

Drivers of seasonal and event-scale DOC dynamics at the outlet of mountainous peatlands revealed by high-frequency monitoring

Thomas Rosset ¹, Stéphane Binet ², Jean-Marc Antoine ³, Emilie Lerigoleur ³, François Rigal ⁴, Laure Gandois ¹

¹ EcoLab, Université de Toulouse, CNRS, Toulouse, 31326, France

² Université d'Orléans, CNRS/INSU, BRGM, ISTO Orléans, 45071, France

³ GEODE, Université de Toulouse, CNRS, Toulouse, 31058, France

⁴ IPREM, Université de Pau et des Pays de l'Adour, CNRS, Pau, 64000, France

Correspondence to: Thomas Rosset (thomas.rosset@ensat.fr)

Abstract. Peatlands store ~20-30 % of the global soil organic carbon stock and are an important source of dissolved organic carbon (DOC) for inland waters. Recent improvements for *in situ* optical monitoring revealed that the DOC concentration in streams draining peatlands is highly variable, showing seasonal variation and short and intense DOC concentration peaks. This study aimed to statistically determine the variables driving stream DOC concentration variations at seasonal and event scales. Two mountainous peatlands (one fen and one bog) were monitored in the French Pyrenees to capture their outlet DOC concentration variability at a high-frequency rate (30 min). Abiotic variables including precipitation, stream temperature and water level, water table depth and peat water temperature were also monitored at high frequency and used as potential predictors to explain DOC concentration variability. Results show that at both sites, DOC concentration time series can be decomposed into a seasonal baseline interrupted by many short and intense peaks of higher concentrations. The DOC concentration baseline is driven, at the seasonal scale, by peat water temperature. At the event scale, DOC concentration increases are mostly driven by a rise in the water table within the peat at both sites. Univariate linear models between DOC concentration and peat water temperature or water table increases show greater efficiency at the fen site. Water recession times were derived from water level time series using master recession curve coefficients. They vary greatly between the two sites but also within one peatland site. They partly explain the differences between DOC dynamics in the studied peatlands, including peat porewater DOC concentrations and the links between stream DOC concentration and water table rise within the peatlands. This highlights that peatland complexes are composed of a mosaic of heterogeneous peat units distinctively producing or transferring DOC to streams.

1. Introduction

Aquatic carbon transfer from terrestrial ecosystems to inland waters is receiving increasing attention as it plays a major role in the watershed carbon balance (Webb et al., 2018) and in the global carbon cycle (Cole et al., 2007; Drake et al., 2017). The origin of aquatic carbon has been tracked and wetlands have been shown to be the main organic carbon suppliers to rivers at both local (Hope et al., 1997; Laudon et al., 2004; Ledesma et al., 2017) and continental scales (Hope et al., 1994; Spencer et al., 2013). Peatlands are specific wetlands which have accumulated organic matter through slow vegetation decomposition

1 processes (Joosten and Clarke, 2002; Limpens et al., 2008). Peatlands grow under different climates (Broder et al., 2012;
2 Dargie et al., 2017; Gorham, 1991; Page et al., 2011) and store between 20 and 30 % of the total global soil carbon stock
3 (Leifeld and Menichetti, 2018; Nichols and Peteet, 2019; Scharlemann et al., 2014). Stream outlets of peatlands have been
4 monitored at different latitudes (Billett et al., 2006; Leach et al., 2016; Moore et al., 2013) in order to quantify and understand
5 the aquatic carbon transfer between these organic carbon rich pools and their draining streams. Dissolved organic carbon
6 (DOC) is a key component of these fluxes as it contributes to more than 80% of the aquatic carbon exported from peatlands
7 (Dinsmore et al., 2010; Hope et al., 2001; Müller et al., 2015; Roulet et al., 2007). At the outlet of peatlands, DOC is not only
8 considered for its role in the carbon balance but also because it may be an issue for water treatment quality (Ritson, 2015) and
9 a conveyor of potentially harmful elements along inland waters (Broder and Biester, 2017; Rothwell et al., 2007; Tipping et
10 al., 2003).

11 Variability in the DOC concentration signals at the outlet of peatlands has been observed at the inter-annual (Fenner and
12 Freeman, 2011; Köhler et al., 2008), the seasonal (Leach et al., 2016; Tipping et al., 2010) and even the event scales (Austnes
13 et al., 2010; Dyson et al., 2011). DOC concentrations were found to be negatively correlated with discharge in boreal systems
14 (Köhler et al., 2008), positively correlated with discharge in temperate areas (Clark et al., 2007) or non-correlated with
15 discharge in mountainous areas (Rosset et al., 2019). Temperature was also reported as an important driver of seasonal
16 variations of DOC concentration in field (Billett et al., 2006) and mesocosm (Pastor et al., 2003) experiments since DOC
17 production is boosted by a greater vegetation and microbial activity during warmer periods. Higher temperatures were also
18 shown to enhance evapotranspiration from peatland resulting in a rise in DOC concentration in peat porewater and stream
19 waters during dry summer periods (Fraser et al., 2001). Studies have highlighted that the heterogeneity of the hydraulic
20 conductivity within peatlands (Rycroft et al., 1975) influences the water table level fluctuations (Bernard-Jannin et al., 2018;
21 Kalbitz et al., 2002; Strack et al., 2008) and the oxygenation of the acrotelm (Freeman et al., 2001) , thus driving DOC
22 production and its transfer to streams.

23 DOC concentration monitoring at the outlet of peatlands has generally consisted in a weekly or monthly stream water sampling
24 routine (Clark et al., 2008; Juutinen et al., 2013). Higher-frequency sampling has been restricted to specific high precipitation
25 events (Austnes, 2010; Clark et al., 2007) or snowmelt (Laudon et al., 2004). Recently, new optical *in situ* sensors (Rode et
26 al., 2016) were used to track DOC concentration at a high-frequency rate (~30 minutes) at the outlet of peatlands (Koehler et
27 al., 2009; Ryder et al., 2014; Tunaley et al., 2016), highlighting the strong variability of the DOC concentration signal over a
28 year. While diel DOC concentration cycles have been analyzed under steady hydrological conditions (Tunaley et al., 2018),
29 no analysis has yet been performed to understand the high-frequency variability of the DOC concentration at a multi-year
30 scale.

31 Mountains host many small peatland areas that are often neglected in global peatland assessments but which drastically
32 influence stream chemistry in headwater catchments (Broder and Biester, 2015; Rosset et al., 2019). The harsh mountainous
33 climatic conditions (from the montane to the alpine belt (Holdridge, 1967)) and the relief of those areas generate high gradients
34 of different abiotic parameters (temperature, precipitation, hydrology) evolving along both seasonal and event (snowmelt,

1 rainstorms) scales. In the present study, a bog and a fen in the French Pyrenees mountains were monitored for stream DOC
2 concentration using an optical high-frequency *in situ* sensor placed at their outlet. The scientific objectives of this study were
3 (1) to statistically identify the main abiotic parameters driving stream DOC concentration variability at each site, (2) to identify
4 the temporal scale of these drivers, and (3) to compare the DOC concentration patterns of two contrasted peatlands regarding
5 their hydrological functioning.

6 **2. Study sites**

7 The peatland of Bernadouze (Fig.1-b) is situated in the Eastern part of the French Pyrenean mountains (42°48'9" N; 1°25'25"
8 E). The peatland lies at 1343 m.a.s.l. It belongs to a 1.4 km² watershed on limestone rocks dominated by the Mont Ceint =2088
9 m.a.s.l. and particularly steep (average slope=50%). From a post-glacial lake, a fen developed for 10 000 years at Bernadouze
10 site, reaching a peat accumulation depth of 2 m in average and more than 9.5 m at extreme locations (Jalut et al., 1982; Reille,
11 1990). As surficial runoff contributes to the water supply of the peatland, it is considered as a soligenous (minerotrophic) fen
12 (Joosten and Clarke, 2002). The fen is subject to an oceanic climatic influence but weather conditions can locally be contrasted
13 due to the specific mountainous topography. For the years 2015 to 2018, the mean annual temperature was 7.9±0.3 °C and the
14 mean annual precipitation was 1797±265 mm. Sub-zero temperatures and snow events are regularly observed at Bernadouze
15 site from mid-October to mid-May with a snow cover lasting around 85 days (Gascoin et al., 2015) from December to April
16 and sometimes exceeding 2m in height. Beech forest is the dominant vegetation cover in the watershed, except for the highest
17 grassland areas (> 1800 m) and the 4.7 ha of the peatland (3% of the watershed area). Vegetation on the peatland is mainly
18 composed of species characteristic of minerotrophic peatlands such as *Carex demissa* and *Equisetum fluviatile*. However, some
19 ombrotrophic species such as *Sphagnum palustre* and *Sphagnum capillifolium* are observed on the southern part of the
20 peatland, forming small hummocks and revealing a progressive disconnection with the stream and the water table supply.
21 Selective logging (one tree out of three was cut) was carried out during autumn 2016 in the lowest forested area surrounding
22 the peatland, producing no clear hydrological and biogeochemical changes at the outlet of the peatland.

23 The peatland of Ech (Fig.1-c) culminates at 710 m.a.s.l. in the west-central part of the French Pyrenees (43°4'59" N; 0°5'39"
24 W). Dominated to the North by mount Cossaout (1099 m.a.s.l.), the peatland depends on a 0.86 km² watershed principally
25 composed of grasslands and grazing areas. The bog area is 5.3 ha (6% of the watershed area) and the peat deposit reaches 3.3
26 m in the center (Millet et al., 2012). Peat formation started about 8200 years ago from a post glacial lake dammed by a
27 recessional moraine in the South (Rius et al., 2012). The peatland is classified as a bog since the surface vegetation depends
28 only on water supplied by precipitation. The site experiences a mountainous oceanic climate characterized by an average
29 annual temperature of 11±0.2 °C and an annual precipitation of 1242±386 mm (data from 2015 to 2018). Sub-zero daily mean
30 temperatures are rare (~10 days a year) and snow events are sparse in Ech. From the model of (Gascoin et al., 2015), the
31 average duration of snow cover does not exceed 10 days at this altitude in the Pyrenees. The vegetation observed is typical of
32 ombrotrophic bogs with a large blanket of *Sphagnum Capillifolium* and *Sphagnum Compactum*. Small birches and hummocks

1 of *Molinia caerulea* have started to develop within the peatland. Many burning events have been reported on the peatland since
2 its formation (Rius et al., 2012). Nowadays, agro-pastoral practices still use fire to limit the vegetation height and *Molinia*
3 *caerulea* extension. The last burning event at the Ech site occurred 8 weeks before the stream monitoring in April 2017 and
4 concerned the North Eastern half of the peatland. A second burning event occurred in February 2019 in the Western area of
5 the site. It was decided to stop data acquisition just before the fire to avoid potential shifts in DOC concentration induced by
6 this anthropogenic disturbance (Brown et al., 2015). According to field observations and a previous study related specifically
7 to DOC exports (Rosset et al., 2019), these two mountainous peatlands are considered as the main DOC contributors in their
8 watershed.

9 **3. Material and methods**

10 **3.1. Site instrumentation**

11 This article presents high-frequency data monitored from the 1st September 2015 to 31st December 2018 at Bernadouze site
12 and from 22nd May 2017 to 19th February 2019 at Ech site. Precipitation (liquid and solid) and air temperature were recorded
13 every 30 minutes at Bernadouze (Gascoïn and Fanise, 2018) and every 60 minutes at Ech by automatic weather stations located
14 respectively 300 and 15 meters from the peatlands in open areas. At both sites, sensor failures prevented data acquisition and
15 gap-filling models were used to complete the datasets. For missing precipitation data in Bernadouze (27% of the monitored
16 timeline), a linear model ($r^2=0.99$, $p\text{-value}< 0.01$) based on cumulative precipitation recorded in Saint Girons (414 m.a.s.l,
17 $42^{\circ}58'58''\text{N}$, $1^{\circ}8'45''\text{E}$) was built to generate total daily precipitation. A similar model was built in Ech ($r^2=0.99$, $p\text{-value}<$
18 0.01) based on data recorded in Ossen (517m, $43^{\circ}4'0''\text{N}$, $0^{\circ}4'0''\text{W}$) to gap fill 80% of the timeline. Missing air temperature
19 data (5% of the timeline) were estimated at Bernadouze from a linear regression model ($r^2=0.99$, $p\text{-value}< 0.01$) based on data
20 monitored at the same rate under the forest canopy 100 m away from the main weather station. In Ech, daily mean temperatures
21 were estimated (80% of the timeline) using a linear regression model ($r^2=0.88$, $p\text{-value}< 0.01$) with daily mean temperature
22 recorded in Tarbes (360 m.a.s.l. $43^{\circ}10'55''\text{N}$, $0^{\circ}0'2''\text{W}$).

23 At the outlet of each peatland, a multiparameter probe (Ysi Exo2, USA) measured fluorescence of the organic matter (fDOM,
24 $\lambda_{\text{excitation}}=365\pm 5$ nm / $\lambda_{\text{emission}}=480\pm 40$ nm), turbidity, water level and temperature every 30 minutes. Wiper sensors
25 prevented the optical sensors from biofouling before each measurement and the probes were inspected and calibrated monthly.
26 In Bernadouze, battery or sensor dysfunctions and wiper failures prevented data acquisition during 14% of the monitored
27 period. At both sites, a network of piezometer wells (8 in Bernadouze and 4 in Ech) was used to record hourly the water table
28 depth and the water temperature with automatic probes (Orpheus Mini Water Level Logger, OTT HydroMet, Germany).
29 Piezometer locations were selected so as to be representative of the different topographic and vegetation surfaces observed on
30 each peatland (hummocks, lawns, river banks) (Figure 1). The piezometer wells are 50 mm diameter PVC tubes slotted from
31 the bottom to 10 cm below the soil surface. The average depth in Bernadouze is about 1.25 ± 0.30 m, except for two piezometers

1 in the center of the peatland which were drilled to 2.18 ± 0.02 m depth. The average depth of the Ech piezometers is 2.35 ± 0.05
2 m (Table S3).

