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Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment

Thibault Lambert,[1] Anne-Catherine Pierson-Wickmann,[1] Gérard Gruau,[1] Anne Jaffrezic,[1,2] Patrice Petitjean,[1] Jean-Noël Thibault,[3] and Laurent Jeanneau[1]

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[1] To obtain better constraints on the control of seasonal hydrological variations on dissolved organic carbon (DOC) dynamics in headwater catchments, we combined hydrometric monitoring with high-frequency analyses of DOC concentration and DOC chemical composition (specific UV adsorption, $\delta^{13}C$) in soil and stream waters during one complete hydrological cycle in a small lowland catchment of western France. We observed a succession of four hydrological periods, each corresponding to specific DOC signatures. In particular, the rise of the upland water table at the end of the rewetting period yielded to a strong increase of the specific UV absorbance (from 2.5 to 4.0 L mg C^{-1} m^{-1}) and of the $\delta^{13}C$ values (from −29 to −27‰) of the soil DOC. Another striking feature was the release of large amounts of DOC during reduction of soil Fe-oxyhydroxides at the end of the high-flow period. Comparison of hydrometric data with DOC composition metrics showed that soils from the upland domains were rapidly DOC depleted after the rise of the water table in these domains, whereas wetland soils acted as quasi-infinite DOC sources. Results from this study showed that the composition and ultimate source of the DOC exported to the stream will depend on the period within the annual hydrological cycle. However, we found that the aromatic DOC component identified during the high-flow period will likely represent the dominant DOC component in stream waters on an annual basis, because most of the annual stream DOC flux is exported during such periods.

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1. Introduction

[2] In streams draining headwater catchments, most of the dissolved organic carbon (DOC) is thought to be primarily of external (allochthonous) origin, resulting from the interaction between biogeochemical and hydrological processes in soils [*Hornberger et al*., 1994; *Schiff et al*., 1997; *Aitkenhead et al*., 1999; *Laudon et al*., 2004; *Sanderman et al*., 2009; *Stutter et al*., 2011]. However, there is still much debate over the details of this interaction and the way it controls DOC sources and DOC export dynamics in catchments. In earlier studies carried out on snow-covered alpine catchments, or on upland peatland catchments, the intake of allochthonous DOC to the drainage network was regarded as resulting from a simple and spatially localized two-stage process involving the production and accumulation of a homogeneous DOC component in riparian soils during the dry season due to the degradation of soil organic matter (SOM) by heterotrophic bacteria, followed by its passive export by drainage during the wet season [*Hornberger et al*., 1994; *Boyer et al*., 1996, 1997, 2000; *Brooks et al*., 1999; *Tipping et al*., 1999]. More recent studies, however, have called this conceptual model into question by showing that (i) the age and composition of the DOC delivered to streams could vary on an intra-annual basis [*Neff et al*., 2006; *Sanderman et al*., 2008, 2009] and (ii) the progressive decrease of DOC concentrations observed in most streams during the wet season could be due to changes in DOC sources in the catchment, including the sporadic mobilization of limited, upland DOC reservoirs [*McGlynn and McDonnell*, 2003; *Sanderman et al*., 2009; *Pacific et al*., 2010], rather than to a limitation of the DOC pool stored in the riparian soils. Additionally, it has long been shown that the prolonged water logging of riparian soils, which remain an essential DOC source in most headwater catchments [*Dosskey and Bertsch*, 1994; *Hope et al*., 1994; *Laudon et al*., 2004; *Morel et al*., 2009; *Lambert et al*., 2011], could lead to the release of large amounts of DOC because of the reductive dissolution of soil Fe-oxyhydroxides [*Fiedler and Kalbitz*, 2003; *Grybos et al*.,

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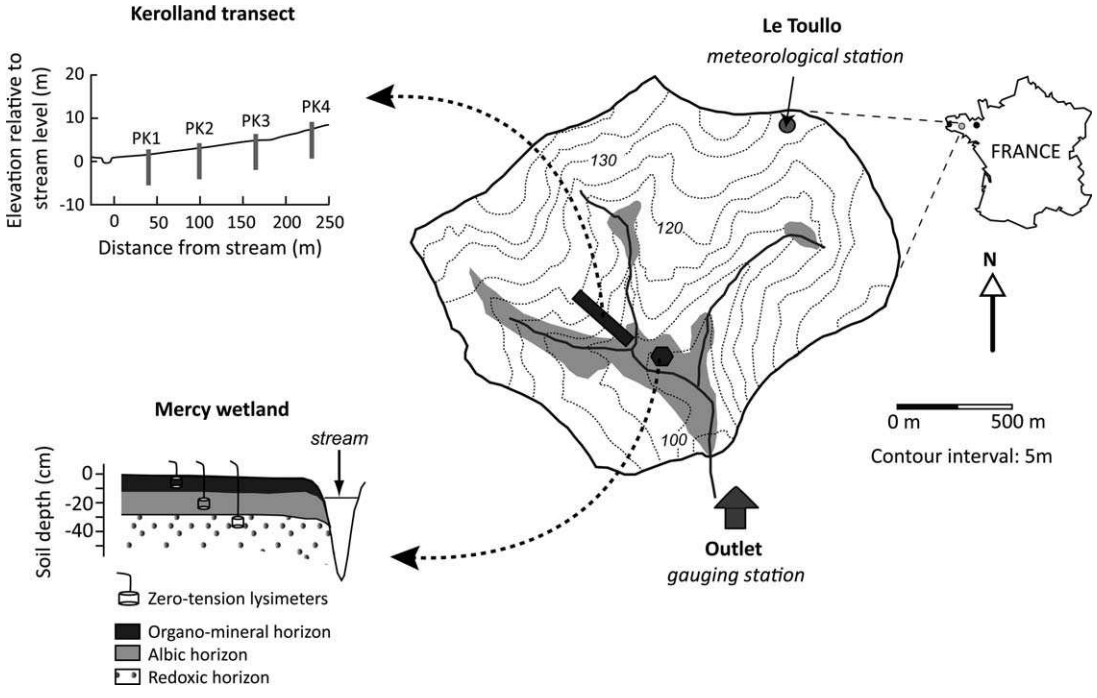


Figure 1. Location map of the Kervidy-Naizin experimental catchment (Brittany, France) showing the different instrumented sites. Gray areas located along the stream channel network indicate the maximum extent of wetland zones.

2009], thereby challenging the hypothesis of the wet period acting mainly as a passive exportation period for DOC, with no, or very little DOC production.

[3] Taken together, these results suggest that the seasonal changes in water pathways and/or water-table level in catchments could exert a hitherto unsuspected control on soil DOC dynamics, either by changing the nature of the organic material from which the DOC is produced or by activating specific biogeochemical DOC production processes depending on the period in the annual hydrological cycle. In this study, we focus on better constraining this control by investigating the variability of DOC concentration and DOC chemical composition (specific UV absorbance and $\delta^{13}C$ values) in the soil and stream waters of a small intensively instrumented lowland catchment during a complete hydrological cycle, from September 2010 to July 2011. Hydrological parameters (rainfall intensity, water table level, and stream discharge) were monitored using high-frequency hydrometric sampling, while Fe(II) concentration data were used to check variations in the redox status of the soil horizons. We use this detailed data set to (i) identify the activation of a series of distinct DOC sources and distinct DOC production processes depending on the period in the annual hydrological cycle and (ii) quantify the contributions of each of these sources and processes to the total annual DOC flux.

