# Factors controlling concentrations and losses of dissolved carbon and nitrogen from disturbed bogs in Lower Saxony (Germany)

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# List of abbreviations

| | |
|---|---|
| AIC | Akaike information criterion for the intercomparison of statistical models |
| ANOVA | Analysis of variance |
| C | Carbon |
| $CH_4$ | Methane |
| $Cl^-$ | Chloride |
| $CO_2$ | Carbon dioxide |
| DOC | Dissolved organic carbon |
| DON | Dissolved organic nitrogen |
| DOM | Dissolved organic matter |
| EC | Electrical conductivity |
| $ET_0$ | Reference evapotranspiration |
| GHG | Greenhouse gas |
| GLS | Linear model fit using generalized least squares |
| LME | Linear mixed-effects models |
| m/z | Mass to charge ratio |
| N | Nitrogen |
| NECB | Net ecosystem carbon balance |
| NEE | Net ecosystem exchange |
| NENB | Net ecosystem nitrogen balance |
| $NH_4^+$ | Ammonium |
| $NO_3^-$ | Nitrate |
| $N_t$ | Total nitrogen |

| | |
|---|---|
| $N_2O$ | Nitrous oxide |
| PVC | Polyvinyl chloride |
| RMSE | Root mean square error |
| SOC | Soil organic carbon |
| $SO_4^{2-}$ | Sulfate |
| $SUVA^{280}$ | Specific ultraviolet absorbance at 280 nm |
| TC | Total carbon |
| TDN | Total dissolved nitrogen |
| TIC | Total inorganic carbon |
| TN | Total nitrogen |
| UV-Vis | Ultraviolet-visible spectral region |
| VPDB | Vienna Pee Dee Belemnite |
| WFPS | Water filled pore space |
| WTD | Water table depth |

# Summary

Peatlands store huge amounts of carbon (C) and nitrogen (N). These stocks are highly vulnerable to drainage. Bogs in Lower Saxony are typically drained and show a variety of land uses, ranging from intensive grassland areas to re-wetted former peat extraction areas under nature conservation. Studies on the impact of common land use types on dissolved C and N concentrations as well as losses from bogs in Lower Saxony, in particular on dissolved organic carbon (DOC) or nitrogen (DON), are largely lacking. The aim of this PhD thesis is to fill this knowledge gap, and to investigate in detail the effect of environmental drivers such as water table depth (WTD) and peat properties.

At first, the impact of land use and associated WTD on pore water concentrations of C and N species were investigated. In an Atlantic bog (“Ahlen-Falkenberger Moor”), the peat soil solutions of common land use types (intensive and extensive grassland, re-wetted peat extraction, near-natural) were sampled. Results showed that concentrations of DOC and N species increased by drainage, in particular by deep drainage (ø DOC > 190 mg $l^{-1}$). In contrast, re-wetting via polder technique, with permanently saturated soil conditions, has led to near-natural DOC and DON concentrations. At all sites, DON was the most important N species.

At the intensively used grassland and the re-wetted peat extraction area, waterborne C and N losses were determined. Measurements of discharge, and of C and N species concentrations were conducted in the drainage network. At both sites GHG emissions were available, which allowed to derive of a full C and N balance. In accordance to the peat pore analysis, water that drained from the grassland was enriched in C and N species. Temporal concentration patterns were solute specific and varied among the two catchments. Elevated C and N losses from the grassland area were rather caused by increased concentrations than by changes of total discharge. Losses from the grassland area represent one of the highest measured values in temperate Europe (> 500 kg $ha^{-1}$ $yr^{-1}$), but contributed less than 10% to the C balance. Finally, DON losses contributed more than 70% to the overall waterborne N losses.

In the last part, the impact of small scale heterogeneities in soil organic carbon (SOC) content and WTD on DOM cycling in the “Großes Moor” peat bog complex was investigated. Three study sites, showing a gradient in SOC und WTD, were established on shallow organic soils used as extensive grassland. The SOC gradient is the result of past peat cultivation measures (peat-sand mixing) in parts of the area. Soil solution was analyzed for DOC and partially for DON, $\delta^{13}C$ and $\delta^{15}N$. Both gradients (SOC, WTD) did not affect DOC concentrations. In general, DOC concentrations were surprisingly high (>160 mg $l^{-1}$). Although average concentrations were the same, DOM quality, temporal patterns and source pool contributions strongly differed between the peat-sand mixture and the pure peat site.

This PhD thesis clearly shows that deep drainage possesses a huge risk of water pollution by dissolved C and N species. Furthermore, off-site $CO_2$ emissions based on DOC losses based on IPCC defaults for drained peatlands in temperate Europe clearly underestimates real losses from intensively used grassland areas. A realistic eutrophication potential from bogs can only be achieved by accounting for DON losses. In contrast, only a successful establishment of permanently wet conditions by re-wetting in the peat layer is beneficial in terms of water quality in the long run.

**Keywords:** peatland, drainage, re-wetting, dissolved organic carbon

# Zusammenfassung

Moore speichern große Mengen Kohlenstoff (C) und Stickstoff (N). Diese Vorräte sind anfällig gegenüber Entwässerung. Niedersächsische Hochmoore sind in der Regel drainiert und zeigen ein breites Nutzungsspektrum. Dieses reicht von intensiv bewirtschaftetem Hochmoorgrünland bis hin zu unter Naturschutz stehenden wiedervernässten Abtorfungsflächen. Arbeiten, die den Einfluss typischer Landnutzungsformen auf die Konzentrationen sowie die Austräge von gelösten C- und N-Verbindungen, im Besonderen gelösten organischen Kohlenstoff (DOC) und gelösten organischen Stickstoff (DON), untersuchen, fehlen weitestgehend. Das Ziel dieser Dissertation ist es, diese Lücke zu schließen und die Auswirkung von Umwelteinflüssen wie z.B. den Wasserstand und die Torfeigenschaften im Detail zu untersuchen.

