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DOC sources and DOC transport pathways in a small headwater catchment as revealed by carbon isotope fluctuation during storm events

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Abstract. Monitoring the isotopic composition ($\delta^{13}C_{DOC}$) of dissolved organic carbon (DOC) during flood events can be helpful for locating DOC sources in catchments and quantifying their relative contribution to stream DOC flux. High-resolution (< hourly basis) $\delta^{13}C_{DOC}$ data were obtained during six successive storm events occurring during the high-flow period in a small headwater catchment in western France. Intra-storm $\delta^{13}C_{DOC}$ values exhibit a marked temporal variability, with some storms showing large variations (> 2 ‰), and others yielding a very restricted range of values (< 1 ‰). Comparison of these results with previously published data shows that the range of intra-storm $\delta^{13}C_{DOC}$ values closely reflects the temporal and spatial variation in $\delta^{13}C_{DOC}$ observed in the riparian soils of this catchment during the same period. Using $\delta^{13}C_{DOC}$ data in conjunction with hydrometric monitoring and an end-member mixing approach (EMMA), we show that (i) > 80 % of the stream DOC flux flows through the most superficial soil horizons of the riparian domain and (ii) the riparian soil DOC flux is comprised of DOC coming ultimately from both riparian and upland domains. Based on its $\delta^{13}C$ fingerprint, we find that the upland DOC contribution decreases from ca. 30 % of the stream DOC flux at the beginning of the high-flow period to < 10 % later in this period. Overall, upland domains contribute significantly to stream DOC export, but act as a size-limited reservoir, whereas soils in the wetland domains act as a near-infinite reservoir. Through this study, we show that $\delta^{13}C_{DOC}$ provides a powerful tool for tracing DOC sources and DOC transport mechanisms in headwater catchments, having a high-resolution assessment of temporal and spatial variability.

1 Introduction

Despite the significant importance of dissolved organic carbon (DOC) in aquatic ecosystems, the processes controlling DOC delivery to stream waters at the catchment scale are still poorly understood (van Verseveld et al., 2008; Pacific et al., 2010; Laudon et al., 2011). In headwater catchments, stream DOC is mainly controlled by allochthonous inputs (Aitkenhead et al., 1999; Billett et al., 2006), with most of the export occurring during snowmelt or rainfall-induced storm events (Hinton et al., 1997; Laudon et al., 2004; Inamdar et al., 2006; Dalzell et al., 2007; Raymond and Saiers, 2010). In upland snow-dominated catchments, stream DOC concentrations are commonly found to peak prior to peak discharge, followed by a rapid decrease in concentrations as snowmelt continues (i.e. Hornberger et al., 1994; Boyer et al., 1997). The resulting hysteresis relationship between stream water discharge and stream DOC concentration has been used to suggest that (i) riparian zones close to the stream network are the dominant DOC sources at the catchment scale and

(ii) the DOC transfer mechanism can be regarded as the flushing of a size-limited DOC pool located in these zones (Boyer et al., 1997; Hornberger et al., 1994). Similar hysteresis has been observed in streams draining rain-dominated catchments (e.g. Hood et al., 2006; Inamdar and Mitchell, 2006; Inamdar et al., 2006) leading to the emergence of an alternative interpretation whereby the DOC flushing process would also affect upland soils, the latter, rather than the riparian soils, being the host of the size-limited DOC pool causing the observed hysteresis (Sanderman et al., 2009; Pacific et al., 2010). To date, however, little direct evidence has been found for the involvement of such a DOC-limited upland reservoir in the stream DOC budget, and this alternative interpretation thus remains a matter of debate.

One way to resolve this issue would be to make use of an absolute tracer to distinguish between riparian-derived DOC and upland-derived DOC, and to monitor it in stream water, along with stream discharge and groundwater level. Among the different potential tracers, the stable carbon isotopes (δ^{13}C) appear particularly promising because of the dominance of aerobic conditions in the well-drained soils of upland domains. Indeed the aerobic decomposition of the soil organic matter (SOM) results in an enrichment of the heavier isotope (^{13}C) of the remaining SOM as the lighter ^{12}C is more often involved in decomposition reactions (e.g. Wynn et al., 2006). By contrast, the dominance of anoxic conditions in riparian soils limits the decomposition processes and consequently the enrichment in ^{13}C of the riparian SOM. Therefore, the δ^{13}C values of SOM in wetland soils can be expected to be lower than in upland soils. Considering that changes in the $\delta^{13}C_{SOM}$ are generally fully transmitted to soil DOC (Ziegler and Brisco, 2004; Amiotte-Suchet et al., 2007; Sanderman et al., 2009; Lambert et al., 2011), we can infer that the predicted spatial variation of δ^{13}C values for SOM should also apply to DOC, thus allowing the use of δ^{13}C to distinguish between upland and wetland DOC sources.

However, the use of carbon isotopes for this purpose is fraught with difficulties. First, the $\delta^{13}C_{SOM}$ values generally increase with soil depth (Wynn et al., 2006; Boström et al., 2007; Sanderman et al., 2009; Lambert et al., 2011). Thus, the high δ^{13}C values expected to be characteristic of upland DOC may overlap with that of deep wetland DOC. Second, seasonal changes in DOC sources and DOC production mechanisms can lead to seasonal changes in the isotopic composition of wetland DOC. For example, the release of microbial DOC may explain the DOC peaks observed in wetland soils after dry summers (Kalbitz et al., 2000). As soil micro-organisms tend to be ^{13}C-enriched by ca. 2 ‰ compared to SOM (Potthoff et al., 2003; Schwartz et al., 2007), such a mechanism could temporarily increase the δ^{13}C of the wetland DOC. Finally, to be able to supply the stream, the upland DOC component must be transported throughout the riparian domains, which occupy the interface between streams and upland zones. Consequently, isotopic mixing between wetland-derived and upland-derived DOC is expected to occur in riparian zones, thus leading to a possible scrambling of the isotopic signal.

One way to overcome these different pitfalls is to thoroughly monitor the spatial and temporal variability of the $\delta^{13}C_{DOC}$ values in the wetland domain, along with the seasonal changes in the hydrological status of the soil and water table depth. This approach has been carried out with a one-year hydrochemical monitoring in the wetland zone of the Kervidy-Naizin catchment, a lowland, rain-dominated agricultural catchment located in western France (Lambert et al., 2013). The results evidenced a strong vertical and temporal variability of the δ^{13}C values of the soil DOC, which could be used to demonstrate the input in this wetland of an upland DOC component. In the present study, we seek to investigate how the spatial and temporal variability of the $\delta^{13}C_{DOC}$ values observed at the scale of the wetland soil profile is transposed to the stream. For this purpose, DOC concentrations and $\delta^{13}C_{DOC}$ values were monitored in the stream during six successive storm events occurring over the same hydrological year covered by our first study (Lambert et al., 2013). In parallel, NO_3, SO_4 and DOC concentrations during storm events are used to deconvolve the contributing water fluxes by the end-member mixing approach (EMMA). Using this database, we want to address three issues:

1. What constraints can be obtained from the monitoring of δ^{13}C variations during storm events relative to the spatial location of DOC sources and to the nature of DOC transport mechanisms in this catchment?

2. What is the proportion of upland DOC in the stream during storm events, and does this proportion vary in relation to the succession of storm events?

3. Can carbon isotopes be used as a robust and universal tool suitable for locating DOC sources in landscapes, and what are the prerequisites for applying such an approach?

