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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.

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Response to Anonymous Referee #2 comments

General Comments

Referee #2: In the manuscript, the authors did not clearly distinguished between the two different 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

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at the same time up to 30% of the DOC should derive from upland soils.

Lambert et al.: A confusion is made here between the relative proportions of DOC that travel through the riparian soil horizons during storms and the proportion of this travelling DOC that is produced in upland soils. As shown in this and our previous study, the rise of the water table in the upland domains of the catchment during the wet season activates an upland DOC flush which transfers upland DOC to the riparian soils by subsurface flow. This downward transport of upland-born DOC is demonstrated by the sudden increase of the δ13C values of the DOC which is collected in the water traps installed in the riparian soil horizons. This sudden increase is due to the fact that DOC from upland soils is isotopically much lighter (ca. -25.0‰ than in-situ produced, wetland DOC (-28.6‰. This sudden increase is however not homogeneous through the soil profile. It is larger in the deep redoxic horizon than in the uppermost organo-mineral horizon (see Fig. 2 in the submitted manuscript), most probably because of existence of a vertical negative gradient in wetland-born DOC concentrations (concentration of wetland-born DOC being lower at depth, the isotopic effect of the upland DOC intrusion is much higher at depth than it is in the shallower soil horizons where wetland-born DOC concentrations are higher). This leads to the development of a vertical gradient with regards to the isotopic composition of the DOC travelling in those horizons during storm events, the DOC travelling in the deep redoxic horizon being lighter than the DOC travelling in the shallow organo-mineral horizon (see also Fig. 2 in the submitted manuscript). Starting from these observations, two mass-balance decompositions can be made from the δ13C values measured in the stream during a storm event. First, one can calculate the proportions of the DOC which ultimately come from the upland and wetland soils, by using the values of ca. -25.0‰ and -28.6‰ as end-member values and by considering that the DOC in the stream is a mixture of upland-born and wetland-born DOC. Second, one can calculate the proportions of DOC that are instantaneously flowing through the shallow, organo-mineral and deep redoxic parts of the riparian which are in way transit zones for both the wetland-born and upland-born DOC components. The end-member values in that case are no more the above source

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δ13C values, but the δ13C values that are recorded in each soil horizon at the moment when occurs the considered storm event, namely for example -28.6‰ and -27.2‰ for the organo-mineral and redoxic horizons, respectively, as in the case of storm event N°4 (see Fig.2 in the submitted manuscript).

Referee #2: 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.

Lambert et al.: There is no direct connection between the DOC/NO3/SO4 EMMA and the isotopic mixing model. Each method is used separately. The key point here, however, is that unlike the EMMA method which can be used for all storm events because of the temporal stability of the difference in DOC/NO3/SO4 ratios between water components, the isotopic method is suitable only in those periods where a sufficient isotopic difference existed between the DOC flowing into the organo-mineral and the DOC travelling into the deeper redoxic horizons. Moreover, unlike the EMMA method for which stream data systematically plot with the space defined by end-members, some storms have stream δ13C values falling outside the range defined by soil end-members, This is the reason why only storm N°4 was isotopically decomposed with regards to the contribution of shallow and deep soil horizons to stream DOC flux (see second paragraph in section 4.2 of the submitted manuscript), as this storm is the only of the six analyzed storms that fulfills both these two necessary prerequisite criteria. The aim of this decomposition is only to show that, when possible, the isotopic decomposition yields results that are comparable to the EMMA technique, which may be viewed as a sort of independent validation of the latter. As regards to Fig. 9 (water component decomposition) and 10 (contributions of the organo-mineral and redoxic horizons to the stream DOC flux), both figures were exclusively constructed using the EMMA method (as indicated in the figure caption), this method being the only method we could apply to all storms.

Referee #2: Most important, the authors did not clearly distinguish flow pathways and DOC sources. This problem becomes evident by comparing figures 9-12.

