappa coefficient, (b) Spearman correlation and its respective $p - value$.

relatively low probability of intermittence to the west, particularly in the central part of the region. The spatial information of the RHT segments containing the ONDE sites was selected. The evaluation required classifying the ONDE sites (discrete observation records), and RHT segment (probability of intermittence) as either perennial or intermittent. ONDE sites classification was conducted as previously (section 2.3.2). When probability of drying of RHT reach was greater than 0.5 we categorised the reach as intermittent, while all others were designated as perennial. A contingency table was used to summarise the comparison between actual (ONDE) and predicted (RHT) classifications. Cohen's kappa coefficient was estimated as previously (section 2.3.2) to measure the agreement between the two categorical variables. Finally, the relative frequency of intermittence at the ONDE sites was compared with the probability of intermittence in the RHT dataset. Spearman's correlation was used to assess the consistency between both percentages.

The Cohen's Kappa coefficient is 0.32, which indicates greater reliability than the previous comparison of ONDE with TOPAGE data. The contingency table shows 54 truly perennial sites, i.e. where both datasets identify the site/stream as perennial, while

there were 31 truly intermittent sites (Fig. 2.7a). Additionally, 33 out of 129 sites are intermittent in ONDE but perennial for RHT. This is classified as a false negative, indicating that RHT might incorrectly classify segments as perennials. There is some concordance in predicting intermittence with RHT modelled data of the river segment. The relative frequency of intermittence from the ONDE site showed a moderate correlation with the probability of intermittence from the RHT (Fig. 2.7b). The sites are mostly related to the low-order Strahler for both datasets.

In conclusion, we showed that discrete-flow state observations from ONDE provide unique data on which to base considerations of the intermittence of low-order streams. Although the RHT modelled data was closer to the ONDE observed data than the TOPAGE dataset, the prediction was not satisfactory. Therefore, it would be of interest to scientist and catchment managers to develop a more accurate map of flow intermittence across Brittany. The next sections explore the feasibility of creating such a map by investigating whether it is possible to identify the controls on the spatial distribution of intermittent rivers from catchment attributes derived from GIS information. Given that Brittany is a relatively homogeneous region in terms of climate, geology, catchment size and land use, we expected the performance of such a model to be better than that of the national RHT model. We also expected that using ONDE observations would improve the model's performance compared to hydrological data from the national gauging network, which undersamples intermittent streams.

2.4 Controls and temporal dynamics of intermittence

The intermittence of streams is controlled by climatic conditions, catchment size, and geomorphological and hydrogeological features in the catchment (Abhervé et al., 2024; Allen et al., 2020). In this section, the spatial features of intermittent and perennial catchments are used to: (*i*) predict intermittence using a random forest classification model; and (*ii*) understand the factors controlling stream intermittence using geomorphological data on river segments. Finally, temporal hydrological data from a headwater catchment are used to: (*iii*) understand the role of the water table in maintaining the presence of water in an intermittent stream.

2.4.1 Predicting stream intermittence using a spatial approach based on a Random Forest algorithm

Given that Brittany is a relatively homogeneous region in terms of climate, geology, catchment size and land use, we expected the performance of such a model to be better than that of the national RHT model. We also expected that using ONDE observations would improve the model's performance compared to hydrological data from the national gauging network, which undersamples intermittent streams. Simulations based on topographic models and existing discharge data, which mainly originate from high-order catchments, are not precise enough to predict intermittence in headwater streams (see section 2.3.3). These intermittent streams have physical characteristics that differ from those of perennial streams. Here, we have developed a random forest (RF) model to estimate intermittence classification using spatial information from the ONDE catchments. A random forest is a machine learning model used for classification and forecasting (Döll et al., 2024).

The ONDE catchments were delimitated from a 25 m resolution DEM using the SIMFEN webservice (Dallery et al., 2022). We then computed numerous catchment attributes from relevant GIS data available across Brittany. Data on flow obstacles was extracted from the national reference database (ROE, Atlas-Catalogue du Sandre). Flow obstacles are water-related structures that cause a change in surface water level; examples include dams and reservoirs. Flow obstacles can play two roles: water reservoirs can promote intermittence, and certain dams can provide support during periods of low water. Only anthropogenic obstacles that are still in operation are considered here. We computed the density of obstacles per km^2 for each catchment. The geology data comes from the French Soil Geographic Database (BDGSF) at a scale of 1:1,000,000, which provides simplified mapping of the region's geology (INRA, 2018). The main focus is on the dominant parent material, with 14 different materials distinguished and grouped into four classes. The extracted data showed the dominant bedrock material per catchment area in relation to the total area of the catchment. The region's main bedrock materials are schist and granite (51.2% and 32.8%, respectively). Alluvium was also included as it could be an important factor in intermittence (2.3%). Other, less extensive bedrock materials, such as loess, silt, sand and limestone, were grouped together (3.1%, 4.7%, 0.8% and 3.9%, respectively).

The hydrology data on potential wetlands was downloaded from the catalogue of geographical data on the French public data platform (*www.data.gouv.fr*). Potential wetlands

Table 2.1 – Descriptors of spatial variables used in the statistical random forest (RF) model

Categories	**Calculated indicators**	**Description**	**Unit**
Flow obstruction reference system	Existing flow obstacles	Obstacles_area	Number/km^2
	Existing flow dams	Dam_area	Number/km^2
Geology	Bedrock material	Mat_Shale	%
		Mat_Granite	%
		Mat_Alluvium	%
		Mat_others	%
Hydrology	Potential wetland surface	Wetland	%
	Strahler order	Strahler	Count
Land use	Agricultural land	Surf_Agriculture	%
	Arable land	Surf_Arable	%
	Artificial land	Surf_Artificial	%
	Forest and seminatural land	Surf_Forest	%
Climate data	Temperature	Tmax / Tmin / Tmean	°C
	Rainfall	Mean rainfall	mm
Topography	Catchment area	Catchment_area	Area (km^2)
	Slope	Slope	%

are areas in which there is a high probability of wetlands being present, as determined by modelling or from mapped data related to the wet nature of the environment. The Strahler order was extracted from the RHT dataset in the segment containing an ONDE site.

Land use data comes from the Corine Land Cover data from 2018 in raster format (European Environment Agency, 2019). Of the 44 thematic classes for the reference year, we regrouped the following: (*i*) areas where agriculture is practised into the 'agricultural surface' class; (*ii*) non-irrigated arable land and areas with complex cultivation patterns into the 'arable surface' class; (*iii*) broad-leaved forests, coniferous forests, mixed forests, natural grasslands, transitional woodland-shrub areas, moors and heathlands into the 'forest surface' class; (*iv*) urban areas and industrial, commercial and transport units into

the 'artificial surface' class (Table 2.1). The calculated indicators for each land use class correspond to the percentage of the catchment's total surface area occupied by each class.

The meteorological data comes from the platform SICLIMA (Climate Data Grid Information System, AgroClim-INRAE) (Maury et al., 2021). The SAFRAN climatic data are provided by Météo-France and were downloaded via the SICLIMA platform developed by AgroClim-INRAE. The shapefile layer brings together the 445 selected grids for the Brittany region, with data covering the period from 2012 to 2022. The climate variables selected were: effective rainfall and temperature (minimum, maximum and average). The grids are intersected for each of the 129 ONDE catchments, then calculated the average of the data present in the intersection (Table 2.1).

Topography data was extracted from a digital elevation model (DEM) at a resolution of $25m$ (BD Alti®) from the departments of the Brittany region in the catalogue of the French National Institute for Geographic and Forest Information (IGN). The slopes were calculated as the average slope per catchment using the Spatial Analyst tool of ArcGIS (ESRI®).

The spatial features of ONDE sites catchments were extracted for each catchment (Table 2.1). A Random Forest model was used to create a decision tree that could predict intermittence based on the studied variables, using the packages caret (Kuhn, 2008), RandomForest (Liaw & Wiener, 2002) and ranger (Wright & Ziegler, 2017) from the R software (Team, 2024). The model was parametrised using a split of 75% of the dataset (comprising 129 observations and 18 predictors) for training and 25% for testing. Two classes are used for classification tasks in the algorithm: Intermittent and Perennial. The algorithm was trained using a cross-validation method of k-fold variation of random samples to find the best parameters, number of trees and maximum number of nodes to be used.

The confusion matrix showed good accuracy for the model. However, the agreement for the test dataset from the Cohen's kappa coefficient of 0.46 was moderate, suggesting that the performance in predicting intermittence remains limited (Fig. 2.8a). On the other hand, the spatial features used for the RF model indicate that the climate variables are the most significant contributors to its predictive power. Maximum temperature and rainfall were the most important features during training, while the geology and flow obstructions such as dams and obstacles contributed the least to the RF prediction model (Fig. 2.8b). In second position after climate, agricultural land use, slope and wetlands also contribute

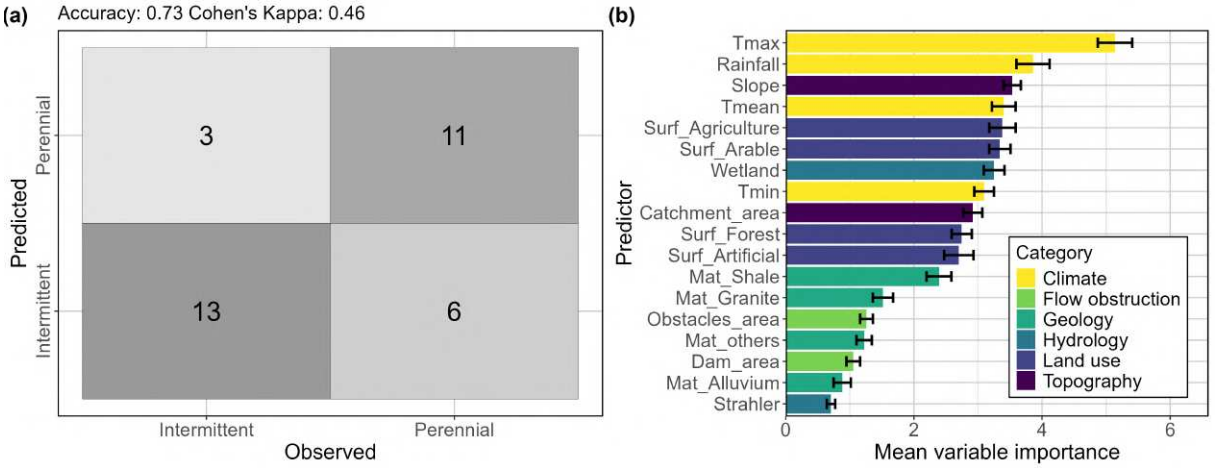

Figure 2.8 – Random Forest (RF) results; (a) Confusion matrix of predicting two classes of hydrology state: Intermittent and Perennial between the training dataset for the algorithm and the test dataset (75% and 25%, respectively), with the Accuracy and Cohen's Kappa coefficients. (b) Mean variable importance for Random Forest (RF). The higher the importance (impurity reduction), the larger the relative importance of a predictor. Error bars show the standard deviation across the cross-validation training sets calculated.

to the model's prediction, which could provide insights into drainage probability and the channelisation of watercourses.

Based on the available mapping data for the region and the ONDE information, is is clear that the spatial distribution of intermittent rivers is not solely controlled by catchment attributes considered in this section. This could be due to the fact that local and unmapped factors play an important role in determining the intermittent nature of streams. For instance, water abstraction could be a cause of intermittence, but there is no data available on small, diffuse abstractions, which dominate headwater rural catchments. Another local factor could be the geomorphology of the channel, as well as the local interactions between the water table and surface water. These factors have a significant influence on streamflow in headwater catchments (Boulton et al., 2017; Costigan et al., 2017; Snelder et al., 2013).

2.4.2 Geomorphology as a driver of intermittence in headwaters streams

In Brittany, there is a strong relationship between groundwater and watercourses, which is believed to be due to the region's geology of impermeable bedrock. Headwater

streams in this region are predominantly found in agricultural landscapes (Bieroza et al., 2024). Intermittence in these headwater streams may be related to local factors, such as tile drainage or the straightening watercourses. These modifications of watercourses could increase the probability of intermittence by either channel incision or relocating them so that they can no longer intercept the groundwater table during the low-flow season. The aim of this section is to analyse whether geomorphological modifications to river geometries in the agricultural landscapes of Brittany are a key factor in causing their intermittent flow. To test this hypothesis, we measured river geometries (width/depth ratio) in two intermittent catchments and compared them to those of reference geometries observed in unmodified rivers. We hypothesised that the analysed intermittent river reaches would have a lower width-to-depth ratio (i.e. be more incised) than the reference rivers.

The CARHYCE database is a reference database containing measurements that enable the hydromorphological characterisation of natural watercourses, as well as observations of bed grain size, bank composition, riparian vegetation type, among others (Baudoin et al., 2017). Data collection began in 2009. For comparison with our study sites, the least altered stations in Brittany were selected (Fig. 2.9) based on the absence of rectification and channelisation, and on the absence or slight modification of the hydrological regime. The other reference database is from the French Biodiversity Agency (OFB). The "OFB data" (LE BIHAN et al., 2025) summarises the same hydromorphological information from 74 reference stations in Brittany (Fig. 2.9), which are located more specifically in headwaters of catchments in the Armorican Massif. These stations target Strahler orders 1 and 2, and are "not or poorly disturbed by human activities". The width-to-depth ratio was estimated for each station using full edge width and full edge height metrics.

The width/depth ratio of a station was estimated according to the same protocol (LE BIHAN et al., 2025) by measuring full-width, full-depth heights as the average of these lengths measured taking into account water height and grain size, as described in Jan (2013), on several (6 in the field measurements we performed) distances from the bank. For each station, 6 replicates (transects) were measured and averaged (Fig. 2.10a).

The full-channel width corresponds to the width of a watercourse's channel before it overflows into the floodplain, i.e. channel width at the lowest edge of the bank to the opposite bank. The full-depth height corresponds to the water level when the stream surface reaches the lowest bank(Fig. 2.10a). Seven stations were chosen per catchment, the 6 replicates were performed over a distance approximately 30 metres. Measurements

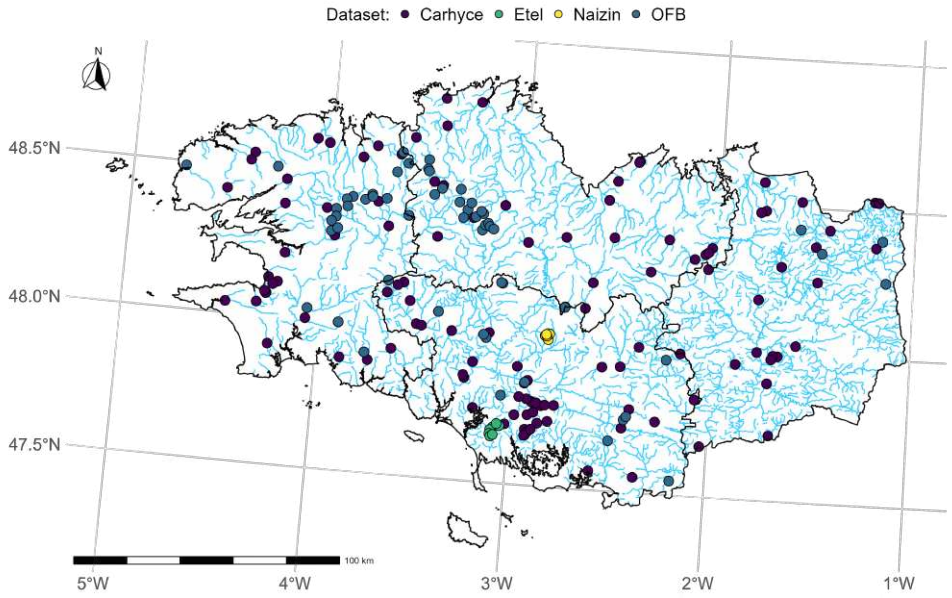

Figure 2.9 – Regional location of measuring stations for calculating the characterisation of river hydromorphology. Blue lines represent the main watercourses. Coloured points represent the different datasets analysed; Carhyce, OFB and stations where field measurements were conducted.

are taken from sections of the two catchments that are in their natural state and from sections that have been straightened or channelised. This provides an approximation of the natural state of the section, which is used to determine whether the watercourse is intermittent due to human modification.

The width-to-depth ratio can be used to characterise the geodynamic activity and bank cohesion of a watercourse. Significant lateral erosion processes and high solid inputs can result in channel incision, thereby increasing the width-to-depth ratio (Jaeger et al., 2017). Furthermore, watercourses with cohesive banks tend to be narrower and deeper. Conversely, if the banks are not very cohesive, the watercourses tend to be wider and shallower. Watercourses with cohesive banks that are narrow and deep have low ratios (Baudoin et al., 2017). Measurements taken from sections of the two study areas (Naizin and ria d'Etel) which are likely to be straightened or recalibrated are compared with the most natural sections of the Carhyce and OFB stations. This indicates the natural state of the section, which is used to determine whether the watercourse is intermittent due to human modification.

Examining the results of the ratios calculated from the field measurements, both Etel and Naizin presented low ratios of 4.6 ± 1.2 and 4.8 ± 1.9, respectively. Both catchments

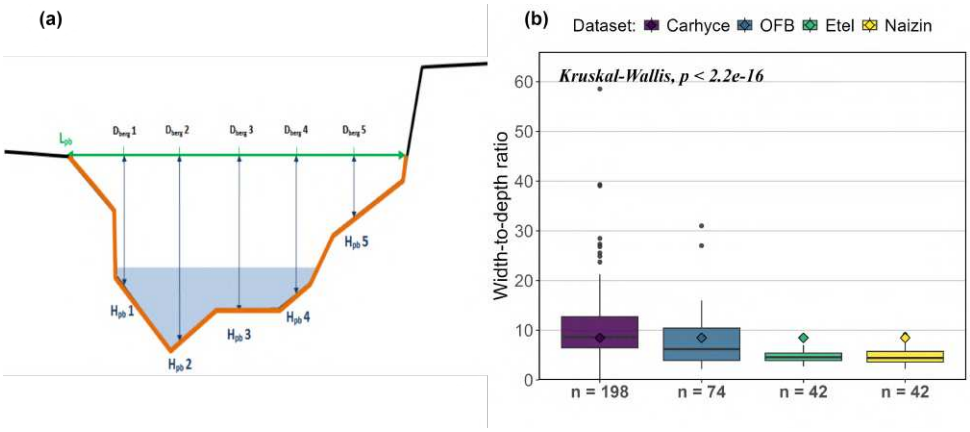

Figure 2.10 – Measurements of river morphology at the selected sites: (a) A cross-section of a river channel showing the river geometry (Jan, 2013). The orange line indicates the riverbank perimeter. The green horizontal line shows the full edge width. The vertical lines show the full edge height measured per transect. (b) Distribution of the width-depth ratio for the two reference datasets (Carhyce and OFB) and the two catchments (Etel and Naizin). Square symbols represent the mean of the data. Total measurements on the X-axis. Non-parametric statistics: Kruskal–Wallis test with its $p - value$.

differ from the reference databases, Carchyce and OFB, which had higher ratios of 10.3 ± 7.2 and 7.7 ± 5.2, respectively. The intermittent rivers of our study sites, Etel and Naizin, are therefore rather incised compared to the reference geometries in two databases of unaltered perennial rivers. However, the first analysis has major limitations because the Carchyce dataset includes rivers with a higher Strahler order than ours, which could partly explain the greater width-to-depth ratio. The OFB database, on the other hand, mostly includes headwater catchments. Therefore, our results do not prove that geomorphological alterations to rivers cause intermittence. They simply demonstrate that intermittent rivers are found in areas where the geomorphology has been modified. Further work is needed to determine whether their intermittence would decrease if they were restored to their natural shape.

2.4.3 Water table controls the intermittence of an agricultural headwaters stream catchment

Groundwater-surface water interactions are a strong control on flow dynamics in headwaters catchments (Molenat et al., 2008). Here, we analyse how the water table level is

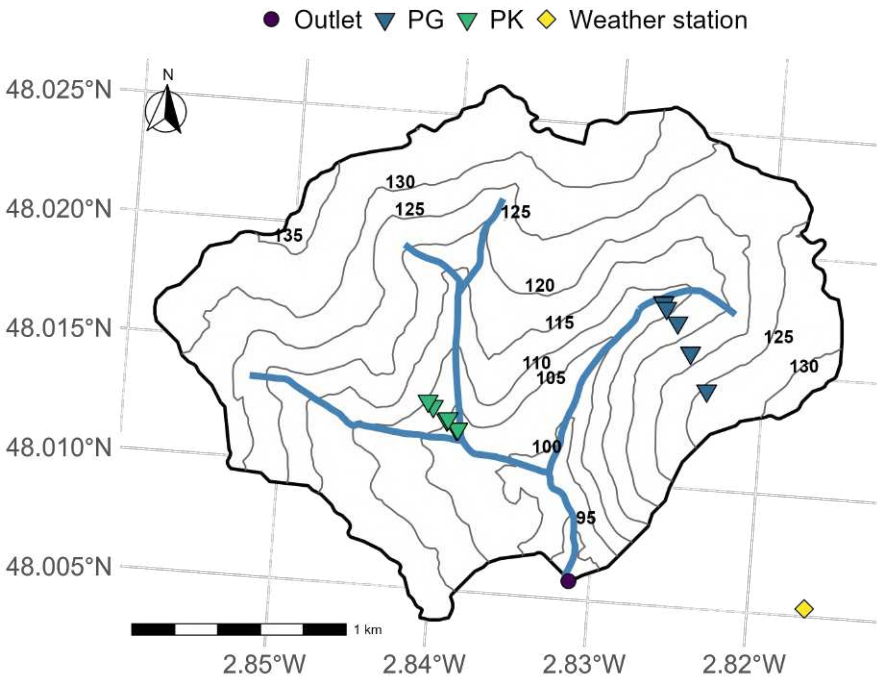

Figure 2.11 – Representation of the Kervidy-Naizin catchment. The blue line represents the river and the grey lines represent the contours with their elevation in metres. The violet dot represents the outlet where the discharge measurement station is located. The blue and green triangles represent the two transects of piezometric water levels and the yellow diamond represents the weather station.

connected to the river using Kervidy-Naizin catchment discharge data, climate data and groundwater levels, to help predict intermittency in schist geology catchments.

The Kervidy-Naizin catchment is 5 km^2 in size, with schist geology and a gentle slope (Fig. 2.11). Two piezometric transects (PK and PG) are located in the eastern and western sub-catchments, respectively at different depths (3 to 10 m), and water loggers record the water level every 15 minutes. The outlet has a discharge measurement station that records the water level at high resolution every minute, and has done so since around the year 2000 (Fovet et al., 2018). A weather station situated east of the catchment records rainfall, temperature, solar radiation, wind speed, moisture hourly among other parameters. The data used in this work are the daily mean precipitations, daily mean discharge measurements and daily mean water level for the piezometric transects. The time series covers the period from 2000 to 2024. The tendency towards intermittent flow is analysed by counting the days with non-flow at the outlet and observing the behaviour

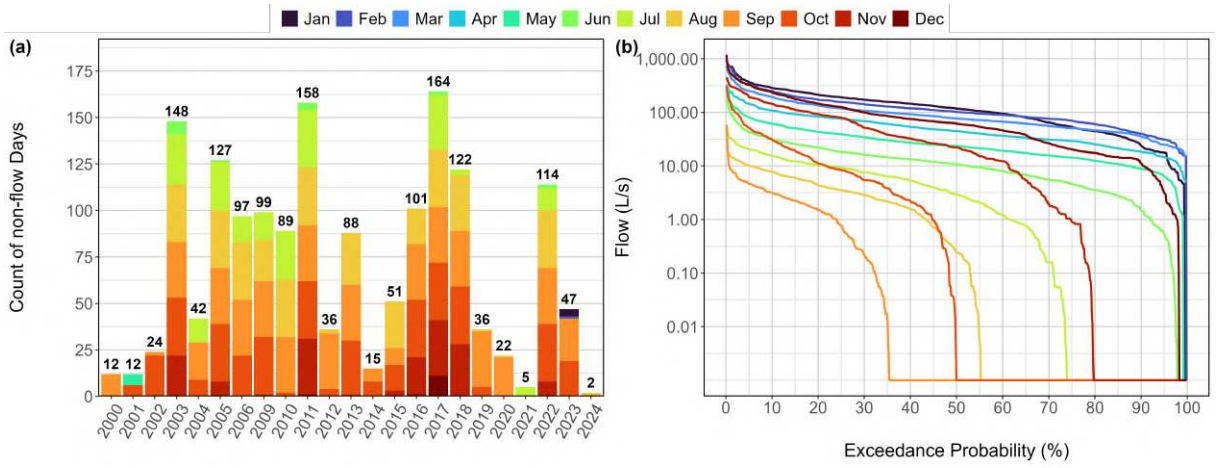

Figure 2.12 – Data on intermittence in Kervidy-Naizin based on daily discharge measurements from 2000 to 2024. (a) Number of non-flow days ($Q \leq 0.001\ L/s$) per year in Kervidy-Naizin; the numbers on top of the bars represent the total number of zero flow days in the respective year. (b) Flow duration curve for the discharge dataset, showing the flow rate per month. The y-axis is in log scale.

of the water table during this period. The analysis of the flow duration was estimated using a flow duration curve for the monthly periods. The flow duration curve shows the percent of time specified discharges were equalled or exceeded during a given period (Searcy, 1959).

Discharge in Kervidy-Naizin varies seasonally, shifting between winter and summer, depending on water table dynamics along the hillslope. Here, the intermittence is characterised by an average of 70 non-flow days per year, with significant variation from year to year (Fig. 2.12a). Non-flow days are likely to occur during late summer and early autumn, from late July to early November in drier years. No apparent trend in the number of non-flow days appear from the data. The flow duration curve is steeper in the drier months of September and October, when non-flow days are more common than in winter (Fig. 2.12b).

