



Effect of past peat cultivation practices on present dynamics of dissolved organic carbon



S. Frank^{a,1}, B. Tiemeyer^{a,*}, M. Bechtold^a, A. Lücke^b, R. Bol^b

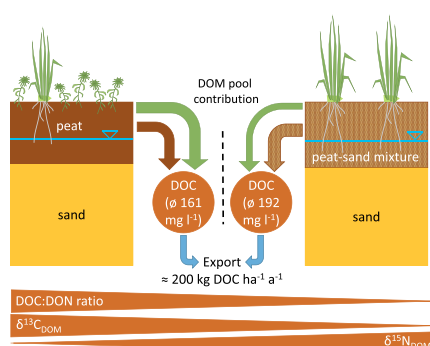
^a Thünen-Institute of Climate-Smart Agriculture, Bundesallee 50, 38116 Braunschweig, Germany

^b Institute of Bio- and Geosciences, IBG-3: Agrosphere, Forschungszentrum Jülich, 52425, Jülich, Germany

HIGHLIGHTS

- First study on DOC dynamics in shallow organic soils with peat-sand mixtures.
- DOC concentrations in soil solution and losses were high compared to natural bogs.
- Peat-sand mixing did not reduce DOC concentrations compared to pure peat.
- DOC concentrations showed delayed response to temperatures and water levels.
- Peat-sand mixing altered DOM cycling and thus the seasonal dynamics.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 May 2016

Received in revised form 7 July 2016

Accepted 9 July 2016

Available online 24 September 2016

Editor: Jay Gan

Keywords:

DOC
Stable isotopes
Deep ploughing
Drainage
Rewetting

ABSTRACT

Peatlands are a major source of dissolved organic carbon (DOC) for aquatic ecosystems. Naturally high DOC concentrations in peatlands may be increased further by drainage. For agricultural purposes, peat has frequently been mixed with sand, but the effect of this measure on the release and cycling of DOC has rarely been investigated. This study examined the effects of (i) mixing peat with sand and (ii) water table depth (WTD) on DOC concentrations at three grassland sites on shallow organic soils. The soil solution was sampled bi-weekly for two years with suction plates at 15, 30 and 60 cm depth. Selected samples were analysed for dissolved organic nitrogen (DON), $\delta^{13}\text{C}_{\text{DOM}}$ and $\delta^{15}\text{N}_{\text{DOM}}$.

Average DOC concentrations were surprisingly high, ranging from 161 to 192 mg l^{-1} . There was no significant impact of soil organic carbon (SOC) content or WTD on mean DOC concentrations. At all sites, DOC concentrations were highest at the boundary between the SOC-rich horizon and the mineral subsoil. In contrast to the mean concentrations, the temporal patterns of DOC concentrations, their drivers and the properties of dissolved organic matter (DOM) differed between peat-sand mixtures and peat. DOC concentrations responded to changes in environmental conditions, but only after a lag period of a few weeks. At the sites with a peat-sand mixture, temperature and therefore probably biological activity determined the DOC concentrations. At the peat site, the contribution of vegetation-derived DOM was higher. The highest concentrations occurred during long, cool periods of waterlogging, suggesting a stronger physicochemical-based DOC mobilisation. Overall, these results indicate that mixing peat with sand does not improve water quality and may result in DOC losses of around 200 $\text{kg DOC ha}^{-1} \text{a}^{-1}$.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

* Corresponding author.

E-mail address: baerbel.tiemeyer@thuenen.de (B. Tiemeyer).

¹ Present address: State Authority for Mining, Energy and Geology, Stilleweg 2, Hannover, Germany.

1. Introduction

Natural peatland offer a number of important ecosystem services such as carbon sequestration and nutrient retention (Bonn et al., 2014). In natural peatlands, the export of dissolved organic carbon (DOC) may be an important part of the total carbon budget (Dinsmore et al., 2010) and changes in DOC export may shift the carbon balance from a sink to a source or vice versa. Drainage for agriculture turns peatlands from a carbon sink into a carbon source due to high carbon dioxide (CO_2) emissions (Maljanen et al., 2010; Tiemeyer et al., 2016) and usually causes nutrient losses (Holden, 2005). Furthermore, drainage usually increases DOC concentrations and losses (Evans et al., 2016). High DOC concentrations can impact the water quality of downstream aquatic systems by changing trace metal transport, light transmittance as well as energy and nutrient supply (Evans et al., 2005).

In the last few decades, numerous studies have been conducted to understand the cycling of dissolved organic matter (DOM) in peatlands. DOC concentrations have been found to be controlled by the C content of the peat (Kalbitz et al., 2002), by oxygen availability or, as a proxy for oxygen availability, by water table depth (WTD) (Frank et al., 2014) and by the degradation status of the peat (Zak and Gelbrecht, 2007). Like DOC concentrations, DOM quality in peatlands has been found to be altered by WTD (Wallage et al., 2006; Höll et al., 2009; Frank et al., 2014) as well as land use history (Kalbitz et al., 2000a; Kalbitz and Geyer, 2002). DOM released from more heavily degraded peat tends to be more strongly microbially degraded, as evidenced by a narrower DOC to dissolved organic nitrogen (DON) ratio (Kalbitz and Geyer, 2002; Frank et al., 2014) and an enrichment of $\delta^{13}\text{C}$ (Kalbitz et al., 2000a). Soil solution properties such as pH value (Evans et al., 2012) and ionic strength (Clark et al., 2011) also affect DOC solubility and concentrations. The seasonal dynamics of DOC concentrations are frequently governed by hydro-meteorological conditions (Dinsmore et al., 2013), which may interact with changes in solution chemistry (Clark et al., 2005).

In north-western Germany, widespread agricultural measures have included covering peat soils with sand and deep-ploughing it into the mineral subsoil (about 79,000 ha or 16% of agriculturally used peatland) (Schulz and Waldeck, 2016) to improve the soil's bearing capacity. Similar agricultural measures have been undertaken in Scandinavia (Sognnes et al., 2006) and the Netherlands (de Bakker, 1978). Another 93,000 ha in north-western Germany alone are SOC-rich soils, which have been developed from peat soils by CO_2 losses due to drainage, but no longer meet the definition of peat (MU, 2016). These soils may also possess a mixed peat-sand horizon in the topsoil. An early laboratory study indicates that mixing peat with sand might increase DOC losses (Ross and Malcolm, 1988), while it does not reduce CO_2 emissions in the field (Leiber-Sauheithl et al., 2014). Although mixing peat and sand is quite a drastic agricultural measure, there have been no field studies so far on the effects of these peat-sand mixtures on DOC concentrations and DOM cycling.

This study investigated the effect of peat-sand mixing on DOM cycling. In a shallow peatland currently used for low-intensity sheep grazing, sites with a peat-sand mixture were compared with a peat site to address the following hypotheses:

- DOC concentrations will be higher at the peat site due to its higher SOC content,
- DOC concentrations will be higher where there are deeper water tables,
- antecedent conditions of environmental variables will be crucial for DOC dynamics,
- properties of DOM in the peat-sand mixture will indicate a stronger microbial degradation due to heavy physical disturbance.

2. Study site

The study was conducted at “Grosses Moor”, a bog-fen complex covering 60 km² near Gifhorn (Germany; 52°34'N, 10°39'E, see Fig. 1). Long-term mean annual temperature and precipitation were 9.6 °C and 656 mm. Peatland formation started in a Pleistocene depression approximately 8000 years ago on gravelly, medium to coarse sand (Schneekloth and Schneider, 1971). The peat thickness reached 5 to 7 m in the centre of the bog.

Industrial cutting of bog peat started in the 19th century and changed peat layer thickness and hydrology. Nowadays, peat layer thickness is highly variable (0 to 5 m) (Schneekloth and Schneider, 1971). Recent vegetation is dominated by extensive grassland, pine and birch forests as well as purple moor-grass (*Molinia caerulea* (L.) Moench), soft rush (*Juncus effusus* L.) and heather (*Calluna vulgaris* (L.) Hull) in former peat harvesting areas.

The study site (Fig. 1) is part of a nature conservation area which was established in 1984 and covers about 2700 ha of the peatland. Since then, it has been managed as low-intensity grassland without fertilisation, and ditches have been partially closed to raise the WTD. The study site is mulched in autumn and grazed by sheep between one to three times per year. The sampling sites were fenced to prevent sheep from damaging the measurement equipment, and grazing was mimicked by cutting the vegetation while the sheep were in the field.

The study area shows a pronounced heterogeneity in peat layer thickness, soil organic carbon (SOC) concentrations and stocks, peat disturbance and WTD (Altdorff et al., 2016). The heterogeneity was caused by differences in peat extraction depth causing ridge-like topographic features and by two different cultivation practices after peat extraction (Fig. 1): While the northern part of the study site was not ploughed, the residual peat in the southern part was mixed with underlying coarse sand by ploughing (30 cm). Differences in mean WTD are mainly caused by the topography, which causes the SOC concentration and WTD to be largely independent of each other.

Three sampling sites were chosen to cover major differences in SOC and WTD. The sites $\text{C}_{\text{low-dry}}$ and $\text{C}_{\text{low-wet}}$ have a relatively low SOC content compared to $\text{C}_{\text{high-wet}}$ while “dry” and “wet” refer to the mean annual water table depth (Table 1). Greenhouse gas fluxes were measured at directly adjacent plots (Leiber-Sauheithl et al., 2014).

