Reply to Anonymous Referee #1 on manuscript “The importance of riparian zones on stream carbon and nitrogen export in a temperate, agricultural dominated landscape” by T. Wohlfart et al.

In the following please find the corrections and comments to the reviewer’s response. For clarity, the comments of the reviewer were copied in black and our comments are in blue.

Anonymous Referee #1

General comments: The manuscript of Wohlfart et al. describes and discusses the results of three sampling campaigns of surface waters, drain waters, and groundwater in the Tyrebaekken catchment in Jutland, Denmark. Concentrations and fluxes of nitrate, dissolved organic nitrogen and dissolved organic carbon are analyzed with respect to their dependency on the spatial distribution of land use and soils as well as topography. The experimental approach is sound and the data have been analyzed appropriately. The analysis revealed that nitrate and DON concentrations and fluxes were enhanced by coarse textured soils and reduced by a larger fraction of organic soils in the catchments of creeks. In contrast, the fraction of cropland in the subcatchments had a much smaller influence on nitrate and DON concentrations, which might also due to the small variation of land use in the Tyrebaekken watershed. Concentrations of DOC were correlated with the fraction of organic soils in subwatersheds. These findings regarding nitrate and DOC dynamics in surface waters are not new and have been documented in numerous studies. Nevertheless, the study has some merit in documenting the strong effect of organic soils on transfers of carbon and nitrogen from terrestrial systems to surface waters not only in landscapes with comparably small land use intensities, such as Scotland, the Canadian Precambrian Shield or forested landscapes of Scandinavia, but also in one of the most intensively used agricultural landscapes in temperate regions: Jutland, Denmark. Nevertheless, I feel that the paper is somewhat long with regard to the novelty of the findings presented. Especially the presentation of results is lengthy and can potentially be shortened by 20-30%. One aspect that is excessively presented and discussed in my opinion is the seasonality of concentrations and fluxes. I think that a time series of three points of time is insufficient to draw any conclusions regarding the seasonality of fluxes or the influence of e.g. precipitation.

We thank to the reviewer for his/her interest in the present study and constructive comments that helped clarify the language. We have tried to accommodate all the following comments in...
the new manuscript version. Despite deletion and shortening of many sections, the paper even increased in its length. This is due to the fact that both reviewers asked for additional clarifications and the inclusion of further literature.

Specific comments:

Title: The current title stresses that role of riparian zones for carbon and nitrogen concentrations and fluxes in adjacent surface waters, but this aspect of riparian buffers is then hardly reflected in the subsequent manuscript. For example, the effect of organic soils was not analyzed with respect to the importance of their distance to the creek. Also the fraction of coarsely textured soils in the subcatchment is not linked to riparian zones. I suggest either to address the aspect of riparian zones more explicitly in the manuscript or to change the title, e.g. into “Spatial distribution of soils determines export of nitrogen and dissolved organic carbon from an intensively managed agricultural landscape”...

The authors would like to thank the referee for pointing this out. We agree that a more suited title was required and therefore changed it to

   Spatial distribution of soils determines export of nitrogen and dissolved organic carbon from an intensively managed agricultural landscape

Abstract: The abstract is a little too long (315 word in my count).
The abstract was shortened to 280 words.

P 7466, Line 14: “electrical onductivity” instead of “Electro-conductivity”? This has been changed and reads now “Electrical conductivity”.

P 7466, Line 16: remove “return”.
This has been corrected.

P 7466, Lines 18, 20 and throughout the manuscript: I have learned that the use of “respectively” is poor style and makes the text hard to follow...
Corresponding lines were deleted in the abstract.
Page 7466, Lines 27-28: The conclusion that soils types affect water quality is not very new and strong. Is it possible to be more specific? For example: The fraction of coarse textured and organic soils determine the fluvial export of nitrogen and DOC from this intensively used landscape.

P2, L14: The conclusion was rephrased to a more specific statement and now reads

For our case study we conclude that the fractions of coarse textured and organic soils have a major influence on nitrogen and DOC export in this intensively used landscape. Meanwhile, the contribution of dissolved organic nitrogen to the total nitrogen losses was substantial.

P7467, L 5: Vitousek et al 1997 is missing in the list of refs...

