

Authors' reply to the comments of referee #1

(Interactive comment on Biogeosciences Discuss., 11, 7079, 2014)

We thank referee #1 for valuable comments on the manuscript.

*1. In line with hypothesis i), higher DOC concentrations were found in the ditches of the agriculturally used fen than in the rewetted one. However, it is difficult to judge whether this difference in DOC concentrations is indeed related to the agricultural management or to other differences between the sampled fens because of the lack of replicates, which precludes a statistical analysis of the data. In my opinion the statistical comparison of concentrations between DOC concentrations at sites RE and AU in figure 3 violates the assumption that the measured concentrations represent an independent random sample. They are not independent because they represent a time-series of concentrations from one or few sampling points.*

We agree with the referee that time series data of concentrations cannot act as replicates, as they are autocorrelated. Therefore, we focused on descriptive statistics, such as Box-Whisker-Plots as seen in figure 3. For a better readability and in order to stress the large difference between Site RE and Site AU in 2011, we inserted an asterisk, as non-overlapping notches are seen as 'strong evidence' for differing medians (Chambers et al., 1983, p. 62). The notches extend to  $\pm 1.58 \text{ IQR}/\sqrt{n}$ . The asterisk is *not* the result of a non-parametric statistical hypothesis test, which indeed would not be appropriate. So as to avoid any misunderstanding, the asterisk was removed.

Referring to the general request for replicates, we don't see the possibility to find real replicates of landscapes or ecosystems that are nearly 100 % equal and differ in one point at the same time. Of course, the integration of further rewetted and agriculturally used fens in our study would have been very informative. However, there would still be the risk of minor differences in substrate quality, hydrologic and climatic conditions or vulnerability influencing the DOC concentrations. Therefore, we had decided to compare only two albeit very similar fen peatlands to reduce site and climatic effects. Furthermore we sampled three points in the large catchment at Site AU to account for spatial variability, and we detected concentrations over a very long period to monitor DOC release from peatlands in the long term.

2. I am aware that the authors strived to sample two sites as similar as possible in terms of site characteristics land use history and climatic conditions. However, important differences remain, for example the blocking of ditches at site AU that prevented discharge (page 7092, lines 17-19). Higher DOC concentrations at site AU could have been caused by water stagnation in the ditches, because we know that DOC release from soil organic matter into water is a kinetic process.

Blocking of ditches did not alter the DOC concentrations at Site AU, as water sampling at the pumping station (where active pumping and free draining induced discharge frequently) showed DOC concentrations similar to other two sampling points: median of 34.9 mg L<sup>-1</sup> compared to 34.7 mg L<sup>-1</sup> and 34.5 mg L<sup>-1</sup>. Furthermore, water stagnation also occurred at Site RE, when discharge was low or the ditch run nearly dry.

3. Due to low discharge at the AU site, the results of the study also do not support the conclusion that rewetting of fens decreases DOC losses with discharge. Actually, the area-specific DOC loss (kg DOC per hectare) from site AU was even smaller than from site RE (page 7091, lines 17-18). Since the catchments differ in size by more than one order of magnitude, it is necessary in my eyes to compare DOC losses that have been normalized to catchment area and not absolute losses.

We agree, that it cannot generally be assumed, that rewetted fens have lower total discharge than agriculturally used fens. What we meant is that the rewetting of a certain fen is usually accompanied by decreasing run-off to raise the water table. Referring to Site AU, we would expect decreasing DOC losses after the rewetting just by closure of the pumping station. Referring to the second point, we are in line with referee #1 to describe area-specific DOC losses. Accordingly, some sentences in this section were rephrased and, in order to have a more accurate approach, DOC losses were related to the proportion of fen area in the catchments.

4. The analysis of temporal patterns of DOC concentrations in the two investigated fens is independent of replicated treatments for comparisons, but rather qualitative and not always comprehensible for me in its current form. For example on page 7088 lines 20-21 it reads that “A rise in water-table (after strong precipitation or rewetting) is accompanied by a flush of DOC-rich water from soil to ditches...”, but when looking at figure 4, I spotted the highest concentrations during periods of falling water tables (e.g., April-May 2011, Oct.-Nov. 2011).