2 Materials and methods

2.1 Pedologic and hydrological context

The Kervidy-Naizin catchment is a 4.9 km^2 lowland catchment located in central Brittany, north-western France (Fig. 1), which belongs to the French network of long-term Environmental Research Observatories (ORE). Numerous hydrological and biogeochemical studies have led to an improved knowledge of water pathways during both "baseflow" and "storm-flow" periods (Mérot et al., 1995; Durand and Torres, 1996; Dia et al., 2000; Molénat et al., 2008) and of the processes governing the production and transfer of DOC in this catchment (Morel et al., 2009; Lambert et al., 2011; 2013). The climate is temperate oceanic, with mean annual (1993–2011) precipitation, runoff and temperature of

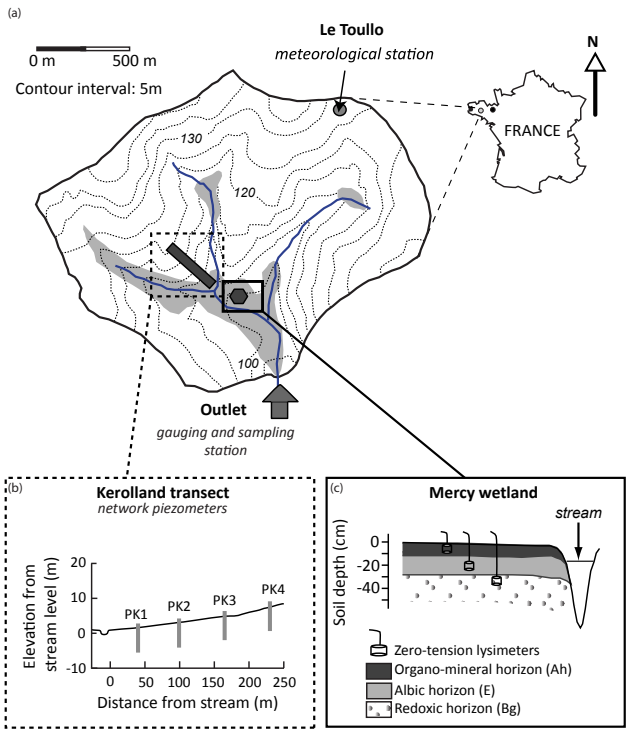

Figure 1. (a) Location and geomorphic map of the Kervidy-Naizin experimental catchment (Brittany, France). Also shown are the sites where the instruments used in this study are installed. Grey areas located along the stream channel network indicate the maximum extent of the interaction zone between the organo-mineral horizon of the soils and the upper layer of the groundwater. **(b)** Piezometer transect in Kerolland site. **(c)** Location in the soil profile of the soil water samples previously analysed and discussed by Lambert et al. (2013). Names of soil horizons in bracket refer to the IUSS Working Group WRB (2006) classification.

814 mm, 328 mm and 10.7 °C, respectively. Rainfall events rarely exceed 20 mm per day, and 80 % of rainfall events have an intensity of less than 4 mm per hour. The high-flow period generally lasts from December to April, with maximum discharges (1000–1200 L s^{-1}) occurring during February–March. Due to the small volume of water stored in the schist bedrock, the stream usually dries out from the end of August to the beginning of November.

The elevation of the catchment area ranges between 93 and 135 m above sea level, with gentle slope gradients of less than 5 %. The bedrock is made up of fissured and fractured Brioverian schists, and is covered by an unconsolidated weathered layer whose thickness ranges from a few metres to 30 m depending on the position in the catchment. The soils at Kervidy-Naizin are silty loams, with depths ranging from 0.5 to 1.5 m, and are classified as Luvisols (IUSS Working Group WRB, 2006). Typically, the soil system can be subdivided into two domains: (i) an upland domain composed of well-drained soils where the water table remains always a few metres below the soil surface and (ii) a riparian wetland domain consisting of highly hydromorphic soils where the water table usually reaches the soil surface during the wet season. The extent of the riparian wetland area is highly variable, ranging from 5 to 20 % of the total catchment surface area depending of the hydroclimatic conditions (Crave and Gascuel-Odoux, 1997). Soils in the riparian domain consists of an upper 10 cm thick Ah horizon overlying a 20 cm thick E horizon, which itself overlies a > 50 cm thick Bg horizon (Curmi et al., 1998). The soil organic carbon (SOC) content 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).

Ninety percent of the catchment area is used for intensive agriculture, mainly pasture, maize and cereals for dairy production and pig breeding. The downward continuous leakage of excess NO_3 brought about by agriculture has caused heavy nitrate pollution in groundwater (up to 80 mg L^{-1}), leading to high NO_3 concentrations in stream water during base-flow periods when groundwater dominates stream flow (Molénat et al., 2002, 2008). During high-flow periods, however, stream NO_3 concentrations decrease as high-NO_3 groundwater flux becomes diluted by lower-NO_3 soil and rain waters (e.g. Mérot et al., 1995). This specificity of agricultural catchments regarding stream NO_3 dynamics greatly differs from non-agricultural catchments, typically forested catchment. In these relatively pristine catchments, no or very little NO_3 is transferred to groundwater and the soils are the natural main reservoir of NO_3 at the catchment scale. Consequently, NO_3 concentrations in streams draining these catchments are typically low during base flow and increase with increasing discharge (e.g. Peterson et al., 2001; Buffam et al., 2001).

The Kervidy-Naizin catchment displays three hydrological and hydrochemical periods during the water year (Molénat et al., 2008). First, after the dry summer, the water table starts to rise in the riparian zone but remains deep in the upland domain (period A). Second, as precipitation increases, the water table rises in the upland domain resulting in the establishment of a hydrological connection between riparian and upland domains and the subsequent increase of upland groundwater flow towards the riparian zone (period B). Third, in late spring and during summer, upland groundwater flow decreases progressively resulting in a gradual air-drying of wetland soils (period C).

Using DOC, NO_3, SO_4 and also Cl, previous studies identified four types of water contributing to storm flow in the Kervidy-Naizin catchment, namely, (i) rainwater (Rw), (ii) DOC-rich shallow riparian groundwater (SRGw, between 0 and 30 cm depth), (iii) NO_3-rich hillslope groundwater (HGw, between 0.3 and 6 m) and (iv) NO_3-poor deep (> 6 m) groundwater (DGw), the latter two types being the only water types present during base-flow conditions (Mérot et al., 1995; Durand and Torres, 1996; Molénat et al., 2002; Morel et al., 2009). The difference between NO_3-rich shallow groundwater in the upland domain and NO_3-poor deep groundwater