We estimated the amount of rainfall necessary to generate a base flow by connecting the water table to the river after a period of non-flow. For this, we considered the lowest measured value of the water table value for each of the two closest piezometer transects (PG and PK) per year. Then, we estimated the amount of rainfall required until the discharge at the outlet overcomes the threshold of $Q > 0.1Ls^{-1}$ and restores the watercourse's hydrological function. Despite the distance between the piezometer sub-catchments and the gauging station at the outlet, it is known that the drying up

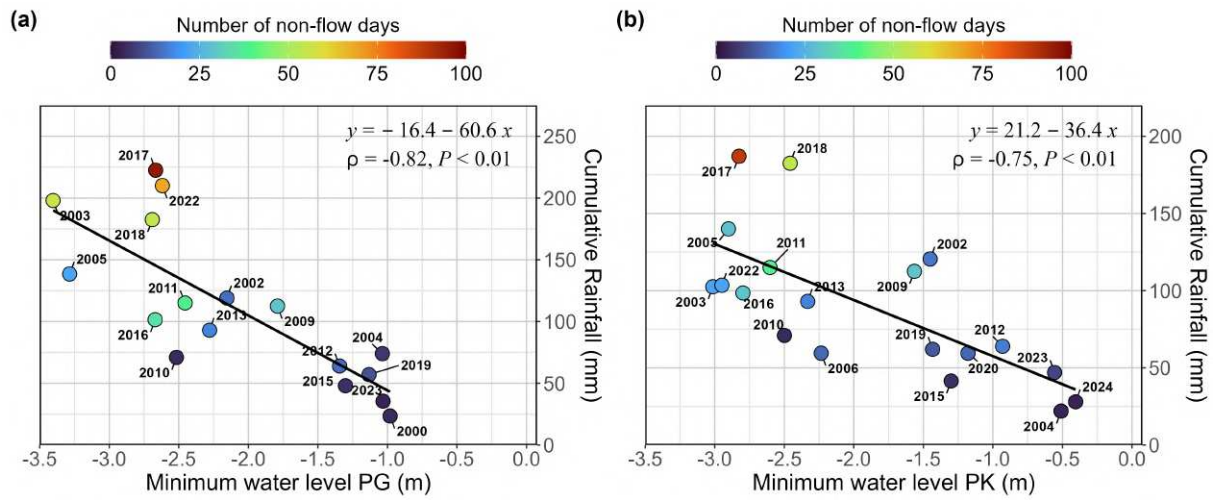

Figure 2.13 – A scatter plot showing the relationship between the minimum water table level for the piezometer closest to the river per transect (a) PG and (b) PK in metres, and the cumulative rainfall during non-flow days ($Q \leq 0.001$). The colour legend shows the number of non-flow days. The statistics show the Spearman's correlation and its respective $p - value$, and the equation of the generalized linear model $Y \sim X$.

of the headwater catchment in the Kervidy-Naizin catchment is a gradual phenomenon, whereas the resumption of flows is rapid. Therefore, we expect that the longer the non-flow periods and the lower the water table, the more rainfall will be needed to reconnect the hydrographic network.

The results show a negative and strong correlation between the cumulative rainfall until the stream flows again and the minimum water table level reaching during the summer for both piezometer of the PG and PK transects (Fig. 2.13). The amount of rainfall required to restore the discharge at the outlet varies depending on the minimum water level for both the PG and PK piezometric transects. The higher non-flow periods in PG in 2017 and 2022 were among the lowest reported water table values (Fig. 2.12a), whereas, the volume of rainfall needed to reconnect the water table to the river was higher in 2017 than in 2011 for PK (Fig. 2.12b). The differences between the two piezometric transects may be due to variations in soil permeability affecting the drainage of the water table downstream. Further analysis is required, taking into account factors such as water usage, drainage from adjacent crop fields, and atmospheric climate variables such as evapotranspiration.

2.5 Discussion and perspectives

This chapter analysed the factors that influence the intermittent nature of headwater streams in agricultural landscapes. This helped to characterise the prevalence of such streams in Brittany's hydrographic network. Furthermore, an attempt was made to predict intermittence and identify the drivers causing it by using the spatial features of diverse headwater intermittent catchments in a random forest model. This showed that unmapped local factors could play an important role in predicting streamflow intermittence. Additionally, exploring the drivers using river geomorphology measurements revealed that recalibrated watercourses may have contributed to the non-permanence of water flow in agricultural landscapes. Finally, high-resolution hydrological data from a headwater catchment helped to identify the role of the water table in controlling discharge.

2.5.1 Spatial distribution of intermittent streams in a temperate oceanic region

Most hydrographic maps systematically underestimate small streams and rivers, making it difficult to estimate the drainage density of river networks (Benstead & Leigh, 2012). This is despite the fact that many rivers experience flow cessation and drying, which disrupts most physical, chemical and biological processes. The flow-state observations from ONDE with 129 sites monitored in Brittany showed an east-west spatial gradient in the region, with more intermittence in the east than in the west. The ONDE database makes it possible to improve the detection of drying events and lead to better understanding the spatial distribution of intermittent streams across the territory (Beaufort et al., 2018; Nowak Céline, 2016). However, the ONDE observations are scarce in space and time, while managers and scientists would need information across the entire river network. Unfortunately, the map of river systems in France (TOPAGE) fails to represent intermittent rivers in Brittany (Fig. 2.5). While TOPAGE is used in practice as a cartographic basis for mapping watercourses in France by department, this is not uniform at the regional level. Messager et al. (2024) emphasised new drainage density in an assembled national map of official watercourses (falling under the Water Law in France) was lower than in TOPO BD 2015 map. They also found that 28% of the missing watercourses were intermittent and headwaters. However, in French Brittany, they calculated a drainage density ratio close to or greater than 1, indicating that in our study region, a substantial effort has been made to complete the mapping of the hydrographic network (see Figure

2D in Messager et al., 2024, p. 6). Nevertheless, a reference map that provides reliable information about the intermittent nature of these hydrographic network segments is still needed.

The next analysis showed that the RHT hydrographic network provided a more accurate representation of the probability of intermittence than TOPAGE (Fig. 2.7). However, estimating the probability of intermittence at gauging stations located mainly on perennial streams using the RHT method could misrepresent intermittence and drying periods, particularly in temperate climates. The disproportionate distribution, together with the limitations of representing low-order streams, also makes it difficult to characterise variability in drying accurately (Beaufort et al., 2018). ONDE's flow-state observations are important for determining intermittence and provide valuable additional insights because its stations are much more prevalent in the headwaters of non-perennial streams and in certain months than the European streamflow gauging station dataset (Döll et al., 2024). Other sources of information about the permanence of flow that are available for managers and scientists and on which recent promising progress have to be noted are sensor networks (Assendelft & van Meerveld, 2019; Kaplan et al., 2020) and citizen science (Truchy et al., 2023, *En Quête d'Eau*, https://enquetedeau.eaufrance.fr). Such observational data must be considered when mapping the hydrological segments of headwater streams, in order to improve the accuracy with which the regional prevalence of intermittent streams can be determined.

2.5.2 Drivers of stream intermittence in a temperate oceanic region

This chapter analysed the factors that influence the intermittent nature of headwater streams in the agricultural landscapes of Brittany. The random forest model showed that higher temperatures and reduced rainfall were associated with greater levels of intermittence (Fig. 2.8b). These climatic predictors are consistent with the literature (Beaufort et al., 2018; Döll et al., 2024; Snelder et al., 2013), in which models predicting intermittence are strongly influenced by aridity. A flat slope was also associated with higher levels of intermittence, most likely because it can influence the relative amount of water exchanged laterally with floodplains. In large catchments, an increase in rainfall and slope resulted in a low frequency of intermittence, but a long duration of non-flow periods, according to a flow regime classification model for France (Snelder et al., 2013). However, agricultural

flat catchments in the Brittany region tend to be tile-drained, which could increase the likelihood of intermittence. As the ONDE dataset is intended to monitor intermittence in predominantly headwater streams, it contains a much higher proportion of non-perennial reaches than the global and European streamflow gauging stations that were used to develop intermittence predictive models (Döll et al., 2024; Messager et al., 2021). However, the catchment area of the sites was not as important in the model whereas topography is a very important explanatory variable specifically for classifying streams as temporary or perennial (Snelder et al., 2013). On the other hand, the model's precision showed good accuracy with a moderate kappa coefficient, meaning it can predict intermittent flow with moderate reliability (Fig. 2.8a). This showed that unmapped local factors, such as water abstraction, alteration of channel geomorphology or small-scale hydrogeology, could play an important role in controlling streamflow intermittence.

Alterations to the natural flow affect the structure and functioning of rivers (Rolls et al., 2012). Reviewing the morphological component of intermittent streams and comparing them with those of natural and low-order streams can help to establish links between human pressures and environmental responses. Streams with active dynamics, characterised by lateral erosion processes and braided rivers, often have a width-to-depth ratio of over 20 (Baudoin et al., 2017). In the Etel and Naizin study field sites, the width/depth ratio is less than 5, indicating that the upstream segments mainly comprise incised riverbanks. This means that the streams tend to be narrower and deeper (Jaeger et al., 2017). These intermittent segments are incised, which could indicate human intervention in the form of channelisation and rectification of a reworked watercourse. Therefore, the driving factors influencing the permanence of the hydrographic network may be related to anthropogenic and biophysical aspects. Then, the channelisation of watercourses may have contributed to the intermittent flow of water in agricultural landscapes. This hypothesis still needs to be tested on a regional scale.

Finally, high-resolution hydrological data from a headwater catchment helped to identify the role of the water table controlling the presence of water in river channels. Spatio-temporal variations in water table depth have been shown to drive surface flow dynamics by other authors (Abhervé et al., 2024; Godsey & Kirchner, 2014). This is a consequence of the geological context of impermeable bedrock and the oceanic climate. The Kervidy-Naizin catchment exhibited stream discharge with seasonal dry periods in late summer and early autumn (Fig. 2.12a), with streamflow primarily dominated by aquifer flow (Molénat et al., 1999). During droughts, when the water table is low, groundwater

flows slowly towards the outlet until it completely dries out. Cumulative rainfall and the estimated water table level determine the rewetting at the outlet (Fig. 2.13). However, it is difficult to predict how much rain is needed before runoff resumes at the outlet, as other factors come into play, such as water withdrawal for irrigation and climatic conditions, such as evaporation that we did not dispose of for this analysis. Although the analysis does not capture the complexity of the hydro-system of the catchment, the spatio-temporal dynamics of the stream network is also related to the water storage in the catchment (Abhervé et al., 2024).

2.5.3 Towards a complementary work on assessing the role of climate change in intermittent streams

Intermittent streams are found in the most hydrologically variable headwater systems, which are particularly sensitive to climate change and human intervention. From our results, climate is not the only driver of intermittence at the regional scale but remains an important one. Most climatic projections in French Brittany agree with an increased warming for all climatic scenarios and this warming is expected to be stronger in the South coast of the region (Amiot et al., 2023). They also agree on a decrease cumulative rainfall in the low flow season in the East of the region (Amiot et al., 2023). These results suggest a potential increase of intermittent stream prevalence at the regional scale in the future as the most impacted areas are those where intermittence is already more frequent.

Data on intermittent streams and their associated ecosystems is scarce (Acuña et al., 2017; Datry et al., 2016) but increasing. Therefore, detailed characterisation of the processes is still to be performed and monitoring the spatial patterns of flow persistence in headwater streams can address the lack of usable data for modelling changes in dynamics of the downstream network due to climate and land use (Van Meerveld et al., 2020). This could help identify the small changes that cause streams to change from perennial to intermittent. The anthropogenic and biophysical factors affecting flow persistence are not easy to disentangle and are probably dependent from each other. Nevertheless, understanding the hierarchy of these factors is crucial for managing and restoring these hydrological systems (Rollet et al., 2014). For effective stream management at a regional scale, the temporal variations of stream intermittence and their climatic controls must be properly considered, bearing in mind the relationships between stream ecology and climate change.

Chapter 3

Spatial variability in nutrient and organic matter concentrations during hydrological fragmentation of an intermittent temperate catchment

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Authors: Andrés Casanova[1], Rémi Dupas[1], Daniel von Schiller[2,3], Laurent Jeanneau[4], Anne Jaffrezic[1], Thibault Lambert[1], Alexandrine Pannard[5], Ophélie Fovet[1]

[1] UMR 1069 SAS, Institut Agro - INRAE, 65 rue de Saint-Brieuc, Rennes, CEDEX 35000, France

[1] Departament de Biologia Evolutiva, Ecologia i Ciències Ambientals, Universitat de Barcelona (UB), Barcelona, Spain

[1] Institut de Recerca de l'Aigua (IdRA), Universitat de Barcelona (UB), Barcelona, Spain

[1] UMR 6118 Géosciences Rennes, University of Rennes, CNRS, Rennes, France

[1] CNRS-UMR 6553 Ecobio, University of Rennes, OSERen, Rennes, France

3.1 Abstract

Intermittent and ephemeral streams are watercourses that cease to flow and/or dry up during part of the year. Their seasonal drying is sometimes preceded by a stream fragmentation phase with formation of isolated pools where the biogeochemistry differs from that of perennial reaches. Our objective was to analyse how hydrological fragmentation alters the spatial variability in dissolved nutrient and organic matter concentrations in a temperate-oceanic and agriculture-impacted headwater stream, where nutrient loadings

are high. We conducted repeated synoptic sampling campaigns at high spatial resolution (150-200 m) along the stream network of the Naizin catchment (7 km^2) during the spring-summer-fall of 2023. We sampled 38 sites and analysed dissolved organic carbon (DOC) concentrations and fluorescence properties, dissolved inorganic nitrogen (DIN) and soluble reactive phosphorus (SRP) concentrations, during four sampling campaigns: stream recession, early and late fragmentation, and reconnection. Our results showed an increase in the spatial variability of concentrations, with monotonic longitudinal gradients along the stream disappearing during hydrological fragmentation. Both DOC and SRP concentrations were higher in isolated pools than in flowing reaches, while DIN concentration was lower. The chemical composition of DIN and DOC also changed with stream fragmentation, with increasing proportions of nitrite and ammonium in DIN and humic-like organic matter in DOC. These results suggest that the main controlling processes in the isolated pools were streambed mobilisation of SRP and DOC, along with denitrification under anoxic conditions. We expect the observed spatio-temporal patterns in nutrient and DOC concentrations to become more widespread in the future as intermittent streams will become more frequent due to climate change.
Keywords: intermittent stream, non-perennial, nutrient, DOM, temperate climate, intensive agriculture

3.2 Introduction

Intermittent and ephemeral streams are watercourses that cease to flow and/or dry during part of the year (Datry et al., 2017a; von Schiller et al., 2011). They have similar human uses as perennial rivers and experience similar impacts from human activities, but they are often considered to have lower aesthetic, recreational, and biological value (Cottet et al., 2023; Fovet et al., 2021; Skoulikidis et al., 2017). Up to 60% of global river networks are estimated to be intermittent (Messager et al., 2021). Climate change is predicted to increase the frequency and duration of droughts in both arid and wet climates, further increasing the frequency of intermittence (Sauquet et al., 2021). In temperate oceanic climates, intermittent streams are mainly headwaters, where stream-flow is sustained by shallow groundwater and often dominated by agriculture associated with high nutrient loadings and legacy storage (Bieroza et al., 2024; Outram et al., 2016).

Hydrological fragmentation (i.e., formation of isolated pools along the river or stream network) results from disruption of hydrological connectivity in three spatial dimensions:

longitudinal (upstream - downstream), lateral (channel - riparian - floodplain), and vertical (surface water - groundwater) (Allen et al., 2020). Isolated pools are patches of stagnant water in the river network separated by patches of dry streambed (Fellman et al., 2011; von Schiller et al., 2011). The spatio-temporal variability in hydrological fragmentation, including the number and size of isolated pools along a river reach, and the frequency and duration of their occurrence, is controlled by interactions between climate conditions, flow regime, fluvial geomorphology, hydrogeology, and biological processes (Abhervé et al., 2024; Bonada et al., 2020; Boulton et al., 2017). Isolated pools can persist from less than one day to several weeks, depending on the presence of groundwater inputs and evaporation rates (von Schiller et al., 2011), and their biogeochemistry can differ from that of flowing reaches due to biotic and abiotic factors (Bonada et al., 2020). Understanding the biogeochemistry of fragmented streams is crucial, as nutrients (nitrogen (N) and phosphorus (P)) and dissolved organic matter (DOM) concentration and composition influence the biodiversity of most taxa that live in these ecosystems (Foulquier et al., 2024; Zimmer et al., 2022).

During hydrological fragmentation, isolated pools act as accumulation sites where the transport and mobilisation of particles slows down, while the retention and removal of nutrients increases (Bonada et al., 2020). In these pools, changes in redox conditions, pH and temperature cause biogeochemical processes to differ from those during the flowing phase (Gómez-Gener et al., 2021; von Schiller et al., 2017; Zimmer et al., 2022). Hydrological fragmentation altered the concentrations of nutrients and dissolved organic matter (DOM) in an arid stream and two Mediterranean streams (Lillebø et al., 2007; Stanley & Boulton, 1995; von Schiller et al., 2011). In these studies, nitrate concentrations decreased under anoxic conditions during stream fragmentation prior to drought, while concentrations of other nitrogen forms, such as ammonium, increased due to oxygen-depleting conditions that favoured ammonification. The response of P concentration to fragmentation varies among studies. Finn et al. (2009) observed a decrease in SRP due to algal uptake concomitant with an increase in total P during fragmentation in two streams in a temperate forest catchment. Others observed an increase in both SRP and total P concentrations due to desorption processes in hypoxic conditions in a seasonal dry stream and a lowland floodplain river (Baldwin & Mitchell, 2000; von Schiller et al., 2011). Several studies have observed an increase in dissolved organic carbon (DOC) concentrations through its release from leaf litter during fragmentation (Abril et al., 2016; Granados et al., 2020; Vazquez et al., 2010). In Mediterranean climates, DOM composition becomes

less aromatic in isolated pools with low dissolved oxygen (DO) concentration and high temperature. This suggest that autochthonous DOM is released and contributes almost a fifth to the total DOM pool, which is mainly dominated by terrestrial inputs (Fellman et al., 2011; Harjung et al., 2018; Vazquez et al., 2010; von Schiller et al., 2015). Others have found that leaching from and decomposition of leaf litter from riparian trees were the dominant source of DOM in isolated pools (Baldwin, 1999; Casas-Ruiz et al., 2015).

Most studies of the biogeochemistry of intermittent streams have been conducted in arid and Mediterranean climates (Skoulikidis et al., 2017). These studies have shown that fragmentation creates biogeochemical hotspots, resulting in high spatial heterogeneity in solute concentrations among isolated pools (Dent & Grimm, 1999; Fellman et al., 2011; Granados et al., 2020; von Schiller et al., 2011). However, intermittent streams are also prevalent in temperate oceanic climates (Messager et al., 2021; Snelder et al., 2013), where intermittent flow is usually limited to headwaters catchments (Fovet et al., 2021; Kaplan et al., 2020; Stubbington et al., 2017). These temperate headwater catchments are often located in regions dominated by urban and agricultural land uses, which are subject to high nutrient loadings and have a major influence on DOM composition that, along with intermittent flow, can have important but often overlooked consequences for stream biogeochemistry (Guillemot et al., 2021; Sarremejane et al., 2024; Stubbington et al., 2017). Research in intensively managed temperate zone catchments has shown that nutrient concentrations are not only higher than in more pristine environments, but also less variable over time and space (Basu et al., 2010; Godsey et al., 2009; Musolff et al., 2015). Such homogeneous temporal and spatial patterns result from the presence of legacy nutrient sources in soils and groundwater (Ebeling et al., 2021). To our knowledge, no study has ever examined whether intermittent streams in temperate-oceanic landscapes impacted by agriculture would display low temporal and spatial variability in concentration, as is commonly observed in their perennial counterparts, or high variability, as is commonly observed in intermittent streams draining drier, less agricultural landscapes.

The aim of this study was therefore to i) examine whether the increasing spatial variability in nutrient and OM concentrations observed during the hydrological fragmentation of Mediterranean and arid streams could also be observed in a temperate-oceanic catchment under intensive agriculture; ii) determine the direction of change in dissolved nutrients and OM concentrations during fragmentation. We hypothesised that i) the spatial variability in nutrients and OM in an intermittent headwater catchment in a temperate-oceanic climate would be lower compared to Mediterranean and arid streams due to the

presence of legacy nutrient sources in its soil and groundwater, and ii) the direction of change in concentrations during the fragmentation of an intermittent stream could be predicted from that observed during the low-flow season of perennial rivers of the same region, i.e., decreasing for DIN and increasing for SRP and DOC (Guillemot et al., 2021).

3.3 Methods

3.3.1 Study area

The Naizin catchment, located in Brittany in western France, is an observatory of response times in agro–hydro systems (AgrHyS), which is part of the French Critical Zone Observatory network (Fig. 3.1a) (Fovet et al., 2018; Gaillardet et al., 2018). The catchment is drained by a second order stream (Strahler) called Coët-Dan. A gauging station located at the outlet of the 5 km^2 catchment uses a float–operated sensor to record stream levels every 1 minute. This study expanded the study area further downstream to assess a 7 km^2 catchment to increase the spatial variability in intermittence compared to that of the 5 km^2 catchment. The discharge reported here, however, still came from the 5 km^2 catchment. The climate is temperate oceanic, with mean rainfall of 800 $\pm$ 219 $mm\ yr^{-1}$ and mean temperature of 11.2 $\pm$ 0.6 °C (1993–2018) measured at the closest weather station (1.1 km away from the gauging station). Rainfall is evenly distributed throughout the year but discharge is highly seasonal due to the seasonality of evapotranspiration: the six wettest months span November-April and the driest months May-October (Fig. 3.1c). Stream flow is seasonally intermittent with a dry season that varies in duration, with a mean of 81 $\pm$ 49 $days\ yr^{-1}$ (2000–2022) at the gauging station, usually in summer and early autumn (Strohmenger et al., 2020). The subsoil consists of Proterozoic schist. The slope is gentle ($< 5\%$), and the soils are silty loams $0.5 - 1.5\ m$ deep (Fovet et al., 2018). Intensive livestock farming (dairy cows and pigs) dominates, with mixed cropping systems of maize, cereals and grassland. Despite the dominant agricultural land use in the Naizin catchment, the entire stream network is surrounded by a strip of riparian deciduous trees ($< 10m$ in width), which keep the surface water shaded throughout the year, particularly during the low-flow and dry seasons.

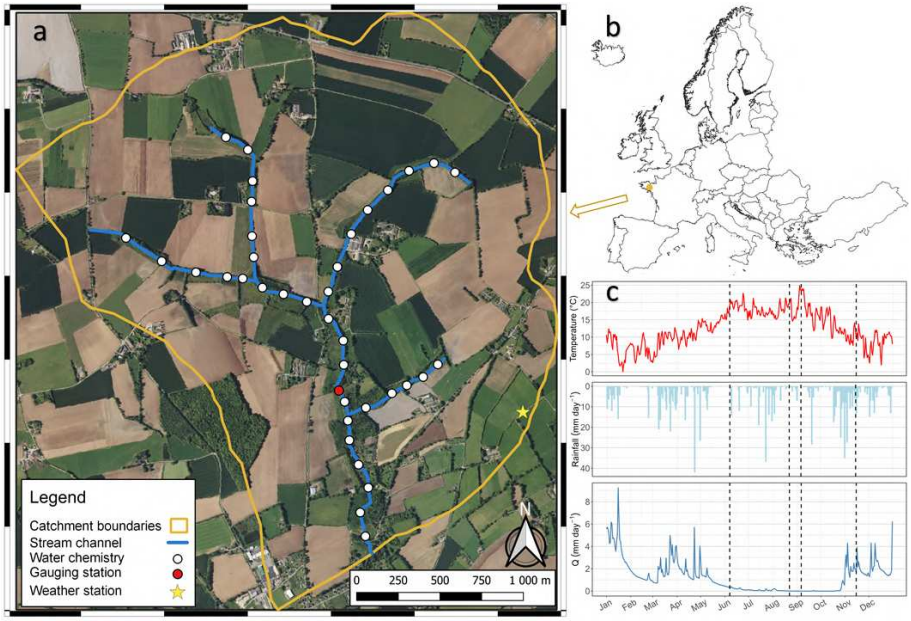

Figure 3.1 – (a) Naizin catchment with the water chemistry sampling sites (n = 38) along the stream channel (b) Location of Naizin catchment in western France. (c) Mean daily temperature (red line), daily rainfall (light blue bars) measured at the weather station, and discharge measured at the gauging station (blue line) for the year of 2023.

3.3.2 Field sampling

We conducted four sampling campaigns targeting four hydrological phases of the stream network: recession, early fragmentation, late fragmentation, and reconnection (Fig. **??**c). The recession phase, sampled on 7 June 2023, was characterised by a fully connected stream network with low discharge. Early fragmentation, sampled on 22 August 2023, was characterised by a longitudinal disconnection in the two upstream tributaries and formation of the first isolated pools. Late fragmentation, sampled on 6 September 2023, was characterised by greater longitudinal disconnection of the main stream channel, with no flow at the outlet, and new isolated pools. In this phase, the reaches that have been disconnected during the previous field campaign were completely dry. The reconnection phase, sampled on 15 November 2023, was characterised by a connected stream network and a winter discharge typical of the Naizin catchment. A total of 38 sampling sites were randomly distributed $150 - 200\ m$ apart along the stream network (Fig. **??**a) using the "random points along a line" algorithm in QGIS (QGIS Development Team, 2020). This algorithm creates a layer of points with a given number of points and a minimum distance between the points placed on the stream segments. For each campaign,

sampling sites were only sampled when water was present (flowing reaches and isolated pools, Fig. A1).

During each of the sampling campaigns, we walked along the whole stream network to precisely map the hydrological states: flowing, dry and fragmented (i.e., presence of isolated pools). We collected stream water in a bucket and filtered the samples on site using a double–rinsed 50 mL syringe at the sampling sites. We filtered samples using a Filtropur S syringe filter with a pore size of 0.45 μm to assess soluble reactive P (SRP), ammonium (N-NH_4^+), nitrite (N-NO_2^-), and nitrate (N-NO_3^-); using a Filtropur S syringe filter with a pore size of 0.20 μm to assess dissolved organic carbon (DOC) and, absorbance and fluorescence measurements of DOM (CDOM and FDOM, respectively). We used a new filter for each sample, and we rinsed them with 5 to 10 mL of river water at each sampling site. The samples were stored in a cooler to keep them at low temperature and prevent light exposure while transporting them to the laboratory. The samples were then stored in a refrigerator at 4 °C until laboratory analysis within 72 h. At the same sampling sites, we measured DO concentration, pH and water temperature using a multiparametric hand–held probe (ODEON®, Aqualabo, Champigny-sur-Marne, France) calibrated the day before sampling.

3.3.3 Laboratory analyses

The concentrations of NH_4^+ and SRP were measured via photometric analysis on an automatic sequential analyser (SmartChem®200, AMS Alliance, France). NH_4^+ was determined based on the reaction with a solution of hypochlorous acid and salicylate (Antweiler et al., 1996). SRP was determined via direct reaction using the phospho-molybdenum blue method (J. Murphy & Riley, 1962). The quantification limits for the analyser were 0.039, and 0.013 mg L^{-1} for NH_4^+, and SRP, respectively. We measured major anions, such as NO_2^- and NO_3^-, using an ion chromatograph (ICS–3000, Dionex, Sunnyvale, California, USA). The quantification limit was 0.05 mg L^{-1} for NO_2^- and NO_3^-. We measured DOC using a carbon analyser (TOC–V 5050A, Shimadzu, Kyoto, Japan) (Petitjean et al., 2004). Quantification limits for the analyser were 0.31 mg L^{-1} for DOC. We calculated dissolved inorganic N (DIN) as the sum of the inorganic N forms (nitrite, nitrate, and ammonium).