Zunächst wurde der Einfluss der Landnutzung und der damit verbundenen Wasserstände auf die C-und N-Konzentrationen in der Bodenlösung untersucht. Dazu wurde im Ahlen-Falkenberger Moor die Bodenlösung aus unterschiedlich genutzten Flächen (Extensiv- und Intensivgrünland, wiedervernässte Abtorfungsfläche, naturnahe Fläche) beprobt. Das Bodenwasser der entwässerten und im Besonderen der tief entwässerten Fläche zeigte dabei deutlich erhöhte DOC- sowie N-Konzentrationen (ø DOC > 190 mg $l^{-1}$). Im Gegensatz dazu wurden in der wiedervernässten Abtorfungsfläche, auf Grund permanenter Wassersättigung, naturnahe DOC- und DON-Konzentrationen gemessen. In der Bodenlösung aller Flächen war DON die wichtigste N-Verbindung.

Aus einer als Intensivgrünland genutzten Fläche sowie einer wiedervernässten Abtorfungsfläche wurden darüber hinaus wassergebundene C- und N-Austräge ermittelt. Dazu wurden die Abflüsse sowie die C- und N-Konzentrationen im Entwässerungssystem gemessen. In Kombination mit vorliegenden Treibhausgasemissionen konnten so vollständige C- und N-Bilanzen für beide Flächen aufgestellt werden. Im Einklang mit den Bodenwasseruntersuchungen zeigte das Dränwasser des Intensivgrünlandes erhöhte C- und N-Konzentrationen. Der zeitliche Konzentrationsverlauf variierte zwischen den gemessenen Stoffen sowie zwischen den Untersuchungsflächen. Erhöhte C- und N-Austräge aus dem Intensivgrünland waren eher auf höhere Konzentrationen als auf höhere Abflüsse zurückzuführen. Obwohl der DOC-Austrag aus dem Intensivgrünland einer der höchsten je gemessenen Werte im temperierten Europa war (> 500 kg $ha^{-1}$ $yr^{-1}$), trug dieser weniger als 10% zur gesamten C-Bilanz bei. Abschließend bleibt festzuhalten, dass die DON-Austräge maßgeblich den wassergebundenen N-Austrag bestimmten (> 70%).

Darüber hinaus wurden die Auswirkungen von kleinräumigen Unterschieden im Gehalt an organischem Bodenkohlenstoff (SOC) sowie im Wasserstand auf den Umsatz an gelöster organischer Substanz (DOM) ermittelt. Auf als Extensivgrünland genutzten und flachgründigen organischen Böden im Großen Moor wurden dafür drei Messstandorte eingerichtet. Diese Standorte waren durch einen Gradienten im SOC-Gehalt sowie im Wasserstand gekennzeichnet. Die Unterschiede im SOC-Gehalt sind auf Kultivierungsmaßnahmen in der Vergangenheit (Vermischung des Torfes mit dem unterlagernden Sand) zurückzuführen. Die Bodenlösung wurde auf DOC sowie teilweise auf DON und stabile Isotopen ($\delta^{13}C$, $\delta^{15}N$) hin untersucht. Beide Gradienten (SOC, Wasserstand) zeigten keinen Einfluss auf die DOC-Konzentrationen. Insgesamt waren die gemessenen DOC-Konzentrationen überraschend hoch (>160 mg $l^{-1}$). Trotz vergleichbarer Konzentrationen waren die DOM-Qualität, der zeitliche Verlauf der DOC-

Konzentrationen und der Beitrag verschiedener DOM-Quellen zwischen einem gestörten (Torf-Sand-Gemisch) und einem ungestörten (Torf) Standort unterschiedlich.

Die vorliegende Dissertation zeigt deutlich, dass tief entwässerte Standorte ein hohes Risiko für den Gewässerschutz darstellen, da sie durch einen hohen Austrag von wassergebunden C- und N-Verbindungen gekennzeichnet sind. Darüber hinaus unterschätzen Basiswerte des IPCC, welche für die Abschätzung der off-site $CO_2$ Emissionen aus gedränten Mooren verwendet werden, die realen Austräge aus tief entwässerten und intensiv genutzten Hochmoorflächen in Niedersachsen. Nur unter Einbeziehung von DON kann eine realistische Risikoabschätzung im Hinblick auf die Gewässereutrophierung durch Hochmoore erfolgen. Abschließend bleibt festzuhalten, dass auf lange Sicht nur Wiedervernässungsvorhaben für den Gewässerschutz von Vorteil sind, die zu einem permanent wassergesättigten Torfkörper führen.

**Schlagworte:** Moor, Entwässerung, Wiedervernässung, gelöster organischer Kohlenstoff

# 1 General introduction

## 1.1 Definitions and environmental functions of peatlands

Peatlands are vulnerable ecosystems. Their formation and maintenance is restricted to waterlogged areas inhabited by peat forming plants. The low oxygen availability under waterlogged conditions prevents plant remnants from decomposition, leading to the formation and accumulation of peat (Succow & Joosten, 2001). In general terms, peatlands are defined as ecosystems with at least 30-40 cm of peat, depending on country or classification system (Charman, 2002). According to the German manual of soil mapping, peat soils are composed of an organic horizon that is at least 30 cm thick and contains at least 30 wt.% of organic substances (AG Boden, 2005).

Peatlands can further be classified depending on *e.g.* vegetation, morphology, hydrology, stratigraphy or chemistry (*e.g.* Charman, 2002, Succow & Joosten, 2001; Göttlich, 1990). Most commonly, peatlands are divided into fens and bogs, indicating the principle hydrology. Fens are ground- and rainwater-fed ecosystems, showing a wide range of nutrient states (eutrophic to oligotrophic), pH values (acidic to alkaline) and hence vegetation compositions (*e.g.* sedges, reed, alder). In contrast, bogs are only rainwater-fed, nutrient-poor (oligotrophic), acidic and inhabits entirely adopted plant species (*e.g. Sphagnum* spp.; Göttlich, 1990).

