

**Transfer of DOM at the soil-stream interface in a lowland headwater catchment**

L. Jeanneau et al.

# Sources and transfer mechanisms of dissolved organic matter during storm and inter-storm conditions in a lowland headwater catchment: constraints from high-frequency molecular data

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

The transfer of dissolved organic matter (DOM) at soil–river interfaces controls the biogeochemistry of micropollutants and the equilibrium between continental and oceanic C reservoirs. Then determining the transfer mechanisms of DOM is of main importance for ecological and geochemical reasons. Is stream DOM the result of the flushing of pre-existing soil DOM reservoirs activated by the modification of water flow paths? The evolution of the chemical composition of stream DOM investigated by thermally assisted hydrolysis and methylation (THM) using tetramethylammonium hydroxide (TMAH) coupled to a gas chromatograph and mass spectrometer (THM-GC-MS) during inter-storm conditions and five storm events with a high-frequency sampling gives new insights on this question. In inter-storm conditions, stream DOM is inherited from the flushing of soil DOM, while during storm events, the modification of the distribution of chemical biomarkers allows the identification of three additional mechanisms. The first one corresponds to the destabilization of microbial biofilms by the increase in water velocity resulting in the fleeting export of a microbial pool. The second mechanism corresponds to the erosion of soils and river banks leading to a partition of organic matter between particles and dissolved phase. The third mechanism is linked to the increase in water velocity in soils that could induce the erosion of macropore walls, leading to an in-soil partitioning between soil microparticles and dissolved phase. The contribution of this in-soil erosive process would be linked to the magnitude of the hydraulic gradient following the rise of water table and could persist after the recession, which could explain why the return to inter-storm composition of DOM does not follow the same temporal scheme as the discharge. Those results are of main importance to understand the transfer of nutrients and micropollutants at the soil–river interfaces during the hot moments that are storm events.

### Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







Moreover those data should be comparable with spectroscopic and molecular data available in the literature. Molecular data generated by thermally assisted hydrolysis and methylation (THM) using tetramethylammonium hydroxide (TMAH) coupled to a gas chromatograph and mass spectrometer (THM-GC-MS) seems to be particularly suitable. This technique can be used to simultaneously analyze phenol markers from lignins (LIG) and tannins (TAN), carbohydrates (CAR) and fatty acids (FA) (Grasset et al., 2009). LIG and TAN are commonly used to monitor the input of terrestrially-derived OM to oceans (Gough et al., 1993) and their investigation has led to the partitioning process invoked for lignin compounds during storm events (Dalzell et al., 2005; Hernes et al., 2008). Analysis of CAR can differentiate between plant-derived and microbial inputs (Rumpel and Dignac, 2006) since the distribution of non-cellulosic monosaccharides is dominated by pentose (C5) for plant-derived inputs and by hexose (C6) and deoxyhexose (deoxyC6) for microbial inputs. Similar to CAR, the distribution of FA differs in plant-derived and microbial inputs (Cranwell, 1974; Lucas García et al., 2001; Matsuda and Koyama, 1977). The combination of those markers allows the investigation of the balance between microbial and plant-derived markers differentiating between soil DOM from organic-rich and organic-poor horizons in a wetland submitted to fluctuating water-table level and being correlated with the specific UV absorbance (SUVA) at 254 nm (Jeanneau et al., 2014). By assuming that protein-like and humic-like fluorophores (C5 and C2, respectively in Knorr, 2013) are representative of DOM from microbial and plant-derived inputs, respectively, it could be possible to compare the data generated by fluorescence excitation-emission matrices and by THM-GC-MS.

In this study, high-frequency molecular data were obtained on five successive storm events that were sampled at the outlet of the Kervidy–Naizin catchment, a lowland headwater catchment occurring in Brittany, France. This catchment was preferentially selected due to previous studies on its hydrological responses to storm events (Aubert et al., 2013; Durand and Juan Torres, 1996; Morel et al., 2009), and on its DOM sources and transfer processes (Lambert et al., 2011, 2013, 2014; Morel et al., 2009). Moreover this study takes advantages of previous knowledge acquired during the hydrologic year

**BGD**

12, 3349–3379, 2015

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





flow stage generally lasts from December to April, with maximum discharges occurring during February and March.

