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# 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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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 researches.

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. 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.

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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 lessdegraded 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.

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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 5 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 terrestriallyderived OM to oceans (Gough et al., 1993) and their investigation has led to the partitioning process invoked for lignin compounds during storm events (Dalzell et al., 2005; Hernes et al., 2008). Analysis of CAR can differentiate between plant-derived and microbial inputs (Rumpel and Dignac, 2006) since the distribution of non-cellulosic monosaccharides is dominated by pentose (C5) for plant-derived inputs and by hexose (C6) and deoxyhexose (deoxyC6) for microbial inputs. Similar to CAR, the distribution of FA differs in plant-derived and microbial inputs (Cranwell, 1974; Lucas García et al., 2001; Matsuda and Koyama, 1977). The combination of those markers allows the investigation of the balance between microbial and plant-derived markers differentiating between soil DOM from organic-rich and organic-poor horizons in a wetland submitted to fluctuating water-table level and being correlated with the specific UV absorbance (SUVA) at 254 nm (Jeanneau et al., 2014). By assuming that protein-like and humiclike 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

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2010–2011 on (i) the temporal variations of the distribution of biomarkers, including lignin phenols, in soil solutions 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, CI<sup>-</sup>, 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  $\delta^{13}$ 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 km<sup>2</sup> lowland catchment located in central Brittany, western France (Fig. 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 day<sup>-1</sup>, 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-

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

The elevation ranges from 93 to 135 m a.s.l., with hillslope gradients of less than 5%. The soils are silty loams, with depths ranging from 0.5 to 1.5 m, and are classified as Stagnic fluvisols (IUSS Working Group WRB, 2006) developed from alluvial material and Brioverian schists. The aquifer in the Kervidy-Naizin catchment consists mainly of the unconsolidated weathered bedrock, the deeper fresh bedrock, though locally fractured, being generally considered impermeable. In this aguifer, the groundwater flows from upland down to bottom land all the year round and feds 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).

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#### 2.2.1 Molecular data on SOM and soil DOM

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

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

#### 2.2.2 Previous data on river samples

The composition of DOM in the river during the five studied storm events was previously investigated using  $\delta^{13}$ 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

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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

#### 2.3 Sampling

DOM pools via the rise of the water table.

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, all samples were freeze-dried and crushed using an agate mortar.

The five studied storm events were sampled between 4 December 2010 and 19 February 2011, during hydrological period B (Fig. 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 4 December, 19 December, 6 January, 13 February and 19 February, 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<sup>-1</sup> in 10 min at the stage recorder. Stream water samples were collected using a refrigerated (4 °C) automatic sampler (Sigma 900 Max) installed in a technical hut located at the outlet of the catchment (Fig. 1). Sampling frequency during the monitored storm events varied from one sample every 30 min to one sample every hour, depending on the hydrograph variations. Base-flow waters between each storm event were collected manually on a daily basis (5 p.m.) for DOC monitoring and fortnightly for isotopic and molecular investigations. Turbidity was monitored using an APC-TU Ponselle sensor with a measure every 30 s averaged every 10 min. Rainfall amounts

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are continuously monitored on an hourly interval basis using a weather station located ca. 300 m away from the catchment outlet.

#### **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<sup>-1</sup>, then rising from 150°C to 310°C (held for 14 min) at 3°C min<sup>-1</sup>. Helium was used as the carrier gas, with a flow rate of 1.0 mLmin<sup>-1</sup>. 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  $^{\circ}$ C. The list of analyzed compounds and m/zratios used for their integration are given in Table S1 in the Supplement. 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

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

#### 2.5 Treatment of molecular data

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

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#### 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 29 November 2010 to 11 March 2011, the C/V ratio ranged from 0.2 to 0.4 in the surface horizon and remained stable at 0.2 in the deep horizon. The Ac/Al (V) ratio ranged from 7.1 to 12.1 (9.1 $\pm$ 1.7, mean value  $\pm$  SD) in the surface horizon and from 3.6 to 6.9 (4.7 $\pm$ 1.2, mean value  $\pm$  SD) in the deep horizon.