Lambert et al.: We agree that Figures 9-12, and notably Figs. 11 and 12 may not be fully explicit with regards this problem of distinguishing between DOC flow pathway decomposition and DOC, ultimate source decomposition. For the purpose of making this distinction clearer we propose to add interpretative sketch to figures 11 and 12, as new Figures 9 and 10 (see here in Figures 1 and 2).

Overall, in order to take into account all the comments made by Referee #2: on the lack of clarity of the manuscript as regards the distinction between hydrological flow path and DOC source decompositions, we plan doing the following modifications: 1) modify section 4.2 and 4.3 titles in order to better highlight and better separate the two decomposition types2) rewrite in part sections 4.2 and 4.3 to better explain the concepts and principles that are being each decomposition method and finally, 3) slightly redraw figure 2 to better highlight the transfer of 13C-enriched DOC from upland soils to riparian wetland soils during period B.

Referee #2: 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.

Lambert et al.: The two other end-members (rainfall and deep groundwater) were removed, for clarity, from the initial manuscript as the contribution of these two end-

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members to the stream DOC flux turned out to be negligible (less than 3% in total). However, we plan to re-introduce the contributions of these two other components in Fig. 11 as shown above, to keep full consistency between the text and the figures.

Referee #2: 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.

Lambert et al.: As already stated above, the isotopic decomposition made in the second paragraph of section 4.2. is not aimed at determining from which exact ultimate source (i.e. wetland vs. upland soils) the stream DOC comes from. The objective of this decomposition is different. It is to identify through which of the two wetland soil horizons (i.e. the shallow, organo-mineral horizon and the deep redoxic horizon) is the soil DOC preferentially transferred to the stream, keeping in mind that the transferred soil DOC is basically a mixture of wetland-born and upland-born DOC.

Referee #2: 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).

Lambert et al.: The decomposition of DOC pathways being not related to the δ13C values used for the ultimate wetland and upland DOC reservoirs, there is no need to perform a sensitivity analysis of the impact the uncertainty that affects these two values would have on this decomposition. Moreover, as pointed out above the decomposition of DOC pathways at the soil/stream interface is not made using the isotopic tool, but relies entirely on the EMMA method results.

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Referee #2: 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).

Lambert et al.: As pointed out in the manuscript and stated above, the principles behind the source and water pathway decompositions are fundamentally different. Indeed and regarding the wetland soils, the source decomposition aims at eliminating the effects of the downward transport in these soils of upland DOC which obscures the isotopic signature of the in-situ produced DOC. As explained in the manuscript, the true isotopic signature of the DOC wetland component (true means here “not polluted by the input of upland DOC”) is obtained either at the early beginning or very end of hydrological period B, when the input of upland-born DOC into the wetland soil was negligible. Doing so, one can see that the variation in δ13C values between the A and B soil horizons of the wetland area becomes very limited. More importantly the -28.6‰ average δ13C value obtained at that time in combining the A and B horizon data corresponds to the δ13C value which has been obtained from laboratory aqueous extraction of the organic carbon contained in the two same soil horizons. This to say that the DOC which is produced in-situ from these two soil horizons may be viewed as a single isotopic entity. This is the reason why we did not separate the A and B soil horizons in the source decomposition procedure, considering that the DOC which is produced in-situ from these two soil horizons could be collectively referred to as the “wetland-born DOC end-member” in the mixing analysis, having an average δ13C value of -28.6‰

Referee #2: 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.