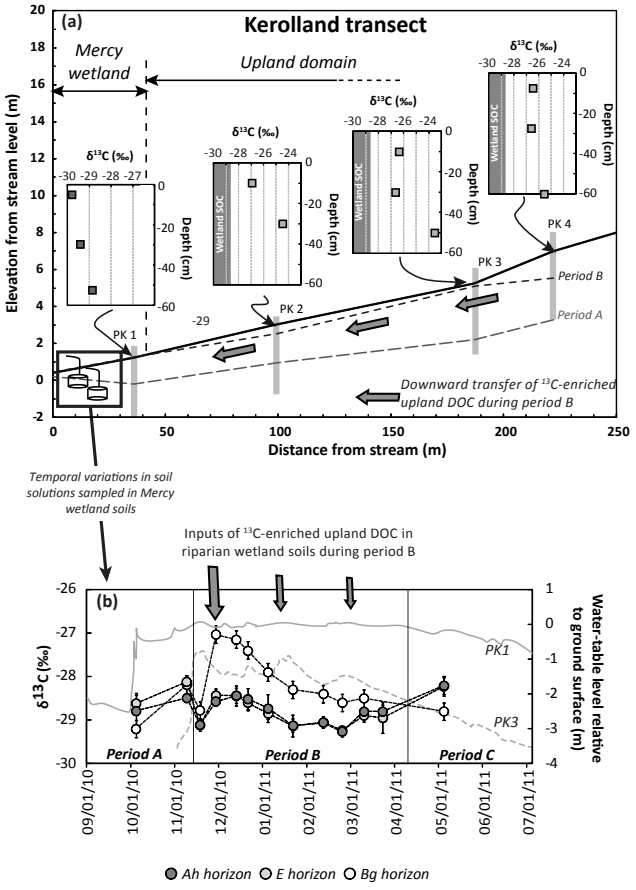

Figure 2. Sketch illustrating: **(a)** spatial variability of $\delta^{13}C_{SOC}$ values for soil organic carbon from the riparian wetland domain to the hillslope domains of the Kervidy-Naizin catchment. Dashed lines represent the water table level along the upland–wetland transect during periods A and B. Grey arrows represent the transfer of ^{13}C-enriched DOC from upland soils to wetland soils ; and **(b)** seasonal variations of the $\delta^{13}C_{DOC}$ values in riparian wetland soils in phase with water table fluctuations. Grey arrows illustrate the mixing between wetland DOC and upland DOC in riparian soils during period B. The gradual decrease in the arrow size symbolises the decrease of upland DOC inputs. Data from Lambert et al. (2011, 2013).

can be explained by the fact that the latter comes from fractured unweathered bedrock containing pyrite, thus giving it a distinct low-NO_3 and high-SO_4 signature (Dia et al., 2000).

2.2 Previous carbon isotopic data

In addition to a concentration gradient (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, 2013; Fig. 2a). Indeed, the $\delta^{13}C_{SOC}$ values decrease from the uppermost soil layer (0–10 cm) to the deeper horizons (50–60 cm), by 1 ‰ in the wetland zones and by 3.5 ‰ in the upland domain. In addition, the $\delta^{13}C_{SOC}$ values are on average lighter in the riparian area (from −29.8 ‰ to −28.9 ‰) compared to those in the upland domains (from −27.0 ‰ to −23.5 ‰).

As pointed out in the introduction, the $\delta^{13}C_{DOC}$ values in wetland soils display a strong spatial and temporal variation along with seasonal changes in the hydrological regime of the catchment (Lambert et al., 2013; Fig. 2b). During period A, the $\delta^{13}C_{DOC}$ values shifted to lighter values, ranging from −29.8 to −28.9 ‰, from the surface to deeper soil horizon in the wetland domain. During the wet period B, a strong isotopic differentiation of progressively decreasing amplitude was observed between the deeper ^{13}C-enriched Bg horizon and the surface Ah and E horizons (Fig. 2b). Finally, during period C, the $\delta^{13}C_{DOC}$ values once again became homogeneous at the scale of the soil profile. As shown by Lambert et al. (2013), the increase and vertical differentiation of $\delta^{13}C_{DOC}$ occurring during period B in the wetland soils provides evidence for the input in these soils of an ^{13}C-enriched DOC component produced in the upland soils. Moreover, the gradual decreasing amplitude of the $\delta^{13}C_{DOC}$ values in riparian soils meanwhile provides evidence for the depletion of the upland DOC pool during the wet period.

2.3 Field instrumentation and water sampling

Water table was continuously monitored (every 15 min) on the Kervidy-Naizin catchment using pressure sensors in piezometers (PK1 to PK4) installed along a 600 m long transect (Kerolland transect; see Fig. 1). Rainfall amounts were continuously monitored at hourly intervals using a weather station located ca. 1400 m away from the catchment outlet. Stream discharge was recorded every minute with an automatic gauge station located at the outlet of the catchment. The beginning and end of a given storm event are determined by an increase and a decrease of the stream discharge of $> 1\,L\,s^{-1}$ in 10 min at the stage recorder, respectively. With this method, the storm flow generally ceases prior to the return to "purely" base-flow conditions regarding DOC concentrations, implying that some of the data referred to here as base-flow DOC could in fact correspond to storm-flow conditions recorded by the receding limb of the storm hydrograph. Six storm events were sampled between 11 November 2010 and 19 February 2011, i.e. during a time interval corresponding to the end of hydrological period A and the first half of hydrological period B. Stream water samples were collected using a refrigerated (4 °C) automatic sampler (Sigma 900 Max) installed at the outlet of the catchment (Fig. 1). Sampling frequency during the monitored storm events varied from one sample every 30 min to one sample every hour, depending on the hydrograph variations. In addition to this high-frequency sampling, a daily sampling of stream water was performed manually at the outlet of the catchment. All water samples were collected in pre-cleaned acid-washed polyethylene bottles. Daily samples were filtered directly on site whereas storm samples were kept at 4 °C, and then transported in the dark to the laboratory for filtration. Filtration

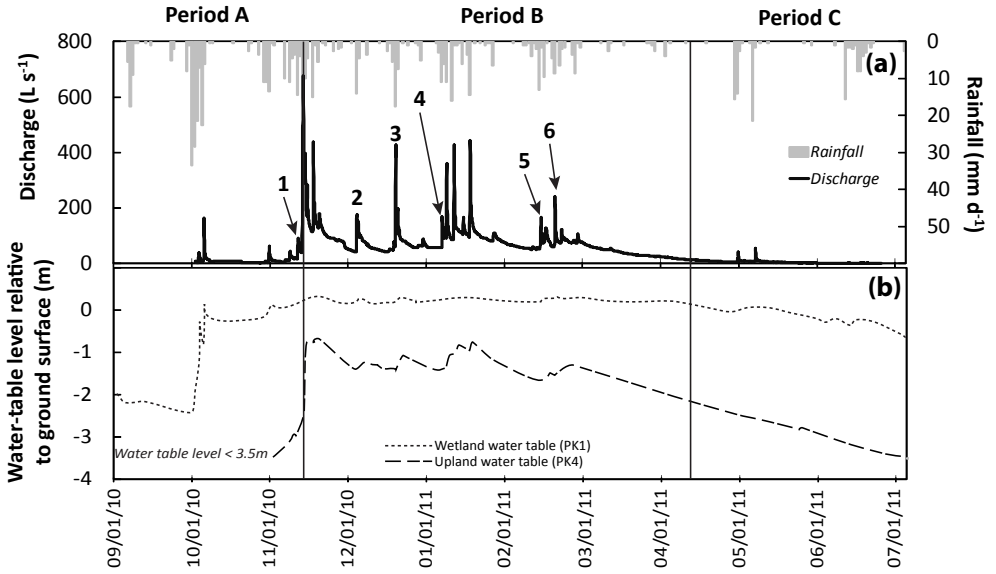

Figure 3. (a) Record of hourly discharge and daily rainfall and **(b)** record of hourly water table levels in the wetland (PK1) and upland (PK4) domains during the investigated periods. Monitored storm events are indicated by numbers.

was performed successively to a mesh size of < 0.7 µm using GF/F filters, then to < 0.2 µm using cellulose acetate filters (Millex-GV, EMD Millipore). All filters (on-site and in-laboratory) were cleaned twice before use: first with 200 mL of deionized water, and then with a few mL of the sample itself.

2.4 Analytical procedures

Dissolved organic carbon concentrations were determined using a Shimadzu TOC-5050A total carbon analyser. Accuracy of DOC measurements is ±5%, based on repeated measurements of standard solutions (K-phthalate). Major anions (Cl^-, NO_3^- and SO_4^-) were measured by ion chromatography (Dionex DX-120), with an accuracy of ±2.5 %.