In the SOC-rich layer, SOC concentrations ranged from around 10% at sites with a peat-sand mixture as topsoil ($\text{C}_{\text{low-dry}}$ and $\text{C}_{\text{low-wet}}$) to around 48% at the site with a residual peat profile ($\text{C}_{\text{high-wet}}$) (Table 1). The peat-sand mixture is loamy sand with 84% sand, 11% silt and 5% clay. Mean WTD ranged from −0.16 to −0.31 m below the surface (Table 2). Differences in peat properties and WTD are reflected by a higher percentage of moss cover at $\text{C}_{\text{high-wet}}$ compared to the grass-dominated sites $\text{C}_{\text{low-dry}}$ and $\text{C}_{\text{low-wet}}$.

3. Methods

3.1. Field measurements and sample collection

Air temperature (2 m), soil temperature (2, 5, 10, 20, 50 cm), global radiation, albedo, wind speed and precipitation were measured at the site (Fig. 1). All hydro-meteorological data were logged at 15 min intervals. Grass reference evapotranspiration ET_0 was calculated according to Allen et al. (1998). At each sampling site, WTD was recorded using a dip well equipped with groundwater level loggers (Mini-Diver, Schlumberger, Delft, Netherlands). WTD below the ground surface was defined as negative and ponding as positive. Soil tension was recorded using T8 tensiometers (UMS, Munich, Germany) at 15, 30 and 60 cm depth at each site.

The soil solution was sampled bi-weekly from June 2011 to June 2013. Solution plates (borosilicate glass, 80 mm diameter, ecoTech, Bonn, Germany) were installed at three depths (15, 30 and 60 cm) in three replicates. The applied suction was chosen on the basis of soil

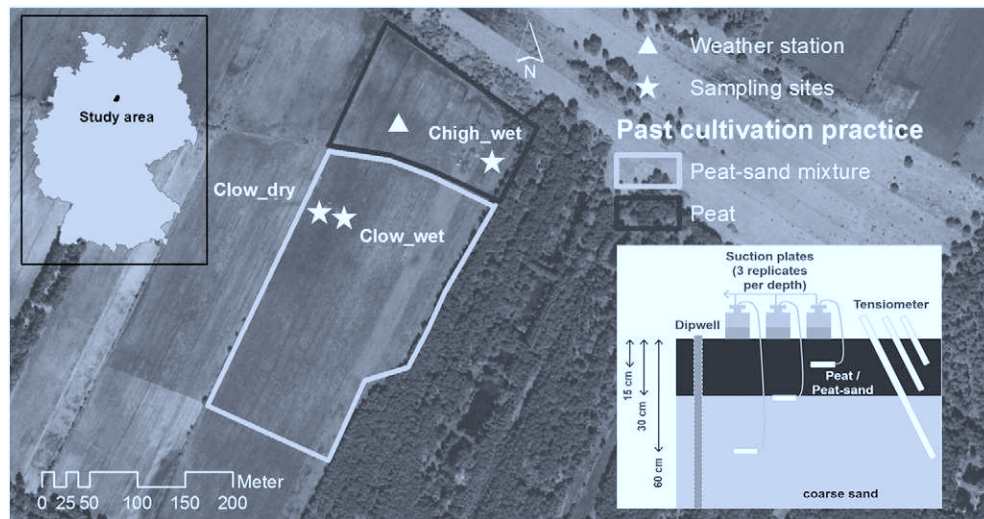


Fig. 1. Map of the study area and sampling sites (aerial image: Federal Agency for Cartography and Geodesy).

water tension measured at the start of each two-week sample collection period.

Vegetation (green biomass) and soil samples were taken adjacent to the sampling sites. Living roots of the herbaceous vegetation were carefully separated from the soil and were mainly present in the upper most 10 cm. Soil samples were taken from each horizon.

3.2. Laboratory measurements

Solution samples were immediately analysed for pH and electrical conductivity (EC) (WTW, Weilheim, Germany). They were then filtered using 0.45 µm PES membrane filters (Pall Life Science, Port Washington, NY, USA) and stored (at 4 °C) until analysis. If it was not possible to conduct the analyses within three days, the samples were frozen at −18 °C.

DOC was measured in each sample in at least three replicates using a DimaTOC 2000 (DIMATEC, Essen, Germany). DOC was calculated as the difference between total carbon (combustion at 850 °C) and total inorganic carbon (combustion at 165 °C after acidification).

Soil and vegetation samples were oven dried (40 °C), sieved and ground. Soil total organic carbon (TOC) and total nitrogen (N_t) contents were measured on a LECO TrueMac CN (LECO Corporation, St. Joseph, Michigan, USA).

Solution samples from the sites C_{low_wet} and C_{high_wet} on twelve dates covering a broad range of hydrological conditions and temperatures were chosen for further analyses (29/08/2011, 12/09/2011, 26/09/2011, 12/03/2012, 26/03/2012, 13/04/2012, 14/08/2012, 27/08/2012, 10/09/2012, 25/09/2012, 08/10/2012, 22/10/2012) (Fig. S1).

Table 1

Soil properties of the sampling sites (Leiber-Sauheitl et al., 2014, amended). Soil type according to IUSS Working Group WRB (2007). SOC = soil organic carbon, N_t = total nitrogen, C:N ratio = SOC:N_t ratio, BD = bulk density, f = porosity, n.d. = not determined.

Depth (cm)	SOC (%)	N _t (%)	C:N ratio	pH	BD (g cm ⁻³)	f (–)	SOC stock (kg m ²)
<i>C_{low_dry}</i> : histic gleysol							
0–30	11.3	0.42	27	4.5	1.06	0.59	36
> 30	0.6	0.02	24	4.7	1.65	0.37	n.d.
<i>C_{low_wet}</i> : histic gleysol							
0–32	9.3	0.39	24	4.5	0.97	0.59	29
> 32	0.4	0.02	21	4.7	1.91	0.31	n.d.
<i>C_{high_wet}</i> : histic gleysol							
0–30	47.9	1.73	28	3.8	0.29	0.88	41
30–34	12.9	0.44	29	4.3	1.00	n.d.	5
> 34	2.7	0.12	23	4.6	1.75	n.d.	n.d.

Dissolved organic nitrogen (DON) was determined from these selected samples as the difference between total dissolved nitrogen (TDN) and mineral nitrogen (nitrate and ammonium). TDN was measured by reduced pressure chemiluminescence detection (TN-100, Mitsubishi, Kagawa, Japan). Nitrate and ammonium were determined by ion chromatography (850 Professional ion chromatograph, Metrohm, Filderstedt, Germany).

DOM stable carbon and nitrogen isotope compositions were determined for these selected solution samples. The solution samples were freeze-dried and the remaining dry matter was used for analysis. Since nitrate concentrations were negligible (<0.9 mg l⁻¹), they did not bias (contaminate) δ¹⁵N isotope measurements. Samples were smoothly homogenised with a spatula prior to analysis. Soil and vegetation samples were freeze-dried and milled prior to analysis. About 250 mg of the sample powder was weighed into tin capsules to provide about 100 µg of carbon. For nitrogen isotope analyses in a separate run, samples were weighed into tin capsules to provide about 60 µg of nitrogen. Samples were combusted at 1080 °C using an elemental analyser (Thermo Scientific Flash 2000) interfaced in-line with an isotope ratio mass spectrometer (Thermo Scientific Delta V Advantage). The carbon or nitrogen contents of each sample were determined by peak integration

Table 2

Vegetation composition (species with a cover >3%), management and mean water table depth (WTD) (01.06.2011–31.05.2013).

Sampling site	Species	Management	Mean WTD (m)
<i>C_{low_dry}</i>	<i>Poa pratensis</i> L.	2011: 3 cuts, one mulching 2012: two cuts	0.31 ± 0.13
	<i>Agrostis stolonifera</i> L.		
	<i>Poa trivialis</i> L.		
	<i>Holcus mollis</i> L.		
	<i>Ranunculus repens</i> L.		
<i>C_{low_wet}</i>	<i>Agrostis capillaris</i> L.	2011: 3 cuts, one mulching 2012: two cuts	0.19 ± 0.14
	<i>Carex leporina</i> L.		
	<i>Ranunculus repens</i> L.		
<i>C_{high_wet}</i>	<i>Agrostis stolonifera</i> L.	2011: one cut, one mulching 2012: two cuts	0.16 ± 0.15
	<i>Carex nigra</i> (L.) Reichard		
	<i>Aulacomnium palustre</i> (Hedw.) Schwägr.		
	<i>Sphagnum fallax</i> H. Klinggr.		
	<i>Drepanocladus fluitans</i>		
	<i>Molinia caerulea</i> (L.) Moench		
	<i>Sphagnum cuspidatum</i> Ehrh. ex Hoffm.		
	<i>Festuca ovina</i> L.		

of m/z 44, 45 and 46, and calibrated against elemental standards analysed in the same run. Isotope ratios are expressed as δ -values in per mil (‰), where $\delta = (R_{\text{sample}} / R_{\text{standard}} - 1) \times 1000$, with R_{sample} and R_{standard} as isotope ratios ($^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$) of samples and standards, respectively, and reported against Vienna Pee Dee Belemnite (VPDB) ($\delta^{13}\text{C}$) and air ($\delta^{15}\text{N}$). Besides calibration standards, additional laboratory standard materials were inserted between field samples to monitor the mass spectrometer performance between single autoruns. The overall precision of replicate analyses of samples was $<0.1\%$ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

3.3. Soil hydrological modelling

Due to instrument failures, there were gaps in the tensiometer data (approximately 11%). Furthermore, measurement fluctuations of a few hPa that are typical for tensiometers hampered the interpretation of low gradients ($<1 \text{ hPa cm}^{-1}$) that occurred at wetter conditions for around 50% of the time. A soil hydrological model (Hydrus 1D) was set up to obtain continuous and consistent time series of soil water tension at the measurement depths. As a first step, soil hydraulic parameters of the van Genuchten-Mualem model (van Genuchten, 1980) were derived from laboratory evaporation experiments (Dettmann et al., 2014). In a second step, root water uptake parameters of the Feddes function (Feddes et al., 1978) and hydraulic conductivity parameters of the van Genuchten-Mualem model were calibrated on the entire range of in situ measured field soil water tension data (ranging from 0 to appr. 140 hPa). Precipitation, potential evapotranspiration and measured WTDs were prescribed. Achieved RMSE were fairly low (6.5 to 9.7 hPa). Absolute values of modelled water fluxes could not be validated and might be less reliable. This paper therefore relies on the modelled fluxes only as a relative measure.

