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New insights from the use of carbon isotopes as tracers of DOC sources and DOC transport processes in headwater catchments

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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 DOC stream flux. High-resolution (< hourly basis) $\delta^{13}C_{DOC}$ data were obtained on six successive storm events occurring during the high-flow period in a small headwater catchment from 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 $\delta^{13}C$ data in conjunction with hydrometric monitoring and an end-member mixing approach, we show that (i) > 80 % of the stream DOC flux flows through the most superficial soil horizons of the riparian domain and (ii) the 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.

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, in particular concerning DOC flushing – and its variability – at the riparian and upland scales (van Verseveld et al., 2008; Pacific et al., 2010; Laudon et al., 2011). In headwater catchments, stream DOC is mainly controlled by allochthonous inputs (Boyer et al., 1996, 1997; Aitkenhead et al., 1999; Billet 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 on the rising limb of the hydrograph, 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, the flushing being triggered by the rise of the water table induced by the snow melting process (Boyer et al., 1996; 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, however, 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 this tracer in stream water, combined with the monitoring of stream discharge and groundwater level. Among the different potential tracers, the δ^{13}C value appears particularly promising for the following reason. Because of the general prevalence of aerobic conditions in the well-drained soils of upland domains, oxidative processes dominate during the decomposition of plant material. Due to isotopic fractionation during extensive aerobic decomposition, soil organic matter (SOM) is increasingly enriched in the heavier isotope (^{13}C) in these soils, while the lighter ^{12}C is preferentially involved in decomposition reactions (e.g. Wynn et al., 2006). By contrast, wetlands are characterized by anoxic conditions. The lack of oxygen results in an incomplete decomposition of organic material by anaerobic bacteria. Carbon compounds are less degraded and thus retain their original (plant) isotopic signature. Therefore, the δ^{13}C values (i.e. the classical notation used to express the relative deviation between the measured ^{13}C/^{12}C of a sample and the ^{13}C/^{12}C of a standard) of SOM in wetland soils can be expected to be lower than in upland soils. Considering that changes in the isotopic composition of 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 to use δ^{13}C values to distinguish between upland and wetland DOC sources.

However, the use of carbon isotopes for the purpose of locating the source of stream DOC in landscapes is fraught with difficulties. Several pitfalls exist. First, the δ^{13}C value of SOM generally increase with depth in the soil profile (Wynn et al., 2006; Boström et al., 2007; Sanderman et al., 2009; Lambert et al., 2011). Thus, the high δ^{13}C value expected to be characteristic of upland DOC may become confused with the isotopic signature of deep wetland DOC. Second, there may have seasonal changes of the isotopic composition of wetland DOC due to changes in DOC sources and DOC production mechanisms. For example, the release of a microbial DOC component has been advocated to explain DOC peaks in wetland soils after dry summers (Kalbitz et al., 2000). Such a mechanism could temporarily increase the δ^{13}C of the wetland DOC component due to the fact that soil micro-organisms tend to be ^{13}C-enriched by ca. 2 ‰ compared with SOM (Potthoff et al., 2003; Schwartz et al., 2007). Finally and most importantly, 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 these interface domains, 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 DOC isotopic composition in the wetland domain of a rain-dominated catchment, along with the seasonal changes in the hydrological status of the soil and water table depth. In a previous paper (Lambert et al., 2013), we presented the results of such a detailed hydro-chemical monitoring study carried out in the wetland zone of the Kervidy–Naizin catchment, a lowland, rain-dominated agricultural catchment located in western France. Results evidenced a strong vertical and temporal variability of the δ^{13}C values of the soil DOC, which we showed 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 which we observed at the scale of the wetland soil profile is transposed to the stream. For this purpose, we analysed DOC concentrations and DOC δ^{13}C values in the stream at the outlet of the Kervidy–Naizin catchment during 6 successive storm events, which occurred over the same hydrological year as that covered by our first study (Lambert et al., 2013). The DOC concentration and δ^{13}C data are combined with high-frequency hydrometric measurements (groundwater level and stream water discharge), as well as with NO_3, SO_4 and DOC concentration data to decompose water fluxes using 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 relatively 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 studied here is a 4.9 km^2 lowland catchment located in central Brittany, north-western France (Fig. 1). This experimental catchment site is particularly suitable for addressing the issues raised in this study for two reasons. First, the Kervidy–Naizin catchment is included in a long-term observatory (so-called ORE AgrHys) aimed at understanding the impact of agricultural intensification on water pathways and water quality, forming part of the French network of Environmental Research Observatories, and has already been the subject of 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). In particular, the detailed study of nitrate transfer on this site has led to an improved knowledge of water pathways during storm events (Mérot et al., 1995; Durand and Torres, 1996). Second, the processes governing the production and transfer of DOC in this catchment have already been investigated in several studies (Morel et al., 2009; Lambert et al., 2011, 2013), providing a valuable foundation for the present work.

The study site has a temperate oceanic climate with mean annual (1993–2011) precipitation, runoff, and temperature of 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. Ninety percent of the catchment area is used for intensive agriculture, mainly pasture, maize and cereals for dairy production and pig breeding, which has caused heavy nitrate pollution with a mean nitrate concentration in the stream of 80 mg L^{-1} NO_3 (Molénat et al., 2002).

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. Typically, the soil system can be subdivided into two domains: (i) an upland domain composed of well-drained soils (average saturated hydraulic conductivity of 10^{-5} m s^{-1}), and (ii) a riparian wetland domain consisting of highly hydromorphic soils (average saturated hydraulic conductivity of 10^{-6} m s^{-1}). Soils in the latter domain are multilayered, consisting of an upper 10 cm-thick organo-mineral horizon, overlying a 20 cm thick albic horizon, which itself overlies a $>$ 50 cm-thick redoxic horizon (Curmi et al., 1998).

The aquifer in the Kervidy–Naizin catchment consists mainly of unconsolidated weathered bedrock, while the deeper fresh bedrock, even though locally fractured, is generally considered impermeable. On hillslopes, the water-table is 0–10 m beneath the ground surface depending on the season and on the position along the toposequence, and increases in depth farther uphill. In bottomland areas, the water table is near the soil surface during the wet season, and the uppermost layer of the groundwater thus flows through the uppermost organic-rich horizon of the soils of these areas during this season. This zone of interaction between the organic-rich soil horizon and the groundwater flow covers an area that depends strongly on the hydroclimatic conditions. During dry hydrological years, this interaction zone may be restricted to the riparian wetland domains, representing less than 5 % of the total catchment area. During wet hydrological years, the upper limit moves upwards in the hillslope domains, and

the surface-area of the interaction zone may increase up to 20 % of the total catchment surface area (Crave and Gascuel-Odoux, 1997).