*I wondered if a more quantitative analysis of the time series of concentrations and potential drivers like climate and groundwater levels using for example wavelet analysis would yield a clearer picture of the crucial factors causing temporal variations of DOC concentrations (see e.g., recent paper of Mengistu, S. G., C. G. Quick, and I. F. Creed, 2013. Nutrient export from catchments on forested landscapes reveals complex nonstationary and stationary climate signals, Water Resour. Res., 49, 3863–3880, doi:10.1002/wrcr.20302).*

According to literature (Lundquist et al., 1999; Kalbitz et al., 2000; Zak and Gelbrecht, 2007), a raise in the water table induces a DOC flush. We assume this process to account for the higher DOC concentrations at Site AU, as water levels were shown to be highly dynamic (e.g. from near-to-surface to WTD of 1 m within six weeks in July/August 2011). Unfortunately, the resolution of DOC concentrations is not high enough to relate them to a single hydrological situation or event. DOC is known to flush with pulsed hydrological events quickly (Wilson et al., 2013), which cannot be monitored with biweekly sampling. Therefore we focused on averaged DOC concentrations (like figure 6 and 7). Referring to the given example in figure 4, one can find very high concentration during periods of rising water tables as well (December 2011). In our opinion, these observations can hardly be interpreted as we have no information of DOC concentrations around this punctual measurement. Figure 4 and 5 are primarily of interest in terms of differing water table and DOC dynamics between Site AU and RE. Time series analyses, like wavelet, seemed inappropriate for our data, as two full years of data are necessary for yearly time series (according to Mengistu et al. 2013) and biweekly resolution is not sufficient for time series of a smaller time scale.

*5. For the interpretation of temporal variations it might be important to account for “dilution effects” as discussed by Schwalm and Zeitz on page 7090, lines 12-14. I suggest normalizing DOC concentrations to concentrations of a rather conservative ion like chloride or bromide to analyze these dilution effects more quantitatively.*

As chloride or bromide ion concentrations have not been detected during the study period, this suggestion must be rejected.

*6. The figures 6 and 7 are not addressed in the text of the manuscript.*

They are addressed in my manuscript for upload. I apologise for not recognising the missing cross references after typesetting.

7. Regarding the relevance of dissolved carbon losses for the carbon budget of peatlands, Schwalm and Zeitz refer to results of Dawson et al. underlining that the contribution of dissolved inorganic carbon is negligibly small in comparison to DOC. I am not convinced that the results of Dawson et al. for rather acidic Scottish peatlands (mean pH 4.8-5.7, Dawson et al., 2002) can be transferred to fens in NE Germany, because the solubility of carbon dioxide in the form of bicarbonate and carbonate is much higher at the pH values of 6.2-8.6 encountered in the investigated sites. Our own unpublished data show average DIC concentrations of 150-170 mg /l in topsoils of agriculturally used fens. Therefore, I would suggest that total dissolved carbon losses from these fens are probably much higher than DOC losses.

Unpublished data from the study sites show TIC concentrations of about 70 mg L<sup>-1</sup>, which is undoubtedly of relevance for the respective carbon budget. A sentence with this recent data was added to the manuscript's 'Results and Discussion' section and to 'Introduction'. As inorganic carbon concentration has a lower sensitivity than DOC against land use changes, we did not focus on it.

## References

- Chambers, J. M., Cleveland, W. S., Kleiner, B. and Tukey, P. A.: Graphical Methods for Data Analysis. Wadsworth & Brooks/Cole, 1983.
- Kalbitz, K., Geyer, S. and Geyer, W.: A comparative characterization of dissolved organic matter by means of original aqueous samples and isolated humic substances., *Chemosphere*, 40(12), 1305–12 [online] Available from: <http://www.ncbi.nlm.nih.gov/pubmed/10789969>, 2000.
- Mengistu, S. G., Quick, C. G. and Creed, I. F.: Nutrient export from catchments on forested landscapes reveals complex nonstationary and stationary climate signals, *Water Resour. Res.*, 49(6), 3863–3880, doi:10.1002/wrcr.20302, 2013.
- Schleier, C. and Behrendt, A.: Kennzeichnung von eigenschaften der folgeböden nordostdeutscher niedermoore, *Arch. Agron. Soil Sci.*, 45(3), 207–221, doi:10.1080/03650340009366123, 2000.
- Wilson, H. F., Saiers, J. E., Raymond, P. a. and Sobczak, W. V.: Hydrologic Drivers and Seasonality of Dissolved Organic Carbon Concentration, Nitrogen Content, Bioavailability, and Export in a Forested New England Stream, *Ecosystems*, 16(4), 604–616, doi:10.1007/s10021-013-9635-6, 2013.
- Zak, D. and Gelbrecht, J.: The mobilisation of phosphorus, organic carbon and ammonium in the initial stage of fen rewetting (a case study from NE Germany), *Biogeochemistry*, 85(2), 141–151, doi:10.1007/s10533-007-9122-2, 2007.