3.4. Statistical modelling

Due to frost or low soil moisture, water samples could not always be taken from all suction plates. As missing DOC concentrations of one suction plate may bias the average DOC concentrations on these dates, gaps ($n = 47$) were filled by linear regression between the concentrations of the replicate suction plates. The same method was applied for missing pH values.

We applied linear mixed effects (LME) and generalized least squares (GLS) models from the nlme (Linear and Nonlinear Mixed Effects Models) package (Pinheiro et al., 2013) in R (R Core Team, 2013) in order to: 1) identify differences in DOC concentrations between sampling sites and depths and 2) analyse the influence of environmental variables on the time series of DOC concentrations individually for each site and depth.

Model building was based on the procedure given in with Zuur et al. (2009). First, an LME model was set up to test the differences of DOC concentrations between the sites, including all depths. Second, separate LME models for each site were built to evaluate the depth-dependency of DOC concentrations. LME models were used to account for the “random effects” induced by the three replicate suction plates. Appropriate variance structures were tested and added if they improved the model. A first-order autocorrelation structure (corAR1) was then tested and added if it improved the model. To test model improvement, the Akaike information criterion (AIC) was used and compared using an analysis of variance (ANOVA) after re-fitting the model with the “maximum likelihood method”. An example of one such model is given in Eq. (1).

$$\begin{aligned} \text{lme}(\text{DOC} \sim \text{sampling site}, \text{random} = 1|\text{suction plate}, \text{weights} \\ = \text{varPower}(\text{form} = \sim 1|\text{sampling site}), \text{correlation} \\ = \text{corAR1}(0.6, \text{form} = \sim \text{date}|\text{suction plate})) \end{aligned} \quad (1)$$

This full model was tested against a “zero” model (Eq. (2)) to test whether the fixed effect (sampling site or depth) had a significant impact on DOC concentrations. For the “zero” model, the fixed effect was substituted by 1, indicating the mean of all data:

$$\begin{aligned} \text{lme}(\text{DOC} \sim 1, \text{random} = 1|\text{suction plate}, \text{weights} \\ = \text{varPower}(\text{form} = \sim 1|\text{sampling site}), \text{correlation} \\ = \text{corAR1}(0.6, \text{form} = \sim \text{date}|\text{suction plate})) \end{aligned} \quad (2)$$

Several models indicated a significant impact of the fixed effects, as shown by significant differences in the model AIC. Thus, for all models a Tukey post-hoc test implemented for generalized linear models in R was applied (Hothorn et al., 2008) to evaluate the sites or depths that differed significantly from one other.

As a first step in the analysis of the effect of environmental variables on DOC concentrations, a cross-correlation with a lag time of up to 140 days was performed. The values of the three suction plates were averaged (DOC_{mean}) for this analysis. Environmental variables included soil temperatures, pH values, modelled water fluxes, modelled water-filled pore space (WFPS) and WTD. Cross-correlation was used to find an optimal set of explanatory variables for further model building and to account for antecedent conditions and a possible delayed response in DOC concentrations. This was conducted separately for each site and depth.

Model building started with full GLS models containing all explanatory variables and plausible interactions. A variance structure and a first-order autocorrelation structure (corAR1) were then tested and added if they improved the model. Again, the AIC of the models was compared by an ANOVA. The structure of an example of a full model is given by Eq. (3) (WTD = water table depth, ST = soil temperature, FLUX = water flow direction, WFPS = modelled water-filled pore space, pH = pH value):

$$\begin{aligned} \text{glS}(\text{DOC}_{\text{mean}} \sim \text{WTD} + \text{ST} + \text{FLUX} + \text{WFPS} + \text{pH} + \text{WTD} : \text{ST}, \\ \text{weights} = \text{varPower}(\text{form} = \sim \text{WTD}), \\ \text{correlation} = \text{corAR1}(0.6, \text{form} = \sim \text{date})) \end{aligned} \quad (3)$$

Potential explanatory variables were dropped when the AIC of a reduced model was not significantly higher than the AIC of the full model ($p > 0.05$).

4. Results

4.1. Hydro-meteorological conditions

Mean air temperatures and precipitation sums during the periods 01/07/2011 to 30/06/2012 and 01/07/2012 to 31/06/2013 were 9.4 and 8.1 °C and 675 and 738 mm respectively. Annual grass reference evapotranspiration sums (ET₀) were 600 and 518 mm for the first and second period respectively. Thus, seepage to groundwater was estimated to be 75 and 220 mm.

During the study period, the driest site (C_{low-dry}) had a mean WTD of -31 cm and the largest water table amplitude (WTD ranging from -1 to -57 cm below surface in the dip well). The wetter sites (C_{low-wet} and C_{high-wet}) had shallower WTDs (-19 and -16 cm) and about the same water table amplitudes (both sites: $+4$ to -50 cm). WTD at the sites with peat-sand mixtures (C_{low-wet}, C_{low-dry}) remained at -15 cm or higher for 28 and 170 days respectively in both periods. At the peat site (C_{high-wet}), this was the case for 265 days. The sand at 60 cm sampling depth remained water saturated throughout the entire study period at all sites.

At C_{low-dry}, the deeper WTD led to a slightly lower modelled WFPS at 15 cm depth but not at 30 cm depth (Table 3). The proportion of dates with upward water fluxes generally decreased in the order C_{low-dry} > C_{low-wet} > C_{high-wet}. At all sites, there was more upward flow at shallower depths than at deeper depths (C_{low-dry}: 62% in 15 cm, 59%

in 30 cm and 57% in 60 cm depth, C_{low_wet} : 47, 45 and 42%, and C_{high_wet} : 33, 32 and 30%).

4.2. DOC concentrations and basic solution properties

Overall average DOC concentrations at C_{low_dry} , C_{low_wet} and C_{high_wet} were 191 ± 97 , 161 ± 54 and 192 ± 70 mg l^{-1} (Fig. 2). DOC concentrations ranged from 95 to 449 mg l^{-1} at C_{low_dry} , 59 to 230 mg l^{-1} at C_{low_wet} and 80 to 400 mg l^{-1} at C_{high_wet} (Fig. 2). Neither the SOC content of the peat (C_{low_wet} vs. C_{high_wet}) nor the water table position (C_{low_dry} vs. C_{low_wet}) had a statistically significant impact ($p > 0.05$) on the measured DOC concentrations.

Within sites, DOC concentrations depended on sampling depth (Fig. 3). At C_{low_dry} and C_{low_wet} , mean DOC concentrations at the boundary between the peat-sand mixture and the sand at 30 cm depth were significantly ($p < 0.05$) higher (274 and 194 mg l^{-1}) than in both the peat-sand mixture (156 and 139 mg l^{-1}) and the underlying sand (130 and 145 mg l^{-1}). Concentrations in the peat-sand mixture and in the sand did not differ significantly. In contrast, mean DOC concentrations in the peat of C_{high_wet} (204 mg l^{-1}) and at the peat-sand boundary (241 mg l^{-1}) did not differ significantly ($p < 0.05$), but were both significantly ($p < 0.05$) higher than in the sand (132 mg l^{-1}).

Basic properties of the soil solution (Table 3) indicated that high EC tended to concur with high DOC concentrations. For the peat-sand mixed sites C_{low_dry} and C_{low_wet} , there was a positive relationship between DOC and EC (Fig. S2). This suggests that DOC determined EC as it is an important solute of the soil solution. The pH values showed clear differences between the three sites. With the exception of C_{low_wet} , pH values tended to increase with depth and were quite similar in the underlying sand at 60 cm at all sites (Table 3).

4.3. Temporal patterns and delayed response of DOC concentrations

At site C_{low_dry} , DOC concentrations at 30 cm depth showed the highest variability between suction plates and with time (Fig. 4a). At C_{low_wet} and C_{high_wet} this was the case at 15 cm (Fig. 4b and c). These depths corresponded to the mean annual WTD, i.e. the depth with the strongest hydrological dynamics.

At C_{low_dry} and C_{low_wet} , the highest DOC concentrations occurred in late summer (Fig. 4a and b). This pattern was clearest in 2011. The lowest DOC concentrations were commonly measured in early summer. In contrast to the peat-sand mixture, DOC concentrations at C_{high_wet} at 15 cm depth were highest in spring and early summer. The lowest DOC concentrations were measured in the autumn. While at this site there were no clear seasonal dynamics at 30 cm depth, DOC concentrations tended to be higher during colder periods.

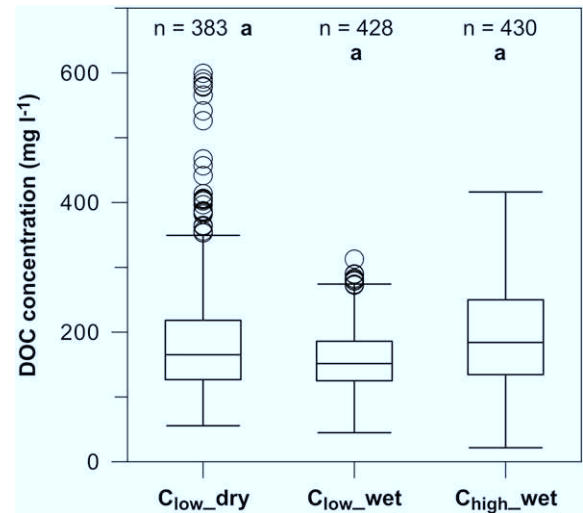


Fig. 2. Boxplots of dissolved organic carbon (DOC) concentrations at the sampling sites summarising all depths (15, 30 and 60 cm). Central crossbars represent the median, the boxes the 75th and 25th percentiles and the circles extreme values; n: number of samples. Letters indicate significant differences between the sites.