2. Materials and Methods

2.1. Site Description

[4] The studied area (so-called Kervidy-Naizin catchment) is a 4.9 km^2 lowland catchment located in central Brittany, western France (Figure 1), belonging to the French network of long-term Environmental Research Observatories (ORE). Numerous hydrological and biogeochemical studies [*Mérot et al*., 1995; *Durand and Torres*, 1996; *Crave and Gascuel-Odoux*, 1997; *Curmi et al*., 1998; *Dia et al*., 2000; *Molénat et al*., 2002, 2008; *Morel et al*., 2009; *Lambert et al*., 2011] have led to a relatively good knowledge of water sources and water pathways, both during base-flow and storm-flow periods, making this catchment a well-suited site for studying the relationships among hydrological conditions, soil biogeochemical processes, and stream water chemistry. The Kervidy-Naizin catchment has a temperate oceanic climate, with a mean annual (1993–2011) precipitation and mean annual runoff of 814 and 328 mm, respectively (mean annual temperature = 10.7°C). Rainfall events rarely exceed 20 mm/d, with 80% of rainfall events having an intensity of less than 4 mm/h. The stream generally dries up from the end of August to October due to the small volume of water stored in the bedrock. The high-flow stage generally lasts from December to April, with maximum discharges (1000–1200 L s^{-1}) occurring during February-March.

[5] Elevation ranges between 93 and 135 m above sea level, with hillslope gradients of less than 5%. The bedrock is made up of fissured and fractured Brioverian schists. Soils are silty loams, with depths ranging from 0.5 to 1.5 m, and are classified as Luvisols. Typically, the soil system can be subdivided into two domains depending on water-table fluctuations: (i) a hillslope domain where the water table remains always a few meters below the soil surface, consisting of well-drained soils associated with essentially vertical water pathways and (ii) a wetland domain where the water table usually reaches the soil surface during the wet season (winter and spring), leading to the development

of hydromorphic soils because of seasonal waterlogging [*Curmi et al*., 1998], with water pathways changing from vertical in autumn and spring to horizontal in winter.

[6] In the Kervidy-Naizin catchment, soil organic carbon (SOC) concentrations exhibit two superimposed spatial gradients, including a strong decrease with depth coupled to a progressive decline with increasing distance to the stream [*Morel et al*., 2009]. The stable carbon isotopic composition of SOC ($\delta^{13}C_{SOC}$) also exhibits vertical and horizontal gradients [*Lambert et al*., 2011]. Indeed, $\delta^{13}C_{SOC}$ values decrease from the top to the base of the soil profile, with the shift increasing from the wetland (1‰) to the hillslope domains (3.5‰). In addition, the $\delta^{13}C_{SOC}$ values are lighter on average in the wetlands (from −29.8‰ to −28.9‰), as compared to the hillslope domains (from −27.0‰ to −23.5‰).

2.2. Field Instrumentation, Monitoring, and Sampling

[7] Stream discharge was recorded every minute with an automatic gauge station located at the outlet of the catchment (Figure 1). Rainfall amounts were recorded at hourly intervals at a weather station located 1400 m north of the catchment outlet. Four piezometers (PK1–PK4) installed along a topographic gradient (Kerolland transect; Figure 1) were used to monitor water-table level both in the upland (PK4) and wetland domains (PK1), each being equipped with shaft encoders connected to an integral datalogger. Water-table levels were measured every 15 min with an error ranging from 1 to 5 mm.

[8] Variations in soil water DOC concentration and composition were monitored using eight zero-tension lysimeters installed in the Mercy wetland zone (Figure 1) at 0–10 cm (organic horizon; O2, O3, and P6), 15–25 cm (albic horizon; E2, A1, A2, A3), and 35–40 cm (redoxic horizon; E3) and set up according to the method developed by *Bourrié et al*. [1999]. After a period of 1 year for equilibration, the lysimeters were sampled every 2 weeks from October 2010 to June 2011. Stream waters were collected manually near the gauge station at the outlet of the catchment. A daily frequency was used for DOC concentration monitoring, while the $\delta^{13}C_{DOC}$ variations were monitored at a lower frequency (weekly). Initially, it was also planned to monitor the SUVA value. However, for logistical and technical reasons, this monitoring could not be implemented, so the use of this compositional parameter is restricted to interpretation of the soil water data.

[9] All water samples were filtered using 0.22 μm cellulose acetate membrane filters (Millipore Millex-GV) previously rinsed twice, first with 200 mL of deionized water, then with a few milliliters of the sample itself. With this decontamination procedure, possible blank contributions of the filters to the sample DOC were negligible, being in the range 1.0 to 0.1% depending on the samples. All filtration were performed directly on site, except for the stream water samples used for $\delta^{13}C_{DOC}$ measurements that were filtered in the laboratory.

2.3. Analytical Procedures

[10] Dissolved organic carbon concentrations were determined using a total carbon analyzer (Shimadzu TOC 5050). Accuracy on DOC measurements is ±5%. Iron (II) was analyzed using the 1.10 phenantroline colorimetric method, according to AFNOR NF T90-017 [*AFNOR*, 1997], with an accuracy of 5%. Specific ultraviolet absorbance (SUVA), used as an indicator of the aromaticity of DOC [*Weishaar et al*., 2003], was calculated as the UV absorbance of a water sample at 254 nm (UV_{254}) normalized to its DOC concentration. UV_{254} absorbance measurements were performed using a UV-visible spectrophotometer (UVIKON XS, Bio-Tek), with distilled water as a blank. Possible interference due to Fe(III) absorbance at $\lambda = 254$ nm is considered negligible (<5%), based on repeated measurements of soil water extracts variably enriched in Fe(III) (SUVA = 4.04 ± 0.14 L mgC^{-1} m^{-1}; Fe(III) ranging from 1.0 to 9.9 mg L^{-1}; n = 9).

[11] The $\delta^{13}C$ value of DOC ($\delta^{13}C_{DOC}$) was determined by isotope ratio mass spectrometry at the Stable Isotope Laboratory of the PEGASE Joint Research Unit of the INRA in Saint-Gilles (France), following the method described in *Lambert et al*. [2011]. The $\delta^{13}C$ values are expressed as the relative deviation between the measured $^{13}C/^{12}C$ ratio (R_{sample}) and the $^{13}C/^{12}C$ ratio of the international standard Vienna Pee Dee Belemnite (V-PDB) ($R_{standard}$), as follows: $\delta^{13}C$ (‰) = $[(R_{sample}/R_{standard}) - 1] \times 1000$. International standards were also measured: (i) USGS 24 ($\delta^{13}C = -16.5 \pm 0.1$‰) and (ii) ANU sucrose ($\delta^{13}C = -10.5 \pm 0.1$‰). The accuracy on $\delta^{13}C$ values measured on both water and soil samples is estimated as better than ±0.2‰, based on repeated measurements.

3. Results

3.1. Hydrology

[12] Total rainfall was 698.5 mm during the studied hydrological year, with 50% of the cumulated rainfall occurring between early September and mid-November. The onset of stream flow occurred when the water table rose in the bottomland domain at the end of October. The most marked rainfall event (cumulated rainfall amount = 50.5 mm on 13 November) caused the maximum peak discharge value in the stream (676.5 L s^{-1}). It also caused the sudden rise of the water table in the upland domain, thereby abruptly increasing the hydraulic gradient between the upland and bottomland domains (Figure 2). Hillslope groundwater flow showed a marked increase from this date, associated with a period of high flow in the stream punctuated by a series of lower intensity storm events. The drawdown of the water table started by the end of February and April in the hillslope and wetland domains, respectively, and occurred more rapidly in the former domain.

