Referee 1.

The intent of this manuscript was to study DOM character during storm events using molecular biomarkers determined using THM-GC-MS. The authors compared this data against – isotopic data, UV and florescence values, and results and EMMA analyses from prior studies in this catchment. The questions were well posed and the paper was generally well written.

The authors report some interesting trends in the molecular biomarkers during storm events and the comparison of this data against isotopic and spectrofluorometric data was valuable. My main concern in this manuscript is about the very specific mechanisms provided to explain the molecular biomarker signatures. These include – destabilization of microbial biofilms from macropores and erosion of macropore walls due to high soil water velocity. I am not sure that the authors have the evidence to back up some of these explanations. There could be alternate, simpler, explanations for some of the results that they see. Such as simple microbial lysis in the soils over the dry period and flushing of these byproducts during the wetting-up phase, destabilization and disaggregation of soil aggregates during storms, etc. I think the authors could include some of these alternate hypotheses to explain their results and tone down the very specific hypotheses they provide.

Both of those alternate hypotheses have been added in the text (page 19; lines 3-8 and page 20; lines 23-24; **Important: the page and line numbering corresponds to this document**).

Some additional description on results from previous studies that have used these biomarkers would have also been beneficial.

A sentence was added in order to describe the results from previous studies (page 19; lines 25-27)

Specific comments – The manuscript could be improved for grammar and overall writing. For example, page 3351, lines 6 and 12 – “research” is singular.

The modification was performed (page 8; line 22).

Page 3350, line 12 – replace “inherited” with “derived”.

The modification was performed (page 7; line 22).

Page 3355, line 9 – feds should be feeds.

The modification was performed (page 12; line 3).

Line 10 – what do you mean by “increases uphill”.

It means that the depth of the watertable increases with the altitude. Whatever, it has been removed from the text (page 12; line 4).

Page 3359, line 1 – no internal standards were used. Does this weaken your methods and approach?

Since no internal standards were used, it is not possible to know what proportion of DOM the analyzed markers represent. However the compositional proxies on lignins and carbohydrates can be interpreted in a qualitative way. As a consequence the approach is not weakened but it is not possible to provide quantitative information from a qualitative analyses. As an example, it is not possible to quantify the proportion of flushing and the proportion of partitioning using those data. To perform such a calculation, quantitative data will be necessary.

Line 17 – can you provide a reference here for your assumption?

This assumption is supported by Rumpel and Dignac, 2006 that was added in the text (page 15; line 31).

Page 3367, line 5 and 6 – you did not provide any specific evidence to support this. This is a speculation or hypothesis.

The term evidence was misused and has been replaced by suggested (page 22; line 22).

Figures 2-7 – please provide legend of the figures so that we can easily associate the symbols with the parameters. We should not have to read the caption to understand the symbols.

Legends of the figures were added.

Referee 2.

The authors use THM-GC-MS to characterize DOM from a headwater stream during 5 successive storm events and during inter-storm conditions, and compare to spectroscopic and isotopic measurements. Emphasis is placed on high-frequency sampling during storm events, leading to exciting and unique results. Additionally, the Kervidy-Naizin catchment is well studied, leading to a wealth of background information to aide interpretation of this study's results.

Biomarker results are analyzed via carboxyC6/C5, C/V, and Ac/Al (V) ratios, and using a biomarker end-member mixing approach. The authors interpret changes in these metrics as representing three DOM export mechanisms: microbial biofilms, partitioning between particulate and dissolved phase, and erosion of macropore walls.

My main concerns are: lack of quantification in in biomarker detection procedure, selection of end-member values for EMMA, and highly specific hypotheses to explain observed trends (specifically periods 1 and 3 involving microbial biofilms and macropore walls). Simpler explanations should be considered to describe observed trends, for example: partitioning from particulate phase could continue in soils once turbidity has decreased without needing to invoke macropore wall erosion.

The partitioning from particulate phase occurs continuously in soils but with a high ratio soil/water creating a specific DOM with a low C/V (around 0.2). During storm event, erosion carries particles in water. These low soil/water conditions induce a displacement of the equilibrium between OM in the solid phase and OM in the dissolved phase, which seems to lead to DOM with a high C/V (higher or equal to 0.8). Since the lignin ratio C/V remains high even after turbidity has decreased to pre-event value, an additional mechanism inducing low soil/water conditions is necessary. This could be the erosion of macropore walls but also as suggested by the first referee, the destabilization and disaggregation of soil aggregates. Those explanations are hypothetic and at this stage need further investigation to be supported.

General comments:

- Grammar and syntax could be improved overall (i.e. confusion between singular and plural nouns, verb/noun agreement, pronoun usage, lengthy paragraphs)

- Much of section 2.1 and 2.2 should be moved to the results section, leaving only general statements about site description in the methods section (i.e. mean temperature, mean rainfall, bedrock lithology, etc.). Discussion on groundwater movement, hydrological periods, and previous results are better placed in the results section.

The discussion on groundwater movement, hydrological periods and previous results are not new results but the framework necessary to analyze the new results presented in this study. For this reason, we believe that it is better to let it in the “materials and methods” section.

- Compound detection and quantification procedure is not quantitative. Compounds should be quantified in SIM mode for maximum sensitivity (e.g.http://www.shimadzu.com/an/sim-mode.html) and compared to an external standard calibration curve run at multiple dilutions for proper quantification. Internal standards or extraction of known mixtures should be used to quantify extraction recovery.

Working in the Single Ion Monitoring mode implies to specifically know in advance what are the compounds that will be investigated without giving a chance to the unknown part of DOM, what has been called the molecularly uncharacterized organic matter. The SIM mode is more dedicated to the analysis of target compounds such as pesticides or hydrocarbons in a given matrix, while the fullscan mode is better to the investigation.

- Justification is needed for end-member definitions in the EMMA. Specifically, attributing FA <C19 to microbial (omitting C16:0 and C18:0) and >C19 to vascular plants is an oversimplification and will likely bias results. Heterotrophs and phytoplankton have been shown to produce an array of FA with chain lengths longer than C19.

I agree some microorganisms can produce fatty acids with more than 19 carbon atoms as described by Volkman et al. (1980) (Geochimica et Cosmochimica Acta, 44, 1133-1143, 1980). However the data described in this latter paper correspond to an intertidal sediment. It is quite sure that the biodiversity of microorganisms in such an environment is different from the soil-river interface that is under investigation in the present paper. Looking at the literature on the phopho-lipid fatty acids (PLFA) in soils and streams justifies the cutting at C20 to differentiate between microbial (<C20) and plant-derived (>C20). As an example, Frostegard et al. (1996) used iC15:0, aC15:0, C15:0, iC16:0, C16:1w9, C16:1w7t, iC17:0, aC17:0, C17:0, cyC17:0, C18:1w7 and cyC19:0 as bacterial PLFA (Biology and Fertility of Soils, 22, 59-65, 1996). More recently, in a study looking at the PLFA composition in different streams, iC15:0, aC15:0, iC16:0 and aC17:0 were attributed to heterotrophic bacteria while polyunsaturated fatty acids (C16:2w4, C18:2w6, C18:3w3 C20:4w6 and C20:5w3) were attributed to algae (Lyon and Ziegler, 2009 in Limnology and Oceanography, 54, 439-449). However those polyunsaturated compounds are not detected in this present study. As a consequence, regard to the literature on soil and stream PLFA, it is reasonable and justified to perform such a classification. Moreover the FAs considered as microbial have been indicated in the text and their classification as microbial FA has been supported by a reference (page 16; lines 3-5).