Nitrate provides an efficient tool for determining hydrological and hydrochemical dynamics in this catchment. Using nitrate concentrations, previous investigations have shown that the Kervidy–Naizin catchment displays three hydrological and hydrochemical states during the water year (Molénat et al., 2008). After the dry summer, the water table starts to rise. During this rise, a period occurs when the water table is very shallow in the riparian zone but remains deep in the upland domain. In soils of the riparian domain, water movements are essentially vertical during this period with low hydraulic gradient and groundwater flow from the upland domain. Since upland groundwater is the main nitrate reservoir at the catchment scale, nitrate concentrations are low in the stream during this period, the latter being fed essentially by low-NO_3, riparian groundwater. As soon as the groundwater table rises in the upland domain in response to increasing precipitation, the hydrology changes. The interaction zone between groundwater and organic-rich soil horizons extends uphill. During this period, upland groundwater forms the main input to base-flow and stream nitrate export. In late spring and during summer, upland groundwater flow decreases progressively and the bottomland hydrological processes become the predominant control on nitrate concentrations and export.

Using nitrate as well as other solute concentrations (Cl, DOC and SO_4), previous studies have revealed the inputs of four types of water to storm flow in this catchment, namely (i) rainwater, (ii) DOC-rich, riparian wetland soil water (between 0 and 30 cm depth), (iii) NO_3-rich upland shallow groundwater (between 0.3 and 6 m) and (iv) NO_3-poor deep ($>$ 6 m, fresh bedrock) groundwater, the latter two types being the only water types present during baseflow 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 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 (Molénat et al., 2008).

2.2 Previous isotopic data

Soil organic carbon (SOC) contents show two well-marked gradients in the Kervidy–Naizin catchment (Morel et al., 2009): (i) a rapid and strong decrease with depth (e.g. from 6.6 % at 0–10 cm depth to 0.1 % at 80–100 cm depth in riparian wetland soils close to the stream network), and (ii) a progressive decline with increasing distance from the stream network (i.e. from 4.4 % at 0–10 cm close to the stream down to 0.9 % at 0–10 cm, 400 m away from the stream). The stable carbon isotopic composition of SOC also exhibits vertical and horizontal gradients (Lambert et al., 2011, 2013; Fig. 2a). Indeed, SOC from the upper soil layer (0–10 cm) shows lighter δ^{13}C values than SOC from deeper horizons (50–60 cm), the difference progressively increasing from the wetland areas (1 ‰) to the hillslope domains (3.5 ‰). Overall, SOC from the riparian wetland domain exhibits lighter δ^{13}C values (from −29.8 ‰ and −28.9 ‰) than SOC from hillslope domains (from −27.0 ‰ and −23.5 ‰). This lateral isotopic gradient provides the basis for using the Kervidy–Naizin site to investigate the relationships between DOC dynamics and composition in the stream, as well as possible changes in DOC sources in the landscape.

As pointed out in the introduction, previous studies have highlighted strong spatial and temporal variations in the δ^{13}C of DOC in the soils of the wetland domain of this catchment (Mercy wetland site; Fig. 1). Three periods are recognized based on the δ^{13}C values and the hydrological status of the catchment (Fig. 2b), namely: (i) a first period coinciding with the water-table rise in the riparian wetland domain after the dry summer (referred to here as hydrological period A), during which the δ^{13}C values of DOC in the organo-mineral, albic and redoxic horizons lie in a narrow range from −29.5 to −28.5 ‰; (ii) a second period starting with the water-table rise in the upland domain and extending until the onset of its drawdown back into the deeper soil horizons (referred to here as hydrological period B); during this period, an isotopic differentiation of progressively decreasing amplitude is observed between the lower redoxic horizon and the upper organo-mineral and albic horizons, the δ^{13}C value of DOC in the latter two horizons being lower than in the DOC from the deeper redoxic horizon; finally (iii) a third period corresponding to the progressive drawdown of the water table and progressive drying of the riparian soils (referred to here as hydrological period C), during which the δ^{13}C value of the DOC once again becomes 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 hydrological period B in the wetland soils of the Kervidy–Naizin catchment provides evidence for the input in these soils of an isotopically heavier DOC component coming from higher up in the catchment.

2.3 Field instrumentation and water sampling

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 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, respectively, by an increase and a decrease of the stream discharge of $> 1\,\mathrm{L\,s^{-1}}$ in 10 min at the stage recorder. With this method, the storm flow generally ceases prior to the return to "purely" base-flow conditions as regard 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. Stream water samples were collected using a refrigerated (4 °C) automatic sampler (Sigma 900 Max) installed in a technical hut located at the outlet of the catchment (see 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. Base-flow waters between each storm event were collected manually on a daily basis (5 p.m.).

Water table is 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 (Kerroland transect; see Fig. 1) extending from the Mercy wetland site, where the above presented isotopic data were obtained, and the plateau domains of the catchment. Rainfall amounts are also continuously monitored at hourly intervals using a weather station located ca. 300 m away from the catchment outlet.

2.4 Analytical procedures

All water samples were collected in pre-cleaned acid-washed polyethylene bottles, kept at 4 °C, and then transported in the dark to the laboratory for filtration. Filtration was performed successively to a mesh size of < 0.7 µm using GF/F filters, then to < 0.2 µm using cellulose acetate filters (millipore, Millex-GV). Base-flow samples were filtered directly on site, immediately after water sampling. All filters were cleaned twice before use: first with 200 mL of deionised water, and then with a few mL of the sample itself.

Dissolved organic carbon concentrations were determined using a Shimadzu TOC 5050 A total carbon analyser. Accuracy on DOC measurements is ±5 %, based on repeated measurements of standard solutions (K-phtalate). Major anions (Cl^-, NO_3^- and SO_4^-) were measured by ion chromatography (Dionex, model X120), with an accuracy of ±2.5 %.