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Lambert et al.: We agree that the water-extractable organic carbon may not strictly correspond to the upland DOC component that was leached from upland soils and further transported downhill into the wetland domains during storms. However, the Kervidy-Naizin catchment does not have the equipment necessary to directly collect this DOC component. Therefore, perform aqueous extraction was the only method we could find to estimate the δ13C value of this component. For the sake of consistency, we used the same water extraction procedure to estimate the isotopic composition of the wetland DOC end-member. At any rate and as we stressed in our responses to Referee #1 comments, our objective in the present paper is not to constrain what was exactly the δ13C value of the upland DOC component that moved into the wetland zone, but to show that the database we collected on the Kervidy-Naizin catchment points to a limited size of the upland DOC component. From our point of view, this conclusion is unambiguously demonstrated by the progressive temporal decrease of soil δ13C values as shown in Fig. 11 of the submitted manuscript, and is independent of the true isotopic composition of the upland DOC component. It seems to us that there is no other way than to call for the input of an upland DOC component into the wetland soils to account for the abrupt increase of the wetland DOC δ13C values seen at the beginning of Period B. The fact that DOC δ13C values gradually increase uphill is consistent with this interpretation, as is also consistent the observation that this abrupt increase occurred when the water table started to rise in the upland domain. Conversely, the hypothesis of an upland DOC reservoir being size limited is the only way we see to explain why the influx of the upland, isotopically heavy DOC stopped, while the water table remained high. however and order to take into account the uncertainty that remains around the true isotopic composition of the moving upland DOC component, we suggest to introduce the term “estimate” to refer to this component both in text and figure 10 in the new version.

Referee #2: 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).

Lambert et al.: We agree but as explained above we prefer the isotopic signature of the water extractable DOC (-24.9±0.7‰ (n=3)) which we think is a better "estimate" of the moving upland DOC component.

Referee #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.

Lambert et al.: We agree. Consistently, we propose to use only the isotopic signature of the water extractable DOC obtained from these uppermost soil horizons in the isotopic mixing calculation model.

Referee #2: 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.

Lambert et al.: That is not true. The δ13C of the DOC which is in-situ produced from the wetland B horizon is -28.6‰ while that of the DOC which is water extractable from the upland, uppermost soil horizon is -25.0 ‰ not -27.0‰ as argued by Referee #2. In fact, -27.0‰ corresponds to the isotopic signature of the soil organic carbon (not the DOC). A δ13C value obtained for SOM cannot be assigned to DOC as the process of

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DOC production is known to fractionate carbon isotopes (see for example Sanderman et al., Biogeochemistry (2008) 89:181–198).

Referee #2: Secondly, please distinguish hydrological pathways and DOC sources as clear as possible.

Lambert et al.: Responses to this comment have already been provided above.

Referee #2: Structure-wise, improvement 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.

Lambert et al.: From a construction point of view, we propose to do the following changes: - Remove Fig.4 as this figure is redundant with Fig. 3. - Move Fig. 5b in a Supplementary Information section. - Consolidate Figs. 6 and 5a in a new Fig. 4 as also suggested by Referee #1 (see the news proposed Fig. 4 in the responses to Referee #1). - Use a darker grey for the discharge line in Fig. 10 in order to help distinction of this line in the figure (see also Referee #1 responses). - Compile and present the whole dataset of stream chemistry during storm events in a table in a Supplementary Information section. - Rewrite in part the discussion section in order to make this section more concise. A 20% shortening is envisaged.

Referee #2: 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.

Lambert et al.: We agree that we the presentation of previously published data could be more concise. A 20% shortening of this part of the paper is envisaged. However, we advocate keeping Fig. 2 which is essential to understand the articulation between the new and already published results, and also essential for interpretation the presented storm data. We think that a table would hardly illustrates the complex spatio-temporal variability of soil water data which need to be presented in order to allow the reader to understand the way the storm data are interpreted. However, we will add in the Supplementary Information Section which we will join to revised version of the paper a table resuming the isotopic data of SOC, WEOC and DOC as this corresponds also to the request of Referee #1.

Specific Comments

Referee #2: 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.

Lambert et al.: We agree with this request to change the title of our paper. The title we envisage for a revised version would be “DOC sources and DOC transport pathways in a small headwater catchment as revealed by carbon isotope fluctuation during storm events”. This new title would be more in phase with the application nature of our study as pointed out by Referee #2.