3 **3.2. Water sampling and DOC calibration**

4 Grab water sampling was performed every two weeks at the outlet of Bernadouze peatland and every two months at the outlet
5 of Ech. Piezometer wells were used to sample peat porewater on four occasions (2013, 2014, 2015, 2018) in Bernadouze and
6 on two occasions (2017, 2019) in Ech during stream baseflow periods. Grab water was collected using a manual peristaltic
7 pump and was directly filtered on site using $0.22 \mu\text{m}$ cellulose acetate filters (GSWP04700, Merck-Millipore, USA). To avoid
8 contamination from cellulose, the first milliliters of filtered water were discarded. Water samples were brought back to the
9 laboratory in a cool box and were stored at 6°C until analysis. High resolution water sampling was performed during 9 flood
10 events at the outlet of Bernadouze and once at Ech using automatic water samplers (ISCO 3700, USA) to collect water during
11 various hydrological conditions. Each sampling event consisted in collecting 24 samples of raw water (950 mL) at a frequency
12 defined thanks to the observed timelag of discharge (1 hour for rainfall and 4 hours for snowmelt driven flood events). Flood
13 water samples were collected within the 48 hours following the previous sampling and processed as grab water samples at the
14 laboratory.

15 For all samples (grab and flood samples), non-purgeable organic carbon (NPOC, referred to hereafter as DOC) concentration
16 was analyzed in filtered samples after acidification to pH 2 with a TOC-5000A analyzer (Shimadzu, Japan). The quantification
17 limit was 1 mg L^{-1} . Above this value, the analytical uncertainty was estimated at $\pm 0.1 \text{ mg L}^{-1}$. Reference material included
18 ION-915 ([DOC]= $1.37 \pm 0.41 \text{ mg C L}^{-1}$) and ION 96.4 ([DOC]= $4.64 \pm 0.70 \text{ mg C L}^{-1}$) (Environment and Climate Change
19 Canada, Canada).

20 The fluorescence of DOM (fDOM) data was explored for potential adjustments for temperature, inner filter effect and turbidity
21 (Downing et al., 2012; de Oliveira et al., 2018; Watras et al., 2011). fDOM data were corrected for temperature as described
22 by de Oliveira et al. (2018). The inner filter effect was adjusted at Ech for data showing absorbance values at 254 nm higher
23 than 0.6 (de Oliveira et al., 2018). Lastly, fDOM data recorded during high turbidity events ($>20 \text{ FNU}$) at the beginning of
24 high discharge events were ignored in the analysis as the fluorescence can be drastically attenuated by the presence of particles
25 (Downing et al., 2012). These periods were sporadic, accounting for only 0.2% of the fDOM time series and they do not alter
26 the fDOM variability which is delayed compared to the turbidity (Rosset et al., 2019). High-frequency DOC concentrations
27 were calculated at each site using a site specific linear model ([DOC]= $a \cdot \text{fDOM} + b$) linking corrected fDOM data to DOC
28 concentration in flood and grab-water samples. The two models (Fig. S1) are respectively described by the following
29 parameters: ($a=0.192$, $b=-0.031$, number of observations =174, $r^2=0.93$, $p\text{-value}<0.001$) for Bernadouze and ($a=0.290$, $b=-$
30 1.359 , number of observations =28, $r^2=0.73$, $p\text{-value}<0.001$) for Ech.

3.3. Water level fluctuation characterization

In order to provide an overall characterization of the peatlands, a mean peat water table depth, as well as a mean water temperature was calculated at each site by averaging peat water table depths and water temperature data at a given time from the set of piezometer probes. Calculations were performed only when all sensors were running (94% of the time period in Bernadouze and 100% in Ech). Hereafter, the mean water temperature in the piezometers is assimilated to peat water temperature.

Master Recession Curve (MRC) analyses were performed on water table and stream level time series, using the MRCTools v3.1 software (Posavec et al., 2017). In order to characterize the hydrodynamic properties of the peat, MRC were preferred to hydraulic conductivity estimations from slug tests because they can be performed directly with the water table level datasets and repeated easily on other peatlands. The MRC represents the average recession of the water level observed when only discharge flow occurs (no recharge). An exponential master recession curve was used to adjust the observed average MRC and to define a specific recession coefficient (α , unit= day^{-1}) characteristic of each monitoring point (Eq.(1)) where B is a constant.

$$\text{Master Recession Curve} \Leftrightarrow \text{Water level} = f(t) = B * e^{-\alpha t} \quad (1)$$

The exponential recession coefficient corresponds to the inverse of the average water recession time, called recession time, in the area of a piezometer or in a stream after a precipitation event. In the following, the recession time coefficient ($1/\alpha$) is used to characterize the hydraulic properties of peatlands and stream.

3.4. DOC peak selection and characterization

Peak selections in the DOC concentration time line were performed by running Python 3.6 (Python Software Foundation, 2019) scripts using the function `find_peak` available in the `Scipy` Signal library (Jones et al., 2001) and the arithmetic mean of the DOC concentration signal (`DOC_mean`) as an input parameter. Peak selection criteria were: to reach `DOC_mean` concentration and have a prominence higher than 0.25 times `DOC_mean`. Peaks occurring during an interval shorter than 12 hours apart were grouped under the highest DOC concentration peak. Each DOC concentration peak was defined by the time period delimited by the two nearest low points surrounding the peak event. Low points were located on the DOC concentration time lines by applying the `find_peak` function on the negatively transformed ($-1*$) DOC concentration signal previously processed with a Savitzky-Golay filter (`window-length=23` and `polyorder=2`). Low points occurring during an interval shorter than 12 hours apart were grouped under the lowest DOC concentration point. Lastly, the DOC peak period could be manually adjusted to fit or correct a peculiar peak pattern. A DOC concentration peak period was characterized by different metrics (Fig.2): its initial value corresponding to the DOC concentration of the low point at the start of the peak period (`DOC_initial`), its maximum value corresponding to the DOC peak value (`DOC_max`), its range (`DOC_increase`) which was calculated by subtracting the initial value from the maximum value and finally by the rising time duration (`rising_limb`) which separates the initial low point time from the peaking time. In this study, initial values and increases of DOC were the targeted variables to

1 be explained. Initial values of DOC were used to determine a DOC concentration baseline (Fig.2). The following classification
2 was used to describe seasonal variations: winter (December, January, February), spring (March, April, May), summer (June,
3 July, August), and autumn (September, October, November).

4 **3.5. Explanatory variables selection and characterization**

5 In order to investigate DOC concentration variabilities (at two temporal scales: peak event and seasonal), nine explanatory
6 variables were chosen (Table 1). Variables were calculated for each DOC concentration peak event using similar metrics to
7 those previously described in the DOC peak characterization section (Fig.2).

8 The variables were abiotic parameters, chosen because they have been reported in the literature to have an explanatory potential
9 for stream DOC concentration variability (Table 1). Two categories of variables were distinguished depending on whether the
10 process they described was related to the production of DOC within peatlands or to the transfer of DOC from peatlands to
11 streams. After sensitivity tests and in accordance with the observations of Tunaley et al. (2018), a mean of seven days prior to
12 the event was defined as the best operator to characterize pre-event conditions of air and stream water temperatures.

13 **3.6. Correlation and statistical modeling**

14 Relationships between targeted variables (DOC_increase and DOC_initial) and the explanatory variables were investigated
15 using ordinary least squares (OLS) multiple regression analyses. Prior to the analyses, variables which did not satisfy a normal
16 distribution were log or square root transformed to improve normality (Table 1). Multicollinearity was assessed among all the
17 predictors using Pearson correlation with a threshold $|r| < 0.7$ following Dormann et al., (2013). When two variables were found
18 to be collinear, we selected the one that displayed the highest absolute correlation with the targeted variables. Then at both
19 sites, all variables were standardized to a mean of zero and a standard deviation of one to derive comparable estimates in the
20 following analysis. We performed a backward stepwise selection procedure on the full model (i.e. the model including the
21 variables retained after removing multicollinearity) to capture the best set of variables explaining each targeted variable. At
22 each step of the procedure, the non-significant variables (p -value > 0.05) with the highest p -value were dropped from the model
23 and the resulting reduced model was re-evaluated. This process was continued until there were no non-significant variables
24 remaining in the final model. To account for the time dependency of the variables in the analyses, time was also included as
25 an explanatory variable in the full model. This variable corresponds to the duration which separates each DOC peak event
26 from the start of the time line. Residuals of the final models were surveyed in order to detect deviations from normality and
27 homoscedasticity and to identify outliers. No specific deviations or outliers were detected. Model residuals were also checked
28 for autocorrelation to verify the absence of any cyclical variation in the variables set. When more than one variable was retained
29 in the final model, the relative contribution of each variable was assessed using hierarchical variance partitioning (Chevan and
30 Sutherland, 1991). According to the previous predictor selections for the MLR models of DOC concentration increases
31 (DOC_increase), OLS regression analyses were performed at each piezometer plot of a peatland site, replacing the mean water
32 table increase variable by the specific water table level increase values of each plot in order to test the importance of recession

1 time heterogeneity in the observed correlations. Similar OLS regression analyses were performed at the outlet of streams by
2 replacing the mean water table increase variable by the stream water level increase when necessary. R^2 and relative importance
3 (%) of the stream or water table level increase variable were reported for each OLS regression tested. All the analyses were
4 undertaken in R (R Core team, 2019) using the package *rms* (Harell, 2019) and *relaimpo* (Groemping and Matthias, 2018).

5 **4. Results**

6 **4.1. Climate, hydrology and DOC dynamics**

7 Climatic variables are contrasted between the two studied areas. In 2018, temperatures were higher in Ech than in Bernadouze
8 with an annual mean air temperature, water temperature and peat water temperature respectively of 11.3, 10.7, 11.9 °C
9 compared to 7.9, 7.1, 7.7 °C. Total precipitation reached 2151 mm in Bernadouze and 1140 mm in Ech. In these steep
10 mountainous headwaters, short and intense flood events were triggered by strong precipitation events and/or the snowmelt.
11 Over the whole timelines, the maximum and mean of the stream water level were respectively 1.36 and 0.35 m in Ech and
12 0.81 and 0.10 m in Bernadouze. These short flood events were followed by recession sequences revealed by the slow decreases
13 in the peat water table at both sites, especially in late summer and autumn (Fig.3-c). The average and minimum of the peat
14 water table depth in the two piezometer networks were respectively -0.23 and -0.43 m at Ech, and -0.15 and -0.45 m in
15 Bernadouze. No clear relationship was observed at either site between the stream water level and the peat water table time
16 series. The peat water levels responded differently to rain events depending on the season. For instance, a strong flood observed
17 in the stream can be contiguous with a low or high peat water table rise (i.e. July 2016 and February 2017 events in Bernadouze)
18 (Fig.3 b -c). Peat porewater, occasionally sampled in the piezometers, showed an average DOC concentration of 12.4 ± 8.3 mg
19 L⁻¹ in Bernadouze while it reached an average of 37.3 ± 18.8 mg L⁻¹ in Ech (Table S3). Peat porewater was in average more
20 acidic in Ech, (pH=5.0±0.4) than in Bernadouze (pH=6.2±0.3)..

21 DOC concentration was highly variable at both sites during the monitored periods as highlighted by the numerous short DOC
22 peak events (~30 hour duration) in the two time series (Fig.3 and Table 2). At Bernadouze site, DOC concentration peaks
23 showing higher values were more frequent from April to November while this was less obvious at Ech site where DOC
24 concentration also peaked during winter. In 2018, the arithmetic means and flow weighted averages of DOC concentration
25 were higher at the outlet of Ech, reaching 7.1 ± 6.1 and 4.6 mg L⁻¹, than in Bernadouze where they were 2.0 ± 1.5 and 1.7 mg L⁻¹.
26

27 **4.2. DOC concentration peaks characterization**

28 Peak characterization (Table 2) revealed that the increases and the maxima of DOC concentration peaks were on average two
29 times higher in Ech than in Bernadouze. However, the ratio between the mean increase and the mean initial value of DOC
30 concentration was higher in Bernadouze (2.3) compared to Ech (1.9). DOC concentration peaks occurred more often at
31 Bernadouze compared to Ech (0.24 vs 0.16 peak per day in average) while their duration was slightly longer (32 ± 14 vs 28 ± 16

1 hours). Rising limbs of DOC concentration peaks lasted on average 10 ± 5 and 13 ± 14 hours at Bernadouze and Ech respectively
2 and they were slightly longer than the stream water rising limb averages monitored at the outlet of the two peatlands. In
3 contrast, rising limb duration of the water table in Ech was clearly longer (22 ± 12) compared to Bernadouze (13 ± 7 hours).