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

In river samples from 28 November 2010 to 8 March 2011, the proportion of plant-derived markers ranged from 34 to 48% of the analyzed compounds (Fig. 3). Among CAR, the ratio deoxyC6/C5 ranged from 1.0 to 1.6 and heptoses have never been detected in those samples. For LIG-TAN, the C/V ratio remained lower than 0.2 with the exception of the sampling of 7 January 2011 with a value of 0.5. The Ac/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 (Figs. 4 and S1, Table 1). The modifications were similar for the five storm events. At the beginning of storm events, the first sample was characterized by low values of SUVA at 254 nm comprised between 2.0 and 2.8, depending of the storm

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

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

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

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#### 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 29 November 2010 to 11 March 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. 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

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

#### 4.3 Soil erosion as a DOM producer

During the five monitored storm events, the compositional ratios calculated on LIG were modified. The C/V ratio increased from 0.2 to 0.8 and the Ac/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). 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).

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

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., <sub>5</sub> 2010; Knorr, 2013; Singh et al., 2014). It is then probable that the succession of DOM producing mechanisms leading to this pattern can be generalized. The combination of previous and present results could be used to decompose this succession into four distinct mechanisms. In inter-storm conditions, DOM would be derived from the passive (without compositional changes of the DOM during transport) flushing of organic-rich and organic-poor wetland soil horizons. The contribution of each soil horizon would be controlled by the water table level. During a rain event, the increase in water velocity would induce the destabilization of microbial biofilms resulting in the export of a microbial pool. This first stage would be followed by the rise of the water table, which in association with the decrease of lateral hydraulic conductivity with depth (Seibert et al., 2009) would induce an increase of the proportion of the water flowing through the upper organic-rich wetland surface horizon. This would result in an increase of the stream DOC concentration. In the same time, erosion of soils and river banks would induce an increase of the turbidity leading to a partition of organic matter between particles and dissolved phase. The contribution of this soil surface erosive process on the DOM chemistry would depend on the concentration in suspended matter and would therefore decrease during the falling limb of the hydrograph. In the same time, the increase in water velocity in soils could induce the erosion of macropore walls, leading to an in-soil partitioning between soil microparticles and dissolved phase. The contribution of this in-soil erosive process would be linked to the magnitude of the hydraulic gradient following the rise of water table. Since the recovery of pre-event conditions is longer for in-soil hydraulic gradient than for discharge (Lambert et al., 2014 - Fig. 3b), this could explain why the compositional proxies, including biomarkers and spectroscopic measurements, do not recover their pre-event values with the same

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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. 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

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

The Supplement related to this article is available online at doi:10.5194/bqd-12-3349-2015-supplement.

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

Event Date		2 4 Dec 2010	3 19 Dec 2010	4 6 Jan 2011	5 13 Feb 2011	6 19 Feb 2011
Discharge (Ls <sup>-1</sup> )	beg.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
$\begin{array}{c} DOC \\ (mg L^{-1}) \end{array}$	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 (Lmg <sup>-1</sup> cm <sup>-1</sup> )	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
$\delta^{13}C^{c}$	beg. <sup>a</sup>	-28.9	-28.9	-28.6	-28.7	-28.8
(‰)	max.b	-28.8	-28.5	-28.8	-28.6	-28.8
	end	-27.2	-27.0	-28.1	-28.5	-28.2
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. <sup>a</sup>	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

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

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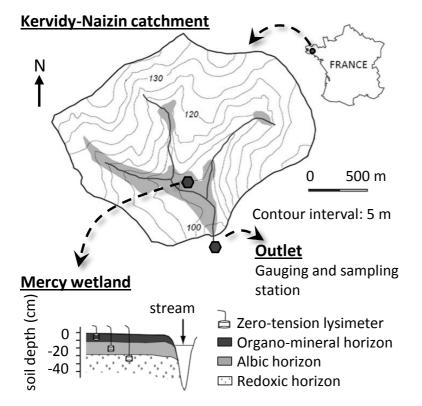
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<sup>&</sup>lt;sup>b</sup> Value recorded at the peak discharge.