- Explanatory mechanisms for DOM trends during storm events seem speculative and highly specific. More evidence is necessary to justify these hypotheses.

It is true that all the evidences needed to be sure of those explanatory mechanisms are not yet available. That is why the sentences are turned into conditional tense. However the modification of the lignin proxies has already been described in other catchments as well as the differentiation between concentration and composition of DOM during the falling limbs of hydrograph. As a consequence, it seems that those mechanisms are not highly specific but could be present in different catchments.

Specific comments:

- Verbose title, should be shortened (e.g. to the shortened title listed in the side bar: “Transfer of DOM at the soil-stream interface in a lowland headwater catchment: Constraints from high-frequency molecular data”)

The title was shortened (page 7; line 1).

- Abstract: Transfer of DOM is but one of many control mechanisms on these processes [page 3350, lines 1-3]. Abstract lists micropollutants and terrestrial v. marine C reservoirs as main motivation to study DOM [page 3350, lines 2-3, 24-25], while introduction lists UV light absorption and food source for bacteria as main motivation [page 3351, lines 2-3].

The two first sentences of the introduction were changed to describe the same motivation as the abstract (page 8; lines 9-12).

- Citation for statement that DOM is controlled by water flow paths? [page 3351, lines 13-15]

A citation was added (page 8; lines 24-25).

- Why not cite original lignin export papers? e.g. Hedges and Mann, 1979; Hedges and Parker, 1976. Similarly original vascular plant fatty acid papers? e.g. Eglinton and Hamilton, 1967 [page 3353, line 8, 14].

Those papers have been cited (page 10, lines 10 and 16-17).

- [page 3353, line 19-22] Is this a valid assumption? This assumption seems critical to the comparison between molecular and spectroscopic data, yet neither citation nor confirmation data are given.

Further investigations will be necessary to test this assumption; as a consequence this sentence was removed from the manuscript (page 10; lines 22-25).

- Is ‘soil solutions’ a synonym for soil DOM? [page 3354, line 2] If so, this should be changed to ‘soil DOM’ throughout. If not, this should be defined.

“soil solutions” was changed to “soil DOM” (page 10; line 33).

- Concentrations should be listed in brackets, e.g. [DOC], [Cl-], etc. [page 3354, line 5]

The modification was performed (page 11; line 4).

- Soil molecular data [page 3356, line 3-19]: Why omit C6 in deoxyC6/C5 ratio, since C6 and deoxyC6 are listed as microbial?

The thermally assisted hydrolysis and methylation (THM) reaction using TMAH allows for the analysis of free and terminal monosaccharides and the differentiation of aldohexoses (C6), 6-deoxyaldohexoses (deoxyC6) and aldopentoses (C5) (Estournel-Pelardy et al., 2011). The distribution of CAR in microorganisms is dominated by C6 and deoxyC6, while that of non-cellulosic CAR in plants is dominated by C5. As a consequence, deoxyC6/C5 (R1) and C6/C5 (R2) ratios can be used to differentiate between DOM from plant-derived sources (R1 and R2 < 0.5) and DOM from microbial (R1 and R2 >2.0) sources (Guggenberger and Zech, 1994; Rumpel and Dignac, 2006). However, these limits of 0.5 and 2 were calculated from data obtained using an analytical method involving the hydrolysis of non-cellulosic carbohydrates. The THM method results in the detection of terminal glucose, an aldohexose included in the C6 signal, in cellulose chains (Estournel-Pelardy et al., 2011), leading to an artificial increase in the proportion of C6. Consequently, R2 cannot be used here to estimate the proportion of plant-derived and microbial CAR. This has already been explained in detail in our previous paper and a brief comment has been added in this present one (pages 15-16; lines31-1).

Estournel-Pelardy et al., Journal of Analytical and Applied Pyrolysis, 92, 401-406, 2011

Guggenberger and Zech, Soil Biology and Biochemistry, 26, 19-27, 1994

Rumpel and Dignac, Soil Biology and Biochemistry, 38, 1478-1481, 2006

How is proportion of plant-derived markers defined, specifically?

This calculation is described in Jeanneau et al., 2014 and also further in the text in the "treatment of molecular data" section (page 16; lines 7-9).

It is unclear what the unit 'L mg-1m-1' is meant to represent.

This is the unit for the specific UV absorbance.

Is SUVA vs. deoxyC6/C5 regression for surface samples, deep, or both?

The regression was performed using data from surface and deep samples. It has been precised in the text (page 13; line 6).

- More detail is needed on "removal of roots and gravels" – i.e. removed by eye? Sieved? If so, to what pore size? [page 3357, line 12]

Roots and gravels were removed by eye, which has been added in the text (page 13; lines 27-28).

- More detail needed on DOC sampling procedure [page 3357, line 21-23] – i.e. depth of sampling in water column, filtration pore size (if filtered?), sample volume, sample storage (bottle material), etc.

The DOC sampling procedure has been detailed (page 14; lines 9-19).

- [page 3358, line 4] 'soil or lyophilizate' implies that stream water samples were freezedried, yet this procedure was never discussed explicitly.

It has been added (page 14; line 19).

- Odd choice for transfer line temperature (321C) [page 3358, line 11]

This is the maximum temperature that can be set for the transfer line between the pyrolyser and the gas chromatograph.

- What is the justification for using full scan mode, rather than SIM mode, for peak detection and integration? Generally, quantitative measurements should be done in SIM mode, as sensitivity is higher, and compared to an external standard calibration curve [page 3358, line 17].

This point has already been discussed previously.

- [page 3359, line 4] 'C/V' and 'Ac/Al' have not been defined.

Since defining those ratios here would have been difficult, the sentence was modified. C/V and Ac/Al are now together under the term “LIG proxies” (page 15; line 19).

- ‘R1 value’ not defined [page 3359, line 17]

It was not necessary to use the term “R1 ratio” because it is redundant with deoxyC6/C5, then it has been removed from the text (page 15; line 30).

- [page 3359, line 18-20] This source separation is an oversimplification. Phytoplankton/ bacteria have been shown to produce >C19 branched and unsaturated FA (see, e.g. Volkman et al., 1980).

This point has already been discussed previously.

- [page 3359, line 20-22] This mixing model description would be made much clearer with a simple equation.

An equation would take more place and this calculation does not need, to my mind, an equation to be understood.

- [page 3362, line 18-20] Is this statement statistically true? Looking at Figures 3 and 5, the fraction of plant-derived markers at the beginning of event 3 looks identical to inter-storm conditions.

With only five events investigated, it is not possible to say if an observed trend is statistically true. What is observed is that during the five recorded storm events the proportion of plant-derived markers increases. However your observation is true and thank you for it. For the events 2, 4, 5 and 6, the proportion of plant-derived markers for the first sample was lower than for the stream DOM in inter-storm conditions sampled before the event. But for the event 3 (19/12/2010) the proportion of plant-derived markers for first sample was 49%, while it was 41% in the pre-event stream DOM (02/12/2010). This can be explained by the discharge recorded during the previous 24 hours. For the events 2, 4, 5 and 6, the relative standard deviation (RSD) was 2, 1, 3 and 2%, respectively, highlighting that the discharge was constant. On the contrary for the event 3, the RSD was 17% with a 62% increase (from 48 to 78 L/s) of the discharge before the recording of the storm event. In such conditions, the microbial biofilms occurring in the river may have been destabilized by the first increase in discharge.

