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10, C8484–C8491, 2014

Interactive Comment

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 #2

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This article describes the hydrometric monitoring and end-member modeling (SO4, NO3, DOC, and 13C-DOC at a later stage) in an agricultural catchment in France, to verify application of δ13C-DOC for identification of DOC sources and transport processes. This manuscript presents an interesting and very extensive dataset on temporal variability of these parameters, including high-resolution data on 13C in DOC.

The manuscript is generally well written. However, the manuscript needs thorough revisions before publishing can be recommended. The following major problems have been identified:

In the manuscript, the authors did not clearly distinguished between the two different

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Interactive Discussion
Discussion Paper

soil horizons of the wetland (deep redoxic horizon vs. shallow organo-mineral horizon) on the one hand and upland soils on the other hand as possible stream water (and DOC) sources. That is already illustrated in the abstract (lines 13-15) with 80% of the DOC flowing through the most superficial soil horizon of the riparian domain (20% of the flux derived from the deeper horizon of the riparian domain) but at the same time up to 30% of the DOC should derive from upland soils. The connection between the "conventional" end member mixing approach (EMMA) and the use of 13C DOC to separate different water sources is not very clear. Most important, the authors did not clearly distinguish flow pathways and DOC sources. This problem becomes evident by comparing figures 9-12. For instance, it is not clear how the partitioning of DOC as represented in Fig. 11 was calculated. The EMMA approach should consider 4 water sources, including hillslope groundwater (illustrated in Figure 9) but in Figure 11 just the two horizons of the riparian zone were considered to be important for the transition of DOC from soils to the stream during the four storm events. For sure, all of the water has to pass the riparian zone before entering the stream but containing DOC originated from e.g. upland soils too. Using 13C of DOC, the estimated contribution of the uppermost horizon of the riparian zone was significantly smaller (second paragraph of section 4.2). I do not understand how DOC input from upland soils (hillslope groundwater) was considered in this estimation. This estimation also indicated the necessity of a sensitivity analysis using 13C DOC to identify DOC sources (even smaller changes than the analytical precision resulted in large effects).

After determination of the main flow pathways in the riparian zone (Fig. 11), the authors calculated the contribution of upland DOC to stream water (results given in Fig. 12; section 4.3). I do not understand how they included the contribution of the B horizon of the riparian zone (called deep redoxic horizon). The used 13C ratios for this calculation (-28.6 for the riparian zone and -25.0 for upland soils) were deduced from aqueous extractions of the respective soil horizons. This approach is particularly questionable for the upland soils because equilibrium conditions were assumed which are not very likely during storm events. 13C ratios of the topsoils of the upland soils would suggests ratios of about -27 in the uppermost soil layer close to the stream (Fig. 2). I do not agree using a 0-40 cm soil layer as the source of upland DOC if most of the water movement took place in 0-15 cm as stated in a previous section (section 3.1, last sentence). It is also reasonable to assume that the uppermost horizon of the upland soil is the most important source of upland DOC taking the strong decline in SOC with depth into account.

Summarizing the most important problems, it seems there is no significant difference in 13C of DOC between the uppermost upland soil horizon (the most likely DOC source of upland soils) and the B horizon of the riparian zone. Therefore, the approach used by the authors seems to be overambitious and not justified by the data. It seems possible to distinguish between two main DOC sources: the upper horizon of the riparian zone and the B horizon of the riparian zone + contribution from upland soils using 13C DOC. Secondly, please distinguish hydrological pathways and DOC sources as clear as possible.

All of my further comments should be considered in the context of my main concern about the suitability of the differences in 13C DOC (and other end members) to distinguish DOC in upland soils from DOC in B horizons of the riparian zone.

Structure-wise, improvements in the order of the discussion is recommended. The manuscript is rather lengthy and could be more concise, the figures need to be critically re-assessed based on their relevance for the text, as some can be merged or better placed in supplementary materials.

