

## ***Interactive comment on “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” by L. Jeanneau et al.***

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Thank you for your contribution to improve this paper and for your remarks. The editing remarks will be considered in preparing the next version of the manuscript and I provide in the following a point by point response with your remarks indicated into brackets.

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[Simpler explanations should be considered to describe observed trends, for example: partitioning from particulate phase could continue in soils once turbidity has decreased without needing to invoke macropore wall erosion.]

The partitioning from particulate phase occurs continuously in soils but with a high ratio soil/water creating a specific DOM with a low C/V (around 0.2). During storm event, erosion carries particles in water. These low soil/water conditions induce a displacement of the equilibrium between OM in the solid phase and OM in the dissolved phase leading 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 hypothetical and at this stage need further investigation to be supported.

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

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

[Justification is needed for end-member definitions in the EMMA. Specifically, attributing FA <C19 to microbial (omitting C16:0 and C18:0) and >C19 to vascular plants is an oversimplification and will likely bias results. Heterotrophs and phytoplankton have

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

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

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

The thermally assisted hydrolysis and methylation (THM) reaction using TMAH allows for the analysis of free and terminal monosaccharides and the differentiation of aldohexoses (C6), 6-deoxyaldohexoses (deoxyC6) and aldopentoses (C5) (Estournel-Pelardy et al., 2011). The distribution of CAR in microorganisms is dominated by C6 and deoxyC6, while that of non-cellulosic CAR in plants is dominated by C5. As a

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consequence, deoxyC6/C5 (R1) and C6/C5 (R2) ratios can be used to differentiate between DOM from plant-derived sources (R1 and R2 < 0.5) and DOM from microbial (R1 and R2 > 2.0) sources (Guggenberger and Zech, 1994; Rumpel and Dignac, 2006). However, these limits of 0.5 and 2 were calculated from data obtained using an analytical method involving the hydrolysis of non-cellulosic carbohydrates. The THM method results in the detection of terminal glucose, an aldohexose included in the C6 signal, in cellulose chains (Estournel-Pelardy et al., 2011), leading to an artificial increase in the proportion of C6. Consequently, R2 cannot be used here to estimate the proportion of plant-derived and microbial CAR. Estournel-Pelardy et al., *Journal of Analytical and Applied Pyrolysis*, 92, 401-406, 2011 Guggenberger and Zech, *Soil Biology and Biochemistry*, 26, 19-27, 1994 Rumpel and Dignac, *Soil Biology and Biochemistry*, 38, 1478-1481, 2006

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

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

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in the manuscript and the figure 5 will be changed in order to avoid any confusion.

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