4
5 General mean and seasonal means of initial DOC concentrations were 2.5 and 3.1 times higher at Ech compared to Bernadouze
6 (Table 3). However, at both sites, initial DOC concentrations showed a clear seasonal variability. The lowest values were
7 observed in spring and the highest in autumn while in summer and winter DOC concentration was close to the annual mean.
8 DOC peak event frequencies also varied at the seasonal scale (Table 3). The highest frequencies were reported in autumn at
9 both sites. The lowest peak frequencies were observed in winter at Bernadouze and in summer at Ech.

10 **4.3. DOC concentration variations models**

11 Prior to multiple regression analyses, the air temperature over 7 days, the maximum stream water level and the initial level of
12 the water table were excluded from the analysis because of their strong correlation with other variables (Pearson's correlation
13 $|r| > 0.7$) (Fig. S2). Multiple linear regressions (MLR) followed by backward stepwise selections showed that respectively 55%
14 and 44% of the seasonal variation of DOC (DOC_initial) was explained by the final models at Bernadouze and Ech (Table 3).
15 Peat water temperature was reported as an important predictor at both sites (72% of the variance explained by the final model
16 at Ech and 44% at Bernadouze). In Bernadouze, variance is similarly explained by the time between two peaks (44%). Along
17 the two years of monitoring in Ech, the strong DOC concentration values observed during the dry autumn 2018 (Fig.2) created
18 a positive general trend in the DOC concentration baseline. This peculiar trend drastically influenced the statistical analysis
19 and consequently the variable "time" became a significant predictor at the seasonal scale. Considering the high relative
20 importance of the peat water temperature in the two final models, two simple linear models (Fig.4 a) were built based on this
21 variable to illustrate the seasonal DOC concentration behavior in Bernadouze (slope=0.08, intercept=-0.16, n=231, $R^2=0.26$,
22 p-value<0.001) and in Ech (slope=0.10 intercept=0.50, n=100, $R^2=0.27$, p-value<0.001). In the final models of increase of
23 DOC concentration, water table increase was the most important variable at Bernadouze (67% of the variance explained) and
24 the single variable at Ech. In Bernadouze, other variables such as stream water temperature, stream water level increase and
25 the time between two peaks were significant enough to be integrated in the final model of DOC concentration increase. The
26 R^2 associated to the models varied strongly between the two sites, reaching 0.77 in Bernadouze and only 0.27 in Ech. Since
27 water table increase was the main explanatory variable for the DOC concentration increase model, two simple linear models
28 were built (Fig.4b) with the following parameters in Bernadouze (slope=8.44, intercept=-1.06, n=231, $R^2=0.68$, p-
29 value<0.001) and in Ech (slope=6.39, intercept=0.84, n=100, $R^2=0.27$, p-value<0.001).

30 **4.4. Relationships between DOC dynamics and recession time**

31 In the fen of Bernadouze the recession times in the peat ranged from 15 to 77 days whereas in the bog of Ech they were longer,
32 ranging from 53 to 143 days (Fig.5). Stream recession times were shorter at both sites reaching 4 days in Bernadouze and 9

1 days in Ech. Results of the OLS regressions conducted at each peat water level monitoring plot using DOC increase final
2 models, revealed that recession time influenced the model's efficiency (Fig.5 a). Piezometers characterized by shorter recession
3 times showed greater determination coefficients R^2 (Fig.5 a). Peat water table increase was the most important predictor (pie
4 charts Fig.5 a) for all piezometer plots, contributing at least 47% of the explained variance of the DOC increase models. In
5 Bernadouze, the model based on stream water level was weaker ($R^2=0.37$) than the models based on peat water table data
6 while in Ech the model based on stream water level was unable to explain at all the DOC increase variation ($R^2=0$). Recession
7 times showed a positive relationship with DOC concentration measured in the piezometers and in the streams, higher
8 concentrations being associated to longer recession times (Fig. 5 b).

9 **5. Discussion**

10 **5.1. Long-term high-frequency monitoring**

11 To our knowledge, this is the first time that stream DOC concentration and abiotic drivers, including peat water table depth
12 fluctuations, have been analyzed at the outlet of peatland sites on a multi-year period at this frequency (30 min). Previously,
13 DOC concentration variability was investigated either at lower frequencies (Clark, 2005; Dawson et al., 2011) or during shorter
14 periods (Austnes et al., 2010; Koehler et al., 2009; Tunaley et al., 2016; Worrall et al., 2002). Recently, high-frequency
15 monitoring of nutrient dynamics in watersheds has developed and has revealed an unexpected variability of mobilization
16 processes for these nutrients (Blaen et al., 2017; Rode et al., 2016; Tunaley et al., 2016). These acquisitions have allowed
17 scientists to characterize the "hot moments" in the biogeochemical cycles of a watershed (McClain et al., 2003). A contribution
18 of our study is to sequence extremely brief DOC concentration peaks and to statistically disentangle their event and seasonal
19 drivers using synchronous high-frequency monitoring of climatic and hydrological parameters. The representativeness of both
20 seasonal and event scale statistical models is enhanced by the large number of events (252 peaks in Bernadouze and 101 peaks
21 in Ech) captured at all seasons (Table 2).

22 **5.2. Peat water temperature controls seasonal DOC concentration baseline**

23 Clear seasonal variations in the DOC concentration baseline were observed at both sites (Figure.3 and Table 2). The DOC
24 concentration baseline increased in late spring, peaked in autumn, decreased during winter and reached the lowest levels in
25 early spring. Similar seasonal DOC concentration patterns have been observed at the outlet of other peatland sites in temperate
26 regions (Austnes, 2010; Broder and Biester, 2015; Clark et al., 2005; Tunaley et al., 2016; Worrall et al., 2006; Zheng et al.,
27 2018) or after the snowmelt event in boreal areas (Jager et al., 2009; Köhler et al., 2008; Laudon et al., 2004; Olefeldt and
28 Roulet, 2012; Whitfield et al., 2010).

29 In this study, linear regression models revealed that the seasonal variations of the DOC concentration baseline are mostly
30 driven by peat water temperature (Table 3). At peatland sites, temperature is often identified as a DOC concentration driver at
31 the seasonal scale (Billett et al., 2006; Clark et al., 2008; Dawson et al., 2011; Koehler et al., 2009). Warmer temperatures

1 directly enhance DOC production by stimulating vegetation and microbial activity (Kalbitz et al., 2000; Pastor et al., 2003).
2 Warmer temperatures are also indirectly linked to DOC production processes in temperate and northern peatlands since they
3 often correspond to dry periods that lower water table levels. When the water table decreases, the “enzymic latch” (Freeman
4 et al., 2001) is initiated on a greater volume of acrotelm (oxygenated peat) and enhances DOC production within the upper
5 peat layers. DOC concentration relationships with peat water temperature have already been described in an acidic fen in
6 France (Leroy et al., 2017) and in blanket peatlands from the North Pennine uplands in the UK (Clark et al., 2005); however,
7 in these cases DOC concentrations were measured in peat porewater. A complementary study in the North Pennines (Clark et
8 al., 2008) showed that peat porewater DOC concentrations and stream DOC concentration were strongly correlated, meaning
9 that, by extension, the relationship between peat temperature and stream DOC concentration could be verified for these sites.

10 **5.3. Water table increase controls DOC concentration peaks at the event scale**

11 This study, coupling high-frequency stream DOC concentration and water table depth monitoring at both peatland sites,
12 revealed that peat water table increase is a strong predictor of stream DOC concentration increase at the event scale (Table 3
13 and Figure 4 b). Until now, stream DOC concentration variability at the event scale has been investigated in terms of discharge
14 but rarely in terms of peat water table variation. Several studies have reported stream DOC concentration increases at the outlet
15 of peatlands during flood events (Austnes, 2010; Ryder et al., 2014; Tranvik and Jansson, 2002; Yang et al., 2015), whereas
16 others showed dilution during high flow events (Clark et al., 2007; Grayson and Holden, 2012; Laudon et al., 2004; Worrall
17 et al., 2002). At the outlet of peatlands, non-linear discharge-DOC concentration relationships have been reported (Roulet et
18 al., 2007; Tunaley et al., 2016) and modelled (Birkel et al., 2017); this seems to be the case at our sites where stream water
19 level explains the variability of DOC increases during flood events only poorly (Bernadouze) or not at all (Ech) (R^2 contribution
20 in Table 3 and Figure .5 a). Non-linear /hysteretic patterns (Hendrickson and Krieger, 1964; Walling and Foster, 1975) between
21 DOC and discharge are commonly observed in upland watersheds (Jeong et al., 2012; Strohmeier et al., 2013) and are analyzed
22 to infer DOC export mechanisms. However, these patterns cannot predict stream DOC concentration as an MLR model
23 integrating water table increase appears to do.

24 The link between DOC dynamics and peat water table has been largely investigated at the seasonal scale (Kalbitz et al., 2002;
25 Strack et al., 2008; Hribljan et al., 2014;) or in mesocosm experiments (Pastor et al., 2003; Blodau et al., 2004). The peat water
26 table is usually considered as a DOC production driver as it controls the oxygenated acrotelm volume (Billett et al., 2006;
27 Freeman et al., 2001; Ritson et al., 2017). Therefore, different studies attempted to quantify the effect of water table position
28 on DOC production rate in peatlands. In fen and bog mesocosms, Pastor et al., (2003) observed no DOC concentration variation
29 in the stream water after long term peat water table decreases. Contrastingly, increasing DOC concentrations were observed
30 during the re-wetting phase of the acrotelm at fen sites in Germany (Kalbitz et al., 2002), in Canada (Strack et al., 2008) and
31 in the USA (Hribljan et al., 2014). Clark et al., (2009) reported similar observations after re-wetting peat cores in controlled
32 laboratory conditions. Our results are in line with these studies. Moreover, thanks to the high-frequency survey, they highlight,

1 in addition to DOC production processes, specific hydrodynamic processes driving DOC export from peatlands at the event
2 scale.

3 The correlation between DOC peak and water table increase can have different origins. First, the water table increase could
4 create a piston flow that expels pre-flood water (Małoszewski et al., 1983), enriched in DOC. At our sites, the delay (a few
5 hours) between stream discharge peaks, peat water table increase and DOC peaks suggests that DOC concentration peaks are
6 not directly related to water pressure. As previously observed in peat-dominated headwater catchments by Rodgers et al.
7 (2005), this observation rejects the piston flow hypothesis. Secondly, as DOC is mostly produced in the oxygenated and
8 unsaturated peat volume above the water table (Billett et al., 2006; Freeman et al., 2001; Ritson et al., 2017), it can be flushed
9 by flood water during a flood event (Boyer *et al.*, 1997). Due to the exponential decrease in hydraulic conductivity properties
10 (Rycroft et al, 1975), pre-flood-water under the water table is less mobile than flood water located above (Quinton *et al*, 2008).
11 Our data support this second hypothesis, with a very fast increase in DOC concentrations, and a rapid DOC concentration
12 recession in the same order of magnitude as sub-surface flow recession. This does not exclude the possibility that a fraction of
13 pre-flood waters may reach the stream during the recession time, but this mixing process is minor compared to flushing
14 processes. These mechanisms are in line with the two layers hydrology-biogeochemistry model developed by Birkel et al.,
15 (2017) at the outlet of a peatland. Moreover, this model emphasizes the positive relationship between the stream DOC
16 concentration and the water table connection to the upper soil horizon. Following this second hypothesis, if DOC production
17 was the limiting factor, the linear regression (Fig.4b) should show a plateau for the high value of water table increase. This is
18 not the case. Thus the limiting factor appears to be the amount of water brought floods and ultimately the full saturation of the
19 peat. These observations support the practices for degraded peatland restoration, where a general rise in the water table is
20 recommended to limit water table increases and the DOC concentration peaks induced at their outlets (Höll et al., 2009; Strack
21 and Zuback, 2013).

22 **5.4. Hydrological influences on DOC concentration at the outlet of peatlands**

23 The higher DOC concentration observed in summer could be explained by evapotranspiration processes that concentrate
24 solutes in stream water. However, the evapotranspiration rates in these mountainous environments are low (<300 mm year⁻¹)
25 compared to precipitation (>1200 mm year⁻¹) and should not drastically influence the seasonal DOC concentration baseline.
26 These Pyrenean peatlands are considered as the main source of DOC in their watershed (Rosset et al., 2019). However, the
27 outlet DOC concentrations are influenced by dilution process resulting from the input of water flowing from upstream non-
28 peaty areas. The hydrographs recorded at the outlet of the peatlands are in favor of uniform contributions of water from the
29 watershed to the outlet discharge. Considering this hypothesis, the different DOC concentration levels between the two sites
30 (Table 2), may be partially explained by the different peatland coverage in the watershed of the two sites (Bernadouze 3% vs
31 Ech 6%).

32 In Bernadouze, DOC concentration remained extremely low when the fen was snow-covered and it did not drop drastically
33 during the spring snowmelt as has been observed in boreal areas (Laudon et al., 2004; Leach et al., 2016). This pattern can be

1 explained by (1) the low initial DOC concentration which prevents a clear dilution being observed during the snowmelt event,
2 (2) the snowmelt regime in this Pyrenean catchment, which may be less sudden than in boreal regions and occurs from the
3 early snow deposit to the beginning of the growing season, continuously diluting the low winter DOC production within the
4 peatland.