We assessed UV–visible absorbance for CDOM using spectra measured from 230–700 nm at 1 nm increments in a 1 cm quartz cuvette using a UV/VIS spectrometer (Lambda20, PerkinElmer Waltham, Massachusetts, USA). Samples whose absorbance

approached 2.0 or exceeded the linear range of the spectrophotometer were diluted to avoid inner–filter effects (K. R. Murphy et al., 2013).

We recorded FDOM excitation–emission matrices (EEMs) using a Fluorescence Spectrophotometer (LS–55, PerkinElmer). The instrument was set for excitation wavelengths of 270–450 nm at 5 nm increments and emission wavelengths of 290–550 nm at 0.5 nm increments at 1200 nm min^{-1}, using a 1 cm quartz cuvette. We used EEMs of Milli–Q water to make blank–subtracted corrections to all of the EEMs obtained on the same day (Vogt et al., 2023), and used CDOM spectra to correct EEMs for inner–filter effects (Ohno, 2002).

3.3.4 Data analysis

We examined differences in concentrations among the four hydrological phases using the non–parametric Kruskal–Wallis test. When this test was significant ($p < 0.05$), we used a post–hoc Dunn test with Bonferroni correction to determine which phase differed from the others. We also examined differences in concentrations between flowing and fragmented reaches for each sampling date when isolated pools were present (i.e., early and late fragmentation) using a Wilcoxon signed–rank test. When this test was significant ($p < 0.05$), we performed a post–hoc Dunn test with Bonferroni correction to adjust the significance level.

Parallel factor (PARAFAC) analysis used EEMs that had been pre–processed (Raman scattering removal and standardisation to Raman units) and normalised to those of a Milli–Q water sample on the day of the analysis. A multi-component PARAFAC model was obtained using the drEEM 0.6.5 Toolbox (K. R. Murphy et al., 2013) for MATLAB (MathWorks, USA). Random initialisation, sum–of–squared–error analysis, and split–half analysis (Fig. A2) were used to test and validate the model. PARAFAC components are normalised by the percentage of total fluorescence. Maximum peak positions of the PARAFAC components were compared to those in other studies of similar temperate oceanic catchments using the open fluorescence database OpenFluor (K. R. Murphy et al., 2014), then filtered by Tucker's congruence coefficient $>$ 0.98. We also calculated two DOM descriptors from FDOM matrices: the fluorescence index (FI) and the biological index (BIX). The FI, which provides information on the source of DOM (e.g., terrestrial or microbial) (McKnight et al., 2001), equalled the emission intensity at 470 nm divided by that 520 nm, both obtained at excitation of 370 nm. The BIX, which indicates the contribution of recently produced DOM (Fellman et al., 2010), equalled the emission

intensity at 380 nm divided by the maximum emission intensity from 420–435 nm, both obtained at excitation 310 nm (Hansen et al., 2016).

To assess changes in the spatial variability in nutrient concentrations, we estimated the spatial coefficient of variation (CV), defined as the standard deviation (σ) divided by the mean (μ), using spatial data from each water chemistry parameter and field campaign. The CV is expressed as a percentage. All statistical analyses were performed in (Team, 2024), using the 'tidyverse' (Wickham et al., 2019), and 'ggpubr' (Kassambara, 2023) packages to visualise and model data, and the 'Simple Features for R' (Pebesma, 2018) package to create spatial plot visualisations.

3.4 Results

3.4.1 Response of longitudinal connectivity to hydrological fragmentation

The four high spatial resolution campaigns covered contrasting hydrological conditions, including two fragmentation dates in which isolated pools were present (Fig. 3.2). During the recession, 100% of the stream network was flowing (6.1 km) and discharge at the gauging station was 16.7 Ls^{-1}. During early fragmentation, 76% of the stream network was flowing (4.7 km) and discharge at the gauging station was lower (0.3 Ls^{-1}); one sampling location was dry and seven presented isolated pools in upstream reaches. During late fragmentation, 10% of the stream network was flowing (0.6 km) and discharge at the gauging station was zero (the flowing reach was downstream of the gauging station); ten sampling locations were dry and twenty–three presented isolated pools in both upstream and downstream reaches (Fig. 3.2). Discharge at the outlet resumed 51 days after the late fragmentation sampling, and the reconnection phase was sampled an additional 19 days later. On the sampling day during the reconnection phase, 100% of the stream network was flowing and discharge was 93.9 L s^{-1}. In total, we collected 141 water samples: 38 during recession, 37 during early fragmentation, 28 during late fragmentation, and 38 during reconnection.

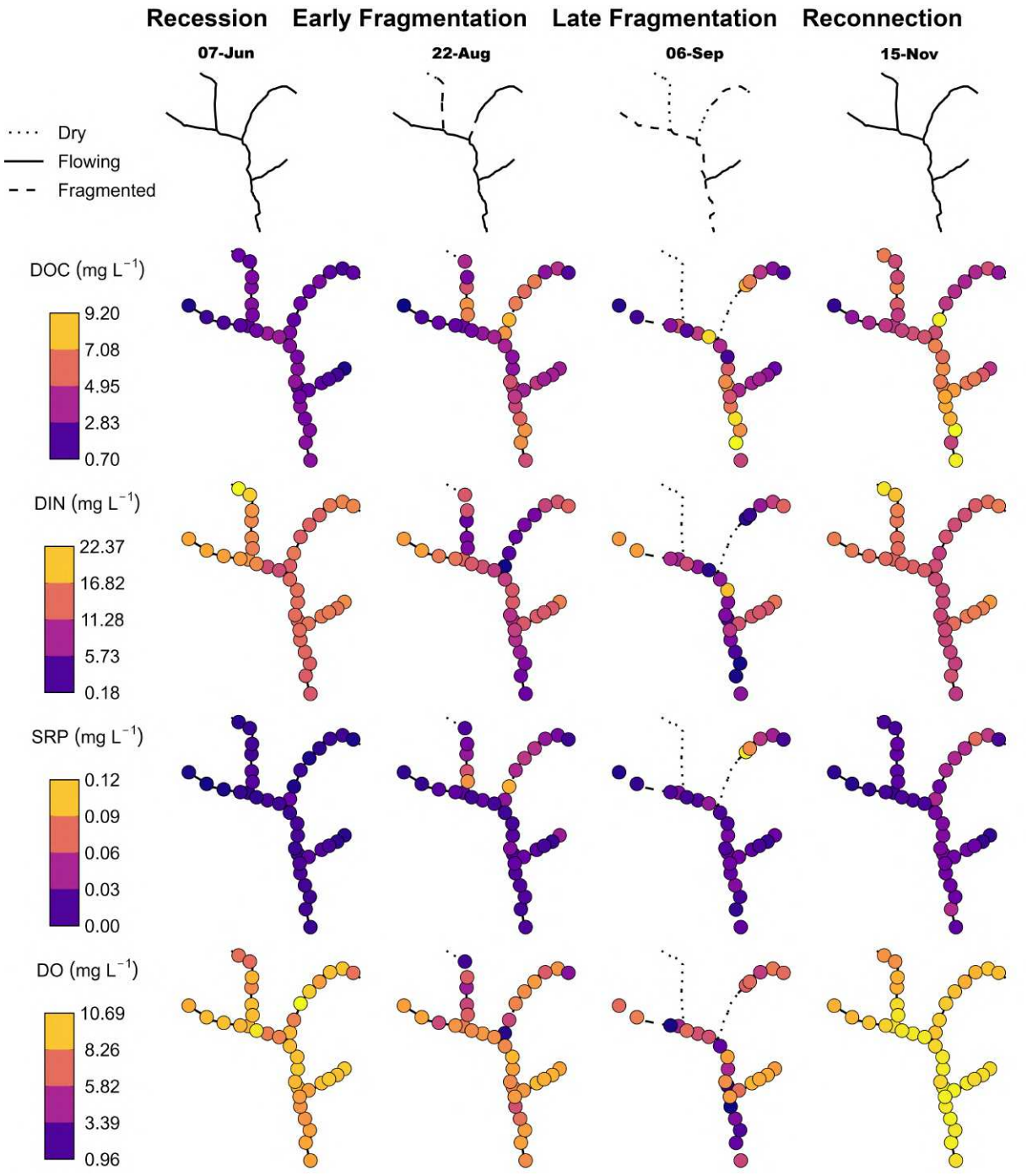

Figure 3.2 – Spatio–temporal variability of hydrological fragmentation and spatial configuration of dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN), soluble reactive phosphorus (SRP) and dissolved oxygen (DO) concentrations in the four sampled hydrological phases: recession ($n = 38$), early fragmentation ($n = 37$), late fragmentation ($n = 28$), and reconnection ($n = 38$). Stream network line types correspond to flowing states: dry (i.e., absence of surface water; dotted line), flowing (i.e., presence of running water; solid line) and fragmented (i.e., presence of isolated pools; dashed line). Dot colours correspond to concentrations.

3.4.2 Temporal dynamics of water chemistry among hydrological phases

Dissolved oxygen, water temperature, nutrient and organic carbon concentrations differed significantly among the four hydrological phases (Kruskal–Wallis test, p–value < 0.05). In contrast, pH did not vary significantly among the sampling campaigns, and remained at 6.9 ± 0.3 (Fig. 3.3).

During recession, mean DO concentration was 8.8 mg L^{-1} and decreased significantly to 7.3 mg L^{-1} during early fragmentation, before decreasing again, albeit not significantly, to 5.9 mg L^{-1} during late fragmentation (Table 3.1, Fig. 3.3). Mean DO concentration then increased significantly to 9.8 mg L^{-1} during reconnection. Mean DO concentrations in isolated pools were 42% and 37% (significantly) lower than in the flowing reaches during early and late fragmentation, respectively. During recession, mean temperature was 15.5 °C and increased significantly to 17.4 °C during early fragmentation, before increasing again, albeit not significantly to 17.7 °C during late fragmentation (Table 3.1, Fig. 3.3). Mean temperature then decreased significantly to 11.9 °C during reconnection. Mean temperature in isolated pools were 7% and 8% (significantly) higher than in the flowing reaches during early and late fragmentation, respectively. During recession, mean pH was 6.8 and increased slightly, but not significantly, to 6.9 during early fragmentation, and then increased again, albeit not significantly, to 7.0 during late fragmentation (Table 3.1, Fig. 3.3). Mean pH then decreased slightly but not significantly during reconnection. Mean pH in isolated pools were similar to those in the flowing reaches during early and late fragmentation.

During recession, mean DOC concentration was 2.4 mg L^{-1} and increased significantly to 4.4 mg L^{-1} during early fragmentation, before increasing again, albeit not significantly, to 4.8 mg L^{-1} during late fragmentation (Table 3.1, Fig. 3.3). Mean DOC concentration then increased again, albeit not significantly, to 5.6 mg L^{-1} during reconnection. Mean DOC concentration in isolated pools was 140% and 150% higher than in the flowing reaches during early and late fragmentation, respectively, but they differed significantly only during early fragmentation. During recession, mean DIN concentration was 15.1 mg L^{-1} and decreased significantly to 10.1 mg L^{-1} during early fragmentation, before decreasing again, albeit not significantly, to 8.5 mg L^{-1} during late fragmentation (Table 3.1, Fig. 3.3). Mean DIN concentration then increased significantly to 13.4 mg L^{-1} during reconnection. Mean DIN concentration in isolated pools was 42% and 41% lower

Table 3.1 – Summary of descriptive statistics for the physicochemical variables measured during the four sampled hydrological phases: recession, early fragmentation, late fragmentation, and reconnection.

Variable	Recession (n = 38)		Early Fragmentation (n = 37)		Late Fragmentation (n = 28)		Reconnection (n = 38)	
	Mean ± SD	CV	Mean ± SD	CV	Mean ± SD	CV	Mean ± SD	CV
DO (mg L^{-1})	8.8 ± 0.8	9.5	7.3 ± 1.9	26.0	5.9 ± 2.6	43.5	9.8 ± 0.6	6.5
pH (-)	6.8 ± 0.4	5.7	6.9 ± 0.3	3.8	7.0 ± 0.3	3.7	6.9 ± 0.3	4.6
Temperature (°C)	15.5 ± 1.3	8.6	17.4 ± 1.1	6.0	17.7 ± 1.3	7.5	11.9 ± 0.9	7.5
DOC (mg L^{-1})	2.4 ± 0.7	26.5	4.4 ± 1.8	40.8	4.8 ± 2.3	49.1	5.6 ± 1.7	30.5
DIN (mg L^{-1})	15.1 ± 2.2	14.7	10.1 ± 4.2	41.6	8.5 ± 5.4	63.6	13.4 ± 2.4	17.8
SRP (mg L^{-1})	0.009 ± 0.005	53.5	0.026 ± 0.021	79.0	0.027 ± 0.024	90.1	0.025 ± 0.015	61.4

Note: Dissolved oxygen (DO), pH, temperature, dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN) equals the sum of nitrogen (N) forms ($N\text{-}NO_2^-$ + $N\text{-}NO_3^-$ + $N\text{-}NH_4^+$) and soluble reactive phosphorus (SRP). SD: standard deviation; CV: coefficient of variation (%).

than in the flowing reaches during early and late fragmentation, respectively, and they differed significantly during both early and late fragmentation. During recession, mean SRP concentration was 0.009 mg L^{-1} and increased significantly to 0.026 mg L^{-1} during early fragmentation, before increasing slightly, albeit not significantly, to 0.027 mg L^{-1} during late fragmentation (Table 3.1, Fig. 3.3). Mean SRP concentration decreased slightly, albeit not significantly, to 0.025 mg L^{-1} during reconnection. Mean SRP concentration in isolated pools was 250% and 150% higher than in the flowing reaches during early and late fragmentation, respectively, but they differed significantly only during early fragmentation.

3.4.3 Temporal variability in nitrogen speciation and organic matter composition

Nitrate was the dominant form of DIN across all dates and sampling locations with a mean concentrations of 11.9 ± 4.5 mg L^{-1}, representing (98.2% ± 7.1% of DIN). The mean concentrations of ammonium and nitrite were 0.04 ± 0.07 mg L^{-1} and 0.03 ± 0.04 mg L^{-1}, respectively, and they represented on average 4.1% ± 6.6% and 2.7% ± 3.6% of DIN, respectively (Fig. 3.4). The proportion of ammonium and nitrite tended to increase during the fragmentation and reconnection phases, compared to the recession (Fig. 3.4). During recession, the mean ± standard–deviation percentage of ammonium in DIN was 2.1% ± 0.9%, and it increased significantly to 2.9% ± 2.2% during early fragmentation,

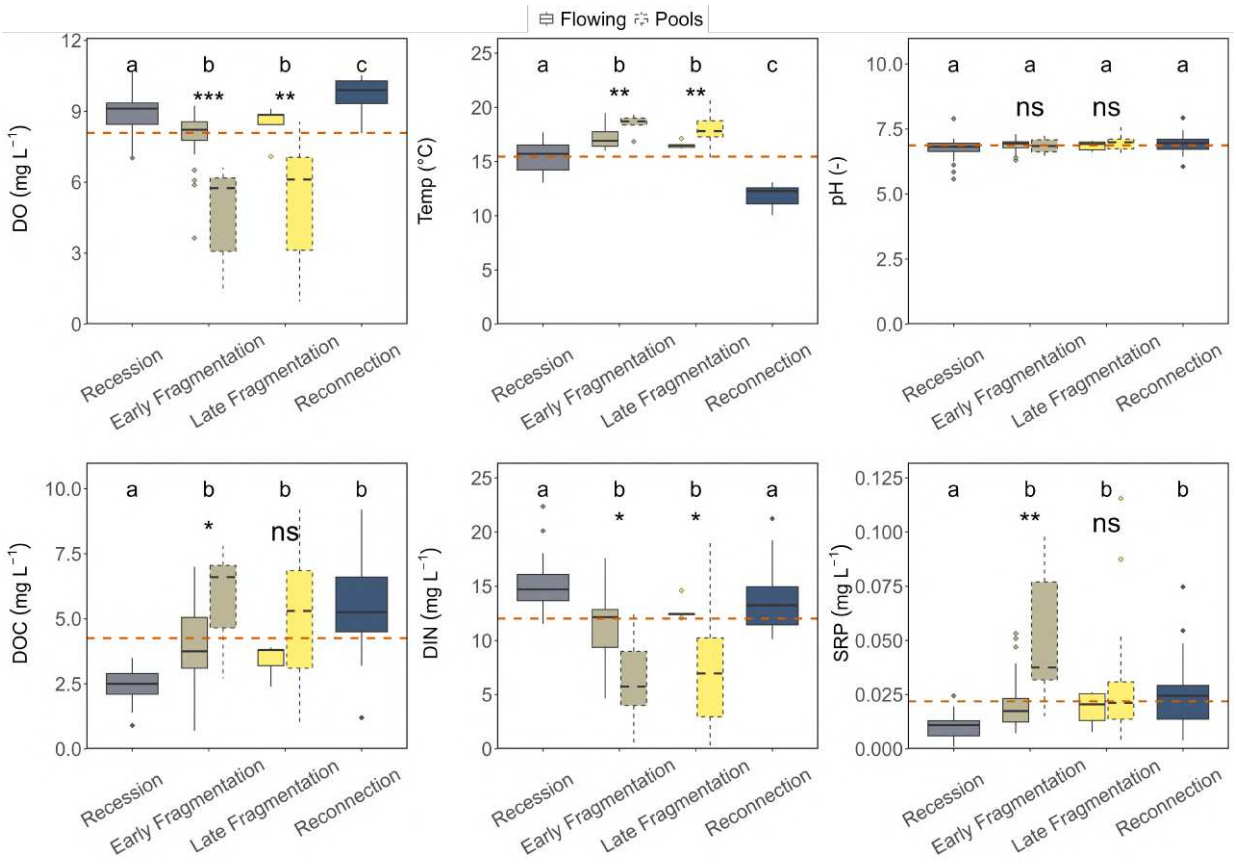

Figure 3.3 – Boxplots of dissolved oxygen (DO), water temperature (Temp), pH, organic carbon (DOC), dissolved inorganic nitrogen (DIN) and soluble reactive phosphorus (SRP) concentrations during the four hydrological phases sampled: recession ($n = 38$), early fragmentation ($n = 37$; where 30 flowing and 7 fragmented), late fragmentation ($n = 28$; where 5 flowing and 23 fragmented), and reconnection ($n = 38$). Whiskers equal 1.5 times the interquartile range. Solid lines represent concentrations in flowing water of the reaches, whereas dashed lines represent those in isolated pools of fragmented reaches during early and late fragmentation. The horizontal orange dashed lines represent the mean concentrations. The letters indicate statistical differences between sampling dates, as determined by the non-parametric Kruskal—Wallis test and post–hoc Dunn test with Bonferroni correction. Asterisks indicate a significant difference when comparing concentrations in flowing reaches and isolated pools during each fragmentation phase, which were analysed using the Wilcoxon signed–rank test. Significance levels are as follows: ns: not significant; *: $p \leq 0.05$; **: $p \leq 0.01$; ***: $p \leq 0.001$.

before increasing again (significantly) to 10.1% ± 13% during late fragmentation. Then it decreased significantly to 2.9% ± 1.4% during reconnection. The proportion of ammonium in DIN also differed between flowing reaches and isolated pools: significantly during early fragmentation (2.7% ± 2.1% and 3.8% ± 2.7%, respectively), but not significantly during late fragmentation (7.8% ± 3.6% and 10.6% ± 14.3%, respectively). During recession, the mean ± standard–deviation percentage of nitrite to DIN was 1.9% ± 0.9%, and it decreased significantly to 0.7% ± 1.9% during early fragmentation, then increased (significantly) to 6.0% ± 6.4% during late fragmentation. It then decreased significantly to 3.0% ± 0.5% during reconnection (Fig. 3.4). There was no significant difference in the proportions of nitrite in DIN between flowing reaches and isolated pools, although the proportions increased in isolated pools compared to the flowing reaches (1.9% ± 4.2% and 0.4% ± 0.6%, respectively) for early fragmentation and (6.5% ± 7.0% and 4.1% ± 0.5%, respectively) for late fragmentation. During the late fragmentation phase, ammonium peaked at 0.6 mg L^{-1} (18.7% of DIN) and nitrite peaked at 0.3 mg L^{-1} (10.8% of DIN).

The PARAFAC analysis of fluorescence spectra yielded six components (Fig. A4). Components C1, C2, and C4 had humic–like fluorescence properties (Fellman et al., 2010), with excitation/emission peaks of 350 nm/452 nm, 270 nm/448 nm and 420 nm/448 nm, respectively. Component C3 also had humic–like fluorescence properties (excitation/emission peaks of 330 nm/404 nm) but with microbial processing as a probable source (Cory & McKnight, 2005). Components C5 and C6 had protein–like fluorescence properties with excitation/emission peaks 290 nm/354 nm and 275 nm/308 nm, respectively (Fellman et al., 2010). The humic–like components C1, C2, C3 and C4 had contributed consistently more to DOM fluorescence (29%, 34%, 22% and 9%, respectively) than the protein–like components C5 and C6 did (4% and 2%, respectively).

Component contributions differed among the four hydrological phases ($p < 0.05$) for the humic–like components C1, C2 and C3, and for the protein–like components C5 and C6 components, but did not vary among phases for the humic–like component C4 (Table 3.2, Fig. A5). We focus on the contributions of the humic–like C2 and protein–like C5 component, which differed significantly ($p < 0.05$) during the early and late fragmentation phases when comparing the fragmented and flowing reaches (Fig. 3.5). From recession to early and late fragmentation, the mean contribution of component C2 increased, whereas that of component C5 decreased (Table 3.2). Mean contributions did not differ significantly between the two fragmentation phases, but during late fragmentation (Fig. 3.5), that of component C2 was lower in isolated pools than that in flowing reaches (33.5% ±

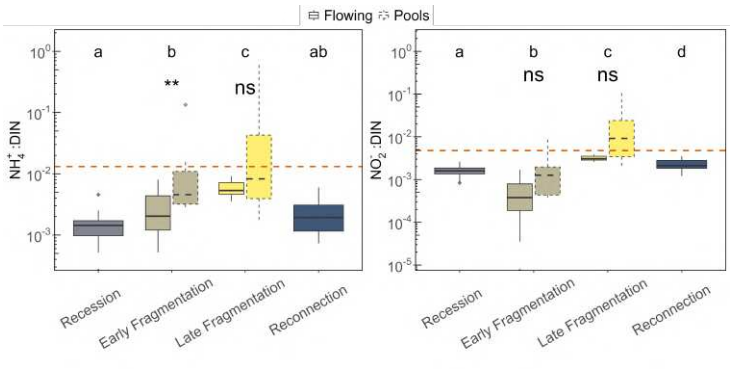

Figure 3.4 – Boxplots showing the ratios of ammonium (NH_4^+) and dissolved inorganic nitrogen (DIN), and nitrite (NO_2^-) and dissolved inorganic nitrogen (DIN) during the four hydrological phases sampled: recession ($n = 38$), early fragmentation ($n = 37$; where 30 flowing and 7 fragmented), late fragmentation ($n = 28$; where 5 flowing and 23 fragmented), and reconnection ($n = 38$). The y-axis is on a log scale. Whiskers equal 1.5 times the interquartile range. Solid lines represent concentrations in flowing water of the reaches, whereas dashed lines represent those in isolated pools of fragmented reaches during early and late fragmentation. The horizontal orange dashed lines represent the mean ratio. The letters indicate statistical differences between sampling dates, as determined by the non-parametric Kruskal–Wallis test and post hoc Dunn test with Bonferroni correction. Asterisks indicate a significant difference when comparing proportions in flowing reaches and isolated pools during each fragmentation phase, which were analysed using the Wilcoxon signed-rank test. Significance levels are as follows: ns: not significant; *: $p \leq 0.05$; **: $p \leq 0.01$.

Table 3.2 – Summary of descriptive statistics for the fluorescence index and PARAFAC components estimated for the four sampled hydrological phases: recession, early fragmentation, late fragmentation, and reconnection.

Variable	Recession (n = 38)		Early Fragmentation (n = 37)		Late Fragmentation (n = 28)		Reconnection (n = 38)	
	Mean ± SD	CV	Mean ± SD	CV	Mean ± SD	CV	Mean ± SD	CV
FI	1.68 ± 0.10	6.0	1.67 ± 0.05	2.7	1.67 ± 0.03	2.1	1.73 ± 0.04	2.57
BIX	0.58 ± 0.12	20	0.48 ± 0.06	13	0.47 ± 0.04	9.3	0.48 ± 0.02	4.4
C1	27.5 ± 2.6	9.4	29.9 ± 1.6	5.3	29.4 ± 1.4	4.6	30.7 ± 3.1	10.2
C2	31.2 ± 4.9	15.6	34.6 ± 3.9	11.3	34.6 ± 5.2	15.1	34.0 ± 3.8	11.1
C3	21.4 ± 1.7	7.7	20.6 ± 1.2	5.74	20.2 ± 1.4	7.13	23.7 ± 2.7	11.4
C4	9.1 ± 1.7	18.9	8.9 ± 0.9	10.3	8.8 ± 1.3	14.8	8.1 ± 1.0	12.3
C5	8.9 ± 6.6	74.6	4.0 ± 4.1	104	4.1 ± 3.1	75.9	1.1 ± 0.6	60.4
C6	1.8 ± 1.0	51.8	2.0 ± 1.6	80.1	3.0 ± 2.1	70.4	2.7 ± 9.9	371

Note: The fluorescence index (FI), the freshness index (BIX), and the percentages (%) of the humic–like (C1, C2, C3 and C4), and protein–like (C5, C6) components. SD: standard deviation; CV: coefficient of variation (%).

