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Biogeosciences Discussions

Interactive comment on "Dissolved organic carbon dynamics in a UK podzolic moorland catchment: linking storm hydrochemistry, flow path analysis and sorption experiments" *by* M. I. Stutter et al.

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Response to reviews bg-2011-451D Interactive comment on "Dissolved organic carbon dynamics in a UK podzolic moorland catchment: linking storm hydrochemistry, ïňĆow-path analysis and sorption experiments" by M. I. Stutter et al. Anonymous Referee #1 Received and published: 3 February 2012 This manuscript presents an interesting study on DOC dynamics in a small Scottish catchment. The detailed consideration of not only DOC but also the characteristics of the carbon as quantiïňĄed by SUVA and the DOC/DON ratio seems especially valuable. The authors claim that the observed

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Interactive Discussion

Discussion Paper

dynamics cannot be explained by hydrological controls as done by previous studies, but that DOC biogeochemistry must be considered in more detail. While this certainly might be true, and thus a valuable contribution to current DOC-catchment research, I have to raise some important issues: 1) The manuscript is mainly based on just two events. These events have different antecedent conditions as the authors highlight, but also occurred in different seasons (and different years) and were caused by different amounts of rainfall. Given this variability I ïňĄnd it difíňĄcult to draw too many conclusions on the difference between these two events. More events would certainly be needed to support the ïňĄndings. From the text it sounds as if more events might have been sampled; if so, it would certainly be useful to include these data. Whilst we only have two events here to consider in detail these were sampled to maximise the different antecedent conditions and look in detail at the nature (quantity and quality of the DOC) delivered to the stream as a result of these different catchment conditions. Our paper therefore should be taken as the initial evidence for a new idea that biological processing must be superimposed onto hydrological delivery processes to explain the nature of the stream DOC. We therefore put these ideas and this preliminary study forwards to encourage further study. We have now sought to make it clear that we are offering preliminary evidence towards this goal of further study by stating this in the abstract and conclusions. The paper is explicit also now in the discussion that the weight of evidence from these two storms is limited, yet they frame perhaps the 'extremes' of biogeochemical processing periods for DOC in the catchment. We do not have further storms analysed for this stream to add into this debate. 2) The spatial coverage of the measurements is rather limited. Basically the integrated catchment response (streamïňĆow) is related to the point observations at a few points. Furthermore, for one central variable, namely groundwater levels, no observations are shown. This data limitation makes it difíňĄcult to test different possible hypotheses about the DOC dynamics and their controls. In particular the potential interaction between different landscape units cannot be fully assessed. While I can ïňĄnd the conclusions of the authors reasonable, one could, thus, also come up with alternative explanations, which

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cannot be falsiïňĄed based on the available data. Our spatial coverage of catchment source waters contributing DOC comprised three locations for soil waters in O, B and C horizons (not all horizons at each location though), a single rainfall sample location, two different spring waters, then three transects totalling 32 points to evaluate differences in topsoil DOC between hillslope and riparian soils. We have now added a new figure to exand on the results of the soil transects previously given as a summary figure and a new text end of section 3.3. We consider this to provide a reasonable representation of spatial variability for key soil types in the 1 km2 catchment. The principal end member composition not covered by this sampling was deep peat subsoil and it is generally accepted that flows from acrotelm peats are limited due to low hydraulic conductivities. 3) There is quite a number of recent publications on DOC catchment dynamics and their hydrological controls. The contribution of the presented manuscript would be clearly of more value if the authors could better link and compare their work to other recent studies such as, for instance, the work of the groups at Western Ontario (Irena Creed et al), Montana State (Tenderfoot study, Brian McGlynn et al), Aberdeen (Chris Soulsby / Doerthe Tetzlaff et al) or SLU Umeå (Krycklan Catchment study, Hjalmar Laudon, Kevin Bishop, Jan Seibert et al). Better and more up to date references are now included and discussed. 4) The end members are not clearly deïňĄned. Water from the O or B horizon could also be groundwater, couldn't it? We considered spring water in this deeply weathered geology to be best representative of deeper ground waters. We also characterised waters from the O, B horizons by tension lysimetry and from O, B and C horizons of soil pits collecting free-draining runoff from those soil layers. As the reviewer notes water from O and B horizons could be groundwater which may be resurgent into upper soil layers from deeper areas anywhere in the catchment and additionally is also often poorly defined in such studies. However, we would consider that the soil waters characterised from the O, B and C horizons would have generally been of sufficient residence time in those horizons to pick up the chemical signatures of those horizons and contribute usefully to the interpretation of end members (Table 4 and Figure 6). This would be especially the case for O and B soil waters sampled