Referee #2: 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.

Lambert et al.: In intend to significantly shorten the Introduction of the paper. However we do not plan to remove entirely the first and second paragraphs. The question of the source of DOC has many important implications that need to be at least briefly summarized.

Referee #2: 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)?

Lambert et al.: This point is discussed in the third paragraph of section 4.4. In fact, the study site investigated by Schaub and Alewell – the Urseren Valley - is markedly different in terms of land use as compared to the Kervidy site (agricultural soils for the Kervidy-Naizin site and forested/pastured soils for the Urseren Valley) and morphologic setting (lowland catchment for Kervidy-Naizin and Alpine Valley for the Urseren Valley). The fact that in these two contrasted study sites the riparian soils are characterized by lower stable carbon isotopic composition compared to their upland counterparts suggest that the riparian-upland isotopic gradients which is observed in both these two sites could be a systematic feature of headwater catchment worldwide. Of course, we cannot prove this to be true. However, we believe important to mention this possibility as one of the output of our study.

Referee #2: Also, for the speciïňĄc catchment discussed in this article, to what extent

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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)?

Lambert et al.: This is a good point. Unfortunately, we do have the data to evaluate the role of vegetation variation in the construction of the observed spatial isotopic gradient. This remains an open question for future work.

Referee #2: 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.

Lambert et al.: This result is not in contrast to literature expectation, nor it is with the expectation we have when starting this study. In fact and as mentioned in the present paper, the study site has already been the subject of a study of DOC dynamics during storm events which gave exactly the same results that those we obtained regarding DOC vs. discharge relationship (see Morel et al, Hydrological Processes 23, 2888–2901, 2009). Furthermore, the present paper is not dedicated to study in details the relationship between DOC and discharge. Doing such detailed study would lengthen the paper, which would be contradictory with Referee #1 and #2 to make it more concise.

Referee #2: In lines 9-10 (page 17968) you stated that the isotopic composition of SOM is 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

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(cf. one of my previous comments).

Lambert et al.: There is a misunderstanding here. What is transmitted to the DOC is not the SOM isotopic composition, strictly speaking. This is the vertical isotopic gradient found in SOM which is transmitted to DOC. As the regard the absolute values, they are different at a given soil depth because of the fractionation event mentioned above. This is the reason which the SOM value found in upland soils cannot be regarded as representative of the isotopic composition of the moving upland DOC component.

Referee #2: Page 17969, line 9-11: give numbers

Lambert et al.: Numbers are provided in Fig.2 and in section 2.2. Give these numbers again here would be contradictory with the general objective of significantly shortening the present paper.

Referee #2: Material and Methods Section 2.1 The first paragraph can be shortened substantially.

Lambert et al.: We agree. A 20% shortening is envisaged.

Referee #2: 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.

Lambert et al.: We will follow Referee #2 recommendation to use the soil horizon names of the WRB, and will change our terminology accordingly.

Referee #2: Please be precise, consistent and short in the description of the hydrology.

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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.

Lambert et al.: These inconsistencies will be corrected.

Referee #2: 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 extent of lateral 13C-DOC variations.

Lambert et al.: The spatial coverage of the variability of δ13C of SOC defined here for riparian and upland soils have been tested by measuring the isotopic composition of SOC along another transect in the catchment (so-called Gueriniec transect, located in the north-east of study site).. The results (Figure 1, below) show comparable vertical and lateral variability of δ13C of SOC, with the SOC of the upland soils being systematically 13C-enriched as compared to the SOC of the riparian soils. Thus, the riparian-upland isotopic variability portrayed in Fig. 2 of the submitted paper is clearly a general characteristic of the study site.

Referee #2: 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?