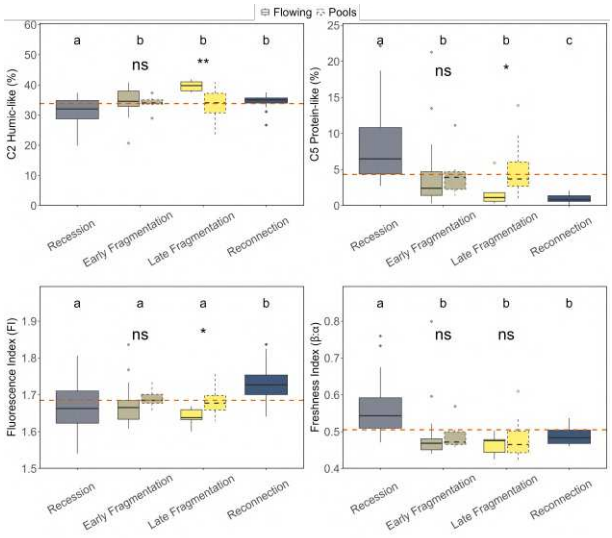

Figure 3.5 – Boxplots of the proportions of humic–like component (C2), protein–like component (C5), and the fluorescence index (FI) and freshness index (BIX) properties values during the four hydrological phases sampled: recession (n = 38), early fragmentation (n = 37; where 30 flowing and 7 fragmented), late fragmentation (n = 28; where 5 flowing and 23 fragmented), and reconnection (n = 38). Whiskers equal 1.5 times the interquartile range. Solid lines represent concentrations in flowing water of the reaches, whereas dashed lines represent those in isolated pools of fragmented reaches during early and late fragmentation. The horizontal orange dashed lines represent the mean concentrations. The letters indicate statistical differences between sampling dates, as determined by the non–parametric Kruskal-–Wallis test and post–hoc Dunn test with Bonferroni correction. Asterisks indicate a significant difference when comparing concentrations in flowing reaches and isolated pools during each fragmentation phase, which were analysed using the Wilcoxon signed–rank test. Significance levels are as follows: ns: not significant; *: $p \leq 0.05$; **: $p \leq 0.01$.

5.1% and 39.7% ± 1.9%, respectively), whereas that of component C5 was higher (4.5% ± 3.1% and 1.9% ± 2.3%, respectively). DOM descriptors also differed among the four hydrological phases (Fig. 3.5). The mean FI increased significantly during reconnection compared to recession, early and late fragmentation ($p < 0.05$) (Table 3.2). In contrast, the mean BIX decreased significantly between recession and the early and late fragmentation phases, and reconnection ($p < 0.05$) (Table 3.2).

3.4.4 Spatial configuration of nutrient and organic carbon concentrations

The hydrological fragmentation of the stream network led not only to changes in mean concentrations or their speciation but also to changes in their spatial configuration (Fig. 3.2). During recession, DO, temperature, DOC and DIN concentrations exhibited a monotonic longitudinal gradient (Fig. 3.2 and Fig. A3), with higher DO, temperature and DOC downstream and higher DIN upstream. In contrast, SRP concentrations and pH exhibited no particular longitudinal gradient. During both the early and late stages of fragmentation, the concentrations of DO, DOC and DIN lost their longitudinal gradients and became more heterogeneous, particularly in the fragmented reaches. During reconnection, the spatial configuration of DO, temperature, pH, DOC, DIN and SRP returned to the initial patterns observed during recession.

The spatial CV of DO was 9.5% during recession, increased to 26% during early fragmentation and to 43% during late fragmentation, before declining again to 6.5%. The spatial CV of water temperature decreased from 8.6% during recession to 6% and 7.5% during early and late fragmentation, respectively. During reconnection the spatial CV of water temperature was 7.5%, similar to the CV during late fragmentation. The spatial CV of pH was 5.6% during recession, decreased to 3.8% and 3.7% during early and late fragmentation, respectively. During reconnection the spatial CV of pH then increased to 4.6%. The spatial CV of nutrient and organic carbon concentrations increased with stream fragmentation compared to the recession phase (Table 3.1). The spatial CV of DOC concentrations was 26.5% during recession, then increased by a factor of 1.5 and 1.8 times during early and late fragmentation, respectively. During reconnection, the spatial CV of DOC decreased to 30.5% (Table 3.1). The spatial CV of DIN concentrations was 14.7% during recession, then increased 2.8 and 4.3 times during early and late fragmentation, respectively. During reconnection, the spatial CV of DIN decreased to 17.8%, which was similar to the level observed during recession. The spatial CV of SRP concentrations was 53.5% during recession, then increased 1.5 and 1.7 times during early and late fragmentation. During reconnection, the spatial CV decreased to 61.4% (Table 3.1). In summary, stream fragmentation increased the spatial variability of water chemistry for the parameters DO, DOC, DIN and SRP but not for temperature and pH.

3.5 Discussion

3.5.1 Effects of stream fragmentation on spatio-temporal patterns of dissolved organic matter and nutrients

The spatial configuration of concentrations in the streams of Naizin catchment during flowing phases (recession and reconnection) exhibited opposite longitudinal gradients for DIN and DOC (i.e., decreasing or increasing downstream, respectively) and a more variable longitudinal gradient for SRP that was independent of the other two (Fig. 3.2). The longitudinal gradients observed during flowing phases (recession and reconnection) were similar to those of other streams in Brittany region (Casquin et al., 2020; Dupas et al., 2021). Several factors can explain these gradients, including the spatial distribution of land–use types and longitudinal changes in groundwater–surface water interaction in the riparian zone (Dupas et al., 2021; Floriancic et al., 2019; Likens & Buso, 2006). Research on longitudinal concentration gradients in headwater streams of the Brittany region has shown that broad land–use categories cannot explain the observed patterns for two non–exclusive reasons: *i)* in catchments where >90% of the land use is agriculture, spatial variability in agricultural management practices can play an important role; *ii)* longitudinal variations in topography can also play an important role in determining groundwater–soil interactions in the riparian zone and influencing riparian processes (Dupas et al., 2021).

During the fragmentation phases, the spatial variability in stream concentrations increased substantially for DIN, SRP and DOC, as indicated by the increase in the spatial CV (Table 3.1). This increasing spatial variability in concentrations during low flow can be caused by discrete groundwater inflow points and/or spatially variable in stream processes, which become more apparent as flow decreases (Floriancic et al., 2019; Hensley et al., 2020; Lupon et al., 2023). In the case of the Naizin catchment, we think that in stream processes play a crucial role in controlling the biogeochemistry of the isolated pools, as no point sources were recorded, and the hydrological characteristics of the catchment suggest that the isolated pools are losing systems (Molenat et al., 2008).

Temporally, the seasonal dynamics of DOC and nutrient concentrations in the intermittent stream of the Naizin catchment were also similar to those of most streams in Brittany and other temperate–climate regions (intermittent or perennial) with *(1)* seasonal maxima of phosphorus and minima of DIN concentrations during the low–flow season and, *(2)* seasonal maxima of DOC concentration during the low–flow season or at the transition

between the low–flow and high–flow seasons (Ebeling et al., 2021; Guillemot et al., 2021; Minaudo et al., 2019). Hence, the direction of change in nutrient and DOC concentrations during stream fragmentation in catchments such as Naizin can be predicted from those during the low–flow season in perennial streams that share temperate oceanic climates, although the changes were larger in the present study. For example, DIN concentrations approached zero in several isolated pools, which rarely occurs in agricultural catchments with perennial flow of the same region (Ebeling et al., 2021; Guillemot et al., 2021).

3.5.2 Biogeochemical controls on dissolved organic matter and nutrient concentrations during stream fragmentation

The DOC and nutrient concentrations observed in the stream of the Naizin catchment during the flowing phases (recession and reconnection) reflect those measured in the shallow groundwater that feeds them (Aubert et al., 2013; Lambert et al., 2024). During the fragmentation phases, the groundwater draws down and surface waters become hydrologically disconnected from lateral groundwater inputs (Molenat et al., 2008). Stream concentrations then diverge from those of the flowing phases, as local biogeochemical processes in the stream gain importance in driving concentration changes in isolated pools (Granados et al., 2020; Zimmer et al., 2022).

The decrease in DIN during fragmentation reflects a decrease in the concentration of nitrate, which is the dominant form of inorganic N form in flowing streams of temperate agricultural catchments (Taylor & Townsend, 2010) including the Naizin catchment (Aubert et al., 2013). Decreasing nitrate concentration can be explained by increasing assimilatory uptake, decreasing mineralisation and nitrification of detrital OM, and/or increasing denitrification (Bernal et al., 2005; Merbt et al., 2016; Woodward et al., 2015). Although all of these processes can occur in isolated pools, we postulate that denitrification exceeded uptake, because we assumed that *(1)* assimilatory N uptake would also decrease SRP concentrations, which was not observed; *(2)* light exposure favours assimilatory N uptake, but the entire stream in the Naizin catchment is shaded during the low–flow season; and *(3)* denitrification increases in the presence of anoxic conditions and OM (Fig. 3.2), which occurred during fragmentation (Table 3.1, Fig. 3.3). The increase in ammonium and nitrite concentrations during fragmentation (Fig. 3.4), can be explained by incomplete mineralisation of the organic N in accumulated detrital OM and anoxia (Acuña et al., 2005; Boulton, 1991; von Schiller et al., 2011). Photodegradation of DOM

also influences ammonium production in streams (Larson et al., 2007); but again, little light penetrated the riparian vegetation over the stream of the Naizin catchment during fragmentation.

The increase in DOC concentration during fragmentation resulted from DOC production exceeding DOC degradation. In the Naizin catchment, previous research studies focusing in the flowing phase have found that stream DOC comes mainly from riparian soils (Humbert et al., 2015; Lambert et al., 2011; Morel et al., 2009). Thus, most DOC in the stream of the Naizin catchment is of terrestrial origin, which is consistent with the knowledge that headwater stream ecosystems are generally heterotrophic (Bernhardt et al., 2022). Because the isolated pools are hydrologically disconnected from the surrounding landscape, lateral inputs from riparian soils are unlikely during fragmentation. Similar to our interpretation of DIN dynamics, we postulate that the lack of light in isolated pools does not favour autotrophy. In contrast, the anoxia and higher temperatures in isolated pools (Table 3.1, Fig. 3.3) do favour reductive dissolution of iron (hydr)oxides and subsequent release of DOC from streambed sediments (Lambert et al., 2013). This process has been emphasised in riparian soils of the Naizin catchment under waterlogged conditions, but could also occur in contexts with lower nutrient legacies (Lambert et al., 2024). According to this interpretation, the sources of DOC are allochthonous materials that have accumulated in the streambed either as litter or as hydrological inputs of OM from the surrounding hillslopes, before fragmentation followed by solubilisation when anoxic conditions set in the isolated pools (Battin et al., 2009; Eder et al., 2022; Harjung et al., 2018). The fluorescence data, which showed a dominance of humic–like PARAFAC components, and even an increase in component C2 in isolated pools, supports this interpretation. Component C2 is associated with terrestrial, degraded, and transformed OM (Groeneveld et al., 2020; Ouyang et al., 2024; von Schiller et al., 2015). In contrast, protein–like DOM, such as component C5, decreased during fragmentation. The fact that this fresh and labile DOM did not increase under low–flow conditions, as would have been expected if autotrophy was high, also supports our interpretation. The decrease in BIX and FI values below 1.8 during fragmentation (Fig. 3.5) suggests a more degraded, less recently produced DOM, and more likely terrestrial source of DOM. This is consistent with our interpretation of the PARAFAC components. The results for DOM composition differ from those of previous studies in a Mediterranean intermittent stream and a coastal plain river system, in both of which non–humic and microbial DOM increased during fragmentation (Ouyang et al., 2024; Vazquez et al., 2010; von Schiller et al., 2015). This

difference could be due to the lack of light in the isolated pools in the Naizin catchment or the high nutrient and OM inputs before fragmentation.

The increase in SRP concentration during fragmentation may have been driven by the same process as DOC release (despite the different spatial patterns): reductive dissolution of iron (hydr)oxides and subsequent release of P and OM from streambed sediment. Synchronous release of DOC and SRP under anoxic conditions is commonly observed in river sediments (Inamdar et al., 2020) and waterlogged riparian soils, including those in the Naizin catchment (Gu et al., 2018; Lambert et al., 2024). Summer release of SRP from lake sediment is also commonly observed, and we suspect that the same mechanism occurs during fragmentation in the Naizin catchment, as the stream switches from a lotic to a lentic system. Photodegradation and mineralisation, which are other processes that can release SRP, are assumed to be limited by the lack of light and oxygen, respectively, as discussed for DIN and DOC.

Upon reconnection, DIN concentrations increased to levels similar to those observed during recession. Meanwhile, DOC and SRP concentrations remained high and were similar to those observed in isolated pools (Fig. 3.3). When we sampled the reconnection phase, the pools' concentrations likely had not contributed to those of the flowing stream, as the volume of water that had flowed since reconnection began (> 2800 m^3) already far exceeded that of the pools (Fig. 3.1c). In addition, previous studies in the Naizin catchment have found that DOM and P accumulated in riparian soils during the low–flow season were flushed for several weeks upon rewetting (Gu et al., 2018; Humbert et al., 2015; Lambert et al., 2024). The fact that the DOM fluorescence properties upon reconnection differed greatly from those of the isolated pools (Fig. A5) supports this interpretation. Determining the influence of the nutrients and OM in isolated pools on stream water upon reconnection requires sampling in a finer temporal resolution (Datry et al., 2018).

Although the processes proposed in this section are hypothetical and could only be confirmed through detailed experimentation, we assume that they do not differ substantially from those observed in less agricultural and drier contexts, since the spatio–temporal patterns and controlling factors appear to be similar (Gómez-Gener et al., 2021; Price et al., 2024; Zimmer et al., 2022).

3.5.3 Implications for the ecology of intermittent streams and downstream water bodies

The interruption of flow in the Naizin catchment caused isolated pools to form, which decreased the number of lotic habitats in the stream network. Several studies have observed that ecological dynamics in these lentic ecosystems are similar to those of temporary wetlands and ponds (Bonada et al., 2020; Datry et al., 2017b). In addition to this major change in physical habitats, results of the present study highlight changes in their biogeochemical characteristics, with the development of anoxia, warming, and changes in trophic conditions. The lower DIN but higher SRP concentration should increase biological (microbial) activity in these environments that are likely to be relatively P–limited. However, the substrate for heterotrophic communities seems less suitable for microbial activity as DOM concentration increases but is likely to be less biodegradable (i.e., more degraded, less recent and more terrestrial). Thus, fragmentation changes the role that streams play in maintaining biodiversity and controlling fluxes of matter (Datry et al., 2014).

The present study highlights the value of high-spatial–resolution data for capturing the heterogeneity of changes in nutrient and DOC concentrations during the fragmentation of headwater streams. We used to think that at the scale of such headwater streams, stream biogeochemistry was dominated by hillslope processes and our results show that in– and near–stream processes can play a crucial role during stream fragmentation. Future studies are still required to determine how this heterogeneity influences the nutrient and OM fluxes to downstream streams and rivers (Brinkerhoff et al., 2024). Several studies observed a flush of mineralisation when intermittent streams reconnected (Datry et al., 2018; Shumilova et al., 2019; von Schiller et al., 2019). We assume that the DOM in isolated pools and litter in intermittent headwater influence the DOM concentration and properties in perennial downstream reaches during reconnection (Price et al., 2024), although the present study's sampling campaigns did not capture this moment. Therefore, we hypothesise that the metabolism (e.g., heterotrophic respiration) of downstream reaches increases when intermittent upstream streams reconnect with downstream reaches. Testing this hypothesis requires more frequent sampling to assess DOM and high–frequency monitoring to estimate metabolism (e.g., continuous monitoring of DO).

Long–term monitoring is required to explore the relation between the climate conditions and biogeochemistry of intermittent streams. In France, the duration and severity of

no–flow events is predicted to increase in future hydroclimatic conditions (Sauquet et al., 2021). Because of their highly dynamic hydrology, responses of intermittent streams to floods and extreme storm events may change faster than in perennial streams under future climate (Dupas et al., 2024; Tramblay et al., 2023). Our results suggest that seasonal fragmentation is associated with larger temporal changes in stream water concentrations compared to changes during the low–flow season in perennial streams, even though the directions of these changes are the same, they were greater in the Naizin catchment. Thus, intermittent headwater streams could serve as sentinels of the future of temperate streams under climate change.

Appendix



Figure A1 – Left: Fragmented reach with an isolated pool during late fragmentation. Right: Flowing reach during reconnection.

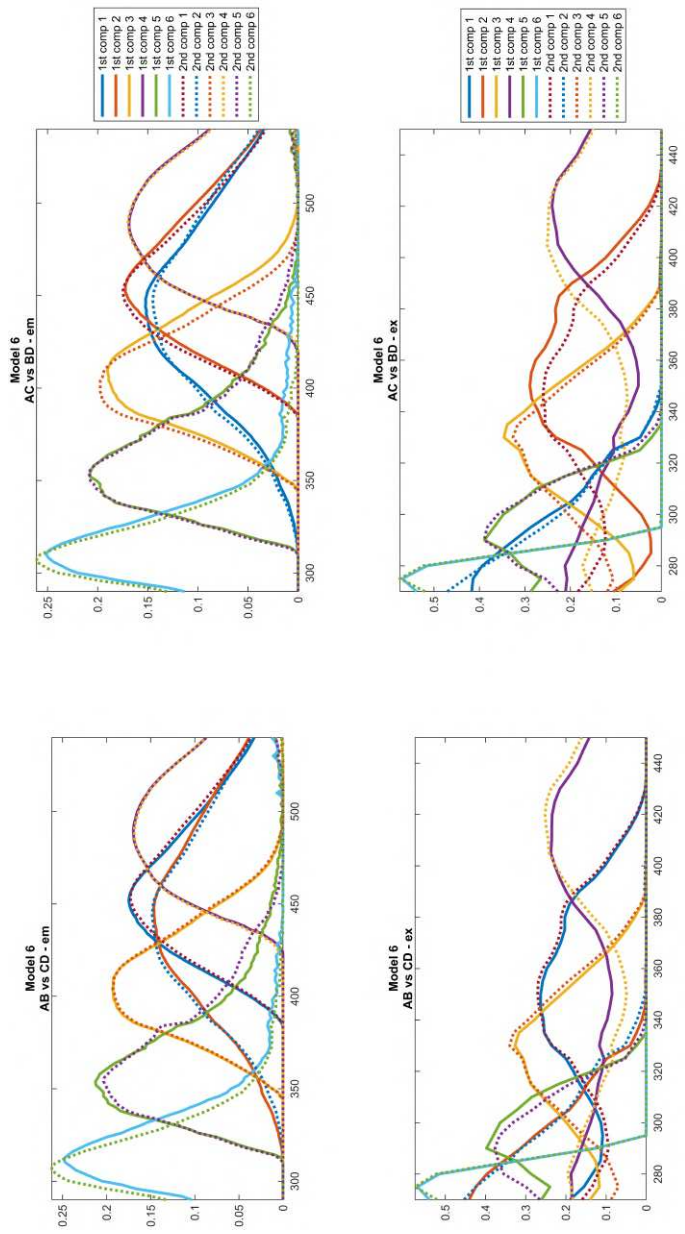

Figure A2 – Split–half validation of the six parallel factor (PARAFAC) modelling components, $n = 181$ samples.

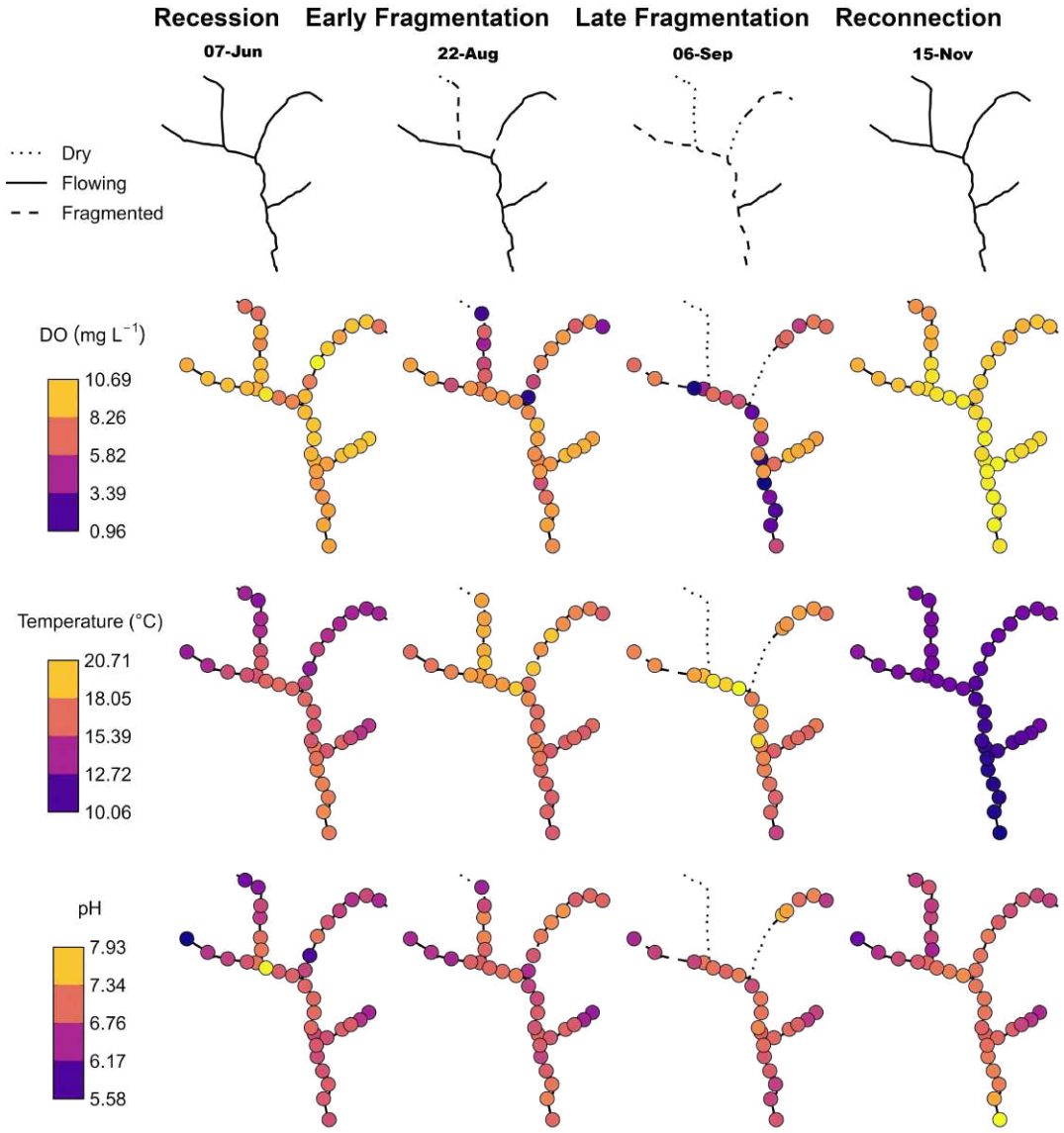

Figure A3 – High–spatial configuration of dissolved oxygen (DO), temperature (Temp) and pH during the four hydrological phases sampled: recession ($n = 38$), early fragmentation ($n = 37$), late fragmentation ($n = 28$), and reconnection ($n = 38$). Stream network line types correspond to flowing states: dry (i.e., absence of surface water; dotted line), flowing (i.e. presence of running water; solid line) and fragmented (i.e., presence of isolated pools; dashed line). Dot colours correspond to concentrations.

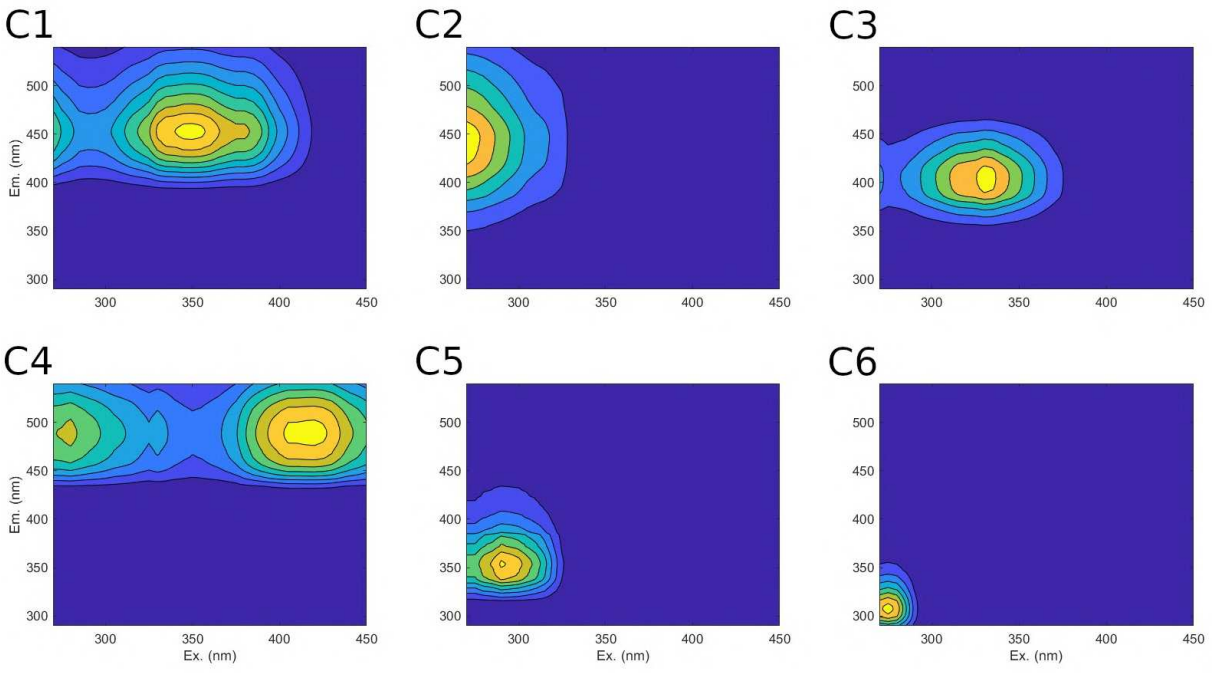

Figure A4 – The six parallel factor (PARAFAC) modelling components identified during the four hydrological phases sampled: recession ($n = 38$), early fragmentation ($n = 37$), late fragmentation ($n = 28$), and reconnection ($n = 38$). Components C1, C2, and C4 had humic-like fluorescence properties, with excitation (Ex.)/emission (Em.) peaks of 350 nm/452 nm, 270 nm/448 nm and 420 nm/448 nm, respectively. Component C3 also had humic-like fluorescence properties (with excitation/emission peaks of 330 nm/404 nm), but with microbial processing as probable source. Components C5 and C6 had protein-like fluorescence properties, with excitation/emission peaks of 290 nm/354 nm and 275 nm/308 nm, respectively.

