

**Report on the manuscript “The importance of riparian zones on stream carbon and nitrogen export in a temperate, agricultural dominated landscape” By T. Wohlfart, J.-F. Exbrayat, K. Schelde, B. Christen, T. Dalgaard, H.-G. Frede, and L. Breuer**

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.

This study deals with an important topic on the links between land use, soil types and water quality in agricultural catchments. The analysis is based on the comparison between two catchments in the same area in Denmark, with different soil types (organic soils vs. mineral soils and different textures among sandy soils). The experimental methods focused on stream water analysis for nitrate, DON and DOC, with samplings made at different locations in two streams, artificial drains and groundwater in the study area. Due to different reasons, the link between the observed concentrations and loads and soil types/land use, as well as the link between the different measured compounds is not easy to establish. This subject is clearly relevant for Biogeosciences.

General comments

This study is well presented and the methods are clearly exposed. The results are clearly presented, even though this section is sometimes difficult to read. The main results are presented in figure 4. However, the discussion should clearly be improved before this manuscript can be accepted for publication. To my opinion, three main concerns arise from this paper:

1. The discussion is often too general and does not give quantitative and convincing arguments to interpret the data or highlight their limits.
  - The discussion provides many comments on processes which could explain the observations, but few/no link is made with the study case. For example in page 7476, line 5-9, an argument is given to explain the constant nitrate concentration at one location, but no argument on the local hydrology is given to prove that it worked so. In page 7477, lines 10-18, the authors mention some agricultural practices as an explanation for nitrate concentration, but no information is provided on these agricultural practices. The soil texture (esp. sandy soils) are often quoted as an explanation but few references are given on the influence of the soil texture on transfer and biotransformation of N and SOM in soils, in a quantitative perspective.

- As a whole, the agricultural practices are mentioned in different place in the text as an explanation for both temporal change in concentration and difference between the northern and southern catchments. However, few information is given on these practices to support the arguments. Considering the previous studies made on this area, these data are certainly available and usable for analysis.

We acknowledge that the original discussion lacks additional references to previous studies, and lacks a more elaborated discussion and documentation of the management practices observed in the watershed, and the relation to the nitrogen measurements reported.

Specifically (and in addition to the Materials and Methods section additions specified below), the text in page 7476, following line 5-9, has been elaborated to:

However, as mentioned in section 2.1, detailed information about site-specific management practices (Dalgaard et al., 2012; Cellier et al., 2011) showed relatively larger areas with extensive grazing (and thereby lower nitrogen fertiliser and manure input) in the northern part, which also included more wet meadows compared to the more steep terrain along the southern stream branch. Despite this, higher  $\text{NO}_3^-$  concentrations exhibited in the northern branch during summer 2009.

Moreover three reference to past management practices (Caspersen and Fritzbøger 2002) has been added to the following section:

Consequently, N leaching is affected by past land use and management practices (Hansen et al., 2011; 2012), which varied a lot in this area during the past 300 years (Caspersen and Fritzbøger, 2002), but a further study of this aspect was out the scope of the present study.

Moreover, in page 7477, after the lines 10-18, we have provided further references and discussion points to the specific agricultural practices referred to:

Maybe the higher  $\text{NO}_3^-$  concentrations in the northern part can be explained by tile drains from the more flat and thereby larger areas of drained agricultural uplands in this area, as compared to the southern part, but this could not be confirmed by the present study. A more elaborated discussion of the hydrology in the area can be found in Dahl et al. (2004), who also discuss the potential effect of clean groundwater from buried valleys, which may affect the  $\text{NO}_3^-$  concentration in the

stream, but no systematic difference between the northern and the southern branch of Tyrebækken was found.

Finally in the discussion section references to the correspondence between soil texture and nitrate leaching is inserted, and in addition, extra information with references to soil type, land use and management data was added to the Materials and Methods section (2.1)

Pasture is the second most frequent land cover (20%), totally dominating the land use along the stream (Cellier et al., 2011). The average fertilisation in the area is  $80 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the form of livestock manure (equal amounts of pig and cattle slurry), and  $74 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the form of synthetic fertilisers with a modelled average  $\text{NO}_3^-$  leaching equal to  $58 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Dalgaard et al., 2011a), correlating to the typical cropping and management practices in this part of Denmark (moraine plateaus with arable land dominated by winter wheat cereals, and with permanent grassland on the lowland organic soils; Dalgaard et al., 2012, Höll et al., 2002).