All $\delta^{13}C_{DOC}$ values were determined at the Stable Isotope Laboratory of the PEGASE Joint Research Unit of the INRA in Saint-Gilles, France. Up to one litre of raw water was collected in-stream and in-soil. After a filtration at 0.2 µm, and an acidification by adding 1 mL of 1N HCl to remove all traces of inorganic carbon, the water samples were frozen and freeze-dried.

The $\delta^{13}C_{DOC}$ values of the freeze-dried samples were determined using an elemental analyser (EA-CE 1500 NA, Carlo Erba) interfaced with an isotope ratio mass spectrometer (IRMS) (VG Isoprime). Tin capsules were used for sample loading. The $\delta^{13}C$ values are expressed as the relative deviations 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:

$$\delta^{13}C(‰) = [(R_{sample}/R_{standard}) - 1] \times 1000, \quad (1)$$

where $R = {}^{13}C/{}^{12}C$. International standards were also measured: (i) USGS 24 ($\delta^{13}C = -16.5 \pm 0.1$ ‰ ($n = 36$)) and (ii) ANU sucrose ($\delta^{13}C = -10.5 \pm 0.1$ ‰ ($n = 53$)). The accuracy of measured $\delta^{13}C$ values is better than ±0.2 ‰, based on repeated measurements of samples and standards.

2.5 End-member mixing approach (EMMA)

The EMMA is a widely used method in catchment hydrology studies for estimating the relative proportion of waters of different geographical origins contributing to stream discharge (Christophersen et al., 1990; Hinton et al., 1998; Katsuyama et al., 2001; Inamdar and Mitchell, 2006). This approach is based on a conservative mixing model where the stream water is regarded as a mixture of water components coming from different end-members or water reservoirs with contrasted and stable chemical compositions. This method has been used successfully in the Kervidy-Naizin catchment (Durand and Torres, 1996; Morel et al., 2009). Since four end-members are assumed to contribute to storm flow in this catchment, three chemical tracers are required. As in Morel et al. (2009), we used DOC, SO_4 and NO_3 due to the strong variability of these tracers between the different water mass bodies. Concentrations used by Morel et al. (2009) were applied for the rainwater and deep groundwater end-members, as their chemical composition is temporally stable in this catchment. For the DOC-rich SRGw and NO_3-rich shallow hillslope groundwater end-members (HGw), temporal variations were taken into account by considering chemical data obtained during the course of the study by Lambert et al. (2013).

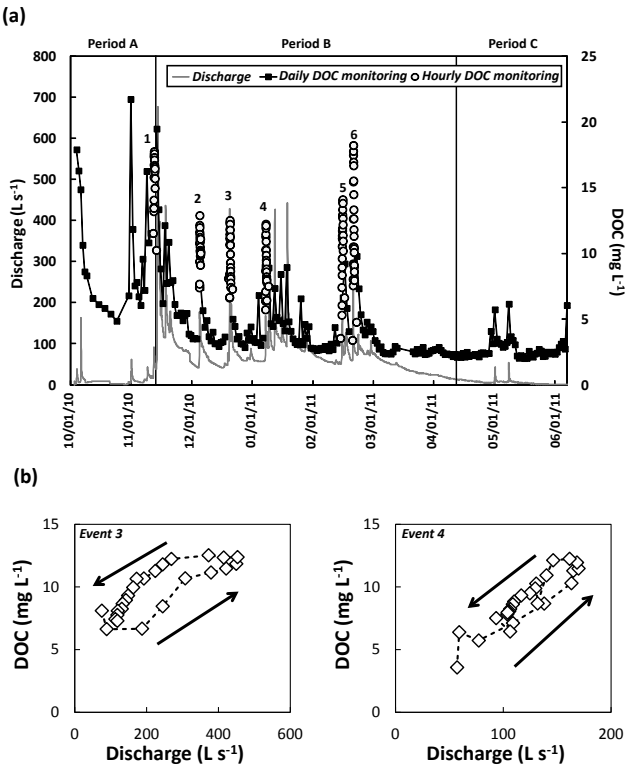

Figure 4. (a) Temporal variations in stream discharge and DOC concentrations at the catchment outlet during the study period and **(b)** example of DOC concentrations versus discharge showing hysteresis patterns (arrows indicate chronology). Monitored storm events are indicated by numbers in box **(a)**.

3 Results

3.1 Hydrology

The first three months of hydrological year 2010–2011 (i.e. from September to November 2010) were relatively wet, with a total precipitation of 356 mm vs. 251 mm on average for the same period over the last 10 years. The heavy rainfall events at the beginning of October 2010 caused a rise of the water table in the riparian domain (PK1), which marked the beginning of hydrological period A. Hydrological period B started on 13 November 2010, when a 50 mm rainfall event caused a rise of the water table in the upland domains (PK4). This period ended in April 2011, when the water table started to fall in the riparian domain, highlighting the beginning of hydrological period C. As can be seen, the Kervidy-Naizin catchment reacts quickly to rainfall, with most storm water being discharged within a day after the rainfall event. Moreover, the water table, both in the riparian and uphill domains, reacts quickly to rainfall in the same way as the stream discharge. Note that the hydraulic gradient between riparian and upland domains was constant from storm events no. 2 to 4. The six monitored storm events took place during hydrological period B, except for storm event no. 1 which occurred during hydrological period A. Peak discharge values were low to moderate for all events (90 to 170 $L\,s^{-1}$), except for storm event no. 3 whose peak discharge reached 430 $L\,s^{-1}$.

3.2 Concentration data

DOC concentrations in the stream varied from 2.5 to 21.5 $mg\,L^{-1}$ during the study period (Fig. 4a). Due to a rapid response to rainfall, the maximum DOC concentrations are reached during storm events, and mostly captured by hourly sampling, while the minimum DOC concentrations occurred during inter-storm periods, and mostly captured by a daily sampling. During storm events, the DOC concentration vs. discharge relationships (Fig. 4b) revealed a slight anti-clockwise hysteresis, with higher DOC concentrations on the descending limb of the hydrograph as compared with the ascending limb, a feature that was already apparent in the eight storm events monitored in 2006 by Morel et al. (2009). As pointed out by these authors, this indicates that water entering the stream during the early part of the storm has lower DOC concentrations than water entering the stream after the peak discharge.

The in-stream NO_3 and SO_4 concentrations were inversely and positively correlated with discharge, respectively (Supplement Fig. S1). In addition, the SO_4 concentrations continuously decreased from the beginning to the end of the study period during base flow accompanied by a decrease in concentration variability during storm events. In the case of NO_3, their concentrations were lower during hydrological period A than during hydrological periods B and C. During the latter two periods, NO_3 concentrations measured after the cessation of rainfall were generally identical to pre-storm concentrations. The whole data set of stream chemistry during storms can be found in Supplement Table 1.

3.3 Carbon isotopic data

In contrast to DOC concentrations which showed a systematic increase with increasing discharge, the carbon isotopic composition of DOC displayed a strong intra-storm variability (Fig. 5). More specifically, while $\delta^{13}C_{DOC}$ varied by ca. 2 ‰ (from −29 to −27 ‰) during storm events no. 2 and no. 3, the isotopic variations were reduced to 1 ‰ or less during the four remaining monitored storm events. The minimum variation was observed during storm event no. 5 with nearly constant intra-storm $\delta^{13}C_{DOC}$. The magnitude of variations in intra-storm $\delta^{13}C_{DOC}$ values was not correlated with the magnitude of variations in intra-storm DOC concentration, or with the magnitude of variations of stream discharge. By contrast, the $\delta^{13}C_{DOC}$ values were systematically lower on the ascending limb of the hydrograph than on the descending limb, the minimum values being observed either during the ascending limb or at the time of maximum discharge.