The $\delta^{13}C$ values of DOC ($\delta^{13}C_{DOC}$) were determined at the Stable Isotope Laboratory of the PEGASE Joint Research Unit of the INRA in Saint-Gilles (France). For the water samples, the procedure was as follows. Filtered water samples were first acidified by adding 1 mL of 1N HCl to remove all traces of inorganic carbon, and then frozen and freeze-dried. Isotopic measurements were performed using an elemental analyzer (EA-CE 1500 NA, Carlo Erba) coupled to 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:

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

where $R = {}^{13}C/{}^{12}C$. 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 measured $\delta^{13}C$ values is better than ±0.2 ‰, based on repeated measurements.

2.5 End-member mixing approach (EMMA)

The end-member mixing approach (EMMA) is a widely used method in catchment hydrology studies for evaluating the relative contributions of waters of different origins to stream discharge (Christophersen et al., 1990; Durand and Torres, 1996; Hinton et al., 1998; Katsuyama et al., 2001; Inamdar and Mitchel, 2006; Morel et al., 2009). This approach, which is based on a simple 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 chemical compositions, has already been successfully used in the Kervidy–Naizin catchment for stormflow decomposition. In particular, Morel et al. (2009) used the EMMA approach to decompose eight storm events occurring in this catchment between February and March 2006. Since four end-members are assumed to contribute to storm flow in this catchment (see above), three chemical tracers are required to perform the mixing analysis. In this study, we used the same tracers as those used by Morel et al. (2009), namely DOC, SO_4 and NO_3. Since the composition of rain water and deep groundwater is temporally stable in this catchment, we applied the same concentrations as those used by Morel et al. (2009) for these two end-members. For the other two end-members – namely, DOC-rich shallow riparian soil water and NO_3-rich shallow upland groundwater – temporal variations were taken into account by considering chemical data obtained during the course of the study by Lambert et al. (2013).

3 Results

3.1 Hydrology

Results of the hydrological monitoring are shown in Fig. 3. 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 yr. The heavy rainfall events at the beginning of October 2010 caused a rise of the water table in the riparian domain (PK1 piezometer), 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 piezometer). This period of high upland groundwater flow ended in April 2011, when the water table started to fall in the riparian domain (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. The six monitored storm events, numbered from 1 to 6 in the following, all 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 $\mathrm{L\,s^{-1}}$), except for storm event No 3 whose peak discharge reached 430 $\mathrm{L\,s^{-1}}$.

Figure 4 shows a detailed view of the water-table fluctuations during each of the six monitored storm events at two different locations: (i) in the riparian domain (PK1 piezometer) and (ii) 190 m uphill in the transition zone between hydromorphic and well-drained soils (PK3 piezometer; Fig. 2a). The figure shows that the water table, both in the riparian and uphill domains, reacts quickly to rainfall in the same way as the stream discharge. In addition, it can be noted that the hydraulic gradient between riparian and hillslope domains was constant from storm events No 2 to 4, with the water table in all three events remaining within the topmost 15 cm of the soil profile in the hillslope domain.

3.2 Concentration data

Dissolved organic carbon concentrations in the stream varied from 2.5 to 21.5 $\mathrm{mg\,L^{-1}}$ during the study period (Fig. 5a). Maximum concentrations were reached during storm events, whereas minimum concentrations occurred during inter-storm periods. There was a marked difference between stream DOC data obtained from daily regular monitoring and from 30 min to hourly monitoring performed during the storm events, the latter showing generally much higher concentrations than the former. This is due to the rapid response of the catchment to rainfall, implying that very high frequency monitoring is required to capture the dynamics of DOC during storm events.

The temporal variations of in-stream NO_3 and SO_4 concentrations show that NO_3 and SO_4 concentrations were respectively inversely and positively correlated with discharge (Fig. 5b). There was a marked temporal evolution of SO_4 concentrations, which showed a continuous decrease from the beginning to the end of the study period during baseflow accompanied by a decrease in concentration variability during storm events. In the case of NO_3, 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, yielding results that are consistent with previous studies of nitrate dynamics in this catchment (i.e. Molénat et al., 2008).

The DOC vs. discharge relationships (Fig. 6) 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 8 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.

3.3 Isotopic data

In contrast to DOC concentrations, which showed comparable and systematic variations during the six monitored storm events (Fig. 6), we observed strong temporal changes in the intra-storm isotopic variability (Fig. 7). More specifically, while $\delta^{13}C_{DOC}$ varies by ca. 2‰ ($\delta^{13}C_{DOC}$ values ranging 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 being observed during storm event No 5 with nearly constant intra-storm $\delta^{13}C_{DOC}$. We found no correlation between the magnitude of variations in intra-storm $\delta^{13}C_{DOC}$ variations and the magnitude of variations in intra-storm DOC concentration or water discharge. By contrast, we noted that $\delta^{13}C_{DOC}$ 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. Thus, there was a comparable and systematic change in DOC composition during the course of the six monitored storm events, with isotopically lighter DOC entering the stream during the early part of each storm event compared with the DOC entering the stream after the peak discharge (Fig. 7).

3.4 Hydrograph separation results

The mixing diagrams (Fig. 8) showed that the stream chemistry was generally within the field defined by the four 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 DOC-rich riparian soil end-member during hydrological period A. Such a hypothesis is consistent with the stream NO_3 chemograph showing that hydrological period A (during which storm event No 1 took place) was characterized by a strong temporal variability of in-stream nitrate concentrations (Fig. 5). Molénat et al. (2008) have shown that this variability is characteristic of riparian wetland soils

during the rewetting period preceding the rise of the water table in the upland domain, variability which is probably not captured satisfactorily by the bi-weekly sampling frequency used in the study of Lambert et al. (2013).

The results of the hydrograph decompositions (Fig. 9) are comparable to those obtained by Morel et al. (2009) for the 2006 storm events. As observed by these authors (op. cit.), we found that (i) the contribution of deep and hillslope groundwaters was fairly constant during the six newly investigated storm events and (ii) the major contribution during the peak discharge came from the riparian wetland soils. We also confirmed a previously noted feature of hydrograph decomposition in this catchment, namely, that the proportional contribution of riparian wetland soil water seems to increase with the magnitude of storm events (Morel et al., 2009).