Both peatland types cover a broad range of ecosystem services. Their consideration in the context of peatland protection and restoration is essential to balance possible benefits and risks of peatland management (Tiemeyer et al., 2015). One important characteristic of pristine peatlands is the carbon (C) sequestration potential. Thus, pristine peatlands are known as a sink for greenhouse gases (GHG; Limpens et al., 2008), in particular $CO_2$. Gorham (1991) estimated an annual C accumulation of 30 g $CO_2$-C m$^{-2}$ yr$^{-1}$ over the last 4,600 years. Today, one third of the global soil C pool is stored in peatlands (250 to 450 Pg C; Gorham, 1991), despite covering only a small portion of Earth´s surface (2 to 3%; Charmann, 2002; Gorham, 1991). Furthermore, pristine peatlands, in particular fens, are referred to as nature´s kidneys (Charmann, 2002). By physical/chemical sorption, peat accumulation and transformation into gaseous products, peatlands 'filter' nutrients and trace elements from groundwater and can thus improve regional water quality (Succow & Joosten, 2001). Additionally, peatlands are important for the catchment hydrology as they sustainably affect water retention and runoff generation (Holden et al., 2004). Furthermore, peatlands are important in terms of biodiversity, local climate regulation and recreational and archeological functions (Göttlich, 1990). Containing up to 97 vol.% water under saturated conditions (Göttlich, 1990), peatlands also represent a huge fresh water resource (Holden, 2005).

Mentioned ecosystem services are affected by state of the peatland. Only under wet conditions, most of them are beneficial (*e.g.* carbon sequestration, water purification, biodiversity). Nowadays, approximately 60% of the European and up to 99% of the German pristine and growing peatlands disappeared over the last decades to centuries, due to drainage for agriculture, forestry or peat-cutting (Succow & Joosten, 2001).

## 1.2 Bog characteristics in Lower Saxony

Peatlands cover approximately 15,682 km² of Germanys land surface, representing 4.4% of the total area (Roßkopf *et al.*, 2015; Fig. 1-1). Classified by peatland type, 3,141 km² of Germany´s land surface is covered by bogs, 9,660 km² by fens and 2,882 by other organic soils (Roßkopf *et al.*, 2015).

In Germany the majority of bogs (approx. 73%) is located in Lower Saxony. Bog development in Lower Saxony started around 6000 BC (Overbeck, 1975) either on previously formed fen peat or directly on the underlying sand (Tüxen, 1978). Originally, 3,500 km² of Lower Saxony was covered by pristine bogs (Overbeck, 1975), thus bogs were a typical scenery in this region. Since the 18th century, the area covered by bogs continuously decreased. After a comprehensive field survey, Schneekloth et al. (1983) reported a bog area of aprox. 2,500 km². Recently MU (2016) reported an area of 2,080 km², representing approximately 4% of the land area of Lower Saxony.

The loss of around 40% of the previous bog area are caused by their utilization in the past and present. Until the 19th century, bogs were used extensively for agriculture mainly as “Moorbrandkulur” (whole Lower Saxony), “Fehnkultur” (Northwestern part of Lower Saxony) or “Hochmoorkultur” (around Bremen; Tacke & Keppeler, 1941) and for energy as “bäuerliche Handtorfstiche” (peat-cutting). Scientific improvements in bog cultivation practices for agriculture (*e.g.* “Deutsche Hochmoorkultur”, “Sandmischkultur”) or the industrialization of peat-cutting fostered the bog cultivation during the 20th century (Göttlich, 1990).

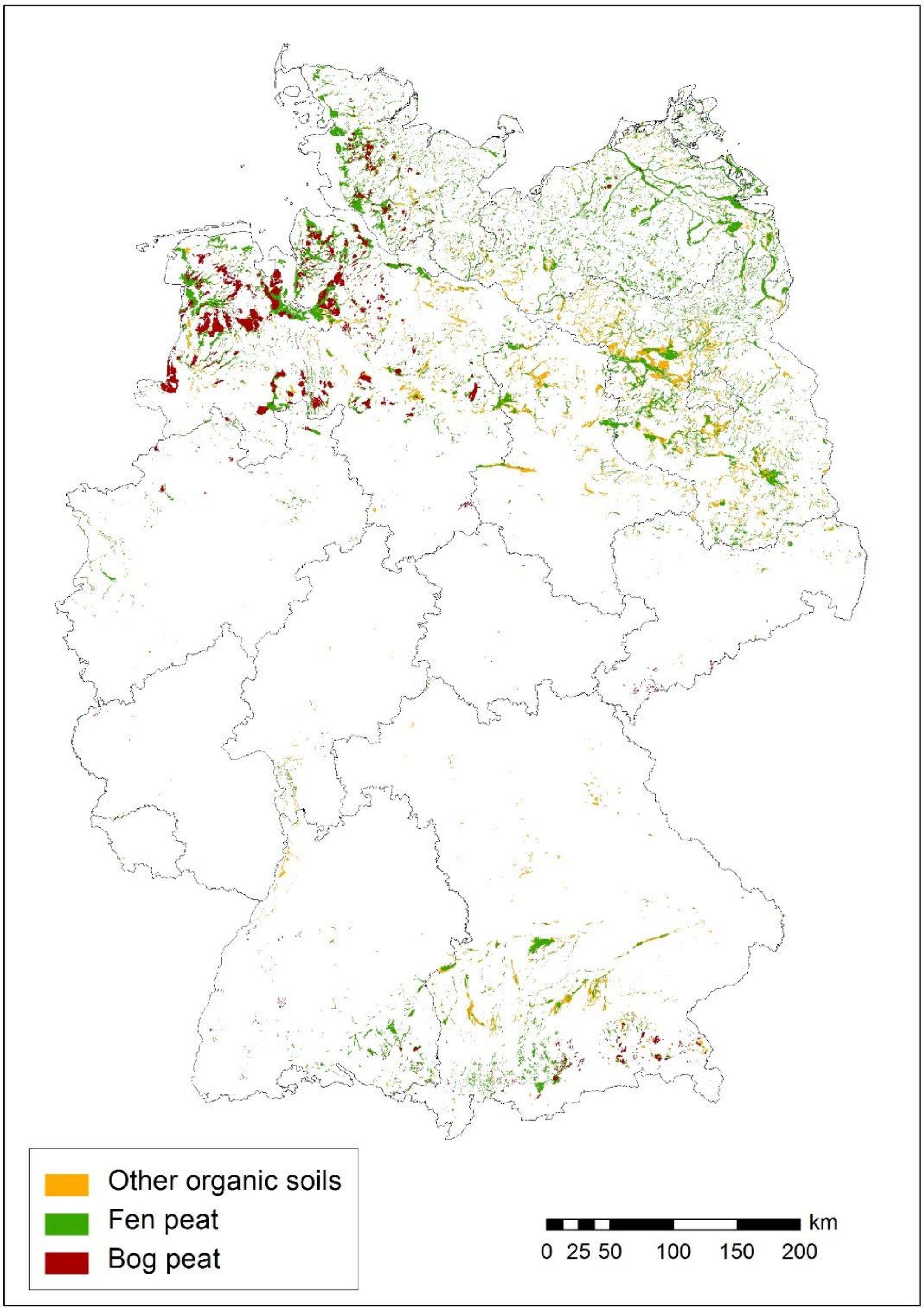

**Fig. 1- 1:** Map of peatlands (bog and fen) as well as potential organic soils in Germany (Geological map 1:200.000; BGR).

