Interactive comment on "Dynamics, chemical properties and bioavailability of DOC in an early successional catchment" by U. Risse-Buhl et al.

U. Risse-Buhl et al.

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A. Butturini (Referee)

Comment: The research by Risse-Buhl and colleagues describes the DOC changes, bioavailability and chemical properties along a hydrological flow path in an artificial catchment. I found the report extremely interesting and attractive. In my opinion the strength of this work is the DOC bioavalability experiments. However I had some difficulties to understand the experimental design and interpretation of results. On the other hand, the most weak part is that focus on carbon mass balance. Below I detailed all questions and doubts raised reading the manuscript.

Comment: Study site: From literature I observed that chicken Creek is a "rectangular" catchment (fig. 1 in Hollander et al., HESS, 13: 2069-2094, 2009). It would be useful for a reader to generate a map of the catchment that indicates the exact position of the sampling sites into the catchment. This might help the reader to have a visual perspective of the water hydrological flow path from the soil to the pond.

Response: We will add an illustrated aerial photograph showing all sampling points as suggested by both Referees (please attached Fig. 1).

Comment: DOC bioavailability: In the Discussion, at the beginning of the section 5.2, authors reported that during incubations, "an initial period characterized by declines in DOC concentrations and relatively high respiration rates between days 0 and 14. . .[ ]. . ..(Fig. 5)." From Fig. 5 the initial DOC decline is clear for incubations with soil and stream sediment microbial communities. Conversely, it is ambiguous the DOC decline when microbial community from pond was used as inoculum. In addition, from Fig. 5 (panels a, b, and c) DOC concentration in pond water (gray diamonds) decreased clearly only in panel b. Therefore I interpret that BDOC for pond water was virtually null in two cases out of three. Similarly, for subsurface (gray squares), DOC decrease is evident in panel a but not really in the other two panels. In synthesis, I detected DOC a robust decline for "upwelling groundwater" only (soil solution is also clear but it was estimated only in one treatment, figure 5a).
I conclude that microbiota from soil and stream sediments are more (approx.) effective in DOC degradation than that from pond water and that pond water seem to me more recalcitrant that that of "upwelling groundwater". Nevertheless, authors stated that "DOC bioavailability was similar across all water types" and focused their explanation on changes on DOC aromaticity, molecular weight and carbohydrates. My questions are: How BDOC was estimated? How change SUVA, a250/a365 ratio and carbohydrates content in the four waters types during incubations?

Response:

- DOC in subsurface and pond water tended to be less bioavailable than that from soil solution and upwelling groundwater. However, the apparent differences among water types or microbial communities were not significant, perhaps partly because of rather large variation among replicates. We will clarify this point in the revised manuscript.
- The fraction of bioavailable DOC was estimated by repeated measurements of the DOC concentration at days 0, 7, 14, 42 and 70 and data were fitted to an exponential decay model to calculate the fraction of recalcitrant (DOC_r) and bioavailable ($1\text{-}DOC_r$) DOC from the total DOC pool:

$DOC_t = DOC_r + (1 – DOC_r) * e^{-k(b) * t}$
where k(b) is the decomposition rate coefficient for the bioavailable carbon, and t is time in days. We will add this information to the procedure described on page 1023.

- We used parameters such as $SUVA_{254}$, the a250/a365 ratio, carbohydrate content and isotopic ratio to generate the NMDS plot shown in Fig. 6. These parameters characterize DOC of a given water type at a certain point in time (i.e. day 7 or 70). The main temporal changes of these parameters are indicated by grey arrows in the NMDS plot. In the revised manuscript, we will indicate all temporal changes in the NMDS plot and better describe these changes in the Results section.