This has been added in the manuscript (page 18; lines 18-23 and table S2) and the figure 5 has been changed in order to avoid any confusion.

- [page 3366, line 20-22] A citation for this claim should be provided.

A citation has been added (page 22; lines 10-11). It deals with the specific sorption of emergent pollutants on hydrophobic black carbon from crop residue-derived hashes.

- [Figure 2] ‘PK1’ is not defined.

Since PK1 was not necessary, it has been removed from the caption.

- [Figure 3-4] These figures would be made much clearer with a legend for symbols. Additionally, measurements should maintain same symbol throughout figures (i.e. C/V data are black circles in Figure 3, but white triangles in Figure 4).

Legends for symbols were added on all figures and the same symbol was maintained for measurements throughout figures.

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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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~~ derived 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.

1 Introduction

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 (Corapcioglu and Jiang, 1993; Raymond et al., 2013). Then determining the transfer mechanisms of DOM is of main importance for ecological and geochemical reasons. ~~Dissolved organic matter (DOM) is recognized as playing a key role on stream biodiversity as an absorbent of biologically harmful ultraviolet light and as a source of energy for heterotrophic bacteria (Jerome and Bukata, 1998; Tranvik, 1992). Understanding the processes that feed rivers with DOM has therefore become a priority of river researches in recent years.~~ The concentration of DOM generally decreasing from headwater to large river catchments (Ågren et al., 2007), there is nowadays a widely accepted consensus that a large proportion of river DOM ultimately come from headwater catchment soils (Billett et al., 2006; Morel et al., 2009). Unraveling the processes by which DOM is transferred from soils to headwater streams and understanding how these processes control the chemistry of the exported DOM are therefore two challenging issues of ~~these~~ this research~~es~~.

The export of soil DOM in headwater catchments is controlled by water flow paths which may change both at seasonal and event scales, depending on hydroclimatic conditions (Hinton et al., 1998). More than 60% of the dissolved organic carbon (DOC) exported annually is transferred during storm events highlighting them as hot moments in the continental C cycle (Morel et al., 2009). During storm events, the increase in discharge is associated with an increase in DOC concentrations (the parameter commonly used to quantify DOM concentrations) associated with changing flow path circulations due to the rise of water table, which results in the leaching of DOM-rich soil horizons (Maurice et al., 2002; McGlynn and McDonnell, 2003).

Storm events are also associated with changes in DOM composition and biodegradability (McLaughlin and Kaplan, 2013). Compositional changes have been recorded using different spectroscopic measurements namely UV-absorbance and fluorescence. The first results were obtained using low frequency spectroscopic measurements and have highlighted that DOM aromaticity increased during storm events (Hood et al., 2006; Maurice et al., 2002). It has been attributed to the mobilization of aromatic DOM from surface soil horizons with the rise of water table. However high frequency spectroscopic measurements have shown that concentration and composition were not linked and that the return to pre-event values was much longer for compositional indices than for concentration (Austnes et al., 2010; Knorr, 2013; Saraceno et al., 2009; Yang et al., 2013). This was interpreted as an evidence for in-stream production of fluorescing DOM (Austnes et al., 2010) or for a continuous contribution of surface soil horizons to the DOM export, even after the return to low-flow conditions (Strohmeier et al., 2013).

Molecular data investigating the differences in DOM composition between low-flow and high-flow conditions are less common than spectroscopic data, and comprise mostly low frequency lignin phenol data (Dalzell et al., 2005; Hernes et al., 2008). Those data on lignin phenols highlight a modification in the DOM composition with less-degraded lignins being mobilized during storm events. Since those modifications were correlated with the amount of suspended sediments in the water column, they have been interpreted as the mobilization of particles by erosion combined with partitioning of the lignin compounds between the solid and dissolved phase. This partitioning process could be linked to the in-stream production of fluorescing DOM suggested by Austnes et al. (2010). However those data have been acquired using low frequency water sampling strategies (one sample per storm event), and cannot be used therefore to investigate the persistence of the DOM aromatic fingerprint after storm events.

Thus, according to the existing database on DOM composition variation during storm events, it appears that the transfer of DOM in headwater catchments could not be regarded as simply the passive transfer of a surface soil DOM component leached by the water table rise. Other processes seems to be involved implying either a modification of the DOM composition on its way from its soil source to the stream or the involvement of additional DOM sources specifically generated and mobilized during the storm events. Answering these questions requires acquiring (i) high-frequency data on DOM composition during storm events, at a level sufficient to allow identification of theses possible additional sources and mechanisms and (ii) background information on the composition of soil organic matter (SOM), soil DOM and inter-storm river DOM. 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)~~(Hedges and Parker, 1976) 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; Eglinton and Hamilton, 1967; Lucas García et al., 2001; Matsuda and Koyama, 1977)~~(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 2010-2011 on (i) the temporal variations of the distribution of biomarkers, including lignin phenols, in soil ~~solutions~~ DOM of the Mercy Wetland (France) that is the main contributor of DOM in the Kervidy catchment (Jeanneau et al., 2014; Morel et al., 2009) and (ii) the high-frequency sampling of stream water during winter storm events with previously investigated isotopic (δ^{13}C) and hydrochemistry ([DOC], [Cl^-], [NO_3^-], [SO_4^{2-}])~~(DOC, Cl^-, NO_3^-, SO_4^{2-})~~ data at the outlet of the Kervidy catchment (Lambert et al., 2014). Three main issues are addressed in this paper: (i) how does the molecular composition of DOM vary during one single storm event, and in between the five investigated storm events; do we see seasonal trends? ; (ii) is there a correlation between the variability of molecular biomarkers during storms and the variation of more global DOM characteristics such as the UV-absorbance and δ^{13}C values? (iii) What new constraints do the molecular data set on the sources and transfer mechanisms of DOM during storms in this catchment?

2 Materials and methods

2.1 Site description

This research was conducted in the Kervidy-Naizin catchment which is a 4.9 km² lowland catchment located in central Brittany, western France (Figure 1). Numerous hydrological and biogeochemical studies have already been undertaken at this site, which belongs to a long-term monitoring research program aimed at understanding the impact of agricultural intensification and climate change on water pathways and water quality (Aubert et al., 2013; Lambert et al., 2013 and references therein). Only the information required for this study is presented here.

The Kervidy-Naizin catchment has a temperate oceanic climate. The mean annual temperature and precipitation (1993-2011) are 10.7°C and 814 mm, respectively. Rainfall events rarely exceed 20 mm per day, with 80% of rainfall events having an intensity of less than 4 mm per hour. The stream generally dries up from the end of August to October due to the small volume of water stored in the bedrock. The high-flow stage generally lasts from December to April, with maximum discharges occurring during February and March.

The elevation ranges from 93 to 135 m above sea level, 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).

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±0.1 (standard deviation) for the ratio deoxyC6/C5 while in the deep horizon, this proportion was lower than 30% with a mean value of 1.3±0.2 (standard deviation) for the ratio deoxyC6/C5. Molecular data were well correlated along the depth profile 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 ± 0.4 $l.mg^{-1}.m^{-1}$) and deep (2.5 ± 0.7 $l.mg^{-1}.m^{-1}$) 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 $\delta^{13}C$ values (Lambert et al., 2014). The intra-storm variability of $\delta^{13}C$ 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 order to determine the contributions of rain water, deep groundwater, shallow riparian groundwater and hillslope groundwater. The storm-flow generation was decomposed in three successive steps: (i) an overland flow above the saturated wetland soil horizons; (ii) a subsurface flow through the uppermost organic-rich horizon of wetland soils; and (iii) a subsurface return flow from shallow hillslope groundwater flowing through deeper organic-poor horizon of wetland soils (Lambert et al., 2011, 2014). Those data tend to support the concept of a storm-DOM flux generated by the mobilization of pre-existing DOM pools via the rise of the water table.

