BG-2015-17 Editorial Review

Major Comments

There is a general problem with data being discussed which are not presented, therefore the statements referring to them are unsupported. For example, SUVA, deoxyC5/C6 and proportion of plant markers are not stated or plotted for the SOM or soil DOM. Therefore the statement at the beginning of section 4.1 about the provenance of inter-storm river DOM is unsupported, as is the end-member mixing model statement that follows it. Please extend figure 3 and Table 1 to include the missing data. The reader should not have to refer to another paper in order to substantiate the claims made in your text.

The values of the proportion of plant-derived markers for soil DOM sampled in the organo-mineral and mineral horizons were added on Figure 3. This value is used to quantify the proportions of DOM flushed from organo-mineral and mineral horizons. The evolution of SUVA and deoxyC6/C5 are not displayed since they are not used in this calculation. Moreover the beginning of the section 4.1 was changed.

You also have the opposite problem of including data which are not discussed. Your discussion does not comment upon or explain the noted changes in SUVA or percentage plant derived markers that you describe in your results section. Please insert a discussion of those data or remove them from your methods and results.

SUVA was not necessary for the discussion. As a consequence the description of the evolution of this parameter in the result section was removed (first paragraph of section 3.3). Moreover the beginning of section 4.4 was re-worded in order to take into account the fact that SUVA was not displayed. SUVA was also removed from Table 1 and Figures 4 and S1. As a result figure 5 was removed.

However the proportion of plant-derived markers is important for two reasons. (1) It is used to approximate the proportion of DOM flushed from organo-mineral and mineral horizons. (2) It is the complementary value of the proportion of microbial markers that is used in the discussion in the section 4.2.

At one point in your response to reviews you use the text copied below. This is a more detailed argument than you employ in your manuscript. Please add the argument given below to the appropriate section of your discussion.

The section 4.3 has been reorganized in order to add this argument to the discussion.

'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.'

Please include the end member mixing model equation as suggested by reviewer 2.

Three equations were added. Equation 1 for the end member mixing approach allows calculating the proportion of microbial CAR. Equation 2 allows the calculation of the proportion of microbial markers. Equation 3 allows the calculation of the proportion of plant-derived markers.

The use of English throughout the manuscript contains minor errors, and these occasionally tend to obscure the intended meaning. Please seek to have the manuscript copy-edited for use of English (the journal can provide this if necessary, but only at additional cost).

The manuscript was copy-edited by Dr BW Abbott, a native English speaker.

Minor Comments

Abstract: Please re-write the first few sentences of the abstract, as the use of English is a little awkward, and one sentence is over-long. This is also true of the first paragraph of the introduction.

The first sentences of the abstract and the first paragraph of the introduction have been reworded.

Page 3 line 26. You begin a sentence with 'Answering these questions...', but no question has actually been posed. Please re-phrase.

This sentence has been reworded.

Page 4 line 12. Be more explicit about how your markers allow distinction between DOM from different soil horizons, At the moment this is simply stated rather than explained.

Soil DOM from surface horizons was characterized by high proportion of plant-derived markers, while soil DOM from deep horizons was characterized by high proportions of microbial markers. This has been added in this sentence.

Page 4 line 29; Delete 'do we see trends?' (unnecessary).

It has been deleted.

Page 16 line 7; replace 'on' with 'in' (October).

It has been performed (Page 7 line 16).

Page 8 line 27. You refer to published data here, so please add in the relevant references.

Two references have been added: Nierop and Verstraten, 2004 and Nierop et al., 2005.

Page 9 line 14. Please add 's' to the end of 'follow'.

It has been performed.

Page 10 line 4-5. This sentence does not make sense. Please re-phrase.

This sentence has been re-phrased.

Section 3.1. This section makes reference to compounds (specific lignins) which were not mentioned in the methods section. Please clarify in the methods section which aspects of the methods (presumably TMAH GC-MS) involved the identification and quantification of these different lignin compounds. Similarly, you also refer to SUVA data in your results section. Please therefore provide your method for measuring SUVA.

A paragraph has been added at the beginning of the section 2.5 in order to clarify where those lignin-tannins (LIG-TAN) compounds come from and how the LIG-TAN proxies were calculated. Moreover the trivial names of the compounds used in the calculation of those proxies were added in table S2.

Figure 4. The legend for this figure needs correcting, as it currently does not distinguish between the line for discharge and the line for DOC concentration.

The legend has been changed.

Please add a note to your results text to explain that data are visually presented for example events rather than for all events.

A precision has been added at the beginning of section 3.3.

Page 12 line 7. The sentence starting 'The highest value..' is unclear. Please re-word to make the meaning clear (do you mean 'higher' instead of 'highest'?).

The beginning of the section 4.2 has been reworded. "Highest" was misused and has been replaced by "higher".

Page 12 line 14. Please state exactly what you mean (i.e. what data) by 'other microbial-derived biomarkers'.

"Other microbial-derived biomarkers" referred to the microbial FA and microbial CAR included in the calculation of the proportion of microbial markers. The sentence has been reworded.

Page 12 line 30. Explain what you mean by 'the extreme value'. Extreme value of which parameter? In which figure can this data be seen? Are these last lines of the section referring to your own study or to other previously reported studies? Please clarify.

The last lines of this section refer to previously reported studies. This point was clarified by rewording the paragraph.

Figure 6 caption please remove the phrase 'Time diagram'.

It has been performed.

Page 13 line 28. Please replace 'liquid' with 'dissolved'.

It has been performed.

Figure 7 caption. Please remove the words 'Difference of'.

It has been performed.

Figure 7 legend. The black diamonds should be labelled 'entire event', not 'falling limb'.

It has been changed.

Page 14, first paragraph. Please explain why disaggregation of aggregates and erosion of macropore walls would transfer lignins into solution but not add to the suspended particle load.

The disaggregation of aggregates and erosion of macropore walls could lead to a modification of the composition of DOM produced within the different soil horizons and flushed to the stream, without adding suspended solid in the stream, the latter particles being physically trapped by the soil matrix. This explanation has been added at the end of the section 4.3.

