

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.

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Linking catchment sources and processes to streamwater chemistry is essential to realizing the full potential of streams and rivers as monitors for changing terrestrial environments. I have spent a lot of time on this topic, and it is not an easy nut to crack. It is great to see others working on this as well, as we need a critical mass of scientists looking at it from different angles. This paper focuses on sources of increased DOM in streams during storm events and presents a conceptual model for mobilization of colloids and particles within the soils and subsequent release of DOM. Based on experiments that we have done in our lab, I agree that simple desorption of OM from

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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 selfserving, 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.

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.) 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.

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.

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.

It is critical to keep in mind phase changes and the potential for fractionation when comparing solids to dissolved. The trends in Opsahl and Benner (1995), for example, may not all be relevant to the dissolved phase.

The delta-H term and water table levels were confusing to me. Delta-H is supposedly

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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?

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