2.3 Sampling

Soils from the Mercy wetland were sampled using a hand auger on October 2010. Three sample subsets were collected in the organo-mineral (0-10 cm) and the mineral (30-40 cm) horizons. After removal of roots and gravels by eye, all samples were freeze-dried and crushed using an agate mortar.~~After removal of roots and gravels, all samples were freeze-dried and crushed using an agate mortar.~~

The five studied storm events were sampled between December 04, 2010 and February 19, 2011, during hydrological period B (Figure 2). Their numbering corresponds to those used in the previous paper by Lambert et al. (2014). Events 2, 3, 4, 5 and 6 were sampled on December 4, December 19, January 6, February 13 and February 19, respectively. Stream discharge was recorded every minute with an automatic gauge station located at the outlet of the catchment. The beginning and the end of a flood are determined respectively by an increase and a decrease of the stream discharge of > 1 l.s^{-1} in 10 min at the stage recorder. Turbidity was monitored using an APC-TU Ponselle sensor with a measure every 30 seconds averaged every 10 minutes. Rainfall amounts are continuously monitored on an hourly interval basis using a weather station located ca. 300 m away from the catchment outlet. ~~Stream~~ Storm stream water samples (1 l) were collected 40 cm above the river bed using a refrigerated (4°C) automatic sampler (Sigma 900 Max) installed in a technical hut located at the outlet of the catchment (Figure 1) and were stored in polypropylene (PP) bottles.~~(Figure 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.) in 60 ml PP bottles for DOC monitoring and fortnightly in 1 l glass bottles for isotopic and molecular investigations. Stream water was filtered at 0.22 µm using cellulose acetate membrane filters previously washed with 200 ml of de-ionized water and few ml of the sample itself. Filtered water samples were then acidified using 1 N HCl (1 mL per L of sample) to remove inorganic carbon, and finally frozen and freeze-dried. ~~Turbidity was monitored using an APC-TU Ponselle sensor with a measure every 30 seconds averaged every 10 minutes. Rainfall amounts are continuously monitored on an hourly interval basis using a weather station located ca. 300 m away from the catchment outlet.~~

2.4 Analytical procedure

Approximately 2 mg of solid residue (soil or lyophilizate) was introduced into an 80 µl aluminum reactor with an excess of solid tetramethylammonium hydroxide (TMAH – ca. 10 mg). The THM reaction was performed on-line using a vertical micro-furnace pyrolyser PZ-2020D (Frontier Laboratories, Japan) operating at 400°C during 1 min. The products of this reaction were injected into a gas chromatograph (GC) GC-2010 (Shimadzu, Japan) equipped with a SLB 5MS capillary column (60 m × 0.25 mm ID, 0.25 µm film thickness) in the split mode. The split ratio was adapted according to the sample and ranged from 15 to 30. The temperature of the transfer line was 321°C and the temperature of the injection port was 310°C. The oven temperature was programmed from an initial temperature of 50°C (held for

2 min) rising to 150°C at 15°C/min, then rising from 150°C to 310°C (held for 14 min) at 3°C/min. Helium was used as the carrier gas, with a flow rate of 1.0 ml/min. Compounds were detected using a QP2010+ mass spectrometer (MS) (Shimadzu, Japan) operating in the full scan mode. The temperature of the transfer line was set at 280°C, and molecules were ionized by electron impact using an energy of 70 eV. The temperature of the ionization source was set at 200°C. The list of analyzed compounds and m/z ratios used for their integration are given in the supplementary materials (Table S1). Compounds were identified on the basis of their full-scan mass spectra by comparison with the NIST library and with published data. They were classified into three categories: lignin (LIG) and tannin (TAN) markers, carbohydrates (CAR) and fatty acids (FA). The peak area of the selected m/z for each compound was integrated and corrected by a mass spectra factor (MSF) calculated as the reciprocal of the proportion of the fragment (used for the integration) relating to the entire fragmentogram provided by the NIST library. The proportion of each compound class was calculated by dividing the sum of the areas of the compounds in this class by the sum of the peak areas of all analyzed compounds 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 standard deviation (RSD) calculated for ~~deoxyC6/C5, C/V, Ac/Al (V)~~CAR proxy, LIG proxies and the proportion of plant-derived markers was 9, ~~10,~~ 10 and 6%, respectively. The uncertainties given in Figures 3, 4, 5 and S1 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~~it is 0.5 and 2.0 for plant-derived and microbial inputs, respectively (Rumpel and Dignac, 2006). C6 were not considered since they can derive from the THM of cellulose leading to an increase of the plant-derived C6 signal. 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 microbial FA were composed of C12:0, C13:0, C14:0, C15:0, C17:0, *anteiso* and *iso* C15:0 and C17:0, *iso* C16:0, C16:1 and C18:1 commonly used as bacterial indicators (Frostegård et al., 1993). 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.

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/Al (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 November 29, 2010 to March 11, 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/Al (V) ratio ranged from 7.1 to 12.1 (9.1 ± 1.7, mean value ± standard deviation) in the surface horizon and from 3.6 to 6.9 (4.7 ± 1.2, mean value ± standard deviation) in the deep horizon.

3.2 River DOM in inter-storm conditions

In river samples from November 28, 2010 to March 8, 2011, the proportion of plant-derived markers ranged from 34 to 48% of the analyzed compounds (Figure 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 January 7, 2011 with a value of 0.5. The Ac/Al (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 (Figures 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 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 (Figure 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 (Figure 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.

4 Discussion

4.1 Inter-storm stream DOM

The molecular composition of inter-storm stream DOM samples was characterized by values comprised between soil DOM from the organic-rich and the organic-poor horizons. This is in agreement with the flowpath geometry during inter-storm conditions, with the wetland being saturated and the lower mineral soil horizon characterized by an hydraulic pressure higher than the upper organic-mineral horizon. Since the proportion of plant-derived markers clearly differentiated soil DOM from organo-mineral and mineral horizons and was fairly stable during the investigated period (Jeanneau et al., 2014), it can be used in an end member mixing approach in order to determine the proportions of DOM coming from organo-mineral and mineral horizons. From November 29, 2010 to March 11, 2011 the proportion of stream DOM originating from organo-mineral horizon ranged from 23 and 59 % (37 ± 13%, average ± standard error), which is in line with the conclusions of Strohmeier et al. (2013) stating that upper organic-rich soils in riparian wetland zones are important DOM contributors, even in non-storm conditions.

4.2 Beginning of floods: export of a microbial pool

At the beginning of the ~~five investigated~~ storm events the proportion of plant-derived markers in stream DOM was lower than in stream DOM during antecedent inter-storm conditions. The highest value recorded for event 3 was probably due to the 62% increase (from 48 to 78 l s^{-1}) of the discharge recorded the day before the event (Table S2). The stream DOM at beginning of storm events was also characterized by higher deoxyC6/C5 ratio than inter-storm stream DOM and by the occurrence of heptoses.~~For the same samples, the deoxyC6/C5 ratio increased as compared to inter-storm samples. Moreover they were the only samples where heptoses were detected.~~ Heptoses have been quantified in microbial exopolysaccharides (Jiao et al., 2010) and lipopolysaccharides (Sadovskaya et al., 1998). This export of a microbial pool as denoted by the high concentrations in heptoses and other microbial-derived biomarkers was the most important for event 5 with 86% of the analyzed biomarkers being from microbial origin during the earliest stages of this event. This was the first 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.

