

## ***Interactive comment on “Dissolved organic matter characteristics of deciduous and coniferous forests with variable management: different at the source, aligned in the soil” by Lisa Thieme et al.***

**Lisa Thieme et al.**

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Dear John Van Stan, thank you for your detailed review of our manuscript. In the following, we hope to adequately address your constructive comments and questions.

"Biodegradability measurement – were the samples spiked with nutrients to achieve N, P > Redfield limitations? All other details of the bioincubation tests look good. But, if we want to test the biolability of the DOC, then it is important to release the microbes from as many common limitations as possible (e.g. the authors set an optimal, controlled temperature: page 6, line 2). As a test of how much DOC is utilizable by microbes, this is a test of DOC quality, not an environmental rate at which one would expect the

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DOC to be utilized. Thus, ensuring the microbes are released from nutrient limitations, arguably, should be standard to allow comparison of DOC quality across studies, sites, between research groups, and independent of differences in C:N:P across environments. If this was not done, I recommend the authors briefly discuss the implications (biodegradation of DOC could have been constrained)."

No additional nutrients were added to our incubation experiment. It was, however, possible to check concentrations of nitrogen (total inorganic N) and phosphorus (ortho-P) in the samples prior pooling for the incubation test.

Calculating maximum nutrient demands for the consumed carbon in our samples by using values for bacterial growth requirement of N and P suggested by Fellman et al. 2008b (40  $\mu\text{g N l}^{-1}$  and 8  $\mu\text{g P l}^{-1}$  to satisfy growth requirements using a bacterial growth efficiency of 0.4 and a bacterial molar ratio for C:N of 10 and C:P of 50), we found that for throughfall (TF) and litter leachate (LL) samples, constrained biodegradation due to nutrient limitation is not likely. Low concentrations of phosphorous in stemflow (SF) samples may have limited biological degradation.

We will expand the discussion paragraph at Page 17 Line 20 as followed.:

Beside other factors, nutrient availability can affect biological degradation in samples of ecosystem fluxes. In our study, no additional nutrients were added to compensate for possible limitations. We calculated maximum nutrient demands for the consumed carbon in our samples by using values for bacterial growth requirement of nitrogen and phosphorous suggested by Fellman et al. (2008b) and measured concentrations of N and P in the solution samples prior to pooling for the incubation experiment. The results suggested that constrained biodegradation of DOM due to nutrient limitation in TF and LL samples was not likely. Low concentrations of phosphorous in SF samples may, however, have limited biological degradation and the potential %BDOC could be higher than measured, thus even increasing the difference in the biodegradability of DOM between the samples of SF and those of TF and LL.

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We will add the table you can find in the supplement to this reply as new Table S5

"There are no measurements/estimates/tests of soil geochemical interactions with infiltrating DOM. As indicated above, biodegradation will likely be limited in natural settings (compared to the bioincubation tests – even for bioincubation tests without the nutrient spiking). I noticed that the other reviewer also believed this to be a shortcoming of the manuscript. As gathering more data along this vein would be difficult (and is, of course, not possible for storms already past unless it was collected at the time), I recommend the other reviewers' solution: provide more discussion of geochemical controls over DOM processes within soils. Perhaps the discussion could have subsections dedicated to biological factors and geochemical factors."

As this comment is similar to referee 1 we give the same answer.

Being part of the DFG priority program 1374 offered the unique opportunity to access various kinds of information about the study sites. Therefore, it was possible to add additional geochemical information like soil texture and elemental composition. We will add the new table S2 you can find in the supplement to this reply to the supporting information.

To assess whether geo-chemical processes controlled the DOM quality in our study, we additionally examined the relation between changes in DOC concentration and the ratio between organic carbon content of the mineral soil and the sum of its oxalate-extractable Fe- and Al-content ( $OC/[Fe+Al]$ ) and compared the results with findings of Kindler et al. (2011).

We will add Fig.1 of these reply as new Fig.2 to the manuscript

caption: Figure 2: Percentage reduction of DOC concentrations between topsoil (TOP) and subsoil leachates (SUB) as a function of carbon saturation of pedogenic Fe- and Al-(hydr)oxides. For the Hainich sites (this study), the reduction of DOC concentrations decreased significantly with increasing  $OC/(Fe+Al)$  ratio (reduction = 84% –

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$34\% \cdot OC/(Fe+Al)$ ;  $p = 0.027$ ,  $r = 0.86$ ). We found no significant correlation for the Schorfheide sites (this study). The relative increase of DOC concentrations at high OC surface loadings was likely caused by a concentration effect because of evapotranspiration, while surface sorption was negligible. The shown site names refer to Kindler et al. (2011).