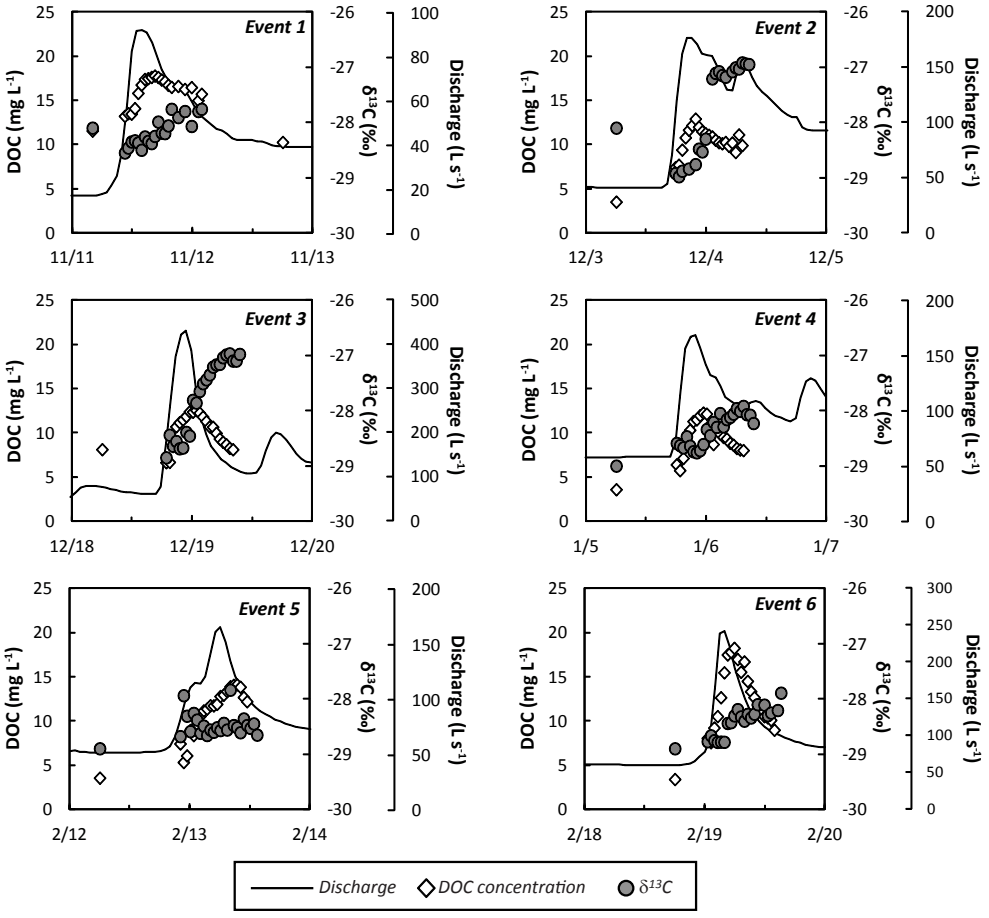

Figure 5. Changes in stream DOC concentrations, stream $\delta^{13}C_{DOC}$ values and stream discharge during the six investigated storm events.

3.4 Hydrograph separation results

The mixing diagrams (Fig. 6) show that the stream chemistry was generally within the field defined by the four identified end-members. The results from storm event no. 1 were difficult to interpret, because some of the data points fell outside the end-member field in the SO_4 vs. NO_3 diagram. This feature is most likely due to high-frequency variations of NO_3 concentration in the riparian wetland soils during the rewetting period (Molénat et al.,2008), variability which is probably not captured satisfactorily by the bi-weekly sampling frequency used in the study of Lambert et al. (2013). Such a hypothesis is consistent with the stream NO_3 chemograph showing that hydrological period A was characterized by a strong temporal variability of in-stream nitrate concentrations (Fig. S1).

The results of the hydrograph separations (Fig. 7) show that (i) the contribution of DGw and HGw was fairly constant during the six newly investigated storm events and (ii) the major contribution during the peak discharge came from the SRGw. Furthermore, the proportional contribution of SRGw seems to increase with the magnitude of storm events

4 Discussion

4.1 Linking soil and stream DOC

Data from this study provide evidence for a strong temporal change in the variability of intra-storm $\delta^{13}C_{DOC}$ values, with a much larger range of values for storm events occurring soon after the transition between hydrological periods A and B (events no. 2 to 4) than those occurring before (event no. 1) or long after (events no. 5 and 6) (Fig. 5). Figure 8 shows that this temporal variability is similar, both in terms of amplitude and absolute values, to the temporal variation of $\delta^{13}C_{DOC}$ taking place in soils of the Mercy wetland zone during the same period. This feature is consistent with what is known about storm-flow generation at this site. Previous studies (e.g. Durand and Torres, 1996; Morel et al., 2009; Lambert et al., 2011) have indeed established that storm-flow generation is dominated successively by (i) an overland flow above the saturated wetland soil horizons; (ii) a subsurface flow through the uppermost Ah horizon of wetland soils; (iii) a subsurface return flow from shallow hillslope groundwater flowing through deeper Bg horizon of wetland soils; and

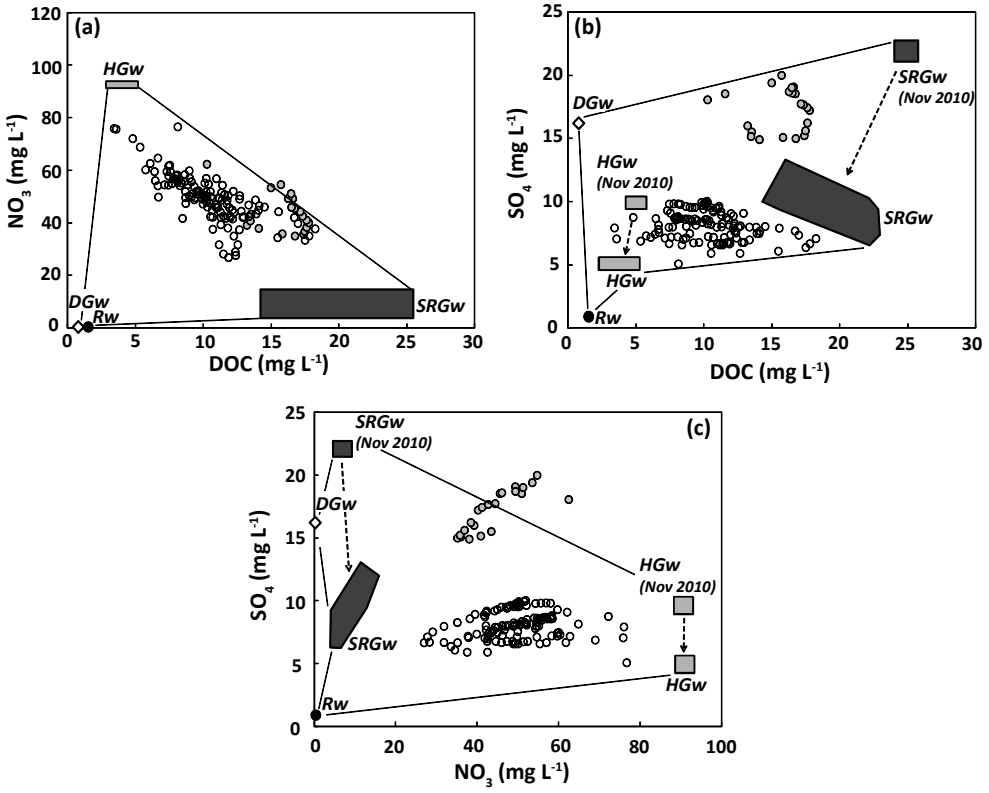

Figure 6. End-member mixing diagrams for the six investigated storm events: **(a)** NO_3 versus DOC; **(b)** SO_4 versus DOC; **(c)** SO_4 versus NO_3. Data from event no. 1 on 11 November 2010 shown as solid grey circles. Rw: rain water; DGw: deep groundwater; SRGw: shallow riparian groundwater; HGw: hillslope groundwater. Filled areas for SRGw and HGw delimit the changes in concentration observed for these two end-members during the study period. Data source: Lambert et al. (2013); Lambert, unpublished data.

finally (iv) when base-flow conditions are restored, a subsurface return flow involving a mixture of shallow hillslope groundwater and deep (< 6 m) groundwater flowing through the Bg part of the wetland soil profile. Thus, the fact that the intra-storm isotopic variability mimics the spatial and temporal of $\delta^{13}C$ variation in the riparian zones is fully consistent with the storm-flow generation pattern, and confirms the currently accepted view that the source of DOC in stream draining headwater catchments is allochthonous, at least during the wet season (Boyer et al., 1996; Hagedorn et al., 2000; Inamdar et al., 2006; Sanderman et al., 2009).

