Reply to the reviewer comments

Referee 3

We are grateful for the thorough review and detailed comments, which will help to improve our manuscript. Furthermore, we are happy that the reviewer believes that the paper is interesting for fluvial ecology and biogeochemistry and that the data are interesting and publishable. Nevertheless, he/she raised a lot of points that must be addressed to improve the manuscript and highlighted the poor language and speculation in the discussion as major points. As stated in our reply to referee 1 and 2, we agree on that and a revised manuscript would of course be professionally corrected by a native speaker and thoroughly revised to delete speculations before resubmission. Furthermore, we will follow the suggestion for referee #3 to reformulate the hypothesis (see response to referee 1).

Besides those general points, referee #3 raised several technical concerns and suggested helpful corrections. Here we answer to the main critical points. We agree with all minor suggestions which are not listed there and will be consider them in the revised manuscript.

P18257, L11-22: "For a good overview of the effects of agriculture on DOM amount and composition, I suggest referring to Graeber et al. (2012) ….".

> Thank you! The paper provides relevant information, e.g. on the effect of different land use forms (agriculture, forest, wetland) on DOM composition and DOC concentration in streams. Their findings are also based on EEM`s and support some of our main statements. Thus we will consider it in a revised version.

P18258, Study area: "…nice to see % land use covers of each catchment":

> We will integrate a more detailed description in a revised version of our paper (see also the detailed response to referee 1).

P18258, L15-16: The referee was "not convinced about the classification of the streams in "non-forestry" and "forestry" streams. He/she suggested "using the "open canopy" and "closed canopy" as classification. It was also suggested using the classification consistently in the whole manuscript and adding PAR data into table 1.

> It was correctly commented that the investigated streams are especially classified based on their contrasting leaf canopy cover which results in different light intensities (see reply to referee 2). We will add the PAR data into table 1. Nevertheless, in the temperate zone "non-forestry" areas are a result of anthropogenic land use changes. This includes deforestation for land use forms like cattle, agriculture, and settlements. The "non-forestry" streams Hassel and Rappbode are affected by cow ranging in different intensity. On the other hand the "forestry" streams Zillierbach and Ochsenbach are pristine streams, running though a dense alder forest (P18258). These are different land use forms, where different DOM quality can be expected. We think that the chosen classification highlights these aspects. We will include a more detailed explanation

into the method chapter of the revised manuscript. And we will use the classification consistently in the total manuscript (including figures and tables) as suggested.

P18260, L18: “Why did you use GF/F filters of 0.7 µm pore size? DOM and DOC are usually considered after filtering with 0.45 µm pore size.”

We are not aware of a strict convention on the pore size and the present literature is divers. Even though some authors use 0.2, 0.3 or 0.45 µm GF/F or Polycarbonate membrane filters, many experts use 0.7 µm GF/F for DOM as well as DOC filtration (refer for instance to Butman et al. (2012, Global Biogeochemical Cycles), Jaffé et al. (2008, Journal of Geophysical Research), van Verseveld et al. (2009, Journal of Hydrology), Parlanti et al. (2000, Organic Geochemistry), and many more).

P1260, L16-17: The referee stated to be “concerned about the way reaeration was measured. Apparently the conservative tracer was injected as a slug, while propane gas was injected at a constant rate. For this type of measurements usually both tracers are injected concomitantly at a constant rate. With the slug it seems relatively easy to correct for dilution between the top and down stations but it seems not so easy to correct for dispersion”.

Conservative tracers can generally be injected by a slug or by permanent injection. Permanent chloride injection is only appropriate in very small streams where sufficient mixing can be assumed and the reservoir for the tracer solution can be handled. The chloride injection with this technique was not possible in the Rappbode (Q=30-37 Ls^{-1}, table 1) and we decided to use the same technique for all streams. Beside this, if injecting both tracers in parallels the increasing chloride concentration can affect the solubility of the gas tracer. In addition, the results of the chloride injection experiment are needed to detect the travel time that defined the minimum injection time for the volatile tracer. That’s why we decided to have the chloride injection first, followed by the gas tracer. This approach is a standard technique and was for example recently described in Bales and Nardi (2007) U.S.G.S. Techniques and Methods 4-C2, 33p, and Reichert et al. (2009) J. Geophys. Res. 114, G03016. We will cite these references as suggested by the referee.