We therefore will expand the discussion section as follows:

Page 13 Line 13: In the study of Kindler et al. (2011), the retention of DOC in mineral soil, expressed as percentage reduction of downward DOC flux, was closely related to the ratio between organic carbon concentration of the mineral soil and the sum of its oxalate-extractable Fe and Al content ( $OC/[Fe+Al]$ ). This suggests that the DOC retention in mineral soils is governed by the sorption to the surfaces of Fe- and Al-(hydr)oxides. Furthermore, organic matter sorption decreased exponentially with increasing organic matter coverage of the hydroxide surfaces (Kindler et al. 2011), which suggests that these hydroxides have a limited DOC sorption capacity (our hypothesis ii). In contrast to the findings of Kindler et al. (2011), we compare DOC concentrations, not fluxes. In order to test whether the data of our study fit the findings of Kindler et al. (2011), we plotted changes in DOC concentrations reported by Kindler et al. (2011) together with the data of this study against the ratio of  $OC/(Fe+Al)$  in one graph (Figure 2). Different from fluxes, which always decreased with increasing soil depth in the Kindler et al. (2011) study, DOC concentrations increased with increasing depth at the Hainich sites with the highest  $OC/(Fe+Al)$  ratios of all study regions (Figure 2). This increase in concentrations can be explained by a concentration effect because of evapotranspiration, if the DOC sorption capacity of pedogenic Fe- and Al-(hydr)oxides is saturated. Overall, the retention of DOC in the Hainich soils of this study fitted well to the DOC retention in the European data set of Kindler et al. (2011), who showed that the regional variation in DOC retention can be as large as the variation at continental scale. The concurrent decrease of DOC concentrations and increase of  $OC/(Fe+Al)$  ratios between TOP and SUB ( $p = 0.027$ ; Figure 2), corroborates the hypothesis that

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sorption to pedogenic Fe- and Al-(hydr)oxides controls DOC retention in mineral soils (Kindler et al. 2011). However, the results for mineral soils of the Schorfheide sites did not meet this pattern, as DOC concentrations decreased from TOP to SUB by 33-72% regardless of the OC/(Feo+Al<sub>o</sub>) ratio (Figure 2). At the Schorfheide sites, other processes than sorption to Fe- and Al-(hydr)oxide surfaces likely governed DOC retention. The Schorfheide soils developed from fluvioglacial quartzitic sands covering carbonate-free glacial till. Because of their poor pH buffering capacity, these soils were very acidic (pH<sub>CaCl2</sub> = 3.0 – 3.6 in topsoils). The mean pH values in soil water samples of the Schorfheide sites was 4.5 in TOP solutions, increasing to 5.5 in SUB solutions. This means that Al-(hydr)oxides were dissolved in the Schorfheide topsoils, increasing Al<sup>3+</sup>-concentrations in soil water and leachates. The pH increase to 5.5 along the way from TOP to SUB likely induced a re-precipitation of Al. We assume that dissolved organic matter transported from TOP to SUB co-precipitated together with Al<sup>3+</sup> as described by Nierop et al. (2002) and Jansen et al. (2003, 2005) for acidic sandy soils from the Netherlands. If DOM was immobilized as insoluble metal-organic matter precipitate in B horizons, sorption sites on surfaces of pedogenic (hydr)oxides may be less important.

The following references will be added to the manuscript:

Jansen, B., Nierop, K.G.J., and Verstraten, J.M.: Mobility of Fe(II), Fe(III) and Al in acidic forest soils mediated by dissolved organic matter: influence of solution pH and metal/organic carbon ratios. *Geoderma*, 113, 323– 340, 2003.

Jansen, B., Nierop, K.G.J., and Verstraten, J.M.: Mechanisms controlling the mobility of dissolved organic matter, aluminium and iron in podzol B horizons. *Eur. J. Soil Sci.*, 56, 537–550. doi: 10.1111/j.1365-2389.2004.00686.x, 2005.

Nierop, K.G.J., Jansen, B., and Verstraten, J.M.: Dissolved organic matter, aluminium and iron interactions: precipitation induced by metal/carbon ratio, pH and competition. *Sci. Total. Environ.*, 300, 201–211, 2002.

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"The meaning of DOM "origin" is unclear. For example, in the abstract: "strong significant effects of origin of ecosystem fluxes" – what is the "origin"? (A) Is it the first contact between precipitation and terrestrial surfaces (in the tree canopy), thus species specific throughfall v. stemflow v. litter leachate? Or, (B) Is it the origin of specific DOM fluorophores/molecular formulas? If (per A) the "origin" variable is used to indicate the initial DOM-enrichment process - throughfall or stemflow or litter leachate (for gap throughfall) - how is this different from the "species" variable? If the "origin" variable is used to indicate the origination of specific indicator fluorophores (like the component C1, "humic-like with terrestrial origin") or FTICR-MS formulas (like the N-rich organic compounds assumed to have atmospheric origins [p. 15, lines 10-15]), then this should be explicitly defined."