This microbial pool could derived from the microbial lysis occurring in soils over the dry period and that would have been flushed during the wetting-up phase (Christ and David, 1996). However the five recorded storm events were during the hydrological phase B characterized by permanent waterlogging of riparian wetland soils. As a consequence the wetting-up phase, denoted A, had already occurred. Moreover heptoses were not detected nor in soil DOM nor in stream DOM sampled in inter-storm conditions. ~~Since they have not been detected nor in soil DOM nor in stream DOM sampled in inter-storm conditions,~~Then 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/Al (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). In both of those watersheds, storm stream DOM was characterized by higher C/V and lower Ac/Al (V) ratios than DOM sampled in inter-storm conditions. 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/Al (V) ratio (Kabuyah et al., 2012; Vane et al., 2005). The aforementioned modifications of C/V and Ac/Al (V) ratios have then been attributed to the mobilization of less-degraded lignins during flood events (Dalzell et al., 2005; Hernes et al., 2008).

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 (Figure 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 (Figure 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. This could come from the destabilization and the disaggregation of soil aggregates during the erosion of macropores walls ~~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~~2015). 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 3.b), this could explain why the compositional proxies, including biomarkers and spectroscopic measurements, do not recover their pre-event values with the same kinetic as stream DOC concentrations. Sampling soil solutions during storm events and up to the recovery of pre-event values at the same high frequency than deployed for monitoring stream variations would be necessary to test this in-soil erosive process.

4.5 Summary and implications

The results from this study thus highlight changes in DOM sources and DOM transfer processes during storm and inter-storm conditions. Although the source of DOM during inter-flow conditions appears to have been the DOM contained in the soil horizons of the riparian wetland zones which was passively transferred into the stream, the DOM source and DOM transfer processes were more complex during storm periods. During these periods, the DOM transferred from soil to the stream was not only due to the flush of DOM already occurring in soils but also to additional sources and production processes that lead to the occurrence of less-degraded molecules in the dissolved phase. Those findings, which appear characteristic of DOM transfer in lowland catchments worldwide as far as the current literature is concerned, have two important implications.

The first one concerns the transfer of micropollutants, which is mainly controlled by the complexing properties of OM. The partitioning between soil particles and the dissolved phase during storm event highlighted in this study induced the occurrence in the dissolved phase of less-biodegraded molecules, that is to say a DOM of more hydrophobic composition (Kleber and Johnson, 2010). SOM hydrophobicity is assumed to be the main driving force of the retention of hydrophobic micropollutants in soils, such as many pesticides and antibiotics (Ji et al., 2011). This DOM producing process could therefore lead to hot moments in the transfer of these harmful compounds from soils to the dissolved phase of stream water increasing their bioavailability and then their potential for creating undesirable effects, such as antibiotic resistance (Hellweger et al., 2011).

The second implication concerns the modeling of the export of DOM from headwater catchment. In lowland headwater catchments, up to 80% of DOM is transferred during storm events (Raymond and Saiers, 2010). In many modeling studies, it is assumed 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~~ suggested 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.

Acknowledgements

We thank the technical staff from INRA and Géosciences Rennes for their assistance during the fieldwork. This research was funded by the University of Rennes 1 through the "Varia-MOD" project and by the CNRS through the EC2CO "Prodynamos" project. We used data provided online by the environmental observatory ORE AgrHys (www6.inra.fr/ore_agrhys_eng/).

References

Ågren, A., Buffam, I., Jansson, M. and Laudon, H.: Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export, J. Geophys. Res. Biogeosciences, 112(G3), G03003, doi:10.1029/2006JG000381, 2007.

Aubert, A. H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., Grimaldi, C., Hamon, Y., Jaffrézic, A., Lecoz-Boutnik, M., Molénat, J., Petitjean, P., Ruiz, L. and Merot, P.: Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study, Hydrol Earth Syst Sci, 17(4), 1379–1391, doi:10.5194/hess-17-1379-2013, 2013.

Austnes, K., Evans, C., Eliot-Laize, C., Naden, P. and Old, G.: Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment, Biogeochemistry, 99(1-3), 157–173, doi:10.1007/s10533-009-9399-4, 2010.

Billett, M. F., Deacon, C. M., Palmer, S. M., Dawson, J. J. C. and Hope, D.: Connecting organic carbon in stream water and soils in a peatland catchment, J. Geophys. Res. Biogeosciences, 111(G2), G02010, doi:10.1029/2005JG000065, 2006.

Birkel, C., Soulsby, C. and Tetzlaff, D.: Integrating parsimonious models of hydrological connectivity and soil biogeochemistry to simulate stream DOC dynamics, J. Geophys. Res. Biogeosciences, 119(5), 2013JG002551, doi:10.1002/2013JG002551, 2014.

Christ, M. J. and David, M. B.: Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol, Soil Biol. Biochem., 28(9), 1191–1199, doi:10.1016/0038-0717(96)00120-4, 1996.

Corapcioglu, M. Y. and Jiang, S.: Colloid-facilitated groundwater contaminant transport, Water Resour. Res., 29(7), 2215–2226, doi:10.1029/93WR00404, 1993.

Cranwell, P. A.: Monocarboxylic acids in lake sediments: Indicators, derived from terrestrial and aquatic biota, of paleoenvironmental trophic levels, Chem. Geol., 14(1–2), 1–14, doi:10.1016/0009-2541(74)90092-8, 1974.

Crave, A. and Gascuel-Odoux, C.: The influence of topography on time and space distribution of soil surface water content, Hydrol. Process., 11(2), 203–210, doi:10.1002/(SICI)1099-1085(199702)11:2<203::AID-HYP432>3.0.CO;2-K, 1997.

Dalzell, B. J., Filley, T. R. and Harbor, J. M.: Flood pulse influences on terrestrial organic matter export from an agricultural watershed, J Geophys Res, 110(G2), G02011, doi:10.1029/2005JG000043, 2005.

Durand, P. and Juan Torres, J. L.: Solute transfer in agricultural catchments: the interest and limits of mixing models, J. Hydrol., 181(1–4), 1–22, doi:10.1016/0022-1694(95)02922-2, 1996.

Eglinton, G. and Hamilton, R. J.: Leaf epicuticular waxes, Science, 156(3780), 1322–1335, 1967.

Frostegård, Å., Tunlid, A. and Bååth, E.: Phospholipid Fatty Acid Composition, Biomass, and Activity of Microbial Communities from Two Soil Types Experimentally Exposed to Different Heavy Metals, Appl. Environ. Microbiol., 59(11), 3605–3617, 1993.

Grasset, L., Rovira, P. and Amblès, A.: TMAH-preparative thermochemolysis for the characterization of organic matter in densimetric fractions of a Mediterranean forest soil, J. Anal. Appl. Pyrolysis, 85(1-2), 435–441, doi:doi: 10.1016/j.jaap.2008.09.004, 2009.

Hedges, J. I. and Parker, P. L.: Land-derived organic matter in surface sediments from the Gulf of Mexico, Geochim. Cosmochim. Acta, 40(9), 1019–1029, doi:10.1016/0016-7037(76)90044-2, 1976.