- The observed concentrations can be explained by a range of variables (soils, climate, agricultural practices, etc.); these are analyzed separately and a synthesis is lacking. For example the nitrate concentration might depend on fertilization and soil tillage practices, soil type and climate. The different effect should be balanced. For example in page 7476, lines 12-15, it is assumed that the differences in nitrate concentration are due to rainfall, but it might be also explained by fertilization (in April) and climate (e.g. influence of temperature on mineralization)). This should be at least discussed.

We agree with the reviewer that the current discussion is lacking some specific reasons for the observed patterns. However, some points were already included (e.g. management) while some other reasons cannot be the reason for the differences we found (e.g. temperatures which so not vary between the two stream sections that are in close vicinity). Nevertheless, we added some points of discussion. The section now reads:

In the Danish stream Tyrebaekken, water analyses showed a quite heterogeneous distribution of  $\text{NO}_3^-$ -N concentrations and fluxes between the three stream sections. In the northern part, they were significantly higher than in the southern part even though the land use distribution according to Table 1 apparently did not vary much. On average  $\text{NO}_3^-$  concentrations measured in the southern part represented about 15% of the concentrations measured on the same day in the

northern part. However, as mentioned in the Materials and Methods section, detailed information about site-specific management practices (Dalgaard et al., 2012; Cellier et al., 2011) showed relatively larger areas with extensive grazing (and thereby lower nitrogen fertiliser and manure input) in the northern part, which also included more wet meadows compared to the more steep terrain along the southern stream branch. Despite this, higher  $\text{NO}_3^-$  concentrations exhibited in the northern branch during summer 2009. However, as pointed out in many studies (Böhlke and Denver, 1995; Ruiz et al., 2002a; Worrall and Burt, 2001) soils are able to store N, leading to poor correlations between N losses from agricultural soils and headwater quality. Consequently, N leaching is affected by past land use and management practices (Hansen et al., 2011; 2012), which varied a lot in this area during the past 300 years (Caspersen and Fritzboøger, 2002), but a further study of this aspect was out the scope of the present study. Furthermore, the  $\text{NO}_3^-$  stored in soils can be released into sub-surface and groundwater after some time. Nutrients are mobilised by mineralisation processes during the growing season when high rates of microbial activity are observed (Böhlke and Denver, 1995; Böhlke, 2002; Schnabel et al., 1993).  $\text{NO}_3^-$  leached to shallow groundwater may be steadily released through time periods of a year or more (Martin et al., 2004; Molénat et al., 2002; Ruiz et al., 2002b). As shown by Schiff et al. (2002),  $\text{NO}_3^-$  concentrations can be traced back to groundwater charges and might give a correct basis to explain the almost constant  $\text{NO}_3^-$  concentrations measured at sampling point 1 over the whole sampling period.

- The variability should be commented more thoroughly, as it is large in several cases, especially for DON and DOC.

We have added several sections to the discussion of our results on DON and DOC. Apart from smaller corrections and amendments, we added the following larger sections.

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  $1.1 \text{ mg N L}^{-1}$ . Siemens and Kaupenjohann (2002) described median DON concentrations of 0.4 to  $2.3 \text{ mg N L}^{-1}$  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.

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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. We assume that the water input by precipitation that influences the in-stream runoff is a driving factor for DOC exports to stream, thus explaining the observed correlation between DOC and discharge. Nevertheless, one has to carefully consider the discharge data obtained with the handheld flowmeter and the uncertainty introduced by the evaluation of the cross-section in the transformation of velocity data to volumes.

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. 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, 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.

- The origin of N in the two catchments (mineral and organic fertilization, atmospheric deposition, plant and soil processes) should be discussed in a more precise and quantitative way, with relation with the natural and anthropogenic processes and their range of variation. For example the authors mention the potential of atmospheric deposition but do not try to consider it in a quantitative way, nor to discuss the N transformation which may apply to this nitrogen.

A description of the amount of organic and inorganic fertilizers applied is already given in the paper in section 2.1, amounting to a total N application rate of  $154 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ .

Atmospheric deposition does not alter the N budget according to a recent estimate from Dalgaard et al. 2012. We added the following sentence to section 2.1:

According to Dalgaard et al. (2012) atmospheric N deposition for the Bjerringbro area derived from EMEP (2010) was around  $12 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , adding another 8% of total N input, which does not significantly change the overall N budget.