[13] Three successive hydrological periods, each corresponding to different hydrological regimes for the wetland soils can be highlighted from these results (Figure 2), i.e., (i) a period of progressive rewetting of the wetland soils after the dry summer season, and of low hillslope groundwater flow and low stream discharge; (ii) a period of prolonged waterlogging of wetland soils, with the water table remaining close to the soil surface in the bottom land domains, and corresponding to high values of hillslope groundwater flow and stream discharge; and (iii) a period of drainage and progressive drying of the wetland soils, leading to the drawdown of the water table in the bottomland domains and to the marked decrease of both the hillslope groundwater flow and stream discharge. This

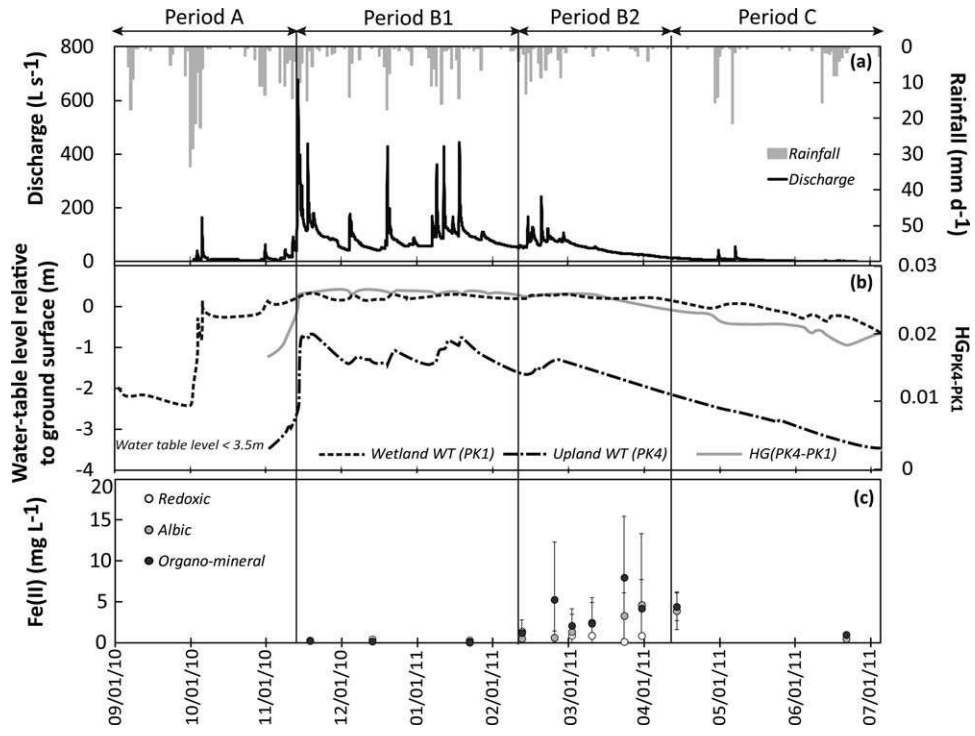


Figure 2. (a) Record of hourly discharge and daily rainfall; (b) record of hourly piezometric levels in wetland (PK1) and upland (PK4) domains (horizontal dashed line indicates local ground surface) and temporal evolution of the hydraulic gradient (HG) between the two domains (calculated as HG=(hPK4-hPK1)/L, with h the hydraulic head in the 2 piezometers and L the distance between them); (c) evolution of Fe(II) concentrations in soil lysimeters. Vertical lines delimit the four defined hydrological periods (see text for further explanation).

seasonal succession of hydrological regimes is repeated each year and is characteristic of this and other headwater catchments developed in temperate regions underlain by shallow impervious bedrock [e.g., *Molénat et al*., 2008].

[14] Hydrological period B was not homogeneous as regards the Fe(II) concentration of waters from the two uppermost soil horizons (organomineral and albic horizons), allowing its subdivision into a low-Fe(II) (period B1) and a high Fe(II) (period B2) period (Figure 2). This change in Fe(II) concentrations indicated a change in the redox status of the soil, which was oxidizing with respect to the Fe(III)-Fe(II) redox couple during period B1, then becoming reducing with respect to this couple during period B2. Note that Fe(II) concentrations always remained very low in the deep redoxic horizon, suggesting the maintenance of oxidizing redox conditions in this horizon throughout period B.

3.2. Soil Water Chemistry

[15] Dissolved organic carbon concentrations were most of the time much higher in the organomineral and albic soil horizons (>10 mg L^{-1}, as against <3 mg L^{-1} in the deep redoxic horizon), except during the beginning of period A (identical concentration of ~20 mg L^{-1} in all three soil horizons, Figure 3). DOC concentrations in the organomineral and albic horizons were also much more temporarily variable than DOC concentrations in the deeper redoxic horizon, showing a progressive decrease during periods A and B1 (from ~20–30 mg L^{-1} to ~10–15 mg L^{-1}), followed by a period of strong and rapid increase during period B2 (DOC concentrations locally as high as 50–60 mg L^{-1}); finally, there was an abrupt decrease of the concentrations at the transition between periods B2 and C (Figure 3). Quite clearly, the period of high DOC concentration observed during hydrological period B2 in the two uppermost soil horizons coincided with the development in these soil horizons of Fe-reducing conditions (Figures 2 and 3).

[16] Compositional metrics (SUVA and $\delta^{13}C_{DOC}$ values) also exhibited variations in phase with changes in hydrologic regimes. Specifically, SUVA values were low in all three soil horizons during periods A and C (i.e., 2.7 ± 0.6 L mgC^{-1} m^{-1} and 2.5 ± 0.6 L mgC^{-1} m^{-1}, respectively), but high in the shallow organomineral and albic horizons during period B (3.9 ± 0.4 L mgC^{-1} m^{-1} as against 2.5 ± 0.7 L mgC^{-1} m^{-1} in the deep redoxic horizon, Figure 4). The abrupt increase of SUVA values in the organomineral and albic horizons at the end of period A was clearly concomitant of the sudden rise of the water table in the upland domain and of the equally sudden rise that affected most DOC concentrations at that time (Figures 2–4). The transition from high to low SUVA values toward the end of period B was more progressive, even though the end of this period was characterized by a brief episode of very low SUVA values (<2.0 L mgC^{-1} m^{-1}), comparable to the values found in the underlying redoxic horizon (Figure 4).