However, a more detailed comparison between intra-storm $\delta^{13}C_{DOC}$ values and temporal changes in riparian soil $\delta^{13}C_{DOC}$ values reveals some inconsistencies (Figs. 7 and 8). During storm events no. 2 and no. 3, the $\delta^{13}C_{DOC}$ values observed at peak flow turned out to be significantly lower than the corresponding $\delta^{13}C_{DOC}$ values in wetland soil Ah horizons, even though groundwater from these horizons contributed predominantly to stream flow at that time. Similarly, the $\delta^{13}C_{DOC}$ values at the end of storm events no. 1, 3 and 6 were higher than the $\delta^{13}C_{DOC}$ values found in groundwater flowing through the Bg horizon, while this horizon was calculated to provide most of the stream water at that time of the storms.

Most likely, these inconsistencies indicate that the Mercy site is not strictly representative of the riparian zone system over the entire catchment. Indeed, lateral variations in the $\delta^{13}C_{DOC}$ in riparian soil horizons may occur at the catchment scale. As already mentioned, the increase in $\delta^{13}C_{DOC}$ values at the transition between hydrological periods A and B in the Mercy soils is related to the input into these soils of an isotopically heavier DOC component derived from upland areas (Fig. 2b) caused by the activation of a hydrological connectivity developed across the riparian–upland continuum (Lambert et al., 2013). In this typical scenario of catchments developed on impermeable basement rocks (McGlynn and McDonnell, 2003; Bishop et al., 2004; Hood et al., 2006; Pacific et al., 2010), spatial variations in the isotopic composition of riparian DOC are to be expected provided that (i) the hydrological connectivity across the riparian–upland continuum is spatially discontinuous and (ii) the flux of isotopically heavier DOC coming from upland areas varies from one riparian zone to another.

We have no data to assess the variability of the hydrological connectivity across the riparian–upland continuum at

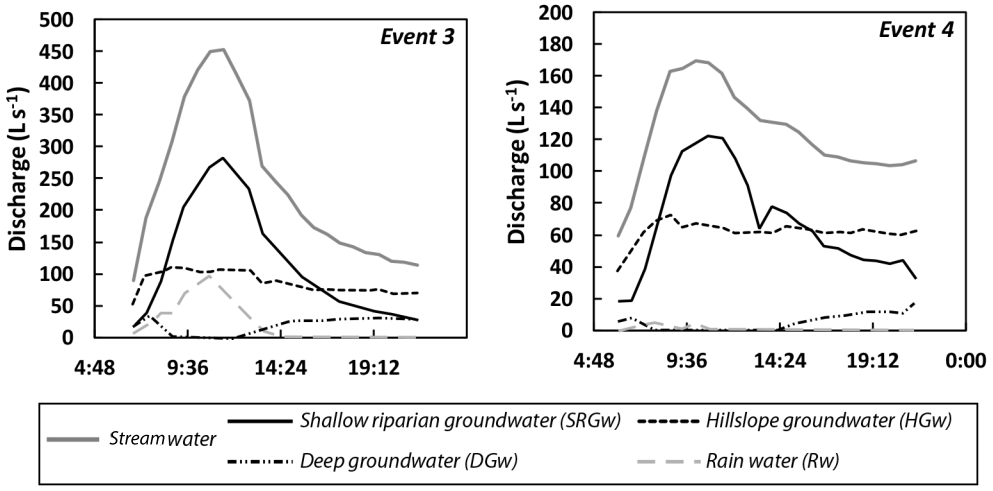

Figure 7. Examples of end-member mixing analysis used to determine the contributing waters during storm events no. 3 and no. 4.

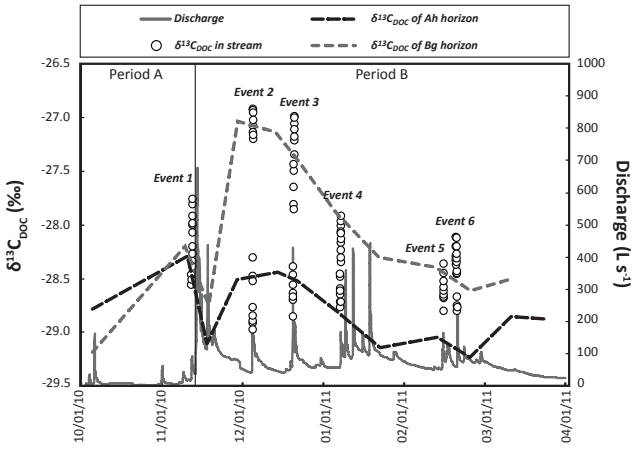

Figure 8. Comparison between storm-flow DOC isotopic data and the seasonal DOC isotopic trend observed in riparian soil waters at the Mercy site. Riparian soil water data are from Lambert et al. (2013).

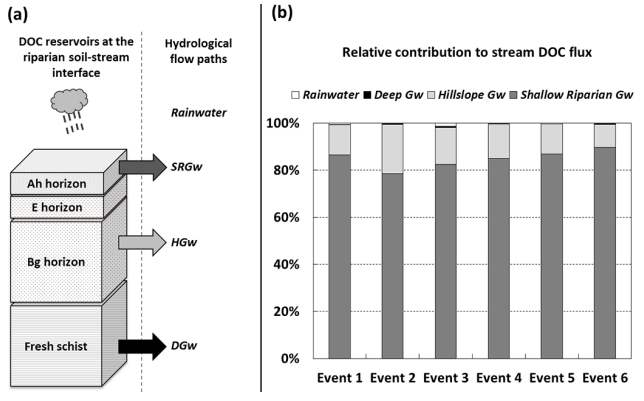

Figure 9. (a) The four identified hydrological flow path and DOC reservoirs at the riparian soil–stream interface and **(b)** Contribution of each hydrological flow paths to the total storm DOC flux as calculated using the NO_3, DOC, and SO_4 concentrations and the EMMA method. Note that DOC in wetland soil horizons is basically a mixture of wetland-borne and upland-borne DOC.

the Kervidy-Naizin catchment scale, nor that of the flux of upland DOC. However, we know that the groundwater rise in upland areas is not uniform over the entire catchment, but more pronounced in its central part at the location of the Mercy site than in areas further upstream with steeper slopes (Molénat et al., 2008). In these latter zones, the upland groundwater only rarely reach the uppermost organic-rich soil horizons, so we can infer that the ratio of upland to riparian DOC should be lower in these zones as compared to the central flat part of the catchment. This would lead to spatial variations in the isotopic signature of the soil DOC flux entering the stream network during storm events, which could account for the differences between the present storm $\delta^{13}C_{DOC}$ values and the Mercy wetland soil data.

