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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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Responses to Anonymous Referee #1 comments

Results section

Referee #1: 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 ïňĆow) 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, ïňĄltration and preservation?

Lambert et al.: The difference in DOC concentrations between the high-frequency and daily sampling procedures is due to differences in the timing of sample collection. Indeed, the high frequency is necessary to capture the rapid DOC concentration variations that occur during storm events, whereas a daily frequency is sufficient during low flow periods, as the variation in DOC concentrations is much more limited during these periods. This in turn explains why DOC concentrations are much higher on average during high-frequency sampling than during daily sampling, concentrations during storm events being systematically higher than during low flow periods (see Fig. 1 below). A sentence will be added in the revised version of the manuscript to clarify this point. ________________________

Referee #1: If you compare the concentration of the daily sample to a high frequency sample taken around the same time are the values comparable?

Lambert et al.: Such a comparison is not feasible to the extent that daily manual sampling is interrupted during storm events, being replaced by high frequency sampling. Anyhow, we find that DOC concentrations measured during low flow periods fit well with those measured during storm events (see Fig. 1).

Referee #1: 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.

Lambert et al.: This statement will be moved in the discussion section as requested, and the text modified in order to eliminate repetition from other sections.

Referee #1: Section 3.2. 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 ïňĄgure (other than the EMMA ïňĄgure, 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.

Lambert et al.: The bibliographic references given by anonymous Referee #1 deal with non-agricultural catchments, including forested catchments as large as the Amazon basin. In these relatively pristine catchments/basins, the N load to soil is low being limited to N inputs from natural vegetation degradation. No massive spreading of N-fertilizers occurs in these soils. Because of this, and because of the rapid recycling of the N by growing vegetation, no or very little NO3 is transferred to groundwater in these pristine catchments; most of the NO3 remained stored in the natural soils. Streams and rivers draining these catchments during low flow periods when the groundwater contribution to streams and rivers is high therefore have low NO3 concentrations. The situation is totally different in agricultural catchments suffering heavy NO3 pollution as is the case of the Kervidy-Naizin catchment. In those catchments, the main NO3 store is indeed not soils but groundwater, due to the downward continuous leakage of excess NO3 bring about by agriculture (in the present case, NO3 concentration in groundwater goes up to 80 mg/L; see Fig. 8 of the submitted manuscript). This explains why NO3 concentrations in streams draining these catchments are high during low flow periods when groundwater is the main streamwater source, but become low during high flow periods, when the high-NO3 groundwater flux becomes diluted by lower-NO3 soil and rainwater. One or two sentences will be added in the revised manuscript to address this specificity of agricultural catchments as regards NO3 concentration variations between high flow and low flow periods. We plan to add these sentences in

the section dealing with the presentation of the study site. We also envisage including some of the references provided by anonymous Referee #1 on that topic in the reference list of the revised manuscript. However, we will not go into deep discussion of this point keeping in mind that 1) the dynamic of NO3 in the Kervidy-Naizin catchment has already been the subject of numerous studies, especially with respect to the transport pathways of NO3 and to the relative variations of shallow and deep groundwater components during base-flow periods and storm events (see Molénat et al., 2008 and other references quoted in section 2.1. of the current manuscript) and 2) the addition of a deep discussion of that point would significantly increase the length of the paper, which would be contradictory with Referee's #1 and #2 request to substantially cut short the present manuscript. Note that figure 5b will be moved into a Supplementary Information section, and modified according to Referee #1 and #2 recommendations.

Referee #1: Section 3.3. Lines 20-25: Again, please discuss/explain the observations in the discussion section and describe the data in the results section.

Lambert et al.: A better separation of what is result and what is discussion will be made in the revised manuscript.