[17] Concurrently with the SUVA variations, a marked vertical differentiation of $\delta^{13}C_{DOC}$ values was observed during period B, the two uppermost soil horizons showing

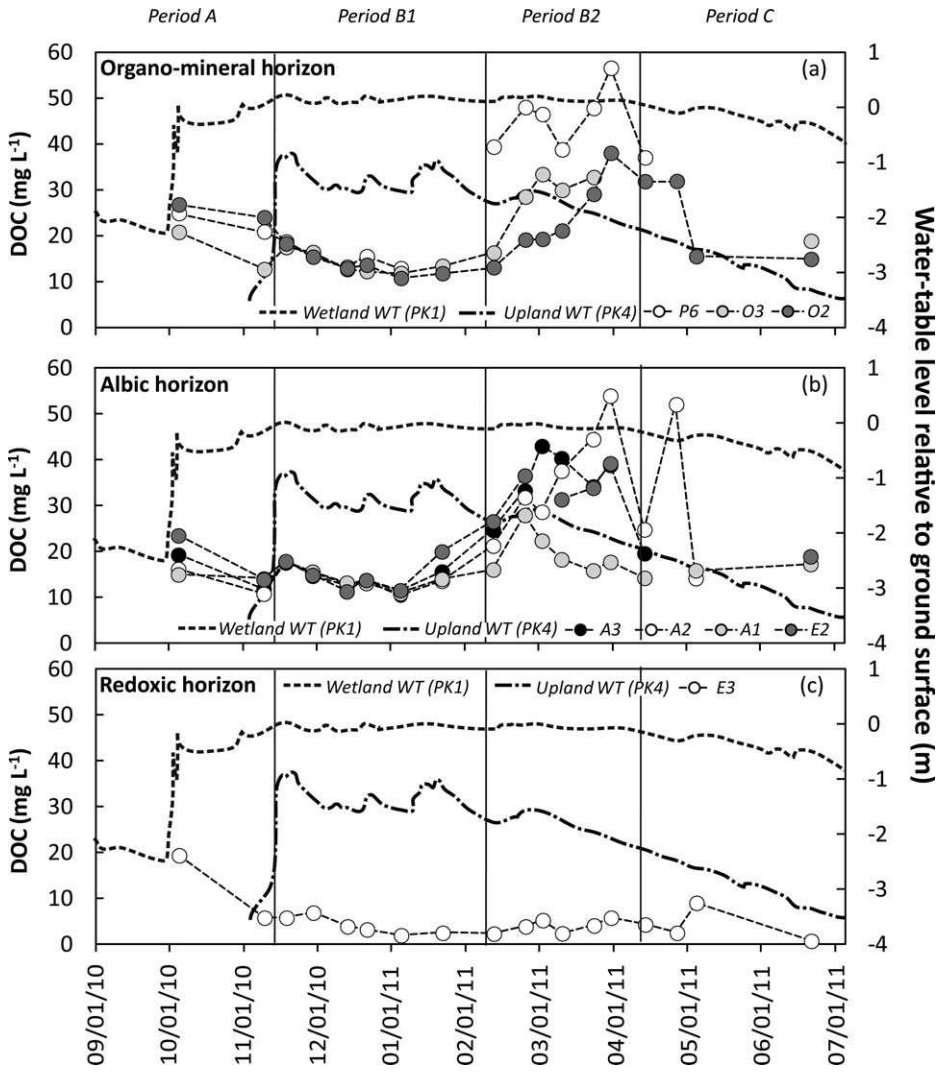


Figure 3. Seasonal trends in soil water DOC values in (a) the organomineral horizon, (b) the albic horizon, and (c) the redoxic horizon. Hourly piezometric levels in wetland (PK1) and upland (PK4) domains are plotted in the background. Vertical lines delimit the four defined hydrological periods.

comparatively lower $\delta^{13}C_{DOC}$ values (Figure 5). However, in contrast to SUVA, the shift in $\delta^{13}C_{DOC}$ did not remain constant, being maximum at the beginning of period B1 ($\sim$1.2‰), then decreasing steadily to reach zero at the end of period B2. In the same way as with SUVA values, the $\delta^{13}C_{DOC}$ values of the three soil horizons during hydrological periods A ($\delta^{13}C_{DOC} = -28.5 \pm 0.3$‰, n = 13) and C ($\delta^{13}C_{DOC} = -28.4 \pm 0.3$‰, n = 8) were comparable between horizons and from one period to another. Also as with the SUVA values, we note that the water table rise at the beginning of period B was at the origin of the profound modification of the $\delta^{13}C_{DOC}$ profile that occurred at that time. A detailed inspection of the data shows that two successive modifications were recorded (Figure 5), including a sudden decrease by $\sim$0.8‰ of the $\delta^{13}C_{DOC}$ values that converged all toward a common, low value ($\delta^{13}C_{DOC} = -29.1 \pm 0.2$‰; n = 8), followed by a general rise of the $\delta^{13}C_{DOC}$ values about 1 week later, the amplitude of this rise being much higher in the deep redoxic horizon (1.8‰) than in the shallower albic and organomineral horizons (between 0.5 and 0.7‰, respectively).

3.3. Stream Water Chemistry

[18] Rainfall events caused large increases of DOC concentrations in the stream (Figure 6), an observation consistent with the general knowledge of water pathways in this catchment that points to the predominance of a DOC-rich wetland water component during stormflow genesis [*Mérot et al*., 1995; *Durand and Torres*, 1996; *Molénat et al*., 2002; *Morel et al*., 2009; *Lambert et al*., 2011]. During periods A and B1, there was a tendency for maximum and minimum DOC concentrations in the stream to decrease, a feature resembling that displayed by soil water DOC (Figures 3 and 6). By contrast, even if period B2 corresponded to a period of high DOC concentrations in the soil, this period was not characterized by particularly high DOC concentrations in the stream.

[19] On average, base-flow $\delta^{13}C_{DOC}$ values of stream waters were higher during periods A ($\delta^{13}C_{DOC} = -27.8 \pm 0.3$‰; n = 8) and C ($\delta^{13}C_{DOC} = -27.9 \pm 0.3$‰; n = 9), than during period B ($\delta^{13}C_{DOC} = -28.4 \pm 0.5$‰; n = 15), leading to a V-shaped pattern of $\delta^{13}C_{DOC}$ variation