The elevation ranges from 93 to 135 m a.s.l., with hillslope gradients of less than 5%. The soils are silty loams, with depths ranging from 0.5 to 1.5 m, and are classified as Stagnic fluvisols (IUSS Working Group WRB, 2006) developed from alluvial material and Brioverian schists. The aquifer in the Kervidy–Naizin catchment consists mainly of the unconsolidated weathered bedrock, the deeper fresh bedrock, though locally fractured, being generally considered impermeable. In this aquifer, the groundwater flows from upland down to bottom land all the year round and feeds the stream. Along hillslopes, the water table depth is typically 0–10 m and increases uphill. In bottom land areas, the water table is near the soil surface during the wet season and the uppermost layer of the groundwater thus flows through the organic-rich horizon of the soils. The surface area of this domain of interaction between the organic-rich part of soils and the groundwater flow depends strongly on the hydroclimatic conditions. During dry hydrologic years, it 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 hillslopes, and the surface area of this domain may increase up to 20% of the total catchment surface area (Crave and Gascuel-Odoux, 1997).

Previous studies have evidenced the occurrence of three distinct hydrological periods in the Kervidy–Naizin on the basis of the seasonality of water table depth fluctuations in wetland and upland domains (Lambert et al., 2013; Molenat 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).

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





## 2.2 Previous data

### 2.2.1 Molecular data on SOM and soil DOM

The molecular composition of SOM and the spatio-temporal variation of the molecular composition of soil DOM were investigated in the central, most widespread wetland zone of the catchment (so-called Mercy wetland) during the hydrologic year 2010–2011 (Jeanneau et al., 2014). Concerning SOM, the proportion of LIG-TAN, CAR and FA were 16, 29 and 55 % and 4, 3 and 93 % in the organo-mineral and mineral horizons, respectively. The deoxyC6/C5 ratio was 0.4 and 0.2 in the organo-mineral and mineral horizons, respectively and the proportion of plant-derived markers was 88 and 71 % in the organo-mineral and mineral horizons, respectively.

During hydrologic period B, when the five studied storm events were sampled, there was a clear differentiation between surface (10 cm) and deep (50 cm) soil DOM. In the surface horizons, the proportion of plant-derived markers remained higher than 70 % with a mean value of  $0.8 \pm 0.1$  (SD) for the ratio deoxyC6/C5 while in the deep horizon, this proportion was lower than 30 % with a mean value of  $1.3 \pm 0.2$  (SD) for the ratio deoxyC6/C5. Molecular data were well correlated with SUVA values at 254 nm (SUVA against deoxyC6/C5,  $R^2 = 0.75$ ,  $p$  value  $< 0.0001$ ,  $n = 37$ ) that exhibited a clear differentiation between soil DOM sampled in surface ( $4.1 \pm 0.4 \text{ L mg}^{-1} \text{ m}^{-1}$ ) and deep ( $2.5 \pm 0.7 \text{ L mg}^{-1} \text{ m}^{-1}$ ) horizons (Lambert et al., 2013).

### 2.2.2 Previous data on river samples

The composition of DOM in the river during the five studied storm events was previously investigated using  $\delta^{13}\text{C}$  values (Lambert et al., 2014). The intra-storm variability of  $\delta^{13}\text{C}$  values ranged between the values recorded in the soil solution of the organic-rich surface horizon at the beginning of storm events and of the organic-poor deep horizon at the end of storm events. Those data were in accordance with the end member mixing approach (EMMA) developed using nitrate, sulfate and DOC concentrations in