5 In Bernadouze, contrary to the initial hypothesis (Table 1), the time between peaks was a negative significant predictor in both
6 seasonal and event DOC concentration models (Table 3). This is considered as an indirect consequence of the seasonal
7 temperature control on DOC concentration. Indeed, snow cover and the low temperatures associated to high water table
8 positions prevent the occurrence of DOC peaks in winter, creating large time gaps between two events (Table 2) of low initial
9 values. In contrast, DOC production is amplified during warmer periods, resulting in more frequent stream DOC concentration
10 peaks starting at higher initial values. In Ech, where average annual temperatures are higher and snow cover is reduced, the
11 initial hypothesis was verified since DOC concentrations were stronger in autumn after the long summer times between peaks
12 (Table 2). However, the variable was not significant enough to be integrated in any final model (Table 3).

13 **5.5. Contrasted DOC dynamics related to recession times**

14 Spatial analysis of water table variation within the peatland revealed that the studied sites are composed of several peat units,
15 characterized by contrasted recession times. In these mountainous peatlands, recession times are related to DOC dynamics,
16 driving model efficiency between DOC concentration increase and peat water table rise and explaining DOC concentration in
17 peat pore water.

18 In the present study, both stream and peat pore water DOC concentrations were higher at Ech compared to Bernadouze (Table
19 2 and S3 and Figure 5 b). This is consistent with mesocosm (Pastor et al., 2003) or field (Chanton et al., 2008; Chasar et al.,
20 2000; Moore, 1988) peat porewater observations which highlighted higher concentrations in bogs compared to fens.

21 Sphagnum species, which are dominant on bogs, usually produce relatively less labile and reactive DOC than vascular plants,
22 which are more abundant on fens (Chanton et al., 2008). Lower pH values are expected to reduce DOC solubility (Clark et al.,
23 2005). However, these relationships are not observed at our sites. As can be seen on Figure 5b, peat porewater DOC
24 concentrations are related to MRC, higher concentrations being associated to longer recession times. Beyond this hydrologic
25 control, other parameters, such as residence time, vegetation cover, linked to bog and fen conditions influence DOC
26 concentration levels in peat pore water.

27 In average the bog of Ech presented a longer recession time (111 days) than the fen of Bernadouze (20 days). However, a large
28 variability is observed within each site. For instance, a specific unit in the fen of Bernadouze was characterized by a long
29 recession time of 77 days. This unit shows surface bog vegetation and topographic patterns but is surrounded by typical fen
30 units characterized by shorter recession times (Fig.5). Thus a peatland complex must be considered as a patchwork of different
31 units and not as a uniform peat entity.

32 At the event scale, the univariate model between DOC concentration and peat water table increase showed a non-negligible
33 intercept at Ech contrasting with the model of Bernadouze (Figure 4 b). This means that in Ech, DOC concentration increases

1 can occur without water table increases. In this case, DOC is transferred from the upper peat layers via fast runoff flows without
2 any water table level fluctuation. Such a phenomenon is consistent with the lower hydraulic conductivities (longer recession
3 times) measured in bogs (Figure 5). In contrast, DOC stored in the upper peat layers of fen units is transferred to the stream
4 by fast percolating water raising water table levels and supplying sub-surface flows (Figure .6). This explains why the DOC
5 increase model based on peat water table increase is particularly efficient for fen units characterized by short recession times
6 (Fig.5 a). Recession times, used as proxies of the hydraulic conductivity, also explain the differences in peat porewater DOC
7 concentration observed between bog and fen sites. In the fen, recession times are short, meaning that the upper peat layers are
8 rapidly washed by precipitations, inducing sudden DOC pool depletions of the peat porewater (Fig.3 c). At the bog site, DOC
9 stored in the upper peat layers is slowly released to the stream after precipitation events and contributes to maintaining a high
10 stream baseline (Fig.3 c) and peat pore water DOC concentrations (Fig.5 a).

11 Thus, stream DOC concentration modelling at the outlet of peatlands must account for different proportions of fen-like or bog-
12 like units in peatland complexes to reflect the real seasonal and event DOC concentration variability. Every unit supplies DOC
13 to the stream at a different rate depending on its volume, distance from the stream and recession time (Fig.6). This end member
14 mix concurs with the model of Binet et al. (2013) describing event and seasonal water table variability in peatlands using a
15 double porosity parametrization. In that sense, recession time appears as a physical parameter able to characterize peatland
16 units beyond the binary typology of bog or fen. This would surely improve the efficiency of hydrological and biogeochemical
17 models. In the case of peatland complexes characterized by long recession times, further investigations of peatland runoffs and
18 sub-surface flows are needed, analyzing denser and stream directed piezometer transects in order to build stronger DOC
19 concentration models.

20 **6. Conclusion**

21 This study reports a statistical analysis of the stream DOC concentration variability at the outlet of two mountainous peatlands.
22 Multi-year *in situ* high-frequency (30 minutes) monitoring revealed that at both sites, DOC concentration time series can be
23 decomposed into a seasonal baseline interrupted by many short, intense peaks of higher concentrations. At the seasonal scale,
24 DOC concentration baseline variations are mainly explained by peat water temperature which controls integrative DOC
25 production processes within the peatland. During the “hot moments” of peak events, DOC concentrations are well explained
26 at both sites by water table increases within the peatlands. Recession time is a relevant parameter to explain peat porewater
27 DOC concentration and the different model performances observed between bog and fen sites. Recession time assessments in
28 different locations on the two studied sites showed that peatlands are composed of different units presenting contrasted
29 hydraulic conductivities Thus, peatlands should not be considered as uniform landscapes. Distinct peatland units within the
30 same peatland complex contribute differently to the DOC transfer processes to inland waters. Recession time assessment in
31 piezometers appears to be a simple and promising tool to investigate hydrological processes occurring in peatlands over time
32 and space. Indeed, water table time series are often under-used and only account for a seasonal mean or minimum depth.

- 1 Assessing recession times on peatlands is a first step to taking peatland water table dynamics into consideration and to
- 2 explaining potentially related biogeochemical processes.

1 **7. Data availability**

2 The data used in this manuscript are described and available on the Pangaea® data repository at:

3 <https://doi.pangaea.de/10.1594/PANGAEA.905838>

4 **8. Author contribution**

	CASRAI role	Rosset	Binet	Antoine	Le rigoleur	Rigal	Gandois
1	<i>Conceptualization</i>	x	x				x
2	<i>Data curation</i>	x			x	x	
3	<i>Formal analysis</i>	x	x			x	x
4	<i>Funding acquisition</i>		x				x
5	<i>Investigation</i>	x	x	x	x		x
6	<i>Methodology</i>	x	x	x			x
7	<i>Project administration</i>	x	x				x
8	<i>Resources</i>	x	x		x		x
9	<i>Software</i>	x			x	x	
1 0	<i>Supervision</i>		x		x		x
1 1	<i>Validation</i>	x	x				x
1 2	<i>Visualization</i>	x	x		x		x
1 3	<i>Writing – original draft</i>	x	x				x
1 4	<i>Writing – review & editing</i>	x	x	x	x	x	x

5

1 **9. Competing interest**

2 The authors declare that they have no conflict of interest.

3 **10. Acknowledgment**

4 All the carbon analyses were performed at the PAPC platform (EcoLab). The authors wish to thank: L.Plagnet for permitting
5 the access to the peatland of Ech, V. Payré-Suc, F. Julien, D. Lambrigot, W. Amblas for assisting in stream organic carbon
6 concentration analysis; F. De Vleeschouwer, D. Allen, P. Durantez Jimenez, T. Camboulive for assisting in water sampling;
7 G.Susong and the Regional Natural reserve of Pibeste-Aoulhet for piezometer maintenance, S. Gascoin, P. Fanise, the CESBIO
8 laboratory and the OSR Toulouse for providing the meteorological data, D. Galop for assisting in site preparation and
9 communication with local policy makers, E. Rowley-Jolivet for English language assistance.

10 This project was made possible with the support of the LabEx DRIIHM , French programme "Investissements d'Avenir" (ANR-
11 11-LABX-0010) which is managed by the ANR and funds the Ph.D of T. Rosset; LabEx DRIIHM OHM Haut Vicdessos/
12 Haute Vallée des Gaves, INTERREG V POCTEFA REPLIM PIRAGUA OPCC, ANR JCJC TRAM (ANR JCJC 15-CE01-
13 008 TRAM), which funded the investigations at both sites.

14 **References**

15 Armstrong, A., Holden, J., Luxton, K. and Quinton, J. N.: Multi-scale relationship between peatland vegetation
16 type and dissolved organic carbon concentration, *Ecol. Eng.*, 47, 182–188, doi:10.1016/j.ecoleng.2012.06.027,
17 2012.

18 Austnes, E.: Effects of storm events on mobilisation of dissolved organic matter (DOM) in a Welsh peatland
19 catchment, *Biogeochemistry*, 99(1), 157–173, doi:10.1007/s10533-009-9399-4, 2010.

20 Austnes, K., Evans, C. D., Eliot-Laize, C., Naden, P. S. and Old, G. H.: Effects of storm events on mobilisation
21 and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment, *Biogeochemistry*,
22 99(1–3), 157–173, doi:10.1007/s10533-009-9399-4, 2010.

23 Bernard-Jannin, L., Binet, S., Gogo, S., Leroy, F., Défarge, C., Jozja, N., Zocatelli, R., Perdereau, L. and
24 Laggoun-Défarge, F.: Hydrological control of dissolved organic carbon dynamics in a rehabilitated *Sphagnum*-
25 dominated peatland: a water-table based modelling approach, *Hydrol. Earth Syst. Sci.*, 22(9), 4907–4920,
26 doi:https://doi.org/10.5194/hess-22-4907-2018, 2018.

27 Billett, M. F., Deacon, C. M., Palmer, S. M., Dawson, J. J. C. and Hope, D.: Connecting organic carbon in stream
28 water and soils in a peatland catchment, *J. Geophys. Res. Biogeosciences*, 111(G2), doi:10.1029/2005JG000065,
29 2006.

- 1 Binet, S., Gogo, S. and Laggoun-Défarge, F.: A water-table dependent reservoir model to investigate the effect of
2 drought and vascular plant invasion on peatland hydrology., *J. Hydrol.*, 499, 132–139,
3 doi:10.1016/j.jhydrol.2013.06.035, 2013.
- 4 Birkel, C., Broder, T. and Biester, H.: Nonlinear and threshold-dominated runoff generation controls DOC export
5 in a small peat catchment, *J. Geophys. Res. Biogeosciences*, 122(3), 498–513, doi:10.1002/2016JG003621, 2017.
- 6 Blaen, P. J., Khamis, K., Lloyd, C., Comer-Warner, S., Ciocca, F., Thomas, R. M., MacKenzie, A. R. and
7 Krause, S.: High-frequency monitoring of catchment nutrient exports reveals highly variable storm event
8 responses and dynamic source zone activation, *J. Geophys. Res. Biogeosciences*, 122(9), 2265–2281,
9 doi:10.1002/2017JG003904, 2017.
- 10 Blodau, C., Basiliko, N. and Moore, T. R.: Carbon turnover in peatland mesocosms exposed to different water
11 table levels, *Biogeochemistry*, 67(3), 331–351, doi:10.1023/B: BIOG.0000015788.30164.e2, 2004.
- 12 Boyer, E. W., Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1997). Response characteristics of DOC
13 flushing in an alpine catchment. *Hydrological processes*, 11(12), 1635-1647.
- 14 Broder, T. and Biester, H.: Hydrologic controls on DOC, As and Pb export from a polluted peatland – the
15 importance of heavy rain events, antecedent moisture conditions and hydrological connectivity, *Biogeosciences*,
16 12(15), 4651–4664, doi:10.5194/bg-12-4651-2015, 2015.
- 17 Broder, T. and Biester, H.: Linking major and trace element concentrations in a headwater stream to DOC release
18 and hydrologic conditions in a bog and peaty riparian zone, *Appl. Geochem.*, 87, 188–201,
19 doi:10.1016/j.apgeochem.2017.11.003, 2017.
- 20 Broder, T., Blodau, C., Biester, H. and Knorr, K. H.: Peat decomposition records in three pristine ombrotrophic
21 bogs in southern Patagonia, *Biogeosciences*, 9(4), 1479–1491, doi:10.5194/bg-9-1479-2012, 2012.
- 22 Brown, L. E., Holden, J., Palmer, S. M., Johnston, K., Ramchunder, S. J. and Grayson, R.: Effects of fire on the
23 hydrology, biogeochemistry, and ecology of peatland river systems, *Freshw. Sci.*, 34(4), 1406–1425,
24 doi:10.1086/683426, 2015.
- 25 Chanton, J. P., Glaser, P. H., Chasar, L. S., Burdige, D. J., Hines, M. E., Siegel, D. I., Tremblay, L. B. and
26 Cooper, W. T.: Radiocarbon evidence for the importance of surface vegetation on fermentation and
27 methanogenesis in contrasting types of boreal peatlands, *Glob. Biogeochem. Cycles*, 22(4),
28 doi:10.1029/2008GB003274, 2008.
- 29 Chasar, L. S., Chanton, J. P., Glaser, P. H., Siegel, D. I. and Rivers, J. S.: Radiocarbon and stable carbon isotopic
30 evidence for transport and transformation of dissolved organic carbon, dissolved inorganic carbon, and CH₄ in a
31 northern Minnesota peatland, *Glob. Biogeochem. Cycles*, 14(4), 1095–1108, doi:10.1029/1999GB001221, 2000.
- 32 Chevan, A. and Sutherland, M.: Hierarchical Partitioning, *Am. Stat.*, 45(2), 90–96,
33 doi:10.1080/00031305.1991.10475776, 1991.