2. One major interest of this paper is to have measured simultaneously nitrate, DON and DOC; however the authors make insufficient link between these chemical species to interpret the data. These interrelations could be used into more detail to explain the spatial and temporal variations in stream concentrations. It must be noticed that the measured pH and EC values are not used in the data analysis.

A summarized comparison of DOC and DON behavior has been implemented at the end of the discussion, see also reply to the comment two bullet points above.

3. The statistical analysis is based on the comparison between two sets of data only as well as limited number of sampling along time. There is a risk that this limits strongly the interpretation. It is mentioned by places (e.g. page 7477, lines 4-8) but this should be commented more precisely.

We do not agree with regard to the limitation of the data set we used. The aim of this study was not to present a time series of measurements – for such an approach the data presented would have been not sufficient. However, we rather present a spatial analyses of 20 waypoints sampled at nine different times in a snap shot fashion. Snap shot sampling provides a viable

tool for spatial analyses and there are a number of published snap shot sampling results that are based on a similar/sometimes larger number of waypoints and similar/sometimes number of replications (e.g. Pohlert et al. 2007, Hydrology and Earth System Sciences, doi:10.5194/hess-11-997-2007; Lyon et al. 2012, Water Resources Research, DOI:10.1029/2011WR011073; Mourad and van der Perk 2009, Hydrological Processes DOI: 10.1002/hyp.7309; Biggs et al. 2004 Biogeochemistry, DOI: 10.1023/B:BIOG.0000025744.78309.2e). We further argue that the interpretation of results is not limited by the number of observation points or replications in itself, but rather (in the case of land use p7477, L4-8) by catchment characteristics (which would not change by sampling more often). Homogeneity in the observed land use (or topography or any other catchment characteristic) is not a statistical problem per se in the evaluation of snap shots. In our case it required to find other catchment characteristics that show more variability and which potentially lead to the observed instream concentrations or loads (e.g. soil types) we observed.

#### Specific comments

- The title is not the same in the manuscript (The importance of riparian zones on stream C and N : : :) and on the Biogeosciences site. I consider that the title on the manuscript is not relevant, as the study do not focus on riparian zones.

This was also pointed out by referee #1 and we changed the title to a more suited one:

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

- Figures 1, 2 and 3: delineation of the sub-catchment should be added to clarify interpretation and link with Tables 1 and 2.

This was changed.

- Figure 5 could be converted to a table (could be added to Table 2). This figure is referred to after Fig. 6 in the text.

The graphical representation chosen in Figure 5 looked clearer to us than a table.

- Figure 6 should be clarified: lines/figures types in order to distinguish between drains, groundwater and pools; include year in the date on the X-axis

Figure 6 was re-created after removing data corresponding from Pool and Tpool. Thick solid lines were kept for groundwater wells and thick dashed lines for drains. All samples have been taken in 2009, the year is just acknowledged in the legend that now reads:

Figure 6. Measured NO<sub>3</sub>-N, DON and DOC concentrations [mg L<sup>-1</sup>] analysed in drains (T), groundwater wells (GW) and pools in 2009. The given numbers of the drains refer to the previous in-stream sampling point, letters indicates the position of each drain between two points (A: first, B: second, C: third).

- The reference Hutchings et al. (2004) is missing in the Reference list

The corresponding reference was added to the bibliography:

Hutchings N, Dalgaard T, Rasmussen BM, Hansen, JF, Dahl M, Jørgensen LF, Ernsten V, von Platen-Hallermund F, Pedersen SS (2004) Watershed nitrogen modelling. In: Hatch DJ et al. (eds.) Controlling nitrogen flows and losses. Wageningen Academic Publishers. ISBN 90-7699-984-34. p. 47-53.

- Page 7474, line 23: it is not explained what are “Pool” and “TPool” (and difficult to see where they are in Figs. 1 and 2) and what is their significance in this context.

Samples were taken at those two locations. This is why they were included in the first version of the manuscript. However, since we do not treat corresponding results in our statistical analysis, we removed the Pool and Tpool from the maps as well as the text.

- It seems that the words “runoff”, “load” and “discharge” are sometimes used for the same thing. Please check and choose one of these words.

We checked the inconsistencies and replaced “runoff” by “discharge” to describe in-stream water throughout the manuscript. However, we always employed the term “specific load” to describe nutrient losses in terms of yields and therefore kept this notation.