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Carbon isotopes as tracers of dissolved organic carbon sources and water pathways in headwater catchments

Thibault Lambert [a,*], Anne-Catherine Pierson-Wickmann [a], Gérard Gruau [a], Jean-Noël Thibault [b], Anne Jaffrezic [c]

[a] Centre Armoricain de Recherches en Environnement, Unité mixte de Recherche CNRS – Université de Rennes I "Géosciences Rennes", Campus de Beaulieu, 35042 Rennes Cedex, France

[b] Unité Mixte de Recherche INRA – Agrocampus Ouest "Systèmes d'Élevage, Nutrition Animale et Humaine", Domaine de la Prise, 35590 Saint-Gilles, France

[c] Centre Armoricain de Recherches en Environnement, Unité Mixte de Recherche INRA – Agrocampus Ouest "Sol, Agronomie, Spatialisation", Route de Saint Brieuc, 35042 Rennes Cedex, France

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SUMMARY

Stable carbon isotopes ($\delta^{13}C$) are assessed in further detail for their potential to (i) trace the relationship between spatial variations in the source of dissolved organic carbon (DOC) in soils and temporal variability of both DOC concentration and composition in streams, and (ii) elucidate water pathway changes during storm events in headwater catchments. For this purpose, we investigated $\delta^{13}C_{DOC}$ values in a wetland soil (0–50 cm), in deep groundwater (until 6 m) and during a storm flow event with high-resolution monitoring ($\leqslant$hourly basis) in a small, lowland catchment in western France (Kervidy-Naizin catchment). The results show a combined increase of stream DOC concentration (from 4 to 14 mg L^{-1}) and decrease of stream $\delta^{13}C_{DOC}$ (from −27 to −29‰) with increasing discharge, suggesting a change in DOC sources between base flow and storm flow periods. Such an interpretation is consistent with the $\delta^{13}C_{DOC}$ values in soils that show a 6‰ vertical variation, with $\delta^{13}C_{DOC}$ values of the uppermost soil horizons (0–10 cm) of the wetland domains being close to those measured in the stream channel during the ascending limb of the hydrograph. Overall, the results presented in this study are consistent with a model in which the water-table rise and wetland runoff caused by rainfall lead to a flushing of the DOC stored in the uppermost soil horizons of the wetland domains near the channel network. Subsequently, these wetland soils become the dominant DOC source during storm events (ca. 70% of the total DOC flux). In this way, the stream DOC isotopic composition reflects the combined effects of the vertical variation of soil organic matter composition as well as the changes in water routing through time. This study demonstrates the ability of the stable isotopes of carbon to serve not only as a tool for the location of stream DOC sources in landscapes but also the reconstruction of water pathways in headwater catchments.

1. Introduction

Allochthonous input of organic carbon is now widely accepted as the dominant process controlling dissolved organic matter (DOM) concentrations in headwater stream ecosystems (Aitkenhead et al., 1999; Brooks et al., 1999). Several studies have reported that in-stream DOC concentrations generally increase with increasing discharge (Boyer et al., 1996; Royer and David, 2005; Dalzell et al., 2007; Morel et al., 2009; Sanderman et al., 2009). Conceptually, this can be explained by the rise in water table that accompanies rainfall or snowmelting, as well as by the increased flow through the DOM-rich upper soil horizons caused by this rise; in this way, DOM-enriched soil waters are flushed towards the stream channel (see Boyer et al., 1996, 1997). This so-called flushing mechanism has been documented in a large number of headwater catchments, including forested, alpine and lowland agricultural catchments (see Boyer et al., 1996, 1997; Royer and David, 2005; Morel et al., 2009).

Thus, it appears there may be a close link between the spatial (essentially, vertical) variability of DOM in soils and the temporal variability of DOM in streams. Unravelling this link is particularly importance since the DOM in topsoil horizons may be different in composition and reactivity compared to the DOM from deeper soil horizons (Amundson, 2001; Sanderman et al., 2009), which could cause marked changes in the composition and reactivity of stream DOM between storm flow and base flow periods. This could be particularly significance in agricultural catchments, where the DOM may act as a carrier of pollutants (e.g. pesticides) (Driscoll et al., 1988; Campbell et al., 1992).

* Corresponding author. Tel.: +33 0 2 23 23 65 89.
E-mail address: thibault.lambert@univ-rennes1.fr (T. Lambert).

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Many of the chemical characteristics of DOM show relatively predictable variations in soil profiles, with the result that these characteristics represent potentially useful tracers of temporal changes of DOM sources in streams. The DOM can be characterized by its molecular weight, C/N ratio, specific UV adsorption, the distribution of functional groups and δ^{13}C value (Maurice et al., 2002; Sanderman et al., 2008, 2009). Among these different potential tracers, the δ^{13}C value appears particularly promising for two reasons: (i) soil organic matter (SOM), whatever the vegetation cover, generally shows a systematic and predictable vertical variation of the δ^{13}C value, which, in most cases, greatly exceeds analytical uncertainty (Wynn et al., 2006; Wynn and Bird, 2007 and references therein); (ii) the few existing studies on the variation of the DOM isotopic signature with depth in soils have shown that the systematic and predictable vertical variation in the isotopic composition of SOM is also observed for the soil DOM (Ziegler and Brisco, 2004; Amiotte-Suchet et al., 2007; Sanderman et al., 2009).