Discussion section

Referee #1: Please include additional justiïňĄcation for why 13C data from storm event N° 4 should be used as mixing model end members

Lambert et al.: The reason why we used this event is that storm event N°4 is the only one among the 6 analyzed storm events whose temporal variations in ïĄď13C values were bracketed by the ïĄď13C values of DOC in the organo-mineral and redoxic soil horizons of the Mercy wetland at corresponding time (see Fig. 10 of the submitted manuscript). This situation makes it possible to use the latter values to calculate the relative contribution of each of these two soil horizon to the stream DOC flux during this storm event, keeping in mind the results of the EMMA analysis that tell us that most of the DOC transported by the Kervidy stream during storms derives from wetland soils. Of course, beyond this use is the assumption that the Mercy soils are representative of all Kervidy-Naizin wetland soils. Such an assumption is obviously questionable on a general basis but appears nevertheless plausible during storm event N°4, because of the coincidence of stream and soil minimum and maximum ïĄď13C values. Clearly, this was not the case during the other 5 analyzed storm events. During those events, the maximum and minimum of ïĄď13C values measured in the stream and in the Mercy soils were indeed not coincidental; the values found in the stream falling outside the soil range (see Fig. 10 of the submitted manuscript). This explains why our attempt to use carbon isotope data to quantify the respective contribution of the organo-mineral and redoxic horizons to the stream DOC flux during storm events was restricted solely to storm event N°4. This type of justification will be added in the revised version of the manuscript.

Referee #1: 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 justiïňĄcation. 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 conïňĄrming the validity of 13C-DOC mixing model, especially considering the uncertainty in endmember values.

Lambert et al.: We agree that the claim that the isotopic tool is an “extremely powerful tool” for tracing DOC sources and transport mechanisms maybe described as relatively exaggerated at first. Following of Referee #1 suggestion, we performed a sensitivity

analysis in order to quantify the sensibility of both the EMMA and isotopic mixing methods and it is true that results showed that the EMMA method is effectively less sensitive to variations in end-member composition than is the isotopic mixing method. However, it should be nevertheless kept in mind that carbon isotopes provide a much more absolute way of tracing DOC sources and DOC pathways in catchments than does the EMMA method. Unlike the EMMA method which relies on concentration variations which do not bring in reality any absolute information about the spatial location of DOC sources, carbon isotopes do have this capacity of bringing such absolute information. Let us consider the increase in δ13CDOC values which is observed in parallel with the rising limb of the hydrograph during storms event 2, 3 and 4 (see Fig. 7 of the submitted manuscript). This increase provides absolute evidence that the source of the DOC was moving from the shallow, organo-mineral soil horizons to the deeper, redoxic ones as the storm events progressed. Quite, clearly this result does not depend on the stability of end-member DOC concentration, nor of DOC/NO3 ratio values as the EMMA result does. It just came out because of the isotopic difference that existed at that time between the DOC that circulated through these two soil horizons. This ability of carbon isotopes to provide an absolute tracer of DOC sources in landscape is exemplified further by the ca. 2 ïĄď units variation that occurs between wetland-born and upland-born DOC. This variation which in combination with the time variation of stream δ13CDOC values provides for the first time the absolute evidence that upland DOC sources contribute to the export of DOC by stream is unique to the carbon isotope system. No such evidence for the involvement of an upland DOC source could have been made possible by using the EMMA method. So, our suggestion is to replace “extremely powerful tool”, by “absolute tracer” or even simpler, if requested, by “a tool for locating DOC sources” and to systematically eliminate the adjective "extremely” from the discussion and conclusion section of the manuscript.

Referee #1: Section 4.4: Carbon isotopes: “a powerful and reliable tool”. Can the authors justify the claim of reliability?

Lambert et al.: The term reliable is used because the difference in carbon isotope composition which is found in this study between wetland and upland domains and which can be used as a basis for tracing DOC sources in landscape was already observed elsewhere (see Schaub and Alewell, 2009), suggesting that it could be a general feature in catchments, worldwide. The adjective "reliable" is used here to point out the fact that, if this feature became effectively a general feature of catchments, then carbon isotopes could be confidently used (more confidently than EMMA mixing methods) to locate DOC sources in landscape. Of course, the reliability of this use of DOC isotopes is based on the assumption that the lateral gradient that exists as regards δ13C values in the Kervidy-Naizin catchment and that Schaub and Alewell's (2009) also reported earlier will be hold true in other catchments, which we cannot guarantee. However, there are good reasons to think that this could be so, as we argue in the discussion section of the submitted manuscript, and this is basically the reason why we claim that carbon isotopes could become a reliable tool for locating DOC sources in landscape. In any case, however, as we cannot prove that this will be true, we agree that the assertion "reliable tool" should perhaps be modulated. Our plan is to add a question mark at the end of section 4.4. subtitle and to remove "Powerful" from this subtitle. Accordingly, the new subtitle of section 4.4. would become: "Carbon isotopes: a Reliable Tool for Locating DOC Sources and Studying DOC Transport Processes in Landscapes?"