Comment: Furthermore, authors stated "high respiration rates between days 0 and 14" (pag 1030, line 14). However, from figure 5, the temporal patter of the respiration rate (0<t<14 days) in soil inoculum (fig. 5 panel d: it gradually decrease) is opposite to that observed in stream sediment inoculum (Fig. 5 panel e: it gradually increase). This is an interesting result. Do you have some hypothesis that might understand these different dynamics in respiration? Does the respiration increase observed at the beginning of the panel e (especially in pond water!!!) a response of new high bioavailable DOM release of microbial origin? This new DOC release might compensate the DOC consumption and determines a low/null net DOC changes (see panel b).

Response: We will draw attention to this difference in a revised Discussion and briefly discuss a possible explanation: The bacterial abundance in treatments inoculated with the stream microbial community was one order of magnitude lower than in treatments inoculated with the microbial community from soil and pond water. This is a plausible simple reason why the respiration rate of the stream microbial community was initially lower than those of the two other microbial communities.

Comment: In the description of equation 4 it is necessary to add the units of the parameters. Furthermore, it is necessary to describe in more detail how data fit this model: are the fits statistically significant?

Response: Please see response to the next comment for the units. The requested detail on the model fit will also be added.

Comment: How is estimated the parameter R (DOM recalcitrant fraction)?

Response: The fraction of recalcitrant DOC (originally referred to as R, now called DOC_r in the revised ms) was estimated by regression analysis of DOC concentration vs time (days 0, 7, 14, 42 and 70) according to an exponential decay model with two carbon fractions (see also response further above):
$DOC_t = DOC_r + (1 – DOC_r) * e^{-k(b) * t}$,
where DOC_t is the DOC fraction remaining from the total DOC pool (expressed in %), DOC_r is the recalcitrant DOC pool (%), ($1-DOC_r$) the bioavailable DOC pool (%), k(b) is the decomposition rate coefficient for the bioavailable carbon (day^{-1}), and t is time (d).We will add this information to the procedure described on page 1023 of the manuscript.

Comment: DOC age: In the last paragraph of the introduction, authors "hypothesized that DOC in the catchment originates primarily from ancient organic matter of the Quaternary substrate, that DOC of ancient origin is the primary substrate for microbial activity" (pag. 1016, line 20). It is evident from results, that old organic matter is "a minor source of DOC" (pag 1028, line 14). However, the hypothesis that old DOC is a relevant substrate for microbiota is not discussed. I have just read that "preferential microbial degradation or sorption of ^{13}C enriched compounds such as recently formed carbohydrates". It would extremely interesting to discuss in more detail why your initial hypothesis is not confirmed by results.

Response: Both reviewers noted seemingly contradictory statements about the age and sources of DOC. The likely reason for our misleading statements is that DOC is a mixture of both recent C from primary productivity in the experimental Chicken Creek catchment and of old C originating from the Quaternary substrate, whose 14C age was found to be 3,000-15,000 years, although the substrate itself was deposited as a terminal moraine much earlier during the Saale-glacial period. We will clarify this ambiguity by estimating the relative contribution of recent and old C by using a mixing model:

$\Delta^{14}C_{DOC} = f_{subst} \times \Delta^{14}C_{subst} + f_{atm} \times \Delta^{14}C_{atm}$

where f_{subst} and f_{atm}, respectively, are the contributions of the Quaternary substrate and vegetation representing current atmospheric CO_2. The $\Delta^{14}C$ values measured in the Chicken Creek substrate (-317‰ and -862‰, corresponding to an age of 3000 and 15,000 yrs) and DOC in soil solution (-280‰ and -297‰, corresponding to an age of 2600 to 2800 yrs) shows that the estimated contribution of recent C was 10% and 60%. These contributions of recent C are likely to be overestimates because DOC leached from a substrate is usually younger than the substrate itself, due to preferential release of younger C components (Fröberg et al., 2003, Geoderma; Sanderman et al., 2008, Biogeochemistry). Additional uncertainty arises from the $\Delta^{14}C$ values of the substrate used to construct the catchment with unknown contributions of charred ^{14}C dead components (i.e. C lacking a ^{14}C signal because it is >50,000 yrs old; Arnold and Libby, 1949, Science) and more recent C. We cannot further elucidate the sources of DOC within the present study but will expand the discussion about the identification of DOC sources and its limitation in the revised manuscript. The estimated DOC sources will be reported consistently throughout the manuscript.