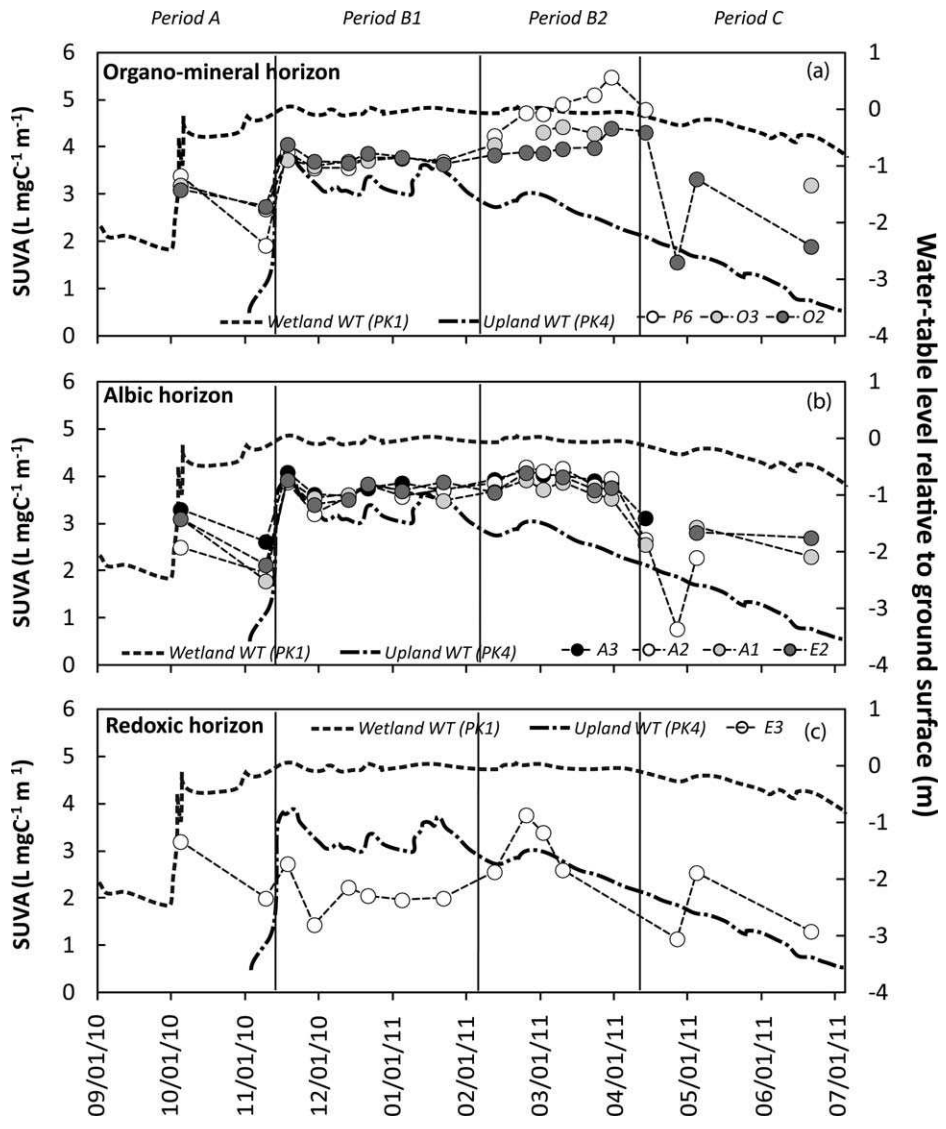


Figure 4. Seasonal trends in soil water SUVA values in (a) the organomineral horizon, (b) the albic horizon, and (c) the redoxic horizon. Hourly piezometric levels in wetland (PK1) and upland (PK4) domains are plotted in the background. Vertical dashed lines delimit the four defined hydrological periods.

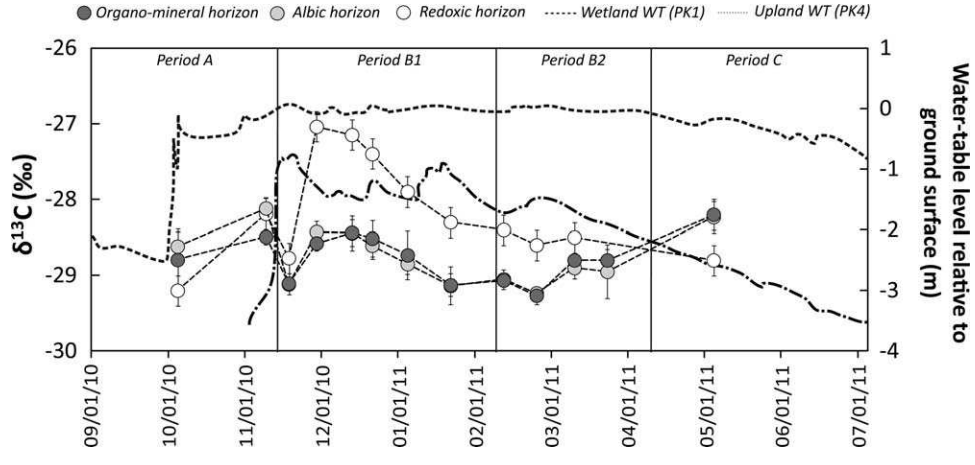


Figure 5. Seasonal evolution of soil water $\delta^{13}C_{DOC}$ values. Hourly piezometric levels in wetland (PK1) and upland (PK4) domains are plotted in the background. Vertical lines delimit the four defined hydrological periods.

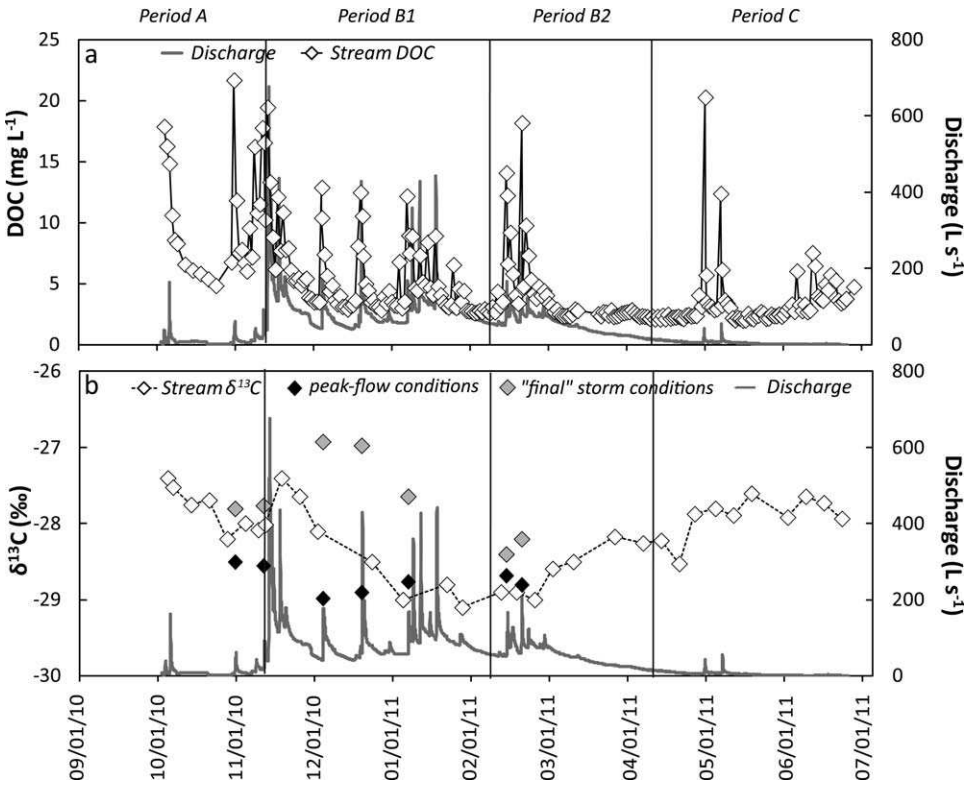


Figure 6. Seasonal trends in stream water (a) DOC concentrations and (b) $\delta^{13}C_{DOC}$ values. For $\delta^{13}C_{DOC}$ values, open diamonds represent base-flow conditions, while black and gray diamonds represent peak-flow and "final" storm conditions, respectively. Vertical lines delimit hydrological periods defined using soil hydrometric data. Hourly stream discharge is shown as solid gray line.

with time (Figure 6). There was a sudden positive shift of 0.5‰ at the transition between periods A and B. While occurring about 1 week later, this shift resembles the shift recorded by the soil water $\delta^{13}C_{DOC}$ at this transition. On average, base-flow $\delta^{13}C_{DOC}$ values were in the range of soil $\delta^{13}C_{DOC}$ values, except at the beginning of period A when the values tended to be higher than soil values by ~1‰ (Figures 5 and 6).

[20] Significant temporal trends in storm flow $\delta^{13}C_{DOC}$ values were also observed, with the values following rather closely the soil $\delta^{13}C_{DOC}$ values, particularly at the transition between periods A and B (Figure 6). Indeed, while the intrastorm variation amounted to only 0.7–0.8‰ during period A, it reached 1.9–2.1‰ at the beginning of period B1, which corresponded to the period of maximum $\delta^{13}C_{DOC}$ variability in the soil. Then, the intrastorm variability started to decline again, dropping to 0.4–0.5‰ at the end of hydrological period B2, as also observed with the variation of soil $\delta^{13}C_{DOC}$ values. Note that peak flow $\delta^{13}C_{DOC}$ values tended to be systematically lower than postpeak flow values.