Referee #1: How easy/difïňĄcult 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? Lambert et al.: The response to this question quite clearly depends on the relationship existing between the size of the internal isotopic variability of each end-member and the external isotopic shift existing between each end-member. In the case where the external shift is small as for example in the case of storms events 5 and 6 (see Fig. 10 of the submitted

manuscript) which occurred when the variations in δ13C between the upper and lower soil horizons was small (<1‰, the internal variability of δ13C values in end-members could well have reached or exceeded the external isotopic shift, making it difficult to calculate end-member contributions using the isotopic tool. This is basically why in section 4.2. we did not use storm event 5 and 6 isotopic data for the purpose of calculating the relative proportion of upper and lower wetland soil horizons to the stream DOC flux. However, the situation becomes different if the isotopic variation between end-members becomes larger than the internal isotopic variability of each end-member. This is the situation that occurred during storm events 2, 3 and 4, when the isotopic variations between DOC circulating through the upper and lower soil horizons was in the range 1 to 1.5‰İn fact, the results obtained during our previous study on the isotopic composition of DOC in the Mercy soil horizons (Lambert et al., 2013, Water Resources Research 49, 1–12; doi:10.1002/wrcr.20466) show that the isotopic variability in both the upper organo-mineral and lower redoxic soil horizons as calculated from the variation between data obtained on soil waters collected from three spatially remote water traps located in each soil horizon was of the order of $\pm$0.1 δ13C units. In this case, the isotopic mixing method can be used to calculate end-member proportions, the important point being to accompany the results of uncertainties based on a sensitivity analysis. This is what we do in section 4.2 of the submitted manuscript where we point out that changing the isotopic composition of the organo-mineral DOC end-member by 0.1‰ will change the proportion of this horizon to the stream DOC flux by 10%, the important point being however that this shift will not change the fact that this soil horizon was by far the main DOC source during storm event 4. Considering the use of carbon isotopes to distinguish between wetland-born and upland-born DOC, we wish to stress that the isotopic variation between these two sources is quite large, being of ca. 3 δ13C units. Although we agree that it is to be recognized that the value of the δ13C of the upland DOC reservoir is not precisely known, we stress that the potential internal variability one can deduce for this reservoir from the available database turns out to be much lower than the above external variation of 3 δ13C units, being of

±0.6 δ13C units as established from the standard deviation of the isotopic analyses of upland soil, water extractable organic carbon. Obviously, this uncertainty on the isotopic composition of upland DOC is a cause of uncertainty with respect to the absolute contribution of upland soils to the stream DOC flux one can calculate using the isotopic database. However, the important point here is that, whatever its extent will be, this uncertainty will not affect the important conclusion stemming from this study and that we point out in the abstract and conclusion of the submitted manuscript, namely that the proportion of the upland DOC reservoir to the stream DOC flux was decreasing during period B, thereby providing evidence of the size-limited character of this reservoir. Anyhow, to the extent that this issue of the impact of uncertainties on the conclusions one can draw from the present study is an important issue, a sensitivity analysis of the role of the likely internal isotopic variability of the upland DOC reservoir on the relative contributions of wetland and upland DOC reservoirs to stream DOC will be included at the end of section 4.2.

Referee #1: The authors do a ïňĄne job of noting that 13C-DOC is only powerful if measured at hi-resolution as done here, but I think that this qualiïňĄer 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.

Lambert et al.: OK. We will modify the manuscript accordingly.