According to our model results, the DOC concentrations showed a delayed response to environmental conditions at all sites. In the peat-sand mixtures, DOC concentration increased with soil temperature, with lag times of 90 to 127 days (Table S1). This was especially the case with C_{low_dry} where the soil temperature at 2 cm depth determined the DOC concentrations at all depths (Table 4). Additionally, lag times at C_{low_dry} increased with depth from 90 to 117 days. Hydrological variables, e.g. water table depth at 15 cm depth or flow direction at 30 cm depth at C_{low_dry} , were also included in the final models. For example, at C_{low_dry} , the highest DOC concentrations at 15 cm depth were measured when high temperatures were followed by deep water tables. Upward flow has been defined as a positive flux, and thus a negative relationship with DOC indicates higher concentrations under infiltration (Table 4). Therefore, the interaction of high temperatures and downward fluxes led to the highest DOC concentrations at C_{low_dry} at 30 cm depth and at C_{low_wet} at 15 cm depth (Table 4). Only two of the final models (C_{low_dry} at 60 cm depth and at C_{low_wet} at 30 cm depth) contained the pH value as an explanatory variable.

At the peat site, the dependency of DOC concentration on explanatory variables clearly differed from the peat-sand mixture sites. Overall, WTD was the most important explanatory variable at C_{high_wet} . In contrast to the peat-sand mixtures, shallow WTD with

Table 3

Basic properties of the soil solution (pH and EC: electrical conductivity) and concentrations of dissolved organic carbon (DOC) of the complete sample set. Concentrations of dissolved organic nitrogen (DON), nitrate ($\text{NO}_3\text{-N}$) and ammonium ($\text{NH}_4\text{-N}$) of selected samples as well as the modelled water-filled pore space (WFPS) at all three depths (means \pm standard deviation), n.d.: not determined.

Sampling site/depth	pH	EC ($\mu\text{S cm}^{-1}$)	DOC (mg l^{-1})	DON (mg l^{-1})	$\text{NO}_3\text{-N}$ (mg l^{-1})	$\text{NH}_4\text{-N}$ (mg l^{-1})	WFPS (%)
<i>C_{low_dry}</i>							
15 cm	4.8 ± 0.3	91 ± 25	156 ± 44	n.d.	n.d.	n.d.	95.2 ± 2.9
30 cm	5.1 ± 0.2	144 ± 50	274 ± 115	n.d.	n.d.	n.d.	98.3 ± 2.7
60 cm	5.5 ± 0.2	104 ± 24	130 ± 27	n.d.	n.d.	n.d.	100.0 ± 0.0
<i>C_{low_wet}</i>							
15 cm	5.8 ± 0.4	111 ± 28	139 ± 55	6.3 ± 1.9	0.0 ± 0.0	0.2 ± 0.3	96.3 ± 3.8
30 cm	6.1 ± 0.3	141 ± 34	194 ± 57	7.2 ± 2.3	0.1 ± 0.2	0.4 ± 0.5	98.2 ± 3.1
60 cm	6.0 ± 0.3	141 ± 26	145 ± 18	5.7 ± 0.7	0.0 ± 0.0	0.4 ± 0.1	100.0 ± 0.0
<i>C_{high_wet}</i>							
15 cm	3.8 ± 0.1	142 ± 28	204 ± 81	4.9 ± 1.7	0.0 ± 0.0	0.1 ± 0.2	97.9 ± 3.4
30 cm	4.4 ± 0.2	140 ± 14	241 ± 34	6.1 ± 0.8	0.0 ± 0.0	0.1 ± 0.2	99.3 ± 1.6
60 cm	5.6 ± 0.4	121 ± 7	132 ± 31	3.2 ± 0.5	0.0 ± 0.0	0.0 ± 0.0	100.0 ± 0.0

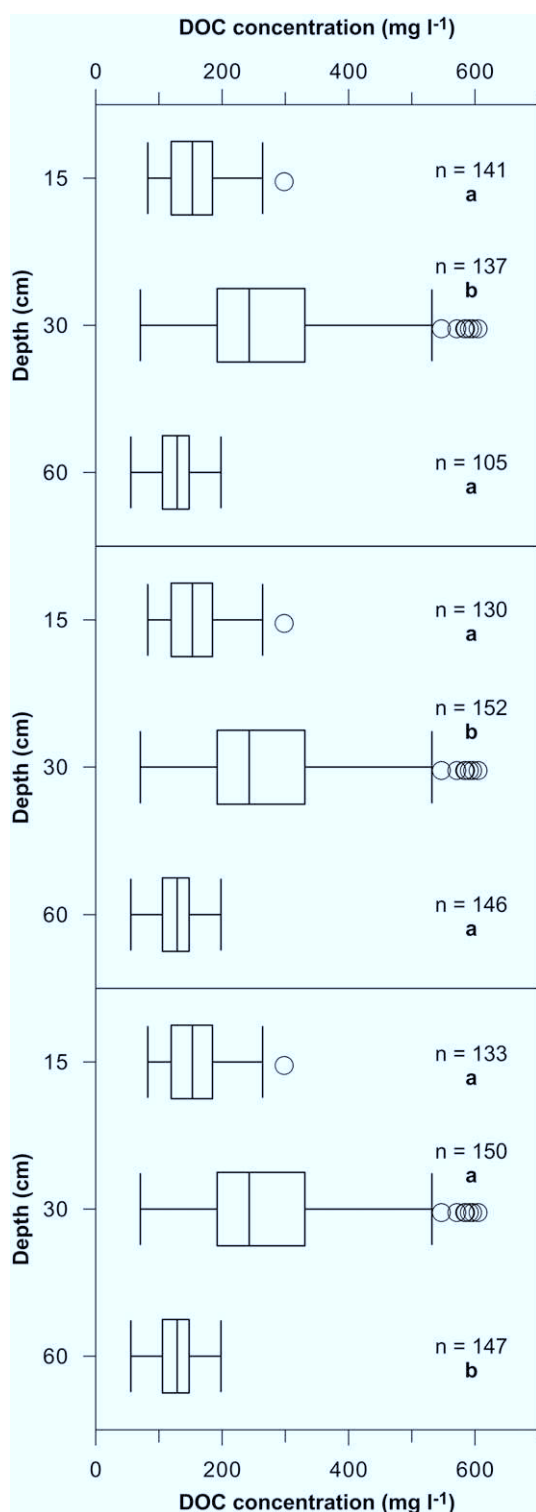


Fig. 3. Boxplots of dissolved organic carbon (DOC) concentrations at the sampling sites: a) $C_{\text{low-dry}}$, b) $C_{\text{low-wet}}$ and c) $C_{\text{high-wet}}$ per depth. Central crossbars represent the median, the boxes the 75th and 25th percentile and the circles extreme values; n: number of samples. Letters indicate significant differences between sampling depths.

lag times of 19 to 38 days increased DOC concentrations at all depth. Furthermore, there was no consistent impact of temperature on DOC concentrations (Table 4). At 15 cm depth, high DOC concentrations even coincided with low temperatures. Furthermore, at 60 cm depth, there were higher DOC concentrations at lower pH values (Table 4).

4.4. DOM properties

To evaluate possible source pools of DOM and differences in DOM cycling between $C_{\text{low-wet}}$ and $C_{\text{high-wet}}$, the solution's DOC:DON ratio, $\delta^{13}\text{C}_{\text{DOM}}$ and $\delta^{15}\text{N}_{\text{DOM}}$ were compared with those obtained in the peat, the underlying sand and the vegetation (Table 5 and Fig. S3).

The C:N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of the peat-sand mixture at $C_{\text{low-wet}}$ and the peat layer at $C_{\text{high-wet}}$ did not differ significantly (Table 5). The underlying sand was also fairly homogenous (Table 5). The strongest differences between the two sites were found for the vegetation, especially regarding the lower $\delta^{15}\text{N}$ values of not only the mosses, but of the herbaceous vegetation as well at site $C_{\text{high-wet}}$. This coincided with wider C:N ratios in the vegetation at this site. At both sites, the $\delta^{15}\text{N}$ values were higher for the SOC-rich layer compared to the subsoil and vegetation compartments.

Average DOC concentrations of the samples chosen for DOM quality analyses at 15, 30 and 60 cm at $C_{\text{low-wet}}$ (139, 174, 139 mg l^{-1}) and $C_{\text{high-wet}}$ (196, 252, 120 mg l^{-1}) were comparable to average DOC concentrations of these sites (Fig. 2). DOM in the soil solution at the peat-sand mixture site ($C_{\text{low-wet}}$) showed a narrower DOC:DON ratio compared to the peat site $C_{\text{high-wet}}$ (Fig. 5). Despite choosing samples with a broad range of climatic and hydrological conditions, the DOC:DON ratios did not show any temporal pattern. Both the slightly lower DOC and slightly higher DON concentrations (Table 3) of the sample subset at $C_{\text{low-wet}}$ compared to $C_{\text{high-wet}}$ contributed to the narrower DOC:DON ratios.