Comment: Water/DOC fluxes: Equation 3 is imprecise. Note that the left hand is a flux (Q_{gs}), meanwhile the right hand is a mix of fluxes (P_{pond}, ET_{pond}, Q_{pond}) and volumes (δV_{pond}). In my opinion the equation water mass should be rewritten in the following way: $dV_{pond}/dt=Q_{gs}+P_{pond}-ET_{pond}-Q_{pond}$

Response: We have revised the mass balance following the suggestions of the reviewer (see response to the next comment).

Comment: It remains confused to me the approach to estimate the DOC input. According the text pag. 1022, line25), DOC input is "calculated multiplying Q_{gs} by mean annual DOC concentration measured at the weir and the H-flume". Are the discharge contribution of stream (Q_s) and groundwater Q_{gw}) identical (i.e. $Q_s = Q_{gs}$)? If Q_s, Q_{gs} and their DOC concentrations are known, DOC input is the sum of the two DOC fluxes? (i.e. $DOC_{input}= Q_s * DOC_s+ Q_{gs} * DOC_{gs}$). It is necessary to explain better how DOC inputs fluxes are estimated.

Response: We have improved the water and DOC budget by calculating the water budget on a daily basis and by using DOC concentrations measured in daily collected samples that were pooled over two-week periods. Furthermore, we have clarified the calculation of water and DOC fluxes as follows:

"A rough DOC budget for the pond was established by first estimating the water budget of the pond followed by multiplying the fluxes with measured DOC concentrations. The water budget of the pond was calculated on a daily basis for the years 2008 to 2010 as:

$$dV_{pond}/dt = Q_{sgs} + P_{pond} - ET_{pond} - Q_{pond} \qquad (3),$$

where dV_{pond}/dt is the in water-volume change of the pond obtained by monitoring the water level, Q_{sgs} is the inflow into the pond by stream water, ground water and subsurface water, P_{pond} is the precipitation on the pond surface, ET_{pond} is the estimated evapotranspiration from the pond surface, and Q_{pond} is the measured outflow from the pond. Inflow via surface runoff (stream water), ground water and subsurface water could not be separately quantified. Therefore, Q_{sgs} was used to calculate the DOC inflow into the pond by multiplying the mean DOC concentrations determined every second week at the H-flume and the weir by the water inflow (Q_{sgs}) over the respective sampling periods.

Likewise, DOC concentrations determined in daily collected samples pooled over two-week periods of the bulk precipitation (P_{pond}) and the pond outflow (Q_{pond}) were multiplied by the precipitation (P_{pond}) and pond outflow (Q_{pond}) cumulated over the respective sampling periods. Finally, DOC removal in the pond was calculated as the difference between total inputs and ouflow as:

$DOC_{removal} = dDOC / dt = Q_{sgs} * DOC_{sgs} + P_{pond} * DOC_{precip} – Q_{pond} * DOC_{pond}$ *(4)."*

Comment: Finally, the DOC mass balance does not take into account the DOC release generated into the pond (mainly by photoautotrophs). This is an important aspect. If this autochthonous DOC input cannot be quantified, in my opinion does not make any sense estimate an incomplete DOC mass balance in pond. Is the apparent decrease of the % removal (from 73 to 29%) the consequence of the increase of the contribution of DOC release from submerged macrophytes? In my opinion these results are the weakest part of the manuscript. If relevance of autochthons DOC cannot be estimated and integrated in the balance, I would suggest removing this section. Removal of this section does not really change the main results of this study.