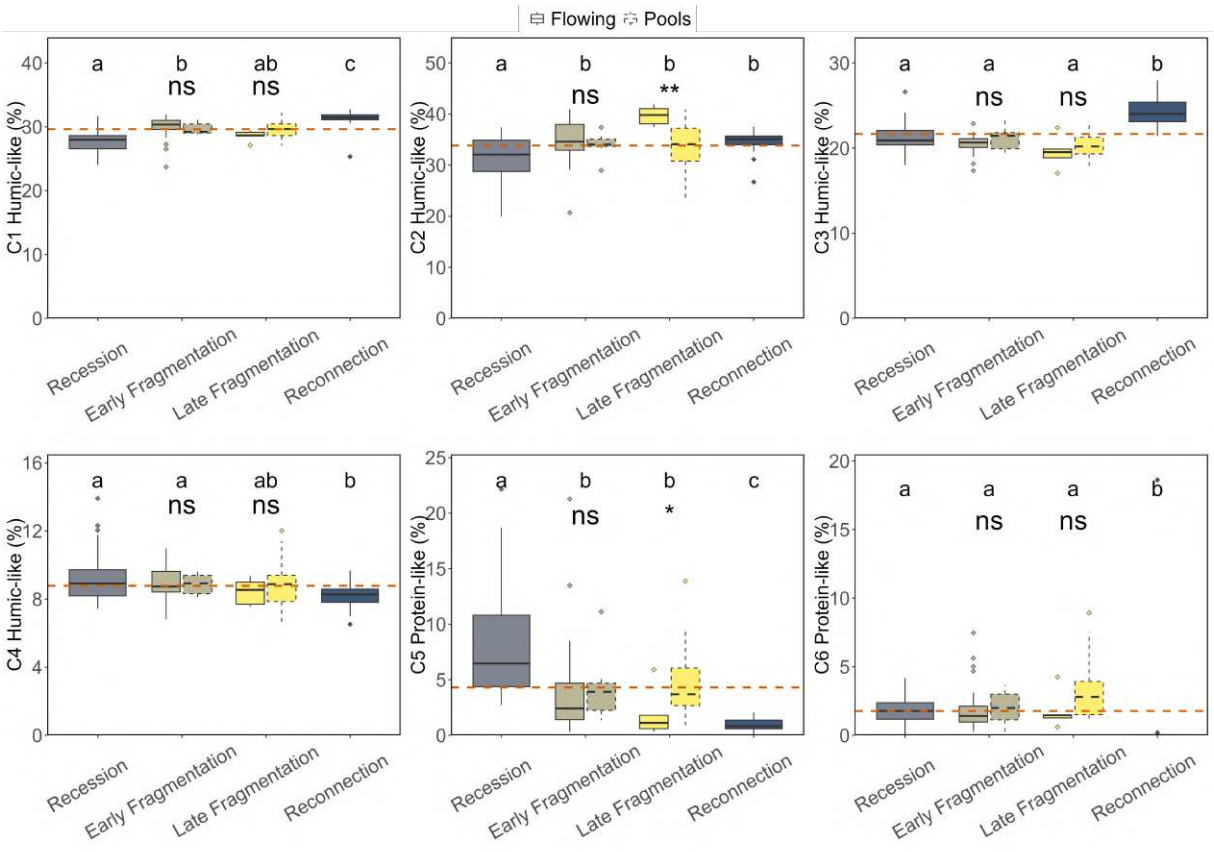

Figure A5 – Boxplots of the contributions of the six parallel factor (PARAFAC) components identified during the four hydrological phases sampled: recession ($n = 38$), early fragmentation ($n = 37$; where 30 flowing and 7 fragmented), late fragmentation ($n = 28$; where 5 flowing and 23 fragmented), and reconnection ($n = 38$). Whiskers equal 1.5 times the interquartile range. Components C1, C2 and C4 had humic–like fluorescence properties. Component C3 also had humic–like fluorescence properties but with microbial processing as probable source. Components C5 and C6 had protein–like fluorescence properties. Whiskers equal 1.5 times the interquartile range. Solid lines represent concentrations in flowing water of the reaches, whereas dashed lines represent those in isolated pools of fragmented reaches during early and late fragmentation. The horizontal orange dashed lines represent the mean ratio. The letters indicate statistical differences between sampling dates, as determined by the non-parametric Kruskal–Wallis test and post hoc Dunn test with Bonferroni correction. Asterisks indicate a significant difference when comparing proportions in flowing reaches and isolated pools during each fragmentation phase, which were analysed using the Wilcoxon signed-rank test. Significance levels are as follows: ns: not significant; *: $p \leq 0.05$; **: $p \leq 0.01$.

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Chapter 4

Hydrological fragmentation alters nutrients and organic matter speciation in intermittent agricultural catchments

Authors: Andrés Casanova[1], Ophélie Fovet[1], Anne Jaffrezic[1], Rémi Dupas[1]

[1] UMR 1069 SAS, Institut Agro - INRAE, 65 rue de Saint-Brieuc, Rennes, CEDEX 35000, France

4.1 Abstract

The speciation of nitrogen (N), phosphorus (P) and organic matter (OM), i.e. the diversity of their chemical forms, plays a key role in regulating the ecological functions of streams and rivers. Speciation influences their bioavailability and how prone they are to being transported to downstream water bodies. While several studies have investigated the influence of land use and seasonal variations in temperature and discharge on nutrients and OM speciation, few have analysed intermittent rivers subjected to seasonal fragmentation. This is a particularly critical knowledge gap in agricultural contexts, where nutrient concentrations are often high and dominated by one form (e.g. nitrate for nitrogen) in perennial catchments. In this study, we conducted repeated synoptic sampling campaigns at 30 locations within three intermittent agricultural catchments (18 to 24 km^2) during the hydrological fragmentation and rewetting period of 2024–2025. Our aim was to analyse how hydrological fragmentation leads to changes in nutrient and OM speciation that may affect export at rewetting. The results showed that hypoxic conditions in the isolated pools during stream fragmentation led to an increase in the concentration of reduced and organic forms of N and P, while nitrate and soluble reactive P (SRP) decreased. Dissolved

OM concentration increased in isolated pools, likely due to pH– or redox–mediated desorption processes, but their fluorescence properties remained similar to flowing reaches. We conclude that monitoring intermittent agricultural streams requires consideration of more nutrient species than are usually measured (e.g. nitrate and SRP) because they present different degrees of bioavailability and toxicity to aquatic ecosystems.
Keywords: intermittent stream, nutrient, DOM, speciation, temperate climate, intensive agriculture

4.2 Introduction

Nutrient dynamics in freshwater ecosystems play an important role in their productivity (Bernal et al., 2012; Elser et al., 2007). The concentration of nitrogen (N) and phosphorus (P) in aquatic ecosystems typically increases with increasing agricultural intensity and population density, which significantly affects the integrity of freshwater systems (Arce et al., 2015; Conley et al., 2009; Lupon et al., 2016). Nutrient and organic matter (OM) concentrations are influenced by regional and local factors, such as climate, hydrology, geology, geomorphology, and land use in the surrounding catchment (Abbott et al., 2018; Fisher et al., 1998; Gómez et al., 2017). These concentrations also vary over time in response to changes in hydroclimatic conditions at long-term, seasonal and event time scales. The predominant control of discharge on water quality has been widely documented for perennial rivers, and since more recently for intermittent rivers and streams (Covino, 2017; Dupas et al., 2024; Godsey et al., 2009).

Climate change is increasing the frequency and intensity of extreme weather events such as droughts with consequences on water quality (Bieroza et al., 2024; Dupas et al., 2024; Van Vliet et al., 2023). One consequence of drought is stream fragmentation and flow cessation, particularly in headwaters. Hydrological fragmentation occurs when hydrological connectivity is disrupted in one or more spatial dimensions and leads to a cessation of flow (Boulton et al., 2017; Datry et al., 2014). Hydrological fragmentation creates isolated pools, which are biogeochemical hotspots where the high spatial variability of physico-chemical conditions leads to biogeochemical reactions that differ from that of flowing reaches. These hotspots are influenced by local environmental conditions including water residence time, organic matter availability (OM) availability, sediment-water interactions and the activity of biological communities (Boulton et al., 2017; Gómez et al., 2017; Gómez-Gener et al., 2021).

In general, the spatial variability in solutes such as nitrate, soluble reactive phosphorus (SRP) and dissolved organic carbon (DOC) increases among isolated pools during stream fragmentation compared to the flowing conditions that usually prevail in winter (Fellman et al., 2011; Gómez et al., 2017; von Schiller et al., 2017). Such increasing variability in concentration during stream fragmentation has been quantified with the spatial coefficient of variation in both arid and temperate contexts (Dent & Grimm, 1999), Casanova et al., submitted. Solute concentrations also vary over time, primarily due to drying and rewetting cycles in both perennial and intermittent streams and rivers (Acuña et al., 2005; Arce et al., 2015; Bernal et al., 2012; von Schiller et al., 2011). In particular, decreases in dissolved inorganic nitrogen (DIN) and increases in DOC concentrations were observed in isolated pools across both forested and agricultural catchments, while the direction of change for SRP varies among studies (Casanova et al., submitted; Skoulikidis & Amaxidis, 2009; von Schiller et al., 2011). The processes hypothesised to drive the changes in nitrate concentrations are denitrification and the decreased mineralisation of OM (Bernal et al., 2005; Merbt et al., 2016; Woodward et al., 2015). Changes in SRP concentrations may be driven by photodegradation, mineralisation, and solubilisation in reductive conditions (Gu et al., 2018; Inamdar et al., 2020; Lambert et al., 2024). Similar processes are related to changes in DOC concentrations, whereby reductive conditions favour the dissolution of iron (hydr)oxides, subsequently releasing DOC from streambed sediments (Lambert et al., 2013; von Schiller et al., 2019).

Nutrients and OM experience different processes of transformation in running waters. These processes may be exacerbated in intermittent streams, where the discontinuity of the hydrological cycle varies in space and time (Arce et al., 2015). An important factor controlling N processes is the residence time of water, which is driven by the climate, land uses and catchment management (Durand et al., 2011). Although nitrate has captivated the interest of researchers seeking to understand the processes behind nitrogen cycling, other forms of nitrogen, such as nitrites and ammonium, as well as dissolved organic nitrogen (DON), are commonly found in all freshwater. Nitrate, nitrite, ammonium and DON are all readily available to plants, supporting the growth of both algae and higher plants. In nutrient-rich rivers, where anthropogenic nitrogen (N) inputs are high, nitrate is the dominant form. In oligotrophic systems, however, dissolved organic nitrogen (DON) is produced as a by-product of the microbial breakdown of organic matter, typically comprising 60% of the total nitrogen (Durand et al., 2011). Microbial transformations of N are determined by biogeochemical conditions. For instance, in respiratory denitrifi-

cation, electrons released by the oxidation of organic matter under anaerobic conditions reduce nitrate to N_2 and N_2O, but also a small fraction of nitrite (Burgin & Hamilton, 2007). Nitrite formation has also been associated to the anaerobic ammonium oxidation, a chemolithoautottrophic process derived from the reduction of nitrate by denitrifying bacteria and to dissimilatory nitrate reduction to ammonium (DNRA) which releases ammonium in nitrate-limited environments, that are rich in labile carbon (Burgin & Hamilton, 2007; Kelso et al., 1997). The reduced form ammonium is more biologically available and less mobile than nitrate, while the oxidised form nitrite accumulated from the sediments might adversely affect aquatic organisms (Kelso et al., 1997). In most aquatic systems, the largest sources and sinks of P are sediments characterised by a high iron content. Iron–rich sediments limit the availability of dissolved phosphorus, but also lead to the release of phosphate into the water column through changes in pH and redox conditions (Baldwin & Mitchell, 2000; Gómez et al., 2017). Studies on P speciation have shown that a high proportion of particulate P is present during the rewetting phase, but also that the proportion of bioavailable dissolved P increases, probably due to sediment drying during stream fragmentation (Kerr et al., 2010; Tzoraki et al., 2007). The dynamics of OM are affected by hydrological fragmentation, resulting in a decrease in the proportion of high-molecular-weight substances (von Schiller et al., 2015). Conversely, the proportion of particulate OM increases due to the retention and accumulation in the riverbed and/or to a decrease in microbial activity (Dewson et al., 2007; Rolls et al., 2012). Concentrations of DOC and DON also tend to increase during stream fragmentation, with an increase in the non-humic, microbial-like DOM composition in a Mediterranean stream (von Schiller et al., 2015). However, another study has shown a prevalence of degraded DOM of a humic and terrestrial nature in a forested intermittent stream (Casas-Ruiz et al., 2015). The importance of nutrient and OM storage and transformation processes in intermittent streams in response to changes in catchment land use is largely uncertain, as is the influence on freshwater ecosystem health.

The aforementioned research studies provide a good understanding of how nutrient and OM concentration and speciation respond to fragmentation in Mediterranean and arid climates with rather low nutrient loadings, while knowledge from temperate and agriculturally–intensive landscape focus on perennial rivers. In perennial streams and rivers of temperate and agriculturally–intensive landscapes, nutrient concentrations are often high and dominated by one form (e.g. nitrate for nitrogen); little is known about intermittent rivers in these contexts. Hence, our research question is how does nutrient

speciation and organic matter composition change during the fragmentation of an intermittent stream draining an agricultural catchment of the temperate zone? We hypothesise that, due to the hypoxic conditions that usually prevails during stream fragmentation, reduced and organic forms of N and P (NH_4^+, DON, DOP) will increase while oxidised forms of N (NO_3^-) will decrease. The response of inorganic P (SRP) may vary depending on sediment redox processes, potentially increasing due to Fe reduction and release from sediments. Finally, we expect microbial and protein forms of dissolved organic matter to increase due to increasing residence time and temperature during stream fragmentation.

4.3 Materials and Methods

4.3.1 Study area

The Ria d'Étel, located on the south coast of Brittany, is an inland sea measuring 22 km^2 and boasting 122 km of coastline. Its catchment area is 360 km^2 and includes over 500 km of river network that supplies it with fresh water (Fig. 4.3). The water quality thus depends on the surrounding land. The local economy is based on oyster farming and leisure activities such as yachting, swimming, and fishing. The area is home to a variety of species, including shellfish, fish and birds. As such, it is part of the Natura 2000 network under the European Union Habitats Directive.

Our study encompasses three intermittent headwaters catchments on the eastern side of the Ria d'Étel. ALl three have a Strahler order of 4, and are distributed from north to south: Cochelin (23.3 km^2), Calavret (23.7 km^2), and Poumen (17.7 km^2). They follow a gradient of intermittence from north to south, with Poumen being the most affected by seasonal drying, followed by Calavret and Cochelin. Seasonal drying generally occurs in late summer/early autumn and is more pronounced in low-order streams.

The topography is dominated by low-granulometric sedimentary formations, with elevations ranging from 1 to 66 meters above sea level, and gentle mean slopes in Cochelin (1.2%), Calavret (1.6%) and Poumen (0.8%). The geology is predominantly Carboniferous granite, consisting of medium-to fine-grained leucogranite with biotite and muscovite from Carnac-Sarzeau, containing numerous small sub-automorphic feldspar phenocrysts **??**. Long-term weather data comes from the nearest Meteo France weather station in the city of Auray, 5 km east of the study area, and covers the period from 2000 to 2023. The climate is temperate oceanic. Temperatures are mild, with an average of 12.5°C through-

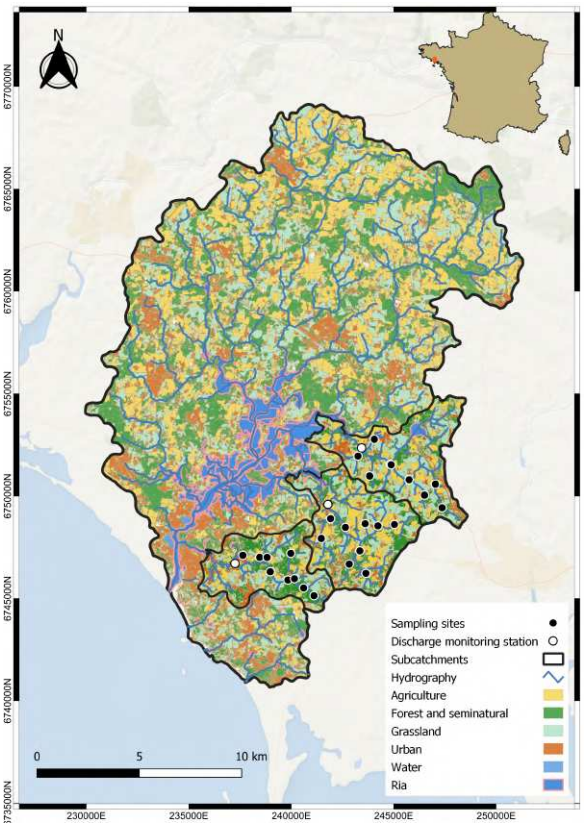

Figure 4.1 – The Ria d'Etel and its catchment area (western France) with the 3 eastern intermittent headwater catchments, from north to south Cochelin, Calavret and Poumen.

out the year, ranging from 7°C during the coldest months (December to February) to 18°C during the warmest months (July and August). The long-term mean annual rainfall is 792 mm. November and December are the wettest months, with an average monthly rainfall of 105 mm, while June and July are the driest months, with an average monthly rainfall of 44 mm.

The Ria d'Étel economy encompasses extensive oyster farming, tourism and agriculture involving mixed livestock farming and the cultivation of winter cereals, maize, temporary grasslands and other crops. There are also small towns and villages, as well as broadleaved and coniferous forests and seminatural areas. These land cover classes vary among catchments. Calavret and Cochelin have the largest agricultural areas at 52% and 56%, respectively, while Poumen has 43%. Calavret and Poumen mostly shared the forested area, with Poumen having approximately 46% and Calavret having 37%, while Cochelin has 28%.The forested area is mostly shared by Calavret and Poumen, with approximately 8 km^2 each. Finally, Cochelin's coverage of roeads, urban sprawl and industrial and commercial zones amounts to 14%, compared to 11% for Calavret and Poumen.

4.3.2 Hydrochemical monitoring

Three discharge monitoring stations equipped with a data logger (CTD-Diver® or TD-Diver®) and water level gauges were installed at the outlet of the three study catchments to estimate the discharge through a rating curve. The water level was measured every 15 minutes from 20 March of 2024 to 28 February of 2025. We conducted four field campaigns to determine water quality during four different hydrological phases: recession, early fragmentation, late fragmentation, and winter discharge (Fig. 4.2). We selected ten sampling sites per catchment for a total of thirty sites per field campaign (Fig. 4.3). These sites were located along accessible stream reaches with a diversity of land uses and Strahler orders.

During the recession phase (sampled on 27 May 2024), the stream network was fully flowing across the three catchments (Fig. 4.2). The early fragmentation phase, sampled on 2 August 2024, was characterised by a low water level, the formation of twelve isolated pools in the upstream reaches of the three catchments and two completely dry sites: one in the uppermost reaches of Poumen, and one in one of the upper reaches of Calavret (Fig. **??**). The late fragmentation phase, sampled on 29 August 2024, was characterised by the lowest water level recorded across the three catchments in 2024. The number of fragmented sites increased to fifteen isolated pools. The isolated pools from the previous sampling campaign remained unchanged in the Cochelin and Calavret catchments, while the stream network in the Poumen catchment was fully fragmented. Three sites were dry: two were the same as during the early fragmentation phase in the Poumen and Calavret catchments, and a third was in the Poumen catchment (Fig. **??**). The winter discharge phase, sampled on 19 February 2025, was characterised by a fully flowing stream network and high water levels across the three catchments, as is typical of the winter season.

For each field sampling date, we collected stream water using a bucket and filtered the samples on site using a 50 ml syringe (flushed twice beforehand) at the sampling sites. We filtered one aliquot using a 0.2 µm filter to measure the dissolved organic carbon (DOC) content, as well as the coloured and fluorescent dissolved organic matter (CDOM and FDOM, respectively). We also filtered a second aliquot using a 0.45 µm filter to measure the concentrations of anions, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), total dissolved nitrogen (TDN), sulphate (SO_4^{2-}), silica (Si) and chloride (Cl^-). A third aliquot was kept unfiltered to measure total phosphorus (TP). All samples were then stored in a cooler to keep them at a low temperature and to prevent light exposure during transport to the laboratory. The samples were refrigerated at 4°C, and analysed within 72 hours.

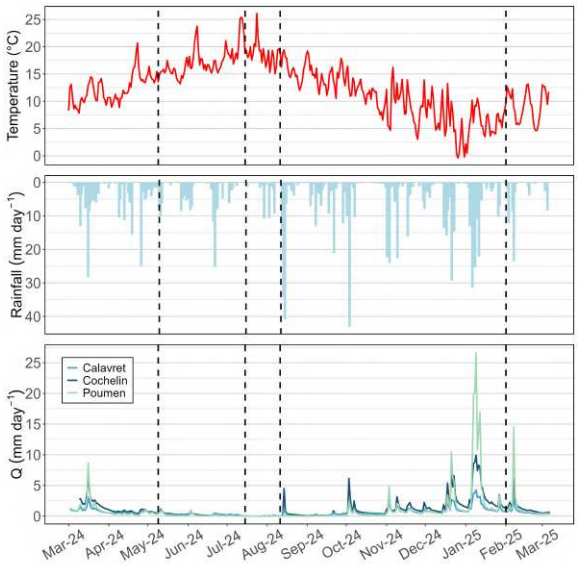

Figure 4.2 – Mean daily temperature (red line), daily rainfall (light blue bars) measured at the weather station, and discharge measured at the gauging station (blue line) for the year of 2024—2025 for the three headwaters catchments. Vertical orange dashed lines represents the sampling dates during four hydrological phases: from left to right, recession, early fragmentation, late fragmentation and winter discharge.

On site, we also measured on site physico-chemical parameters such as dissolved oxygen (DO) concentration and saturation, pH, water temperature, redox potential, and electrical conductivity (Eh) using a multiparametric probe (ODEON®, Aqualabo, Champigny-sur-Marne, France) calibrated with buffer solutions at the laboratory the day before.

4.3.3 Laboratory analysis

The concentrations of several nutrient and OM forms: NO_3^-, NO_2^-, NH_4^+ and total dissolved N (TDN), soluble reactive P (SRP) and total P (TP), DOC and DOM fluorescence properties for OM, SO_4^{2-}, Si, and Cl^- were carried out on the water samples on the four sampling dates. Dissolved inorganic N (DIN) was computed as the sum of NO_2^-, NO_3^-, and NH_4^+, while dissolved organic N (DON) as the difference between TDN and DIN. Non-reactive P (NRP) as the difference between TP and SRP, this includes dissolved organic phosphorus, particulate phosphorus and other forms of phosphorus that are either dissolved or colloidal but not molybdate reactive (Gu et al., 2020).

The concentrations of ammonium, TP, SRP and Si were measured via photometric analysis using an automatic sequential analyser (SmartChem® 200, AMS Alliance,

France). Ammonium concentration was determined based on its reaction with a hypochlorous acid and salicylate solution (Antweiler et al., 1996). SRP was determined via a direct reaction using the phosphomolybdenum blue method (J. Murphy & Riley, 1962). TP was determined by digesting all forms of inorganic and organic phosphorus to orthophosphate in acidic potassium persulfate, followed by the phosphomolybdenum blue method (Hosomi & Sudo, 1986). Silica concentrations were determined based on the reaction of silicates with molybdate ions under acidic conditions (Kahler, 1941). The quantification limits for the analyser were 0.039, 0.013, 0.016, and 0.1 $mg.L^{-1}$ for ammonium, SRP, TP, and Si respectively. Major anions, such as nitrite, nitrate, sulphate and chloride were measured using an ion chromatograph (ICS-3000, Dionex, Sunnyvale, California, USA). The quantification limits were 0.05 $mg.L^{-1}$ for nitrite, and 1 $mg.L^{-1}$ for nitrate, sulphate and chloride. Total dissolved nitrogen (TDN) was estimated using the oxidative mineralisation method with potassium peroxodisulphate (Ebina, 1983), and analysed using the same sequential analyser as for ammonium, TP and SRP. The quantification limit was 0.1 $mg.L^{-1}N$ for TDN. We measured DOC using a carbon analyser (TOC-V 5050A, Shimadzu, Kyoto, Japan) (Petitjean et al., 2004). The quantification limits for the analyser were 0.31 $mg.L^{-1}$ for DOC.

The optical properties of DOM were analysed by evaluating the UV-visible absorbance of colored DOM using spectra measured at 1 nm increments between 230–700 nm in a 1 cm quartz cuvette with a UV/VIS spectrometer (Lambda20, PerkinElmer Waltham, Massachusetts, USA). Samples with an absorbance approaching 2.0 or exceeding the spectrophotometer's linear range were diluted to avoid inner filter effects (K. R. Murphy et al., 2013). We recorded fluorescent DOM excitation-emission matrices (EEMs) using a spectrometer (LS–55, PerkinElmer). The instrument was set to measure excitation wavelengths between 270 and 450 nm at 5 nm intervals and emission wavelengths between 290 and 550 nm at 0.5 nm intervals at a speed of 1200 $nm.min^{-1}$, using a 1 cm quartz cuvette. We made blank-subtracted corrections to all the EEMs obtained the same day using Milli–Q water EEMs (Vogt et al., 2023), and corrected EEMs for inner-filter effects using CDOM spectra (Ohno, 2002).

4.3.4 Data analysis

All samples per sampling date were selected and analysed together, regardless of the catchment. To evaluate the changes in nutrient speciation and organic matter composition across the four hydrological dates, non–parametric Kruskal–Wallis tests. When this

test yielded a significant result ($p < 0.05$), a post–hoc Dunn test to identify the dates that differed the others was used. Differences in nutrient speciation and organic matter composition during stream fragmentation were also evaluated. The comparison between the isolated pools and the flowing reaches, during the early and late fragmentation periods were performed using a Wilcoxon signed–rank test. If this test yielded a significant result ($p < 0.05$), a post–hoc Dunn test with Bonferroni correction to adjust the significance level was performed. We compared the results and correlations with those of the other anions measured (Si, Cl^-, SO_4^{2-}) and $C : N$ ratio, to help identify the processes involved.

Additionally, we performed Parallel factor Analysis (PARAFAC) on pre-processed fluorescence EEM signals (Raman scattering removal and standardisation to Raman units) and normalised to the values of a Milli–Q water sample on the day of analysis. The analysis was performed in MATLAB (MathWorks, USA) using the drEEM 0.6.5 Toolbox (K. R. Murphy et al., 2013). To test and validate the model, random initialisation and sum–of–squared–error and split–half analysis were performed. The PARAFAC components were normalised by the percentage of total fluorescence. PARAFAC analysis of the fluorescence spectra yielded five components. Components C1, C3 and C4 exhibited humic-like fluorescence properties (Fellman et al., 2010), with excitation/emission peaks of 345 nm/450 nm, 270 nm/448 nm and 275 nm/490 nm, respectively. Component C2 also exhibited humic-like fluorescence properties, with excitation/emission peaks at 315 nm/402 nm; however, it has microbial processing as a probable source (Cory & McKnight, 2005). Component C5 exhibited protein-like fluorescence properties, with excitation/emission peaks at 290 nm/352 nm (K. R. Murphy et al., 2006). We aggregated the humic-like components (C1, C3 and C4) and analysed them alongside the microbial component C2 and the protein-like component C5. We then compared them across sampling dates and between the flowing reaches and isolated pools. We performed the same statistical analysis as for the nutrient concentrations to analyse the effect of stream fragmentation to the DOM in the catchments.