The isotopic signatures of DOM from the two sites were also clearly different (Fig. 5). DOM at $C_{\text{low-wet}}$ was consistently higher in $\delta^{15}\text{N}_{\text{DOM}}$ by on average 1.5‰ and lower in $\delta^{13}\text{C}_{\text{DOM}}$ by on average 1.1‰ when compared to DOM from the peat site $C_{\text{high-wet}}$. Within and across the sites, DOC:DON ratios were positively related to $\delta^{13}\text{C}_{\text{DOM}}$ (Fig. 5a). This relation was clearer for the peat-sand mixture than for the peat site. Across sites, there was also a negative relationship between DOC:DON ratios and $\delta^{15}\text{N}_{\text{DOM}}$ (Fig. 5b). However, within a single site or depth this was either not the case ($C_{\text{high-wet}}$) or went against expectations (i.e. $C_{\text{low-wet}}$).

The DOC:DON ratio and $\delta^{13}\text{C}_{\text{DOM}}$ of soil solution were comparable to the C:N ratio and $\delta^{13}\text{C}$ of the peat and, in the case of $\delta^{13}\text{C}$, to the herbaceous vegetation at the peat-sand mixture site $C_{\text{low-wet}}$ (Table 5). The $\delta^{15}\text{N}_{\text{DOM}}$ values at 30 and 60 cm depth were intermediate between $\delta^{15}\text{N}$ values of the peat and the vegetation. At 15 cm depth, average $\delta^{15}\text{N}_{\text{DOM}}$ values were lower than all investigated pools (Table 5). At the peat site, DOC:DON ratios and $\delta^{15}\text{N}_{\text{DOM}}$ values were intermediate between the values of vegetation and peat, but $\delta^{13}\text{C}_{\text{DOM}}$ values were consistently higher than all the investigated pools except herbaceous vegetation (Table 5).

Within the profile, the DOC:DON ratios and $\delta^{13}\text{C}_{\text{DOM}}$ in solution remained almost constant with depth, whereas $\delta^{15}\text{N}_{\text{DOM}}$ tended to increase slightly with depth.

5. Discussion

5.1. Impact of SOC content and water table depth on DOC quantity

As DOC concentrations did not differ significantly between the sites, the hypotheses that at the field site mean DOC concentrations are determined by WTD or by the SOC content of the SOC-rich layer were rejected. At the same site, Leiber-Sauheilt et al. (2014) found no relationship between GHG emissions and SOC content, but noted a tendency for a higher net ecosystem exchange at peat-sand mixture sites, which might suggest faster C cycling. This may also encourage enhanced production of DOC (Chow et al., 2006). However, the differences in SOC stocks were less pronounced than in SOC content: while the SOC content at $C_{\text{high-wet}}$ was four times higher than at $C_{\text{low-dry}}$ and $C_{\text{low-wet}}$, the SOC stock was only 1.2 to 1.6 times higher due to a concurrence of high bulk density and low C content (Table 1). A study by Kalbitz et al.

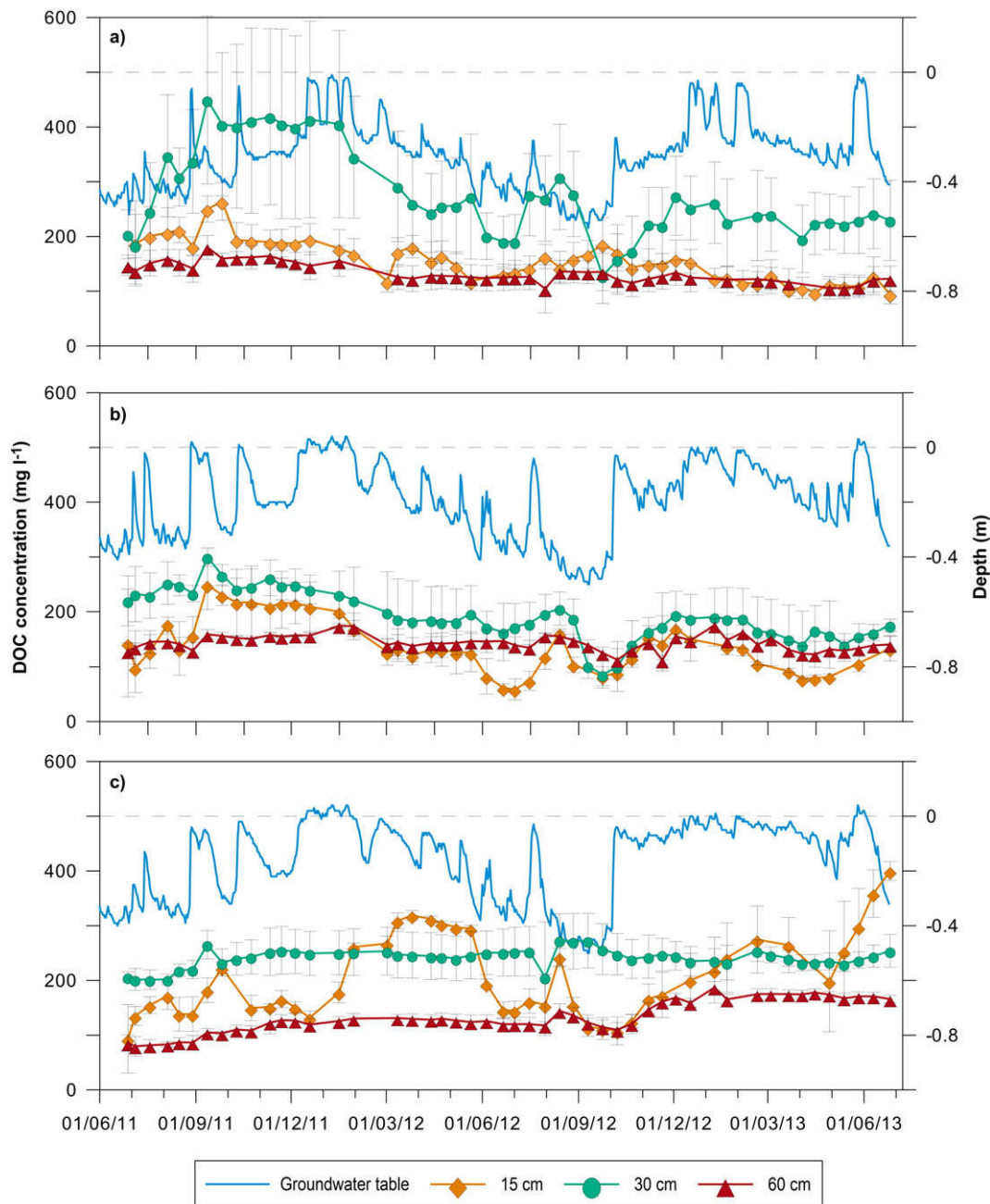


Fig. 4. Temporal pattern of the dissolved organic carbon (DOC) concentrations of the soil solution at three depths (15, 30 and 60 cm) and water table dynamics over the study period (28.06.2011–26.06.2013) at the sampling sites: a) $C_{\text{low-dry}}$, b) $C_{\text{low-wet}}$ and c) $C_{\text{high-wet}}$. Horizontal dotted lines represent the soil surface. Error bars indicate the standard deviation of the three suction plate replicates.

(2002) showed a clear dependency of DOC concentration on the SOC content of the remaining peat, which might be caused by an interaction of land use, recent land use change and WTD. Therefore, more studies focussing on soils at the boundary between organic and minerals are needed to identify drivers for DOC concentrations beyond SOC.

At this study site, a difference of 12 cm in mean WTD ($C_{\text{low-wet}}$ vs. $C_{\text{low-dry}}$) did not cause significant differences in DOC concentration levels (Fig. 2). This was somewhat surprising since there was a clear effect of WTD on CO_2 emissions and thus microbial activity at this site (Leiber-Sauheitl et al., 2014). In previous field studies, differences in mean WTD of 5 to 17 cm were sufficient to find differences in DOC concentrations (Strack et al., 2008; Frank et al., 2014). However, these changes in WTD are frequently associated with a change in land use or different topsoil properties (Höll et al., 2009; Frank et al., 2014). In contrast, incubation experiments by Chow et al. (2006) do not establish

the impact of soil water content on DOC concentrations. Furthermore, the lysimeter study of Schwalm and Zeitz (2015) showed that a common geographical origin determines the DOC concentration level more greatly than WTD or management. Previous field studies finding clear effects of WTD on DOC concentrations have focused on deep peat soils, but in the present study heavy physical disturbance (e.g. mixing with sand) of the shallow peat seemed to outweigh the effects of WTD or SOC content. This is also stressed by very low DOC concentrations in a shallow, but not ploughed peatland in the UK (Grand-Clement et al., 2014).

Besides these two aforementioned factors, pH values have been shown to be crucial for DOC concentrations (Clark et al., 2005; Evans et al., 2012). Higher pH values at the sites with a peat-sand mixture might be related to more frequent periods of upward flow of less acidic deep groundwater (average pH 5.9), but this does not explain the

Table 4

Explanatory variables for DOC concentrations determined by a GLS model. Up arrows indicate positive relation to DOC; down arrows indicate negative relation to DOC at significance levels of $p \leq 0.05$ (*), $p \leq 0.01$ (**) and $p \leq 0.001$ (***). ST = soil temperature; WTD = water table depth (above surface: positive values, below surface: negative values); WFPS = water-filled pore space; Flux = modelled water flux (upward flux: positive values, infiltration: negative values); ST:Flux = interaction of soil temperature and modelled water fluxes.