In 1981, only 4 % of the bogs in Lower Saxony were found to be in near-natural conditions. The majority, approximately 65%, was used for agriculture, mainly as grassland. About 13% were used for peat extraction and another 18% were agriculturally unused areas in different stages of succession (ML, 1981). In 2016, approximately 54 % of the bogs were used for agriculture, mainly as grassland. Around 26% were agricultural uncultivated areas in succession, 6% were forested and another 8% were used for peat extraction (MU, 2016).

This increase of area of bogs without utilization (agricultural or peat-cutting) in different stages of succession visualizes the progress of previous bog protection programs in Lower Saxony from 1981 and 1994. A subsequent agricultural utilization of peat extraction, areas was common prior 1981 to increase the area of arable land, especially in the Western parts of Lower Saxony (*e.g.* “Emslandplan”). After the termination of the peat extraction arable land was commonly created on deeply ploughed bog remnants (“Deutsche Sandmischkultur”; Göttlich, 1990). In association with sand covered peatlands (“Sanddeckkultur”), these deeply ploughed peatlands cover about 790 km² of Lower Saxony (Schulz and Waldeck, 2015). Since the start of the bog protection program in 1981, the subsequent utilization of newly claimed peat extraction areas was restricted to re-wetting. This measure was established to save approximately 300 km² of peat extraction areas for nature protection (MU, 1981). The bog protection program was extended in 1986 to smaller bogs, without peat extraction, and in 1994 to grassland areas.

The typical land use sequence of bogs in Lower Saxony is illustrated in Fig. 1-2. Previously pristine peatlands were either utilized for agriculture (mainly grassland) or peat extraction. Both measures are associated with peatland drainage (Göttlich, 1990). Furthermore, both utilization measures could be transferred into each other, as peat extraction sites could have been formerly used agriculturally and agricultural areas could have been established on former peat extraction areas (the later mainly prior 1981). Since 1981, the re-wetting of former peat extraction areas and the extensification of agricultural areas were conducted for nature conservation.

Since the discourse about global warming, the importance of peatlands as enormous C pool as well as source and sink of greenhouse gases (GHG) has been recognized. Drained peatlands are known as huge GHG source (Tiemeyer *et al.*, 2016, Höper, 2007). Höper (2015) calculated a GHG release of 10.6 Gg $CO_2$-eq. $ha^{-1}$ $yr^{-1}$ from peatlands in Lower Saxony. The majority of the GHG emissions was caused by agriculturally used peatlands. Additionally, about 930 km² of soils in Lower Saxony did not meet the definition of peat soils (AG Boden, 2005), but may fit the IPCC definition of organic soils (10 cm thick diagnostic horizon with ≥ 12% soil organic carbon (SOC); IPCC, 2006). GHG measurements by Leiber-Sauheitl *et al.* (2014) showed that these soils emit similar amounts of GHG like drained bogs. A recently started program "Niedersächsische Moorlandschaften" focused on the reduction of GHG emissions from drained and agriculturally used bogs and fens (MU, 2016).