- 1 Clark, J. M.: Environmental Controls on the Production and Export of Dissolved Organic Carbon in an Upland
2 Peat Catchment, Ph.D., University of Leeds. [online] Available from:
3 <https://ethos.bl.uk/OrderDetails.do?uin=uk.bl.ethos.503248> (Accessed 17 May 2019), 2005.
- 4 Clark, J. M., Chapman, P. J., Adamson, J. K. and Lane, S. N.: Influence of drought-induced acidification on the
5 mobility of dissolved organic carbon in peat soils, *Glob. Change Biol.*, 11(5), 791–809, doi:10.1111/j.1365-
6 2486.2005.00937.x, 2005.
- 7 Clark, J. M., Lane, S. N., Chapman, P. J. and Adamson, J. K.: Export of dissolved organic carbon from an upland
8 peatland during storm events: Implications for flux estimates, *J. Hydrol.*, 347(3–4), 438–447,
9 doi:10.1016/j.jhydrol.2007.09.030, 2007.
- 10 Clark, J. M., Lane, S. N., Chapman, P. J. and Adamson, J. K.: Link between DOC in near surface peat and stream
11 water in an upland catchment, *Sci. Total Environ.*, 404(2), 308–315, doi:10.1016/j.scitotenv.2007.11.002, 2008.
- 12 Clark, J. M., Ashley, D., Wagner, M., Chapman, P. J., Lane, S. N., Evans, C. D. and Heathwaite, A. L.: Increased
13 temperature sensitivity of net DOC production from ombrotrophic peat due to water table draw-down, *Glob.*
14 *Change Biol.*, 15(4), 794–807, doi:10.1111/j.1365-2486.2008.01683.x, 2009.
- 15 Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M.,
16 Kortelainen, P., Downing, J. A., Middelburg, J. J. and Melack, J.: Plumbing the Global Carbon Cycle: Integrating
17 Inland Waters into the Terrestrial Carbon Budget, *Ecosystems*, 10(1), 172–185, doi:10.1007/s10021-006-9013-8,
18 2007.
- 19 D’Andrilli, J., Chanton, J. P., Glaser, P. H. and Cooper, W. T.: Characterization of dissolved organic matter in
20 northern peatland soil porewaters by ultra high resolution mass spectrometry, *Org. Geochem.*, 41(8), 791–799,
21 doi:10.1016/j.orggeochem.2010.05.009, 2010.
- 22 Dargie, G. C., Lewis, S. L., Lawson, I. T., Mitchard, E. T. A., Page, S. E., Bocko, Y. E. and Ifo, S. A.: Age,
23 extent and carbon storage of the central Congo Basin peatland complex, *Nature*, 542(7639), 86–90,
24 doi:10.1038/nature21048, 2017.
- 25 Dawson, J. J. C., Tetzlaff, D., Speed, M., Hrachowitz, M. and Soulsby, C.: Seasonal controls on DOC dynamics
26 in nested upland catchments in NE Scotland, *Hydrol. Process.*, 25(10), 1647–1658, doi:10.1002/hyp.7925, 2011.
- 27 Dinsmore, K. J., Billett, M. F., Skiba, U. M., Rees, R. M., Drewer, J. and Helfter, C.: Role of the aquatic pathway
28 in the carbon and greenhouse gas budgets of a capeatland tchment, *Glob. Change Biol.*, 16(10), 2750–2762,
29 doi:10.1111/j.1365-2486.2009.02119.x, 2010.
- 30 Dormann, C. F., Elith, J., Bacher, S., Buchmann, C., Carl, G., Carré, G., Marquéz, J. R. G., Gruber, B.,
31 Lafourcade, B., Leitão, P. J., Münkemüller, T., McClean, C., Osborne, P. E., Reineking, B., Schröder, B.,
32 Skidmore, A. K., Zurell, D. and Lautenbach, S.: Collinearity: a review of methods to deal with it and a simulation
33 study evaluating their performance, *Ecography*, 36(1), 27–46, doi:10.1111/j.1600-0587.2012.07348.x, 2013.

- 1 Downing, B. D., Pellerin, B. A., Bergamaschi, B. A., Saraceno, J. F. and Kraus, T. E. C.: Seeing the light: The
2 effects of particles, dissolved materials, and temperature on in situ measurements of DOM fluorescence in rivers
3 and streams, *Limnol. Oceanogr. Methods*, 10(10), 767–775, doi:10.4319/lom.2012.10.767, 2012.
- 4 Drake, T. W., Raymond, P. A. and Spencer, R. G. M.: Terrestrial carbon inputs to inland waters: A current
5 synthesis of estimates and uncertainty, *Limnol. Oceanogr. Lett.*, n/a-n/a, doi:10.1002/lol2.10055, 2017.
- 6 Dyson, K. E., Billett, M. F., Dinsmore, K. J., Harvey, F., Thomson, A. M., Piirainen, S. and Kortelainen, P.:
7 Release of aquatic carbon from two peatland catchments in E. Finland during the spring snowmelt period,
8 *Biogeochemistry*, 103(1), 125–142, doi:10.1007/s10533-010-9452-3, 2011.
- 9 Fenner, N. and Freeman, C.: Drought-induced carbon loss in peatlands, *Nat. Geosci.*, 4(12), 895–900,
10 doi:10.1038/ngeo1323, 2011.
- 11 Fraser, C. J. D., Roulet, N. T. and Lafleur, M.: Groundwater flow patterns in a large peatland, *J. Hydrol.*, 246(1–
12 4), 142–154, doi:10.1016/S0022-1694(01)00362-6, 2001.
- 13 Freeman, C., Ostle, N. and Kang, H.: An enzymic “latch” on a global carbon store, *Nature*, 409(6817), 149–149,
14 doi:10.1038/35051650, 2001.
- 15 Gascoin, S. and Fanise, P.: Bernadouze meteorological data, , doi:10.6096/DV/UQITZ4, 2018.
- 16 Gascoin, S., Hagolle, O., Huc, M., Jarlan, L., Dejoux, J.-F., Szczypta, C., Marti, R. and Sánchez, R.: A snow
17 cover climatology for the Pyrenees from MODIS snow products, *Hydrol. Earth Syst. Sci.*, 19(5), 2337–2351,
18 doi:https://doi.org/10.5194/hess-19-2337-2015, 2015.
- 19 Gorham, E.: Northern Peatlands: Role in the Carbon Cycle and Probable Responses to Climatic Warming, *Ecol.*
20 *Appl.*, 1(2), 182–195, doi:10.2307/1941811, 1991.
- 21 Grayson, R. and Holden, J.: Continuous measurement of spectrophotometric absorbance in peatland streamwater
22 in northern England: implications for understanding fluvial carbon fluxes, *Hydrol. Process.*, 26(1), 27–39,
23 doi:10.1002/hyp.8106, 2012.
- 24 Groemping, U. and Matthias, L.: relaimpo: Relative Importance of Regressors in Linear Models. [online]
25 Available from: <https://CRAN.R-project.org/package=relaimpo> (Accessed 22 May 2019), 2018.
- 26 Harell, F. E.: rms: Regression Modeling Strategies. [online] Available from: [https://CRAN.R-](https://CRAN.R-project.org/package=rms)
27 [project.org/package=rms](https://CRAN.R-project.org/package=rms) (Accessed 22 May 2019), 2019.
- 28 Hendrickson, G. E. and Krieger, R. A.: Geochemistry of natural waters of the Blue Grass region, Kentucky, US
29 Govt. Print. Off., 1964.
- 30 Holdridge, L. R.: Life zone ecology., *Life Zone Ecol.*, ((rev. ed.)) [online] Available from:
31 <https://www.cabdirect.org/cabdirect/abstract/19670604180> (Accessed 23 July 2018), 1967.

- 1 Höll, B. S., Fiedler, S., Jungkunst, H. F., Kalbitz, K., Freibauer, A., Drösler, M. and Stahr, K.: Characteristics of
2 dissolved organic matter following 20years of peatland restoration, *Sci. Total Environ.*, 408(1), 78–83,
3 doi:10.1016/j.scitotenv.2009.08.046, 2009.
- 4 Hope, D., Billett, M. F. and Cresser, M. S.: A review of the export of carbon in river water: fluxes and processes,
5 *Environ. Pollut.*, 84(3), 301–324, 1994.
- 6 Hope, D., Billett, M. F. and Cresser, M. S.: Exports of organic carbon in two river systems in NE Scotland, *J.*
7 *Hydrol.*, 193(1), 61–82, doi:10.1016/S0022-1694(96)03150-2, 1997.
- 8 Hope, D., Palmer, S. M., Billett, M. F. and Dawson, J. J. C.: Carbon dioxide and methane evasion from a
9 temperate peatland stream, *Limnol. Oceanogr.*, 46(4), 847–857, doi:10.4319/lo.2001.46.4.0847, 2001.
- 10 Hribljan, J. A., Kane, E. S., Pypker, T. G. and Chimner, R. A.: The effect of long-term water table manipulations
11 on dissolved organic carbon dynamics in a poor fen peatland, *J. Geophys. Res. Biogeosciences*, 119(4), 577–595,
12 doi:10.1002/2013JG002527, 2014.
- 13 Jager, D. F., Wilmking, M. and Kukkonen, J. V. K.: The influence of summer seasonal extremes on dissolved
14 organic carbon export from a boreal peatland catchment: Evidence from one dry and one wet growing season,
15 *Sci. Total Environ.*, 407(4), 1373–1382, doi:10.1016/j.scitotenv.2008.10.005, 2009.
- 16 Jalut, G., Delibrias, G., Dagnac, J. and Mardones, M.: A palaeoecological approach to the last 21 000 years in the
17 Pyrénées: the peat bog of Freychinède (alt. 1350 m, Ariège, south France), *Palaeogeogr. Palaeoclimatol.*
18 *Palaeoecol.*, 1982.
- 19 Jeong, J.-J., Bartsch, S., Fleckenstein, J. H., Matzner, E., Tenhunen, J. D., Lee, S. D., Park, S. K. and Park, J.-H.:
20 Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream,
21 investigated by high-frequency, in situ optical measurements, *J. Geophys. Res. Biogeosciences*, 117(G3),
22 G03013, doi:10.1029/2012JG001999, 2012.
- 23 Jones, E., Oliphant, T. and Peterson, P.: *SciPy: Open Source Scientific Tools for Python*. [online] Available from:
24 <https://www.scipy.org/> (Accessed 1 July 2019), 2001.
- 25 Joosten, H. and Clarke, D.: *Wise use of mires and peatlands: background and principles including a framework*
26 *for decision-making*, International Peat Society ; International Mire Conservation Group, Jyväskylä] :
27 [Greifswald., 2002.
- 28 Juutinen, S., Väiliranta, M., Kuutti, V., Laine, A. M., Virtanen, T., Seppä, H., Weckström, J. and Tuittila, E. -S.:
29 Short-term and long-term carbon dynamics in a northern peatland-stream-lake continuum: A catchment approach,
30 *J. Geophys. Res. Biogeosciences*, 118(1), 171–183, doi:10.1002/jgrg.20028, 2013.
- 31 Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B. and Matzner, E.: Controls on the dynamics of dissolved
32 organic matter in soils: a review, *Soil Sci.*, 165(4), 277, 2000.
- 33 Kalbitz, K., Rupp, H. and Meissner, R.: N-, P- and DOC-dynamics in soil and groundwater after restoration of
34 intensively cultivated fens, in *Wetlands in Central Europe: Soil Organisms, Soil Ecological Processes and Trace*

- 1 Gas Emissions, edited by G. Broll, W. Merbach, and E.-M. Pfeiffer, pp. 99–116, Springer Berlin Heidelberg,
2 Berlin, Heidelberg., 2002.
- 3 Koehler, A.-K., Murphy, K., Kiely, G. and Sottocornola, M.: Seasonal variation of DOC concentration and
4 annual loss of DOC from an Atlantic blanket bog in South Western Ireland, *Biogeochemistry*, 95(2–3), 231–242,
5 doi:10.1007/s10533-009-9333-9, 2009.
- 6 Köhler, S. J., Buffam, I., Laudon, H. and Bishop, K. H.: Climate’s control of intra-annual and interannual
7 variability of total organic carbon concentration and flux in two contrasting boreal landscape elements, *J.*
8 *Geophys. Res. Biogeosciences*, 113(G3), doi:10.1029/2007JG000629, 2008.
- 9 Laudon, H., Köhler, S. and Buffam, I.: Seasonal TOC export from seven boreal catchments in northern Sweden,
10 *Aquat. Sci.*, 66(2), 223–230, doi:10.1007/s00027-004-0700-2, 2004.
- 11 Leach, J. A., Larsson, A., Wallin, M. B., Nilsson, M. B. and Laudon, H.: Twelve year interannual and seasonal
12 variability of stream carbon export from a boreal peatland catchment, *J. Geophys. Res. Biogeosciences*, 121(7),
13 2016JG003357, doi:10.1002/2016JG003357, 2016.
- 14 Ledesma, J. L. J., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., Laudon, H., Bishop, K.
15 H. and Köhler, S. J.: Towards an Improved Conceptualization of Riparian Zones in Boreal Forest Headwaters,
16 *Ecosystems*, 1–19, doi:10.1007/s10021-017-0149-5, 2017.
- 17 Leifeld, J. and Menichetti, L.: The underappreciated potential of peatlands in global climate change mitigation
18 strategies, *Nat. Commun.*, 9(1), 1071, doi:10.1038/s41467-018-03406-6, 2018.
- 19 Leroy, F., Gogo, S., Guimbaud, C., Bernard-Jannin, L., Hu, Z. and Laggoun-Défarge, F.: Vegetation composition
20 controls temperature sensitivity of CO₂ and CH₄ emissions and DOC concentration in peatlands, *Soil Biol.*
21 *Biochem.*, 107, 164–167, doi:10.1016/j.soilbio.2017.01.005, 2017.
- 22 Limpens, J., Berendse, F., Blodau, C., Canadell, J. G., Freeman, C., Holden, J., Roulet, N., Rydin, H. and
23 Schaeppman-Strub, G.: Peatlands and the carbon cycle: from local processes to global implications—a synthesis,
24 *Biogeosciences*, 5(5), 1475–1491, 2008.
- 25 Maloszewski, P., Rauert, W., Stichler, W., and Herrman, A.: Application for flow models in an alpine catchment
26 area using tritium and deuterium data, *J. Hydrol.*, 66, 319–330, 1983
- 27 McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M., Hart, S. C., Harvey, J.
28 W., Johnston, C. A., Mayorga, E., McDowell, W. H. and Pinay, G.: Biogeochemical Hot Spots and Hot Moments
29 at the Interface of Terrestrial and Aquatic Ecosystems, *Ecosystems*, 6(4), 301–312, doi:10.1007/s10021-003-
30 0161-9, 2003.
- 31 Millet, L., Rius, D., Galop, D., Heiri, O. and Brooks, S. J.: Chironomid-based reconstruction of Lateglacial
32 summer temperatures from the Ech palaeolake record (French western Pyrenees), *Palaeogeogr. Palaeoclimatol.*
33 *Palaeoecol.*, 315–316, 86–99, doi:10.1016/j.palaeo.2011.11.014, 2012.

