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Interactive comment on "New insights from the use of carbon isotopes as tracers of DOC sources and DOC transport processes in headwater catchments" *by* T. Lambert et al.

Anonymous Referee #1

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This study explored the transfer pathways of DOC in the Kervidy-Naizin catchment over the course of six successive storms. The authors observe a positive correlation between DOC concentrations and river discharge during every sampled storm and a negative correlation between nitrate concentrations and discharge. The isotopic composition of DOC also varies with discharge, showing somewhat variable patterns between each storm. Through the use of several endmember mixing model approaches (e.g. DOC vs. NO3 vs SO4, and 13C-DOC) the authors demonstrate that the majority of the stream DOC flux in this catchment flows through the most surficial soil layers and the contribution of wetland soils to DOC export progressively increases during periods of high flow relative to upland soils. This study demonstrates the utility of carbon iso-

topes in determining sources and transfer pathways of watershed DOC and highlights the importance of high-resolution sampling schemes to capture the highly variable nature of river DOC. In general this is a nice study with a lot of background information given, but could arguably be made slightly more concise.

Comments:

Results section

3.2 concentration data Line 5-9: Please clarify this statement. Did the high frequency samples have higher concentrations due to timing of collections (e.g. the daily sample was collected during times of lower flow) or were the samples treated differently (there are no details given on daily sample collections in the methods section). Were samples treated the same in terms of collection, filtration and preservation? If you compare the concentration of the daily sample to a high frequency sample taken around the same time are the values comparable? Also the statement that high frequency sampling is necessary to capture DOC dynamics belongs in the discussion section rather than here results...although true, this statement is repeated too much throughout the text.

Lines 10-19: It is interesting that the authors observe an inverse relationship between NO3 and discharge, as many studies have observed the opposite. Again there are brief explanations of the data here in the results section that should be moved to the discussion section. The results section should be used for reporting the data of this study; references to literature and discussion of explanations should be in the discussion section. Further, aside from the several sentences in the results section, there is no further discussion of the NO3/SO4 data (other than in the context of EMMA). Understandably DOC is the main focus of the study, but if the NO3/SO4 concentrations are to be included in their own figure (other than the EMMA figure, which receives adequate discussion) it needs to be properly discussed and also put in the context of the many studies showing the opposite relationship between NO3 and discharge. Some references that may be worth including in your discussion for example:

Sigleo AC, Frick WE (2003) Seasonal variations in river flow and nutrient concentrations in a Northwestern USA watershed. In: Proceedings of the first interagency on research in the watersheds, USDA, Benson, Arizona, pp 370–376

Ward, N.D.; Keil, R.G.; Richey, J.E. (2012). Temporal variation in river nutrient and dissolved lignin phenol concentrations and the impact of storm events on nutrient loading to Hood Canal, Washington, USA. Biogeochemistry. doi: 10.1007/s10533-012-9700-9

Peterson BJ, Wolheim WM, Mulholland PJ, Webster JR, Meyer JL, Tank JL, MartÄś0 E, Bowden WB, Valett HM, Hershey E, McDowell WH, Dodds WK, Hamilton SK, Gregory SV, Morrall DD (2001) Control of nitrogen export from watersheds by headwater streams. Science 292:86–90

McClain ME, Elsenbeer H (2001) Terrestrial inputs to Amazon streams and internal biogeochemical processing. In: McClain ME, Victoria RL, Richey JE (eds) The biogeochemistry of the Amazon basin. Oxford University Press, New York, pp 185–208

Buffam I, Galloway JN, Blum LK, McGlathery KJ (2001) A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appala- chian stream. Biogeochemistry 53:269–306

Lines 20-25: Again, please discuss/explain the observations in the discussion section and describe the data in the results section.

Discussion.

4.2: Please include additional justification for why 13C data from storm event No 4 should be used as mixing model end members

The authors note that a 0.1 per mil change in 13C-DOC endmembers results in a large change in the calculated organo-mineral contribution. With this in mind as well as the inherently variable nature of 13C-DOC shown here and elsewhere, can the authors support their conclusion that the analysis of 13C-DOC, alone, is an “extremely powerful tool for tracing DOC sources and transport mechanisms”? The authors somewhat

overstate this point without adequate justification.

It seems that the more traditional DOC:NO3:SO4 EMMA was more reliable, and without this information we would not have the proper context for confirming the validity of 13C-DOC mixing model, especially considering the uncertainty in endmember values.

4.4: Carbon isotopes: “a powerful and reliable tool”. Can the authors justify the claim of reliability? How easy/difficult is it to reliably determine discreet 13C endmembers considering that in general endmembers represent a range of 13C values that exceed the 0.1 per mil sensitivity of the endmember mixing model? The authors do a fine job of noting that 13C-DOC is only powerful if measured at hi-resolution as done here, but I think that this qualifier needs to be added to each sentence stating: “the results of this study indicate that carbon isotopes. . . (e.g. abstract, intro, 4.4 and conclusion). The end of that sentence should read something like “assuming we have a hi-resolution assessment of temporal/spatial variability”, rather than saying this several sentences later.

Figures: There are quite a few figures. Some can be consolidated (e.g. Figure 4 is somewhat redundant since discharge is shown in other figures) and some data presented in figures is not discussed in the text (e.g. Figure 5b). Is it necessary to show each of the storms in each figure to tell the story or could some of this be consolidated into a table?.

Figures 3 and 4 seem somewhat redundant. The plots look nice, but the key partâĂŤdischarge is shown in other figures 5,7,9, and 10. Figure 4 could be eliminated/merged with figure 3.

Figure 5:

The scale for SO4 data should be adjusted so that the peaks are more obvious (perhaps use a break between NO3 and SO4 data and adjust the scales). It would also be easier to see the correlation between SO4/NO3 and discharge if the discharge data

was overlaid on the bottom frame (b). It would make more sense to have the discharge y-axis on the right of both (a) and (b) and have DOC/NO3/SO4 axes on the left since the concentrations are the main emphasis.

Figure 6: Is it necessary to show all 6 hysteresis plots, or would showing just one get the same idea across? I don't believe there is discussion of the difference between each storm that necessitates showing all six plots.

Figure 10: A slightly darker grey for the discharge line would be nice.

Interactive comment on Biogeosciences Discuss., 10, 17965, 2013.