Lambert et al.: The samples collected manually and automatically were treated in the same way and the sampling frequency has virtually no influence on the results. The use of two sampling strategy is simply that the high frequency is necessary to capture the rapid DOC concentration variations that occur during storms, which are generally short events lasting no more than 24 hours. Such rapid events are hard to sample adequately manually.

Referee #2: 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.

Lambert et al.: Sections 2.3 and 2.4. will be rewritten to make these points clearer.

Referee #2: Section 2.4. 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?

Lambert et al.: Among the different standards used in this study, the USGS24 was prepared using the same procedure as that used for the natural water samples. After solubilization in deionized water, USGS24 samples were acidified, then frozen and freeze-dried. As quoted in the submitted manuscript, measured values were consistent with the reference values published for this standard. Therefore, we argue that the freeze-drying procedure we used had no measurable effects on the DOC isotopic composition of the analyzed water samples.

Referee #2: 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 specific adjustments required? Information on the amount of sample to be freeze-dried would be a valuable asset, to provide insight in the application of such a 13C-DOC approach on large scales.

Lambert et al.: The EA-IRMS device we used is specified to be linear for ionic currents in the range 1 to 13-14 nA, and the quantity of freeze-dried samples has been adjusted in all cases to reach at least 2 nA. For samples with high %Corg (for example for the WEOC samples), a dilutor was installed online in order to have a signal below 10 nA. Samples whose signal has exceeded the limit of 13-14 nA were re-analyzed, either using the dilutor, or by reducing the amount of sample in the tin capsules. Moreover, in addition to the USGS 24 and ANU standards, we used internal, laboratory standards, especially glutamic acid and atropine with δ13C values of -27.6 and -28.6‰ respectively. The volumes of water sample freeze-dried will be specified in section 2.4 of the revised manuscript.

Referee #2: Section 2.4. Line 28: Precision is meant instead of accuracy. Repeated measurements. . . The amount of replicates should be deïňĄned, and if this precision was obtained for standards as well as for water samples.

Lambert et al.: OK. The revised manuscript will be corrected accordingly.

Referee #2: 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.

Lambert et al.: Ok for using “identify component” instead of decompose.

Referee #2: Why is δ13CDOC not mentioned in the EMMA approach?

Lambert et al.: As described in the manuscript and specified above, the EMMA approach does not rely on δ13CDOC values. Only DOC, NO3 and SO4, concentrations are used as was done during the previous hydrograph separation made on this catchment (see Durand and Torres, 1996; Morel et al., 2009).

Referee #2: Please explain also the end-member modeling approach applied for the δ13C-DOC data and how it is connected to the conventional EMMA (cf. first paragraphs describing the main problems of the manuscript).

Lambert et al.: As stated above the EMMA and isotopic-mixing approaches were conducted independently from each other. They are not connected in any manner, except that both were developed with the same attempt of valuating water contribution proportions (see above for more details).

Referee #2: 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.

Lambert et al.: The present paper does not rely on time series analyses. This means that the statistical tools commonly used for analyzing such data (running average, smoothing of data, potentially missing data points) would not bring any supplementary constraints for interpreting the current dataset. As regards error bars, we stress that error bars are generally smaller than the symbols used, and are thus not visible in the presented diagrams (this point will be specified in figure captions, when necessary).

Referee #2: Results Section 3.2 The temporal variations in SO4 are not clearly visible in Fig. 5b with its current scaling.

Lambert et al.: Fig. 5b will be moved in the Supplementary Materials section (request of Referee #1), meanwhile being redrawn with the appropriate scaling to make the temporal variability of SO4 more visible.

Referee #2: Section 3.2. (1) 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. (2) Might that be an indication that at first uplands contributed to DOC and later the riparian zone?

Lambert et al.: As pointed out above, it is not so quite interesting that NO3 was inversely correlated with discharge, this being an already well known feature of this catchment which was already apparent in previous studies (see for example the paper by Morel et al., (2009). As regard, referee #2 suggestion that this might be an indicator that uplands contributed first and later the riparian zones, this cannot be so. Indeed, and as shown in Fig. 8 of the submitted manuscript, upland groundwater is not NO3-poor as should be the case in this hypothesis, having instead NO3 concentrations as high as 100 mg/L. .