Hellweger, F. L., Ruan, X. and Sanchez, S.: A Simple Model of Tetracycline Antibiotic Resistance in the Aquatic Environment (with Application to the Poudre River), Int. J. Environ. Res. Public. Health, 8(2), 480–497, 2011.

Hernes, P. J., Spencer, R. G. M., Dyda, R. Y., Pellerin, B. A., Bachand, P. A. M. and Bergamaschi, B. A.: The role of hydrologic regimes on dissolved organic carbon composition in an agricultural watershed, Geochim. Cosmochim. Acta, 72(21), 5266–5277, doi:10.1016/j.gca.2008.07.031, 2008.

Hinton, M. J., Schiff, S. L. and English, M. C.: Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield, Biogeochemistry, 41(2), 175–197, doi:10.1023/A:1005903428956, 1998.

Hood, E., Gooseff, M. N. and Johnson, S. L.: Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon, J Geophys Res, 111(G1), G01007, 2006.

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(G3), G03043, 2011.

IUSS Working Group WRB: World reference base for soil resources 2006, World Soil Resources Reports No. 103. FAO, Rome, 2006.

Jeanneau, L., Jaffrezic, A., Pierson-Wickmann, A.-C., Gruau, G., Lambert, T. and Petitjean, P.: Constraints on the Sources and Production Mechanisms of Dissolved Organic Matter in Soils from Molecular Biomarkers, Vadose Zone J., 13(7), doi:10.2136/vzj2014.02.0015, 2014.

Jiao, Y., Cody, G. D., Harding, A. K., Wilmes, P., Schrenk, M., Wheeler, K. E., Banfield, J. F. and Thelen, M. P.: Characterization of Extracellular Polymeric Substances from Acidophilic Microbial Biofilms, Appl. Environ. Microbiol., 76(9), 2916–2922, doi:10.1128/AEM.02289-09, 2010.

Ji, L., Wan, Y., Zheng, S. and Zhu, D.: Adsorption of Tetracycline and Sulfamethoxazole on Crop Residue-Derived Ashes: Implication for the Relative Importance of Black Carbon to Soil Sorption, Environ. Sci. Technol., 45(13), 5580–5586, doi:10.1021/es200483b, 2011.

Kabuyah, R. N. T. M., van Dongen, B. E., Bewsher, A. D. and Robinson, C. H.: Decomposition of lignin in wheat straw in a sand-dune grassland, Soil Biol. Biochem., 45(0), 128–131, doi:10.1016/j.soilbio.2011.10.014, 2012.

Kleber, M. and Johnson, M. G.: Advances in Understanding the Molecular Structure of Soil Organic Matter: Implications for Interactions in the Environment, in Advances in Agronomy v106, vol. Volume 106, pp. 77–142, Academic Press. [online] Available from: http://www.sciencedirect.com/science/article/B7CSX-4YNV3J6-7/2/0601e6ab50127f09e54b0df6822be945, 2010.

Knorr, K.-H.: DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths – are DOC exports mediated by iron reduction/oxidation cycles?, Biogeosciences, 10(2), 891–904, doi:10.5194/bg-10-891-2013, 2013.

Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Thibault, J.-N. and Jaffrezic, A.: Carbon isotopes as tracers of dissolved organic carbon sources and water pathways in headwater catchments, J. Hydrol., 402(3–4), 228–238, doi:10.1016/j.jhydrol.2011.03.014, 2011.

Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J.-N. and Jeanneau, L.: Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment, Water Resour. Res., 49, 1–12, doi:10.1002/wrcr.20466, 2013.

Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J. N. and Jeanneau, L.: DOC sources and DOC transport pathways in a small headwater catchment as revealed by carbon isotope fluctuation during storm events, Biogeosciences, 11(11), 3043–3056, doi:10.5194/bg-11-3043-2014, 2014.

Lucas García, J. A., Barbas, C., Probanza, A., Barrientos, M. L. and Gutierrez Mañero, F. J.: Low molecular weight organic acids and fatty acids in root exudates of two Lupinus cultivars at flowering and fruiting stages, Phytochem. Anal., 12(5), 305–311, doi:10.1002/pca.596, 2001.

Matsuda, H. and Koyama, T.: Early diagenesis of fatty acids in lacustrine sediments—II. A statistical approach to changes in fatty acid composition from recent sediments and some source materials, Geochim. Cosmochim. Acta, 41(12), 1825–1834, doi:10.1016/0016-7037(77)90214-9, 1977.

Maurice, P. A., Cabaniss, S. E., Drummond, J. and Ito, E.: Hydrogeochemical controls on the variations in chemical characteristics of natural organic matter at a small freshwater wetland, Chem. Geol., 187(1–2), 59–77, doi:10.1016/S0009-2541(02)00016-5, 2002.

McGlynn, B. L. and McDonnell, J. J.: Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, Water Resour Res, 39(4), 1090, 2003.

McLaughlin, C. and Kaplan, L. A.: Biological lability of dissolved organic carbon in stream water and contributing terrestrial sources, Freshw. Sci., 32(4), 1219–1230, doi:10.1899/12-202.1, 2013.

Molenat, J., Gascuel-Odoux, C., Ruiz, L. and Gruau, G.: Role of water table dynamics on stream nitrate export and concentration in agricultural headwater catchment (France), J. Hydrol., 348(3–4), 363–378, doi:10.1016/j.jhydrol.2007.10.005, 2008.

Morel, B., Durand, P., Jaffrezic, A., Gruau, G. and Molenat, J.: Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment, Hydrol. Process., 23(20), 2888–2901, doi:10.1002/hyp.7379, 2009.

Raymond, P. and Saiers, J.: Event controlled DOC export from forested watersheds, Biogeochemistry, 100(1-3), 197–209, doi:10.1007/s10533-010-9416-7, 2010.

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P. and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503(7476), 355–359, 2013.

Rumpel, C. and Dignac, M.-F.: Gas chromatographic analysis of monosaccharides in a forest soil profile: Analysis by gas chromatography after trifluoroacetic acid hydrolysis and reduction–acetylation, Soil Biol. Biochem., 38(6), 1478–1481, doi:10.1016/j.soilbio.2005.09.017, 2006.

Sadovskaya, I., Brisson, J.-R., Lam, J. S., Richards, J. C. and Altman, E.: Structural elucidation of the lipopolysaccharide core regions of the wild-type strain PAO1 and O-chain-deficient mutant strains AK1401 and AK1012 from Pseudomonas aeruginosa serotype O5, Eur. J. Biochem., 255(3), 673–684, doi:10.1046/j.1432-1327.1998.2550673.x, 1998.

Saraceno, J. F., Pellerin, B. A., Downing, B. D., Boss, E., Bachand, P. A. M. and Bergamaschi, B. A.: High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes, J Geophys Res, 114, G00F09, 2009.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M. and Bishop, K.: Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration Model, Hydrol Earth Syst Sci, 13(12), 2287–2297, doi:10.5194/hess-13-2287-2009, 2009.

Singh, S., Inamdar, S. and Mitchell, M.: Changes in dissolved organic matter (DOM) amount and composition along nested headwater stream locations during baseflow and stormflow, Hydrol. Process., 29(6), 1505-1520, 2015.

Strohmeier, S., Knorr, K.-H., Reichert, M., Frei, S., Fleckenstein, J. H., Peiffer, S. and Matzner, E.: Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements, Biogeosciences, 10(2), 905–916, doi:10.5194/bg-10-905-2013, 2013.

Trulear, M. G. and Characklis, W. G.: Dynamics of biofilm processes, J. Water Pollut. Control Fed., 54(9), 1288–1301, 1982.