BGD

12, 3349–3379, 2015

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion









multiplied by 100 in order to express it as a percentage. Since no internal standard were used, these data must be handled in a qualitative way. Five samples were analyzed in triplicate in order to investigate the experimental repeatability of the analysis. The relative SD (RSD) calculated for deoxyC6/C5, C/V, Ac/Al (V) and the proportion of plant-derived markers was 9, 10, 10 and 6%, respectively. The uncertainties given in Figs. 3–5 and S1 in the Supplement correspond to these mean RSD values. The use of THM-GC-MS to investigate the temporal variability of the DOM composition meant that it was necessary to assume that the ionization efficiency and matrix effects are equivalent for all analyzed compounds in all samples.

## 2.5 Treatment of molecular data

The classification of molecular markers generated by THM-GC-MS into microbial and plant-derived markers has been performed according to Jeanneau et al. (2014). Briefly, the analyzed compounds were classified as follow. LIG-TAN are characteristic of DOM inherited from plant-derived inputs whereas CAR and FA can be inherited from both plant-derived and microbial sources. The proportion of microbial CAR was calculated using an end-member mixing approach (EMMA) based on the deoxyC6/C5 ratio, assuming that the R1 value is 0.5 and 2.0 for plant-derived and microbial inputs. The proportion of microbial FA was calculated as the % low molecular weight FA (<C19) by excluding C16:0 and C18:0 that can be inherited from plant-derived or microbial inputs. The proportion of microbial markers was calculating as the sum of the proportion of microbial CAR multiplied by the proportion of CAR plus the proportion of microbial FA multiplied by the proportion of FA. From this value, it is possible to calculate the proportion of plant-derived markers among the analyzed compounds. For this calculation, it is assumed that the modification of the distribution of CAR and FA would only be due to the relative proportion between these plant-derived and microbial inputs. Although these assumptions still need to be validated by investigating pure and known mixtures of vegetal and microbial sources, this approach can be used to approximate the proportions of plant-derived and microbial CAR.

BGD

12, 3349–3379, 2015

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3 Results

#### 3.1 Soils and soil solution

Compared with its companion study (Jeanneau et al., 2014), compositional ratio on  
LIG-TAN markers were calculated for SOM and soil DOM. In SOM, the ratio C/V,  
that is the ratio of the sum of coumaric acid and ferulic acid on the sum of vanillic  
acid, vanilline and acetovanillone, was 1.3 and 1.6 in surface and deep horizons,  
respectively. The ratio Ac/AI (V), that is the ratio of vanillic acid on vanilline, was 2.6 and  
1.6 in surface and deep horizons, respectively. In soil DOM from 29 November 2010  
to 11 March 2011, the C/V ratio ranged from 0.2 to 0.4 in the surface horizon and  
remained stable at 0.2 in the deep horizon. The Ac/AI (V) ratio ranged from 7.1 to 12.1  
( $9.1 \pm 1.7$ , mean value  $\pm$  SD) in the surface horizon and from 3.6 to 6.9 ( $4.7 \pm 1.2$ , mean  
value  $\pm$  SD) in the deep horizon.

#### 3.2 River DOM in inter-storm conditions

In river samples from 28 November 2010 to 8 March 2011, the proportion of plant-  
derived markers ranged from 34 to 48% of the analyzed compounds (Fig. 3). Among  
CAR, the ratio deoxyC6/C5 ranged from 1.0 to 1.6 and heptoses have never been  
detected in those samples. For LIG-TAN, the C/V ratio remained lower than 0.2 with  
the exception of the sampling of 7 January 2011 with a value of 0.5. The Ac/AI (V) ratio  
ranged from 4.5 to 7.7.

#### 3.3 River DOM during storm events

During the five recorded storm events, the composition of DOM was modified as  
highlighted by isotopic (Lambert et al., 2014), spectroscopic and molecular markers  
analyses (Figs. 4 and S1, Table 1). The modifications were similar for the five storm  
events. At the beginning of storm events, the first sample was characterized by low  
values of SUVA at 254 nm comprised between 2.0 and 2.8, depending of the storm

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



event. Then this value increased from the second sample and remained stable up to the end of the sampling. The higher SUVA values were 3.0 (event 6), 3.2 (event 2), 3.3 (event 5), 3.4 (event 3) and 3.5 (event 4).