Authors' reply to the comments of referee #2

(Interactive comment on Biogeosciences Discuss., 11, 7079, 2014)

We thank referee #2 for valuable comments on the manuscript.

### **General comments**

*1. How the catchment boundaries were defined is not explained, and yet the calculation of DOC fluxes per unit is critically dependent on these terms, and so therefore are the conclusions about the effects of land-management on DOC export.*

Catchment boundaries for Site RE were defined by 'HYK 50' (Hydrogeological Map 1:50000), and accord to catchment boundaries reported by Zauft (2008) for this rewetted fen. For Site AU, catchment boundaries were adopted from 'WBV Nauen' (Water and Soil Association of the district *Nauen*). Due to intensive land use and complex melioration in the GDR, hydrological conditions are well documented for the *Havelländisches Luch*. We therefore assume the catchment boundaries to be reliable. However, catchment size estimation has some uncertainty by nature, though, from our point of view, the DOC export calculations are more affected by uncertainty of discharge measurement (as discussed in the paper). We therefore agree that reporting of DOC flux per unit must be done with caution. An explanation of the catchment size definition will be added to the text.

The effects of land use change on DOC export were assumed as follows: Site RE has lower DOC concentrations as does Site AU, and moreover, concentrations decreased since 2007. We therefore concluded that rewetting of degraded peatlands leads to a decrease in DOC concentrations. Because rewetting is usually initiated by drain blocking in order to raise the water table, a decrease in discharge can be assumed as well. Lower DOC concentrations at a lower discharge means a reduction of DOC flux in the long term.

*2. From Table 1, 35 % of the agricultural site is not peat, but which areas, and how do these areas influence results?*

35 % of the area AU is not *peatland*, but peaty soils that do not fulfil the WRB key for Histosols (WRB, 2006), or islands of mineral soils spread over the area. As a result of

long lasting agricultural use, Site AU is strongly degraded and fen soils converted to post fen soils in the *Havelländisches Luch* (Schleier and Behrendt, 2000). The proportion of peatland in a catchment strongly influences the DOC concentrations (Dillon and Mollot, 1997; Koprivnjak and Moore) and DOC fluxes should be related to hectares of peatland. More precisely, it is not only the peatland area but also the peat layer thickness that needs to be taken into consideration, which is mostly not practicable lacking sufficient data.

*3. Additionally, the authors refer to the use of pumps in the agricultural catchment, without explaining what the pump are doing (removing water? If so how much?), where they are located, or wether pumped water was included in the flux calculations.*

One pumping station drains Site AU (page 7085, line 25 and 7092, line 18) which is located at the outlet of the catchment. The two pumps of the pumping station get enabled on demand to lower the water table (e.g. to enhance soil trafficability in spring). On account of these circumstances, no water level-discharge-relationship could be interpolated.

*4. I am not particularly keen on the mixing up of results and discussion. This results in some subjective statements during the reporting of results – e.g. ‘interestingly’ on the first line of this section, ‘we assume that’ later on, and ‘in our opinion’ on page 7088, where the authors propose a hydrological explanation for observed differences in DOC between sites, without having first described their hydrological results. Similarly, results from previous publications are interspersed with and sometimes described before the authors’ own results, which makes it difficult to work out what is new here.*

The respective sections will be rephrased and results and discussion will be more clearly segregated.