4. Discussion

4.1. Linking Hydrological Variations and Soil DOC Dynamics

[21] We found that there was a significant correlation between the rise of the water table in the upland domain and the strong and sudden increase of SUVA values in the two uppermost soil horizons. More specifically, the installation of a high hydraulic gradient due to this rise led to a longlasting change in the SUVA values in these two soil horizons, with values remaining high until the progressive drawdown of the upland water table, despite strong temporal variations of the DOC concentrations. This key role of hydrology in controlling DOC concentration and DOC composition in these soil horizons is confirmed by the isotopic record. Indeed, the sudden divergence of $\delta^{13}C_{DOC}$ values observed between deep and shallow soil horizons at the transition between periods A and B also coincided clearly with the rise of the upland water-table level.

[22] We may hypothesize that these changes in DOC composition were caused by the radical changes in water pathways that occurred at the transition between each hydrological period. As shown earlier for this and other lowland catchments developed on low-permeability basement rocks [*Molénat et al*., 2002, 2008; *Martin et al*., 2004], the low streamflow periods in autumn and spring (i.e., periods A and C) correspond to periods of deep water table in upland domains. The transmissivity and hydraulic gradient of the upland water table being low, upland groundwater flow is generally limited during these periods, with the water movements remaining essentially vertical in the riparian areas. The vertical fluctuations of the wetland water table that is generated by the succession of rainy and dry episodes that characterize these periods should thus lead to a vertical homogenization of the DOC in the soil profile, both in terms of concentration and composition.

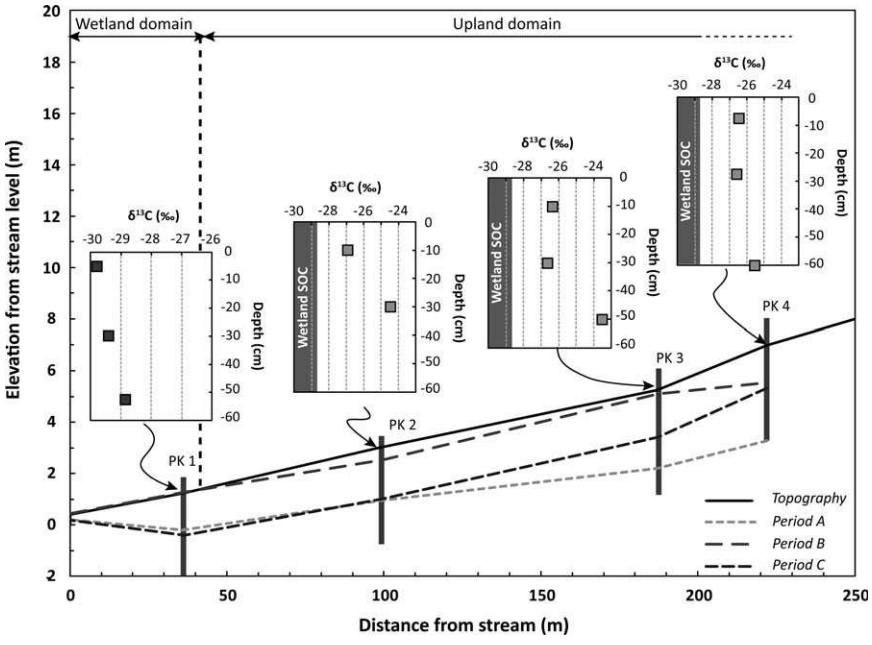


Figure 7. Block diagram comparing the seasonal evolution of the water-table level along the Mercy (wetland)–Kerolland (upland) continuum, along with the spatial variability of $\delta^{13}C$ for soil organic carbon [from *Lambert et al*., 2011]. Indicated water-table levels correspond to mean depths recorded over the hydrological periods A, B, and C.

[23] The situation was quite different during the wet season (i.e., period B). The higher hydraulic gradient induced by the rise of the upland water-table level increased the upland groundwater flow. The hydrological connection thus established between the upland and riparian domains induced a change in water pathways from a generally vertical to an essentially horizontal direction. Under these conditions, the different riparian soil horizons could become vertically isolated from one another with regard to water flow, and a vertical differentiation could develop in both DOC concentration and composition, particularly if (i) the earlier formed vertically homogeneous DOC pool was flushed away by the horizontal water flow and (ii) some DOC from upland domains was transported into the wetland soils due to the increased upland groundwater flow.

[24] The isotopic record supports the occurrence of both of these processes. Indeed, the strong $\delta^{13}C_{DOC}$ vertical gradient encountered in the Mercy soils during period B1 looks more like the gradient expected for an upland soil profile than that of a wetland soil. In fact, the $\delta^{13}C$ values of soil organic carbon (SOC) generally vary little with depth in wetland soils (usually by 1‰), while the variation is much more pronounced in upland soils (usually >2‰) [*Wynn et al*., 2006; *Schaub and Alewell*, 2009; *Lambert et al*., 2011]. In addition, a lateral gradient of $\delta^{13}C_{SOC}$ is generally observed across the wetland-upland continuum, with values in wetland soils being generally much lower on average than in the upland domain [*Schaub and Alewell*, 2009; *Lambert et al*., 2011]. Both of these features occur in the Kervidy-Naizin catchment, where analyses of upland soil SOC yield $\delta^{13}C_{SOC}$ values ranging from −27‰ to −24‰ with increasing depth, as compared to −30‰ to −29‰ for wetland soils (Figure 7) [*Lambert et al*., 2011]). Thus, both the $\delta^{13}C_{DOC}$ value > −29‰ and the strong vertical isotopic gradient recorded in the Mercy wetland soils at the beginning of period B clearly argues in favor of the input of an upland DOC component into these soils, reflecting the establishment of a hydrological connection across the riparian-upland interface at that time.

[25] Conversely, the DOC component identified in the Mercy soils during period A does not exhibit the isotopic signature typical of upland DOC. However, the mean $\delta^{13}C_{DOC}$ value obtained for this component was not strictly equivalent to the $\delta^{13}C$ signature of local SOC (−30 to 29‰ [*Lambert et al*., 2011]), particularly on 9 November 2010, when the three soil horizons yielded tightly grouped $\delta^{13}C_{DOC}$ values (-28.5 ± 0.1‰; Figure 5). In fact, it is only during the sudden rise of the groundwater table in the upland domain that the Mercy soils yielded $\delta^{13}C_{DOC}$ values in accordance with the isotopic signature of local SOC (-29.1 ± 0.1‰; Figure 5). The hypothesis proposed here is that the relatively isotopically homogeneous and heavy DOC component present in these soils during period A corresponded to a particular DOC pool of limited size, that was flushed away by the horizontal groundwater flow induced by the rise of water table in the upland domain.

4.2. Nature of DOC Sources and DOC Production Mechanisms

[26] We found that the DOC released during periods A and C was relatively homogeneous in composition throughout the soil profile and from one period to another, showing SUVA values much lower than those of the DOC released during period B in the two uppermost soil horizons (Figure 4). In most catchments, SOM turns to more aromatic in shallow soil horizons as compared to deeper ones. This explains why in catchments where SUVA values on stream waters are available, these values generally increase during

high flow when streamflow is largely sustained by groundwater passing through the upper organic-rich horizons of the soil [*Hood et al*., 2006; *Maurice et al*., 2002; *Vidon et al*., 2008; *Sanderman et al*., 2008, 2009]. The low SUVA values recorded here during periods A and C in the Mercy albic and organomineral soil horizons are at variance with this anticipated vertical pattern in SUVA values, arguing for the existence at that time of a specific DOC component in these soils, composed of poorly aromatic molecules. This component can be contrasted with the highly aromatic DOC that is released from these same horizons in cases where water flows laterally through them during period B.