Sources 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~~Understanding the mechanisms controlling this transfer ~~mechanisms of DOM~~ is ~~of main importance for~~fundamental to ecology and geochemistry ~~ecological and geochemical reasons~~. ~~Is stream~~ DOM delivery to streams during storms is assumed to come from the flushing of ~~the result of the flushing of~~ pre-existing soil DOM reservoirs ~~activated~~ mobilized by the modification of water flow paths~~?~~. We tested this hypothesis by investigating the ~~The~~ evolution of the ~~chemical~~ composition of stream DOM during inter-storm conditions and five storm events monitored with a high-frequency sampling. The composition of DOM was ~~investigated~~ analyzed using~~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 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~~ due to 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~~ across soil-river interfaces is a globally relevant carbon flux (Cole et al., 2007) and a major control~~s~~ on the biogeochemistry of micropollutants ~~and the equilibrium between continental and oceanic C reservoirs~~ (Corapcioglu and Jiang, 1993; Raymond et al., 2013). ~~Then determining~~While the mechanisms governing this transfer ~~mechanisms of DOM is of main importance for~~have clear ecological, societal and geochemical ~~reasons~~implications, key unknowns persist concerning the production and transfer of DOM across terrestrial-aquatic interfaces (Kicklighter et al., 2013; Lambert et al., 2014). Understanding DOM dynamicsin headwater catchments is particularly important because over 90% of stream length occurs in small catchments (Bishop et al., 2008) and DOM yield per square meter is highest in headwaters ~~. The concentration of DOM generally decreasing from headwater to large river catchments~~ (Ågren et al., 2007~~),~~), resulting in a large proportion of river DOM ultimately coming from headwater catchment soils (Billett et al., 2006; Morel et al., 2009). ~~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 this research.~~

Organic matter sources are typically abundant in headwater catchment soil, meaning that DOM flux depends primarily on water flow path (McDonnell, 2003; Morel et al., 2009), which changes at seasonal and event scales in response to hydroclimatic conditions ~~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). Because storm events connect a larger portion of the landscape with surface waters, more than 60% of annual dissolved organic carbon (DOC; the parameter commonly used to quantify DOM concentration) load can occur ~~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 concentration~~s~~ typically increases during storm events as elevated water table and enhanced near-surface flow cause leaching of ~~(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).

The shift in flow paths during ~~S~~storm events can also cause ~~are also associated with~~ changes in DOM composition and biodegradability (McLaughlin and Kaplan, 2013). Low frequency spectroscopic measurements of ~~Compositional changes have been recorded using different spectroscopic measurements namely~~ UV-absorbance and fluorescence suggested that ~~. The first results were obtained using low frequency spectroscopic measurements and have highlighted that~~ DOM aromaticity ~~increased~~ increases during storm events, potentially due to mobilization of aromatic DOM from surface soil horizons (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~~ are not always linked and that compositional differences in DOM can persist long after concentration returns to pre-event levels ~~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~~ shift in DOM signature has been attributed to ~~interpreted as an evidence for~~ in-stream production of fluorescing DOM (Austnes et al., 2010) or ~~for a continuous~~sustained hydrologic contribution ~~of~~ from surface soil horizons ~~to the DOM export, even~~ after the return to low-flow conditions (Strohmeier et al., 2013).

~~Molecular~~ Analysis of the molecular composition of DOM during low and high-flow conditions is considerably less ~~data investigating the differences in DOM composition between low-flow and high-flow conditions are less~~ common than spectroscopic data due to analytical cost and complexity. However, ~~and comprise mostly~~ low frequency lignin phenol data indicate that less-degraded lignins are mobilized during storm events potentially due to the mobilization of particles by erosion combined with partitioning of the lignin compounds between the solid and dissolved phase (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 because molecular data are typically collected ~~those data have been acquired~~ using low frequency water sampling strategies (one sample per storm event), it is not possible to evaluate the persistence of shifts in DOM ~~and cannot be used therefore to investigate the persistence of the DOM~~ aromatic fingerprint after storm events.

~~Thus, according to the existing database on~~These asymmetrical shifts in DOM composition ~~variation~~ during and after storm events suggest~~, it appears~~ that in addition to changing flow path and DOM transport, storm events alter mechanisms of DOM production or processing. To test this hypothesis, we collected high-frequency molecular data during five successive storm events and we compared them with ~~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 molecular composition of soil organic matter (SOM), soil DOM and inter-storm river DOM in a lowland headwater catchment in Brittany, France. ~~Moreover those data should be comparable with spectroscopic and molecular data available in the literature.~~

Among the different techniques available to study the molecular composition of DOM, ~~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 (LIG-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 (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). The combination of those markers allows the investigation of the balance between microbial and plant-derived markers differentiating between soil DOM from organic-rich, characterized by high proportion of plant-derived markers, and organic-poor horizons, characterized by high proportion of microbial markers, 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).

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 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 ($\delta^{13}C$) and hydrochemistry ([DOC], [Cl^-], [NO_3^-], [SO_4^{2-}]) data at the outlet of the Kervidy catchment (Lambert et al., 2014). Three Two main issues are addressed in this paperquestions motivated our work. First,: (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)Second, what new insights can molecular data provide on the sources and transfer mechanisms of DOM during storms? 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? (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

We collected samples from the outlet of the Kervidy-Naizin catchment, a 4.9 km² lowland catchment located in central Brittany in western France (Figure 1). The catchment is a part of a long-term monitoring research program aimed at understanding the impact of agricultural intensification and climate change on hydrologic processes and water quality. Numerous hydrological and biogeochemical studies have already been undertaken at this site (Lambert et al., 2013 and references therein) including investigating the effect of storm events on hydrology (Aubert et al., 2013; Durand and Juan Torres, 1996; Morel et al., 2009) and DOM sources and transfer processes (Lambert et al., 2011, 2013, 2014; Morel et al., 2009).~~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~~. ~~ with ~~The ~~mean annual temperature and precipitation (1993-2011) ~~are ~~of 10.7°C and 814 mm, respectively. Rainfall events rarely exceed 20 mm per day, ~~with ~~and 80% of rainfall events ~~having ~~have an intensity of less than 4 mm per hour. The stream is ephemeral and aften does not flow ~~generally dries up ~~from the end of August to October due to the small volume of water stored in the bedrock. ~~The h~~High-flow ~~stage ~~generally lasts from December to April, with maximum discharges ~~occurring during~~in February and March. Catchment topography is gentle, with hillslope gradients of less than 5% and elevation ranging from 93 to 135 m above sea level. Soil depth ranges from 0.5 to 1.5 m with soils classified as silty loams, specifically Stagnic fluvisols (IUSS Working Group WRB, 2006) developed from alluvial material and Brioverian schist.

