Biogeosciences
Discussions

Interactive comment on "New molecular evidence for surface and sub-surface soil erosion controls on the composition of stream DOM during storm events" *by* Marie Denis et al.

Marie Denis et al.

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Thank you for your suggestions and comments to improve this manuscript. Your remarks will be considered to the next version of the manuscript. You will find below a point by point response to your comments reported into square brackets.

[Based on experiments that we have done in our lab, I agree that simple desorption of OM from soils is not a strong enough source to account for increased DOM concentrations in streams, and so it is a bit unclear as to how the authors think that the conceptual model in Fig. 8 is fundamentally different from desorption of OM from soils in terms of generating enough to account for the increase? Clearly, there is a mass balance issue

that needs to be factored in – it's not just about matching chemical composition, there has to be enough DOM from the various sources as well. At the risk of appearing self-serving, I would encourage the authors to have a look at the recently published Hernes et al. (2017) in Frontiers in Earth Sciences, which also focuses on rain events, also has subsurface flow/sampling, also involves lignin chemistry, and argues that simple litter/duff leaching (or leaching during stemflow and canopy throughfall) can produce all the DOM needed to account for increases in stream DOM, and that perhaps the main role of the soils is simply to modify and reduce the pulse of DOM flowing through to the streams. Granted, there are significant differences between the two systems, and the soil desorption experiments demonstrate that it does not have to be mechanistically either/or, but at a minimum, the authors need to address the conflict between Fig. 8 and the soil desorption results].

The analogical modelling of the in-stream process simulated by shaking 1g of soil with 1 L of water was conducted in order to assess the potential contribution of the so called "in-stream process" which was proposed to explain the changes of molecular composition in stream water. This analogical modelling is fundamentally different from the conceptual model proposed in Figure 8 as it takes place in soil macroporosity. These two processes are fundamentally different because of the difference in the soil/water ratio observed in these two location of the soil/stream continuum. The soil/water ratio observed in saturated soils is 1/1.5 when the soil/water ratio used in the in-stream process simulation is 1/1000. This difference in soil/water ratio will therefore impact the solubilization of organic molecules. Following the results of in-stream process simulation we concluded that this mechanism could not explain the changes of molecular composition and the increase of DOC concentration during storm events. However, the determination of relative sources contribution demonstrated that combination of surface runoff (erosion of soil surface and litter leaching) and subsurface erosion (Fig. 8) can explain the increase of DOC observed in the river during storm events.

[Regarding the sourcing, the way in which the pyrolysis target compounds have been

normalized to the total response of all target compounds introduces some fundamental problems in the data analysis in that any change in one component percentage necessitates the opposite change in at least one other component. It's a zero sum game, and not always straightforward on how to interpret those changes – does an increase in the %LIG mean that more lignin was produced, or does it simply mean that carbohydrates or fatty acids were degraded or produced less? There are at least two interpretations for every change in a single component, and you have to be extremely careful to sort out which is which. Rather than interpreting the percentages straight up, it might be beneficial to multiply the percentages times the DOM concentrations and makes some plots of those concentrations with time to better evaluate what is increasing vs. what might be decreasing or degrading. (Of course, there is also an inherent assumption that the yield efficiency of your target compounds is constant across sample types and concentrations.)]

I fully agree about the precautions which must be taken with this type of results, especially when they are used to discuss about biogeochemical functioning. During the discussion of our manuscript, all these results of %LIG, %CAR and %FA are not interpreted in terms of biogeochemical processes. These results are only used to present the differences of DOM composition during the two hydrological conditions (storm event / base flow) and between the different compartments (soil solutions / stream water / surface runoff). The different way you proposed to process the data were used for the interpretation of datas presented in the first submission of Jeanneau et al. (2014) and was highly criticized by the reviewers. For these reasons we chose not to go further for in the interpretation of the data, and to present the data as percentages.

[Again, the conceptual problem that I wrestled with in Hernes et al. was the capacity of the soils to modify chemical composition during lateral flow through the soils. The mass balance says that there has to be significant sorption or degradation (or both) happening, and that almost any of the plant litters/duffs was producing enough lignin to account for streamwater chemistry.]

The three storm events we followed in this study occurred when soils are completely saturated, even during base-flow period. Therefore, water circulation in these soils is only horizontal circulation, so we cannot hypothesize vertical circulation of litter leachate to explain the modification of soil solution molecular composition. This precision may be added in the discussion section. However, in the riparian area of the transect, litter leachate will contribute to the increase of DOC concentration in the stream as surface runoff is one of the three sources considered in this study.