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by tension lysimeters. A note about GWs is added at the end of section 4.1. 5) Previous studies have found riparian zone dynamics to be of importance. Here the authors found no signiïĭňĄcant difference in DOC between the riparian and hillslope sites for one snapshot sampling (for which measurement details are not fully clear), but this does of course not mean that they contribute in the same way. The important issue is the interplay between different landscape units and the ïňĆow pathways within those, including the question of connectivity. The lack of difference between riparian and hillslope topsoil waters in terms of the chemical signatures used (Fig. 5) makes the EMMA approach difficult to use to define the (potentially important) role of contributing waters from riparian areas. These areas have been found especially important during overall drier conditions across wider catchment areas. One aspect to test would be whether riparian gleyed soils have distinct DOC compositions from hillslopes (contrary to what we observed), or that riparian soils have non-unique DOC compositions, but continue to act as DOC sources during drier summer months (as probably occurred in this study in Aug, but could not be tested by the EMMA approach). The only way to add this in would be by soil hydraulic monitoring/modelling of water contributions and this was outwith the scope of this present study. New text is added to the discussion in the middle of section 4.1. 6) More observation, especially also in some spatially distribution, would be needed to better test the hypotheses raised in this manuscript. Without such data, one has to be more careful with conclusions on the importance of different hydrological and biogeochemical processes. We have noted this as a restriction of the study in the discussion and in summing up. Particularly we would advise future studies to concentrate on (a) soil spatio-temporal data differentiating hillslope organo-mineral soil DOC contributions against wetland peat and riparian gleyed soils, (b) hydrological and biogeochemical 'transition periods' between the drier summer storms when smaller areas of the catchment contribute water and the autumn when the whole system is rewet and connected and has a considerably different degree of biological processing of DOC. Minor comments: P214,12ff: could you comment on the local topographic setting of these measurement locations? The soil solution samplers and soil moisture monitor-

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ing is on a 5 degree slope on a broad ridge, with soils peaty to humus iron Podzols. New text added in section 2.2. P216, 16: as you introduce most other abbreviations, it would be suitable to do this also for DOM. DOC is used instead now for consistency. P220, 3ff: the information about the two events might better ïňĄt in the material part. In anyway, please clarify the rainfall amounts of the two events, I could not ïňĄnd this information. Total event rainfall was 15 mm (Aug-05) and 22 mm (Nov-06). Now included in the text. P220, 17ff: please provide the time period for which the 1.5 respective 5.7 mm are computed, ïňĆow should have the unit mm/time. These runoff sums are determined from the time of flow rise to the midnight at the close of the storm day (when flow was deemed to have reached almost steady decline rate (end of period for each storm in figure 2). P222, 23: this should be mentioned already in the method section. How was this sampling done, at which depths, spatial resolution. This is already in P215, L19-26. This will be made more obvious in the text. Table 4: Can you explain the high value of DOC in the B horizon pit water? This is likely to be due to preferential flowpath transfer of O horizon runoff into the B horizon just upslope of the gravity draining runoff water collection face. So this does not really indicate the true nature of B horizon matrix flow. However, this composition was not used as an end member in the EMMA approach (see Fig. 6) so does not affect the results of Fig. 7. Note now added in section 3.3. Fig 1 : could you show land cover (peat!) in this map New panel (b) added to Fig. 1. Fig 2: Hourly rainfall has the unit mm/h Ok, this will be changed. Fig 3 add text about dates on x-axis. Ok, this will be changed.