Figures

Referee #1: There are quite a few ïňĄgures. Some can be consolidated (e.g. Figure 4 is somewhat redundant since discharge is shown in other ïňĄgures) and some data

presented in ïňĄgures is not discussed in the text (e.g. Figure 5b). Is it necessary to show each of the storms in each ïňĄgure to tell the story or could some of this be consolidated into a table?

Lambert et al.: We plan to modify the manuscript as follows to account for these comments and suggestions: 1) Remove Fig. 4 as this figure appears redundant with Fig. 3 2) Move Fig. 5b into a Supplementary Information section as the data presented in this figure are not essential to understand the carbon story that stem out from this study, and consequently not thoroughly discussed in the paper. 3) Consolidate Figs. 5a and 6 in the new Fig. 4. Fig. 5a becoming Fig. 4 a and Fig. 6 becoming Fig. 4b; we agree that it may be not necessary to present DOC vs. discharge relationship for each of the storms as all relationships are similar; we plan accordingly to present examples for two storms, only (e.g. storms 3 and 4), in the new Fig. 4b (see below). 4) Provide a table in the Supplementary Information section resuming the SOC, WEOC and DOC data 5) Figure the discharge using a darker grey line in Fig. 10. 6) Compile the whole dataset of stream chemistry during storms in a table that will be inserted in the Supplementary Information section.

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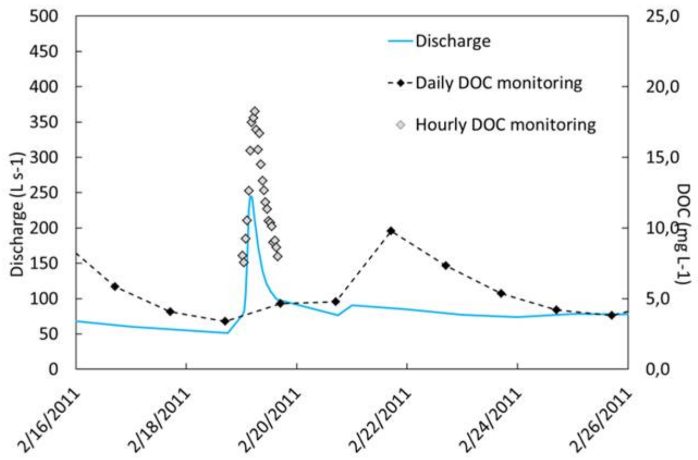

Fig. 1. Evolution of DOC concentrations of daily and hourly sampling in stream at the Kervidy outlet. Water discharge is also given in order to highlight the storm event period.

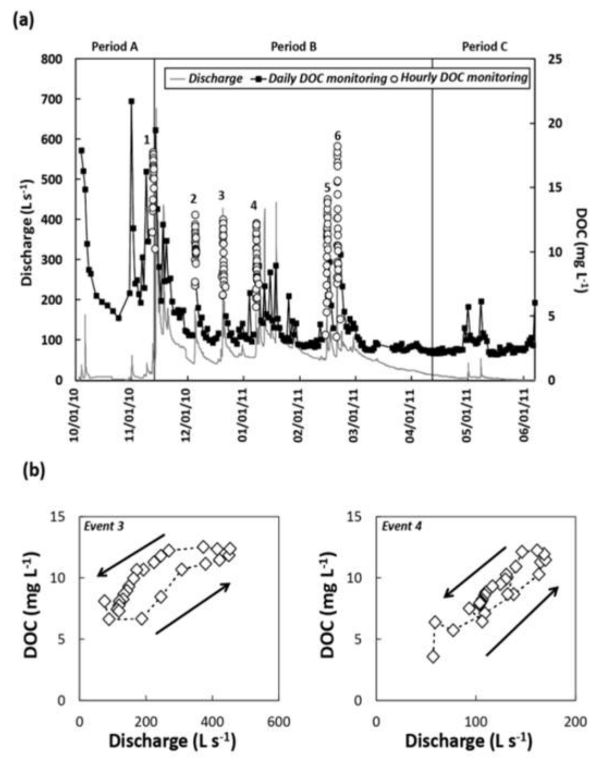

Figure 4

Fig. 2. Proposed new Fig. 4