The aquifer in the catchment consists of unconsolidated weathered bedrock, underlain by a locally fractured but generally impermeable unmodified bedrock.

~~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.~~

Mis en forme : Éviter veuves et orphelines, Espacement automatique entre les caractères asiatiques et latins, Espacement automatique entre les caractères asiatiques et les chiffres, Taquets de tabulation : Pas à 0,99 cm + 1,98 cm + 2,96 cm + 3,95 cm + 4,94 cm + 5,93 cm + 6,91 cm + 7,9 cm + 8,89 cm + 9,88 cm + 10,86 cm + 11,85 cm

The hydrologic regime is characterized by three distinct periods (Lambert et al., 2013; Molenat et al., 2008). First, in the autumn, the water table reaches the riparian zone but remains below the surface in the upland domain (period A). Second, as precipitation increases through the winter, the water table rises in the upland domain, connecting upland and riparian areas hydrologically and consequently increasing upland groundwater flow towards the riparian zone (period B). Third, in late spring and summer, upland groundwater flow decreases progressively resulting in a gradual air-drying of wetland soils (period C).

The extent of interaction between the organic-rich soils and groundwater fluctuates strongly with hydroclimatic conditions within and between years. During dry hydrologic years, it may be restricted to riparian or wetland areas, which represent less than 5% of the total catchment area. Conversely, during wet hydrological years, water table may be in contact with 20% of the total catchment surface area (Crave and Gascuel-Odoux, 1997).

~~Along hillslopes, the water table depth is typically 0-10 m. 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 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. We separated the storm-flow hydrograph into three successive components: 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 passing through deeper organic-poor soil horizons in of wetlands 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.These patterns supported the hypothesis that a portion of DOM flux during storm is generated by mobilization of pre-existing DOM pools during water table rise.

2.3 Sampling

Soils from the Mercy wetland were sampled using with a hand auger on in 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 eyehand, all samples were freeze-dried and crushed using an agate mortar.

The five studiedFive storm events were sampled between December 04, 2010 and February 19, 2011, during hydrological period B, when wetland soils are most hydrologically connected to stream flow (Figure 2). Their nNumbering corresponds to those used in the previous paper byof storm events follows 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. An automatic gauge station at the outlet of the catchment recorded stream discharge 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 was determined respectively by an increase and a decrease of the stream discharge of > 1 L s^{-1} in over 10 minutes at the stage recorder. Turbidity was monitored using anby a APC-TU Ponselle sensor with a measure every 30 seconds, with averaged every 10 minute averages reordeds. Cumulative rainfallRainfall amounts arewas continuously monitoredrecorded every hour at on an hourly interval basis using a weather station located ca. 300 m away from the catchment outlet. Storm stream water samples (1 L) were collected 0.4 m above the river bed using a refrigerated (4°C) An automatic sampler (Sigma 900 Max) collected 1 L stream water during storms which were stored at 4°C in polypropylene (PP) bottles in a shed at the outlet of the catchment installed in a technical hut located at the outlet of the catchment (Figure 1) and were stored in polypropylene (PP) bottles. 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 flowDuring baseflow conditionsbetween storms, we collected manual samples daily 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 every two weeks in 1 L glass bottles for isotopic and molecular investigationsanalyses. Stream water was filtered at 0.22 µm using cellulose acetate membrane filters previously pre-washed with 500 mL of de-ionized water and rinsed with a 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 and then were frozen and freeze-dried.

2.4 Analytical procedure

Approximately We introduced 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 for 1 minute. The products of this reaction were injected into a gas chromatograph (GC) GC-2010 (Shimadzu, Japan) equipped with a SLB 5MS capillary column in the split mode (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 to maintain an initial temperature of 50°C (held for 2 minutes, then rise) rising to 150°C at 15°C /min^{-1}, and then rise rising from 150°C to 310°C at 3 °C min^{-1} where it stayed for 14 minutes(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, the ionization source at 200°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-

Mis en forme : Exposant

Mis en forme : Exposant

scan mass spectra by comparison with the NIST library and with published data (Nierop et al., 2005; Nierop and Verstraten, 2004). They were classified into three categories: lignin ~~(LIG)~~ and tannin (LIG-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 and ~~(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~~ expressed ~~it~~ as a percentage. Since no internal standards were used, ~~these~~ data ~~must be handled in a qualitative way~~were interpreted qualitatively. Five samples were analyzed in triplicate ~~in order to investigate the experimental repeatability of the analysis~~to quantify reproducibility of the analysis. The relative standard deviation (RSD) calculated for ~~CAR~~ carbohydrate proxy, ~~LIG~~lignin-tannin proxies and the proportion of plant-derived markers was 9, 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~~ Analysis of molecular data

We used two metrics to investigate the distribution of lignin-tannin markers produced by the THM reaction. First, we used the ratio of the sum of coumaric and ferulic acid to the sum of vanillic acid, vanillaldehyde and acetovanillone (C/V ratio). Second, we used the ratio of vanillic acid to vanillaldehyde (Ac/Al (V) ratio).