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 storm events occurring soon after the transition between hydrological periods A and B (events No 2 to 4) showing a much larger range of values than storms occurring before (event No 1) or long after (events No 5 and 6) this transition (Fig. 7). Figure 10 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 confirms the currently accepted view that the source of DOC in streams draining headwater catchments is allochthonous, at least during the wet season (Boyer et al., 1997; Hagedon et al., 2000; Inamdar et al., 2006; Sandermann et al., 2009), a view also consistent with what is known about changes in water pathways and water sources during storm flow generation at this site. At the Kervidy–Naizin catchment 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) overland flow above the saturated wetland soil horizons (this occurs generally throughout the duration of the rainfall); (ii) subsurface flow through the uppermost (i.e. organo-mineral) horizons of wetland soils; (iii) subsurface return flow from shallow hillslope groundwater flowing through deeper (i.e. redoxic) wetland soil horizons; and (iv) finally, when base-flow conditions are restored, subsurface return flow involving a mixture of shallow hillslope groundwater and deep (< 6 m) groundwater flowing through the redoxic part of the soil profile. Previous isotopic results from the Mercy riparian wetland zone have also shown that (i) the DOC flowing through the uppermost, organo-mineral part of the soil profile tends to have systematically lower δ^{13}C values than the DOC flowing through the deeper, redoxic part of the soil profile (Fig. 2b) (Lambert et al., 2011, 2013), and (ii) the vertical difference in δ^{13}C values of the DOC flowing through this riparian zone changes on a seasonal basis (Fig. 2b) (Lambert et al., 2013). Therefore, the storm flow generation pattern described above is fully consistent with the following points: (i) $\delta^{13}C_{DOC}$ values vary within each individual storm event, (ii) $\delta^{13}C_{DOC}$ values tend to be lower during the rising limb of the hydrograph and at peak flow than during the decreasing limb of the hydrograph or/and during pre-event conditions, and (iii) the range of $\delta^{13}C_{DOC}$ values during individual storm events changes on a seasonal basis in the same way as the vertical range of $\delta^{13}C_{DOC}$ values in the soil profile.

Even if the observed temporal change in intra-storm $\delta^{13}C_{DOC}$ values appears globally consistent with temporal changes in riparian soil $\delta^{13}C_{DOC}$ values, comparison of Figs. 9 and 10 reveals some inconsistencies. For example, the $\delta^{13}C_{DOC}$ values observed at peak flow during storm events No 2 and 3 turn out to be significantly lower than the corresponding $\delta^{13}C_{DOC}$ values in wetland soil organo-mineral 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 redoxic 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. Lateral variations in the isotopic composition of DOC may occur in the soil horizons of this system at the catchment scale, which could explain why the $\delta^{13}C_{DOC}$ values of stream DOC do not strictly correspond to the values obtained from the Mercy wetland soils. In fact, it is very likely that riparian wetland zones in the Kervidy–Naizin catchment differ spatially as regards their $\delta^{13}C_{DOC}$ values. 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) (Lambert et al., 2013). This input is caused by the activation of a hydrological connectivity developed across the riparian-upland continuum in response to the rise of the water table in the upland domains (Lambert et al., 2013). In this scenario, which is typical of catchments developed on impermeable basement rocks (McGlynn and McDonnald, 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 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, being more marked in its central part at the location of the Mercy site, than in areas further upstream with steeper slopes. 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 Transport pathway of DOC at the soil-stream interface

Using the EMMA results, we can estimate the total contribution of each riparian soil horizon to the DOC flux exported by the stream during the six studied storm events, bearing in mind that (i) these riparian soil horizon are transit zones for DOC coming from upland zones, and (ii) the Mercy zone is not strictly representative of the entire riparian domain across the catchment. Figure 11 shows that that the contribution of the uppermost organo-mineral soil horizons represents between 78 and 89 % of the total DOC exported by the stream. This result compares well with the 65–90 % contribution calculated by Morel et al. (2009) from the EMMA-based decomposition of 8 successive storm events that occurred in this catchment during hydrological-year 2005–2006.

We can also attempt to determine the pathways through which DOC is transferred from the soil to the stream using the isotopic results obtained for storm event No 4 that occurred on 5–6 January 2011, and for which there is a fairly good consistency between stream and soil isotopic data (Fig. 10). 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, which can allow to use these data along with the hourly measured stream $\delta^{13}C_{DOC}$ values to calculate the relative contribution of the organo-mineral and redoxic horizons to the total stream DOC. Assuming $\delta^{13}C_{DOC}$ values of −28.7 and −27.2 ‰ for the DOC circulating in the organo-mineral and redoxic soil horizons, respectively, we can calculate that the uppermost organo-mineral horizons 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, we should point out that 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 organo-mineral DOC end-member by 0.1 ‰ (−28.6 instead of −28.7 ‰) 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 organo-mineral horizons of the riparian soils of this catchment to the DOC fluxes exported during storm events.

4.3 Contribution of riparian vs. upland DOC sources

As pointed out in the introduction, recent studies have shown that the transport of DOC from soil to stream is not simply the result of the flushing of the DOC generated in the riparian soils close to the stream network, but can also result from the mobilization of DOC produced in upland soils (McGlynn and McDonnald, 2003; Sandermann et al., 2009; Pacific et al., 2010). This scenario involving the mobilization of proximal and distal sources during DOC transfer in catchments was first proposed for mountainous catchments in New Zealand and the Western United States (McGlynn and McDonnald, 2003; Bishop et al., 2004; Hood et al., 2006; Sandermann et al., 2009; Pacific et al., 2010) and recently extended to lowland catchments such as the present Kervidy–Naizin site (Lambert et al., 2013). The mobilization of DOC is driven by the water table rise, which firstly affects the wetland domains, and then extends further upslope if the water table rise is sufficient. 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. In the past, the recognition of this transfer process was achieved essentially by coupling the results obtained from monitoring hydrological parameters (stream and groundwater flow) and water chemistry (DOC concentrations in stream and soil water) (e.g. Pacific et al., 2010). Although the combination of these data may provide convincing evidence for the existence of a relay between wetland and upland DOC sources, no study has so far attempted to quantify precisely the contribution of each source to the total DOC flux exported by streams, nor 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 riparian and upland sources to the stream DOC flux. This estimation is possible because of the difference in $\delta^{13}C_{DOC}$ values between these two DOC sources, which can be used to calculate their respective contributions by means of mass balance equations. For this purpose, the $\delta^{13}C_{DOC}$ values of wetland- and upland-derived components were set as equal to −28.6 and −25.0 ‰, respectively. The first value corresponds to the average $\delta^{13}C_{DOC}$ value of water-extractable DOC measured in samples of the Mercy wetland upper organo-mineral soil horizon (Lambert et al., 2013). It also corresponds to the average measured value of $\delta^{13}C_{DOC}$ in Mercy soils sampled at the transition between hydrological periods A and B, just before the shift caused by the input of isotopically heavier DOC form upland soils (Fig. 2b) (Lambert et al., 2013). The second value (−25.0 ‰) corresponds to the average $\delta^{13}C_{DOC}$ values measured on water-extractable DOC obtained on soil samples collected along the Kerolland Transect (0–40 cm depth), between piezometers PK2 and PK4 (Lambert et al., 2013). Fig. 12 presents the results for storm events No 2 to 5, while storm event 1 is excluded from the calculation because the water table was still deep in the upland domain when this storm event occurred, thus preventing the transfer of any upland DOC to the stream. The results show that the contribution of upland DOC was maximal during storm events No 2 and 3, averaging 33 % of the total DOC flux exported at the catchment outlet, and then decreased during storm events No 4 to 6, when this component represented 10 % or less 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 when the rise in water table is maximum in the upland domains – the riparian wetland zones remain by far the dominant DOC sources. Our estimates also show that the relative contribution of upland DOC sources was not constant during the studied period, since it decreased abruptly after storm event No 3 (Fig. 12). Interestingly, this 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 soils so-