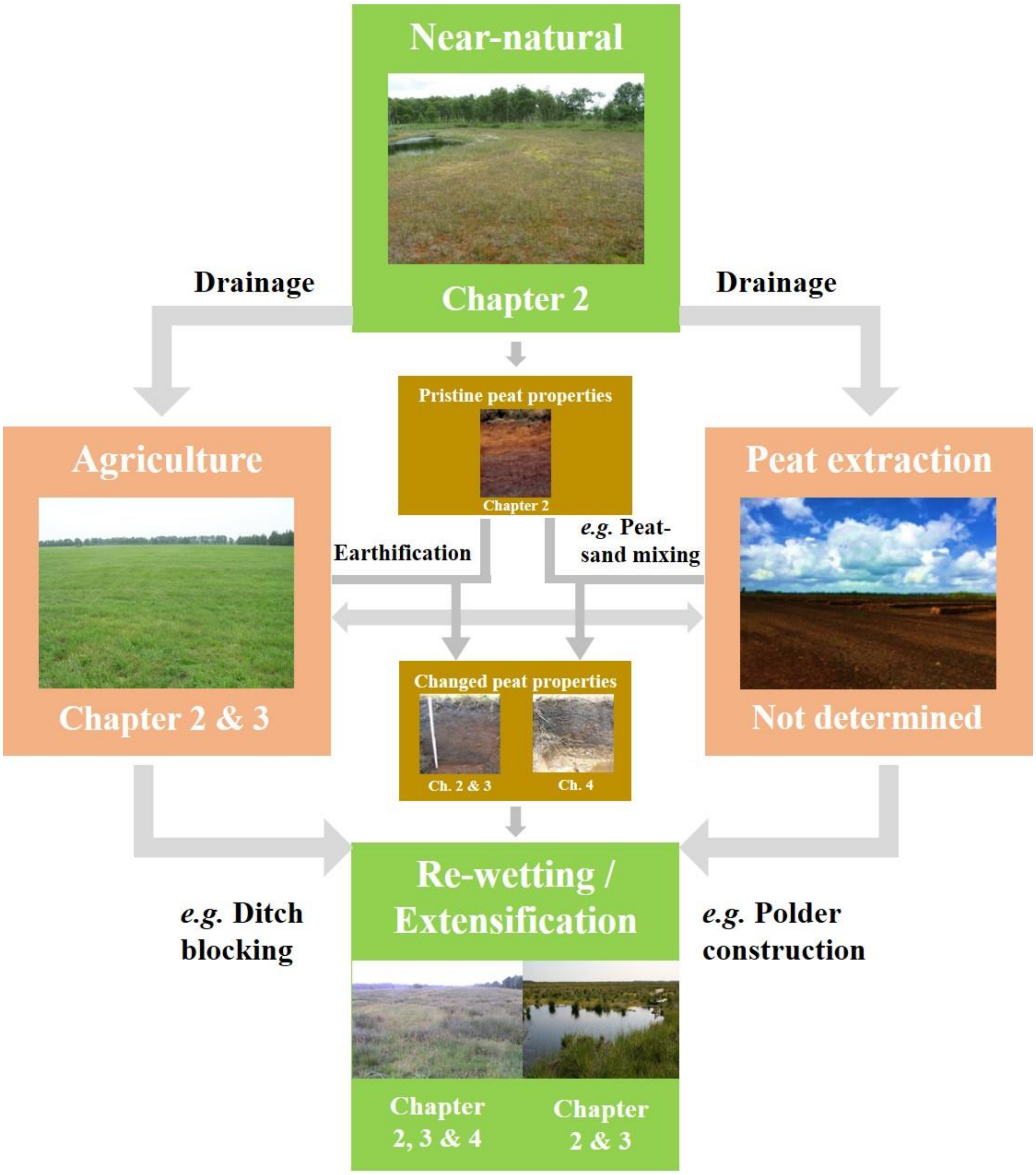

**Fig. 1- 2:** Schematic land use sequence on bogs in Lower Saxony and their investigation in this thesis (light grey arrows: indicate possible pathways; small grey arrows: impact of land use on peat properties as precondition for re-wetting; dark yellow squares: peat layer properties, green squares: wet conditions, orange squares: drained conditions; Photos: S. Frank; B. Tiemeyer and MU, 2016).

## 1.3 Dissolved carbon and nitrogen in peatlands

Beside the release and uptake of GHG, the allocation of dissolved organic matter (DOM) is important for the nutrient cycling in peatlands and their nutrient balances. Common land use types on bogs Fig. 1-2 are associated with different water table depths as well as peat properties, depending on past cultivation practices. The past and present utilization alters factors (production, adsorption, transport) driving C and N concentrations and losses. Basic aspects in the C and N cycling of natural, drained and re-wetted peatlands are outlined in this section.

Waterborne carbon from peatlands consists of several species (*e.g.* dissolved organic carbon = DOC, particulate organic carbon = POC, dissolved inorganic carbon = DIC and dissolved gases = $CO_2$ or $CH_4$; *e.g.* Dinsmore *et al.*, 2010). DOC can further be divided into several species, as DOC is solely defined as dissolved carbon passing a filter with a pore size of 0.45 µm (Thurman, 1985). Generally, DOC is the most important waterborne C species (*e.g.* Billett *et al.*, 2004; Dinsmore *et al.*, 2010). Waterborne nitrogen consists of inorganic nitrogen species (nitrate or ammonium) and dissolved organic nitrogen (DON; *e.g.* Cundill *et al.*, 2007; Bragazza & Limpens, 2004).

*Natural conditions*

Under natural conditions (Fig. 1-2, upper green square), waters that drains from peatlands are enriched in DOC (Evans *et al.*, 2015). The enrichment is caused by the higher C pool of peats, a reduced mineralization and a lacking retention potential on the mineral phase or metal-ions. Schwalm & Zeitz (2011) reviewed DOC concentrations between 14-70 mg $l^{-1}$, with a tendency of higher concentrations in bogs. On a global scale, Evans *et al.* (2015) reported DOC fluxes between 50 to 600 kg C $ha^{-1}$ $yr^{-1}$. The magnitude of C losses depends on climate, peatland hydrology and biochemistry. Global DOC fluxes showed a latitudinal and climate (temperature, precipitation) response, with highest values in the tropical climate (Evans *et al.*, 2015). Regarding peatland hydrology, peatlands with higher discharge release more DOC (Dawson *et al.*, 2004, Dinsmore *et al.*, 2013). Further, highest DOC concentrations tend to occur during peak discharge (Koehler *et al.*, 2009). As often in peatlands, in particular blanket bogs, flow paths change during high flow situations (Austnes *et al.*, 2010). Regarding biogeochemical factors, the production and consumption of DOC is microbially-driven and thus temperature-dependent (Kalbitz *et al.*, 2000a). A typical seasonality, with highest values in summer and lowest in winter, was often reported for DOC concentrations (Dinsmore *et al.*, 2013, Clark *et al.*, 2005). The clarity of temperature impacts could be altered by induced changes in pH or ionic strength, *e.g.*

due to drought (Clark *et al.*, 2005). Decreasing pH and increasing ionic strength are key factors controlling the solubility of DOC (Evans *et al.*, 2012; Clark *et al.*, 2012). Drivers controlling DOC concentrations and losses are strongly interacting and scale dependent (Clark *et al.*, 2010). This difficulty is one of the main reasons why the fundamental relations between DOC concentrations and possible drivers are still a matter of ongoing research.

In many peatlands, in particular in bogs, N is an important and growth-limiting nutrient (Aerts *et al.*, 1992, Berendse *et al.*, 2001). N inputs into bogs occur mainly via dry and wet deposition and $N_2$ fixation by microbes (Hemond, 1983). Natural peatlands showed N losses between 5 to 21 kg N $ha^{-1}$ $yr^{-1}$, depending on peatland type (Göttlich, 1990, Koerselman & Verhoeven, 1992). Under wet conditions, dissolved inorganic N in bogs is dominated by ammonium (Hemond, 1983, Moore *et al.*, 2005). In nutrient-rich peatlands (fens; Bourbonniere, 2009) and peatlands with higher amplitudes of water table fluctuations, nitrate may occur (Daniels *et al.*, 2012). Losses of nitrate are 'flow path-dependent', as nitrate is denitrified when passing anaerobic peat layers (Kieckbusch *et al.*, 2006). As bogs are acidic, nitrification is hampered and nitrate is typically of minor importance (Dancer *et al.*, 1973; Wind-Mulder *et al.*, 1996). Concentrations of inorganic N species in natural peatlands were found to be low (< 2 mg $l^{-1}$), as N demand exceeds N supply (Reynolds & Edwards, 1996; Wind-Mulder *et al.*, 1996; Bragazza & Limpens, 2004). Besides inorganic N, DON was reported as the most important dissolved N species (McKenzie *et al.*, 2016). Like for DOC, the increased concentrations of DON may occur with peak discharge (Edokpa *et al.*, 2015). The importance and concentrations of DON were additionally found to be higher in bogs with an increased atmospheric N input (Bragazza & Limpens, 2004).