At the molecular level, during the five recorded storm events, the proportion of plant-derived makers among the analyzed compounds has increased (Fig. 5). The initial value was 31 (events 2, 4 and 6), 49 (event 3) and 14 % (event 5). It increased with the discharge and reached its maximum with the peak flow. This maximum value ranged from 63 (event 6) to 82 % (event 3). After the peak flow, the proportion of plant-derived markers decreased regularly of approximately 10 % (events 2, 4, 5 and 6) or remained stable (event 3) up to the end of the recording.

The composition of CAR, recorded by the deoxyC6/C5 ratio, was also modified during storm events. The initial value was 1.5 (event 3), 1.6 (event 2 and 4), 1.9 (event 6) and 2.7 (event 5). This ratio decreased with the increase of discharge, reached its minimal value at the peak flow and remained stable up to the end of the recording. Among CAR, heptoses were detected in the first sample at the beginning of the storm events and up to the fifth sample for the event 2 (Fig. S2).

The composition of LIG-TAN, recorded by the C/V and Ac/Al (V) ratios, was modified during storm events. The C/V ratio increased with the discharge from 0.2 at the beginning of storm events to 0.5 (event 5), 0.6 (events 2 and 4), 0.7 (event 3) and 0.8 (event 6). Depending of the storm event, this value slightly decreased or remained stable up to the end of the recording. The evolution of the Ac/Al (V) ratio was storm-dependant. For the events 2, 4 and 6, it remained stable around 5.0 with extreme values that could be considered as outliers, while for the events 3 and 5, it decreased from 7.0 to 5.0 with the increase of the discharge and then remained stable up to the end of the recording.

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





flood after the establishment of reducing conditions in wetland soils (Lambert et al., 2013), when the riparian wetland zones located at the soil–river interface played the role of a hotspot for iron biogeochemical reduction processes. Since they have not been detected nor in soil DOM nor in stream DOM sampled in inter-storm conditions, those compounds could be characteristic of microbial biofilms that likely developed in these zones at that time either directly in the soil macroporosity or at the wetland–stream interface (Knorr, 2013), and that could have been destabilized and transported into the stream by the increase of water velocity (Trulear and Characklis, 1982) at the beginning of storm events. The export of this microbial pool at the beginning of storm events could perhaps be responsible for the extreme value recorded using high-frequency fluorescence measurements. The first storm samplings are often associated with high contributions of protein-like chromophore and low contribution of humic-like chromophores (Knorr, 2013), high fluorescence index and low SUVA (Inamdar et al., 2011; Vidon et al., 2008).

### 4.3 Soil erosion as a DOM producer

During the five monitored storm events, the compositional ratios calculated on LIG were modified. The C/V ratio increased from 0.2 to 0.8 and the Ac/AI (V) ratio decreased from 7 to 5 with the exception of event 6 where it remained stable around 5. Those modifications of the composition of LIG transferred from soils to rivers during flood events are in accordance with data on lignin phenols obtained along the Big Pine Creek watershed (Dalzell et al., 2005) and the Willow Slough watershed (Hernes et al., 2008). Although the differences in analytical techniques makes the comparison of data difficult (Wysocki et al., 2008), the compositional ratios evolve similarly during the biodegradation process with a decrease for the C/V ratio and an increase for the Ac/AI (V) ratio (Kabuyah et al., 2012; Vane et al., 2005). The aforementioned modifications of C/V and Ac/AI (V) ratios have then been attributed to the mobilization of less-degraded lignins during flood events (Dalzell et al., 2005; Hernes et al., 2008).