~~The classification of~~We classified molecular markers generated by THM-GC-MS into microbial and plant-derived markers as described by ~~has been performed according to~~ Jeanneau et al. (2014). Briefly, ~~the analyzed compounds were classified as follow. LIG-TAN~~lignin-tannins were ~~are~~ characteristic of DOM ~~inherited~~ derived from plant~~-derived inputs~~ sources whereas ~~CAR~~ carbohydrates and fatty acids~~FA~~ can ~~be inherited~~come from both plant~~-derived~~ and microbial sources. The proportion of microbial ~~CAR~~ carbohydrates was calculated using an end-member mixing approach (EMMA; Equation 1) based on the deoxyC6/C5 ratio, assuming ~~that it is~~ 0.5 and 2.0 for plant-derived $(deoxyC6/C5_{plant})$ and microbial $(deoxyC6/C5_{mic})$ inputs, respectively (Rumpel and Dignac, 2006):

$$f_{mic}^{CAR} = \left(\frac{deoxyC6}{C5} - \frac{deoxyC6}{C5}_{plant}\right) \div \left(\frac{deoxyC6}{C5}_{mic} - \frac{deoxyC6}{C5}_{plant}\right) \quad (1)$$

~~.~~ 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~~ fatty acids was calculated as the % low molecular weight ~~FA~~ fatty acids (< C19) by excluding C16:0 and C18:0, which ~~that~~ can be ~~inherited~~ derive 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, which are commonly used as bacterial indicators (Frostegård et al., 1993). The ~~proportion~~ fraction of microbial markers (f_{mic}) was calculated as the sum of the proportion of microbial CAR (f_{mic}^{CAR}) multiplied by the proportion of CAR $(\%_{CAR})$ plus the proportion of microbial FA (f_{mic}^{FA}) multiplied by the proportion of FA $(\%_{FA})$ (Equation 2):~~.~~

$$f_{mic} = f_{mic}^{CAR} \times \%_{CAR} + f_{mic}^{FA} \times \%_{FA} \quad (2)$$

From this value, it is possible to calculate the proportion of plant-derived markers among the analyzed compounds (f_{plant}) (Equation 3):

$$f_{mic} + f_{plant} = 100 \quad (3)$$

~~.~~ For ~~this~~ those calculations, ~~it is assumed~~ we assume that ~~the modification of~~ the distribution of ~~CAR~~ carbohydrates and fatty acids was conserved during transport, attributing all differences to the ~~FA would only be due to the~~ relative proportion ~~between these~~ of 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~~ f_{mic} and f_{plant}.~~.~~

3 Results

3.1 Soils and soil solution

Ratios of lignin-tannin composition were poorly associated with spatio-temporal variations of the composition of soil DOM in the Mercy wetland ~~Compared with its companion study~~

(Jeanneau et al., 2014),). However they can differentiate stream DOM between inter-storm and storm conditions (Dalzell et al., 2005; Hernes et al., 2008) leading to the assumption of stream DOM produced by an erosive processcompositional ratio on LIG-TAN markers were calculated for SOM and soil DOM. In SOM from the Mercy wetland, the ratio C/VC/V ratio, 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) ratio, 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 deviationSD) in the surface horizon and from 3.6 to 6.9 (4.7 ± 1.2, mean value ± standard deviationSD) in the deep horizon.

3.2 River DOM in inter-storm conditions

In river samples from November 28, 2010 to March 8, 2011, $f_{plant}$the proportion of plant-derived markers ranged from 34 to 48% of the all analyzed compounds (Figure 3). Among CARcarbohydrates, the ratio deoxyC6/C5 ranged from 1.0 to 1.6 and heptoses have never been detected in those samples. For LIG-TANlignin-tannin, the C/V ratio remained lower than 0.2 with the exception of the sampling of January 7, 2011, which had 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 sampled storm events, the composition of DOM composition showed shifts in isotopes was modified as highlighted by isotopic (Lambert et al., 2014), spectroscopic and molecular markers analyses (Figures 4 and S1, Table 1). The modifications, displayed on Figure 4 for the events 3 and 4, were similar relatively consistent 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, d~~During ~~the five recorded~~ storm events, f_{plant} ~~the proportion of plant-derived makers among the analyzed compounds has~~ increased from an initial value of 31% (events 2, 4 and 6), 49% (event 3) and 14 % (event 5), reaching maximal values of 63% (event 6) to 82 % (event 3) during peak flow (Figure ~~5~~ 4 and Table 1). ~~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, f_{plant} ~~the proportion of plant-derived markers~~ decreased ~~regularly of~~by approximately 10 % (events 2, 4, 5 and 6) or remained stable (event 3) ~~up to~~until the end of the ~~recording~~sample collection.

~~The c~~Composition of ~~CAR~~carbohydrate, ~~recorded~~ as reflected in~~by~~ the deoxyC6/C5 ratio, ~~was~~ also ~~modified~~ varied during storm events, decreasing with discharge from initial values ranging from 1.5 to 2.7, and reaching its ~~. 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 then ~~remained~~ remaining stable ~~up to~~through the end of the ~~recording~~sampling. ~~Among CAR, h~~Heptoses were detected in the first samples at the beginning of ~~the~~ all 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, metrics of the composition of lignin-tannin were~~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~~through the end of the sampling~~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 a few 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~~through the end of the ~~recording~~sampling.

4 Discussion

4.1 Inter-storm stream DOM

The f_{plant} ~~molecular composition~~ of inter-storm stream DOM ~~samples~~ was ~~characterized by values comprised between~~composed of a mix of soil DOM from the organic-rich and ~~the~~

organic-poor horizons (Figure 3). ~~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 f_{plant}~~the proportion of plant-derived markers~~ of ~~clearly differentiated~~ soil DOM differed strongly between~~from~~ organo-mineral and mineral horizons and was fairly stable during the investigated period (Figure 3~~Jeanneau et al., 2014~~), it can be used in an end member mixing approach ~~in order~~ to determine the ~~proportions of~~relative DOM contributions of ~~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~~ to 59 % (37 ± 13%, ~~average~~ mean ± ~~standard error~~SE). This confirms previous findings that near-surface, organic-rich soils in riparian wetland zones are important DOM sources event during non-storm conditions (Strohmeier et al., 2013).~~, 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~~A pulse of microbial DOM at the beginning of storms