[27] Since periods A and C commonly follow or comprise dry periods, this poorly aromatic DOC component could be related to the development of relatively low moisture conditions in the soil profile. Both laboratory and field studies show that DOC concentrations generally increase in soils following rewetting after dry periods [*Christ and David*, 1996; *Lundquist et al*., 1999; *Tipping et al*., 1999; *Kalbitz et al*., 2000; *Chow et al*., 2006; *Stutter et al*., 2007]. In the present case, the highest DOC concentrations in the stream were observed during the storm events after the dry summer (period A), or after the relatively dry period that developed at the beginning of period C. This coincidence highlights the possibility of enhanced DOC release during soil rewetting. Release of DOC after soil rewetting has been attributed to the solubilization of labile organic molecules derived from lyzed microbial cells [*Christ and David*, 1994, 1996], a process that would account for the low SUVA values recorded in the Mercy soil waters during periods A and C, and also perhaps for the positive shift observed at that time between $\delta^{13}C_{DOC}$ and $\delta^{13}C_{SOC}$ values. Indeed, published data have shown that the soil microbial biomass is generally ^{13}C-enriched by 2‰ compared with the total soil organic C [*Potthoff et al*., 2003; *Schwartz et al*., 2007].

[28] During the wet period (period B), groundwater flowed laterally within the riparian soils, and SUVA values were consistent with the expected changes in SOM composition with depth [*Sanderman et al*., 2008, 2009]. During this period, the DOC source consisted mainly of aromatic SOM. As suggested by *Worrall et al*. [2008], three steps could be involved in the release of aromatic DOC at that time, including (i) the microbially mediated production of DOC in soil aggregates, (ii) the diffusion of the DOC so produced toward the surface of the aggregate, and (iii) its release into mobile water that flushes the DOC away. It is noteworthy that the SUVA profiles remained essentially unchanged throughout the phase of upland DOC input. This suggests that the source and production mechanisms of this aromatic, highly processed DOC were probably essentially similar in the riparian and upland zones during this period, despite the strong variation in $\delta^{13}C$ values.

[29] A phase of strong DOC release occurred in the two uppermost soil horizons at the end of the wet period (period B2), which coincided with the establishment of Fe-reducing conditions. The release of DOC due to the reduction of soil Fe-oxyhydroxides is a classical feature of wetland soils [*Hagedorn et al*., 2000; *Olivié-Lauquet et al*., 2001; *Gruau et al*., 2004]. The exact nature of this process has been studied in the laboratory for the Mercy soils [*Grybos et al*., 2007, 2009]. Results have shown that (i) 60% of the release is due to DOC desorption caused by the pH increase that accompanies the reduction of Fe-oxyhydroxides in these soils, the remaining 40% being due to the dissolution of Fe-oxyhydroxides that strongly adsorb the DOC [*Kaiser et al*., 1996], and (ii) the process of DOC release is accompanied by an increase of the SUVA (up to $\sim$5.0 L mgC^{-1} m^{-1}), evidencing that the source pool is composed of highly aromatic organic molecules [*Grybos et al*., 2009]. Incidentally, a significant increase in SUVA value was observed in the present study as the reduction of soil Fe-oxyhydroxides proceeded (Figure 4). Clearly, this mechanism of DOC release caused by Fe reduction during period B2 must be viewed as a supplementary DOC production mechanism, superimposed on the three-step desorption/dissolution mechanism mentioned above.

[30] The establishment of Fe-reducing conditions implies that soil waters in the horizons involved were relatively confined, being isolated from the inflow of oxidizing species (mainly oxygen and nitrate) from outside. Isolation from atmospheric oxygen occurred because of the almost total absence of rain, particularly during the second half of the period (Figure 2). Regarding nitrate input, which represents an important strongly oxidizing species given the agricultural land use [*Molénat et al*., 2008], the confinement was ensured by (i) the very low vertical hydraulic conductivity of the albic horizon [*Curmi et al*., 1998], which strongly limited the upward migration of nitrate from deeper groundwaters and (ii) the onset of drawdown of the upland water table, which reduced the upland groundwater flow and thus the lateral influx of nitrate in the riparian soils [*Molénat et al*., 2008]. Thus, the activation of the "Fe-reducing" DOC release process can be viewed as resulting from the interaction between specific hydroclimatic conditions and particular pedologic characteristics, which may lead to the temporary confinement of the uppermost part of the soil profile.

[31] To summarize, our results highlight the presence of different DOC sources and different DOC production mechanisms, whose successive activation reflects a complex response of soil DOC dynamics to seasonal hydrological changes. There is no clear evidence in the studied riparian soil sequence that the annual cycle of rewetting and subsequent water saturation periods caused the progressive flushing of a single finite DOC pool of homogeneous composition that would have formed during the dry season. We observed that the poorly aromatic DOC component accumulated during the summer dry season was quickly flushed and replaced by a more aromatic DOC component, once the wet conditions have been established. We also observed that, instead of decreasing as expected in the flushing scenario, the concentration of the soil DOC even went to increase during the installation of Fe-reducing conditions.

4.3. Impact of the Seasonality of Soil Processes on Stream DOC Export

[32] Previous studies have suggested that shifts in water source and water flow path are the primary factors driving temporal changes of DOC concentration in streams draining rain-dominated catchments [*Hood et al*., 2006; *McGlynn and McDonnell*, 2003; *Inamdar et al*., 2006],

while the primary factors would the limited size of the soil DOC pools in streams draining snowmelt catchments [*Hornberger et al*., 1994; *Boyer et al*., 1996, 1997]. However, this does not necessarily mean that all DOC sources in rain-dominated catchments behave as a near-infinite DOC-source pool [*McGlynn and McDonnell*, 2003; *Pacific et al*., 2010]. In fact, *Sanderman et al*. [2009] recently provided evidence of seasonal flushing of the DOC-source pool on most of the hillslope domain of a small grassland catchment in California, a situation different from that of the riparian soils of this catchment, which behaved as a near-infinite shallow DOC source. Results from the present study point to the same contrasted situation. Evidence for a depletion of the hillslope DOC pool in the Kervidy-Naizin catchment is provided by comparing the time evolution of $\delta^{13}C_{DOC}$ values in the redoxic horizon during period B1 with variations in the upland water-table level (Figures 2 and 5). The occurrence of a rapid decrease of the $\delta^{13}C_{DOC}$ values in the redoxic horizon while the hydraulic gradient—and thus the upland groundwater flow—remained high points indeed to a rapid decrease of the upland DOC flux during this period. This decrease of the external DOC flux indicates that period B1 corresponded to a period of depletion or flushing of the upland DOC-source pool.