Depth	ST	WTD	WFPS	Flux	pH	ST:Flux
<i>C_{low-dry}</i>						
15 cm	↑***	↓**				
30 cm	↑***			↓**		↑**
60 cm	↑***				↑*	
<i>C_{low-wet}</i>						
15 cm	↑***			↓**		↑***
30 cm			↑***		↑*	
60 cm	↑*			↓**		
<i>C_{high-wet}</i>						
15 cm	↓*	↑**				
30 cm	↑**	↑*	↓***			
60 cm		↑***		↓*	↓***	

differences between *C_{low-dry}* and *C_{low-wet}*. Surprisingly, pH values (Table 3) did not have any obvious impact on DOC concentrations.

The distribution of DOC concentrations with depth (Fig. 3) indicated the highest DOC concentrations at the boundary between the SOC-rich layer and the underlying sand. This deviated from the common concept that DOC concentrations decrease with depth due to sorption and dilution (Kaiser and Kalbitz, 2012). These observations could be explained by a combination of different factors. DOC is likely to be produced in the temporarily unsaturated zone. Due to the relatively coarse material at the peat-sand mixture sites in particular, not only DOC, but larger, coagulated molecules as well might be transported downwards and then be re-dissolved when the pH rises due to the inflow of groundwater. Furthermore, the frequent alternation between upward and downward flow might cause (temporary, by means of an increased residence time) enrichment of DOC. This effect is likely to be especially pronounced at *C_{low-wet}*, the site with the strongest depth-dependent pattern. Finally,

mineralisation of DOC will decrease with depth due to more frequent water saturation. However, the exact reason for this enrichment is not entirely clear. Finally, DOC, which was leached from the SOC-rich layer, was diluted by groundwater inflow at 60 cm depth.

Overall, mean DOC concentrations clearly exceeded 150 mg l^{-1} and were between three to four times higher than concentrations in semi-natural and re-wetted bog sites in Germany (Frank et al., 2014) and the United Kingdom (Wallage et al., 2006) or in agriculturally used and re-wetted fens in Germany (Kalbitz et al., 2002; Höll et al., 2009; Tiemeyer and Kahle, 2014). However, comparably high average DOC concentrations in soil solution were measured in a more intensively used bog in northern Germany (Frank et al., 2014).

Applying the estimated annual seepage into the saturated zone of 75 and 220 mm and the overall average DOC concentrations at 60 cm (134 and 135 mg l^{-1}), total annual DOC losses of 100 to $297 \text{ kg ha}^{-1} \text{ a}^{-1}$ were estimated. The annual water balance controlled the interannual variability of DOC losses, as concentrations at 60 cm depth tended not to react to the higher precipitation during the second year of this study. The estimated values were, on average, slightly lower than the DOC export values given by the IPCC (2014) and Evans et al. (2016) for drained peatlands. Depending on the site and the year, DOC losses add around 2 to 8% to the net ecosystem exchange measured at the three sites (Leiber-Sauheitl et al., 2014). This percentage was similar to a grassland on fen peat (Hendriks et al., 2007), but low compared to semi-natural peatlands in the UK (Dinsmore et al., 2010), where DOC fluxes dominate the overall C balance.

5.2. Peat disturbance effects on the temporal dynamics of DOC concentration

Previous studies in peatlands have frequently found clear seasonal and temperature-driven patterns of DOC concentration, with the highest values in late summer and autumn (e.g. Clark et al., 2005; Dinsmore et al., 2013). Comparable dynamics were observed at the peat-sand mixture sites (*C_{low-wet}*, *C_{low-dry}*). Here, DOC concentrations at all depths were clearly controlled by soil temperature (Table 4), stressing the importance of microbial activity. Enhanced DOC production probably took place in the uppermost centimetres of the soil profile, as best model fits could be achieved using the temperature in 2 to 10 cm soil depth. The long time lag between DOC and temperature or flow direction indicates the delayed response of these systems in either the production of DOC or the redistribution of DOC downwards to the soil profile (Adamson et al., 2001; Clark et al., 2005).

DOC dynamics at *C_{high-wet}* differed from the observations previously discussed. DOC concentrations at *C_{high-wet}* increased in the dormant season with low biological activity and probably also reduced DOC processing (Dawson et al., 2011). Thus, further processes have to be considered for DOC mobilisation. The positive relationship to WTD suggests that organic carbon bound on the solid phase may be re-dissolved (Riedel et al., 2013). Such effects are already known from re-wetting

Table 5

Isotopic signatures ($\delta^{13}\text{C}$ vs. VPDB and $\delta^{15}\text{N}$ vs. air) and carbon-to-nitrogen ratios (C/N) of the solid compartments at the study site (vegetation, SOC-rich layer and coarse sand) as well as the isotopic signatures ($\delta^{13}\text{C}_{\text{DOM}}$ vs. VPDB and $\delta^{15}\text{N}_{\text{DOM}}$ vs. air) and the dissolved organic carbon-to-dissolved organic nitrogen ratio (DOC/DON) of dissolved organic matter (DOM) in the soil solution at three different depths from the two sample sites differing in the soil organic carbon content (mean \pm standard deviation).

<i>C_{low-wet}</i>				<i>C_{high-wet}</i>		
	C:N	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	C:N	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
Pools						
Herbaceous Vegetation	11	-28.6 ± 0.6	0.7 ± 1.0	23	-27.9 ± 0.3	-3.9 ± 0.4
Mosses	not present at the site			49	-29.9 ± 1.3	-3.3 ± 0.4
Roots	34	-29.3 ± 0.2	1.7 ± 0.2	47	-28.3 ± 0.1	0.1 ± 0.2
SOC-rich layer ^a	24	-28.5 ± 0.1	2.1 ± 0.1	28	-28.6 ± 0.6	2.6 ± 1.3
Sand	21	-27.7 ± 0.1	0.9 ± 0.3	23	-28.2 ± 0.3	0.7 ± 0.2
Solution	DOC:DON	$\delta^{13}\text{C}_{\text{DOM}}$	$\delta^{15}\text{N}_{\text{DOM}}$	DOC:DON	$\delta^{13}\text{C}_{\text{DOM}}$	$\delta^{15}\text{N}_{\text{DOM}}$
15 cm	22 ± 2	-28.9 ± 0.2	0.3 ± 0.3	39 ± 4	-27.7 ± 0.1	-1.1 ± 1.1
30 cm	24 ± 2	-28.6 ± 0.2	0.8 ± 0.5	41 ± 2	-27.6 ± 0.1	-0.8 ± 1.0
60 cm	24 ± 2	-28.7 ± 0.1	1.1 ± 0.3	38 ± 2	-27.7 ± 0.1	-0.5 ± 0.2

^a Peat-sand mixture at *C_{low-wet}* and peat layer at *C_{high-wet}*.

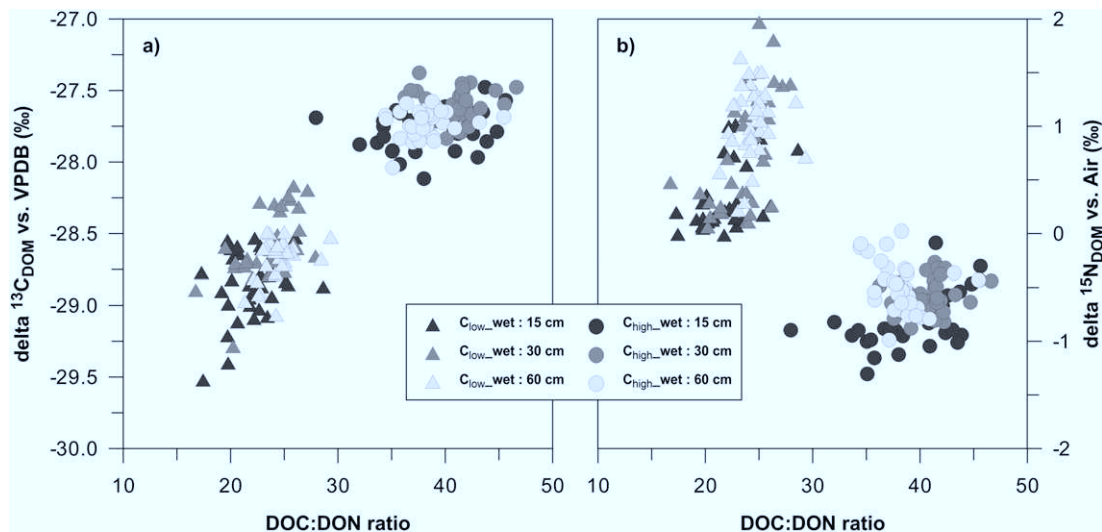


Fig. 5. Relationship between the ratio of dissolved organic carbon (DOC) to dissolved organic nitrogen (DON) and the isotopic signature of $\delta^{13}\text{C}_{\text{DOM}}$ and $\delta^{15}\text{N}_{\text{DOM}}$ of DOM in the soil solution at all depths from the sampling sites $C_{\text{low_wet}}$ and $C_{\text{high_wet}}$.

projects, where DOC concentrations increase after raising the water table (Zak and Gelbrecht, 2007). The pronounced DOC concentration dynamics at 15 cm depth suggest frequently changing redox conditions which might favour re-dissolution and precipitation.

At all sites and depths, correlations between environmental variables and DOC concentrations were only found for antecedent conditions of different lag times, but never for the instantaneous values. These delayed responses seem to be even more important in the flat landscape in this study than in a catchment with rapid hydrological responses (Grand-Clement et al., 2014) and should be taken into account when analysing DOC data.