Response: It is correct that our mass balance ignores potentially important DOC fluxes WITHIN the pond. That is, it gives an account of the net fluxes to and from this pond. This estimate is useful in view of the fact that similar information on DOC fluxes from terrestrial to aquatic systems is notably scarce (e.g. Goodman et al., 2011, Journal of Geophysical Research). Therefore, we prefer keeping this section in the manuscript. However, we will amend it as follows (pages 1031-1032):

"The estimated DOC input to the pond by stream, ground and subsurface water (16 to 62 g DOC m^{-2} y^{-1}) is within the range of mature ecosystems (e.g. Hagedorn et al., 2000; Raymond and Saiers, 2010). In the pond, the DOC mass balance suggests a net removal of the received DOC on the order of 30 to 50%. This is more than can be readily accounted for by microbial utilization, given that an average of only about 20 % of the DOC was found to be bioavailable during our DOC incubation experiment over 70 days. Potential reasons for the discrepancy could be photomineralization, flocculation (e.g. von Wachenfeldt & Tranvik, 2008) or adsorption of DOC to surfaces. Additionally, periphytic and benthic bacterial communities present in the pond but not during our incubations could be more effective at utilizing the imported DOC than the suspended and biofilm bacterial communities considered in our incubation experiments. Irrespective of the predominant removal processes, it is clear that considerably more DOC was removed in the pond than implied by our mass balance, because phytoplankton and macrophytes generated additional DOC within the pond that was not considered in our mass balance. Detailed measurements taking account of within-pond DOC release and microbial carbon utilization and fate, both in the pond water column and other ecosystem compartments would be needed to refine our budget and identify the principal mechanisms responsible for the observed DOC removal in the pond."

Minor questions:

Comment: In Material & methods section, authors identified four water types: 1) Soil; 2) Upwelling groundwater; 3) Subsurface water in the alluvial fan; 4) Pond. Therefore, what is the "perched flow" (line 11, page 1018, Figure 1b)?

Response: The perched-flow sites will be shown in the added aerial photograph and renamed to 'sites of ground water – surface water exchange'.

Comment: Figure 5d, e, f: Respiration: units?

Response: Units are mg O_2 per respiration chamber, which corresponds to the combined oxygen consumption by microbes in 47 mL of water and 11.9 cm^2 of biofilm. The unit given on the y-axis will be amended.

Literature cited

Arnold, J.R., and Libby, W.F.: Age determinations by radiocarbon content: checks with samples of known age. Science, 110, 678–680, 1949.

Fröberg, M., Berggren, D., Bergkvist, B., Bryant, C., and Knicker, H.: Contributions of Oi, Oe and Oa horizons to dissolved organic matter in forest floor leachates, Geoderma, 113, 311-322, 2003.

Goodman, K.J., Baker, M.A., and Wurtsbaugh, W.A.: Lakes as buffers of stream dissolved organic matter (DOM) variability: Temporal patterns of DOM characteristics in mountain stream-lake systems, J. Geophys. Res.-Biogeosciences, 116, G00N02, 2011.

Hagedorn, F., Schleppi, P., Waldner, P., and Flühler, H.: Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments - The significance of water flow paths, Biogeochemistry, 50, 137–161, 2000.

Raymond, P. A., and Saiers, J. E.: Event controlled DOC export from forested watersheds, Biogeochemistry, 100, 197–209, 2010.

Sanderman, J., Baldock, J.A., and Amundson, R.: Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils, Biogeochemistry, 89, 181-198, 2008.

von Wachenfeld, E., and Tranvik, L.J.: Sedimentation in boreal lakes - the role of flocculation of allochthonous dissolved organic matter in the water column, Ecosystems, 11, 803–814, 2008.