[33] The input of upland DOC also affected the $\delta^{13}C_{DOC}$ values of DOC in the uppermost soil horizons of the wetland domain (organomineral and albic horizons), but the impact was less marked, probably because of the combined effect of (i) a reduced isotopic difference between the DOC produced locally in these soil horizons and the external DOC produced in the upper soil horizons of the upland domains (Figure 7) and (ii) higher SOC concentrations in this part of the wetland soil profile. Interestingly, the DOC concentrations in the uppermost soil horizons of the wetland domain showed little change between the flushing of the labile component (end of period A) and the apparent end of the input of the upland DOC component (end of period B1; Figure 3). Thus, unlike the hillslope domain, the seasonal depletion of the DOC pool was moderate in the wetland domain, suggesting in turn that the wetland domain itself behaved as a near-infinite DOC-source pool. This result suggests that, as in the grassland catchment studied by *Sanderman et al*. [2009], DOC export in the Kervidy-Naizin catchment is primarily transport limited given the dominant role of shallow riparian DOC sources in contributing the bulk of the annual DOC flux [see also *Morel et al*., 2009].

[34] The seasonal flushing of the DOC source pool in the upland domains is manifest in the storm flow $\delta^{13}C_{DOC}$ record. In particular, the progressive decrease observed in the amplitude of variation of $\delta^{13}C_{DOC}$ of storm events during period B1 (Figure 6) was likely a direct consequence of this flushing. Indeed, as the DOC-upland pool became depleted, the stream waters received a decreasing proportion of DOC with upland-type isotopic signatures. This logically led to a decrease in the variability of $\delta^{13}C_{DOC}$ values and the maximum $\delta^{13}C_{DOC}$ values during storm flow. This is because local $\delta^{13}C_{DOC}$ values in wetland domains were consistently lower than in the upland domains and varied little with depth.

[35] While the $\delta^{13}C_{DOC}$ record in the soil indicated a gap of about 2 weeks between the rise of the upland water table and activation of the upland DOC-source pool, we found that the stream isotopic data (positive shift in November 2010) reflected a closer synchronism between the two events (Figure 6). One hypothesis is that the shorter response time recorded in the stream reflects the spatial discontinuity of the riparian domain, which is almost absent in the eastern part of the catchment (Figure 1). It is possible that the reduced lateral extent of the wetland domain in the eastern part of the catchment, which is due to steeper slopes, significantly decreased the subsurface travel time of the upland DOC component. This would accelerate the transfer of part of this component, which could reach the stream before reaching the more remote parts of the wetland domains. Another possibility is the existence of a bypass of the wetland domains by overland flow originating from the upland domains. This hypothesis is not to be excluded insofar as the existence of such a hydrological component has already been demonstrated in this catchment [*Durand and Torres*, 1996].

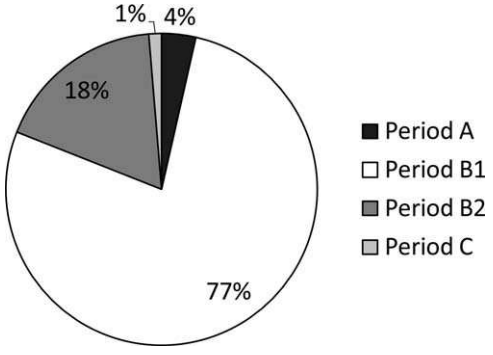


Figure 8. Relative contribution of each of the four defined hydrological periods to the total flux of DOC exported by the Kervidy-Naizin stream during the study period.

[36] Based on the high-frequency monitoring of streamflow and stream DOC concentrations, it is possible to calculate fairly accurately the amounts of DOC exported at the outlet of the Kervidy-Naizin catchment during each hydrological period. This provides quantitative estimates of the contribution of each period to the total DOC flux (Figure 8). The total annual DOC flux is estimated at 13.0 kgC^{-1} ha^{-1}, which is in the range of the DOC fluxes annually exported by temperate and boreal catchments [e.g., *Hope et al*., 1994]. Interestingly, 77% of this flux was exported during period B1, although the soil DOC concentrations during this period were the lowest values for the entire monitored hydrological year. The second most important flux occurred during period B2, representing 18% of the total annual DOC flux. On the contrary, fluxes exported during periods A and C were insignificant, representing only 4 and 1% of the total annual flux, respectively.

[37] These results clearly show that there is no direct correlation between DOC concentrations in soils and DOC fluxes in stream as evidence by period B2 with very high DOC concentrations in the upper organic-rich soil horizons but only limited contribution to the total stream DOC flux. Such a decoupling is, however, not surprising since the establishment of reducing conditions necessary to enhance the DOC concentrations requires the hydrological

confinement of the soil horizons. This implies, in turn, that reducing conditions can only develop during periods of relatively low stream flow. Reducing conditions were also favored by the absence of any major rainfall events during the considered period, which strongly decreased the amount of DOC that could be transferred to the stream, as rainfall events are known to be the main periods during which soil DOC is exported to the stream [*Hood* et al., 2006; *McGlynn and McDonnell*, 2003; *Inamdar et al*., 2006; *Sanderman et al*., 2009; *Morel et al*., 2009; *Lambert et al*., 2011]. Besides, our results show that hydrological periods A and C, during which the specific, low-SUVA DOC component was released from the soils, corresponded to episodes of insignificant DOC export. Most of the annual flux (95%) took place when the soil water was dominated by the more common, high-SUVA DOC component (period B). The establishment of dry conditions, which appear necessary for the formation of the low-SUVA DOC component, can lead to high DOC concentrations in the stream waters, as, for example, during early autumn or/and late spring storm events (Figure 6), but this component is not capable of supplying large DOC fluxes to the stream on an annual basis. This result is consistent with the apparent rapid flushing of this component from the soil during the postsummer water-table rise. In turn, this implies that wet conditions are not only required to create hydrologically favorable conditions for the export of soil DOC towards the stream but also for soil bacteria to produce the large amounts of the soil, highly processed DOC component necessary to sustain the high winter and early spring DOC fluxes.

5. Conclusion

[38] In this lowland headwater catchment with stream DOC of predominantly allochtonous origin, soil DOC was found to vary in composition and concentration both vertically and temporarily on a seasonal scale. Striking features of this variability are changes in DOC composition (SUVA and $\delta^{13}C_{DOC}$ values) between dry and wet periods, as well as the occurrence of a DOC release episode following the establishment of Fe-reducing conditions in the uppermost part of the soil profile. These changes reflect modifications in soil water pathways along with changes in the nature and location of DOC sources along the wetland-upland continuum. We have shown that the seasonal variation in upland water-table level is the main driver of these variability and changes, as evidenced by a comparison between hydrometric data and DOC parameters.

[39] Temporal variations in soil DOC concentration and chemistry thus reflect the succession of particular DOC production mechanisms and DOC pool sources, whose activation is directly related to the seasonal succession of hydrological states. During relatively dry periods of low water table level in the upland domains, DOC was found to consist mainly of poorly aromatic organic molecules—likely derived from lysed microbial cells—the latter being replaced by more aromatic, SOM-derived, highly processed DOC during wetter periods with high upland water table level. Changes in soil DOC composition and concentration were also regulated on a seasonal scale by the progressive flushing of an upland-derived DOC component—similar to the above, SOM-derived, strongly aromatic DOC—which was rapidly depleted and exported to the stream in response to the upland water-table rise. Comparison of the soil and stream data show that composition of the DOC entering the stream in this small lowland will depend on the position within the annual hydrological cycle. However, one can predict that, on average, the more aromatic, SOM-derived DOC component will be dominant on an annual basis, regardless of the interannual climatic variability. This is because this component is the main DOC product in soils during periods of high hydraulic gradient, i.e., when most of the soil DOC is exported to the stream.

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