lution, with $\delta^{13}C_{DOC}$ values decreasing gradually during hydrological 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 with a comparably low level of autochthonous stream production (Sandermann et al., 2008, 2009). In this catchment, the seasonal depletion of the hillslope DOC reservoir is accompanied by a change in radiocarbon ages of the DOC indicative of 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 as an open question for future work.

Unlike upland soils, wetland soils in headwater catchments developed on impervious bedrocks (such as the Kervidy–Naizin catchment) appear to behave as a near-infinite DOC source pool (e.g. Hinton et al., 1998; McGlynn and McDonnel, 2003; Sandermann et al., 2008, 2009; Pacific et al., 2010). This result was already obtained in previous studies carried out in the Kervidy–Naizin catchment by Morel et al. (2009), who noted the constancy of DOC concentrations in the riparian soils of this catchment, despite the continuous succession of storm events. This conclusion has been recently re-inforced by Lambert et al. (2013), who monitored the DOC concentration in soils of the Mercy wetland on a bi-weekly basis during an entire hydrological year. Moreover, these authors found no evidence of seasonal exhaustion of the DOC store built up in the soils of this zone. 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 the results obtained on the Kervidy–Naizin site (Morel et al., 2009; Lambert et al., 2011, 2013; this study) suggest that DOC is primarily transportlimited in this catchment, given the dominant role of shallow riparian DOC-sources in contributing the major part of the exported DOC.

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

The results of this study indicate that carbon isotopes provide a powerful tool for locating DOC sources in the landscape, enabling us to model and quantify DOC transport processes at the catchment scale. At Kervidy–Naizin, the combined monitoring of the temporal and spatial evolution of the isotopic composition of soil water DOC and of the temporal evolution of the isotopic composition of stream DOC during storm events proves effective for unravelling the transport pathways of DOC in the soil profile and locating the ultimate DOC sources in the landscape. We should stress that 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 and continuous monitoring of the water table movements across the stream-wetland-upland continuum. Also, they could not have been obtained without a detailed exploration of the variability of the isotopic composition of SOM and DOC along this continuum. 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, which is a prerequisite condition for using the isotopic tool to trace DOC sources and DOC transport processes, is met in other headwater catchments, thus allowing the implementation of the carbon isotope tool with the same efficiency than in the present case? (2) Why is it so important to determine the ultimate source of DOC in the landscape? What are the issues related to such a determination?

We can probably answer positively to the first question. Indeed, and as mentioned above, the wetland-upland gradient observed at Kervidy–Naizin ($\delta^{13}C_{DOC}$ varying from −28.7 ‰ in the wetland to −25.2 ‰ 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 gradient observed at Kervidy–Naizin will be reproduced elsewhere. The existence of a systematic DOC isotopic gradient across topographic slopes is corroborated by comparing the Kervidy–Naizn catchment with 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, as against forested/pastured alpine soils in the Urseren Valley. This comparison clearly indicates that we should consider 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., 2001). The challenge faced here concerns agricultural catchments such as Kervidy–Naizin, 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 McDonnel, 2003; Pacific et al., 2010). Carbon isotopes are expected to provide a valuable tool to test this hypothesis, 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.

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 published data on the isotopic composition of DOC in the soils of this catchment. We showed that the observed temporal change in the range of intra-storm δ^{13}C values closely reflected the temporal change of δ^{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 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. 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 during 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 an extremely powerful tool for tracing DOC sources and DOC transport mechanisms in headwater catchments. 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 – as well as the corresponding water flows – 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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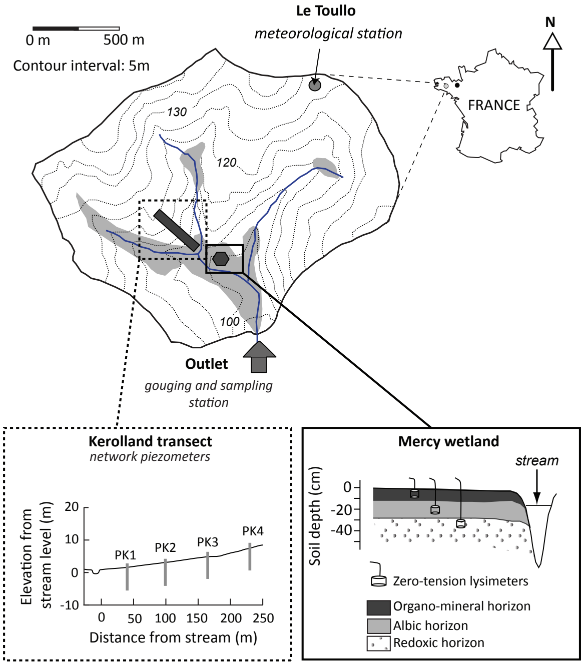

Fig. 1. Location and geomorphic map of the Kervidy–Naizin experimental catchment (Brittany, France). Also shown are the sites where the instruments used in this study are installed. Grey areas located along the stream channel network indicate the maximum extent of the interaction zone between the organo-mineral horizon of the soils and the upper layer of the groundwater. The sketch at bottom right shows the locations in the soil profile of the soil water samples previously analysed and discussed by Lambert et al. (2013).