4.2 Hydrological flow paths and DOC transport mechanisms at the soil–stream interface

Using the EMMA results, the relative contribution of each riparian soil horizons to the stream DOC flux can be estimated for all six storms events (Fig. 9a), bearing in mind that (i) the riparian soil horizons contain both "autochthonous" riparian DOC and "allochthonous" upland DOC and (ii) the Mercy zone is not strictly representative of the entire riparian domain across the catchment. Thus we estimated that the SRGw flowing through the uppermost Ah horizons contributed between 78 and 89 % of the total DOC exported by the stream (Fig. 9b). This result is consistent with the 65–90 % contribution calculated by Morel et al. (2009) from the EMMA-based decomposition of eight successive storm events in this

same catchment during hydrological year 2005–2006. This suggests that the DOC-rich Ah horizon reservoir in the riparian zone is the main contributor of the total stream DOC flux during storm events.

In addition to EMMA results, an isotopic mixing model using $\delta^{13}C_{DOC}$ values for storm events can be used to identify through which of the two wetland soil horizons (shallow Ah horizon and deep Bg horizon) is the soil DOC usually transferred to the stream, assuming that the Mercy wetland soils are representative of all the Kervidy-Naizin wetland soils. In fact, this assumption appears to be valid only for storm no. 4. Indeed, this storm is the only one of the six analysed storms for which the temporal variations in stream $\delta^{13}C_{DOC}$ were bracketed by the $\delta^{13}C_{DOC}$ values in the Ah and Bg soil horizons at the corresponding time (Fig. 8). More specifically, the $\delta^{13}C_{DOC}$ values obtained at that time in the Mercy soils can be taken as possible end-member values for the storm DOC. Assuming $\delta^{13}C_{DOC}$ values of -28.7 and -27.9 ‰ for the DOC circulating in the Ah and Bg soil horizons, respectively, we can calculate that the Ah horizon contribute 61 % of the total DOC flux. This is significantly lower than the proportion obtained using the EMMA method for this same storm event (85 %). However, the isotopic decomposition approach is extremely sensitive to the isotopic composition chosen for the soil DOC end-members. For example, increasing the $\delta^{13}C_{DOC}$ values of the Ah horizon end-member by 0.1 ‰ would increase this proportion from 61 % to 70 %, a result which is within the 65–90 % range obtained for the 14 Kervidy-Naizin storm events decomposed so far using the EMMA method (Morel et al., 2009; this study). Thus, the new results confirm the dominant contribution of DOC circulating through the uppermost horizons of the riparian soils of this catchment to the DOC fluxes exported during storm events.

4.3 Riparian versus upland origin of stream DOC

As pointed out in the introduction, the transport of DOC from soil to stream is not simply the result of the flushing of the DOC generated in the riparian soils, but it can also result from the mobilization of DOC produced in upland soils (McGlynn and McDonnell, 2003; Sanderman et al. 2009; Pacific et al., 2010). This scenario was first proposed for mountainous catchments (McGlynn and McDonnell, 2003; Bishop et al., 2004; Hood et al., 2006; Sanderman et al., 2009; Pacific et al., 2010) and was recently extended to lowland catchments (Lambert et al., 2013). In this scenario, a hydrological connectivity needs to be developed across the upland–riparian–stream continuum to allow transport of upland DOC to the stream network. However, no study has so far attempted to quantify the contribution of each source to the total DOC flux exported by streams, or to evaluate how the relative contribution of each source evolves through time.

For the first time, the isotopic data obtained at the Kervidy-Naizin catchment provide the possibility of quantifying the relative contributions of wetland and upland sources to the stream DOC flux at the catchment scale. This estimation is possible because of the difference in the $\delta^{13}C_{DOC}$ values between these two DOC sources which can be used to estimate their respective contributions by means of a two-end-members isotopic mass-balance mixing (Fig. 10a). For this purpose, the $\delta^{13}C$ values for both wetland-derived and upland-derived DOC soils were estimated from those of water-extractable DOC obtained on the uppermost soil horizons (0–15 cm) collected along the Kerolland transect (data in Supplement Table 2). The estimated $\delta^{13}C_{DOC}$ values of the wetland- and upland-derived DOC were -28.6 ± 0.1 ‰ ($n = 1$) and -24.9 ± 0.7 ‰ ($n = 3$), respectively. The estimated $\delta^{13}C_{DOC}$ for wetland soils corresponds to the average value of wetland-borne DOC (Supplement Table 2). Although the value of the $\delta^{13}C_{DOC}$ of the upland DOC is not precisely known, the potential internal variability deduced for this reservoir (±0.7 ‰) is much lower than the external variation between the $\delta^{13}C_{SOC}$ of wetland and upland soils. Figure 10b presents the results for storm events no. 2 to 5, while storm event 1 is excluded from the calculation because the deep water table in the upland domain during the rewetting period prevented the transfer of any upland DOC to the stream. Due to the uncertainties on the true isotopic composition of upland DOC, our calculations should not be considered as the absolute contribution of upland soils. However, the results clearly show that the contributions of upland-derived DOC reached maxima during storm events no. 2 and 3, estimated at 27 ± 5 % and 19 ± 4 % of the total DOC flux exported at the catchment outlet, respectively, and then decreased during storm events no. 4 to 6 where it represents less than 10 % of the total DOC flux.

Thus, although it appears that upland DOC significantly contributes to DOC export during storm flows – especially at the beginning of hydrological period B – the riparian wetland zones remain by far the dominant DOC sources. Also, the relative contribution of upland DOC sources was decreasing during hydrological period B (Fig. 10b). Interestingly, this

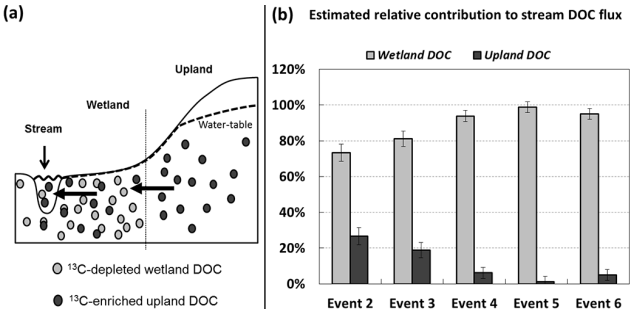

Figure 10. (a) Sketch illustrating the opportunity offered by stable carbon isotopes to quantify the relative contribution of riparian and upland DOC sources and **(b)** estimated relative contribution of riparian and upland DOC sources to stream DOC flux.

decrease occurred for storm events whose maximum peak flow values were comparable (e.g. events no. 2, 4 and 5) and while the water table was still high in the upland domains (Fig. 3). This suggests that the DOC reservoir in these domains is rapidly depleted or flushed during the course of the rainy season. The seasonal depletion of the upland DOC pool in the Kervidy-Naizin catchment was also apparent in the $\delta^{13}C_{DOC}$ records in Mercy soil solutions, with $\delta^{13}C_{DOC}$ values decreasing gradually during period B despite the fact that the hydrological connectivity remained elevated (Fig. 2b; Lambert et al., 2013). A similar behaviour has been observed in a coastal catchment in California (Sanderman et al., 2008, 2009). In the present catchment, the seasonal depletion of the hillslope DOC reservoir is accompanied by a change in the radiocarbon ages of the DOC, indicative of a shift from recent to aged SOM sources. Certain authors consider that this shift towards aged SOM sources for DOC, which occurs along with depletion of the hillslope domain, is due to plant productivity that is insufficiently rapid to meet the microbial demand for organic substrate, thus leading to solubilization of older organic matter sources by the microbial community (Zogg et al., 1997; Andrews et al., 2000). In the present case, we do not have the necessary data to elucidate the precise cause of the observed rapid flush of the hillslope DOC component. This evidently remains an open question for future work.