W. Worrall (Referee) Received and published: 26 March 2012 Review of Stutter et al. This is a good study that well deserves publication. I have a few general comments and then some more speciïňĄc comments below. General comments i) The paper seems to want to comment on the dynamics of peat soils whilst it is based upon an organo-mineral soil. I think the authors should revisit the places in the manuscript where they make this link and be certain it is not stretched too far. ii) The paper really only presents data from two events and so it is not surprising that they are different and although the level of detail in which each event is considered is admirable the au-

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thors should be cautious about concluding to strongly when compared to studies that have considered statistically powerful numbers of events. i). In the response to the first reviewer's comment number 2. It is true that deep peats are a major soil type (40% of the catchment area). However they are not represented by soil solution end member which was clearly defined in space and time. Our argument against this was that acrotelm peats were unlikely to contribute waters from other than shallow surface horizons. In our study O horizons of the peaty Podzols are the surrogate for the surface horizons of peat. The differences in how the Podzol and deep peat topsoils react hydrologically is discussed with reference to Clark et al. (2008). ii). This is answered by the response to the first reviewer's comment number 1. We have added a caveat on this into the end of the abstract and in the discussion. Our intention is that this paper presents new results to justify further examination that biogeochemical processing is at least as important as hydrological delivery in determining variation in DOC compositions. SpeciïňĄc comments P211 line 19 – incomplete sentence P212 line 1 – This sentence implies that the result of this paper is already known in the literature? This section describes what the current state of knowledge in the hydrological processes for the different types of moorland systems. This is trying to portray a science area dominated by hydrological impacts on DOC quality and quantity, whereas we then add to this with our biogeochemical processing argument. P212 line 17 – sentence implies there are examples and so these should be cited. There are two key references given here already. P212 line 21 – please can you break up this sentence into more palatable parts. OK this will be done. P213 line 4 – what is meant by biogeochemical processing? By biogeochemical processing we mean a combination of processes where geochemistry (sorption and alteration by interaction of solutes with soil surfaces) and biological (where mainly microbial processing and plant exudation) interact to alter DOC amounts and compositions. This is clarified in the text at the beginning of the last paragraph of introduction. P215 – can we have the percentile ïňĆow of the antecedent ïňĆow conditions? This was 86%ile and 40%ile flow for Aug and Nov, respectively (based on the period start of Aug-05 to end of Nov-06). P217 line 9 – the bracket

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needs re-phrasing as I don't know which reference has the full equations. This is now done. P217 line 15 – how were endmembers deïňĄned? In EMMA a PCA is used, was that done here? This was determined by graphical interpretation (as in Fig. 6). P217 line 26 – does deïňĄning seasonal variation mean that you accounted for it, if so how and did it ïňĄt well to the data? Differences were looked for between Aug and Nov concentrations of DOC in the source waters. This was found significant for O and B horizon piezometer solutions and different end member concentrations were used in the analyses for the different periods. The variation of the end members was also quantified and accounted for in a Monte-Carlo approach to define the 10 and 90%ile bounds of the end member contributions. P218 line 10 - remove phrase "August 2005 and November 2006". This is done. P219 line 21 – this sentence begs a reference. Kalbitz et al., 2000 is applied here. P220 1st para – was soil moisture data mentioned in the methods? Yes, briefly in section 2.2. P221 line 23 – "This could show : : :", this what? Change in Ph, now stated. P222 last para – not sure any of this was in the methods. Yes. It is at the end of section 2.4. P224 2nd para – should this not be in the past tense? This is done. P226 line 1 – not a sentence. Now amended. P226 line 12 – undeïňĄned acronym. C-Q now defined as Concentration-Discharge P226 - numbered points are poorly punctuated, eg. some need question marks? Now amended. P229 line 6 – not too surprising that two events are different from each other. This sort of question could only be answered if there were more events. The language of this has been toned down now to be less conclusive and the caveats summarised. There is new text in two blocks to explain the novelty of the present study in relation to what has been focussed on before. P231 line 1 – poor English. Now altered. P231 2nd para – should also included impact upon ïňĆocculation during water treatment. Done P233 1st para – given that only two events were considered the results discussed here are somewhat inevitable and I don't think this has been demonstrated. New text has been used in the conclusion to highlight how these results and such methodologies should be further used to explore the strength of biogeochemical processing over hydrological controls.

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