- 1 Moore, S., Evans, C. D., Page, S. E., Garnett, M. H., Jones, T. G., Freeman, C., Hooijer, A., Wiltshire, A. J.,
2 Limin, S. H. and Gauci, V.: Deep instability of deforested tropical peatlands revealed by fluvial organic carbon
3 fluxes, *Nature*, 493(7434), 660–663, doi:10.1038/nature11818, 2013.
- 4 Moore, T. R.: Dissolved iron and organic matter in northern peatlands, *Soil Sci.*, 145(1), 70, 1988.
- 5 Müller, D., Warneke, T., Rixen, T., Müller, M., Jamahari, S., Denis, N., Mujahid, A. and Notholt, J.: Lateral
6 carbon fluxes and CO₂ outgassing from a tropical peat-draining river, *Biogeosciences*, 12(20), 5967–5979,
7 doi:<https://doi.org/10.5194/bg-12-5967-2015>, 2015.
- 8 Nichols, J. E. and Peteet, D. M.: Rapid expansion of northern peatlands and doubled estimate of carbon storage,
9 *Nat. Geosci.*, 1–5, doi:10.1038/s41561-019-0454-z, 2019.
- 10 Olefeldt, D. and Roulet, N. T.: Effects of permafrost and hydrology on the composition and transport of dissolved
11 organic carbon in a subarctic peatland complex, *J. Geophys. Res. Biogeosciences*, 117(G1),
12 doi:10.1029/2011JG001819, 2012.
- 13 de Oliveira, G., Bertone, E., Stewart, R., Awad, J., Holland, A., O'Halloran, K. and Bird, S.: Multi-Parameter
14 Compensation Method for Accurate In Situ Fluorescent Dissolved Organic Matter Monitoring and Properties
15 Characterization, *Water*, 10(9), 1146, doi:10.3390/w10091146, 2018.
- 16 Page, S. E., Rieley, J. O. and Banks, C. J.: Global and regional importance of the tropical peatland carbon pool,
17 *Glob. Change Biol.*, 17(2), 798–818, doi:10.1111/j.1365-2486.2010.02279.x, 2011.
- 18 Pastor, J., Solin, J., Bridgham, S. D., Updegraff, K., Harth, C., Weishampel, P. and Dewey, B.: Global warming
19 and the export of dissolved organic carbon from boreal peatlands, *Oikos*, 100(2), 380–386, doi:10.1034/j.1600-
20 0706.2003.11774.x, 2003.
- 21 Posavec, K., Giacometti, M., Materazzi, M. and Birk, S.: Method and Excel VBA Algorithm for Modeling Master
22 Recession Curve Using Trigonometry Approach, *Groundwater*, n/a-n/a, doi:10.1111/gwat.12549, 2017.
- 23 Python Software Foundation: Python.org, Python Software Foundation. [online] Available from:
24 <https://www.python.org/> (Accessed 24 June 2019), 2019.
- 25 Quinton, W. L., Hayashi, M., & Carey, S. K. (2008). Peat hydraulic conductivity in cold regions and its relation
26 to pore size and geometry. *Hydrological Processes: An International Journal*, 22(15), 2829-2837.
- 27 R Core team: R: A Language and Environment for Statistical Computing., [online] Available from:
28 <https://www.r-project.org/> (Accessed 18 March 2019), 2019.
- 29 Raymond, P. A., Saiers, J. E. and Sobczak, W. V.: Hydrological and biogeochemical controls on watershed
30 dissolved organic matter transport: pulse-shunt concept, *Ecology*, 97(1), 5–16, doi:10.1890/14-1684.1, 2016.
- 31 Reille, M.: Nouvelles recherches pollenanalytiques à Freychinède, Pyrénées ariegoises, France, *Lab. Bot. Hist.*
32 *Palynol.* Novembre 1990 Pp 1-10 Annex., 1990.

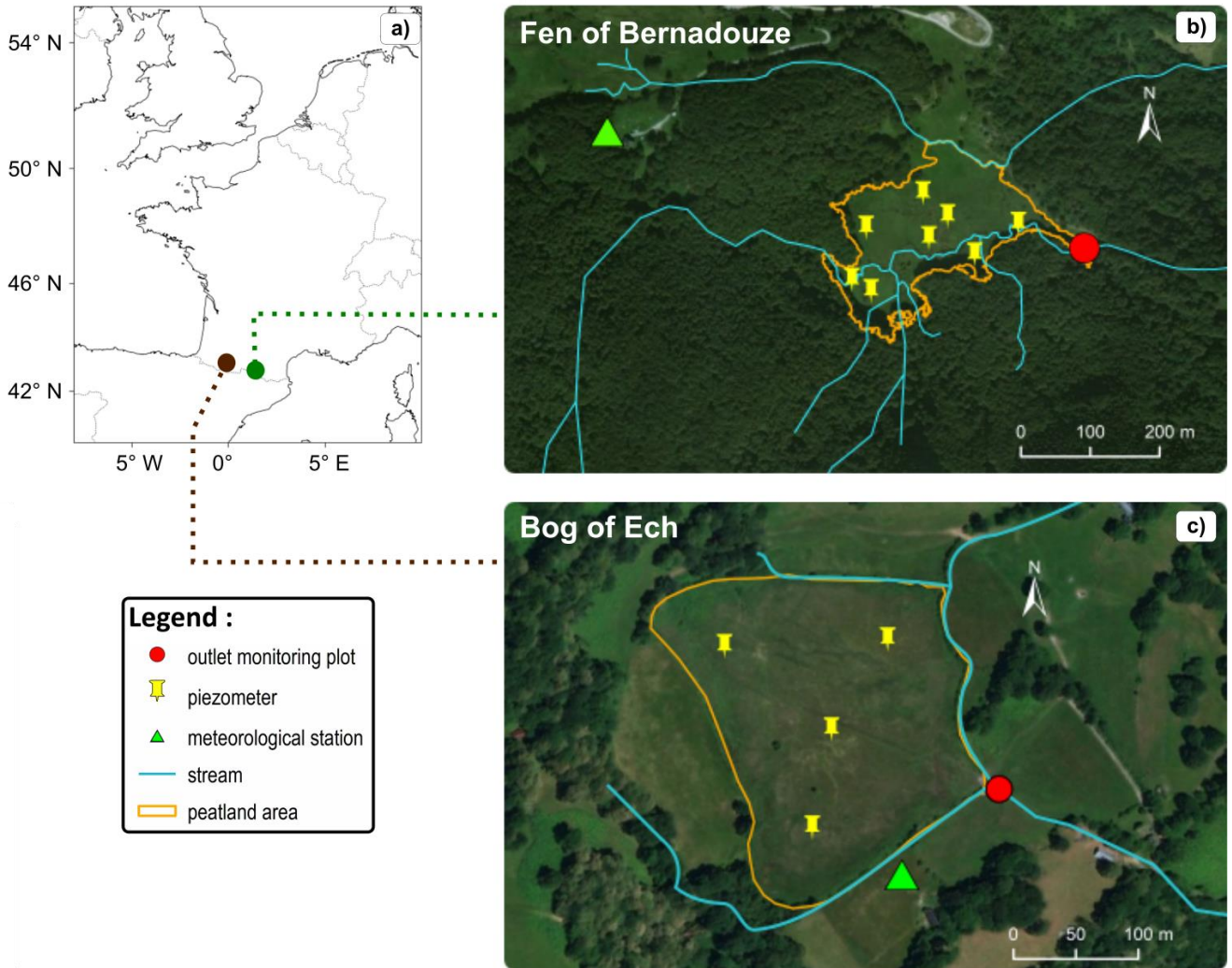
- 1 Ritson, J. P.: The impact of climate change and management practices on dissolved organic carbon (DOC) flux
2 and drinking water treatment in peatland catchments., 2015.
- 3 Ritson, J. P., Brazier, R. E., Graham, N. J. D., Freeman, C., Templeton, M. R. and Clark, J.: The effect of drought
4 on dissolved organic carbon (DOC) release from peatland soil and vegetation sources, *Biogeosciences Discuss.*,
5 (10.5194/bg-2016-517) [online] Available from: <http://dx.doi.org/10.5194/bg-2016-517> (Accessed 30 January
6 2017), 2017.
- 7 Rius, D., Vanni re, B. and Galop, D.: Holocene history of fire, vegetation and land use from the central Pyrenees
8 (France), *Quat. Res.*, 77(01), 54–64, doi:10.1016/j.yqres.2011.09.009, 2012.
- 9 Rode, M., Wade, A. J., Cohen, M. J., Hensley, R. T., Bowes, M. J., Kirchner, J. W., Arhonditsis, G. B., Jordan,
10 P., Kronvang, B., Halliday, S. J., Skeffington, R. A., Rozemeijer, J. C., Aubert, A. H., Rinke, K. and Jomaa, S.:
11 Sensors in the Stream: The High-Frequency Wave of the Present, *Environ. Sci. Technol.*, 50(19), 10297–10307,
12 doi:10.1021/acs.est.6b02155, 2016.
- 13 Rodgers P., Soulsby C., Waldron S., Tetzlaff D.: Using stable isotope tracers to assess hydrological flowpaths,
14 residence times and landscape influences in a nested mesoscale catchment. *Hydrology and Earth System Sciences*
15 *Discussions*, European Geosciences Union, 2005, 9 (3), pp.139-155.
- 16 Rosset, T., Gandois, L., Le Roux, G., Teisserenc, R., Durantez Jimenez, P., Camboulive, T. and Binet, S.:
17 Peatland contribution to stream organic carbon exports from a montane watershed, *J. Geophys. Res.*
18 *Biogeosciences*, 2019.
- 19 Rothwell, J. J., Evans, M. G., Daniels, S. M. and Allott, T. E. H.: Baseflow and stormflow metal concentrations
20 in streams draining contaminated peat moorlands in the Peak District National Park (UK), *J. Hydrol.*, 341(1), 90–
21 104, doi:10.1016/j.jhydrol.2007.05.004, 2007.
- 22 Roulet, N. T., Lafleur, P. M., Richard, P. J. H., Moore, T. R., Humphreys, E. R. and Bubier, J.: Contemporary
23 carbon balance and late Holocene carbon accumulation in a northern peatland, *Glob. Change Biol.*, 13(2), 397–
24 411, doi:10.1111/j.1365-2486.2006.01292.x, 2007.
- 25 Rycroft, D. W., Williams, D. J. A. and Ingram, H. A. P.: The Transmission of Water Through Peat: I. Review, *J.*
26 *Ecol.*, 63(2), 535–556, doi:10.2307/2258734, 1975.
- 27 Ryder, E., de Eyto, E., Dillane, M., Poole, R. and Jennings, E.: Identifying the role of environmental drivers in
28 organic carbon export from a forested peat catchment, *Sci. Total Environ.*, 490, 28–36,
29 doi:10.1016/j.scitotenv.2014.04.091, 2014.
- 30 Scharlemann, J. P., Tanner, E. V., Hiederer, R. and Kapos, V.: Global soil carbon: understanding and managing
31 the largest terrestrial carbon pool, *Carbon Manag.*, 5(1), 81–91, doi:10.4155/cmt.13.77, 2014.
- 32 Spencer, R. G. M., Aiken, G. R., Dornblaser, M. M., Butler, K. D., Holmes, R. M., Fiske, G., Mann, P. J. and
33 Stubbins, A.: Chromophoric dissolved organic matter export from U.S. rivers, *Geophys. Res. Lett.*, 40(8), 1575–
34 1579, doi:10.1002/grl.50357, 2013.