Unlike upland soils, wetland soils in headwater catchments developed on impervious bedrock appear to behave as a near-infinite DOC source pool (e.g. Hinton et al., 1998; McGlynn and McDonnell, 2003; Sanderman et al., 2008, 2009; Pacific et al., 2010). For the Kervidy-Naizin catchment, the constancy of DOC concentrations in the riparian soils observed by Morel et al. (2009) despite the continuous succession of storm events and the lack of seasonal exhaustion of the DOC store built up in the riparian soils during an entire hydrological year reported by Lambert et al. (2013) support this conclusion. This lack of seasonal depletion of the wetland DOC source pool is likely due to the significantly higher organic carbon contents in the wetland soils, which accumulate significantly more organic matter that the surrounding cultivated uplands. Taken together, all these results suggest that DOC is primarily transport-limited in the Kervidy-Naizin catchment, given the dominant role of shallow riparian DOC-sources in contributing the major part of the exported DOC.

4.4 Carbon isotopes: a reliable tool for locating DOC sources and studying DOC transport processes in landscapes?

The results of this study indicate that carbon stable isotopes provide a reliable tool for locating DOC sources in the landscape and unravelling the DOC transport pathways from the soil profile to the stream. The quantification of DOC transport processes was based on the high-resolution monitoring of the temporal and spatial evolution of the $\delta^{13}C_{DOC}$ values during storm events and in soil solutions. Importantly, these results could not have been obtained without detailed previous studies involving high-frequency (bi-weekly) and continuous monitoring of the isotopic composition of DOC in soil waters, as well as SOM in the soil profile, and continuous monitoring of the water table movements across the stream–wetland–upland continuum (Lambert et al., 2013). All these constraints concerning the type, frequency and location of the data are necessary preconditions for interpreting the isotopic signal and implementing the carbon isotopic tool for tracing sources and transport mechanisms of DOC in catchments.

Two questions arise at this stage: (1) Is it possible that the wetland–upland isotopic continuum observed at Kervidy-Naizin is found in other headwater catchments, thus allowing the implementation of the carbon isotope tool with the same efficiency as in the present case? (2) Why is it so important to determine the ultimate source of DOC in the landscape?

We can probably answer positively to the first question. As mentioned above, the wetland–upland gradient observed at Kervidy-Naizin ($\delta^{13}C_{SOC}$ varying from -29.4 ‰ in the wetland to -26.4 ‰ in the upland domains) may be explained by the difference in the conditions of degradation of soil organic matter between the water-saturated anaerobic wetland areas and the better drained, more aerobic upland domains. Insofar as this difference in organic matter degradation conditions is expected to occur in all headwater catchments developed on impervious basement rocks, we can reasonably assume that the wetland–upland isotopic gradient will be reproduced elsewhere. Indeed, a comparable isotopic gradient was observed in the Urseren valley in Switzerland, where a variation of 2 ‰ has been reported between wetland organic matter ($\delta^{13}C = -28.6$ ‰) and upland organic matter ($\delta^{13}C = -26.6$ ‰) (Schaub and Alewell, 2009). This similarity between the two situations is particularly noteworthy, since the physiographic and land-use settings are markedly different, i.e. cultivated lowland soils in the case of Kervidy-Naizin, and forested/pastured alpine soils in the Urseren valley. This comparison clearly indicates that we should consider it feasible to transpose the approach developed at Kervidy-Naizin to other catchments with similar final results.

Regarding the importance of identifying DOC sources in landscape, we can see at least two important issues. The first concerns water quality protection and the well-known role of dissolved organic matter as a vector for micropollutants such as metals and pesticides (e.g. Graber et al., 2001; Williams et al., 2006; Grybos et al., 2007; Pédrot et al., 2008; Du Laing et al., 2009; Thevenot et al., 2009; Taghavi et al., 2010). The challenge faced here concerns agricultural catchments, where cultivated fields on the slopes are likely to receive surface loading of heavy metals and/or pesticides due to agricultural practices. Given the role of dissolved organic matter in controlling the mobility of micropollutants, we anticipate that these substances might become a threat for downstream ecosystems if the upland domains to which they are applied

become hydrologically connected to the stream network. In this way, the micropollutants would form soluble complexes with organic molecules, thus leading to their transfer downstream. Determining the fraction of stream dissolved organic matter likely to come from upland areas using carbon isotopes would enable us, in this case, to quantify the potential risk of water contamination by agricultural pollutants.

The second issue concerns testing the hypotheses that have been proposed for the transfer of DOC in the landscape and the factors controlling the pathways and efficiency of this transfer. Based upon catchment-scale topography analysis and measurements of stream and groundwater DOC, it has been suggested that temporal and spatial changes in the hydrological connectivity between upland and wetland domains could be one of the dominant factors, and that the maximum DOC export occurs in areas combining both large DOC sources with high stream–wetland–upland hydraulic conductivity (e.g. McGlynn and McDonnell, 2003; Pacific et al., 2010). Carbon isotopes are expected to provide a valuable tool to test this hypothesis at the catchment and upland scales, since regions characterized by high hydrological connectivity between stream, wetland and upland areas should yield DOC with a carbon isotope composition more enriched in ^{13}C than regions showing a low hydrological conductivity along this continuum. Carbon isotopes should therefore provide direct evidence of a mixing process than can occur in riparian zones between wetland- and upland-derived DOC, while allowing the unravelling of DOC pathways at the soil–stream interface.

5 Conclusions

Using the carbon isotopic composition of DOC sampled at the outlet of a small lowland agricultural catchment in western France during six successive storm events between November 2010 and February 2011, we were able to reconstruct the transfer pathway of DOC in this catchment and locate the ultimate sources of DOC in the landscape. This was achieved by comparison with previously published isotopic composition of DOC in the soils of this catchment. We showed that the observed temporal change in the range of intra-storm $\delta^{13}C$ values closely reflected the temporal change of $\delta^{13}C$ values observed in soils of the riparian zone of the catchment over the same period. Combining the carbon isotopic data with hydrometric monitoring results and an end-member mixing analysis based on DOC, SO_4 and NO_3 concentrations, we showed that (i) more than 80 % of the DOC flux transiting through the outlet of the basin has passed via the uppermost organo-mineral soil horizons of the riparian domain and (ii) this flux is composed of DOC derived ultimately from both riparian and upland source regions. Moreover, we found that the proportion of upland DOC component decreased rapidly after the rise in water table in the upland domains of the catchment, corresponding to ca. 20–30 % of the total DOC flux exported at the outlet of the catchment during storms events taking place soon after the water table rise. This proportion decreased to less than 10 % of the total DOC flux for storm events occurring later on in the hydrological year. These results indicate that (i) upland domains can be significant contributors of stream DOC flux in headwater catchments and (ii) wetland domains represent more sustainable sources of DOC than upland regions, the DOC-source pool of the latter being rapidly depleted during the course of the rainy season.

Through this study, we demonstrate that the isotopic composition of DOC is a powerful tool for tracing DOC sources and DOC transport mechanisms in headwater catchments if measured at high-resolution. At the same time, to produce accurate results, this tool requires an accurate knowledge of the temporal and spatial variability of the isotopic signatures of all potential DOC sources in the catchment. Providing that this condition is met, the carbon isotopic tool can be used to quantify the proportions of DOC coming from different areas of supply. This approach may be of great importance in achieving a better understanding and improved modelling of DOC transport processes in catchments.

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