At the beginning of the storm events f_{plant}~~the proportion of plant-derived markers in~~ of stream DOM ~~was lower than in stream DOM during antecedent inter-storm conditions~~decreased, with the exception of event 3. The ~~highest~~ higher value recorded for event 3 was ~~probably~~ likely due to an increase in discharge the previous day ~~the 62% increase~~ (from 48 to 78 l s^{-1}~~) of the discharge recorded the day before the event (~~; Table S2), which could have mobilized microbial compounds before the first sampling. ~~The s~~Stream DOM at beginning of storm events was also characterized by higher deoxyC6/C5 ratio than during inter-storm ~~stream DOM~~conditions and by the occurrence of heptoses. Heptoses have been ~~quantified~~ detected in microbial exopolysaccharides (Jiao et al., 2010) and lipopolysaccharides (Sadovskaya et al., 1998). ~~This~~ The export of ~~a~~ microbial ~~pool as denoted~~DOM, evidenced by the ~~high concentrations in~~presence of heptoses and ~~other~~ high f_{mic}~~microbial-derived biomarkers~~ was ~~the most important~~most prevalent for event 5 ~~with~~ where 86% of the analyzed biomarkers ~~being from~~were of microbial origin during the earliest stages of ~~this event~~the storm. This was the first flood after the ~~establishment~~ onset 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~~were a hotspot ~~for~~ of iron ~~biogeochemical~~ reduction ~~processes~~.

This ~~microbial~~ pool of microbial DOM could ~~derived~~come from the flushing of ~~from the~~ microbial lysis products accumulated ~~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~~ sampled storm events ~~were~~ occurred during the hydrological phase B, where ~~characterized by permanent waterlogging of~~ riparian wetland soils are continuously waterlogged, precluding the possibility of lysis from dessication. ~~As a consequence the wetting up phase, denoted A, had already occurred.~~ Moreover, heptoses were not detected ~~nor~~ in soil DOM or~~nor~~ in stream DOM ~~sampled~~ samples ~~in~~ during inter-storm conditions. Alternatively, microbbially-derived DOM ~~Then those compounds~~ could come from ~~be characteristic of~~ microbial biofilms in soil macropores or at the wetland-stream interface ~~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~~are destabilized and transported into the stream by the increase of water velocity at the beginning of storm events (Trulear and Characklis, 1982)~~ at the beginning of storm events~~. Regardless the mechanism, this pulse of microbial DOM

~~The export of this microbial pool~~ at the beginning of storm events could ~~perhaps be responsible~~ account for the ~~extreme value~~compositional shift in stream DOM observed with ~~recorded using~~ high-frequency fluorescence measurements and displayed in the literature. ~~The~~ Indeed soil DOM of the first storm ~~samplings~~ samples ~~are~~ is often ~~associated with~~characterized by high ~~contributions~~ proportions of protein-like chromophores, ~~and~~ low ~~contribution~~ proportions 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

Storm events caused a shift in the compositional ratios of lignin-tannin. 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. These modifications of lignin-tannin transfer 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, stream DOM during storms was characterized by higher C/V and lower Ac/Al (V) ratios than DOM sampled during inter-storm conditions. Although the differences in analytical techniques makes direct data comparison difficult (Wysocki et al., 2008), the compositional ratios show the same pattern during biodegradation with a decrease in the C/V ratio and an increase in 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 consequently been attributed to the mobilization of less-degraded lignins during flood events (Dalzell et al., 2005; Hernes et al., 2008).

In soils, the partitioning of OM between the particulate phase (SOM) and the soil solution (soil DOM) occurs continuously with a high soil/water ratio producing soil DOM characterized by low C/V (around 0.2). During storm events, the values of the C/V ratio in stream DOM increased to values higher than those recorded in the soil solutions. Thus stream DOM during storms cannot only result from the passive transfer of pre-existing soil DOM to the stream. Of all the known DOM sources in the catchment, only SOM has C/V values that could explain the elevated storm DOM values (Figure 5). In the Willow Slough catchment, the concentration in lignin markers is correlated with the concentrationof suspended matter indicating that a portion of DOM during storm events can be inherited from the partitioning of organic compounds between solid and dissolved phases (Hernes et al., 2008). Lignin-tannin and suspended sediment were also correlated in the present study, as seen in the regression between turbidity and C/V ratio (Figure 6). During storm event, erosion carries particles in water. These low soil/water conditions could induce a displacement of the equilibrium between OM in the solid phase and OM in the dissolved phase, which would lead to DOM with a high C/V (higher or equal to 0.8). Soil erosion and the equilibrium between solid (soil particles) and dissolved (river) phases is likely an additional source of DOM transfer from soil to rivers during storm events.

However, the positive relationship between turbidity and C/V ratio occurs primarily during the rising limb of the hydrograph (grey square, $R^2 = 0.68$, p-value < 0.0001, $n = 23$), whereas after peak discharge, turbidity decreased while the C/V ratio remained high leading to a weaker correlation when all the samples are considered (black square, $R^2 = 0.11$, p-value $= 0.008$, $n = 64$). The persistence of high C/V ratios during the falling limb of the hydrograph highlights how other DOM production mechanisms inducing low soil/water conditions are also active during storms in addition to soil erosion. This could come from the exposure of new surfaces within soil structure following destabilization and the disaggregation of soil aggregates during the erosion of macropores walls during storm flow (Wilson et al., 2005). Such a mechanism could modify DOM production in soil profile, causing a shift in DOM composition persisting past peak flow, without adding suspended solid in the stream, the latter particles being physically trapped by the soil matrix.