**BGD**

12, 3349–3379, 2015

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





---

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The values of the C/V ratio recorded during storm events were higher than the values in soil solutions. Thus stream DOM recorded during storm events cannot be viewed simply as resulting from the passive transfer of soil DOM to the stream. Among the different constituents analyzed so far in the catchment, only the SOM presented C/V values that could explain the high storm DOM values (Fig. 6). In the Willow Slough catchment, the concentration in lignin markers has been shown to be correlated to the concentration in suspended matter indicating that DOM transferred during storm events can be, in part, inherited from the partitioning of organic compounds between solid and dissolved phases (Hernes et al., 2008). Such a correlation between lignin compounds and suspended sediment was also found in the present study, as highlighted by the regression between turbidity and the C/V ratio (Fig. 7). Thus, soil erosion and the equilibrium between solid (soil particles) and liquid (river) phases is likely to be an additional source of DOM transferred from soil to rivers during storm events. However, this positive relationship was only found for the samples collected during the rising limb of the hydrograph (grey square,  $R^2 = 0.68$ ,  $p$  value  $< 0.0001$ ,  $n = 23$ ). After the peak discharge, turbidity decreased while the C/V ratio remained high leading to a poor correlation when all the samples are considered (black square,  $R^2 = 0.11$ ,  $p$  value = 0.008,  $n = 64$ ). This highlights that the aforementioned soil erosion process alone cannot explain the persistence of high C/V ratios during the falling limb of the hydrograph. Since the complementary DOM production process must have let the C/V ratio high and that the only component that brings a high C/V is SOM, it should be similar to soil erosion, that is to say consisting of a transfer of SOM-born components into the circulating water. A hypothesis could come from the erosion of macropores walls due to the increase in water velocity during storm event (Wilson et al., 2005) that could lead to a modification of the composition of DOM produced within the different soil horizons.

#### 4.4 Temporal scheme of DOM producing processes during storm events

The increase in the proportion of aromatic DOM during the rising limb of the hydrograph that remained high even after the recession as observed in the present study has been described under different climates and for different catchments (Austnes et al., 2010; Knorr, 2013; Singh et al., 2014). It is then probable that the succession of DOM producing mechanisms leading to this pattern can be generalized. The combination of previous and present results could be used to decompose this succession into four distinct mechanisms. In inter-storm conditions, DOM would be derived from the passive (without compositional changes of the DOM during transport) flushing of organic-rich and organic-poor wetland soil horizons. The contribution of each soil horizon would be controlled by the water table level. During a rain event, the increase in water velocity would induce the destabilization of microbial biofilms resulting in the export of a microbial pool. This first stage would be followed by the rise of the water table, which in association with the decrease of lateral hydraulic conductivity with depth (Seibert et al., 2009) would induce an increase of the proportion of the water flowing through the upper organic-rich wetland surface horizon. This would result in an increase of the stream DOC concentration. In the same time, erosion of soils and river banks would induce an increase of the turbidity leading to a partition of organic matter between particles and dissolved phase. The contribution of this soil surface erosive process on the DOM chemistry would depend on the concentration in suspended matter and would therefore decrease during the falling limb of the hydrograph. In the same time, the increase in water velocity in soils could induce the erosion of macropore walls, leading to an in-soil partitioning between soil microparticles and dissolved phase. The contribution of this in-soil erosive process would be linked to the magnitude of the hydraulic gradient following the rise of water table. Since the recovery of pre-event conditions is longer for in-soil hydraulic gradient than for discharge (Lambert et al., 2014 – Fig. 3b), this could explain why the compositional proxies, including biomarkers and spectroscopic measurements, do not recover their pre-event values with the same

**BGD**

12, 3349–3379, 2015

### Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





that the DOM transfer process during storm events consists of the flushing of pre-existing soil pools. Since the latter are calibrated in term of size (concentration) and nature (composition) using samples taken in inter-storm conditions, these models don't take into account additional DOM producing processes which could occur during the water transfer process, such as the surface and subsurface erosion processes evidenced here. This lack could explain why modeling studies succeed in reproducing inter-storm DOM concentrations, but not storm flow DOM contents (Birkel et al., 2014). Increased interactions between geochemists and modelers should help in improving DOM export modeling.

