Reply to Anonymous Referee #1 on manuscript "The importance ofriparian zones on stream carbon and nitrogenexport in a temperate, agricultural dominatedlandscape" 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 resultsof three sampling campaigns of surface waters, drain waters, and groundwater inthe Tyrebaekken catchment in Jutland, Denmark. Concentrations and fluxes of nitrate,dissolved organic nitrogen and dissolved organic carbon are analyzed with respect totheir 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 enhancedby coarse textured soils and reduced by a larger fraction of organic soils in the catchmentsof creeks. In contrast, the fraction of cropland in the subcatchments had a muchsmaller influence on nitrate and DON concentrations, which might also due to the smallvariation of land use in the Tyrebaekken watershed. Concentrations of DOC were correlatedwith the fraction of organic soils in subwatersheds. These findings regardingnitrate and DOC dynamics in surface waters are not new and have been documented innumerous studies. Nevertheless, the study has some merit in documenting the strongeffect of organic soils on transfers of carbon and nitrogen from terrestrial systems tosurface waters not only in landscapes with comparably small land use intensities, suchas 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 withregard to the novelty of the findings presented. Especially the presentation of resultsis lengthy and can potentially be shortened by 20-30%. One aspect that is excessivelypresented 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 conclusionsregarding 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 carbonand nitrogen concentrations and fluxes in adjacent surface waters, but this aspectof riparian buffers is then hardly reflected in the subsequent manuscript. For examplethe effect of organic soils was not analyzed with respect to the importance of their distanceto the creek. Also the fraction of coarsely textured soils in the subcatchment is notlinked to riparian zones. I suggest either to address the aspect of riparian zones moreexplicitly in the manuscript or to change the title, e.g. into “Spatial distribution of soilsdetermines export of nitrogen and dissolved organic carbon from an intensively managedagricultural 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 itto

> 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 inmy 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”.

P7466, 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 tofollow...

Corresponding lines were deleted in the abstract.

Page 7466, Lines 27-28: The conclusion that soils types affect water quality isnot very new and strong. Is it possible to be more specific? For example: The fractionof 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 inthe list of refs...

The mentioned article has been added to the reference lists:

> Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H. and Tilman, D. G.: Human alteration of the global nitrogen cycle: sources and consequences, Ecological Applications, 7(3), 737–750, doi:10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2, 1997.

P7467, L 19ff: You cite references from pristine forest ecosystemsthat are hardly comparable to the situation in Jutland. On the other hand, the study ofSiemens et al. (J. Plant Nutr. Soil Sci. 165, 675-681, 2002) is not considered despitethe fact that the Pleistocene parent material of the underground as well as the intensiveagricultural management including the intensive use of manure is similar to the situationin Jutland. This seems odd to me. Interestingly, the DON concentrations leachedfrom intensively managed sandy croplands in the study of Siemens et al resemble theconcentrations 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}.Siemensand 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 theimpact 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 clayeysand, 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? Theproblem in Pleistocene areas with glacial till is often that the topography of the land surfacenot necessarily determines the boundaries of catchments because the topographyof 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 informationon 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: LDPEis the more common abbreviation for low density polyethylene. Avoid the abbreviationto avoid misunderstandings?
The abbreviation has been removed.

P7471, L2: “Specific loads”. What is specific about theseloads?
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 catchmentsof different size.

P 7471, L14: “cropland distribution”: Do you mean areal fraction of croplandin subcatchments? A distribution would suggest to me that in addition the mere areaother 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 don0t understand “positive correlations between the sampling date and the sandysoil 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.

P 7475, L 23ff: I think the speculation about the influence of land usehistory on present nitrate concentrations presented here leads nowhere. Such discussionwould make sense in the case that historical data on land use were available incombination with detailed information on hydrological flow paths and water travel times.

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) describeN_2O 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_2O 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 N_2O 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, L 27: “Copper et al. (2007)pointed out that the leaching of DON occurs when water drains through soils.” Isn0tthis trivial?

We deleted this sentence.

P7479, L26: Do you mean DON concentrations or fluxes? I could not spotthe coefficients of –0.15 and –0.22 in table 3. How do you explain a negative influenceof 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 ofboth 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 differbetween 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.

P 7480: Wouldn0t itbe more logical to present DOC results prior to DON results since DON is a part ofdissolved 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.

P7480, L 22: “According to that”...Strange formulation. Accordingto what?
We replaced with Accordingly.

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

P7481, L16ff: What about the role of (near)surface runoffthrough O and A-horizons for transferring DOC from land into streams?
We considered this as well and added it into the discussion.

> 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 asdriving factor for changes in N fluxes. What about seasonal changes in N uptake byplants for example. As pointed out earlier, I would be careful to avoid over-interpretinga 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 significantincrease 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 Hydrochemistryin 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 valuesas 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 thesubcatchments influenced DOC concentrations, but not DOC fluxes? Or that the fractionof cropland does not affect DOC concentrations, but positively DOC fluxes? Is thisrelated to low groundwater recharge in organic soils in depressions and high groundwaterrecharge 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 thered 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 don0t mean the contribution ofDON to the TDN budget, but to TDN concentrations. A budget would consist of inputsand 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.