Referee #2: Fig. 6 may be redundant, as similar information is conveyed by Fig 7 also depicting the temporal trends in DOC.

Lambert et al.: Figure 6 and 5a will be consolidated in the new figure 4, keeping only 2 storms as an example of the types of DOC vs. discharge relationships that characterized the 6 studied storm events.

Referee #2: Section 3.3 The statements given in line 1 (‘Comparable and systematic’), line 11 (‘systematically’), line 13-14 (‘Comparable and systematic’) seem very strong

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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 13CDOC 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.

Lambert et al.: Ok, we agree. The terms "comparable and systematic" are a little bit too strong. They will be removed from section 3.3.

Referee #2: Section 3.3 Line 8: It is not entirely clear which variations and correlation between which factors are meant.

Lambert et al.: This part will be rewritten to clarify this point.

Referee #2: 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?

Lambert et al.: The results presented here deal with water proportions (as established using the EMMA method), not with DOC relative fluxes. This paragraph will be slightly rewritten to make this point clearer, including the removal of the abbreviation 'opt.cit.'.

Referee #2: Discussion. As elaborated above, the discussion needs major revisions taking into account my main concerns.

Lambert et al.: Ok. The discussion will be rewritten, taking into account the requests made by both Referees #1 and #2 (better organization; better separation of results and discussion statements; shortening of certain sub-sections,. . .)

Referee #2: 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 value at the outlet.

Lambert et al.: Once again there is a confusion made here between the ultimate sources of the DOC, which includes the upland soil domains of the catchment, and the zones through which the soil DOC is transferred to the stream. These transfer zones where wetland-born DOC and upland-born DOC mixed together and flow towards the stream, are clearly the riparian zones which stand at the interface between land and stream. In this respects Fig. 10 is not confusing. It demonstrates that the mixing process which occurs in the riparian zones controls also the temporal variability of stream DOC signatures during storms. Unlike being confusing, Fig. 10 demonstrates, in our opinion, how strongly li soil and stream processes are connected in the study site with regards to DOC.

Referee #2: Throughout the discussion, care should be taken that riparian subsoil and upland DOC contribution are ultimately linked and both contributions cannot be discussed separately.

Lambert et al.: Not true. The isotopic data allow to separate DOC pathways from DOC sources (see response above).

Referee #2: Page 17981, line 15/16: Please avoid just a repetition of the results.

Lambert et al.: OK. These repetitions will be removed of the corrected version of the

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paper.

Referee #2: I would recommend to discuss the implications of findings (i.-iii.) with regard to the robustness of 13C-DOC as tracer of DOC sources and pathways, and using it on broad spatial and temporal scales on catchment scale.

Lambert et al.: OK. The last part of the Discussion section which already addresses several implications of the findings of this study will be rewritten to integrate this request.

Referee #2: 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.

Lambert et al.: DOC concentration are effectively higher in the A horizon. However, the anti-clockwise relationship indicates that water entering the stream during the early part of the storm has lower DOC concentrations than water entering the stream after the peak discharge. This feature, which was already apparent in the previous work by Morel and coworkers, is likely due to the fact that the rising does not consist only of waters coming from the A horizon, but comprises also a significant proportion of low-DOC rain/runoff waters (see EMMA results).

Referee #2: Line 23: really lower???

Lambert et al.: Yes, absolutely.

Referee #2: Section 4.3 The first paragraph is very lengthy.

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Lambert et al.: Ok. We could to cut it short by 30%.

Referee #2: Section 4.. You discussed your results with results published by Schaub and Alewell. Are the results of the studies really comparable in term of soil conditions and land use?