~~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 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

Divergent behavior in the response of DOM concentration and composition to storms as we observed here has been documented in other catchments in various climates, with modifications to DOM composition typically persisting after concentration has returned to pre-event levels 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., 2015). This suggests that the mechanisms controlling DOM transport during different hydrologic conditions are general. Our work, in combination with previous results suggests a succession of four distinct mechanisms.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. First, between storms, DOM comes from the flushing of wetland soils horizons without major compositional changes of DOM during transport. The water table level would determine the contriution of organo-mineral and mineral soil horizons during this period. 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 Second, at the beginning of a rain events, the increase in water velocity would could induce the destabilization of microbial biofilms, resulting in the export release of a pulse of microbially-derived DOMof a microbial pool. Third, the rise of the water table, 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 in the wetland, causing~~. This would result in~~ an increase of the stream DOC concentration. ~~In~~ At 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~~ magnitude of the effect of this soil surface erosive process on ~~the~~ DOM chemistry would depend on the concentration ~~in~~ of suspended matter and would therefore decrease during the falling limb of the hydrograph. ~~In the same time~~Finally, the increase in water velocity in soils could ~~induce the erosion~~erode ~~of~~ macropore walls in the soil profile, 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~~ return to~~of~~ pre-event conditions ~~is~~ takes longer in the soil profile ~~for in-soil hydraulic gradient~~ than for discharge (Lambert et al., 2014 – Fig 3.b), this could explain why ~~the~~ compositional proxies of DOM~~, including biomarkers and spectroscopic measurements,~~ do not recover ~~their pre-event values with the same kinetic~~as quickly as stream DOC concentrations. High-frequency sampling~~Sampling~~ of soil solutions during and after storm events ~~and up to the recovery of~~until return to pre-event values ~~at the same high frequency than deployed for monitoring stream variations~~ would be necessary to test ~~this~~ these proposed mechanisms~~in-soil erosive process~~.

4.5 Summary and implications

~~The results from this study thus highlight~~We observed striking changes in DOM sources and ~~DOM~~ transfer processes during and between storm ~~and inter-storm conditions~~events. ~~Although the source of~~While DOM during inter-~~flow~~ storm conditions appears to be derived from the passive transfer of DOM from riparian wetland soils, during storm periods the DOM ~~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~~flushing of DOM already ~~occurring~~ present in soils but also to additional sources and production processes that ~~lead to the occurrence~~increase the proportion of less-degraded molecules in the dissolved phase. Based on the current literature, these~~Those~~ findings~~, which~~ appear ~~characteristic~~ to quite general of DOM transfer in lowland catchments worldwide ~~as far as the current literature is concerned,~~and have two important implications.

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

~~The second~~Secondly, our work has implications for ~~concerns the~~ modeling ~~of the export of~~ DOM ~~from~~ export in headwater catchments. In lowland headwater catchments, up to 80% of DOM is transferred during storm events (Raymond and Saiers, 2010), and~~. In~~ many modeling studies~~, it is~~ assume~~d~~ that ~~the~~ DOM transfer ~~process~~ during storm events consists of the flushing of pre-existing soil pools. Since these soil DOM pools~~ latter~~ are calibrated for concentration and composition ~~in term of size (concentration) and nature (composition)~~ using samples taken in inter-storm conditions, these models don't ~~take into~~ account for ~~additional~~alternative DOM producing processes ~~which could occur during the water transfer process~~activated during storms, such as the surface and subsurface erosion processes proposed~~suggested~~ here. ~~This lack~~ This oversight could explain why modeling studies succeed in reproducing inter-storm DOM concentrations, but not storm flow DOM ~~contents~~ dynamics (Birkel et al., 2014). Increased interaction~~s~~ between geochemists and modelers could accelerate the conceptualization of temporally and spatially variant DOM production mechanisms and~~should help in~~ ~~improving~~ improve modeling of 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/). The authors thank Dr B.W. Abbott who copy-edited the manuscript for the use of English.

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Table 1. Changes in discharge, DOC concentration and metrics of DOM composition~~al proxies~~ during ~~the~~ storm events. ~~The v~~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
~~Plant-derived markers~~ f_{plant} (%)	beg. [a]	31	49	31	14	31
	max. [b]	67	78	70	71	59
	end	57	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.

1

Tableau mis en forme

Mis en forme : Police :Italique

Mis en forme : Police :Italique, Indice

Mis en forme : Police :Italique

Figure captions

Figure 1. Location mMap 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 cCoordinates of the outlet are 48.0057 North, 2.8313 East (decimal degrees).

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

Figure 3. Temporal changeVariation of the molecular composition of inter-storm stream DOM in stream (: compositional ratios included C/V (white triangles – LIG-TAN), deoxyC6/C5 (black square – CAR) and the proportion of f_{plant}) (black triangles). The grey area is delimited by the f_{plant} in soil DOM from the organo-mineral and mineral horizons.

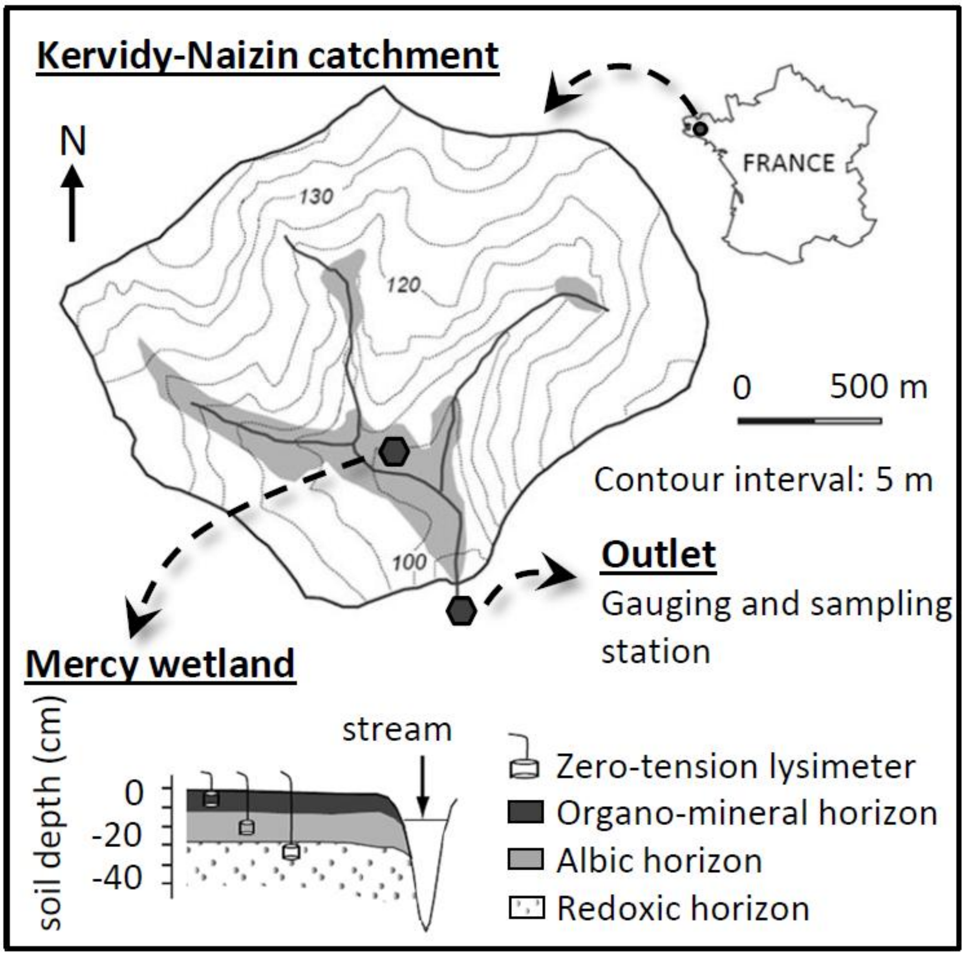
Figure 4. Temporal change in flow and DOC concentration and composition during storm events 3 and 4. The Various units are givenindicated in on the axesaxis labels. The uncertainties for deoxyC6/C5, f_{plant}, C/V and Ac/Al (V) are the mean RSD calculated for five samples analyzed in triplicate.