The mentioned article has been added to the reference lists:


P7467, L 19ff: You cite references from pristine forest ecosystems that are hardly comparable to the situation in Jutland. On the other hand, the study of Siemens et al. (J. Plant Nutr. Soil Sci. 165, 675-681, 2002) is not considered despite the fact that the Pleistocene parent material of the underground as well as the intensive agricultural management including the intensive use of manure is similar to the situation in Jutland. This seems odd to me. Interestingly, the DON concentrations leached from intensively managed sandy croplands in the study of Siemens et al resemble the concentrations found in the Northern branch of the Danish catchment....

P12, L15: To underline the importance of DON losses from agricultural sites two studies were cited. The paragraph in the discussion now reads

Besides, Mattsson et al. (2009) found an averaging proportion of organic nitrogen of 21% in Danish catchments that were dominated by agricultural land. The study points out a mean DON concentration of 1.1 mg N L\(^{-1}\). Siemens and Kaupenjohann (2002) described median DON concentrations of 0.4 to 2.3 mg N L\(^{-1}\) for leaching losses of an agricultural site in north-western Germany and concluded that DON
contributes significantly to nitrogen losses from agricultural soils. Considering these findings together with our results we conclude that DON can contribute substantially to the total N budget, even under highly intensive land use systems such as those of the Bjerringbro landscape.

P7468, L 21: Strange wording at the beginning of the sentence. Replace by: In order to unravel the impact of...

P4, L10: The replacement has been done and the mentioned sentence now reads

In order to unravel the impact of soil properties and land use on in-stream chemistry, measurements of different C and N solutes with a high spatial and temporal resolution are required.

P7469, L 16: Delete "(

Deleted.

P7469, L 20ff: coarse sandy clay, coarse clayey sand, and fine clayey sand are not soils types, but soil textures...

This has been corrected.

P7470, L 10: Wasa hydrological flow path analysis carried out to delineate the contributing areas? The problem in Pleistocene areas with glacial till is often that the topography of the land surface not necessarily determines the boundaries of catchments because the topography of the underlying impermeable glacial till can differ substantially...

A hydrological flow path analysis does not provide information about contributing areas, but it rather helps in identifying runoff generation processes. As indicated in the legend of Figure 3, contributing areas were delineated based on a surface DEM (2x2m) that was derived from airborne laser scanning by Hansen (2004). The reviewer indeed raises an interesting point of discussion, i.e. the mismatch surface derived catchment boundaries and subsurface ones. For a direct comparison of these potentially different watershed boundaries a full recognition of the subsurface hydrogeological structure would be needed, which we do not have. A hydrological flow path analysis as suggested by the reviewer would not solve this problem as it does not consider the lateral (spatial) composition of runoff (where does the water come from in space?) but rather gives information on the vertical contribution of water sources (is the runoff...
consisting of quick flow components from surface/subsurface or low flow components from
deeper soil or bedrock horizons?) in runoff generation. Even though the latter topic would be
an interesting issue for the discussion of results, data for such a hydrological flow path
analyses are not at hand (e.g. stable water isotopes to calculate mixing models).

P7470, L 16: LDPE is the more common abbreviation for low density polyethylene. Avoid the
abbreviation to avoid misunderstandings?
The abbreviation has been removed.

P7471, L2: “Specific loads”. What is specific about these loads?
Specific loads is a technical term in hydro-biogeochemistry. Equivalent to specific discharge
in hydrology, specific loads refer to yields (loads, or the mass of nutrient exported) per unit of
area. This allows to compare losses from catchments of different size.

P 7471, L14: “cropland distribution”: Do you mean areal fraction of cropland in
subcatchments? A distribution would suggest to me that in addition the mere area
other features like the distance to creeks etc. were analyzed...
This has been clarified in the revised manuscript and now reads:

The independent variables were the areal fraction of contributing area
covered by cropland, the portions covered by coarse clayey sandy and
organic soils, two GIS-derived landscape characteristics (mean slope
and mean Topographic Wetness Index (TWI) of each sub-basin) and
the sampling period (April, August, September).

P7472, L21: replace “increased with values from...” with “increased from 2.1 to 25.4 l s⁻¹ ...”
P7, L18: This has been corrected.

P7472, L 27: Why do the DON concentrations “correspond” to the nitrate concentrations?
This has been clarified in the revised manuscript:

DON concentrations (Figure 4c) showed a similar distribution with
highest values in the northern stream between <0.01 and 4.3 mg N L⁻¹.

P 7475, L1: I don’t understand “positive correlations between the sampling date and the
sandy soil properties”.
This was rephrased to

For DON we found positive correlations with both the sampling date and the portion of contributing area covered by sandy soils.