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



**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.

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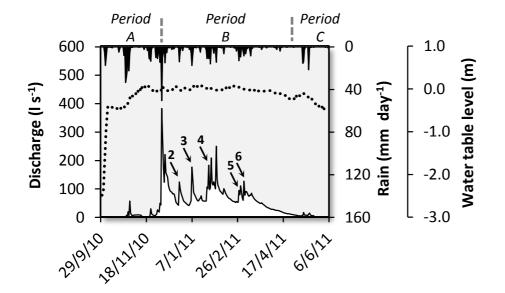


Figure 2. Discharge (white area), daily rainfall (black area) and water table level in the wetland domain (PK1) (dashed line) during the hydrologic year 2010-2011. Monitored storm events are indicated by numbers and arrows.

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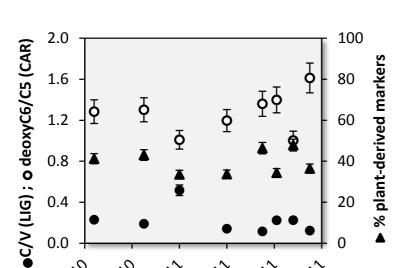
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**Figure 3.** Temporal change of the molecular composition of inter-storm stream DOM: compositional ratios included C/V (black circles – LIG-TAN), deoxyC6/C5 (white circles – CAR) and the proportion of plant-derived markers among the analyzed compounds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

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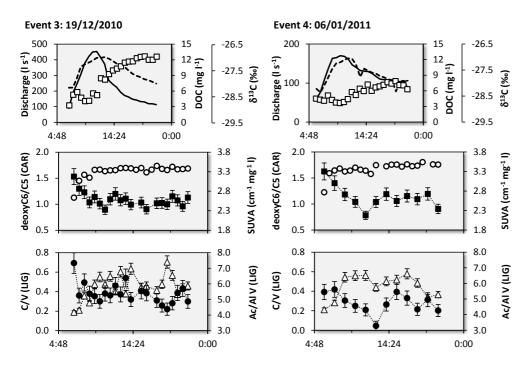


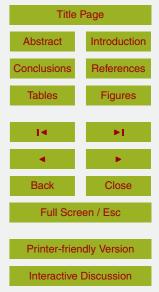
Figure 4. Temporal change in flow and DOM concentration and composition during storm events 3 and 4. Black solid line, dashed line, white squares, white circles, black squares, black circles and white triangles represent discharge, DOC concentration,  $\delta^{13}$ C, SUVA 254, deoxyC6/C5, Ac/Al (V) 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.

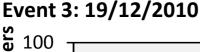
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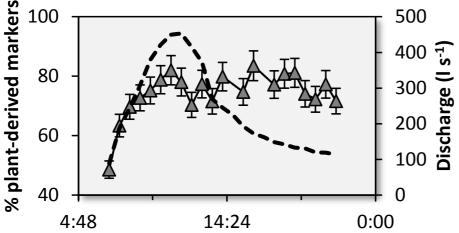
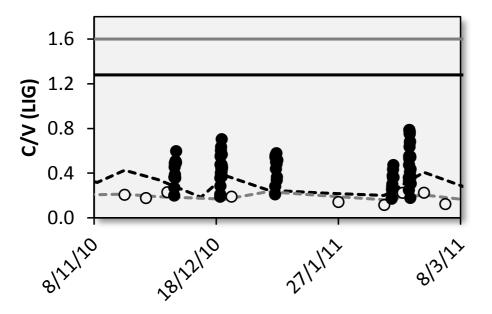


Figure 5. Temporal change in flow (dashed line) and proportion of plant-derived markers (grey triangles) expressed as the percentage of analyzed compounds during storm event 3. The uncertainties are the mean RSD calculated for five samples analyzed in triplicate.



**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.

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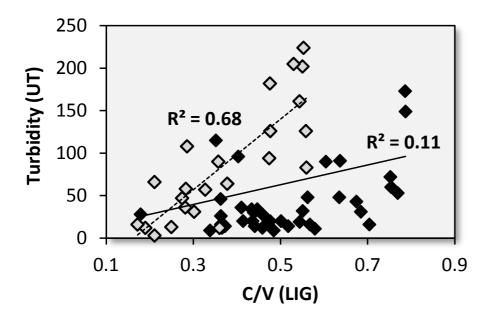


Figure 7. Difference of the correlation between turbidity and the C/V ratio (lignin proxy) during the rising limbs (grey diamonds – p value < 0.0001) and during entire storm events (black diamonds – p value = 0.008).

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