Vane, C. H., Drage, T. C., Snape, C. E., Stephenson, M. H. and Foster, C.: Decay of cultivated apricot wood (Prunus armeniaca) by the ascomycete Hypocrea sulphurea, using solid state 13C NMR and off-line TMAH thermochemolysis with GC–MS, Int. Biodeterior. Biodegrad., 55(3), 175–185, doi:10.1016/j.ibiod.2004.11.004, 2005.

Vidon, P., Wagner, L. and Soyeux, E.: Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses, Biogeochemistry, 88(3), 257–270–270, 2008.

Wilson, G. V., Xu, M., Chen, Y., Liu, G. and Römkens, M. J. M.: Macropore flow and mass wasting of gullies in the Loess Plateau, China, Int. J. Sediment Res., 20(3), 249–258, 2005.

Wysocki, L. A., Filley, T. R. and Bianchi, T. S.: Comparison of two methods for the analysis of lignin in marine sediments: CuO oxidation versus tetramethylammonium hydroxide (TMAH) thermochemolysis, Org. Geochem., 39(10), 1454–1461, doi:10.1016/j.orggeochem.2008.06.004, 2008.

Yang, L., Guo, W., Chen, N., Hong, H., Huang, J., Xu, J. and Huang, S.: Influence of a summer storm event on the flux and composition of dissolved organic matter in a subtropical river, China, Appl. Geochem., 28(0), 164–171, doi:10.1016/j.apgeochem.2012.10.004, 2013.

~~Ågren, A., Buffam, I., Jansson, M. and Laudon, H.: Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export, J. Geophys. Res. Biogeosciences, 112(G3), G03003, 2007.~~

~~Aubert, A. H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., Grimaldi, C., Hamon, Y., Jaffrézic, A., Lecoz-Boutnik, M., Molénat, J., Petitjean, P., Ruiz, L. and Merot, P.: Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study, Hydrol Earth Syst Sci, 17(4), 1379–1391, 2013.~~

~~Austnes, K., Evans, C., Eliot-Laize, C., Naden, P. and Old, G.: Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment, Biogeochemistry, 99(1-3), 157–173, 2010.~~

~~Billett, M. F., Deacon, C. M., Palmer, S. M., Dawson, J. J. C. and Hope, D.: Connecting organic carbon in stream water and soils in a peatland catchment, J. Geophys. Res. Biogeosciences, 111(G2), G02010, 2006.~~

~~Birkel, C., Soulsby, C. and Tetzlaff, D.: Integrating parsimonious models of hydrological connectivity and soil biogeochemistry to simulate stream DOC dynamics, J. Geophys. Res. Biogeosciences, 119(5), 2013JG002551, 2014.~~

~~Cranwell, P. A.: Monocarboxylic acids in lake sediments: Indicators, derived from terrestrial and aquatic biota, of paleoenvironmental trophic levels, Chem. Geol., 14(1–2), 1–14, doi:10.1016/0009-2541(74)90092-8, 1974.~~

~~Crave, A. and Gascuel-Odoux, C.: The influence of topography on time and space distribution of soil surface water content, Hydrol. Process., 11(2), 203–210, 1997.~~

~~Dalzell, B. J., Filley, T. R. and Harbor, J. M.: Flood pulse influences on terrestrial organic matter export from an agricultural watershed, J Geophys Res, 110(G2), G02011, 2005.~~

~~Durand, P. and Juan Torres, J. L.: Solute transfer in agricultural catchments: the interest and limits of mixing models, J. Hydrol., 181(1–4), 1–22, 1996.~~

~~Gough, M. A., Fauzi, R., Mantoura, C. and Preston, M.: Terrestrial plant biopolymers in marine sediments, Geochim. Cosmochim. Acta, 57(5), 945–964, 1993.~~

~~Grasset, L., Rovira, P. and Amblès, A.: TMAH-preparative thermochemolysis for the characterization of organic matter in densimetric fractions of a Mediterranean forest soil, J. Anal. Appl. Pyrolysis, 85(1–2), 435–441, 2009.~~

~~Hellweger, F. L., Ruan, X. and Sanchez, S.: A Simple Model of Tetracycline Antibiotic Resistance in the Aquatic Environment (with Application to the Poudre River), Int. J. Environ. Res. Public. Health, 8(2), 480–497, 2011.~~

~~Hernes, P. J., Spencer, R. G. M., Dyda, R. Y., Pellerin, B. A., Bachand, P. A. M. and Bergamaschi, B. A.: The role of hydrologic regimes on dissolved organic carbon composition in an agricultural watershed, Geochim. Cosmochim. Acta, 72(21), 5266–5277, 2008.~~

~~Hood, E., Gooseff, M. N. and Johnson, S. L.: Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon, J Geophys Res, 111(G1), G01007, 2006.~~

~~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(G3), G03043, 2011.~~

~~Jeanneau, L., Jaffrezic, A., Pierson-Wickmann, A.-C., Gruau, G., Lambert, T. and Petitjean, P.: Constraints on the Sources and Production Mechanisms of Dissolved Organic Matter in Soils from Molecular Biomarkers, Vadose Zone J., 13(7), 2014.~~

~~Jerome, J. H. and Bukata, R. P.: Tracking the Propagation of Solar Ultraviolet Radiation: Dispersal of Ultraviolet Photons in Inland Waters, J. Gt. Lakes Res., 24(3), 666–680, 1998.~~

~~Jiao, Y., Cody, G. D., Harding, A. K., Wilmes, P., Schrenk, M., Wheeler, K. E., Banfield, J. F. and Thelen, M. P.: Characterization of Extracellular Polymeric Substances from Acidophilic Microbial Biofilms, Appl. Environ. Microbiol., 76(9), 2916–2922, 2010.~~

~~Kabuyah, R. N. T. M., van Dongen, B. E., Bewsher, A. D. and Robinson, C. H.: Decomposition of lignin in wheat straw in a sand-dune grassland, Soil Biol. Biochem., 45(0), 128–131, 2012.~~

~~Kleber, M. and Johnson, M. G.: Advances in Understanding the Molecular Structure of Soil Organic Matter: Implications for Interactions in the Environment, in Advances in Agronomy v106, vol. Volume 106, pp. 77–142, Academic Press. 2010.~~

~~Knorr, K.-H.: DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths – are DOC exports mediated by iron reduction/oxidation cycles?, Biogeosciences, 10(2), 891–904, 2013.~~

~~Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J.-N. and Jeanneau, L.: Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment, Water Resour. Res., 49, 1–12, 2013.~~

~~Lambert, T., Pierson-Wickmann, A. C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J. N. and Jeanneau, L.: DOC sources and DOC transport pathways in a small headwater catchment as revealed by carbon isotope fluctuation during storm events, Biogeosciences, 11(11), 3043–3056, 2014.~~

~~Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Thibault, J.-N. and Jaffrezic, A.: Carbon isotopes as tracers of dissolved organic carbon sources and water pathways in headwater catchments, J. Hydrol., 402(3–4), 228–238, 2011.~~

~~Lucas García, J. A., Barbas, C., Probanza, A., Barrientos, M. L. and Gutierrez Mañero, F. J.: Low molecular weight organic acids and fatty acids in root exudates of two Lupinus cultivars at flowering and fruiting stages, Phytochem. Anal., 12(5), 305–311, 2001.~~