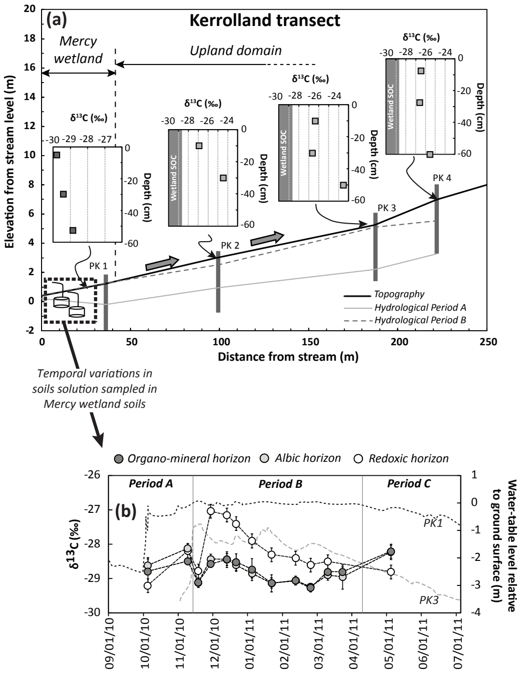

Fig. 2. Sketch illustrating **(a)** spatial variability of δ^{13}C for soil organic carbon from the riparian wetland domain to the hillslope domains of the Kervidy–Naizin catchment and **(b)** seasonal variations of the δ^{13}C value of DOC in riparian wetland soils in phase with water table fluctuations. The average measured water-table levels during hydrological period A and B are also shown in box **(a)**, illustrating upwards migration of shallow groundwater flow into the organic-rich horizons of upland soils with high δ^{13}C values during hydrological period B (arrows). Data source: Lambert et al. (2011, 2013).

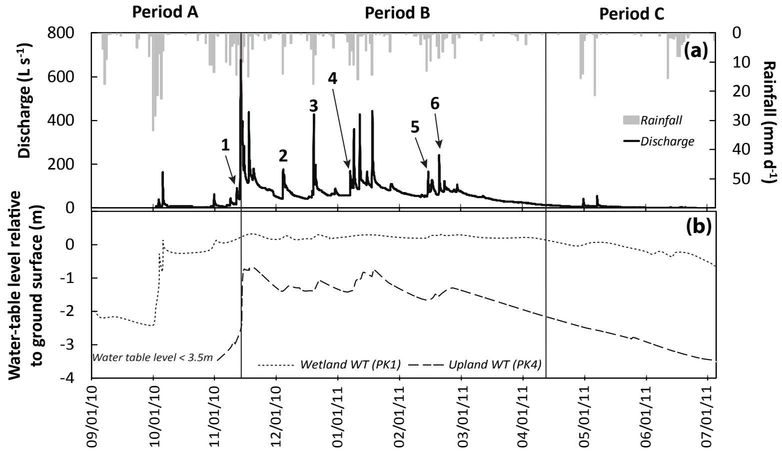

Fig. 3. (a) Record of hourly discharge and daily rainfall and **(b)** record of hourly water table levels during the investigated periods. Monitored storm events are indicated by numbers.

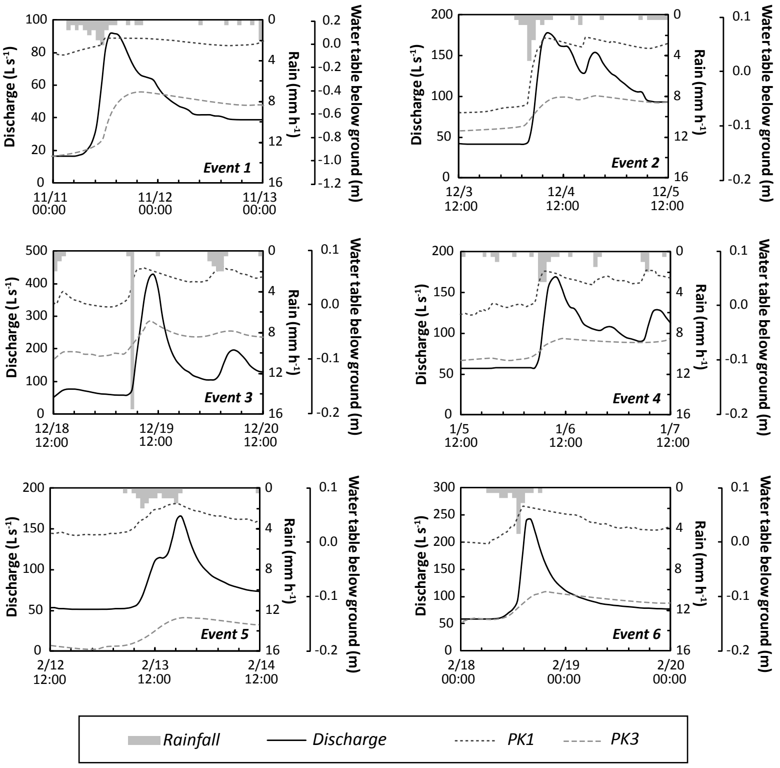

Fig. 4. Stream discharge (black line), rainfall (bars) water table fluctuations (dashed lines) during each of the six studied storm events. The precise position of the two piezometers from which groundwater data come from (PK1 and PK3) can be found in Fig. 2a.