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

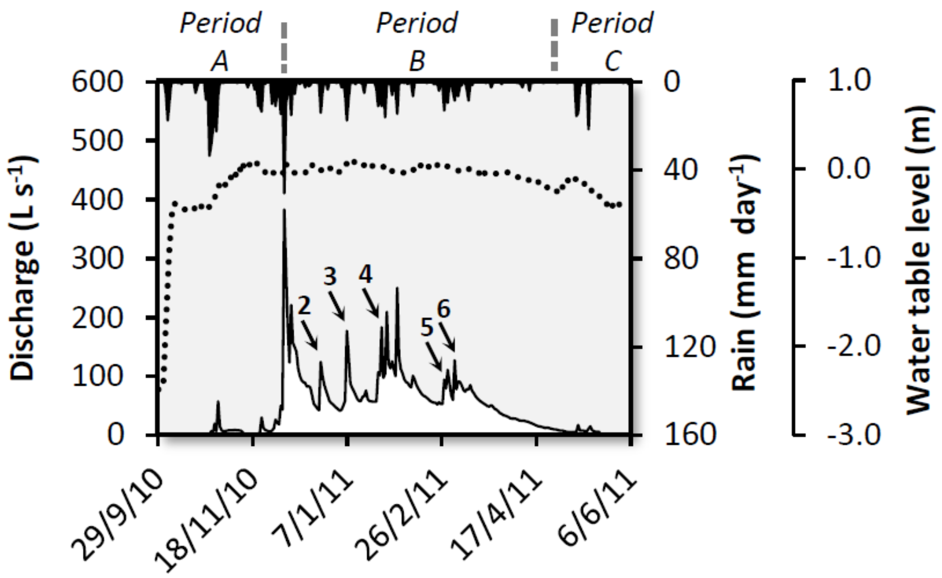
Figure 65. Time diagram comparing the vVariation of the C/V ratio (lignin proxy) in SOM, soil DOM and DOM from organo-mineral and mineral horizons, and the variation of the C/V ratio in riverstream DOM sampled during inter-storm and storm conditions.

Figure 76. Difference of the cCorrelation 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).

Figure 1


Kervidy-Naizin catchment
N
FRANCE
130
120
100
0
500 m
Contour interval: 5 m
Outlet
Gauging and sampling station
Mercy wetland
soil depth (cm)
0
-20
-40
stream
Zero-tension lysimeter
Organo-mineral horizon
Albic horizon
Redoxic horizon

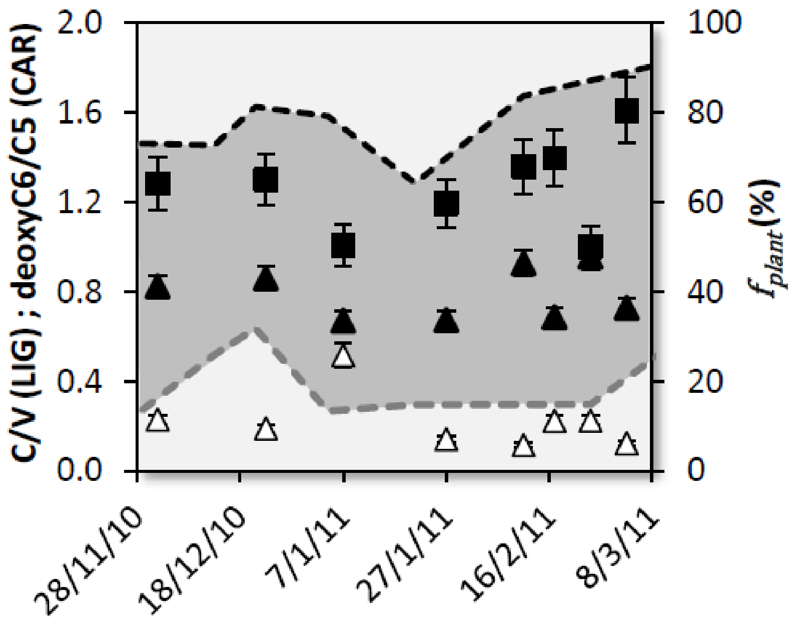
1 Figure 2


Period
A
Period
B
Period
C
Discharge (L s-1)
600
500
400
300
200
100
0
Rain (mm day-1)
0
40
80
120
160
Water table level (m)
1.0
0.0
-1.0
-2.0
-3.0
2
3
4
5
6
29/9/10
18/11/10
7/1/11
26/2/11
17/4/11
6/6/11

