

## ***Interactive comment on “Biotic controls on solute distribution and transport in headwater catchments” by E. M. Herndon et al.***

### **Anonymous Referee #2**

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The paper “Biotic controls on solute distribution and transport in headwater catchment” by Herndon et al fits well to the HESSD journal context. Its strength is in multi-disciplinarily as the paper is written on the borderline between hydrology and soil chemistry. In this review I assume that the main audience for the paper is from the field of hydrology. From this respect I would rather see it as a skillful attempt to learn more about the flow pathways and runoff contributing areas for 3 catchments with similar lithology but different topographical settings and placed in different climate and vegetation zones. It uses the established empirical (and unique for each catchment) relationships between the soil pore water source and chemistry in vertically and horizontally heterogeneous landscape (mixing model). The study also shows that SOM distribution within the catchment, its placement and connectivity to streams has a strong predictive

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power for DOC and other solutes. The approach is quite novel and deserve publication and the only major comment I have to the presentation of hydrology is that the catchments have been well studied before, as authors says, e.g. with an isotopes technique. So I would advise to extent the comparison between the authors' conclusions about the flow path with what previously have been found using other techniques. The authors also pursued another purpose – to develop key conceptual component for predictive model of solute transport in headwater catchment. If that has to be evaluated I feel little confidence in my own expertise and would rather advice to send the paper for an additional reviewer whose major would be in pure soil chemistry. I could advice Ed Tipping's group at the Centre for Ecology & Hydrology in Lancaster Environment Centre, but certainly there many others. My concern here is that the key for understanding of why particular solute behaves differently in different geographical settings has to be based on detailed analysis of the cation binding and dissociation by humic and fulvic acids. Few aspects can be critical: 1) Cation exchange sites are saturated with different exchangeable cations in podzol and peat soils 2) The degree of saturation by exchangeable cations differs between the studied soils and is indeed a factor of vegetation and soil water regime (P-E). It also varies largely vertically being maximum in illuvial horizons. 3) The ability of mineral soil particles to adsorb organic molecules depends on the solution Fe, Al, Ca and Mg concentration. On the other side complexes can be formed between the fulvic acids and metals. So it is not straight forward to see causality (DOC vs. metals). 4) The lateral transport trough inhomogeneous soil is will modify the chemistry that simple source mixing model would propose

In p. 228 authors provide the cation exchange capacity for different soils, but the statement “degree of chemostatis was inversely related to the elements' relative strength of adsorption to cation exchange sites” seems critical for the process understanding, and yet no figure or table support it. I would also think it is fruitful to follow this consideration while explaining why one element is chemostatic in one setting and is not in another.

Minor comments:

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I would advice writing the solutes with a charge because they all are ions, e.g.  $\text{Ca}^{2+}$  not just Ca

Abstract: L7. I would suggest "by patterns of vegetation and SOM" I would also explain already here that there are 2 catchments within Plynlimon catchment: one is peatland (heath) dominated and another is forest dominated

P.217 Please provide a soil type for the Shale Hills watershed.

P.228 L.14 "on mineral surfaces". Also on fulvic and humic acids surfaces and organo-mineral complexes.

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