- 1 Strack, M. and Zuback, Y. C. A.: Annual carbon balance of a peatland 10 yr following restoration,
2 *Biogeosciences*, 10(5), 2885–2896, doi:10.5194/bg-10-2885-2013, 2013.
- 3 Strack, M., Waddington, J. M., Bourbonniere, R. A., Buckton, E. L., Shaw, K., Whittington, P. and Price, J. S.:
4 Effect of water table drawdown on peatland dissolved organic carbon export and dynamics, *Hydrol. Process.*,
5 22(17), 3373–3385, doi:10.1002/hyp.6931, 2008.
- 6 Strohmeier, S., Knorr, K.-H., Reichert, M., Frei, S., Fleckenstein, J. H., Peiffer, S. and Matzner, E.:
7 Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high
8 frequency measurements, *Biogeosciences*, 10(2), 905–916, doi:10.5194/bg-10-905-2013, 2013.
- 9 Tipping, E., Smith, E. J., Lawlor, A. J., Hughes, S. and Stevens, P. A.: Predicting the release of metals from
10 ombrotrophic peat due to drought-induced acidification, *Environ. Pollut.*, 123(2), 239–253, doi:10.1016/S0269-
11 7491(02)00375-5, 2003.
- 12 Tipping, E., Billett, M. F., Bryant, C. L., Buckingham, S. and Thacker, S. A.: Sources and ages of dissolved
13 organic matter in peatland streams: evidence from chemistry mixture modelling and radiocarbon data,
14 *Biogeochemistry*, 100(1–3), 121–137, doi:10.1007/s10533-010-9409-6, 2010.
- 15 Tranvik, L. J. and Jansson, M.: Climate change (Communication arising): Terrestrial export of organic carbon,
16 *Nature*, 415(6874), 861–862, doi:10.1038/415861b, 2002.
- 17 Tunaley, C., Tetzlaff, D., Lessels, J. and Soulsby, C.: Linking high-frequency DOC dynamics to the age of
18 connected water sources, *Water Resour. Res.*, 52(7), 5232–5247, doi:10.1002/2015WR018419, 2016.
- 19 Tunaley, C., Tetzlaff, D., Wang, H. and Soulsby, C.: Spatio-temporal diel DOC cycles in a wet, low energy,
20 northern catchment: Highlighting and questioning the sub-daily rhythms of catchment functioning, *J. Hydrol.*,
21 563, 962–974, doi:10.1016/j.jhydrol.2018.06.056, 2018.
- 22 Vestgarden, L. S., Austnes, K. and Strand, L. T.: Vegetation control on DOC, DON and DIN concentrations in
23 soil water from a montane system, southern Norway, 2010.
- 24 Walling, D. E. and Foster, I. D. L.: Variations in the natural chemical concentration of river water during flood
25 flows, and the lag effect: Some further comments, *J. Hydrol.*, 26(3), 237–244, doi:10.1016/0022-1694(75)90005-
26 0, 1975.
- 27 Watras, C. J., Hanson, P. C., Stacy, T. L., Morrison, K. M., Mather, J., Hu, Y.-H. and Milewski, P.: A
28 temperature compensation method for CDOM fluorescence sensors in freshwater, *Limnol. Oceanogr. Methods*,
29 9(7), 296–301, doi:10.4319/lom.2011.9.296, 2011.
- 30 Webb, J. R., Santos, I. R., Maher, D. T. and Finlay, K.: The Importance of Aquatic Carbon Fluxes in Net
31 Ecosystem Carbon Budgets: A Catchment-Scale Review, *Ecosystems*, doi:10.1007/s10021-018-0284-7, 2018.
- 32 Whitfield, C. J., Aherne, J., Gibson, J. J., Seabert, T. A. and Watmough, S. A.: The controls on boreal peatland
33 surface water chemistry in Northern Alberta, Canada, *Hydrol. Process.*, 24(15), 2143–2155,
34 doi:10.1002/hyp.7637, 2010.

- 1 Worrall, F., Burt, T. P., Jaeban, R. Y., Warburton, J. and Shedden, R.: Release of dissolved organic carbon from
2 upland peat, *Hydrol. Process.*, 16(17), 3487–3504, doi:10.1002/hyp.1111, 2002.
- 3 Worrall, F., Burt, T. P. and Adamson, J. K.: Trends in Drought Frequency – the Fate of DOC Export From
4 British Peatlands, *Clim. Change*, 76(3–4), 339–359, doi:10.1007/s10584-006-9069-7, 2006.
- 5 Yang, L., Chang, S.-W., Shin, H.-S. and Hur, J.: Tracking the evolution of stream DOM source during storm
6 events using end member mixing analysis based on DOM quality, *J. Hydrol.*, 523, 333–341,
7 doi:10.1016/j.jhydrol.2015.01.074, 2015.
- 8 Zheng, Y., Waldron, S. and Flowers, H.: Fluvial dissolved organic carbon composition varies spatially and
9 seasonally in a small catchment draining a wind farm and felled forestry., *Sci. Total Environ.*, 626, 785–794,
10 doi:10.1016/j.scitotenv.2018.01.001, 2018.

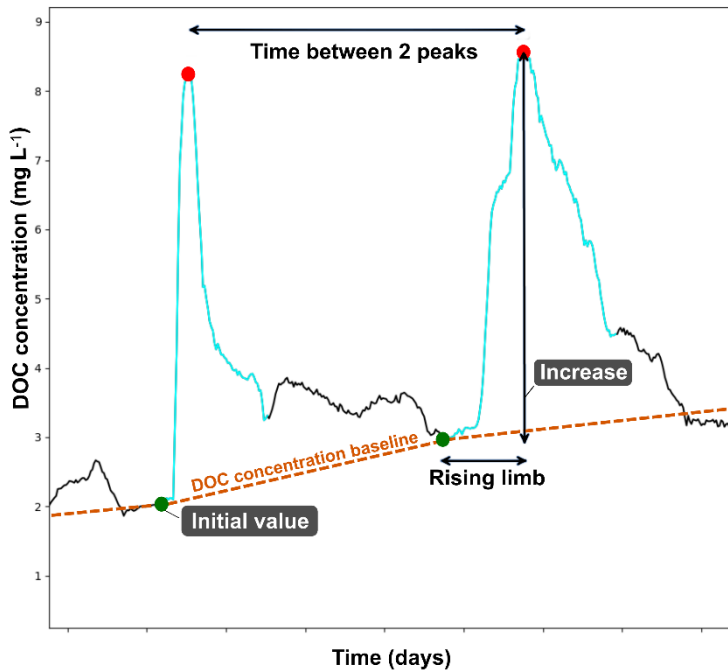
11

1



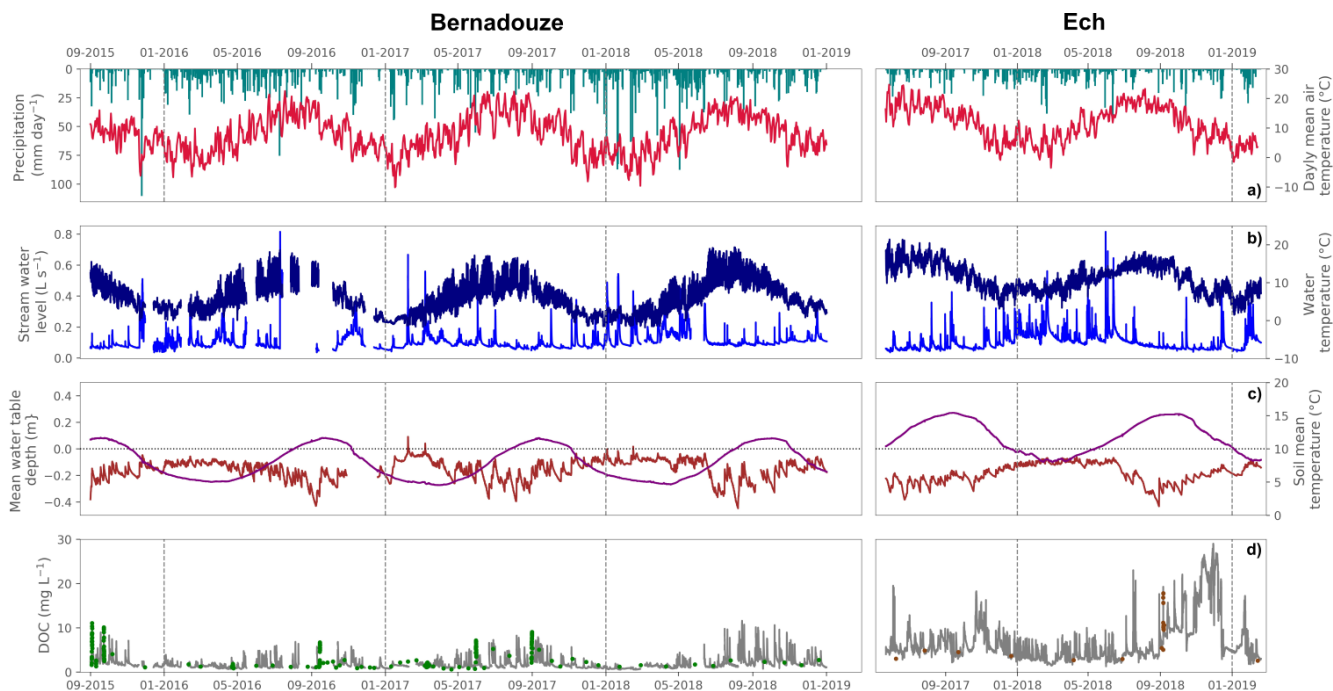
2

3 **Figure 1:** a) Location map of Ech Bog (brown plot) and Bernadouze fen (green plot) in South Western Europe. Satellite views of the
4 peatlands of b) Bernadouze (1343 m.a.s.l.) and c) Ech (706 m.a.s.l.) and location of the site instrumentation. Map source: Esri,
5 DigitalGlobe, Geoeye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo,
6 and the GIS User Community.



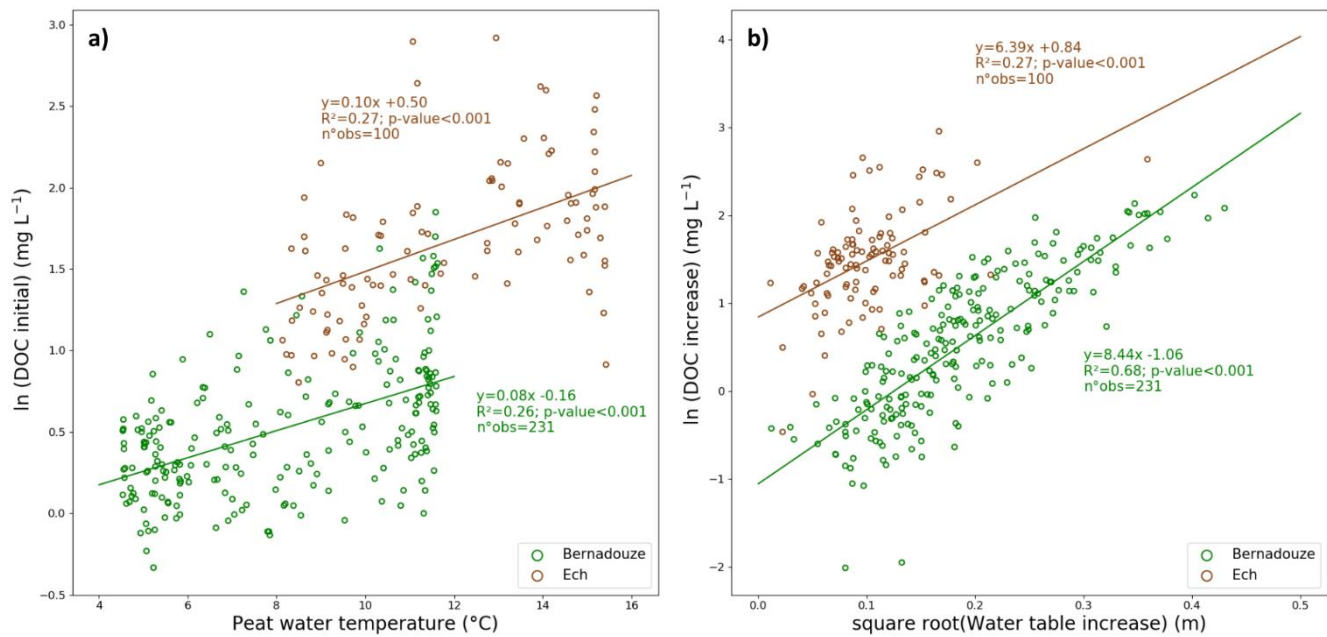
1

2 **Figure 2: Characterization of DOC concentration peaks. Peak events are identified on the DOC concentration time line in blue. Each**
 3 **DOC concentration peak event is defined by an initial concentration (green points) and a maximum one (red points). DOC**
 4 **concentration increase is calculated by subtracting the initial from the maximum concentration. The time between 2 maximum DOC**
 5 **concentrations corresponds to the duration (seconds) separating two events and is used as an explanatory variable. The DOC**
 6 **concentration baseline (orange dotted line) corresponds to the time series defined by all the initial values of each DOC concentration**
 7 **peak.**



1
 2 **Figure 3:** Precipitation and air temperature (a), stream temperature and water level (b) high frequency DOC concentration (c),
 3 mean water table depth variation and peat water temperature (d). Time series observed at the outlet of the Bernadouze fen (left
 4 panel) from 1st September 2015 to 31st December 2018, at the outlet of Ech bog (right panel) from 22nd May 2015 to 13th February
 5 2019. The vertical grey lines represent a change of year. Green (for Bernadouze) and brown (for Ech) plots in time series (c) refer
 6 to DOC concentration measured in grab water samples and automated flood samples.