The difference between the peat-sand mixtures and the peat site indicates an influence of past cultivation practices on the dominant processes for DOC mobilisation. Generally, total porosity decreases due to drainage (Schwärzel et al., 2002; Hallema et al., 2015), but mixing with sand was rarely investigated. This could possibly be caused by a shift in pore size distribution and a higher contribution of macropores at the peat-sand mixture sites (Kuntze and Djakovic, 1970), which may in turn affect oxygen availability and both the production and mineralisation of DOC. Furthermore, the mixture of peat and sand could increase the contact area of the peat remnants (Ross and Malcolm, 1988). These changes may possibly favour a stronger direct impact of microbial processes on DOC dynamics at the peat-sand-mixture sites compared to the peat site. Interactions between soil hydraulic properties and DOM cycling should receive further research attention.

5.3. DOM properties in relation to peat cultivation practice

DOM properties were only analysed for the two wet sites ($C_{\text{low_wet}}$ and $C_{\text{high_wet}}$). The chosen subsamples for DOM quality measurements were considered to be representative as DOC concentrations did not differ significantly from the whole sample set. Despite different CO_2 emissions, aerobic decomposition of SOC at both sites (Leiber-Sauheitl et al., 2014) still led to comparable isotopic signals and C:N ratios in the SOC-rich layer (Table 5). Measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in the SOC-rich layer at these sites were comparable to values reported by Krüger et al. (2015) for the topsoil of a drained bog that is also used as extensive grassland. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of different species were highly variable, as previously described by Ménot and Burns (2001), while the $\delta^{13}\text{C}$ values of *Sphagnum* spp. were in the range of values reported by Price et al. (1997).

Isotopic signatures of different pools can be used to estimate their contribution to DOM. However, this was not possible in this study due

to the high variability of, for example, $\delta^{15}\text{N}$ in the vegetation or a lack of possible end members ($\delta^{13}\text{C}$ vs. $\delta^{13}\text{C}_{\text{DOM}}$ at $C_{\text{high_wet}}$) (Table 5).

Nevertheless, the data suggest different contributions of the source pools to DOM at $C_{\text{low_wet}}$ and $C_{\text{high_wet}}$. At $C_{\text{high_wet}}$, intermediate DOC:DON ratios and $\delta^{15}\text{N}_{\text{DOM}}$ value in soil solution compared to peat and mosses (Table 5) indicate a mix of plant and peat-derived DOM. DOM in peatlands was found to be of recent origin and linked to the decomposition of SOM in the aerobic peat layer (Palmer et al., 2001). Furthermore, Fenner et al. (2004) showed that recently fixed C by *Sphagnum* rapidly contributes to the DOM pool. The DOC:DON ratio as well as the $\delta^{15}\text{N}_{\text{DOM}}$ value of DOM in soil solution suggest a higher contribution of vegetation-derived DOM. However, the DOC concentrations were too high to be mainly derived from exudates. For example, Hagedorn et al. (2004) found a contribution of newly formed DOC of 5–10% in a forest ecosystem after a four-year tracer experiment.

In contrast, at the peat-sand mixture site ($C_{\text{low_wet}}$), DOM derived from the SOC-rich layer contributed most to the DOM pool, as indicated by the identical C:N ratios of DOM in soil solution and the SOC-rich layer. In grassland ecosystems root exudates are an important pathway for C input into soils (Paterson et al., 1997), but this may be outweighed by the enhanced SOM mineralisation (Leiber-Sauheitl et al., 2014).

All DOM properties (DOC:DON, $\delta^{13}\text{C}_{\text{DOM}}$ and $\delta^{15}\text{N}_{\text{DOM}}$) clearly differed between the two sites (Fig. 5, Table 5) and thus show that past cultivation practices do indeed have an effect on DOM cycling. These differences in DOM quality could be caused by overlapping processes such as: 1) DOM properties being determined by contributing sources (Kalbitz et al., 2000b; Kalbitz et al., 2003), thus the shift in DOM pool contribution as well as DOM pool quality changes (e.g. a higher contribution from $\delta^{15}\text{N}$ depleted mosses) may be responsible for the differences; 2) DOM properties also possibly being altered by degradation (Kalbitz et al., 2003), thus higher $\delta^{15}\text{N}_{\text{DOM}}$ values at $C_{\text{low_wet}}$ could also indicate enhanced microbial DON alteration by microbes (Högberg, 1997). Furthermore, the positive correlation between DOC:DON ratios and $\delta^{13}\text{C}_{\text{DOM}}$ (Fig. 5) suggests a change in DOM quality during decomposition at each site, as both parameters indicate stronger degradation (Kalbitz and Geyer, 2002), possibly due to a higher contribution of hydrophobic compounds (Kalbitz et al., 2003). The steeper slope at $C_{\text{low_wet}}$ may therefore indicate a more pronounced accumulation of hydrophobic compounds during biodegradation of DOM at the peat-sand mixture site. Such differences may also affect the water quality of downstream aquatic ecosystems as hydrophobic DOM is less biodegradable (Kalbitz et al., 2003), but prone to photo-degradation (Köhler et al., 2002).

6. Conclusions

The organic soils investigated in this study were characterised by:

- (i) much higher DOC concentrations ($>150 \text{ mg l}^{-1}$) than usually measured in natural or semi-natural peatlands or drained shallow organic soils,
- (ii) the absence of an effect of water table depth on mean DOC concentrations,
- (iii) the absence of an effect of SOC content on DOC concentrations,
- (iv) strongly delayed effects of the main environmental variables of temperature (peat-sand mixtures) and water table depth (peat site),
- (v) and a shift in DOM sources from a decreasing contribution of the vegetation (peat site) to an increasing contribution of the soil (peat-sand mixture).

Finally, the results of this study clearly show that mixing peat with sand did not alter the DOC losses ($200 \text{ kg ha}^{-1} \text{ a}^{-1}$) compared to unmixed peat soils. Therefore, this practice does not reverse the negative impact of agriculture on ecosystem services provided by peatlands: Carbon is not only lost as CO_2 (Leiber-Sauheitl et al., 2014), but also as DOC, which might additionally impact downstream water bodies.

Acknowledgements

The joint research project “Organic Soils in the Emission Reporting” was funded by the Thünen Institute. We thank M. Hunziger, J. Ehe, S. Wathsack, U. Tambor and H. Wissel for field and laboratory support and N. Roßkopf for experiments on the soil hydraulic properties of the peat. Furthermore, we are grateful to Mr. Horny and Schäfer Paulus for giving their permission to undertake research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.07.121>.