To confirm that water chemistry responded to local processes during stream fragmentation, while it was controlled by land–to–stream transfer processes during the flowing phases, we calculated Pearson's correlations between solute concentrations and land cover indices. We used the CESBIO land cover database (Inglada et al., 2017) as raster data with a spatial resolution of 10 m and 20 m. We focused on five land cover classes: agricultural land, arable land, urban surfaces, grassland, forest and seminatural areas. We estimated the percentage of each land cover type within each subcatchment. Water

concentrations are expected to correlate with the relative surface of the subcatchments' land cover, indicating a strong control by land-to-stream transfer processes. In contrast, during the fragmented dates, such correlation would be lost due to a lack of hydrological connectivity with the surrounding landscape, and the increasing importance of local biogeochemical processes within the isolated pools.

All statistical analyses were performed in R (Team, 2024), with the packages "tidyverse" (Wickham et al., 2019), and "ggpubr" (Kassambara, 2023) to visualise and model data, and "Simple Features for R" (Pebesma, 2018) to spatial data manipulation.

4.4 Results

4.4.1 Hydrological and physico-chemical conditions across sampling dates

We observe the same seasonal dynamics of hydrological fragmentation in the three catchments but differences in their magnitude (Fig. **??**). During the recession date the stream network of the three catchments were flowing at all sampling points (Fig. 4.2). During the early fragmentation date, all three catchments exhibited dry site and/or isolated pools in their upstream reaches. However, the Poumen catchment exhibited more isolated pools than Calavret and Cochelin, consistently with local knowledge of the study area. 12 sampling sites were located in isolated pools and 2 sites were dry out of 30 sampling sites for the Calavret and Poumen catchments (Fig. **??**). During the late fragmentation date, the three catchments exhibited more dry sampling sites and/or isolated pools, with 15 isolated pools and 3 dry sites out of 30 sampling sites. The Poumen catchment was entirely fragmented with 8 isolated pools and 2 dry sites, while the Calavret catchment presented 4 isolated pools and 1 dry site in its upstream part. Hydrological fragmentation in the Cochelin catchment was similar to the early fragmentation date, and presented the same sampling sites fragmented minus one upstream (Fig. **??**). During the "winter discharge" date, the stream network of the three catchments were fully flowing with the highest discharge of the four sampling dates (Fig. 4.2).

The physicochemical parameters measured varied among the sampling dates (Table 4.1). The mean water temperature increased significantly from recession to early and late fragmentation, then decreased significantly during winter discharge conditions. During early fragmentation, the mean temperature was significantly higher in the isolated

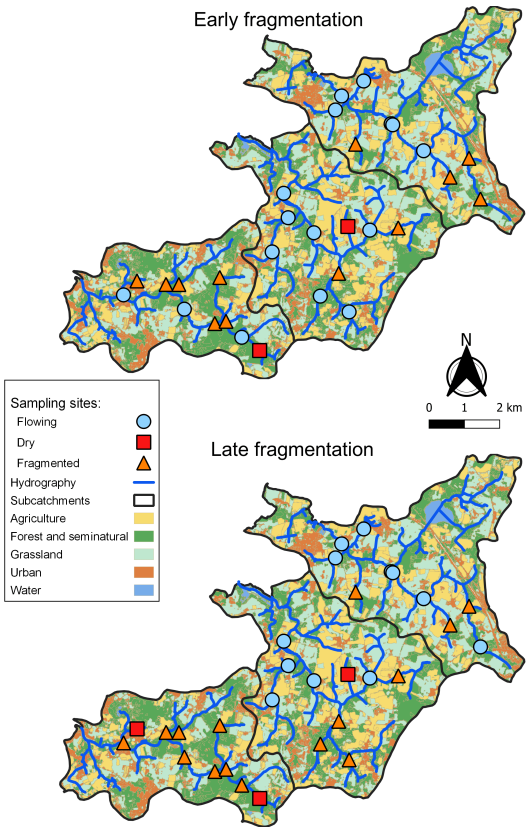

Figure 4.3 – Hydrological state of sampling sites during both fragmentation dates. Early fragmentation had 12 isolated pools and 2 dry sites. Late fragmentation had 15 isolated pools and 3 dry sites. All sampling sites were flowing during the "recession" and "winter discharge" dates.

pools than in the flowing reaches (19řC and 17.8 řC, respectively). However, during late fragmentation there was no significant difference in the water temperature between the isolated pools and flowing reaches (17.1řC and 16.1řC, respectively). The mean dissolved oxygen concentration decreased significantly from recession to early and late fragmentation, then increased significantly during winter discharge conditions. During both early and late fragmentation, the mean concentration of DO was significantly lower in the isolated pools compared to the flowing reaches, 6.1 mgL^{-1} compared to 1.9 mgL^{-1}, during early fragmentation, and 6.3 mgL^{-1} compared to 2.8 mgL^{-1}, during late fragmentation.

The mean redox potential did not vary significantly among the four sampling dates. However, during the two fragmentation dates, the mean Eh was significantly lower in the isolated pools compared to the flowing reaches, from 195 mV to 106 mV, during early fragmentation, and from 229 mV and 112 mV, during late fragmentation. The mean pH increased significantly from recession and early fragmentation to late fragmentation and decreased significantly in winter. During early fragmentation, the mean pH was significantly lower in the isolated pools than in the flowing reaches (6.95 and 7.11, respectively). However, during late fragmentation there was no significant difference in the pH between

Table 4.1 – Descriptive statistics of physicochemical parameters during the four sampled dates.

Variable	RC	EF	LF	WD	H test
Temperature (°C)	14 ± 0.9	18.3 ± 1.5	16.6 ± 0.9	9.21 ± 1	***
O_2 (mgL^{-1})	7.84 ± 1.8	4.3 ± 2.9	4.3 ± 2.8	9.9 ± 1.6	***
Eh (mV)	195 ± 36.4	157 ± 87.3	164 ± 104	200 ± 32.7	ns
pH (-)	7.1 ± 0.2	7 ± 0.2	7.3 ± 0.3	7.1 ± 0.2	***
EC (μScm^{-1})	310 ± 74.1	405 ± 124	432 ± 216	288 ± 69.9	***

Note: RC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge. Temperature, dissolved oxygen (O_2), redox potential (Eh), pH and electrical conductivity (EC). Values are presented as mean ± SD. Significance: ns: non significant, * p-value <= 0.05, ** p-value <= 0.01, *** p-value <= 0.001.

the isolated pools and the flowing reaches (7.23 and 7.38, respectively). The mean electrical conductivity increased significantly from recession to early fragmentation. It then decreased significantly between the two fragmentation periods and winter discharge. During both early and late fragmentation, the mean EC did not vary significantly between the isolated pools and the flowing reaches, during early fragmentation (426 μScm^{-1} and 389 μScm^{-1}, respectively), and during late fragmentation (443 μScm^{-1} and 418 μScm^{-1}, respectively).

4.4.2 Nutrients and organic matter concentrations during hydrological fragmentation

We compared the correlations between DOC and DIN concentrations and land cover in 30 subcatchments (Fig. 4.4). High and positive correlations were observed between DOC concentrations and forest and seminatural areas across the catchments during recession and winter discharge ($r = 0.81$ and $r = 0.83$, respectively). However, these correlations were no longer apparent during early and late fragmentation ($r = 0.27$ and $r = 0.37$, respectively). Similarly, there were high and positive correlations between DIN concentrations and agricultural land cover (comprising arable land and grasslands), with $r = 0.71$ and $r = 0.55$ during recession and winter discharge, respectively. Once again, these correlations were no longer apparent during early and late fragmentation ($r = 0.38$ and $r = 0.21$, respectively). No significant correlations with land cover were found for P forms, even during the recession and winter discharge dates.

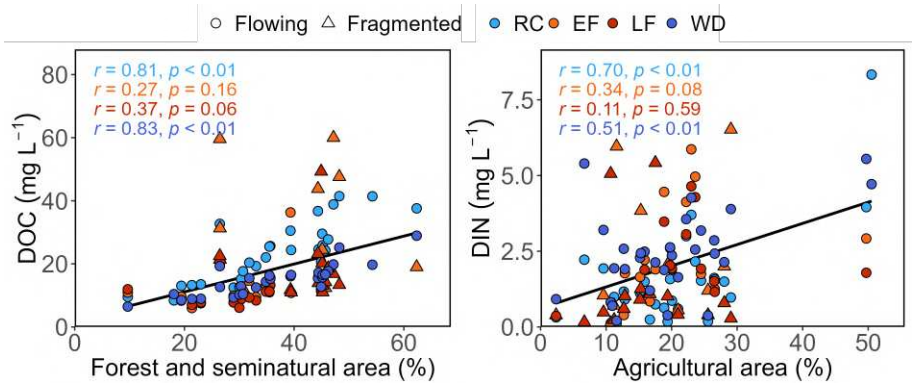

Figure 4.4 – Relationships between dissolved organic carbon (DOC) concentrations and forest and seminatural area, and between dissolved inorganic nitrogen (DIN) concentrations and agricultural areas, for the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). The dots represent samples collected in flowing reaches, triangles represents samples collected from isolated pools. The solid black line shows the general relationship between the data for all samples combined. The statistics show Pearson correlations between solute concentrations and land cover area, with their respective $p - value$.

Most of the measured solutes varied among the sampling dates, but differences were even more significant when comparing isolated pools and flowing reaches (Fig. 4.5). The mean nitrate concentration increased from recession to early fragmentation (from 1.41 $mg.L^1$ to 1.60 $mg.L^1$), then decreased to 1.22 $mg.L^1$ during late fragmentation. It then increased significantly to 2.33 $mg.L^1$ during winter discharge. During the fragmentation dates, nitrate concentration was significantly lower in the isolated pools compared to the flowing reaches (2.3 $mg.L^1$ vs 0.7 $mg.L^1$ during early fragmentation, and 2.25 $mg.L^1$ vs 0.4 $mg.L^1$ during late fragmentation). The mean nitrite concentration increased from recession to early fragmentation (from 0.018 $mg.L^1$ to 0.044 $mg.L^1$), before decreasing to 0.027 $mg.L^1$ during late fragmentation. It subsequently decreased significantly to 0.014 $mg.L^1$ during winter discharge. However, the nitrite concentration did not vary between the isolated pools and the flowing reaches during either early or late fragmentation dates. The mean ammonium concentration increased from recession to early fragmentation (from 0.071 $mg.L^1$ to 0.65 $mg.L^1$), then decreased to 0.5 $mg.L^1$ during late fragmentation. It then decreased significantly to 0.08 $mg.L^1$ during winter discharge. During the fragmentation dates, ammonium concentration was significantly higher in the isolated pools compared to the flowing reaches (0.17 $mg.L^1$ vs 1.3 $mg.L^1$ during early fragmentation, and 0.06 $mg.L^1$ vs 0.85 $mg.L^1$ during late fragmentation).

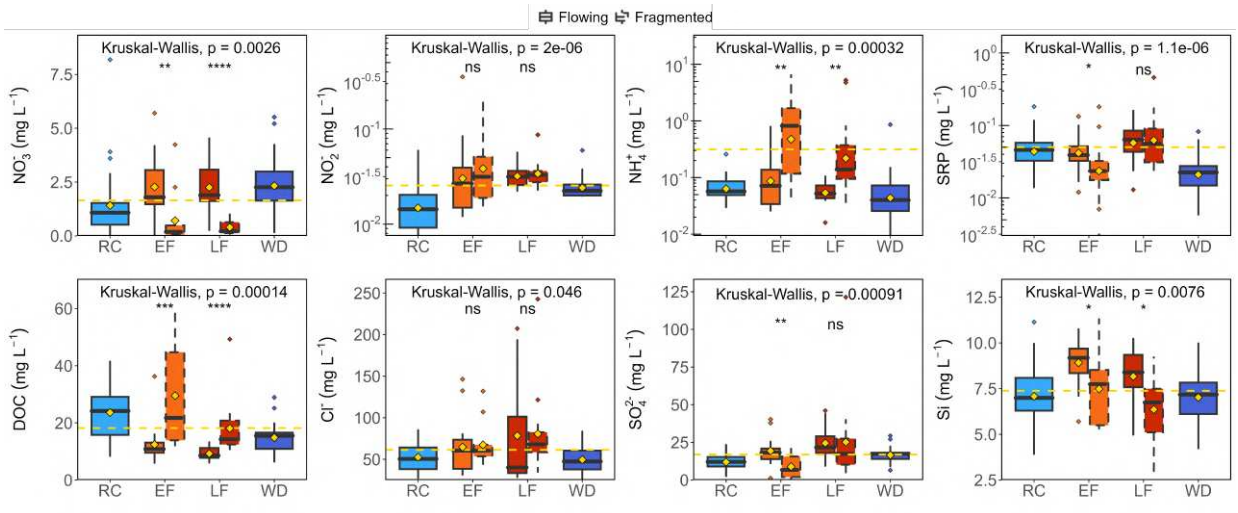

Figure 4.5 – Distribution of nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), soluble reactive phosphorous (SRP), dissolved organic carbon (DOC), chloride (Cl^-), sulphate (SO_4^{2-}), and silica (Si) concentrations during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). Dashed boxplots during fragmentation dates represents the fragmented samples (i.e. isolated pools). Dashed orange lines represent the mean (all dates included) while diamond orange shape is the mean for each of the sampled dates. Non–parametric test Kruskall–Wallis to test differences among the sampling dates. During the early and late fragmentation, non–parametric test Wilcoxon signed–rank test to compare the two hydrological states (i.e. Flowing and Fragmented). Significance: ns: non significant, * p-value <= 0.05, ** p-value <= 0.01, *** p-value <= 0.001.

The mean SRP concentration decreased from recession to early fragmentation (from 0.051 $mg.L^1$ to 0.046 $mg.L^1$), then increased to 0.082 $mg.L^1$ during late fragmentation. It then decreased significantly to 0.025 $mg.L^1$ during winter discharge. During the fragmentation dates, SRP concentration was significantly lower in the isolated pools compared to the flowing reaches (0.05 $mg.L^1$ vs 0.04 $mg.L^1$ during early fragmentation), but there was no significant variation during late fragmentation. The mean DOC concentration decreased significantly from recession to early fragmentation (from 23.6 $mg.L^1$ to 19.8 $mg.L^1$), and then decreased further to 14.2 $mg.L^1$ during late fragmentation. It then stabilised at 14.9 $mg.L^1$ during winter discharge. During the fragmentation dates, DOC concentration was significantly higher in the isolated pools compared to the flowing reaches (12.4 $mg.L^1$ vs 29.5 $mg.L^1$ during early fragmentation, and 9.3 $mg.L^1$ to 18.1 $mg.L^1$ during late fragmentation). The mean chloride concentration increased from recession to early fragmentation (from 52.5 $mg.L^1$ to 65.8 $mg.L^1$), and then increased further to 79.6 $mg.L^1$ during late fragmentation. It then decreased to 49.5 $mg.L^1$ during winter discharge. However, the chloride concentration did not vary between the isolated pools and the flowing reaches during either early or late fragmentation dates.

The mean sulphate concentration increased from recession to early fragmentation (from 12 $mg.L^1$ to 15 $mg.L^1$), and then increased further to 25 $mg.L^1$ during late fragmentation. It then decreased to 17 $mg.L^1$ during winter discharge. During the fragmentation dates, sulphate concentration was significantly lower in the isolated pools compared to the flowing reaches (8.9 $mg.L^1$ vs 19.4 $mg.L^1$ during early fragmentation), but there was no significant variation during late fragmentation. The mean silica concentration increased significantly from recession to early fragmentation (from 7.1 $mg.L^1$ to 9.3 $mg.L^1$), then decreased to 7.2 $mg.L^1$ during late fragmentation. It then decreased to 7 $mg.L^1$ during winter discharge. During the fragmentation dates, silica concentration was significantly lower in the isolated pools compared to the flowing reaches (8.9 $mg.L^1$ vs 7.5 $mg.L^1$ during early fragmentation, and 8.2 $mg.L^1$ vs 6.4 $mg.L^1$ during late fragmentation).

4.4.3 Nutrient speciation and organic matter composition during hydrological fragmentation

The speciation of nutrients changed with the stream fragmentation (Fig. 4.6). Both organic and inorganic nitrogen concentrations changed considerably among the sampling dates. The mean proportion of nitrate in DIN was significantly lower in the recession

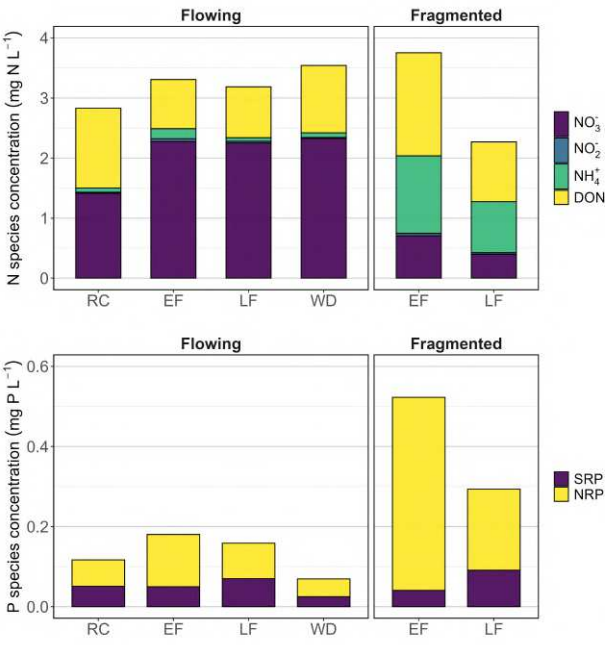

Figure 4.6 – Mean concentrations of N and P species (NO_3^-: nitrate, NO_2^-: nitrite, $NH4^+$: ammonium, DON: dissolved organic nitrogen, SRP: soluble reactive phosphorus, NRP: non-reactive P) during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). The flowing plot shows water samples taken from sites where the water was flowing. The fragmented plot shows water samples taken from isolated pools during early and late fragmentation.

recession, early and late fragmentation dates compared to winter conditions (84%, 65%, 72% and 96%, respectively). During the fragmentation dates, the proportion of nitrate in DIN was significantly higher in the flowing reaches (88% and 94% during early and late fragmentation, respectively) than in the isolated pools (34% and 54% during early and late fragmentation, respectively). Conversely, the mean proportion of nitrite in DIN decreased significantly from recession, early and late fragmentation to winter discharge (2.3%, 2.1%, 2.4% and 0.5%, respectively). However, during both early and late fragmentation, there was no significant variation in the mean proportion of nitrite in DIN when comparing the isolated pools and the flowing reaches. The mean proportion of ammonium in DIN decreased significantly from recession, early and late fragmentation to winter discharge (14%, 33%, 26% and 3.7%, respectively). During both early and late fragmentation, the mean proportion of ammonium in DIN increased significantly from 10% in the flowing reaches to 63% in the isolated pools, during early fragmentation; and from 4% in the flowing reaches to 43% in the isolated pools, during late fragmentation.

The mean proportion of DON in TDN decreased from recession to early and late fragmentation, but it was significantly lower during winter discharge (56%, 40%, 44% and 36%, respectively). During both early and late fragmentation, the mean proportion of DON in TDN was significantly higher from 30% in the flowing reaches to 54% in the isolated pools, during early fragmentation; and from 31% in the flowing reaches to 55% in the isolated pools, during late fragmentation. The proportions of SRP and NRP also changed considerably among the sampling dates (Fig 4.6). The mean proportion of SRP in TP decreased significantly from recession to early fragmentation (44% and 24%, respectively). Then, the mean proportion of SRP in TP increased significantly from early fragmentation to late fragmentation and winter discharge (37% and 36%, respectively). During both early and late fragmentation, the mean proportion of SRP in TP was significantly lower from 29% in the flowing reaches to 17% in the isolated pools during early fragmentation; and from 43% in the flowing reaches to 32% in the isolated pools, during late fragmentation. Thus, there was a significant increase in NRP during early and late fragmentation.

PARAFAC components showed small but statistically significant variations in proportions across the sampling dates (Fig. 4.7). On average for all campaigns, the humic-like components represented $71\% \pm 5\%$, the microbial humic-like component represented $25\% \pm 2\%$, and the protein-like component represented $4\% \pm 5\%$ on average for all campaigns. The proportion of the humic-like component decreased significantly from 72% during recession to 69% during late fragmentation. Conversely, the proportion of the microbial-like component increased significantly, rising from 23% during recession to 26% during early fragmentation and late fragmentation, and finally to 25% during winter discharge. The proportion of the protein-like component decreased significantly from 4.5% during late fragmentation to 2.2% during winter discharge. However, no significant variation in the proportions of the PARAFAC components was observed when comparing the isolated pools and the flowing reaches during both early and late fragmentation.

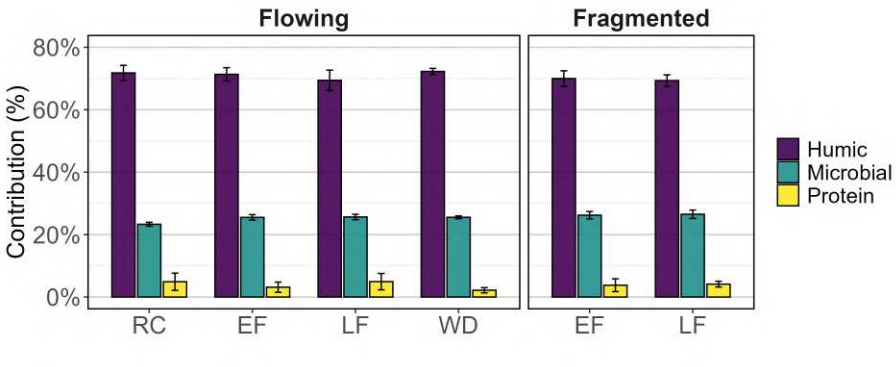

Figure 4.7 – Mean contributions of PARAFAC components: Humic-like components (C1, C3 and C4), Microbial humic-like component C2, and Protein-like component C5 during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). Error-bars represent confidence intervals at 95%. The flowing plot shows water samples taken from sites where the water was flowing. The fragmented plot shows water samples taken from isolated pools during early and late fragmentation.

4.5 Discussion

4.5.1 Change in nutrient and organic matter concentration and speciation during stream fragmentation

The degree of stream fragmentation during the study year was moderate compared to dry years in the region, where all the stream network regularly dries out in Poumen and to a lesser extent in Calavret catchments. Despite the rainy late summer and early autumn, our monitoring design was successful at capturing two phases of stream fragmentation (Fig. 4.2). The isolated pools and/or dry sampling sites were mainly located in the upstream part of the three catchments (Fig. **??**). These drying patterns are commonly observed in other stream networks of the Brittany region during low-flow periods (Snelder et al., 2013). The patterns observed in relation to stream fragmentation and biogeochemical characteristics are: (i) a loss of correlation between DIN/DOC concentrations and land cover indices. (ii) a decrease in NO_3^-, SO_4^{2-} and Si concentrations, and an increase in DOC and SRP concentrations in the isolated pools compared to the flowing reaches, as hypothesised, and (iii) an increase in the proportions of NH_4^+ in DIN, and DON in TDN, and decrease in the proportion of SRP in TP in the isolated pools compared to the flowing reaches without notable change in the proportion of the PARAFAC component.

The loss of correlation between the DIN/DOC concentrations and the land cover indicates a hydrological disconnection between the stream and catchment inputs (Fig. 4.4). This pattern is commonly observed in intermittent streams, where fragmentation is associated with a disruption of lateral hydrological connectivity (Allen et al., 2020; Boulton et al., 2017; Gómez et al., 2017). The decrease in NO_3^- and SRP concentrations that we observed during stream fragmentation, was also observed in US arid and Greek Mediterranean streams (Dent & Grimm, 1999; Skoulikidis & Amaxidis, 2009; Warren et al., 2022), except for an increase in inorganic P in a forested Mediterranean stream in Spain (von Schiller et al., 2011). The increase in NH_4^+ concentrations that we observed during stream fragmentation, was also observed in an upland stream in East Australia site during summer and Mediterranean streams (Baldwin et al., 2005; Marti & Sabater, 1996). An increase in DOC concentrations and a higher proportion of DON in TDN was also observed in Mediterranean streams under stream fragmentation before drought (Acuña et al., 2007; Bernal et al., 2005; Butturini et al., 2016; Vazquez et al., 2010). Therefore, we conclude that the observed spatio-temporal patterns in water chemistry during fragmentation could be attributed to local (in–stream) processes rather than to inputs from terrestrial part of the catchment. Despite large differences in land use and climate conditions, the observed spatio-temporal patterns in water chemistry across ria d'Etel sub–catchments were surprisingly similar to those in more arid and less agricultural contexts.

4.5.2 Biogeochemical processes in fragmented river networks

Changes in the speciation of nutrients and OM properties were also observed during stream fragmentation in the Etel catchment. The observed increase in DON concentrations during stream fragmentation may be due to the nitrate reduction coupled with iron or manganese oxidation, whereby nitrate reacts with Fe or Mn to form nitrite, which then binds with organic substances to produce DON (Burgin & Hamilton, 2007), as the redox potential decreases during this phase (Table 4.1). This increase was potentially due to abrupt lysis of microbial biofilms or by DON exudation under reductive conditions (von Schiller et al., 2011). Although these processes can occur in isolated pools, nitrate reduction coupled with iron reduction is more commonly observed in environments where nitrates is limited, such as in isolated pools formed during stream fragmentation (Fig. **??**) (Arce et al., 2015; Burgin & Hamilton, 2007).