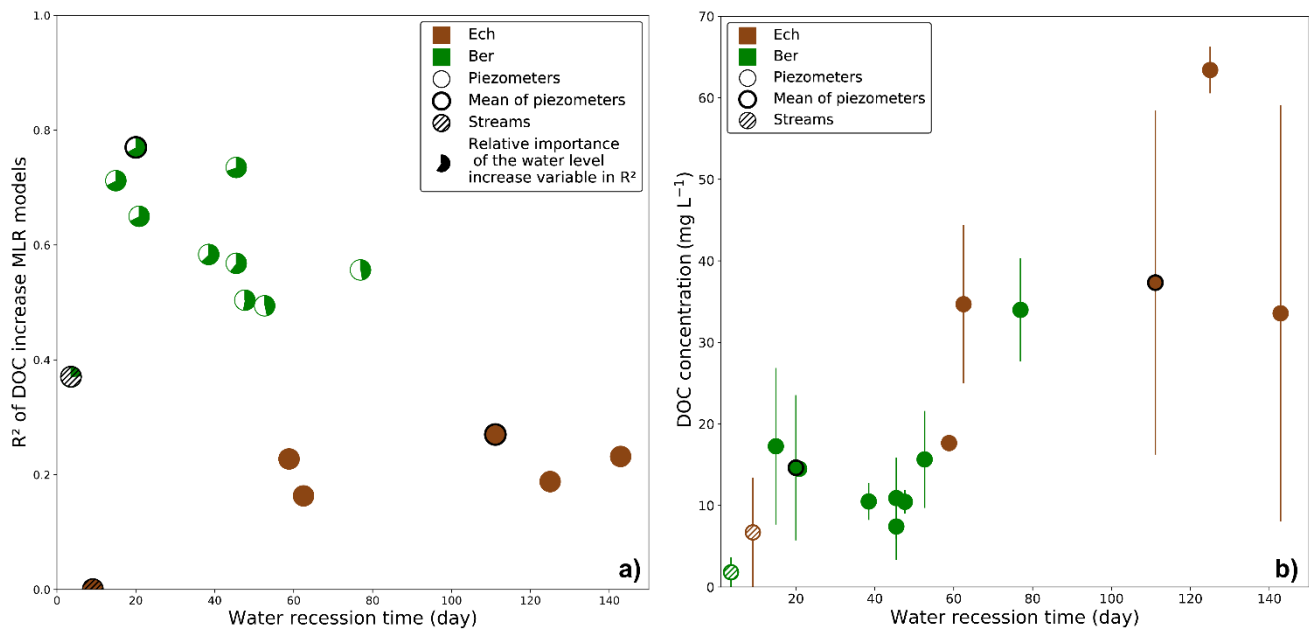
7



1

2 **Figure 4: Relationships between (a) peat water temperature and natural logarithm of DOC concentration initial value and (b) square**
 3 **root of water table increase and natural logarithm of DOC concentration increase during peak events at Bernadouze (green) and**
 4 **Ech (brown). Regression coefficients (intercept and slope), p-values and R^2 are given in each panel.**

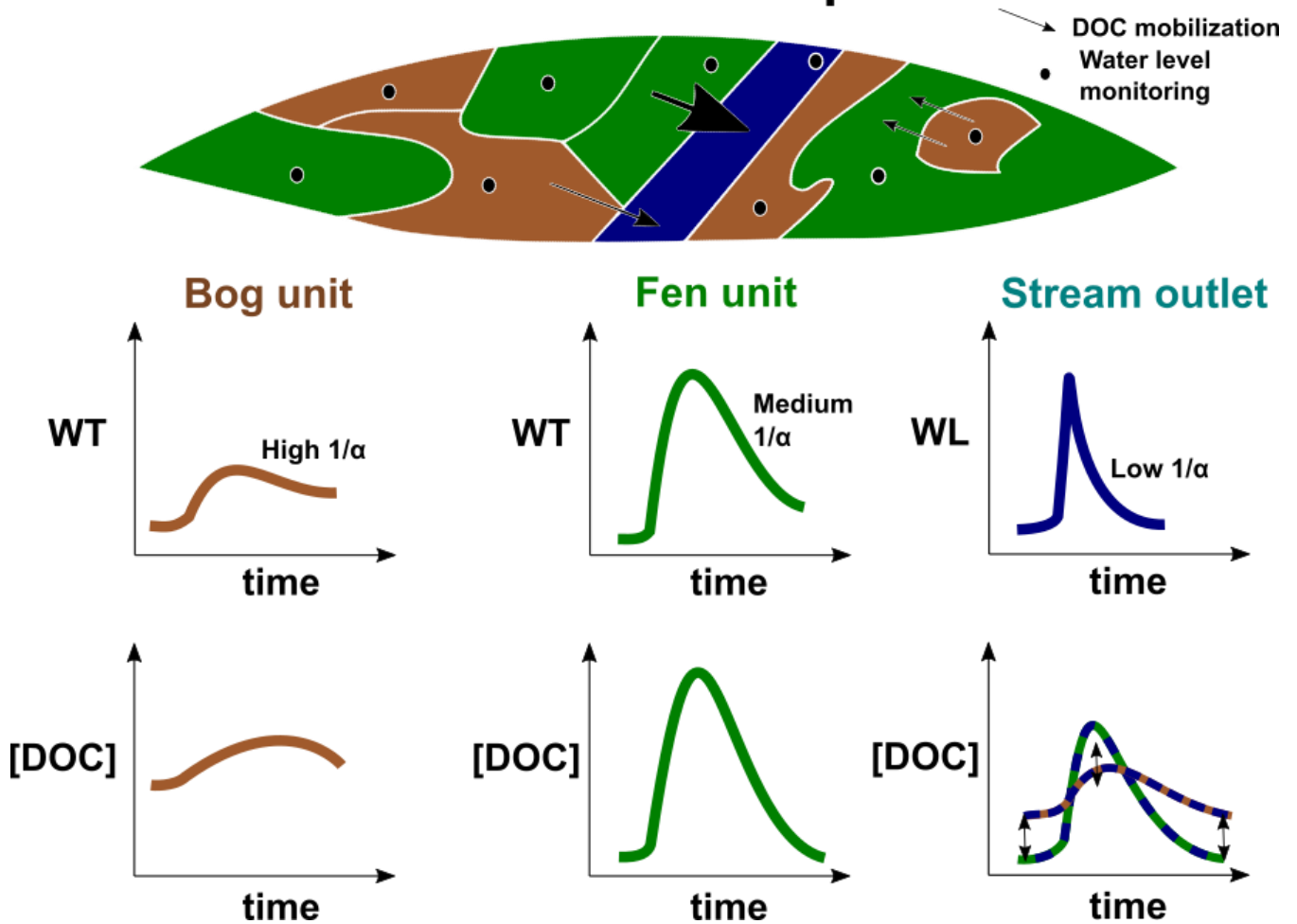
5



1

2 **Figure 5: Relationship between water recession time coefficients and a) the R² of the DOC_increase MLR models or b) the DOC**
 3 **concentration of each water level monitoring plots at the peatland of Bernadouze (green) or Ech (brown). In both graphs, p**
 4 **piezometer plots are represented by solid circles while the mean of the piezometers at each site is surrounded in black. Stream plots**
 5 **correspond to the two black striped circles in each graph. In graph a), pie charts represent the relative importance of the water level**
 6 **increase variable in the R² of each model. In graph b), a marker represents the mean DOC concentration of a plot and vertical**
 7 **segments the standard deviation.**

Peatland complex



1
 2 Figure 6: Schematic overview of a peatland complex. Size of the arrows corresponds to DOC quantity mobilized from distinct
 3 peatland units. The DOC concentration observed in the stream depends on the contribution of the different peat units within the
 4 peatland complex.

5

1 **Table 1. Targeted and explanatory variables description**

	Designation	Variable description	Hypothesis	References	Statistical transformation
Targeted variables					
Seasonal scale	DOC initial	DOC concentration at the start of a DOC peak event	Define the stream DOC concentration baseline		Logarithmic
Event scale	DOC increase	Range between DOC concentration initial value and maximum observed during a DOC peak event			Logarithmic
Explanatory variables					
Production	Time between peaks	Duration between two DOC concentration peaks	Longer intervals between peaks promote DOC production and induce higher stream DOC concentration elevations during the next rewetting	(Fenner and Freeman, 2011; Ritson et al., 2017; Worrall et al., 2006)	Logarithmic
	Air temperature 7	Weekly mean of the water temperature prior to the DOC peak event	High temperatures enhance microbial and vegetation activity which increase DOC production within the peat and DOC concentration in the stream	(Billett et al., 2006; Clark et al., 2005, 2008, 2009; Koehler et al., 2009; Pastor et al., 2003)	
	Water temperature 7	Weekly mean of the water temperature prior to the DOC peak event			
	Peat water temperature	Water temperature observed at the beginning of the DOC peak event (from the mean water temperature of the piezometers)			

	Water table initial	Water table value at the beginning of the DOC peak event (from the mean water table level of the piezometers)	Initial water table value is an indicator of the non-saturated peat depth. A lower initial water table is related to a higher volume of oxygenated peat, where most of the DOC is produced.	(Bernard-Jannin et al., 2018; Billett et al., 2006; Clark et al., 2009; Fenner and Freeman, 2011; Ritson et al., 2017; Tunaley et al., 2016)	
Transfer	Stream level increase	Stream water level increase during the DOC concentration peak	DOC concentration increases with stream water elevations	(Austnes, 2010; Ryder et al., 2014)	Square-root
	Stream level maximum	Water level maximum during the DOC peak event			logarithmic
	Precipitation	Total daily precipitation recorded during the rising period of the peak and the day prior to the DOC peak event	Precipitation triggers lateral transfer of DOC-rich water from peatland to surface water. Amount of precipitation is assumed to be representative of the surface runoff	(Raymond et al., 2016)	Square-root
	Water table increase	Water table increase during the DOC peak event (from the mean water table level of the piezometers)	Water table rise promotes DOC transfer to the stream through sub-surface flows. The greater the re-wetted peat volume (water table range), the stronger the stream DOC concentration	(Clark et al., 2009; Kalbitz et al., 2002; Strack et al., 2008)	Square-root

1

2

1 **Table 2. Time series and DOC concentration peak metrics in Bernadouze over the 1st September 2015 to 31st December 2018 period**
 2 **and in Ech over the 22nd May 2015 to 13th February 2019 period. Mean notations correspond to arithmetic means which are given**
 3 **with standard deviations.**

		Unit	Bernadouze	Ech
Time series	Days of study	Days	1218	638
	DOC data available	% time	86	99
	DOC (arithmetic mean)	mg L ⁻¹	1.8±1.2	6.7±4.9
	Discharge (arithmetic mean)	L s ⁻¹	34.1±74.2	8.4±12.0
	DOC concentration (flow weighted mean)	mg L ⁻¹	1.6	5.0
DOC concentration peaks	Number of peaks		252	101
	DOC maximum (maximum)	mg L ⁻¹	11.6	23.3
	DOC maximum (mean)		4.3±2.2	11.1±4.6
	DOC increase (maximum)		9.3	19.2
	DOC increase (mean)		2.4±1.9	5.2±3.3
	Water table increase (mean)	M	0.04±0.03	0.01±0.01
	DOC peak duration (mean)	H	32±14	28 ±16
	DOC peak rising duration (mean)		10±5	13±10
	Stream water level rising duration (mean)		10±7	12±11
	Water table rising duration (mean)		13±7	22±12
DOC concentration baseline	DOC initial (mean)	mg L ⁻¹	1,9±1.0	5,9±3.1
	Autumn		2,5±1.2	7,9±3.4
	Winter		1,7±0.7	5,3±3.5
	Spring		1,4±0.4	3,5±1.1
	Summer		1,7±0.9	5,6±1.2
	Time between peaks (Mean)	H	116±169	149±179
	Autumn		97±144	133±132
	Winter		196±221	140±219
	Spring		122±214	152±212
	Summer		105±111	180±172

1
2
3
4
5
6

Table 3. Reduced models explaining DOC concentration during peak events (DOC_initial and DOC_increase) at the outlet of Bernadouze and Ech peatlands. Reduced models were obtained after a backward stepwise selection procedure applied on the full model (See details in Methods). Adjusted R² of each model are given as the predictors and their associated coefficient, p-value and R² contribution.

Response variable	Site	Adjusted R ² of the reduced models	Reduced models			
			Coefficients	Predictors	p-value	R ² contribution
DOC initial	Bernadouze	0.55	0.62	Peat temperature water	<0.001	0.24
			-0.50	Time between peaks	<0.001	0.24
			0.16	Precipitation 1	0.002	0.02
			-0.25	Water temperature 7	<0.001	0.03
			-0.14	Stream level increase	0.009	0.02
	Ech	0.44	0.84	Peat temperature water	<0.001	0.32
			0.24	Time	0.004	0.05
			-0.33	Water temperature 7	0.004	0.04
0.16			Precipitation 1	0.017	0.03	
DOC increase	Bernadouze	0.77	0.74	Water table increase	<0.001	0.52
			0.26	Water temperature 7	<0.001	0.17
			0.09	Stream level increase	0.019	0.07
			-0.14	Time between peaks	<0.001	0.02
	Ech	0.27	0.52	Water table increase	<0.001	0.27

7