*Land use impacts - drainage*

Göttlich (1990) pointed out the importance of drainage prior peatland utilization in either way, agriculture or peat extraction (Fig. 1-2; orange squares). Drainage is known to have several effects on peatlands. Firstly, the loss of water induces peat subsidence and shrinkage, alters pore size distribution and leads to an increased bulk density (Göttlich, 1990). Secondly and most important, drainage increases the input of oxygen into the peat layer, enhancing aerobic peat decomposition. The elevated microbial peat decomposition further alters chemical and physical peat layer properties (Göttlich, 1990). Furthermore, peat decomposition is influenced by management practices (*e.g.* pH value shift by fertilization; Eggelsmann, 1960). At last, GHG emissions based on peat decomposition were found to be controlled by water table depth associated with land use intensity (Drösler *et al.*, 2013).

As well as peat degradation, DOC concentrations tend to increase after drainage (IPCC, 2014; Evans *et al.*, 2015). The production of DOC by peat degradation after drainage exceeds DOC export or consumption. Evans *et al.* (2015) summarized a global increase in DOC by drainage of 60% compared to natural peatlands, but noted that given studies are not suitable to separate by peatland type (bog, fen) or land use (agriculture, peat extraction). For temperate climates, IPCC (2014) noted an increase in DOC concentrations of 49 to 118%. In contrast to former findings, some studies reported decreasing DOC concentrations after drainage (*e.g.* Kalbitz *et al.*, 2002; Moore *et al.*, 2013). A decrease in concentrations could occur due to exhaustion of a mobilizable peat C-pool, after longtime of drainage (Kalbitz *et al.*, 2002), or by dilution of DOC concentrations associated with increased water fluxes (Moore *et al.*, 2013). The impact of drainage on total discharge is discussed controversially in literature and seems to be very peatland-specific (Holden, 2004). Only if elevated average DOC concentrations were not superimposed by decreasing total discharge, DOC losses would increase after drainage.

Peatland drainage and utilization additionally affect waterborne N losses. In an incubation experiment by Venterink *et al.* (2002), N mineralization increased due to water table draw down and lead to an elevated inorganic N content. In his review, Holden (2004) reported that after drainage, ammonium concentration increased in particular, while nitrate concentrations only increased in less acidic peatlands. Especially in tile-drained fens, high nitrate concentrations were found, due to a rapid export without passing anaerobic peat layers (Kieckbusch *et al.*, 2006, Tiemeyer & Kahle, 2014). In such peatlands, nitrate concentrations can exceed drinking water limits (Tiemeyer *et al.*, 2007). Göttlich (1990) reported inorganic N losses of 2 to 80 kg ha$^{-1}$ yr$^{-1}$, depending on peatland type (fens > bogs) and land use (arable > grassland). These reported losses did not include DON, as focus was often on nitrate in studies about effects of peatland drainage.

### *Land use impacts – re-wetting*

In Germany, re-wetting of former peat extraction and grassland areas were conducted for nature conservation purposes (Fig. 1-2 – lower green square). Nowadays, re-wetting is additionally conducted to re-establish the C and N sequestration potential of previously drained peatlands. These measures are also beneficial for water quality, if the water table can be established near the soil surface.

A recent review about impacts of re-wetting on DOC revealed that re-wetting is a suitable measure to decrease DOC concentrations and DOC losses from peatlands (Evans *et al.*, 2015).

On average, re-wetting reduced DOC by about -37% compared to drained ones (Evans *et al.*, 2015). In contrast to this overall long-term trend, several authors reported higher DOC concentrations at the beginning of the re-wetting measure (Worrall *et al.*, 2007, Zak & Gelbrecht, 2007; Waddingtion *et al.*, 2008). According to Zak & Gelbrecht (2007), this initial increase in DOC concentrations depends on the state of peat degradation. On longer time scale (> 4 years) DOC concentrations tend to decrease (Wallage *et al.*, 2006; Höll *et al.*, 2009), due to DOC pool exhaustion after re-wetting and a decreasing DOC production under permanently wet conditions (Worrall *et al.*, 2007). Even if DOC concentrations increased after re-wetting, a reduced discharge may led to a decrease in DOC fluxes (Waddingtion *et al.*, 2008). Thus, whether DOC loss is successfully reduced by re-wetting depends on DOC concentration and discharge development after re-wetting.

With regard to nitrate, re-wetting is a well-known measure to reduce diffuse nitrate losses (Trepel & Palmeri, 2002). Main reasons are a reduced N mineralization and an enhanced denitrification potential under wet conditions (Kieckbusch & Schrautzer, 2007), especially in degraded peatlands (Cabezas *et al.*, 2013). Nitrate losses, however, depend on flow paths (Sapek *et al.*, 2007). Even after re-wetting, N mineralization can persist at an increased level (Venterink *et al.*, 2002). This may keep ammonium concentrations high compared to natural areas (Wind-Mulder *et al.*, 1996). Like for DOC, an initial increase in ammonium after re-wetting can occur (Zak & Gelbrecht, 2007).

### *DOM properties*

DOM is a mixture of several compounds ranging from simple compounds (*e.g.* carbohydrates) to complex humic substances (*e.g.* fulvic acids; Thurman, 1985). In peatlands, DOM mainly consists of humic substances (*e.g.* McKnight *et al.*, 1985). However, DOM that drains from more natural peatlands was found to be of young age and possibly plant-derived (Evans *et al.*, 2007, Moore *et al.*, 2013). In degraded and drained peatlands, older DOM was found, which is probably related to the destabilization of the peat C pool (Moore *et al*. 2013). In addition, DOM from drained peatlands was found to be more microbially altered, stronger humified and showed an increased aromaticity (*e.g.* Kalbitz *et al.*, 1999; Höll *et al.*, 2009). Consequently, altered DOM quality by drainage may influence DOM biodegradation, DOM retention as well as photo-oxidation during and after export, as these processes were found to be dependent on DOM quality (Kalbitz *et al.*, 2003; Kaiser *et al.*, 1996; Lindell *et al.*, 2000). The age and quality of DOC in the water that drains from peatlands were found to be highly variable, depending on source pool contribution by changing flow paths (Evans *et al.*, 2007; Austnes *et al.*, 2010).