“P18263, L2: The correction for the inner-filter effect is usually done based on the absorption. Please clarify.” The referee asked also “Did you minimize potential effects of pH and temperature on fluorescence measurements?”

Mobed et al. (1996) described in Environmental Science & Technology absorbance correction as an essential tool “for accurate representation and comparison of the EEMs of the humic substances at high concentrations”. DOM (including humic substances) measured in our samples was not that high that an inner-filter correction would be appropriate. In detail, the maxima fluorescence intensity was 1196, detected for the Hassel and we detected for all samples a low absorbance between 300 and 600 nm (cp. reply to referee 4). Furthermore, also dilution tests showed that inner filter effects can be neglected in our case. In addition, the investigated streams were generally neutral with respect to their pH (Table 1) and our samples are generally not acidified. A pH correction is therefore not appropriate (see Weishaar et al. 2003). We minimized potential temperature effects by measuring all samples at room temperature (~20°C). We clarify these points in the revised manuscript.

P18264, L11-12: “If you already measured DOC concentration, this measure of DOM concentration (a375) seems unnecessary. Also, why did you not measure absorbance spectra in order to estimate absorbance indexes (e.g, SUVA, spectral slope, etc.)?”

The absorption at 375 is a predictor of the total amount of DOM (P18264, Stedmon et al. (2006, Estuaries and Coasts)). We used a375 to test the relationship between CDOM and DOC, which has the main fraction in the DOM matrix. The regression was highly significant (P18267, compare also Stedmon et al. (2006)). We will explain the background of this approach in more detail. However, we measured absorbance between 200 and 800 nm (P18264) to consider whether it is necessary to correct for inner-filter effects. We don’t think that the absorption indices SUVA254 (dissolved aromatic carbon content, humification), spectral slope (molecular weight and source) and so on could provide further relevant information. The fluorescence indices (FI, HIX, beta:alpha) give us all needed information about CDOM and its composition.

P18264, L16: “Why both parametric and non-parametric analyses? It seems that you later only use parametric correlations.”

We used parametric analysis for normally distributed data and non-parametric analyses for non-normally distributed data. However, in the meanwhile we tested all data with Spearman correlation test. This has not changed the statistical statements we have driven in our manuscript. In a revised manuscript we will only show the results of this test.

P18266, L25: “If the correlation is also good for TP why is only the correlation with light shown (Fig. 5).”

And P18271, L21-22: “I do not agree. I do not think that this correlation is indicative of P limitation”

In this context also referee 1 stated that our investigation “does not provide new insights” on seasonality of stream metabolism and the influence on land use on metabolism. Therefore, we will reduce statements regarding this topic (including Fig. 5) and will focus on our central topic – the linkage between the temporal and spatial variability of DOM and metabolism - in a revised version (compare also reply to referee 1).

Fig. 7: “All 3 correlations seem statistically significant. Another thing is that some of the data are not normally distributed and fail to meet the assumptions of parametric statistics. Please clarify.”

We used a non-parametrical test to analyze the significance of this correlation. It is correct, that all correlations are significant (Fig. 7). Furthermore, we tested if a linear model is valid to describe these correlations as described at P 18264. The assumption of a normally distribution of the residuals was only valid for the correlation C1:C3. In order to avoid confusions, we will focus on the significant correlations and delete the information on significant linearity.

Fig. 8: “The significant correlations between PARAFAC component ratios and fluorescence indexes seem quite logical since those indexes are often estimated from the ratio between fluorescence-emission peaks. So, how do these correlations advance our knowledge of DOM dynamics in the system?”

Following relevant information can be drawn from these ratios (P18268, Fig.8):

i) From HIX: C1 is indicated with a higher aromaticity and higher humification than C3.
ii) From beta/alpha: C2 is indicated as rather recently produced and autochthonous, both C1 and C3 seems to be rather decomposed and allochthonous.
iii) From FI: C2 is indicated as originated from a microbial/autochthonous carbon production and C3 seems to be terrestrially derived.

We will describe these findings more clearly in the revised manuscripts.