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**BGD**

12, 3349–3379, 2015

## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H., and McHale, P.: Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed, *J. Geophys. Res.*, 116, G03043, doi:10.1029/2011JG001735, 2011.

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## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Table 1.** Changes in discharge, DOC concentration and DOM compositional proxies during the storm events. The values are given for the first, peak discharge and final samples.

Event Date		2 4 Dec 2010	3 19 Dec 2010	4 6 Jan 2011	5 13 Feb 2011	6 19 Feb 2011
Discharge (Ls <sup>-1</sup> )	beg. <sup>a</sup>	79.8	88.8	59.1	72.8	77.7
	max.	177.3	453.1	169.8	167.3	245.1
	end	127.4	113.1	104.0	96.2	102.5
DOC (mgL <sup>-1</sup> )	beg. <sup>a</sup>	7.4	6.6	6.4	7.4	8
	max. <sup>b</sup>	11.6	12.4	11.5	12.8	15.5
	end	9.8	7.4	8.0	11	9.1
SUVA (Lmg <sup>-1</sup> cm <sup>-1</sup> )	beg. <sup>a</sup>	2.0	2.6	2.8	2.0	2.4
	max. <sup>b</sup>	3.1	3.3	3.4	3.2	2.9
	end	3.0	3.4	3.5	3.0	2.9
$\delta^{13}\text{C}^c$ (‰)	beg. <sup>a</sup>	-28.9	-28.9	-28.6	-28.7	-28.8
	max. <sup>b</sup>	-28.8	-28.5	-28.8	-28.6	-28.8
	end	-27.2	-27.0	-28.1	-28.5	-28.2
deoxyC6/C5	beg. <sup>a</sup>	1.6	1.5	1.6	2.7	1.9
	max. <sup>b</sup>	0.9	1.1	1.0	1.1	1.3
	end	1.1	1.1	0.9	1.2	1.4
C/V	beg. <sup>a</sup>	0.2	0.2	0.2	0.2	0.3
	max. <sup>b</sup>	0.4	0.6	0.6	0.4	0.8
	end	0.5	0.5	0.4	0.4	0.3
Ac/Al (V)	beg. <sup>a</sup>	5.0	7.3	5.5	6.6	5.2
	max. <sup>b</sup>	5.2	5.3	4.6	5.5	4.5
	end	4.7	4.9	4.3	4.8	4.6

<sup>a</sup> Value recorded at the beginning of storm events.

<sup>b</sup> Value recorded at the peak discharge.

<sup>c</sup> Data from Lambert et al. (2014).

**Transfer of DOM at the soil-stream interface in a lowland headwater catchment**

L. Jeanneau et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

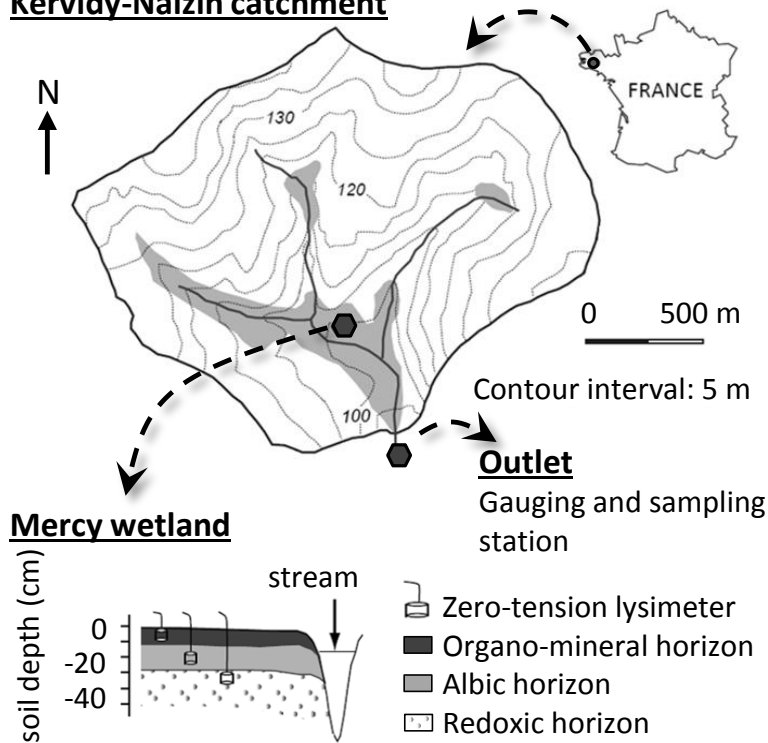
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Printer-friendly Version