During stream fragmentation, the loss of NO_3^- was concomitant with an increase in NH_4^+ in the isolated pools (Fig. 4.6). The production of ammonium during stream fragmentation could result from two main processes. First, an incomplete mineralisation of the organic N in accumulated organic matter, which can result in an increase in NH_4^+ where nitrification is inhibited by a lack of oxygen in the isolated pools (Baldwin & Mitchell, 2000). Second, the dissimilatory nitrate reduction to ammonium (DNRA) process. The DNRA is favoured by a low redox potential (< 50 mV) and high organic C/NO_3^- ratio in the isolated pools (Arce et al., 2015; Burgin & Hamilton, 2007; Rütting et al., 2011). These conditions applied to ten sites in the upstream reaches of the three subcatchments that were isolated pools during early and late fragmentation. Furthermore, the decrease of NO_3^- and SO_4^{2-} concentrations in the isolated pools compared to the flowing reaches during early fragmentation suggest a link to microbial sulfate reduction, which promotes DNRA (Burgin & Hamilton, 2007). Under NO_3^- limiting and reducing conditions in the isolated pools, the lack of electron acceptors mostly limits microbial growth (Rütting et al., 2011). However, the decrease in NO_3^- concentrations in the isolated pools, could also suggest an abiotic pathway involving a reaction between Fe^{2+} and reaction NO_3^- to produce NO_2^- (Burgin & Hamilton, 2007). During stream fragmentation, the NO_2^- concentrations did not vary significantly between the isolated pools and the flowing reaches, but DON concentrations increased. The protein-like component from PARAFAC showed a slight, albeit insignificant, increase in isolated pools during stream fragmentation, which prevents us from affirming this statement. Thus, both denitrification and DNRA can occur simultaneously (Morley & Baggs, 2010). Measurement of N_2 production could give more insights to distinguish between the two processes. The presence of organic matter in protein form or carbohydrates can alter the fate of NO_3^-, possibly through competition between nitrate ammonifiers and denitrifiers for the available NO_3^- pool (Morley & Baggs, 2010).

The inorganic form of phosphorus, as measured by SRP, decreased during stream fragmentation. Meanwhile, the organic forms of phosphorus, as measured by NRP, increased in the isolated pools during both early and late fragmentation (Fig. 4.6). Under hypoxic conditions and at high DOC concentrations in the isolated pools, we attribute these variations in P speciation by a combination of mechanisms, such as: (i) incomplete mineralisation and sediment desorption in increasing DOP in the isolated pools (Skoulikidis & Amaxidis, 2009; von Schiller et al., 2011); (ii) uptake or transformation of readily available P in decreasing SRP concentrations during early fragmentation (Lillebø et al., 2007), and,

(iii) mobilisation of P in sediments releasing iron-bound phosphorus as iron is reduced. Thus, NRP becomes bound to particles or aggregates, as has also been observed in waterlogged soils with a high organic carbon content in an agricultural headwater catchment (Gu et al., 2018; Lambert et al., 2024). During late fragmentation, the increase in SRP concentrations in the isolated pools could be caused by the release of orthophosphates, which are readily available to the microbiota and come from leaf litter in the sediments under hypoxic conditions (Baldwin, 1999; Lillebø et al., 2007).

The increase in DOC during fragmentation was concomitant with minor changes in DOM properties. The humic-like PARAFAC components were the most prevalent in the DOM pool, accounting for over 60% of total fluorescence, and were predominantly associated with wetlands and forested environments (Fellman et al., 2010). Secondly, the microbial-source humic-like component increased by an average of 25% in isolated pools, as observed in a Mediterranean intermittent stream (von Schiller et al., 2019). Conversely, a protein-like component was present in the DOM and exhibited some of the highest values during the recession date (Fig. 4.7). Therefore, we were unable to confirm our hypothesis that microbial and protein components would increase during stream fragmentation. However, we observed a legacy effect in the microbial DOM due to similar contributions in summer and winter samples. This may be because microbial DOM is produced during periods of low flow and remains in the system afterwards. Alternatively, it may come from the soil once the hillslope is connected to the stream during precipitation events. In contrast, the contribution of protein-like DOM remains relatively constant from the spring low flows to summer stream fragmentation, as observed during the hydrological contraction of a Mediterranean stream (von Schiller et al., 2015). The production of DOM during stream fragmentation could be explained by the solubilisation of OM present in the streambed, which has accumulated in the sediments from riparian soils, as occurs in temperate climate catchments (Humbert et al., 2015; Lambert et al., 2011; Reverey et al., 2016). The loss of longitudinal connections and stream fragmentation increases the DOM retention in the system (e.g. through leaf litter accumulation), resulting in reduced organic matter breakdown and limited transport of material and ecosystem production (Acuña et al., 2007; Butturini et al., 2016; Rolls et al., 2012). Therefore, we conclude that despite the differences in climate conditions and high nutrient inputs in the Etel catchment; it seems that the in-stream processes involved in the speciation of nutrients and OM during stream fragmentation seem to resemble the heterotrophic processes that occur under anaerobic conditions in arid and Mediterranean streams.

4.6 Conclusions

In this study, we analysed changes in the concentration and speciation of nutrients and dissolved organic matter during the hydrological fragmentation of three intermittent streams in a temperate, agriculturally intensive region. While perennial streams in such regions are often dominated by inorganic and oxidised nutrient forms (e.g. nitrate and SRP), our results show that hydrological fragmentation in the catchments studied led to the formation of organic and more reduced nutrient forms (e.g. NH_4^+, organic N and P). Thus, the chemistry of streams in intermittent agricultural catchments in temperate regions more closely resembles that of intermittent catchments in less agricultural and Mediterranean regions than that of their perennial counterparts. However, the fluorescence properties of OM remained rather stable across hydrological conditions (flowing and fragmented), contrary to past observations in Mediterranean contexts. Our observations suggest that these changes in nutrient and OM concentration and speciation were controlled by local redox processes within the isolated pools rather than by transport processes. As the spatial extent of intermittent streams in the temperate zone is expected to increase due to climate change, we anticipate that these processes will become more widespread in the future. Therefore, when monitoring intermittent streams in agriculturally intensive temperate regions, a wider range of chemical forms should be considered than is usually measured (e.g. nitrate and SRP), as these forms exhibit varying degrees of bioavailability and toxicity to aquatic ecosystems.

Using silica values as a tracer could help to trace the evolution of such nutrients and organic carbon in the stream network, as in-stream processes transition from aerobic to anoxic conditions, which disrupts the desorption of nutrients. Unknown inputs could also disrupt the continuity of each fragmented reach of the stream. Finally, future research evaluating the speciation of nutrients and the side effects of NO_3^- transformations may require tools, techniques and models in the design of robust water quality management strategies in the face of more frequent and severe hydroclimatic extremes when restoring agricultural systems.

Appendix

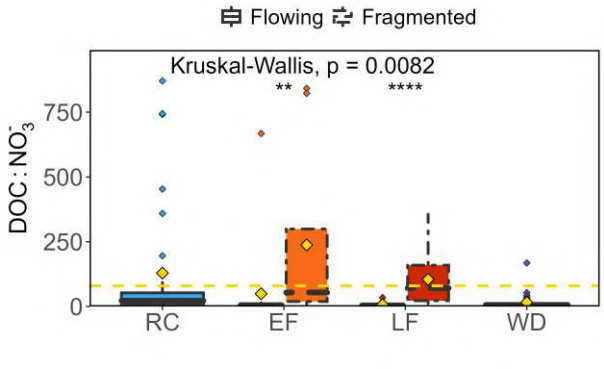

Figure B1 – Distribution of C:N ratio; as dissolved organic carbon (DOC) and nitrate (NO_3^-) concentrations during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). Dashed boxplots during fragmentation dates represents the fragmented samples (i.e. isolated pools). Dashed orange line represent the mean (all dates included) while diamond orange shape is the mean for each of the sampled dates. Non–parametric test Kruskall–Wallis to test differences among the sampling dates. During the early and late fragmentation, non–parametric test Wilcoxon signed–rank test to compare the two hydrological states (i.e. Flowing and Fragmented). Significance: ns: non significant, * p-value <= 0.05, ** p-value <= 0.01, *** p-value <= 0.001.

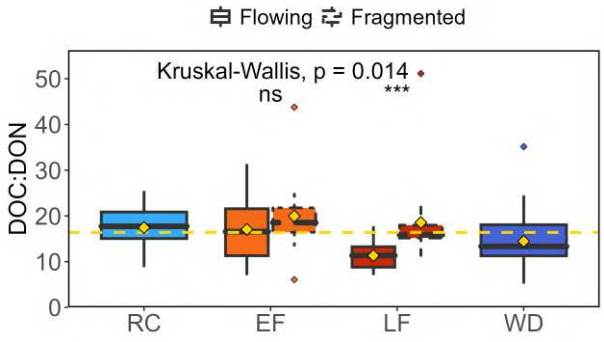

Figure B2 – Distribution of C:N ratio; as dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). Dashed boxplots during fragmentation dates represents the fragmented samples (i.e. isolated pools). Dashed orange line represent the mean (all dates included) while diamond orange shape is the mean for each of the sampled dates. Non–parametric test Kruskall–Wallis to test differences among the sampling dates. During the early and late fragmentation, non–parametric test Wilcoxon signed–rank test to compare the two hydrological states (i.e. Flowing and Fragmented). Significance: ns: non significant, * p-value <= 0.05, ** p-value <= 0.01, *** p-value <= 0.001.

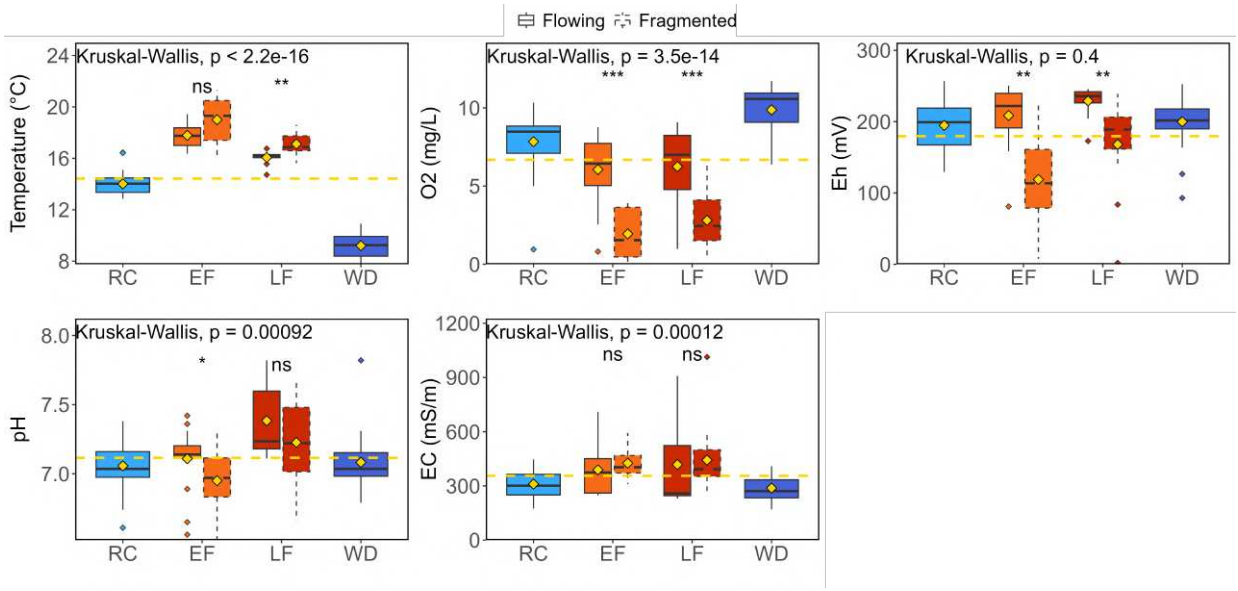

Figure B3 – Distribution of water temperature, dissolved oxygen concentrations, redox potential (Eh), pH and electrical conductivity (EC) during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). Dashed boxplots during fragmentation dates represents the fragmented samples (i.e. isolated pools). Dashed orange lines represent the mean (all dates included) while diamond orange shape is the mean for each of the sampled dates. Non–parametric test Kruskall–Wallis to test differences among the sampling dates. During the early and late fragmentation, non–parametric test Wilcoxon signed–rank test to compare the two hydrological states (i.e. Flowing and Fragmented). Significance: ns: non significant, * p-value <= 0.05, ** p-value <= 0.01, *** p-value <= 0.001.

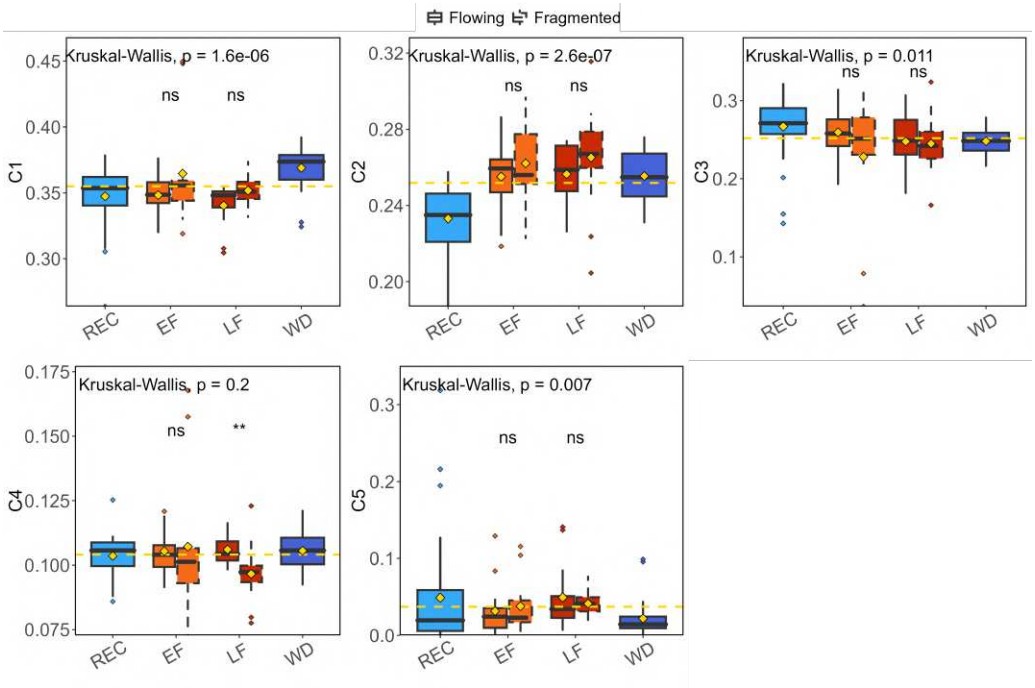

Figure B4 – Distribution of PARAFAC components: humic–like components (C1, C3 and C4), microbial–source humic-like component (C2) and protein–like component (C5), during the four hydrological phases (REC: Recession, EF: Early Fragmentation, LF: Late Fragmentation, WD: Winter Discharge). Dashed boxplots during fragmentation dates represents the fragmented samples (i.e. isolated pools). Dashed orange lines represent the mean (all dates included) while diamond orange shape is the mean for each of the sampled dates. Non–parametric test Kruskall–Wallis to test differences among the sampling dates. During the early and late fragmentation, non–parametric test Wilcoxon signed–rank test to compare the two hydrological states (i.e. Flowing and Fragmented). Significance: ns: non significant, * p-value <= 0.05, ** p-value <= 0.01, *** p-value <= 0.001.

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Chapter 5

Discussion and perspectives

5.1 Introduction

Intermittent streams are an inherent feature of river networks, and the recurrent cessation of flow has become the subject of interdisciplinary research in hydrology, ecology, biogeochemistry, socioeconomics, and resource management, with increased focus over the last decade (Datry, Truchy, et al., 2023). The aim of this thesis was to develop an approach to increase understanding of these hydro-systems in an oceanic temperate region where agriculture has a significant impact on biogeochemical cycles with high nutrient inputs and diffuse pollution, abundant rainfall and mild temperatures. In the following sections, I review the main contributions of my research, discussing the difficulty of representing headwater intermittent stream networks from a spatial point of view (section 2), and summarising the main characteristics of biogeochemical patterns in agriculturally–intensive and temperate catchments in comparison with less–agricultural and drier contexts (section 3). In section 2, I consider the limitations of predicting intermittent flow in a river network based on its catchment's spatial features. In section 3, studying two headwater catchments in the region with different geologies and spatial characteristics, sampled in a drier and wetter year respectively, showed similarities and differences from which I gained insight. In section 4, the discussion covers the gaps and potential future research perspectives that could advance the study of biogeochemical processes in intermittent rivers and streams.

5.2 Challenges in mapping hydrological intermittence

What are the drivers of intermittence in the Brittany region?

We conduct the identification of intermittent rivers and streams in the Brittany region using discrete flow state observations and the available information regarding intermittence. We expect the following: *(i)* the spatial distribution of intermittent rivers and streams in Brittany is structured, and *(ii)* the controls of this spatial structure of hydrological intermittence can be predicted based on local geographical characteristics at the catchment scale.

The oceanic-temperate climate zone, with mild temperatures and abundant rainfall, presents a substantial amount of intermittent streams in their river networks, similar to other biomes. In Chapter (2), we characterise the spatial distribution of intermittent streams in the Brittany region, using discrete flow state observations. The data from the ONDE observations, showed that the intermittent sites were mainly located in headwater streams. The data from the 129 stations from 2012 to 2022 showed an east-west gradient of intermittence, with a higher probability of streams with no flow in the eastern part of the region than in the western part. These observations are consistent with the climate gradient in the region (see Chapter 1, Section 4), which has less annual rainfall and warmer temperatures in the east. However, the ONDE observations have a low spatial and temporal resolution. Therefore, the potential to derive information about the entire river network from this data, as required by managers and scientists, remains limited.

A comparison of different sources of information on stream intermittence showed that the TOPAGE hydrographic reference system does not match the ONDE observations. With a Kappa coefficient of 0.05, TOPAGE's intermittent and perennial stream categories underestimated intermittence compared to field observations of the ONDE data. The RHT hydrographic network represents more accurately the intermittent nature of headwater reaches, with a Kappa coefficient of 0.32. Nevertheless, low-order streams are underrepresented in RHT, since the probability of intermittence was estimated based on data from gauging stations located mainly on perennial streams (Beaufort et al., 2018). In this manner, the results do not entirely confirm our hypothesis that the characterisa-

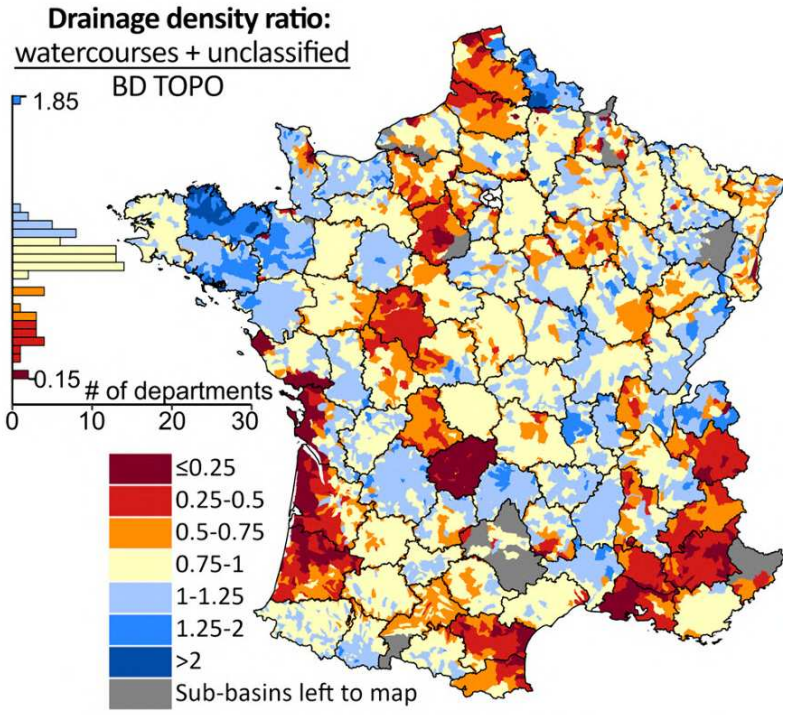

Figure 5.1 – Drainage density ratio between the regulatory maps of watercourses (under the Water Law in France) and reference hydrographic data from BD TOPO. Source: modified from Messager et al. (2024).

tion and spatial distribution of intermittent rivers and streams in Brittany is consistent with the available information regarding intermittence.

As several studies have shown, intermittent streams are found in all biomes and comprise over half of the global river network (Datry, Boulton, et al., 2023; Messager et al., 2021). A perennial stream may have become intermittent due to climate change and not been mapped, or an intermittent stream may not be considered a watercourse due to its lower aesthetic value (Cottet et al., 2023; Fovet et al., 2021). In Brittany however, the drainage density of regulatory of regulatory maps approximately matches that of TOPO 2015 maps, suggesting that, contrary to others regions, regulatory maps are rather complete or even improved in the newest versions (Fig. 5.1) (Messager et al., 2024). Nevertheless, the classification used to determine whether a reach is perennial or intermittent is still unreliable. Representing hydrographic features on topographic maps requires an understanding of the interactions between climate, geology, and the land uses and management. On the other hand, RHT provides a more accurate estimation of intermittent streams than TOPAGE due to the climatic variables used in the modelling. This

is because models that predict intermittency are strongly influenced by aridity indices, while the east–west gradient of intermittence in Brittany matches the well–documented gradient of rainfall and temperature (Beaufort et al., 2018; Döll et al., 2024; Snelder et al., 2013). However, uncertainties may arise in this classification from the difficulty of extrapolating discharge flow gauged mainly at downstream perennial rivers to headwater streams. This makes it challenging to accurately characterise spatial variability in drying.

Therefore, we expected that using ONDE temporal observations located on headwater reaches for the classification of flow intermittence, would provide a more accurate prediction of intermittence patterns than the classification on the French hydrometric data (HYDRO) of gauging records for the RHT model used by Snelder et al. (2013). The hydrological connectivity of stream reaches is determined by local factors such as climatic conditions, the underlying geology, human activities, biological processes, and fluvial geomorphology (Boulton et al., 2017). Using a random forest classification model with the spatial features of intermittent headwater catchments showed, however, moderate estimation of intermittence (Kappa coefficient of 0.46) in low-order catchments. In the study region, climate, agricultural land use and topography were the most relevant spatial features for predicting which catchments were prone to intermittence. The spatial distribution of intermittent streams in the region is not solely determined by these catchment attributes; unmapped factors such as water abstraction, alteration of channel geomorphology or small-scale hydrogeology, may also influence the intermittent nature of the flow regime in certain areas. When the analysis is downscaled to the reach scale, the geomorphological data may reveal changes in the flow regime in the region's agricultural landscapes. The width–to–depth ratio of two intermittent headwater catchments (Etel and Naizin), reported low values of 4.5 $\pm$ 1.5 compared to the regional stations without human geomorphological alteration (Chapter 2, section 3.2). The studied reaches are therefore more incised than the reference geometries in more pristine rivers of the region. Many headwater streams in the region have been straightened and raised above its original course, whose original path remains visible in the vegetation. In general, these watercourses tend to have cohesive banks, which are narrower and deeper of the channel (Baudoin et al., 2017). Deeper river channels and modified river meanders may alter the catchment's response to wetter events (Jaeger et al., 2017). This suggest that alteration of the river morphology may have increased intermittence in the Brittany region, in addition to the regional factors identified by the random forest analysis.

Interactions between the water table and surface water strongly influences the flow dynamics of headwater catchment with impervious bedrock (Molenat et al., 2008). We found that the amount of rainfall needed to reconnect the water table with surface water is greater during drier summers, when the water table is low (Chapter 2, section 3.3). However, the hydrological regime of intermittent rivers are extremely diverse, spanning a spectrum of distinct drivers, processes and forms (Boulton et al., 2017; Jaeger et al., 2017). Predicting these patterns seems to require more local and also probably temporal information. Although modelling approaches that use wetting and flow cessation cycles as variables for calibrating the model show promise in predicting such flow patterns in gaining streams (Abhervé et al., 2024), assessing the consistency of the temporal simulation of the expansion/contraction of the hydrographic network with the temporal observations must be considered.

5.3 Nutrient and dissolved organic matter dynamics in intermittent headwater streams

5.3.1 Changes in nutrients and dissolved organic matter concentration, patterns, and interpreted processes

How does hydrological fragmentation alter the spatial variability of dissolved nutrients and organic matter concentrations along the stream in an agricultural catchment?

We i sam-
pling of nutrient and organic matter concentrations at a high spatial resolution during the fragmentation of a headwater stream network. We can hypothesise the following: *(i)* the increase of spatial variability of nutrient and OM concentrations observed during the fragmentation of Mediterranean and arid streams could also be observed in a temperate-oceanic catchment subject to intensive agricultural practices. *(ii)* the direction of change in nutrient and organic matter concentrations during the fragmentation of an intermittent stream could be predicted based on observations of perennial streams in the same region during the low-flow season.

Most studies on the geochemistry of intermittent rivers have focused on arid and semi-arid regions, covering less than 20% of the world's area (Gómez et al., 2011). The oceanic-temperate climate of the Brittany region is characterised by impervious bedrock, mainly composed of crystalline (granite) and metamorphic (schist) rocks, which have the feature of being rather impermeable. In this context, the hydrological disruption includes low-flow periods, and eventually droughts when the water table becomes disconnected from the surface water. This fragmentation regime offers a valuable opportunity to study the biogeochemical processes occurring in these river networks. The two study sites, Naizin and Etel (presented in Chapters 3 and 4, respectively), confirmed the hydrological processes related to the disconnection of the stream network. During the early summer recession period, the flow rate was low, followed by longitudinal disconnection between the upstream and downstream reaches during late summer. The formation of isolated pools then took place. This was followed by a quick reconnection as a response to precipitation between the water table and surface water during the expansion phase.