Results of previous studies are extensively described/repeated in this article. Although current findings need to be placed in context by summarizing earlier studies (in this particular catchment or others) – to which the authors pay careful attention –, this can be arguably be more concise. Focus should be put on information important in relation to the findings of this study. A brief summary of the results of previous studies would suffice. I suggest a table summarizing the majority of details for the sampling sites including 13C ratios of the different soil horizons and corresponding DOC data inclusive 13C DOC data obtained by water extractions.

Title: The title of the study is a little bit misleading. It suggests that new insights of DOC sources and DOC transport were obtained by the use of 13C-DOC although it is an application study demonstrating the advantages and limitations of the use of 13C of DOC.

Introduction: The introduction is very lengthy. It needs re-structuring and a better focus also in terms of existing data (cf. one of my previous comments). The last paragraph of the discussion might be a good starting point for re-writing the introduction.

Isotopic fractionation during degradation in wetlands and soils is reasoned to cause pronounced differences in 13C signatures on spatial scale, making a 13C approach valuable. Are such distinct differences (lower values in upland and higher in wetlands) generally found on catchment-scale as also shown by other studies (in the discussion one other catchment is mentioned to demonstrate 13C-DOC differences, but can this be used as a universal approach)? Also, for the specific catchment discussed in this article, to what extent are the observed differences in 13C between upland and riparian areas controlled by differences in input by vegetation (as upland soils are cultivated with both maize (C4) and other cereals)?

One of the motivations of the current study may be the hysteresis between discharge and DOC concentrations, i.e. peak of DOC concentrations at the ascending limb of the hydrograph. I wonder why the authors did not discuss their important result of peaks in DOC concentrations at the descending limb of the hydrograph which is in contrast to the literature and their own expectations. It might be helpful to include 13C and nitrate patterns in this discussion.

In lines 9-10 (page 17968) you stated that the isotopic composition of SOM are generally fully transmitted to soil DOC. Although I am not fully convinced by this statement you did not apply that in your end member calculation for upland soils (cf. one of my

BGD

10, C8484–C8491, 2014

Interactive Comment

previous comments).

Page 17969, line 9-11: give numbers

Material and Methods Section 2.1 The first paragraph can be shortened substantially. I suggest to improve your terminology and use the soil horizon names of the WRB. The upper 10 cm thick organo-mineral horizon of the riparian zone might be an Ah horizon and the redoxic horizon a Bg horizon. Please be precise, consistent and short in the description of the hydrology. On page 17972, you described the four types of water. On page 17973, there is some overlap and in figure 9 you are using other names for these four water sources.

Section 2.2 The variability of 13C of SOC defined for riparian and upland soils should be specified with regard to spatial coverage inclusive vegetation type and replicates, to adequately support the 13C-DOC values used as end-members later on. Moreover, this would provide some indications on the extend of lateral 13C-DOC variations.

Section 2.3 line 15: To be addressed in the discussion: what are the implications of this deviation by the sampling method for the recorded results on DOC and 13C-DOC samples?

Section 2.4 Line 4: All water samples. . .. For the analyzed parameters, the type of sample(s) taken as well as the sampling location need to be mentioned clearly, as well as the sampling frequency (which appears later on to differ for NO3, SO4 measurements) with regard to temporal trends.

Line 15: 13C-DOC analysis by IRMS Did you apply the same procedure for the measured standards as for the samples by following the equal-treatment principle by Werner and Brandt (2001)? If not, how is a potential effect of the preparation procedure (e.g. by freeze-drying, acid addition) on 13C values measured for the water samples ruled out? DOC concentrations were fairly low. How did this correspond with the detection limit for analysis by the EA-IRMS, as well as the linearity of the system? Were

BGD

10, C8484–C8491, 2014

specific adjustments required? Information on the amount of sample to be freeze-dried would be an valuable asset, to provide insight in the application of such a 13C-DOC approach on large scales.