Over the summer 2009, NO$_3^-$ concentrations were always higher in the northern branch while land use distributions, and respective proportion of land-use classes, are similar over the contributing areas of both southern and northern branches. Therefore, past management practices could explain differences in water quality. Actually, soils may store organic components from manure and slowly release them throughout time. Unfortunately, only few data were available to treat this hypothesis that falls outside the scope of our current study.

We agree that further research in this direction is of great interest. We rephrased this part of the manuscript to redefine our views on this issue as following

Despite comparable land use distributions in the two main subcatchments, higher NO$_3^-$ concentrations exhibited in the northern branch during summer 2009. This may be further explained by differences in past or present management practices, although corresponding data were not available and out of the scope of the present study.

P7476, L 10ff: What about the relevance of denitrification in riparian organic soils? Is this insignificant for the findings presented here?

P10, L29: Denitrification certainly is important for Nitrate reductions in organic soils and along streams. We added a study which was carried out in the area between 2007 and 2009. Schelde et al. (2012) describe N$_2$O emission measurements during April 2009 under the present dry conditions. The paragraph in the manuscript reads now

In the described study area Schelde et al. (2012) measured nitrous oxide (N2O) emissions during the study period 2007 to 2009. N$_2$O emissions were found to be higher during periods with moist soil, suggesting higher denitrification rates and therefore lower input rates of nitrate with the water draining through soil and into stream water.
An intensive field campaign was carried out in April 2009 when \( \text{N}_2\text{O} \) emissions were found to be relatively low due to dry weather conditions (Schelde et al. 2012) leading to the assumption that denitrification rates were low in April. Low denitrification rates in spring 2009 might explain higher nitrate concentrations in the southern stream during August and September 2009.

P7477, L27: “Copper et al. (2007) pointed out that the leaching of DON occurs when water drains through soils.” Isn’t this trivial?

We deleted this sentence.

P7479, L26: Do you mean DON concentrations or fluxes? I could not spot the coefficients of –0.15 and –0.22 in table 3. How do you explain a negative influence of the area of organic soils on DON concentrations and fluxes?

The reviewer raises here a crucial point of discussion. In our study, organic soils do have opposite influences on in-stream concentrations of DOC and DON. With concentrations higher in the southern than in the northern stream, DOC concentrations are positively correlated with the percentage area corresponding to organic soils. Conversely, organic soils have a negative effect on DON concentrations as a result of more adsorption or faster degradation.

Actually, adsorption of dissolved organic matter depends on molecular weight, acidic group and aromatic structure (Kaiser and Zech, 2000). The adsorption of DOC and DON also depends on their respective concentrations in the draining water (Lilienfein et al., 2004). According to Lilienfein et al. (2004), at low initial concentrations in soil solution, the soil releases potentially more dissolved organic matter (DOM) than at higher concentrations for which it is more likely to retain these substances. Meanwhile, Lilienfein et al. (2004) also state that adsorption mechanisms of both species are controlled by similar factors. Nevertheless in other studies that compare the behaviour of these two DOM components, conclusions are drawn that the tendency for adsorption and degradation probably differ between DOC and DON (Michalzik and Matzner, 2001; Kalbitz et al., 2000). It is worth noting that DON has different characteristics in these controlled laboratory experiments than in field studies (Michalzik and Matzner, 2001).

Both these previous studies and our current results may indicate the existence of at least two different pools of organic matter with heterogeneous composition in the organic soils.
In the manuscript, we first corrected the coefficients for DON concentrations to their correct values of -0.17 for land use and -0.24 for organic soil (Table 3). Previous thoughts about the negative influence of organic soils on DON are included as follows in a new discussion paragraph:

Interestingly, organic soils have opposite influences on in-stream concentrations of DOC and DON. With concentrations higher in the southern than in the northern stream, DOC concentrations are positively correlated with the percentage area corresponding to organic soils. Conversely, organic soils have a negative effect on DON concentrations as a result of more adsorption or faster degradation. Actually, adsorption of dissolved organic matter depends on molecular weight, acidic group and aromatic structure (Kaiser and Zech, 2000). The adsorption of DOC and DON also depends on their respective concentrations in the draining water (Lilienfein et al., 2004). According to Lilienfein et al. (2004), at low initial concentrations in soil solution, the soil releases potentially more dissolved organic matter (DOM) than at higher concentrations for which it is more likely to retain these substances. Lilienfein et al. (2004) also state that adsorption mechanisms of both species are controlled by similar factors. Nevertheless in other studies that compare the behaviour of these two DOM components, conclusions are drawn that the tendency for adsorption and degradation probably differ between DOC and DON (Michalzik and Matzner, 1999; Kalbitz et al., 2000). It is worth noting that DON has different characteristics in these controlled laboratory experiments than in field studies (Michalzik and Matzner, 1999). Both these previous studies and our current results may indicate the existence of at least two different pools of organic matter with heterogeneous composition in the organic soils. However, this would require further field investigations to be confirmed or refuted.