While I decided to use the data from Naizin in 2023 to analyse how stream fragmentation disrupts spatial concentration patterns (Chapter 3) and data from Etel 2024-2025 to analyse how stream fragmentation alters nutrient and dissolved organic matter speciation (Chapter 4), the two scientific questions could be addressed with both study sites. In Naizin, we showed that, during the flowing phases, nutrients and DOM spatial patterns (in particular nitrate and DOC) were characterized by strong longitudinal gradients which we explained by differences between the upstream and downstream part of the catchment in terms of groundwater-surface water interactions in the riparian zone. In Etel, we showed that, during the flowing phases, nutrients and OM spatial patterns (in particular nitrate and DOC) were controlled by land use. In both Naizin and Etel, spatial patterns for P forms during the flowing phases were neither organized according to longitudinal gradients or land use. The effect of stream fragmentation was the same in both Naizin and Etel, as it caused a disruption of spatial patterns observed during the flowing phase and an increase in the spatial variability in concentrations (Fig. 5.2). The only exception to this general observation was nitrate in Etel, whose spatial variability was already high during the flowing (recession) phase, arguably because of the high variability in land use within the three catchments. At both study sites, we interpreted these changes in spatial patterns as the result of in-stream processes within isolated pools, which became dominant controlling factors during fragmentation, as opposed to land-to-stream transfer processes during the flowing phases. As these pools become isolated from each other and

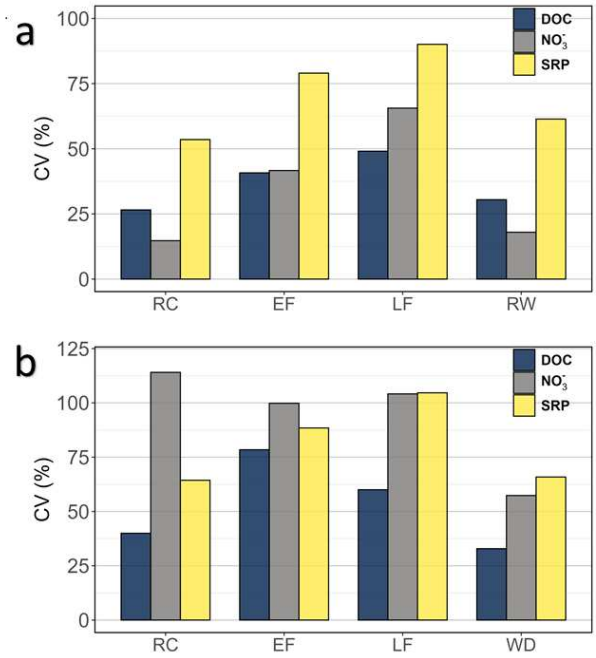

Figure 5.2 – Spatial coefficient of variation, estimated in percentage and defined as the standard deviation (σ) divided by the mean (μ) in: (a) Naizin catchment and (b) Etel catchment during the hydrological phases sampled. RC: Recession, EF: Early fragmentation, LF: Late fragmentation, RW: Reconnection and WD: Winter discharge. The solutes measured are DOC: Dissolved organic carbon, NO_3^-: Nitrate and SRP: Soluble reactive phosphorus.

are exposed to different physico-chemical conditions (e.g. light, temperature, oxygen), the solute concentrations are likely to vary according to local factors, resulting in the increasing spatial variability observed. Conversely, during the reconnection/expansion period, the system generally becomes more homogeneous.

The two study study sites also presented several common features in terms of temporal variability among sampling dates and differences between isolated pools and flowing reaches. Although the nitrate inputs were different for the two catchments, with higher levels in Naizin than in Etel, the temporal variability of concentrations was similar, being high during the flowing dates of recession and reconnection/expansion and decreasing in isolated pools during the fragmentation phases. Similarities were also observed with DOC for both catchments but in opposite directions than for nitrate. Etel had higher inputs of DOC than Naizin, but the concentrations decreased from recession to the fragmentation phases and later to reconnection/expansion. While in Naizin the DOC concentrations increased from recession to fragmentation. In both catchments however, the concentrations

of DOC experienced an increase in the isolated pools during both fragmentation dates. Nevertheless, SRP concentrations showed less similarity in temporal variability between the two catchments. There was a slight increase in SRP concentrations from recession to the stream fragmentation dates in Naizin, while there was no notable variation in Etel. During the early fragmentation phase, however, SRP concentrations increased in isolated pools in Naizin while decreasing in Etel. The ccontrasting temporal patterns for SRP in Naizin and Etel is consistent with our literature review (Chapter 4), which showed that all not catchments exhibited the same response to fragmentation for soluble P forms.

These similarities and differences between two rather contrasting catchments in Brittany during three different years suggest that our observations were representative of different catchment types and climatic conditions in Brittany. The disruption to the spatial patterns of nutrients and OM observed in the two intermittent stream networks studied in Brittany can be explained by the spatial distribution of land use types, as well as by longitudinal changes in the interaction between groundwater and surface water in the riparian zone (Dupas et al., 2021; Floriancic et al., 2019). The increasing spatial variability in concentrations during low flow can be caused by discrete groundwater inflow points; however, as flow decreases, in-stream processes become more important in controlling the biogeochemistry of solutes. While these changes in the spatial variability of nutrient concentrations were observed during stream fragmentation in intermittent arid and Mediterranean catchments (Dent & Grimm, 1999; von Schiller et al., 2011), the patterns were also present in temperate-oceanic catchments. However, nutrient and OM concentration levels were higher in the Brittany region due to legacy nutrients from years of intensive agriculture. Therefore, the direction of change in these concentrations during the fragmentation of intermittent headwater streams in Brittany, could be predicted based on observations of perennial streams in the same region during the low-flow season.

Under stream fragmentation, the formation of isolated pools created anaerobic conditions (i.e. a decrease in dissolved oxygen) prior to complete drought. In these circumstances, the reductive processes enhanced the transformation of the water physicochemistry. In the headwater catchment of Naizin, we observed strong nitrate concentration decrease due to denitrification processes in isolated pools under anoxic conditions and the presence of DOM. During the summer, the riparian vegetation in the catchment increases its canopy, which shades the stream network and decreases the assimilatory uptake, as would be expected in a more arid environment. Similarly, denitrification processes were observed in the Etel's headwaters, alongside perhaps less significant dissimilarity nitrate

reduction to ammonium. Here, N is conserved as ammonium rather than released as N_2 gas. The behaviour of inorganic P was more variable during stream fragmentation. In the isolated pools during the first fragmentation phase, SRP concentrations increased in Naizin and decreased in Etel. The increase of SRP in Naizin could be explained by the dissolution of P from streambed sediments under reductive conditions and presence of iron (hydro)oxides. While the decrease of SRP in Etel could be explained by microbial uptake or adsorption of readily P. During the late fragmentation, a combination of both processes may determine the low variation in the concentrations between the isolated pools and flowing reaches. In this way, the results confirm our hypothesis on the spatial variability of nutrient and OM concentrations observed during the fragmentation of Mediterranean and arid streams could also be observed in a temperate-oceanic catchment subject to intensive agricultural practices. However, the magnitude of the concentration levels are higher in the Brittany region subjected to intensive agriculture.

5.3.2 Changes in nutrient speciation, in organic matter nature and associated processes

How do the speciation of nutrients and the composition of dissolved organic matter change during the stream fragmentation in an agricultural catchment?

We investigate this question by analysing repeated synoptic characterization of N forms, dissolved reactive versus total P, and DOM optical properties during the fragmentation of three headwater coastal streams. During stream fragmentation, stagnant water in the channel typically exhibits hypoxic conditions. We therefore expect the following: *(i)* the reduced and organic forms of N and P will increase, while the more oxidised and inorganic forms will decrease. *(ii)* the microbial and protein forms of dissolved organic matter will tend to increase due to the increased residence time and temperature in isolated pools during hydrological fragmentation.

Similar changes in nutrient speciation were observed in both catchments, with for example an increased proportion of ammonium in DIN during stream fragmentation. These proportions were higher in Etel than in Naizin, where nitrate remained the dominant component of DIN except in a few isolated pools in the small headwater catchment. Notably,

in Etel, a significant proportion of ammonium exceeded 50% of the total DIN, reflecting nitrate depletion in the isolated pools. By contrast, the proportion of nitrite in DIN was more consistent across the two catchments, with similar levels observed during the flowing phases of recession and reconnection. However, the proportion of nitrite in DIN increased, albeit not significantly, in the isolated pools of Naizin and Etel. The proportions of organic and particulate P were reflected in the variations of SRP in the P pool during the stream fragmentation. The proportion of SRP increased in the isolated pools of Naizin, while it decreased in the isolated pools of Etel, reflecting the heterogeneity of the two catchments. The properties of the organic matter were mainly composed of humic-like DOM in both catchments. However, only notable changes in DOM composition were observed in Naizin. During stream fragmentation, the amount of humic-like DOM of microbial origin decreased in isolated pools, while the amount of protein-like DOM in those pools increased.

Our observations suggest that denitrification and dissimilarity nitrate reduction increased levels of reduced nitrogen forms in the isolated pools during stream fragmentation (Fig. 5.3). The speciation of N was also influenced by local processes in the isolated pools. In both catchments, the ammonium concentrations increased during the stream fragmentation, primarily due to OM mineralisation and moderate dissimilarity nitrate reduction to ammonium. In Naizin, despite the high nitrate levels, ammonium levels accounted for up to 60% of the total dissolved inorganic nitrogen in some isolated pools, whereas in the upstream reaches of the Etel catchment, it represented over 90%. Consequently, the increase in DON in the dissolved N pool during stream fragmentation may be due to reduced microbial uptake and/or the high levels of DOM in isolated pools (Fig. 5.3). However, DON was only measured in Etel; it is a shame that it was not also measured in Naizin, as this would have provided more insight into N speciation under stream fragmentation. However, we suppose that DON would have been lower then in Etel, because DOM concentrations where much lower than in Naizin (4.3 ± 2.1 $mg\ L^{-1}$ DOC) while in Etel (18.2 ± 10.8 $mg\ L^{-1}$ DOC). Conversely, organic and particulate phosphorus concentrations increased in the isolated pools during the two fragmentation events in the Etel catchment. In the Naizin catchment, in contrast, SRP increased by a greater proportion than organic and particulate P in the isolated pools (Fig. 5.3). This could be explained by the spatial origin of dissolved P in the Naizin catchment landscape, which comes from adjacent riparian soils, where the alternation of dry and wet cycles fosters P solubilisation (Dupas, Gascuel-Odoux, et al., 2015). Hence, we confirm the hypothesis

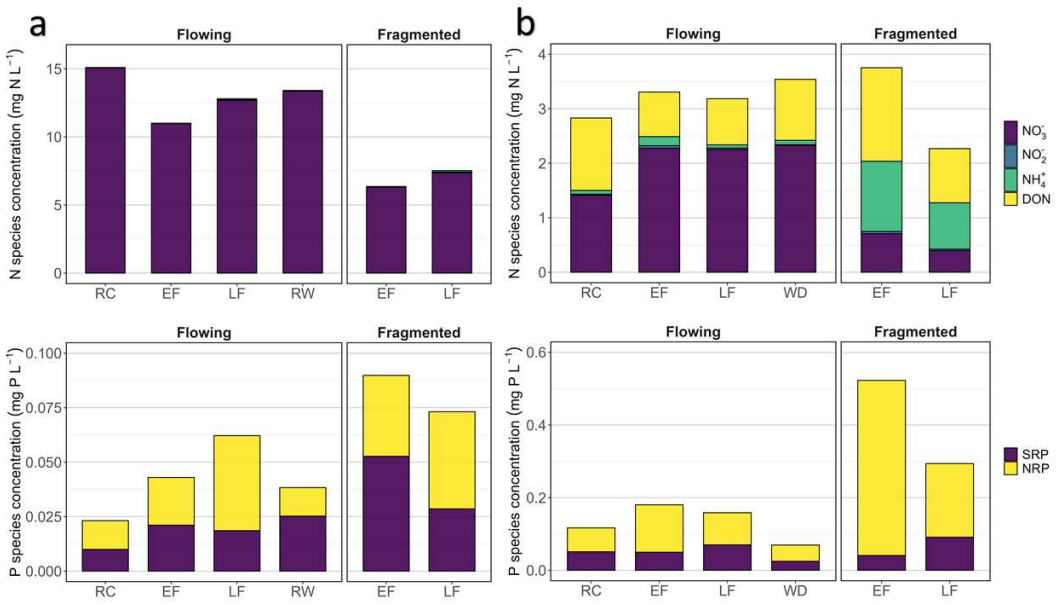

Figure 5.3 – Nitrogen (N) and phosphorus (P) speciation in: (a) Naizin catchment and (b) Etel catchment during the hydrological phases sampled. RC: Recession, EF: Early fragmentation, LF: Late fragmentation, RW: Reconnection and WD: Winter discharge. The solutes measured are NO_3^-: Nitrate, NO_2^-: Nitrite, NH_4^+: Ammonium, DON: Dissolved organic nitrogen, SRP: Soluble reactive phosphorus and NRP: Non–reactive phosphorus (accounting for particulate and organic phosphorus).The y–axis in the N species barplot is in log–scale.

on the speciation of N and P under anaerobic conditions in the isolated pools, where the reduced and organic forms of N and P increased while the more oxidised and inorganic forms decreased.

Dissolved organic matter composition was identified by Excitation Emission Matrices (EEM) fluorescence and PARAFAC modelling. The composition of DOM was mainly composed of humic-like components for both catchments. Their contribution was estimated to be over 60% of the total DOM for each hydrological phase. Microbial humic-like and protein-like components were also found in the DOM pool of the two catchments. The contribution of the humic–like component derived from microbial sources was observed to increase during stream fragmentation for both catchments. During winter, the contribution of this component remained similar to that observed during the fragmentation phase, probably due to a legacy effect in the system. The proportion of the protein-like component also varied, but not in the same way between the catchments. In Naizin, the protein-like DOM was significant during the recession phase and then decreased with

stream fragmentation. In the isolated pools, there was a small yet significant increase in this component compared to the flowing reaches. Meanwhile, in Etel the protein-like DOM was more variable (high at some sites) during the recession phase; then, during the stream fragmentation, its contribution remained similar without any notable change in the isolated pools. As the stream fragments, the loss of longitudinal connections can reduce the energy inputs and transport of material, resulting in DOM retention and reduced microbial activity in isolated pools. In this manner, our results do not confirm entirely our hypothesis on the increases of microbial and protein forms of dissolved organic matter in the isolated pools. Despite the increase in these pools during stream fragmentation, the higher proportions were during the recession phase, where the low-flow and longitudinal connectivity presented better conditions of residence time and temperature to enhanced microbial activity.

In both catchments, our sampling campaigns did not perfectly align with the rewetting period — the period during which the stream network is expanding — as this is difficult to predict. Future work in Naizin and Etel should therefore focus on the rewetting time, and less on spatial variability. Concentrations of nutrients and organic matter tend to be much higher during rewetting (Arce et al., 2015; Shumilova et al., 2019; N. T. Skoulikidis, Vardakas, et al., 2017). While periods of high flow favour the transport of energy and materials in a river continuum along the stream network, periods of stream fragmentation depend on the characteristics of the water, such as dissolved oxygen and temperature (Price et al., 2024). However, the load of nutrients and OM and the rate of reconnection of the stream also determine the biogeochemical and community ecological responses.

5.3.3 Implications of research results: is fragmentation mitigating or exacerbating issues of diffuse water pollution?

The functional responses of intermittent river communities to drying suggest a reduction in biodiversity in drying river networks, which may threaten their functional integrity as their habitat size and connectivity decrease (Crabot et al., 2021; Sarremejane et al., 2021). This emphasises the importance of conserving the natural drying regimes of intermittent streams in order to preserve their ecological integrity. In the Brittany region, which experiences high nutrient loads and subsequent problems of eutrophication, catchment managers have struggled to reduce the impact of excessive nutrients in freshwater systems by lowering nitrate and phosphorus concentrations. Studies in intermittent

headwater streams have shown that nitrate concentrations can be reduced during stream fragmentation, under reductive conditions in the isolated pools. This could be seen as an alternative means of controlling water quality downstream; however, other solutes such as DOC and phosphorus could also increase in these isolated pools.

Whether stream fragmentation mitigates or exacerbates diffuse pollution also depends on which water body is targeted. In intermittent headwater streams, the increasing storage of phosphorus and organic matter may pose a risk during reconnection, as these solutes are quickly mobilised downstream. Consequently, recent literature reports a deterioration in river quality during droughts and heatwaves, with increased water temperatures and algae, and increased concentrations of nutrients and other pollutants such as pharmaceuticals under climate change (Van Vliet et al., 2023). Therefore, reducing the extent to which human activity disturbs headwater streams could prevent the degradation of the physical and chemical conditions of these stream networks and the subsequent transmission of these impacts to downstream systems. Studies on the influence of spatiotemporal patterns of rewetting at the scale of river networks are essential for assessing the future hydrological and biogeochemical state of intermittent rivers. Regardless of the effect of stream fragmentation on N and P, unnatural fragmentation is mostly bad news for aquatic ecosystems because it degrades the criteria required for good ecological status in freshwater, such as a decrease in dissolved oxygen, changes to the hydrological regime, and changes to the morphology.

5.4 Limitations and perspectives

This thesis demonstrated how the forms of nutrients and organic matter vary over time during the hydrological fragmentation of intermittent agricultural catchments. Important changes in the studied elements were observed in the two catchments during stream fragmentation. In addition to the differences in bedrock between the Naizin and Etel catchments, the sampling years of 2023 and 2024 were also different. Temperatures were higher and precipitation was less frequent in 2023 than in 2024, which was wetter. Similarly, the spatial resolution of the sampling for the two catchments enabled similar spatial patterns to be identified during the disconnection of the stream network for Naizin and Etel (see Section 3.1). However, it was interesting that the spatial variations in solute concentrations were not driven by the same factors. For instance, the longitudinal gradi-

ents in Naizin were disrupted, whereas the connection to hillslope processes and land use was lost in Etel.

More data could have been helpful to identify more precisely the processes behind the CNP cycles. Although monitoring changes in isolated pools is challenging, measuring the activity of microorganisms on leaf litter degradation under anaerobic conditions in isolated pools (Abril et al., 2016; Boulton, 1991; Mariluan et al., 2015), followed by drought and subsequent rewetting, could help support or disprove our hypothesis. Studies on the decomposition of leaf litter in headwater streams have shown that the priming effect of labile carbon exudates from primary producers increases the mineralisation of more recalcitrant organic matter in pools (Danger et al., 2013). But also, the evolution of the stoichiometry of primary producers in freshwater, affected by levels of phosphorus and nitrogen concentrations (Beck et al., 2024), could provide insights into nutrient variation by a community of consumer macroinvertebrates in isolated pools. Similarly, direct measurements of organic phosphorus could have helped to interpret the direction of change and identify the processes behind the speciation of phosphorus during stream fragmentation, which differed between the early and late stages in both catchments. The transformation of DOM properties during the solubilisation-bounding process with sediment minerals has been proven in the case of P binding Fe in wetlands (Lambert et al., 2024).

The dynamics of biogeochemical processes in intermittent rivers and streams, organised in space and time, need to be expanded to achieve a more mechanistic understanding of nutrient and DOM dynamics. This can be achieved by addressing the mechanisms that drive changes in nutrients and DOM under natural conditions and field experiments. Future research that could advance this field of study could focus on the transformation pathways of nutrients and OM in dry sediments, as these are important sources of materials downstream during rewetting events (Wilson & Baldwin, 2008). They also contribute to gas emissions (e.g. Carbon dioxide) to the atmosphere (Gómez-Gener et al., 2015; López-Rojo et al., 2024). In this sense, estimating the effects of drying and rewetting on stream metabolism using high-frequency dissolved oxygen measurements could help to clarify the impact on critical ecosystem processes in intermittent streams that are expected to experience a pulse of respiration during rewetting (Diamond et al., 2021; López-Rojo et al., 2025). Preliminary work has been conducted in the Etel catchment area as part of a six-month Master's internship. This work showed variable respiration responses among three catchments but these do not appear to be related to the degree of intermittence.

New data on the drying and rewetting of 2025 physico-chemical parameters could help to clarify the drivers of ecosystem respiration and the effects of stream fragmentation. Another approach would be to consider intermittent rivers that are supported by sewage discharge during low flows in summer, as is the case in some eastern headwater catchments in Brittany. This could result in limited dilution of treated sewage effluents, which could have serious consequences for nutrient concentrations downstream, particularly with regard to extra inputs of ammonium and phosphorus (David et al., 2011). Furthermore, coupled hydro-biogeochemical models could be used to predict how intermittent stream networks respond, the consequences this has for nutrient concentrations in the main river, and how resilient the networks are to climate change.

Conclusion

The main research question of this thesis was the following:

> What are the biogeochemical patterns and processes associated with hydrological intermittence in a temperate oceanic context?

This thesis responds to the research question through the analysis of nutrients in the form of N and P, and also dissolved organic matter during different phases of hydrological fragmentation in headwater intermittent streams in the oceanic–temperate region of Brittany in France. This work involved fieldwork, laboratory analysis and data analysis.

Firstly, I analysed the prevalence of intermittent streams in a wetter region, by examining discrete data on observations on the flow state of 129 monitoring sites in the region. The results showed a gradient of intermittent streams, with higher probability of intermittence in the eastern part of the region compared to the western part. I also compared this intermittence data with a hydrological mapping reference system. This showed an underestimation of intermittent reaches on the hydrographic map. However, when this information on intermittence was compared with a hydrological model based on topographic and discharge data from gauging stations, the results showed better accuracy. These exploratory analysis showed the prevalence of intermittent streams in the region, providing an opportunity to understand the nature of the intermittence in the region by using a random forest classification model. Spatial data on the 129 selected catchments was used, including information on area, mean annual precipitation and temperature, slope, land use, bedrock geology, and presence of dams. The model showed that the relationship between climatic variables and catchment properties was more important for determining intermittence in the region. However, its predictive accuracy was not flawless. This suggests that there are local properties that are not mapped and which influence the nature of intermittence of these streams.

Further analysis of the unmapped properties of intermittence was conducted to evaluate whether the geomorphology of watercourses could indicate intermittence in streams.

This was achieved by analysing the depth-to-width ratio of two intermittent headwater catchments and comparing the results to public data on the geomorphology of watercourses in the region. The results showed that our study sites were more incised than the reference data for the region. However, these results do not prove that geomorphological alterations to rivers cause intermittence. Further work is needed to establish whether restoring them to their natural shape would reduce their intermittent nature. In addition, I evaluated the influence of the water table on the flow dynamics of the surface stream in the intermittent headwater catchment of Naizin. Using statistical regression on 20 years of high-frequency data on discharge, water table level and precipitation. The results showed that the lower the water table, the more precipitation is needed for the stream to flow.

In order to assess the biogeochemical patterns and processes associated with hydrological intermittence, fieldwork was conducted in two intermittent headwater catchments: Naizin and Etel. High spatial resolution sampling in Naizin and lower–resolution sampling in Etel, we capture four phases targeting flow intermittence, stream recession and an early and late stages of stream fragmentation, (i.e. the presence of isolated pools), as well as the reconnection/expansion phase during periods of high flow in winter. We analysed major anions, nutrients (N and P) and dissolved organic matter. The results showed that during stream fragmentation the spatial patterns of solutes are disrupted increasing the heterogeneity of solute concentrations across the stream network. In addition, we observed a decrease in nitrate levels during stream fragmentation, and an increase in the formation of organic and more reduced nutrient forms, such as NH_4^+ and organic N, as well as dissolved organic carbon. However, concentrations of dissolved inorganic phosphorus varied between the catchments, increasing in Naizin and decreasing in Etel. Similarly, the fluorescence properties of OM showed an increase in the protein and microbial forms of DOM in the isolated pools in Naizin, while remaining rather stable across stream fragmentation in Etel. The latter results contrasts with past observations in Mediterranean contexts. Our observations suggest that the changes in nutrient and dissolved OM concentration and speciation were controlled by local redox processes within the isolated pools rather than by transport processes.

As the extent of intermittent streams in temperate zones is expected to increase due to climate change, these processes are anticipated to become more widespread in the future. Therefore, it is important to monitor the presence or absence of water throughout the stream network, and to develop spatiotemporal analysis approaches that can reveal

the mechanisms of biogeochemical processes within these systems. New approaches were proposed to improve our understanding of the biogeochemical processes involved in estimating stream metabolism. In addition, monitoring intermittent agricultural streams requires consideration of more nutrient species than are usually measured (e.g. nitrate and SRP), as these species present different degrees of bioavailability and toxicity to aquatic ecosystems.

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COLLEGE ECOLOGIE
DOCTORAL GEOSCIENCES
BRETAGNE AGRONOMIE ALIMENTATION

L'INSTITUT agro Rennes Angers

Titre : Dynamiques des concentrations en nutriments et en matière organique dans des cours d'eau intermittents tempérés

Mot clés : cours d'eau intermittent, non pérenne, nutriments, MOD, climat tempéré, agriculture intensive

Résumé : Les cours d'eau intermittents et éphémères sont des cours d'eau qui cessent de couler et/ou s'assèchent à certaines périodes de l'année le long de leur cours. Il est donc essentiel de comprendre la biogéochimie des cours d'eau intermittents, compte tenu du rôle clé joué par les nutriments et la matière organique dans la régulation des fonctions écologiques de ces écosystèmes. L'objectif de cette thèse est de faire progresser notre compréhension des motifs spatio-temporels et des processus biogéochimiques associés à la fragmentation hydrologique dans un contexte océanique tempéré. Le chapitre 2 analyse la prévalence des cours d'eau intermittents en Bretagne. Les chapitres 3 et 4 examinent les motifs et processus biogéochimiques liés à la fragmentation des cours d'eau dans les bassins versants de Naizin (5 km^2) et d'Etel (18 à 24 km^2). Les résultats ont montré une augmentation de la variabilité spatiale des concentrations pendant la fragmentation hydrologique, c'est-à-dire la présence de mares isolées. Les mares isolées présentaient des conditions hypoxiques, entraînant une augmentation des concentrations de formes réduites et organiques d'azote (N) et de phosphore (P). La matière organique dissoute (MOD) présentait des propriétés de fluorescence différentes. Nous attribuons ces variations aux processus redox qui se produisent dans des conditions anoxiques, tels que la dénitrification, la réduction dissimilatoire des nitrates en ammonium et la désorption du phosphore réactif dissous et de la MOD, dans les mares isolées des deux bassins versants. Nous pensons que les variations spatio-temporelles observées des concentrations en nutriments et en MOD vont se généraliser à l'avenir, car les cours d'eau intermittents vont devenir plus fréquents en raison du changement climatique.

Title: Patterns of nutrients and organic matter concentrations in temperate intermittent streams

Keywords: intermittent stream, non-perennial, nutrient, DOM, temperate climate, intensive agriculture

Abstract: Intermittent and ephemeral streams are watercourses that cease to flow and/or dry at some period of the year along their course. Understanding the biogeochemistry of intermittent streams is crucial, given the key role played by the presence of nutrients and organic matter in regulating the ecological functions of these ecosystems. The aim of this thesis is to advance our understanding on the biogeochemical patterns and processes associated with hydrological fragmentation in a temperate oceanic context. Chapter 2 analyses the prevalence of intermittent streams in Brittany. Chapters 3 and 4 examine the biogeochemical patterns and processes during stream fragmentation in the Naizin (5 km^2) and Etel (18 to 24 km^2) headwater catchments. The results showed an increase in spatial variability of concentrations during hydrological fragmentation, i.e. when isolated pools were present. These pools exhibited hypoxic conditions, leading to increased concentrations of reduced and organic forms of nitrogen (N) and phosphorus (P). The fluorescence properties of the dissolved organic matter (DOM) differed. We attribute these variations to redox processes occurring under anoxic conditions, such as denitrification, dissimilatory nitrate reduction to ammonium and the desorption of soluble reactive phosphorus and DOM, in the isolated pools. We expect the observed biogeochemical patterns in nutrient and DOM concentrations to become more widespread in the future, as intermittent streams will become more frequent due to climate change.