In this study, we focus on testing whether carbon isotopes can be used to assess and quantify temporal changes in DOM sources in headwater catchments. For this purpose, we measured (on an hourly basis) the δ^{13}C values of stream DOM during a storm event that affecting a small (500 ha) agricultural catchment (the so-called Kervidy-Naizin catchment) located in Brittany, western France, and then compared the observed variations in the stream with the vertical variability of soil DOM δ^{13}C values. We also investigated the vertical variability of SOM δ^{13}C values. Combined with previous published results on this catchment, we used the present detailed isotopic data set to demonstrate a close correlation between vertical variations in SOM and soil DOM isotopic composition, changes in water pathways and temporal variations in δ^{13}C of stream DOM.

2. Materials and methods

2.1. Site description

The Kervidy-Naizin headwater catchment (500 ha) is located about 100 km southwest of Rennes in Central Brittany, western France (Fig. 1). This site was selected for three reasons: (i) it belongs to a long-term monitoring programme of water dynamics and water quality as part of the French network of Environmental Research Observatories (ORE), jointly set up and managed by Cemagref, INRA and CNRS (Durand and Torres, 1996; Pauwels et al., 1998; Molénat et al., 1999, 2002, 2008; Dia et al., 2000); (ii) early studies of nitrate transfer on this site has led to a relatively good knowledge of water pathways during base flow and storm flow periods (Mérot et al., 1995; Durand and Torres, 1996); (iii) a recent study of DOC dynamics in this catchment shows that between 60% and 85% of the DOC entering the stream during storm events originates from the upper layers (between 0 and 20 cm) of the riparian wetland soils (Morel et al., 2009); this latter study provides a comprehensive framework for testing the isotopic tracer presented and discussed in this paper.

The bedrock of the Kervidy-Naizin catchment is made up of fissured and fractured upper Brioverian schists. The catchment elevation ranges between 93 and 135 m above sea level and the steepest slopes do not exceed 10%. The climate is humid temperate: the mean annual rainfall recorded over the last 22 years is 713 mm, while the mean annual temperature and mean annual runoff recorded over the same period are 11 °C and 305 mm, respectively (Morel et al., 2009). Rainfall events rarely exceed 20 mm per day, and 80% of precipitations have intensity less than 4 mm per hour. Most of the storm events occur between November and March. Due to the small volume of water stored in the schist bedrock, the stream usually dries up from the end of August to the beginning of November. Ninety percent of the catchment area is dedicated to intensive agriculture, being composed mainly of pastures, maize and cereals for dairy production and pig breeding. Note that the intensive agriculture carried out on the Kervidy-Naizin catchment has led to heavy nitrate pollution with a mean nitrate concentration in the stream of around 70 mg L^{-1} NO_3^- (Molénat et al., 2008).

Soils in the catchment have developed into a loamy material derived from bedrock weathering and aeolian Quaternary deposits. All the soils are classified as Luvisols. Nevertheless, the poor drainage in the bottomland domain leads to seasonal waterlogging with the development of hydromorphic soils. The hydrology of the catchment can be summarized by the contrast of two domains depending on water-table fluctuations: (i) a hillslope domain, where the water table always remains a few metres below the soil surface and is associated with essentially vertical water pathways, and (ii) a wetland domain where the water table usually reaches the soil surface during the wet season, namely, winter and spring (Molénat et al., 2008). The extent of this wetland domain is highly variable, ranging from 5% to 20% of the total surface area of the catchment depending on hydroclimatic conditions (Gascuel-Odoux et al., 1998).

Soil organic carbon (SOC) contents show two well marked gradients (Morel et al., 2009): (i) a rapid and strong decrease with depth: e.g. from 4.4% at 0–10 cm depth to 0.1% at 80–100 cm depth in wetland areas close to the stream network, and (ii) a progressive decline with increasing distance to the stream network: e.g. 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.

Previous studies focusing on water pathways and solute sources in the Kervidy-Naizin catchment showed that the uppermost soils of the wetland areas (between 0 and 30 cm depth) are the main sources of DOC and waters during storm events, accounting for 60–85% and 35% of the DOC and water fluxes, respectively (Mérot et al., 1995; Durand and Torres, 1996; Gascuel-Odoux et al., 1998; Molénat et al., 1999; Morel et al., 2009). More specifically, four water reservoirs have been identified as contributing to the stream flow in this catchment: (i) rainfall; (ii) deep (>3 m) groundwater; (iii) wetland soil water (including wetland runoff); and (iv) shallow (between 1 and 3 m deep), hillslope groundwater (Mérot et al., 1995; Durand and Torres, 1996; Morel et al., 2009). Of these four end-members, only the last two contribute significantly to the stream DOC, while the contribution of the deep groundwater and rainfall end-members always remains very low (<3%; see Morel et al., 2009).

2.2. Hydrometric monitoring

Since 1993, the outlet of the Kervidy-Naizin catchment has been equipped with an automatic gauge station providing stream discharge measurements every minute, while a weather station located 300 m away from the outlet provides a record of the rainfall at hourly intervals. A network of six piezometers installed along a direction parallel to the expected groundwater flow (so-called Kerolland transect; see Fig. 1) is used to monitor water-table fluctuations and follow up variations of groundwater chemistry in space and time. Water levels in these piezometers are measured and recorded automatically every 15 min and read manually every month. These piezometers allow groundwater collection at depths ranging from 1.5 m (pK1 and pK2) to 6 m (pK6).

2.3. Water sampling

On the 3rd March 2009, a storm event was sampled using an automatic sampler (Sigma 900 max) located at the outlet of the