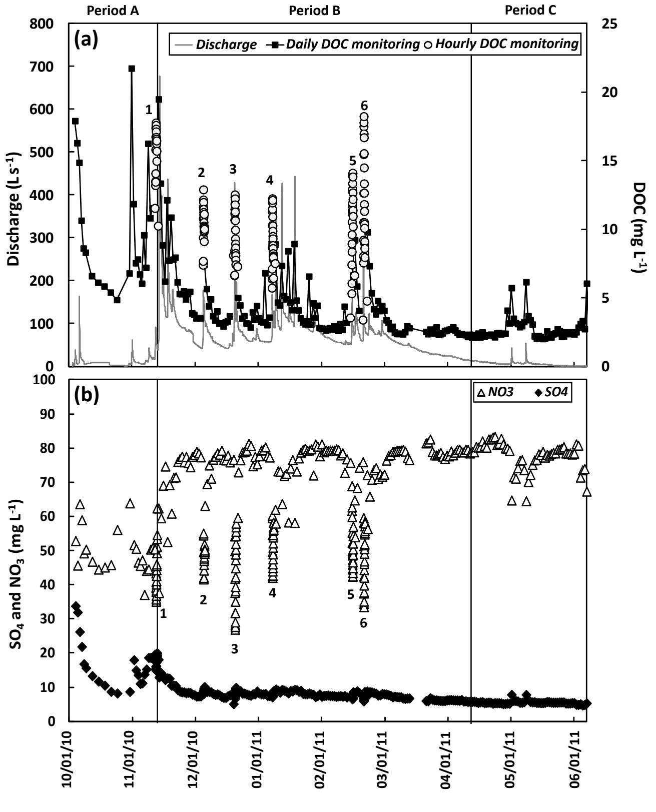

Fig. 5. Temporal variations in **(a)** stream discharge and DOC concentrations, and **(b)** nitrate and sulphate concentrations at the catchment outlet during the study period. Monitored storm events are indicated by numbers.

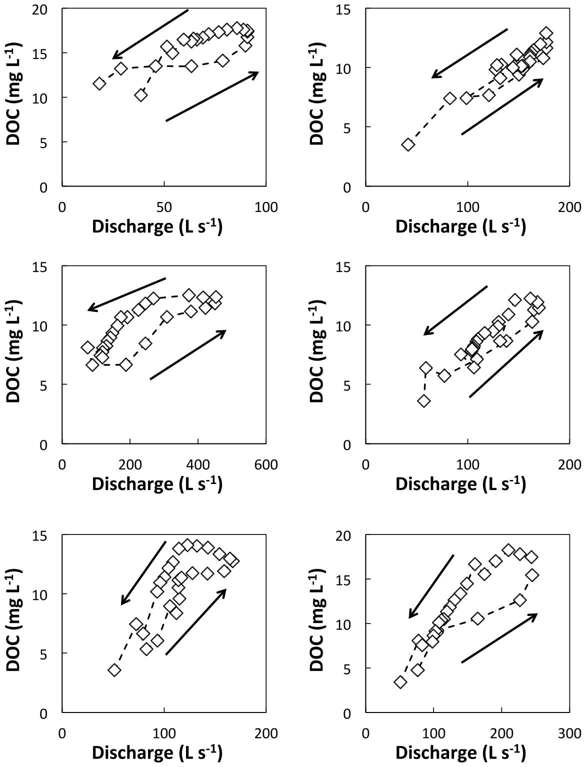

Fig. 6. Discharge vs. DOC concentrations showing hysteresis patterns (arrows indicate chronology) for the six investigated storm events.

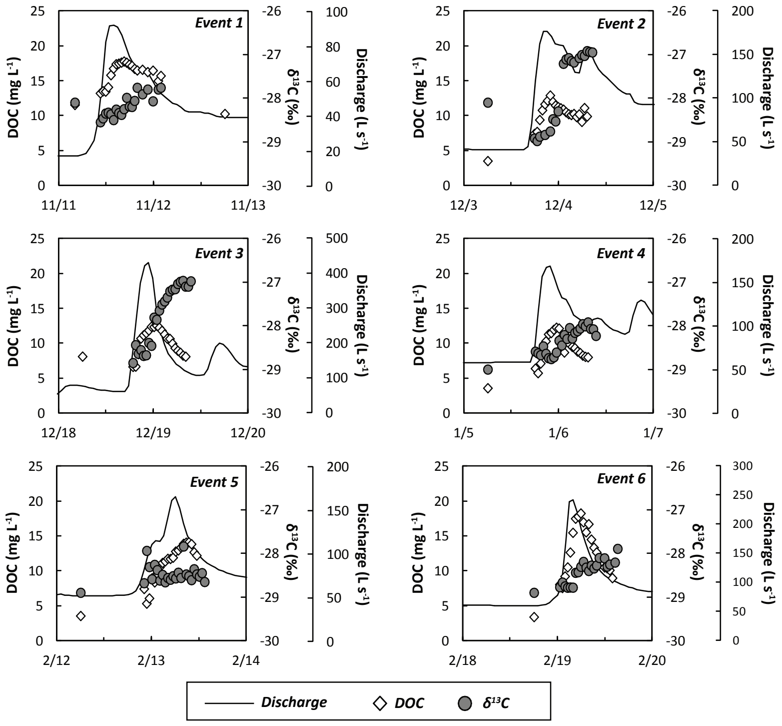

Fig. 7. Changes in stream DOC concentrations, stream $\delta^{13}C_{DOC}$ values and stream discharge during the six investigated storm events.

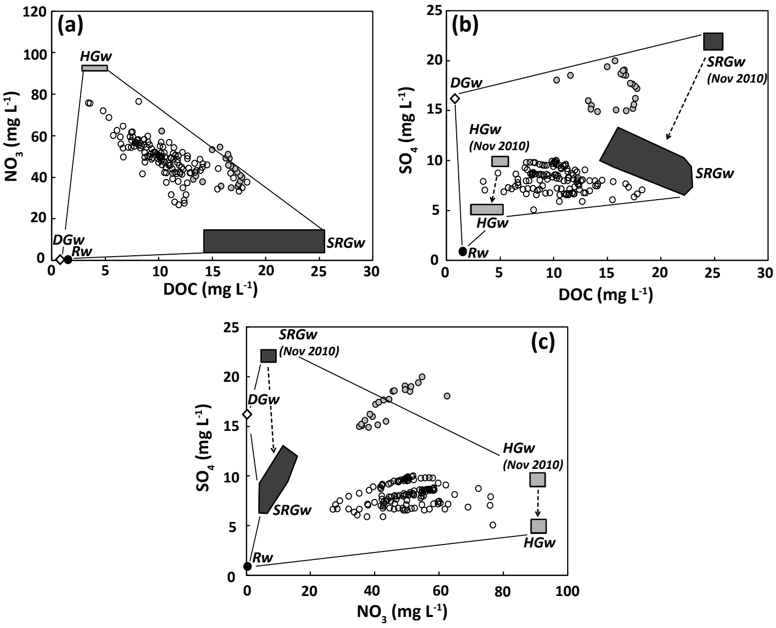

Fig. 8. End-member mixing diagrams for the six investigated storm events: **(a)** NO_3 vs. DOC; **(b)** SO_4 vs. DOC; **(c)** SO_4 vs. NO_3. Data from event No 1 on 11 November 2010 shown as solid grey circles. RW: rain water; DGw: deep groundwater; SRGw: shallow riparian groundwater; HGw: hillslope 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).