Stable isotopes ($\delta^{13}C$, $\delta^{15}N$) are a common technique that allows to investigate DOM source pool contributions in streams draining catchments including peatlands (*e.g.* Lambert *et al.*, 2013). This method requires DOM source pools with different $\delta^{13}C$ or $\delta^{15}N$ signatures as possible end members. Data should be generally interpreted with care, as $\delta^{13}C$ or $\delta^{15}N$ are also influenced by DOM quality, degradation and adsorption (*e.g.* Kalbitz *et al*., 2000b; Kaiser *et al.*, 2001).

## 1.4 Motivation and research gaps

Over the last decades, DOC research focused on the increased release of DOC. The increasing loss of DOC from peatlands over the last decades and the contributing discussion about possible drivers (Evans *et al.*, 2005; Monteith *et al.*, 2007) emphasize the need of further studies to obtain a complete and consistent picture of the various impacts of environmental drivers on DOC dynamics in peatlands. In contrast, less attention was focused on the release of DOC from German peatlands over the last decades. Available studies were limited to fens (*e.g.* Kalbitz *et al.*, 2002; Fiedler *et al.*, 2008; Höll *et al.*, 2009; Tiemeyer & Kahle, 2014; Schwalm & Zeitz, 2015). Information on DOC dynamics in German bogs, in particular in raised bogs of Lower Saxony, are scarce (*e.g.* Glatzel *et al.*, 2006).

The impact of drainage and re-wetting on DOC is not easily transferable from published studies to conditions in German bogs. Effects of drainage and re-wetting on DOC are highly variable and depend on peatland type and climate region (Evans *et al.*, 2015). Furthermore, baseline DOC values are closely related to temperature and precipitation (Evans *et al.*, 2015). In addition, bogs in Lower Saxony are used more intensively (*e.g.* “Deutsche Hochmoorkultur”) compared to most study sites of published research. Several measures (*e.g.* peat-sand mixing) of bog cultivation are very specific for Germany and have not been common practice in other countries where DOC losses from peatlands were more frequently reported. The impact of peat-sand mixing on DOC cycling has not been analyzed yet. GHG measurements by Leiber-Sauheitl *et al.* (2014) indicated enhanced $CO_2$ emissions from peat-sand mixture sites compared to adjacent pure peat sites.

There is an increasing need to understand off-site $CO_2$ emissions, to fully assess anthropogenic impacts on GHG emissions from peatlands (IPCC, 2014). 90% of DOC that drained from peatlands is assumed to be mineralized to $CO_2$ (IPCC, 2014), adding an additional and possibly significant source to the on-site GHG emissions. As observations from German bogs are lacking, a reliable estimation of off-site $CO_2$ emissions, in particular from intensively used or-re-wetted bogs, is not yet possible. Application of the IPCC (2014) default value (Tier 1), may lead to an under- or overestimation of the real losses. It can be noted that in natural peatlands with low soil to atmosphere fluxes, DOC fluxes of > 300 kg $ha^{-1}$ $a^{-1}$ may exceed gaseous C fluxes and can significantly contribute to the overall C balance (Dinsmore *et al.*, 2010, Billet *et al.*, 2004). The lack of knowledge on DOC fluxes thus may lead to a biased C source/sink assumption of a given peatland. At the very common highly-disturbed peatlands in Lower Saxony (drained or re-wetted; Fig. 1-2) higher gaseous C fluxes were reported (Drösler et al, 2013; Höper, 2015), possibly altering the contribution of waterborne C losses (*e.g.* Hendriks *et al.*, 2007).

Bogs in Lower Saxony are often located in areas of an intense animal husbandry and are thus exposed to an elevated atmospheric N input (Hurkuck *et al.*, 2014). The amount of atmospheric N input to peatlands was shown to affect dissolved N concentrations (Bragazza & Limpens, 2004). The increased atmospheric inputs may thus negatively affect near-natural bog sites. Further, it may weaken the success of re-wetting measures in case of N retention (Yesmin *et al.*, 1995). Long time series of waterborne N losses (> 10 years) are not available for re-wetted bogs. It is thus not possible to evaluate neither the success of bog re-wetting on all dissolved N species nor whether near-natural N conditions could be established.

Former studies on waterborne N export from German peatlands were focused on the release and retention of inorganic N, in particular nitrate, after drainage and re-wetting (*e.g.* Kuntze & Eggelsmann, 1972; Göttlich, 1990; Trepel & Palmeri, 2002; Kieckbusch *et al.*, 2006; Kieckbusch & Schrautzer, 2007; Tiemeyer *et al.*, 2007). Recent studies on dissolved N dynamics showed that up to 99% of N in soil and up 75% in drainage water is DON (McKenzie *et al.*, 2016). The contribution of DON to waterborne N losses is dependent on land use and very peatland-specific (*e.g.* Adamson *et al.*, 1996; Reynolds & Edwards, 1996; Kløve *et al.*, 2010; Tiemeyer & Kahle, 2014). Neglecting DON as major dissolved N species, particularly in drained bogs, may underestimate the real N losses (Kløve *et al.*, 2010). This is crucial for determining the real eutrophication potential of drained and re-wetted peatlands on downstream water bodies and ecosystems, as DON may, like DOC, be mineralized in large parts after having been exported from the peatlands. Thus, giving a full N balance, including the majority of waterborne N species (nitrate, ammonium, DON), may help to classify different land use types on bogs regarding their risk or benefits in terms of surface water eutrophication.

Many studies either report dissolved C or dissolved N dynamics. Kalbitz & Geyer (2002) showed that DOC and DON may have different responses to drainage, but knowledge gaps still exist in the interaction between DOC and DON in peatlands. Furthermore, shifts in the ratio of DOC to DON or stable isotopes ($\delta^{13}$C or $\delta^{15}$N) of DOM may help to identify changes in DOM quality, in source pools for DOM as well as DOM cycling, with respect to re-wetting and drainage.

## 1.5 Thesis outline and research questions

Research in this thesis was conducted to address the research gaps raised in the previous section. In this thesis common land use types on bogs of Lower Saxony with varying WTD, land use histories and thus peat layer properties were investigated (Fig. 1-2). At seven sites soil waters and at two sites ditch and pipe waters were analyzed for dissolved C and N species. At each of the chosen land use types either only solute concentrations or both solute concentrations and fluxes were determined.