Wouldn't it be more logical to present DOC results prior to DON results since DON is a part of dissolved organic matter?
That is a good point and we agree on that with the reviewer. Nonetheless, as the results of DON in our study show similar characteristics with nitrate we prefer to keep the represented order to present N related solutes together.


P7481, L3: “Mineral soils contain...” Do you mean organic soils here? Otherwise the following sentence makes no sense... We thank the reviewer to have highlighted this non-sense to us. We corrected the sentence with

Organic soils contain a high proportion of degradable organic matter that can be eventually released by different physicochemical processes into streams (Kennedy et al., 1996).

P7481, L 12ff: “...the dissolution of C into surface water through sorption...”. Sorption reduces the release of C into the aqueous phase, or not? P15, L5: We have replaced the word “affect” by the word “reduce” to clear the instance.

Rewetting through rain and storm events seems to play an important role on the release of carbon. During these events quick discharge components such as surface and sub-surface runoff rapidly transport C laterally, reducing time for microbiological degradation in the upper soil horizons (Cooper et al., 2007) and releasing dissolved organic matter into streamwater.

P7482, L2ff: I am skeptical that the experimental approach allows identifying the precipitation as a driving factor for changes in N fluxes. What about seasonal changes in N uptake by plants for example. As pointed out earlier, I would be careful to avoid over-interpreting a time series of three points...

Yes, we agree with that. We adapted the sentence which reads now
Additionally, DON contributed up to 81% to the TDN losses during the wetter periods of August and September and might therefore play an important role in the nitrogen budget of intensively managed agricultural catchments.

P7490, Table 2: How do you interpret the significant increase in pH in the converged part of the creek? Outgassing of CO2 from streamwater?
In our stream, pH is increasing from source to outlet. This is a natural phenomenon due to photosynthesis by in-stream primary producers that take up dissolved CO2, indirectly reduce HCO3- and therefore free H+, thereby increasing the pH (Liu Z et al. 2006, Diurnal Variations of Hydrochemistry in a Travertine-depositing Stream at Baishuitai, Yunnan, SW China, Aquatic Geochemistry DOI 10.1007/s10498-005-2962-2). In our study, water that has a longer residence time (e.g. water after the convergence compared to headwater) tends to show higher pH values as photosynthesis has been going on for a longer period of time in the water column. A further reason for the differences also related to photosynthetic processes, is that samples were not taken at the same moment, but rather consecutively along the stream reach one after the other during the snap shot sampling. Thus, diurnal variation of pH due to different times of sampling might also have occurred. Nevertheless, pH is not in the focus of this study and thus we tend to not over-discuss our pH measurements.

P7491, Table 3: How do you explain that the fraction of organic soils in the subcatchments influenced DOC concentrations, but not DOC fluxes? Or that the fraction of cropland does not affect DOC concentrations, but positively DOC fluxes? Is this related to low groundwater recharge in organic soils in depressions and high groundwater recharge in elevated mineral soils?
With 0.25, the multi-linear regression model for DOC yields is the lowest one. We may see here a limitation of using a statistical model to describe nutrient fluxes. Probably, some information is missing to correctly DOC losses, especially due to the uncertainties in the handheld measurements of discharge. Limitations of the method have been added in the discussion:

Nevertheless, one has to carefully consider the discharge data obtain with the handheld Flo-meter and the uncertainty introduced by the evaluation of the cross-section in the transformation of velocity data to volumes.
P7495: Figure: What is the meaning of the red color of the letters?
Figure 4: An explanation was added in the legend

Colours indicate the compared groups of either date or stream section.

P7496: Figure title: I guess you don't mean the contribution of DON to the TDN budget, but to TDN concentrations. A budget would consist of inputs and outputs...
Figure 5: The legend was clarified and now reads

Figure 1. Contribution (%) of DON (dark grey) and DIN (light grey) to total dissolved nitrogen losses for every stream section and every sampling period.

P7497: Can this figure be incorporated into figure 4?
We would like to avoid integrating Figure 6 into Figure 4 as both figures already provide a lot of information in it and we would like to keep it comprehensible.