#### **Specific comments:**

*5. I think the statement about DOC ‘harming’ water quality and diminishing carbon storage is questionable – the ‘harm’ is only really true for water treatment, and the connection between DOC and carbon storage is not straightforward – see e.g. Evans et al., Geophysical Research Letters 2007.*

We think, DOC does harm ‘drinking water quality’, as high levels of DOC affect odour, flavour and colour, and as water treatment is impeded and can provoke the formation of carcinogenic substances (Chow et al., 2003; Krasner et al., 1999).

Regarding the second point, Evans et al. (2007, page 1) say, referring to DOC losses: “Reported C losses may to a significant extent be explained by mechanisms other than climate change, e.g. recovery from acidification in peatlands, and agricultural intensification in managed systems.” Since we do not argue for the relationship between DOC concentrations and climate change but for concentrations linked with land use intensity, we don’t see a contradiction.

6. Page 7080: Line: ‘conducted’ mis-spelt.

We corrected the mistake.

7. Line 22: I think Parish et al. is a secondary reference for this figure.

The reference was removed from the text.

8. Page 7081: Line 9: Driscoll is mis-spelt.

We corrected the mistake.

9. Line 15: ‘17 % of the total carbon exchange’ does not make much sense to me – net C exchange can be positive or negative, and is the balance of two large gross fluxes (photosynthesis and respiration) plus some smaller ones (DOC loss being usually the most important).

Net peatland carbon balances mostly do not take DOC into consideration, which is a problem as the given example says that DOC accounted for 17 % of the total carbon exchange.

10. Line 18: This is not the correct final reference for the IPCC Wetland Supplement – also elsewhere. I suggest using IPCC (2014) as reference in the text.

We changed the citations as suggested.

11. Page 7082: Line 10: The reference to acidification due to declining water table requires some explanation, i.e. that is the result of sulphur oxidation.

We added an explanation: “[...] a drop in the water table is considered to be a factor for declining DOC concentrations due to acidification after sulphur redox reactions (Clark et al., 2012) [...]”

12. Line 19-24: The two sentences here about DOC response to re-wetting appear to contradict each other. This whole paragraph seems a little confused, throwing a lot of references together without a clear structure. The seasonality issue should be more clearly differentiated from the discussion of drainage and re-wetting effects.

After dry periods, DOC gets washed out directly after a raise in the water table. In the long term, constantly near-to-surface water levels stabilise soil organic matter turnover and thus reduce DOC concentrations. We improved these two sentences, and added a word wrap to segregate the seasonality issue from water level effects.

13. Page 7083: Line 23: *I think these are hypotheses, not assumptions? Hypothesis 2 seems so well-established that I wonder of it is worth including here? Also, why nothing about fluxes here?*

We replaced ‘assumptions’ with ‘hypothesis’. Hypothesis 2 indeed is well-established. Although we had to reject this hypothesis it as we found highest concentrations during winter months and not during growing season. That made it worth to be included as hypothesis.

14. Page 7084: Line 14: *Use m or cm rather than dm for depth. How far apart are the study sites? It would be good to know this without having to process the latitude/longitude data from Table 1.*

Unit of peat layer thickness changed to cm, as suggested. The distance between both study sites (90 km) was added to the text.

15. Line 21: *‘Mainly peatland specific plants’ and ‘a little swamp forest’ is completely inadequate – what species are present, what is the management? Similarly, what is the management of the agricultural site – livestock? arable?*

A more detailed description of the study sites was integrated into the manuscript.

Present, peatland specific plant species at Site RE are: *Alnus glutinosa*, *Betula pubescens*, *Phragmites australis*, *Carex* sp., *Galium palustre*, *Stellaria palustris*, *Typha angustifolia*, *Utricularia vulgaris*, *Lemna minor*, *L. trisulca*, *Potentilla palustris*, *Lythrum salicaria*, *Thelypteris palustris*, *Epilobium palustre*, *Sphagnum* sp. Species inventory was added to the manuscript. There is no management but natural succession after rewetting in 2003 (page 7084, line 19).