[There may be some interpretive value in considering the DOC hysteresis of the flow events: For any given discharge, was the DOC higher on the rising or the falling limb? If it's higher on the falling limb, this could indicate a lag time in whatever processes are at play in mobilizing new DOM from the litters or soils. If it's higher on the rising limb, this suggests that the source of DOM was already mobilized and perched in the soils, waiting for a flush.]

Lambert et al. (2014) and Morel et al. (2009) reported 10 different storm events sampled on the Kervidy-Naizin catchment for which the DOC concentrations in stream waters were higher during the falling limb of the hydrograph. Moreover, 6 storm events which were not added to this study were sampled on the Kervidy-Naizin catchment. 5 of them are also characterized by higher DOC concentrations during the falling limb of the hydrograph. For these 6 storm events, temporal evolution of DOC and discharge are available in the document in supplement. The first event of this study was only sampled during the rising limb of the hydrograph. Consequently it is not possible to see a hysteresis. The second event is characterized by a different evolution with higher DOC concentrations in the rising limb of the hydrograph. The third event is characterized by a small hysteresis where higher DOC concentrations were observed on the falling limb of the hydrograph. For these 3 storm events, temporal evolution of DOC and discharge are available in the document in supplement. The DOC exported at the outlet during storm events came from the surface runoff and the soil solution present in soil macroporosity. Considering the size of the Kervidy-Naizin catchment (4.9 km^2), a storm event

characterized by intense rains at the beginning of the event could be responsible of the rapid generation of surface runoff, especially during winter when soils in the riparian area are still saturated. These conditions could induce higher concentrations on the rising limb of the hydrograph. For smaller storm events with lower rain amounts, soil solutions are responsible for a larger part of DOC increase. As transfer of soil solutions to river is a process which occurred more slowly than surface runoff generation, this could be in favor of the observation of higher DOC concentrations in the falling limb of the hydrograph. Consequently, depending of the storm event, the proportion of these two sources changes and could explain why some events are characterized by higher DOC concentrations in the rising limb of the hydrograph while some events are characterized by higher DOC concentrations in the falling limb of the hydrograph.

[Figures 4 and 5 are not all that helpful, in my opinion, as there is too much going on and they are hard to interpret. I don't know what the random circles are – data points that are being arbitrarily excluded from the statistics? If so, why? It's confusing how the Event 2 %LIG in Fig. 4 can have the "a" label in common with the soil – they barely look like they overlap. Baseflow %LIG surely looks like it should overlap with "e", especially if the extra data points are factored in. There are numerous examples of confusing similarities or differences within these two figures. Also conspicuously missing from these plots are any indication of the number of samples/datapoints per box. Statistics are merely an interpretive tool, but they can also be very misleading at low n, or when outliers are being excluded, or countless other factors when running regressions, so you want to include the information necessary so that we can evaluate whether the statistics are meaningful or meaningless.]

In the box-plot representation used in Fig. 4 and 5, the white circles represent the values considered as outliers by the statistical software. However, these values were not excluded from the datasets to perform the statistical tests. The statistical test used to determine the statistical differences is the Dunn's test, a non-parametric test. We chose to use this test because some of the series of data do not follow a normal

distribution. The number of samples per box will be added to the Figures 4 and 5. For soil solutions, there are 10, 9, 10 and 13 samples during events 1, 2, 3 and base-flow respectively. For stream water, there are 14, 25, 18 and 8 samples during events 1, 2, 3 and base-flow respectively. Surface runoff is composed of 5 samples and soil of 3 samples. As we used a non-parametric test for datasets with variable number of samples, this could explain some apparent confusions you listed.

[The delta-H term and water table levels were confusing to me. Delta-H is supposedly the difference between the two piezometers, and yet when I look at Fig. 2, for example, the difference between the water tables seems to be 0.1 to 0.5 m most of the time. Yet delta-H is presented as 1.0 to >1.5 m. I am obviously missing something. What is the 0 reference point for the water table in Fig. 2?]

In Fig. 2, water table level is measured by taking the 0 reference point as soil surface. Consequently, the water table level does not take into account the altitude (above sea level) of the soil surface for the two piezometers implemented along the soil profile. In the contrary, the ΔH value take into account the difference of altitude between the wetland piezometer and the mid-slope piezometer. Therefore the 0 reference point to calculate the ΔH is the see level. The 0 reference for the water table level and ΔH can be specified in the material and method section (Page 3 Line 31) and "water table level" can be changed into "water table depth" in order to clarify this point.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2017-252/bg-2017-252-AC1-supplement.pdf