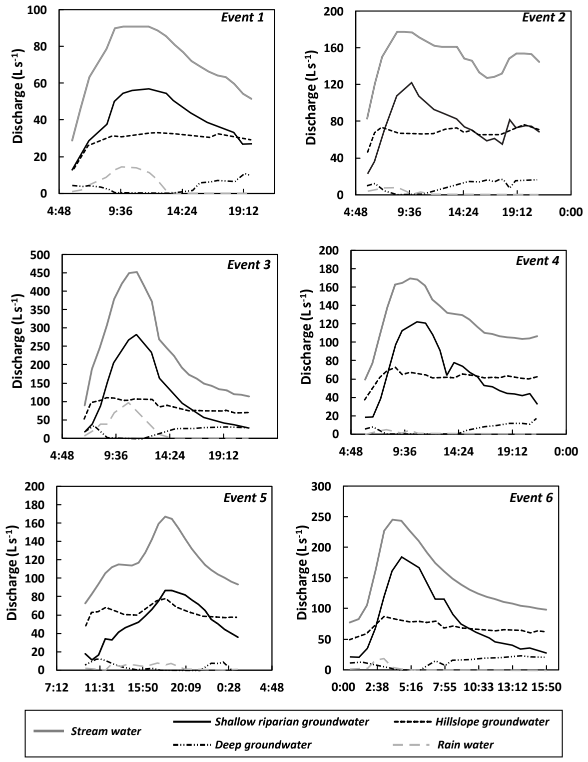

Fig. 9. End-member contributions during the six investigated storm events.

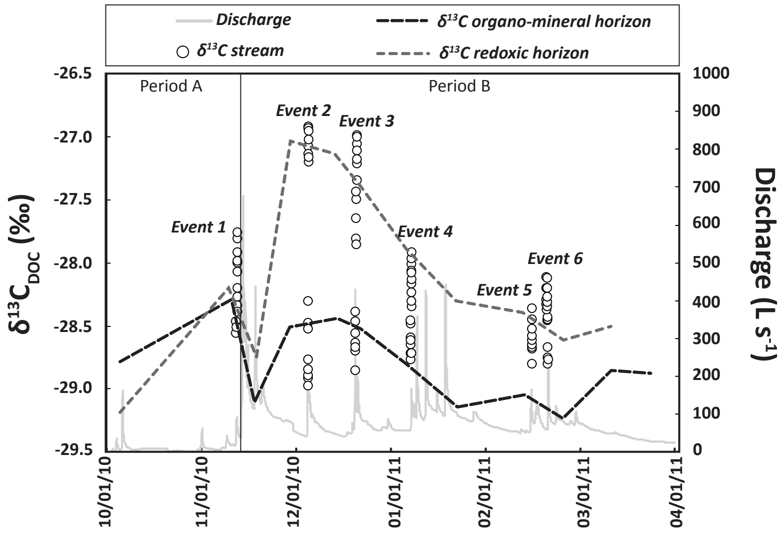

Fig. 10. Comparison between storm flow DOC isotopic data and the seasonal DOC isotopic trend observed in riparian soil waters, at the Mercy site. Riparian soil water data are from Lambert et al. (2013).

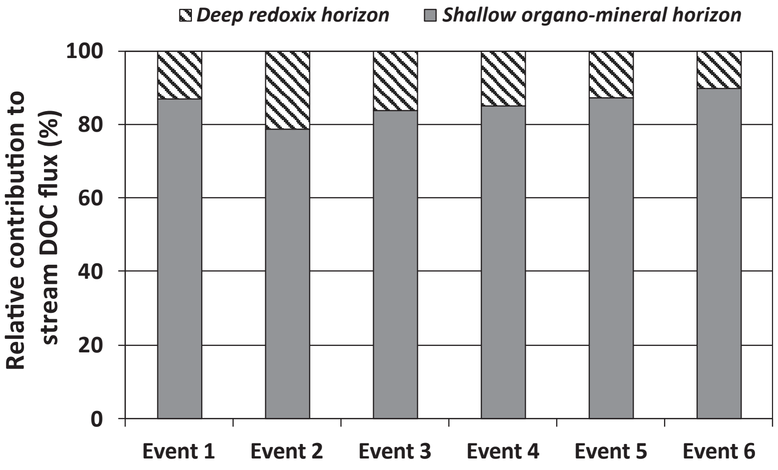

Fig. 11. Contribution of the DOC transiting through the organo-mineral and redoxic riparian soil horizons, respectively, to the total storm DOC flux as calculated using the NO_3, DOC, and SO_4 concentrations and the EMMA method.

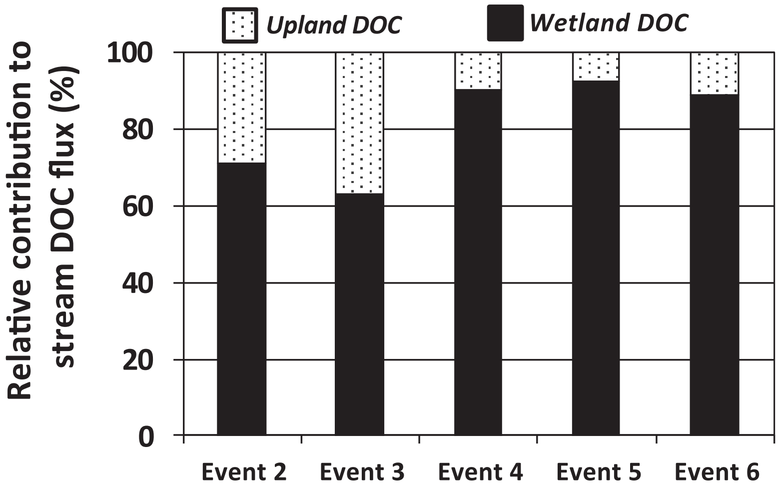

Fig. 12. Relative contribution of riparian and upland DOC sources as calculated from isotopic data.