2

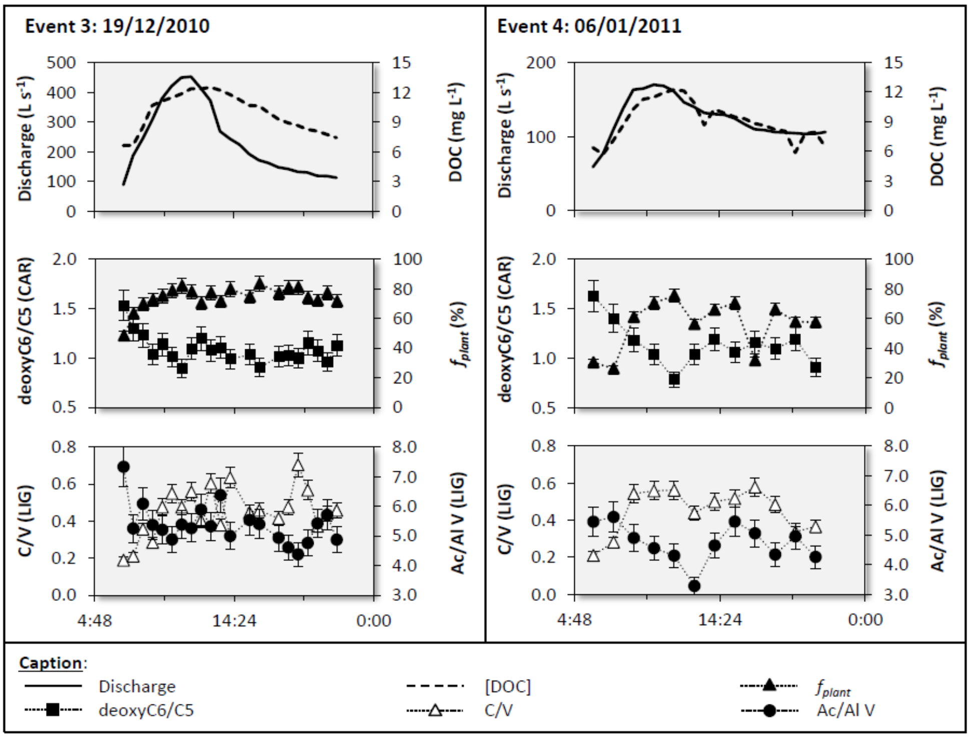
3

Figure 3



Caption:
Inter-storm stream DOM
■ deoxyC6/C5
△ C/V
▲ f_{plant}
Soil DOM: f_{plant}
– – – Organo-mineral horizon
– – – Mineral horizon

Figure 4



Event 3: 19/12/2010
Event 4: 06/01/2011
Discharge (L s-1)
DOC (mg L-1)
deoxyC6/C5 (CAR)
fplant (%)
C/V (LIG)
Ac/Al V (LIG)
4:48
14:24
0:00
Caption:
Discharge
[DOC]
fplant
deoxyC6/C5
C/V
Ac/Al V

Figure ~~6~~5

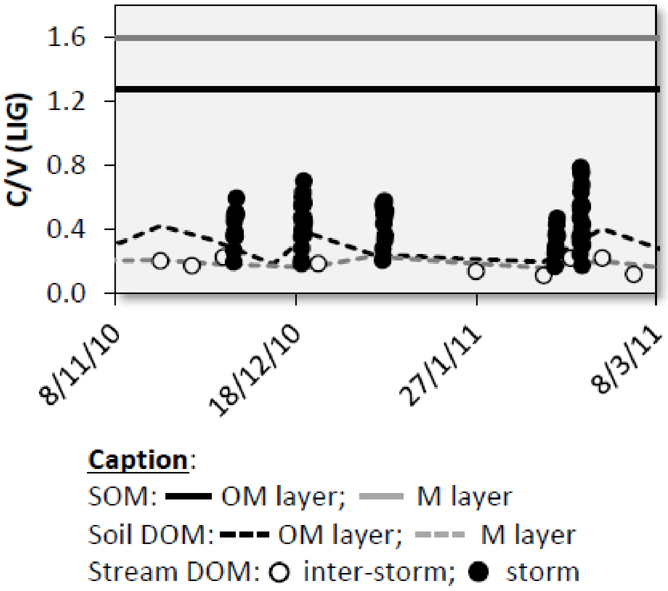
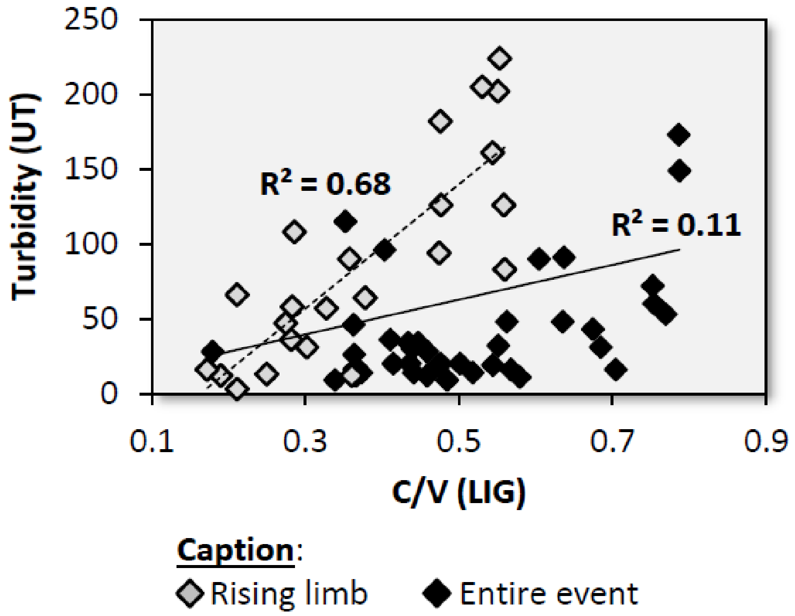

1.6
1.2
0.8
0.4
0.0
C/V (LIG)
8/11/10
18/12/10
27/1/11
8/3/11
Caption:
SOM: OM layer; M layer
Soil DOM: OM layer; M layer
Stream DOM: inter-storm; storm

Figure ~~7~~6


250
200
150
100
50
0
Turbidity (UT)
0.1
0.3
0.5
0.7
0.9
C/V (LIG)
R² = 0.68
R² = 0.11
Caption:
Rising limb
Entire event