Grassland of Site AU is mostly managed as meadow (2-3 cuts per year) and pasture (cattle and doe), with a small area (< 50 ha) of *Zea mays* (page 7085, line 8). Due to the heterogeneous relief (wet and dry microforms) a broad range of plant species occur: *Lolium perenne*, *Festuca arundinacea*, *Alopecurus geniculatus*, *Agrostis stolonifera*, *Phalaris arundinacea*, *Poa pratensis*, *Bromus mollis*, *Linaria vulgaris*, *Silene alba*, *Carex* sp., *Juncus* sp.



16. Page 7085: Line: 12: What method was used to estimate DOC – total C minus inorganic C, or non-purgeable organic carbon? This is important – the NPOC method is problematic for high pH because some of the organic carbon tends to precipitate out when the sample is acidified. On this subject, it seems to me that inorganic C has been largely ignored in the paper, but in a fen it may be a large part (the majority?) of the carbon export, even if it does not all necessarily derive from the peat.

DOC was estimated by measuring NPOC. Preliminary tests showed that the difference between NPOC and TOC minus TIC was negligible. Inorganic carbon was about 70 mg L<sup>-1</sup> and therefore undoubtedly plays a significant role regarding carbon export. As inorganic carbon concentration has a lower sensitivity to land use changes than DOC, we did not focus on it. The idea of our study was to link land use intensity with DOC losses in order to determine avoidable carbon losses. Although concentrations of inorganic carbon are higher than these of organically bound carbon, the amount of carbon lost via DOC is substantial and contributes significantly to the carbon budget (page 7091, 7092).

17. Line 13: What depth were soil waters collected from within the wells (see also later comment about the results)?

Soil water was sampled within the peat layer, i.e. in a depth of up to 1 m.

18. Line 15: Was a baro-diver used to correct for atmospheric pressure? Line 21: Use of 'interval' is here unclear. Line 23: Where is the rating curve? A figure, or regression equation with accompanying statistical information should be provided. Line 27: What was R used for? I can't see any statistics in the paper.

The use of a Baro diver was added to the text. The "interval" refers to the biweekly discharge measurements mentioned above (page 7085, line 19) . A figure of the rating curve will be added to the manuscript. R was used for the graphics and mathematical operations.

19. 7086: The information on sources of weather data should be in the site description or methods. Line 3: Delete 'interestingly' – better just report the results here. Line 9: Hard to distinguish negatives from dashes – suggest using 'to' instead of '-'. Line 14: 'Unordinary' should be 'atypical' or similar.

The source of weather data is mentioned in the site description now. Verbal expressions were changed as suggested.

20. Page 7087: Line 22: *I think higher DOC concentrations in porewaters could also be explained by low mobility of water within the peat, particularly if samples were collected from deeper within the peat profile.*

The water collected from wells was from a maximum depth of 1 m.

21. Page 7088: Line 10: *It seems highly questionable to use literature data from a fen in Canada as a natural reference condition for the re-wetted site in Germany. It is reasonable to compare the data, but I would be more cautious about the statement that DOC concentrations at the RE site are only marginally elevated. You would need data from a natural site in Germany with similar site characteristics and water balance to support this conclusion.*

As more than 95 % of German fens are disturbed, it is difficult to find a natural site that should, moreover, be similar regarding site characteristics and hydrological conditions. We therefore rephrased this paragraph to express the geographic distance between both sampling points.

22. Page 7089: Line 1: *Unless you have some data on either phenolic concentrations or enzyme activities, the reference to enzyme latch is no more than speculation - I suggest removing this, and restricting the discussion to what the measured data actually do or don't show.*

At this point, we aimed to give a few explanations about decreasing DOC concentrations. We decided to keep this argument but included the following:

“However, this is rather speculative as we did not record phenolic concentrations”.

23. Line 3: *I think possibly the ditches at the study site of Kalbitz and Geyer intersect the mineral soil? I believe their sites were shallow relict peats, which could explain reduced DOC concentrations in drained sites due to greater mineral DOC retention.*

Kalbitz and Geyer (2002) bring forward the argument that the decreasing carbon content during degradation leads to lowering of DOC concentrations. We could not find a hint that the respective ditches intersect the mineral soil.

23. Line 24 (and elsewhere): *Use full site names or acronyms, but don't mix them up, especially not in the same sentence.*

We changed them as suggested.