Line 28: Precision is meant instead of accuracy. Repeated measurements... The amount of replicates should be defined, and if this precision was obtained for standards as well as for water samples.

Section 2.5 'decompose' may be a strange term in this context, could be: identify components (see above) please specify which four components are meant Why is d13-DOC not mentioned in the EMMA approach? Please explain also the end-member modeling approach applied for the d13C-DOC data and how it is connected to the conventional EMMA (cf. first paragraphs describing the main problems of the manuscript).

Statistical analysis An explanation on how the data were statically analyzed is currently not described. This should include the approach applied for time series analyses (running average, smoothing of data, potentially missing data points). In the results and discussion, trends are often described as 'strong' or 'marked', however a statistical significance would further support such statements. The number of replicates, and for graphs the error bars, need to be provided for all analyzed parameters, particularly for 13C-DOC values as their variability is of prime interest in this paper. Moreover, the results on the 13C-DOC end-member modeling approach would need a sensitivity analysis.

Results Section 3.2 The temporal variations in SO4 are not clearly visible in Fig. 5b with its current scaling. It is quite interesting that NO3 was inversely correlated with discharge, peaking at the rising limb of the hydrograph as expected for DOC. Please use these two observations (low DOC and high NO3 concentrations) in your discussion about the contribution of the different DOC sources to stream water. Might that be an indication that at first uplands contributed to DOC and later the riparian zone? Fig. 6 may be redundant, as similar information is conveyed by Fig 7 also depicting the

BGD
10, C8484–C8491, 2014

temporal trends in DOC.

3.3 The statements given in line 1 ('Comparable and systematic'), line 11 ('systematically'), line 13-14 ('Comparable and systematic') seem very strong based on the presented results in Fig 7. Although a trend is apparent, there seems to be considerable variation among the different storm events, e.g. for event 5 13C-DOC variation is minimal and does therefore not correspond to the stated trend. Is the precision in 13C-DOC measurements taken into account for the mentioned variations? Would there be statistical evidence to confirm 'comparable and systematic'? Otherwise, a more moderate statement on the apparent trend is arguably more applicable.

Line 8: It is not entirely clear which variations and correlation between which factors are meant.

3.4 Line 6: 'opt.cit.')??? How does the finding that hillslope groundwater contribution is rather constant, correspond to the later end-member modeling with 13C-DOC to determine the contribution of upslope DOC?

Discussion As elaborated above, the discussion needs major revisions taking into account my main concerns.

Section 4.1 Fig. 10. The display of 13C-DOC trends in the redoxic and organo-mineral horizons of the riparian wetland gives the impression that 13C-DOC trends in outlet water during the storm events are directly related to isotopic values observed in the riparian soils. This causes confusion, as also the contribution of upslope DOC with a different isotopic signature plays a role in determining the final 13C-DOC values at the outlet. Throughout the discussion, care should be taken that riparian subsoil and upland DOC contribution are ultimately linked and both contributions cannot be discussed separately.

Page 17981, line 15/16: Please avoid just a repetition of the results. I would recommend to discuss the implications of findings (i.-iii.) with regard to the robustness of

BGD

10, C8484–C8491, 2014

13C-DOC as tracer of DOC sources and pathways, and using it on broad spatial and temporal scales on catchment scale. I am also a little bit confused because I would expect the opposite. DOC concentrations should be higher in the A horizon and at the rising limb of the hydrograph.

Line 23: really lower???

Section 4.3 The first paragraph is very lengthy.

Section 4.4 You discussed your results with results published by Schraub and Alewell. Are the results of the studies really comparable in term of soil conditions and land use?

Conclusions Please avoid terms as “extremely powerful”. In lines 23-25 you mentioned the positive results only but your results illustrated the problem as well.

Figures: Use consistent terminology (e.g., water sources, soil horizons) Figures 6 and 8 might be omitted

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