Interactive Discussion



## Kervidy-Naizin catchment

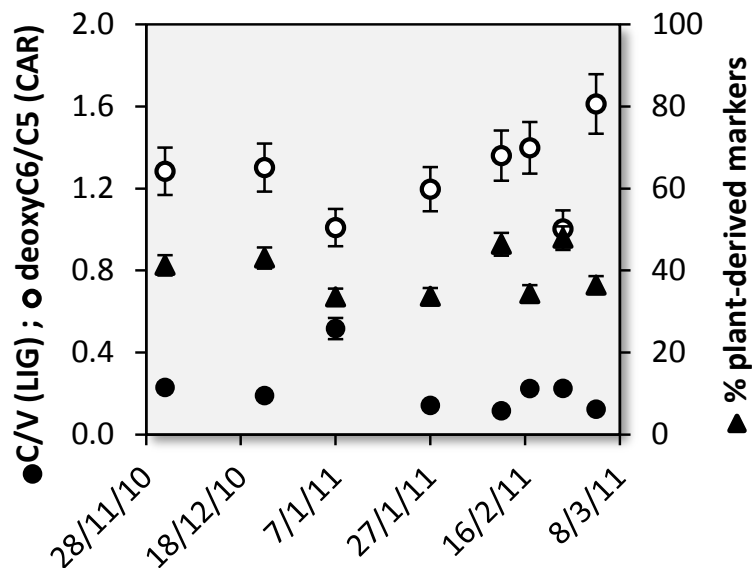


**Figure 1.** Location map of the Kervidy–Naizin critical zone observatory (Brittany, France). Grey areas located along the channel network indicate the maximum extent of the wetland zones.



## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.



**Figure 3.** Temporal change of the molecular composition of inter-storm stream DOM: compositional ratios included C/V (black circles – LIG-TAN), deoxyC6/C5 (white circles – CAR) and the proportion of plant-derived markers among the analyzed compounds (black triangles).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

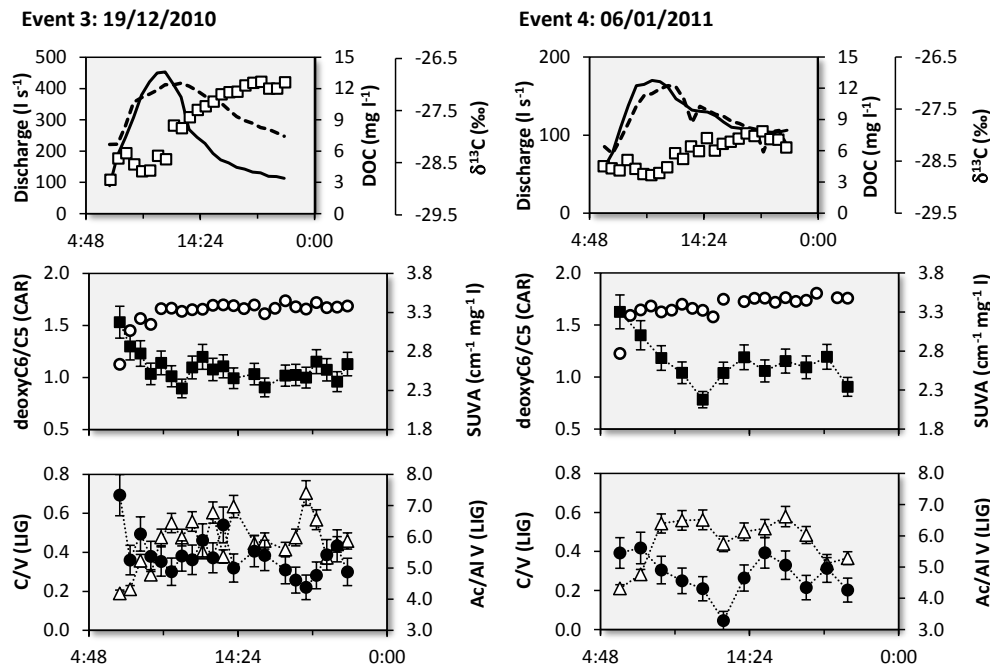
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Interactive Discussion



## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.



**Figure 4.** Temporal change in flow and DOM concentration and composition during storm events 3 and 4. Black solid line, dashed line, white squares, white circles, black squares, black circles and white triangles represent discharge, DOC concentration,  $\delta^{13}\text{C}$ , SUVA 254, deoxyC6/C5, Ac/Al (V) and C/V, respectively. The units are given on the axes. The uncertainties for deoxyC6/C5, C/V and Ac/Al (V) are the mean RSD calculated for five samples analyzed in triplicate.

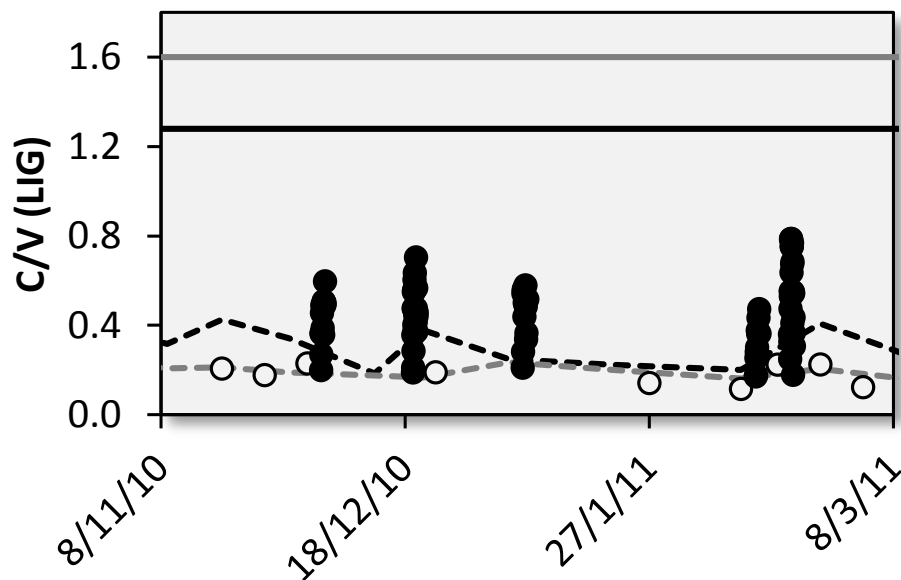
[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)





## Transfer of DOM at the soil-stream interface in a lowland headwater catchment

L. Jeanneau et al.



**Figure 6.** Time diagram comparing the variation of the C/V ratio (lignin proxy) in SOM and DOM from organo-mineral and mineral horizons, and the variation of the C/V ratio in river DOM during inter-storm and storm conditions. Black solid and grey solid lines: SOM from soil organo-mineral and mineral horizons, respectively; black dashed and grey dashed lines: DOM from soil organo-mineral and mineral horizons, respectively; white and black circles: inter-storm and storm stream DOM, respectively.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