24. 7091: Line 3: *The hypothesis that ‘concentrations of DOC underlie seasonality’ does not make much sense.*

We do not know what exactly is meant by this comment. Nevertheless, we rephrased the sentence to: “Overall, our hypothesis that concentrations of DOC underlie seasonality – in terms of high concentrations during growing season and low concentrations during winter – must be rejected”.

25. Line 22, 23: *‘Billet’ should be ‘Billett’. Also, ‘has shown’ should be ‘showed’.*

We changed that as suggested.

26. Page 7092: Line 1: *I don’t really understand how a paper from 1998 could have questioned the peat C accumulation rates published in 2004-2007? Also, there are numbers of recent cull carbon budgets for peatlands that could be referenced here, several of which included DOC and some of which (e.g. Dinsmore et al. 2011) highlight the importance of aquatic C losses.*

Moore et al. (1998) questions the accuracy of carbon accumulations rates in general, not those from 2004 and 2007, of course. We rephrased this misleading sentence and added some recent literature.

27. Line 9: *‘Balancing’ should be ‘balances’.*

We corrected it as suggested.

28. Figures 1 and 2: *These are very uninformative – what are all the lines supposed to show (ditches? natural streams? dams in figure 2?). I would have liked a far more detailed map showing (for example) the boundaries of the peat area, field boundaries, detailed location of pumps, elevation, geographic location. In figure 2 the lake is obviously just a hand-drawn oval, and I don’t understand how the water is moving – does water drain from the lake into the fen (in which case surely this is part of the catchment area) or is the lake hydrologically isolated from the fen (in which case there is perhaps no point in showing it on the figure). Arrows showing flow lines would also be helpful.*

We’ll add a more informative map to the revised manuscript.

29. Figures 6 and 7 do not seem to be referenced or discussed anywhere in the manuscript, and I cannot really see any relationship between the climate anomalies and the DOC concentrations. *If no relationship can be demonstrated and the figures are not important*

*enough to be discussed in the text, I suggest that they are removed. At the least, I think that these two figures could be merged.*

These figures were addressed in our manuscript but the cross reference got lost after typesetting. DOC concentrations by quarter are very valuable in our opinion, as the results contradict the frequently reported seasonality of DOC concentrations (highest concentrations during growing season, page 7089, line 26). We therefore would like to keep these figures.

## References

- Evans, C.D., Freeman, C., Cork, L.G., Thomas, D.N., Reynolds, B., Billett, M.F., Garnett, M.H., Norris, D.: Evidence against recent climate-induced destabilisation of soil carbon from <sup>14</sup>C analysis of riverine dissolved organic matter, *Geophysical Research Letters*, 34(7), L07407, 2007.
- Chow, A.T., Tanji, K.K., Gao, S., 2003. Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. *Water Res.* 37(18), 4475–4485.
- Clark, J.M., Heinemeyer, A., Martin, P., Bottrell, S.H.: Processes controlling DOC in pore water during simulated drought cycles in six different UK peats, *Biogeochemistry*, 109 (1–3), 253–270, 2012.
- Dillon, P. J. and Molot, L. A.: Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. -*Wat. Resour. Res.* 33(11): 2591–2600, 1997.
- Koprivnjak, J.-F. and Moore, T. R.: Sources, sinks and fluxes of dissolved organic carbon in subarctic fen catchment. - *Arc. Alp. Res.* 24(3): 201–210, 1992.
- Krasner, S. W., 1999. Chemistry of disinfection by-product formation, in: Singer, P. C. (Eds.), *Formation and Control of Disinfection By-Products in Drinking Water*, American Water Works Association, Denver, USA.
- Moore, T.R. (1998): Dissolved Organic Carbon: Sources, Sinks and Fluxes and Role in the Soil Carbon Cycle, in: *Soil processes and the carbon cycle*, by: Lal, R., Kimble, J. M., Follett, R. F. and Stewart, B. A. (Eds.), CRC Press, Florida, USA, 624 pp., 1998.
- Schleier, C. and Behrendt, A.: Kennzeichnung von Eigenschaften der Folgeböden Nordostdeutscher Niedermoore, *Arch. Agron. Soil Sci.*, 45(3), 207–221, 2000.