With 'DOM origin' we mean the location where the sample was taken, thus meaning the different ecosystem fluxes in our study (species independent throughfall, stemflow, litter leachate, topsoil and subsoil solution). We will define this more precisely in the manuscript.

The changes will be as follows:

Page2 Line2: The DOM concentration and properties along the water flow path through forest ecosystems depend on the location of sampling and hence the type of sampled ecosystem flux, reflecting production and consumption of DOM during the ecosystem passage on transformation processes.

Page2 Line10: Multivariate statistics revealed strong significant effects of ecosystem fluxes and smaller effects of main tree species on DOM quality.

Page12 Line11: We found a significant effect of ecosystem fluxes on DOM composition variables including SUVA<sub>254</sub> and %PARAFAC components (PERMANOVA,  $p = 0.001$ ) explaining 67 % of sample variance.

The term 'origin' associated with the description of fluorescence components and

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FT-ICR MS formulas is adopted from the literature and we will keep it through the manuscript.

"Although there is little literature covering throughfall and stemflow DOM quality, the authors missed some studies. Normally, one cannot cite all the studies on a particular topic; however, in this case, since so few studies exist, I recommend their inclusion. Please note that, for one of these papers, I am the lead author and it is not my intention to push my own work, only to account for the few studies on the topic. Introduction and discussion: Throughfall and stemflow DOM concentration, flux and quality (including potential sources and fates) have been reviewed and evaluated by Van Stan & Stubbins, 2018, <https://doi.org/10.1002/lol2.10059>. Page 16, lines 26-30: The authors only reference Qualls & Haines (1992) biodegradation estimates for throughfall. But, they do not discuss the only study reported stemflow BDOC in Qualls' recent Special Issue (Howard et al., 2018, <https://doi.org/10.3390/f9050236>)."

Thank you, for pointing us at these studies, which we indeed missed. We will include information from van Stan and Stubbins (2018) as reference in the introduction section of our manuscript (Page 3 Line 2). We will include the results of Howard et al. (2018) in the discussion section (Page 16 Line 30) as follows:

With a cumulative degradation of up to 40 % of the initial DOC concentration as well as the highest degradations rates, DOM from SF samples was most bioavailable. TF samples with BDOC up to 36 % contained DOM, which seemed slightly less bioavailable. This is within the results from Howard et al. (2018) reporting BDOC in an interquartile range of 36-73% for cedar throughfall and stemflow samples.

Both references will be added to the reference list.

Please also note the supplement to this comment:

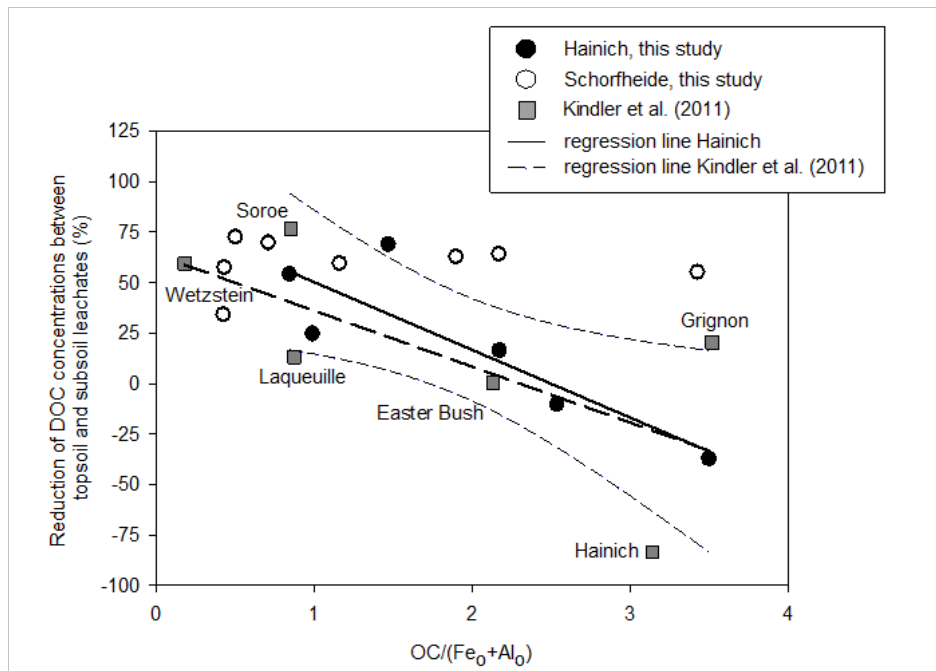
<https://www.biogeosciences-discuss.net/bg-2018-478/bg-2018-478-AC2-supplement.pdf>

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Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-478>, 2018.

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**Fig. 1.** Figure 2: Percentage reduction of DOC concentrations between topsoil (TOP) and subsoil leachates (SUB) as a function of carbon saturation of pedogenic Fe- and Al-(hydr)oxides. For the Hainich sites (t