Lambert et al.: As stated above the land use and the soil types are different, but the hydrologic status (well-drained in hillslope domains and hydromorphic in bottomland zones) are identical. Unlike being a problem, these differences/similarities are of prime importance, since evidencing that the topographic variation in hydrologic status is likely the cause of the observed spatial isotopic gradient. Since similar topographic variation in soil hydrologic gradient are expected to occur in many catchments, this comparison between our and Urseren Valley strengthen our conclusion that the isotopic tool could maybe become a universal tool suitable to locate DOC source in landscapes.

Referee #2: 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.

Lambert et al.: Ok, we agree. The term “extremely powerful” is a little bit too strong. This term will be removed from the Conclusion section.

Referee #2: Figures: Use consistent terminology (e.g., water sources, soil horizons) Figures 6 and 8 might be omitted

Lambert et al.: OK. These points will be carefully checked, and corrections made where necessary.

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

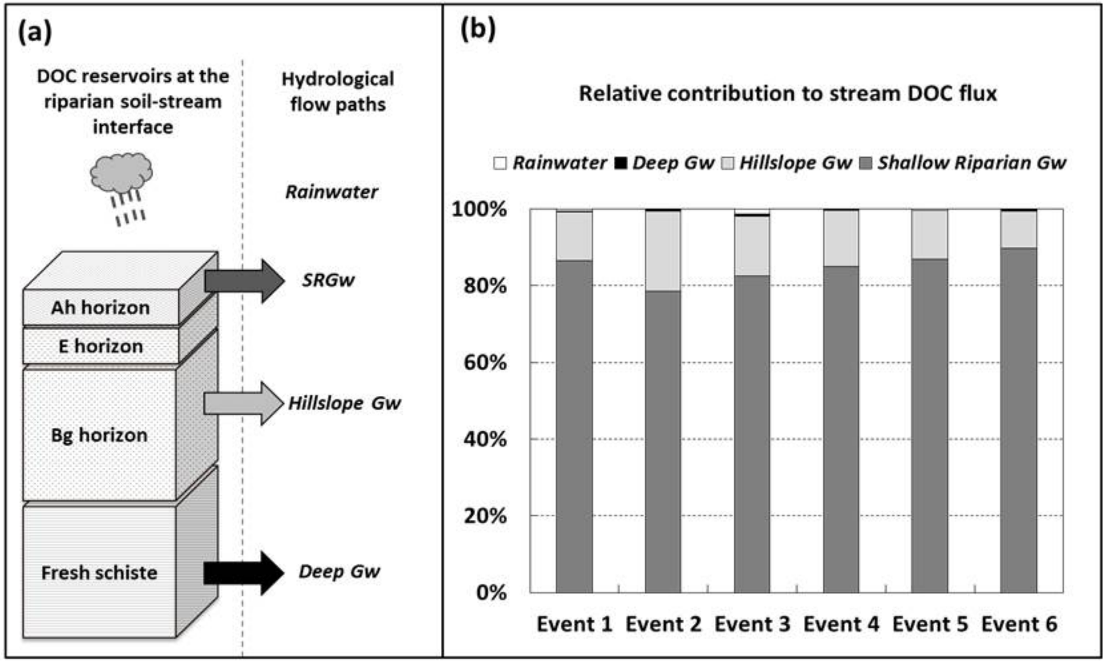

Fig. 1. Proposed new Fig. 9

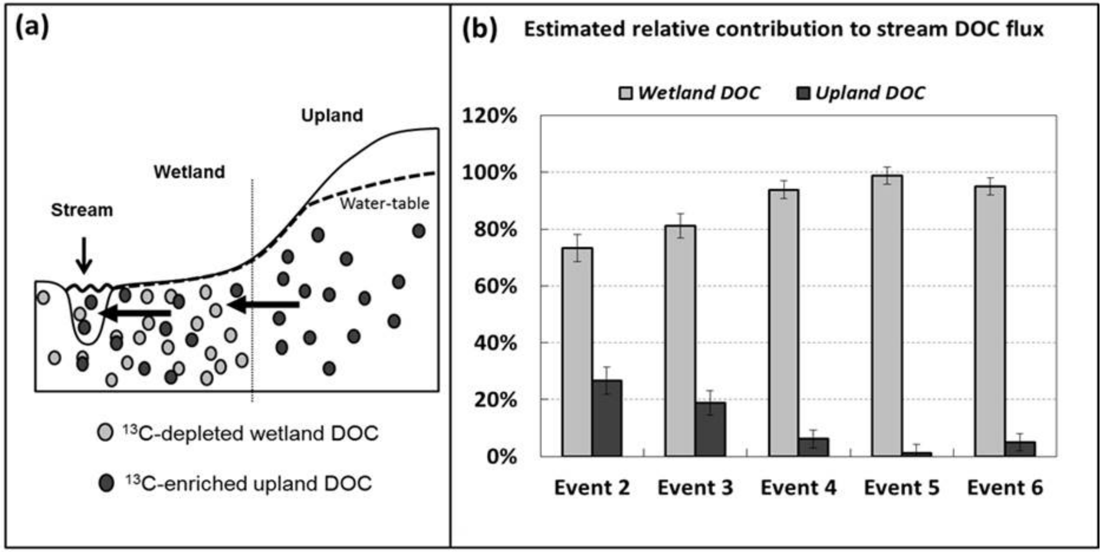

Fig. 2. Proposed new Fig. 10

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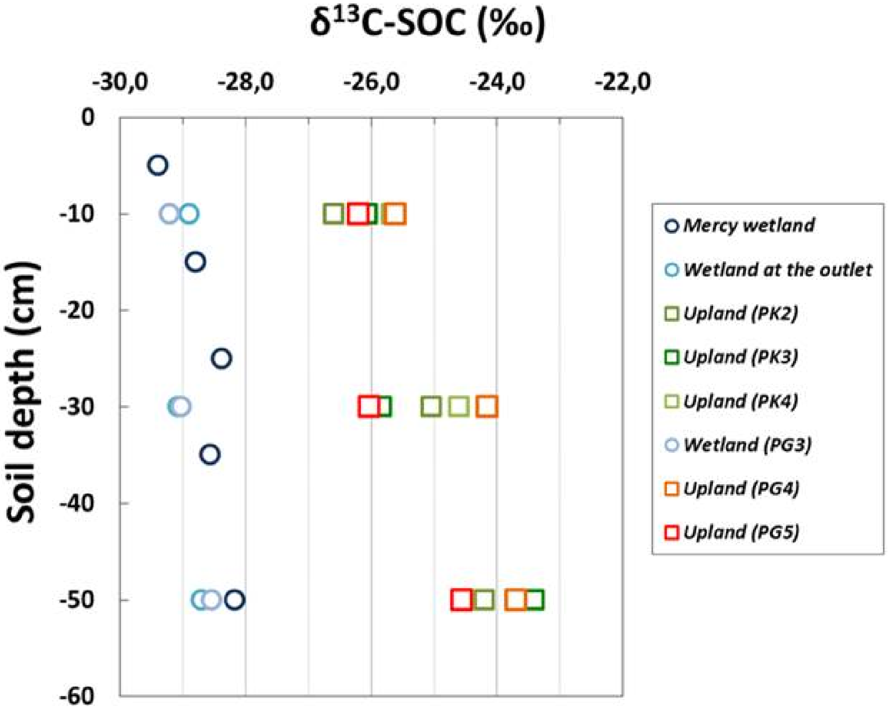

Fig. 3. Depth profile of δ13C for SOC from soils from the Kerolland (PK) and Gueriniec (PG) transects. Riparian soils are portrayed by circles, whereas squares refer to upland soils.

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