References

- Adamson, J.K., Scott, W.A., Rowland, A.P., Beard, G.R., 2001. Ionic concentrations in a blanket peat bog in northern England and correlations with deposition and climate variables. *Eur. J. Soil Sci.* 52, 69–79.
- Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop evapotranspiration. Guidelines for computing crop water requirements. FAO Irrigation and Drainage Paper 56. FAO, Rome.
- Aldorf, D., Bechtold, M., van der Kruk, J., Vereecken, H., Huisman, J.A., 2016. Mapping peat layer properties with multi-coil offset electromagnetic induction and laser scanning elevation data. *Geoderma* 261, 178–189.
- Bonn, A., Reed, M.S., Evans, C.D., Joosten, H., Bain, C., Farmer, J., Emmet, I., Couwenberg, J., Moxey, A., Artz, R., Tanneberger, F., von Unger, M., Smyth, M.-A., Birnie, D., 2014. Investing in nature: developing ecosystem service markets for peatland restoration. *Ecosyst. Ser.* 9, 54–65.
- Chow, A.T., Tanji, K.K., Gao, S., Dahlgren, R.A., 2006. Temperature, water content and wet-dry cycle effects on DOC production and carbon mineralization in agricultural peat soils. *Soil Biol. Biochem.* 38, 477–488.
- Clark, J.M., Chapman, P.J., Adamson, J.K., Lane, S.N., 2005. Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Glob. Chang. Biol.* 11, 791–809.
- Clark, J.M., van der Heijden, G.M.F., Palmer, S.M., Chapman, P.J., Botrell, S.H., 2011. Variation in the sensitivity of DOC release between different organic soils following H_2SO_4 and sea-salt additions. *Eur. J. Soil Sci.* 62, 267–284.
- Dawson, J.J., Tetzlaff, D., Speed, M., Hrachowitz, M., Soulsby, C., 2011. Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland. *Hydrol. Process.* 25, 1647–1658.
- de Bakker, 1978. Major Soils and Soil Regions in the Netherlands. Springer Science + Business Media, Dordrecht, The Netherlands.
- Dettmann, U., Bechtold, M., Frahm, E., Tiemeyer, B., 2014. On the applicability of unimodal and bimodal van Genuchten–Mualem based models to peat and other organic soils under evaporation conditions. *J. Hydrol.* 515, 103–115.
- Dinsmore, K.J., Billett, M.F., Dyson, K.E., 2013. Temperature and precipitation drive temporal variability in aquatic carbon and GHG concentrations and fluxes in a peatland catchment. *Glob. Chang. Biol.* 19, 2133–2148.
- Dinsmore, K.J., Billett, M.F., Skiba, U.M., Rees, R.M., Drewer, J., Helfter, C., 2010. Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment. *Glob. Chang. Biol.* 16, 2750–2762.
- Evans, C.D., Jones, T.G., Burden, A., Ostle, N., Zielinski, P., Cooper, M.D., Peacock, M., Clark, J.M., Oulehle, F., Cooper, D., Freeman, C., 2012. Acidity controls on dissolved organic carbon mobility in organic soils. *Glob. Chang. Biol.* 18, 3317–3331.
- Evans, C.D., Monteith, D.T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environ. Pollut.* 137 (1), 55–71.
- Evans, C., Renou-Wilson, F., Strack, M., 2016. The role of waterborne carbon in the greenhouse gas balance of drained and re-wetted peatlands. *Aquat. Sci.* <http://dx.doi.org/10.1007/s00027-015-0447-y>.
- Feddes, R.A., Kowalik, P.J., Zaradny, H., 1978. Simulation of Field Water Use and Crop Yield. John Wiley & Sons, New York, NY.
- Fenner, N., Ostle, N., Freeman, C., Sleep, D., Reynolds, B., 2004. Peatland carbon efflux partitioning reveals that Sphagnum photosynthate contributes to the DOC pool. *Plant Soil* 259, 345–354.
- Frank, S., Tiemeyer, B., Gelbrecht, J., Freibauer, A., 2014. High soil solution carbon and nitrogen concentrations in a drained Atlantic bog are reduced to natural levels by 10 years of rewetting. *Biogeosciences* 11, 2309–2324.
- Grand-Clement, E., Luscombe, D.J., Anderson, K., Gatis, N., Benaud, P., Brazier, R.E., 2014. Antecedent conditions control carbon loss and downstream water quality from shallow, damaged peatland. *Sci. Total Environ.* 493, 961–973.
- Hagedorn, F., Saurer, M., Blaser, P., 2004. A ^{13}C tracer study to identify the origin of dissolved organic carbon in forested mineral soils. *Eur. J. Soil Sci.* 55, 91–100.
- Hallema, D.W., Lafond, J.A., Périard, Y., Gumiére, S.J., Sun, G., Caron, J., 2015. Long-term effects of peatland cultivation on soil physical and hydraulic properties: case study in Canada. *Vadose Zone J.* 14 (6). <http://dx.doi.org/10.2136/vzj2014.10.0147>.
- Hendriks, D.M.D., Van Huissteden, J., Dolman, A.J., Van der Molen, M.K., 2007. The full greenhouse gas balance of an abandoned peat meadow. *Biogeosciences* 4, 277–316.
- Högberg, P., 1997. Tansley review no. 95 ^{15}N natural abundance in soil-plant systems. *New Phytol.* 137, 179–203.
- Holden, J., 2005. Peatland hydrology and carbon release: why small-scale process matters. *Phil. Trans. R. Soc. A* 363, 2891–2913.
- Höll, B.S., Fiedler, S., Jungkunst, H.F., Kalbitz, K., Freibauer, A., Drösler, M., Stahr, K., 2009. Characteristics of dissolved organic matter following 20 years of peatland restoration. *Sci. Total Environ.* 408, 78–83.
- Hothorn, T., Bretz, F., Westfall, P., 2008. Simultaneous inference in general parametric models. *Biom. J.* 50, 346–363.
- IPCC (Intergovernmental Panel on Climate Change), 2014: 2013 supplement to the 2006 IPCC guidelines for National Greenhouse Gas Inventories: wetlands, in: Hiraiishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M., Troxler, T.G. (Eds.), (Switzerland).
- IUSS Working Group WRB, 2007. World Reference Base for Soil Resources 2006, first update 2007. World Soil Resources Reports No. 103. FAO, Rome.
- Kaiser, K., Kalbitz, K., 2012. Cycling downwards—dissolved organic matter in soils. *Soil Biol. Biochem.* 52, 29–32.
- Kalbitz, K., Geyer, S., 2002. Different effects of peat degradation on dissolved organic carbon and nitrogen. *Org. Geochem.* 33, 319–326.
- Kalbitz, K., Geyer, S., Gehre, M., 2000a. Land use impacts on the isotopic signature (^{13}C , ^{14}C , ^{15}N) of dissolved humic substances in a German fen area. *Soil Sci.* 165, 728–736.
- Kalbitz, K., Rupp, H., Meissner, R., 2002. N-, P- and DOC-dynamics in soil and groundwater after restoration of intensively cultivated fens. *Wetlands in Central Europe*. Springer, Berlin, pp. 99–116.
- Kalbitz, K., Schwesig, D., Schmerwitz, J., Kaiser, K., Haumaier, L., Glaser, B., Ellerbrock, R., Leinweber, P., 2003. Changes in properties of soil-derived dissolved organic matter induced by biodegradation. *Soil Biol. Biochem.* 35, 1129–1142.
- Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000b. Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Sci.* 165, 277–304.
- Köhler, S., Buffam, I., Jonsson, A., Bishop, K., 2002. Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden. *Aquat. Sci.* 64, 269–281.
- Krüger, J.P., Leifeld, J., Glatzel, S., Szidat, S., Alewell, C., 2015. Biogeochemical indicators of peatland degradation—a case study of a temperate bog in northern Germany. *Biogeosciences* 12, 2861–2871.
- Kuntze, H., Djakovic, B., 1970. Einfluss mineralischer und organischer Komponenten auf physikalische Eigenschaften von Sandmischkulturen. *Zeitschrift für Kulturtechnik und Flurbereinigung* 11, 72–87.
- Leiber-Sauheitl, K., Fuß, R., Voigt, C., Freibauer, A., 2014. High CO_2 fluxes from grassland on historic Gleysol along soil carbon and drainage gradients. *Biogeosciences* 11, 749–761.
- Maljanen, M., Sigurdsson, B.D., Guðmundsson, J., Óskarsson, H., Huttunen, J.T., Martikainen, P.J., 2010. Greenhouse gas balances of managed peatlands in the Nordic countries – present knowledge and gaps. *Biogeosciences* 7, 2711–2738.
- Ménot, G., Burns, S.J., 2001. Carbon isotopes in ombrogenic peat bog plants as climatic indicators: calibration from an altitudinal transect in Switzerland. *Org. Geochem.* 32, 233–245.
- MU [Niedersächsisches Ministerium für Umwelt, Energie und Klimaschutz], 2016K. Programm Niedersächsische Moorlandschaften. Grundlagen, Ziele, Umsetzung. Hannover.
- Palmer, S.M., Hope, D., Billett, M.F., Dawson, J.J., Bryant, C.L., 2001. Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies. *Biogeochemistry* 52, 321–338.
- Paterson, E., Hall, J.M., Rattray, E.A.S., Griffiths, B.S., Ritz, K., Killham, K., 1997. Effect of elevated CO_2 on rhizosphere carbon flow and soil microbial processes. *Glob. Chang. Biol.* 3, 363–377.

- Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., the R Development Core Team, 2013. *nlme: linear and nonlinear mixed effects models*. R Package Version. 3, pp. 1–110.
- Price, G.D., McKenzie, J.E., Pilcher, J.R., Hoper, S.T., 1997. Carbon-isotope variation in sphagnum from hummock-hollow complexes: implications for Holocene climate reconstruction. *The Holocene* 72, 229–233.
- R Core Team, R., 2013. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria <http://www.R-project.org/>.
- Riedel, T., Zak, D., Biester, H., Dittmar, T., 2013. Iron traps terrestrially derived dissolved organic matter at redox interfaces. *Proc. Natl. Acad. Sci.* 110, 10101–10105.
- Ross, S.M., Malcolm, D.C., 1988. Modelling nutrient mobilisation in intensively mixed peaty heathland soil. *Plant Soil* 107, 113–121.
- Schneekloth, H., Schneider, S., 1971. Die Moore Niedersachsens. 2. Teil, Bereich des Blattes Braunschweig der Geologischen Karte der Bundesrepublik Deutschland (1:200.000), Göttingen.
- Schulz, S., Waldeck, A., 2016. Kohlenstoffreiche Böden auf Basis hochauflösender Bodendaten in Niedersachsen. *GeoBerichte* 33, 85 (Hannover).
- Schwalm, M., Zeitz, J., 2015. Concentrations of dissolved organic carbon in peat soils as influenced by land use and site characteristics – a lysimeter study. *Catena* 127, 72–79.
- Schwärzel, K., Renger, M., Sauerbrey, R., Wessolek, G., 2002. Soil physical characteristics of peat soils. *J. Plant Nutr. Soil Sci.* 165, 479–486.
- Sognnes, L.S., Fystro, G., Øpstad, S.L., Arstein, A., Børresen, T., 2006. Effects of adding moraine soil or shell sand into peat soil on physical properties and grass yield in western Norway. *Acta Agric. Scand. Sect. B* 56, 161–170.
- Strack, M., Waddington, J.M., Bourbonniere, R.A., Buckton, E.L., Shaw, K., Whittington, P., Price, J.S., 2008. Effect of water table drawdown on peatland dissolved organic carbon export and dynamics. *Hydrol. Process.* 22, 3373–3385.
- Tiemeyer, B., Kahle, P., 2014. Nitrogen and dissolved organic carbon (DOC) losses from an artificially drained grassland on organic soils. *Biogeosciences* 11, 4123–4137.
- Tiemeyer, B., Albiac Borraz, E., Augustin, J., Bechtold, M., Beetz, S., Beyer, C., Drösler, M., Ebli, M., Eickenscheidt, T., Fiedler, S., Förster, C., Freibauer, A., Giebel, M., Glatzel, S., Heinichen, J., Hoffmann, M., Höper, H., Jurasinski, G., Leiber-Sauheitl, K., Peichl-Brak, M., Roßkopf, N., Sommer, M., Zeitz, J., 2016. High emissions of greenhouse gases from grasslands on peat and other organic soils. *Glob. Chang. Biol.* <http://dx.doi.org/10.1111/gcb.13303>.
- van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 892–898.
- Wallage, Z.E., Holden, J., McDonald, A.T., 2006. Drain blocking: an effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. *Sci. Total Environ.* 367, 811–821.
- Zak, D., Gelbrecht, J., 2007. The mobilisation of phosphorus, organic carbon and ammonium in the initial stage of fen rewetting (a case study from NE Germany). *Biogeochemistry* 85, 141–151.
- Zuur, A., Ieno, E.N., Walker, N., Saveliev, A.A., Smith, G.M., 2009. *Mixed Effects Models and Extensions in Ecology with R*. Springer Science & Business Media, New York, USA.