Figure

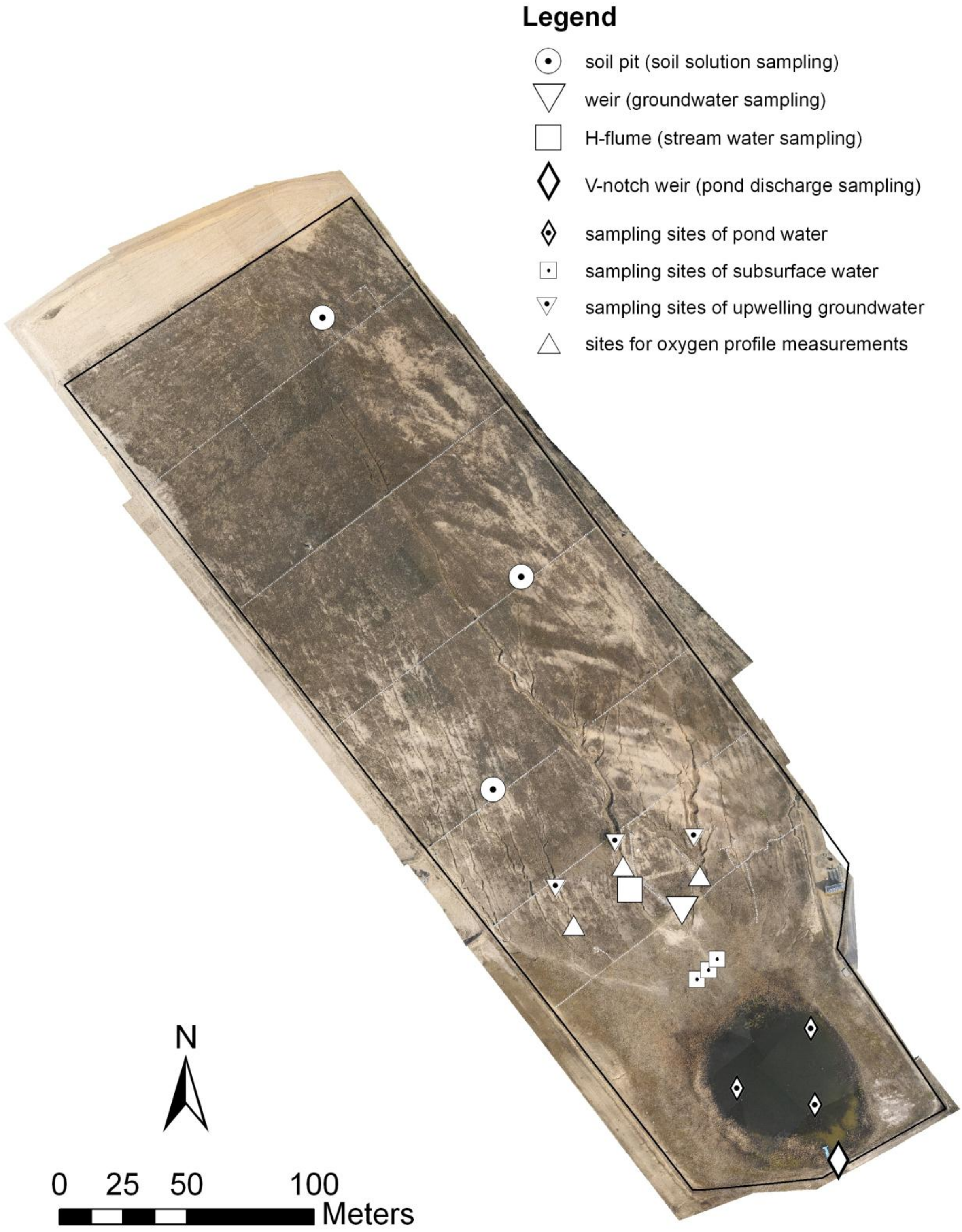

Fig. 1. Aerial photograph of the Chicken Creek catchment that indicates the position of the sampling sites of soil solution, ground water, stream water, subsurface water and pond water to estimate DOC bioavailability and DOC flux, and sites of oxygen profile measurements.