~~Matsuda, H. and Koyama, T.: Early diagenesis of fatty acids in lacustrine sediments—II. A statistical approach to changes in fatty acid composition from recent sediments and some source materials, Geochim. Cosmochim. Acta, 41(12), 1825–1834, 1977.~~

~~Maurice, P. A., Cabaniss, S. E., Drummond, J. and Ito, E.: Hydrogeochemical controls on the variations in chemical characteristics of natural organic matter at a small freshwater wetland, Chem. Geol., 187(1–2), 59–77, 2002.~~

~~McGlynn, B. L. and McDonnell, J. J.: Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, Water Resour Res, 39(4), 1090, 2003.~~

~~McLaughlin, C. and Kaplan, L. A.: Biological lability of dissolved organic carbon in stream water and contributing terrestrial sources, Freshw. Sci., 32(4), 1219–1230, 2013.~~

~~Molenat, J., Gascuel-Odoux, C., Ruiz, L. and Gruau, G.: Role of water table dynamics on stream nitrate export and concentration in agricultural headwater catchment (France), J. Hydrol., 348(3–4), 363–378, 2008.~~

~~Morel, B., Durand, P., Jaffrezic, A., Gruau, G. and Molenat, J.: Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment, Hydrol. Process., 23(20), 2888–2901, 2009.~~

~~Raymond, P. and Saiers, J.: Event controlled DOC export from forested watersheds, Biogeochemistry, 100(1-3), 197–209, 2010.~~

~~Rumpel, C. and Dignac, M.-F.: Gas chromatographic analysis of monosaccharides in a forest soil profile: Analysis by gas chromatography after trifluoroacetic acid hydrolysis and reduction–acetylation, Soil Biol. Biochem., 38(6), 1478–1481, 2006.~~

~~Sadovskaya, I., Brisson, J.-R., Lam, J. S., Richards, J. C. and Altman, E.: Structural elucidation of the lipopolysaccharide core regions of the wild-type strain PAO1 and O-chain-deficient mutant strains AK1401 and AK1012 from Pseudomonas aeruginosa serotype O5, Eur. J. Biochem., 255(3), 673–684, 1998.~~

~~Saraceno, J. F., Pellerin, B. A., Downing, B. D., Boss, E., Bachand, P. A. M. and Bergamaschi, B. A.: High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes, J Geophys Res, 114, G00F09, 2009.~~

~~Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M. and Bishop, K.: Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration Model, Hydrol Earth Syst Sci, 13(12), 2287–2297, 2009.~~

~~Singh, S., Inamdar, S. and Mitchell, M.: Changes in dissolved organic matter (DOM) amount and composition along nested headwater stream locations during baseflow and stormflow, Hydrol. Process., doi:10.1002/hyp.10286, 2014.~~

~~Strohmeier, S., Knorr, K.-H., Reichert, M., Frei, S., Fleckenstein, J. H., Peiffer, S. and Matzner, E.: Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements, Biogeosciences, 10(2), 905–916, 2013.~~

~~Tranvik, L.: Allochthonous dissolved organic matter as an energy source for pelagic bacteria and the concept of the microbial loop, in Dissolved Organic Matter in Lacustrine Ecosystems, vol. 73, edited by K. Salonen, T. Kairesalo, and R. I. Jones, pp. 107–114, Springer Netherlands. 1992.~~

~~Trulear, M. G. and Characklis, W. G.: Dynamics of biofilm processes, J. Water Pollut. Control Fed., 54(9), 1288–1301, 1982.~~

~~Vane, C. H., Drage, T. C., Snape, C. E., Stephenson, M. H. and Foster, C.: Decay of cultivated apricot wood (Prunus armeniaca) by the ascomycete Hypocrea sulphurea, using solid state 13C NMR and off-line TMAH thermochemolysis with GC–MS, Int. Biodeterior. Biodegrad., 55(3), 175–185, 2005.~~

~~Vidon, P., Wagner, L. and Soyeux, E.: Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses, Biogeochemistry, 88(3), 257–270, 2008.~~

~~Wilson, G. V., Xu, M., Chen, Y., Liu, G. and Römkens, M. J. M.: Macropore flow and mass wasting of gullies in the Loess Plateau, China, Int. J. Sediment Res., 20(3), 249–258, 2005.~~

~~Wysocki, L. A., Filley, T. R. and Bianchi, T. S.: Comparison of two methods for the analysis of lignin in marine sediments: CuO oxidation versus tetramethylammonium hydroxide (TMAH) thermochemolysis, Org. Geochem., 39(10), 1454–1461, 2008.~~

~~Yang, L., Guo, W., Chen, N., Hong, H., Huang, J., Xu, J. and Huang, S.: Influence of a summer storm event on the flux and composition of dissolved organic matter in a subtropical river, China, Appl. Geochem., 28(0), 164–171, 2013.~~

Mis en forme : Bibliographie

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		**2**	**3**	**4**	**5**	**6**
Date		**Dec 4, 2010**	**Dec 19, 2010**	**Jan 6, 2011**	**Feb 13, 2011**	**Feb 19, 2011**
Discharge ($l\ s^{-1}$)	beg. [a]	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 ($mg\ l^{-1}$)	beg. [a]	7.4	6.6	6.4	7.4	8
	max. [b]	11.6	12.4	11.5	12.8	15.5
	end	9.8	7.4	8.0	11	9.1
SUVA ($l\ mg^{-1}\ cm^{-1}$)	beg. [a]	2.0	2.6	2.8	2.0	2.4
	max. [b]	3.1	3.3	3.4	3.2	2.9
	end	3.0	3.4	3.5	3.0	2.9
~~**$\delta^{13}C$ [c] (‰)**~~ **Plant-derived markers (%)**	beg. [a]	31~~-28.9~~	49~~-~~	31~~-~~	14~~-~~	31~~-~~
	max. [b]	67~~-28.8~~	78~~-~~	70~~-~~	71~~-~~	59~~-~~
	end	57~~-27.2~~	72~~-~~	58~~-~~	60~~-~~	25~~-~~
deoxyC6/C5	beg. [a]	1.6	1.5	1.6	2.7	1.9
	max. [b]	0.9	1.1	1.0	1.1	1.3
	end	1.1	1.1	0.9	1.2	1.4
C/V	beg. [a]	0.2	0.2	0.2	0.2	0.3
	max. [b]	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. [a]	5.0	7.3	5.5	6.6	5.2
	max. [b]	5.2	5.3	4.6	5.5	4.5
	end	4.7	4.9	4.3	4.8	4.6

[a] Value recorded at the beginning of storm events.

[b] Value recorded at the peak discharge.

~~[c] Data from Lambert et al., 2014.~~

Figure captions

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. The global positioning system coordinates of the outlet are 48.0057 North, 2.8313 East (decimal degree).

Figure 2. Discharge (white area), daily rainfall (black area) and water table level in the wetland domain ~~(PK1)~~ (dashed line) during the hydrologic year 2010-2011. Monitored storm events are indicated by numbers and arrows.

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

Figure 4. Temporal change in flow and ~~DOM~~ DOC 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, δ^{13}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.

Figure 5. Temporal change in flow (dashed line) and proportion of plant-derived markers (~~grey~~ black triangles) expressed as the percentage of analyzed compounds during storm event ~~3~~5. The uncertainties are the mean RSD calculated for five samples analyzed in triplicate.

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.~~

Figure 7. Difference of the correlation between turbidity and the C/V ratio (lignin proxy) during the rising limbs (grey diamonds – *p*-value < 0.0001) and during entire storm events (grey and black diamonds – *p*-value = 0.008).