Chapters 2 to 4 are based on published or submitted papers to peer-reviewed journals. Each chapter is divided into sections depending on the journal of publication (*e.g.* Abstract, Introduction, Materials, Method, Results, Discussion and Conclusion).

Chapter 2: 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 re-wetting. Biogeosciences, 11, 2309-2324.

In this chapter, the focus was set on the determination of baseline data of dissolved C and N concentrations in temperate raised bogs depending on four common types of land use: two grassland areas with varying intensities, a re-wetted peat extraction site and a near-natural reference site. Typical water table depths of these land use types determine peat degradation and redox processes. Thus, another focus was on the depth-pattern of dissolved C and N species as well as DOM quality in relation to mean water table position (permanently wet vs. periodically unsaturated). To consider all possible C and N species in solution, dissolved gases were also measured.

General hypotheses were:

- Drained sites are characterized by elevated dissolved C and N species in pore water, due to an increased C and N mineralization.
- The degradation of the uppermost peat layer by drainage alters the quality (DOC to DON ratio, aromaticity) of the DOM that is released to the pore water.
- 10 years of re-wetting are too short to establish quasi natural DOM concentrations and quality in peat pore water.

Chapter 3: Frank, S. & Tiemeyer, B.: Drivers of nitrogen and dissolved organic carbon (DOC) concentrations and losses from drained and re-wetted catchments in a temperate raised bog. Submitted to Biogeochemistry.

In this chapter, the impacts of two common land use systems (intensively used grassland vs. re-wetted peat extraction area) on losses of dissolved C and N species were investigated. Drainage water analysis was conducted for selected sites of Chapter 2. Solute concentrations and water fluxes were measured in three drainage ditches and one drainage pipe. In addition to land use impacts, climate and water chemistry variables were recorded. This was done to evaluate important drivers for annual solute concentration patterns. At both sites GHG losses were measured in previous studies and allowed the calculation of a full C and N balance at both systems.

Research questions:

- How do dissolved C and N concentrations depend on land use?
- Which are the most important drivers of C and N concentrations?
- How much dissolved C and N are exported from the two land use systems?
- How much do waterborne C and N losses contribute to the total carbon and nitrogen budgets of these two systems?

Chapter 4: Frank, S., Tiemeyer, B., Bechtold, M., Lücke, A. & Bol, R.: Past cultivation practice of a disturbed peatland determines quality and temporal dynamics of dissolved organic carbon but not its mean concentration. Submitted to Science of the Total Environment.

In this chapter, the impact of small scale heterogeneity of the water table position and the SOC content on DOC concentrations was investigated. To exclude land use impacts on DOC concentrations, chosen study sites were located in an extensively used grassland area. Differing SOC contents occur in some parts of the area due to historical peat-sand mixing. At the peat-sand mixture sites, SOC contents were in transition between mineral and peat soils. The peat site showed typical SOC values for bogs. In addition, climate and hydrological (*e.g.* flow direction) as well as DOM quality variables were recorded to investigate the impact of peat-sand mixing on temporal DOC pattern and DOM cycling.

General hypotheses were:

- DOC concentrations are higher at the peat site because of its higher SOC content.
- DOC concentrations are higher at deeper water tables.
- Antecedent conditions of environmental variables are crucial for DOC dynamics.
- Due to the heavy physical disturbance, DOM is microbially more degraded at the peat-sand mixture sites.

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# 2 Publication no. 1

## High soil solution carbon and nitrogen concentrations in a drained Atlantic bog are reduced to natural levels by 10 years of rewetting

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## 2.1 Abstract

Anthropogenic drainage of peatlands releases greenhouse gases to the atmosphere and dissolved carbon (C) and nutrients to downstream ecosystems. Rewetting drained peatlands offers a possibility to reduce nitrogen (N) and C losses. In this study, we investigate the impact of drainage and rewetting on the cycling of dissolved C and N as well as on dissolved gases over a period of 1 year and 4 months, respectively. We chose four sites within one Atlantic bog complex: a near-natural site, two drained grasslands with different mean groundwater levels, and a former peat cutting area rewetted 10 years ago.

Our results clearly indicate that long-term drainage has increased the concentrations of dissolved organic carbon (DOC), ammonium, nitrate and dissolved organic nitrogen (DON) compared to the near-natural site. DON and ammonium contributed most to the total dissolved nitrogen. Nitrate concentrations below the mean groundwater table were negligible. The concentrations of DOC and N species increased with drainage depth. In the deeply drained grassland with a mean annual water table of 45 cm below surface DOC concentrations were twice as high as in the partially rewetted grassland with a mean annual water table of 28 cm below surface. The deeply drained grassland had some of the highest ever observed DOC concentrations of 195.8 ± 77.3 mg $l^{-1}$ with maximum values of >400 mg $l^{-1}$. In general, dissolved organic matter (DOM) at the drained sites was enriched in aromatic moieties and showed a higher degradation status (lower DOC to DON ratio) compared to the near-natural site. At the drained sites, the C to N ratios of the uppermost peat layer were the same as of DOM in the peat profile. This suggests that the uppermost degraded peat layer is the main source of DOM. Nearly constant DOM quality through the profile furthermore indicated that DOM moving downwards through the drained sites remained largely biogeochemically unchanged. Unlike DOM concentration, DOM quality and dissolved N species distribution were similar in the two grasslands and thus unaffected by the drainage depth.

Methane production during the winter months at the drained sites was limited to the subsoil, which was quasi permanently water-saturated. The recovery of the water table in winter months led to the production of nitrous oxide around mean water table depth at the drained sites.

The rewetted and the near-natural site had comparable DOM quantity and quality (DOC to DON ratio and aromaticity). 10 years after rewetting quasi pristine biogeochemical conditions have been re-established under continuously water logged conditions in the former peat cut area. Only the elevated dissolved methane and ammonium concentrations reflected the former

disturbance by drainage and peat extraction. Rewetting via polder technique seems to be an appropriate way to revitalize peatlands on longer timescales and to improve the water quality of downstream water bodies.

## 2.2 Introduction

Biogeochemical cycling of carbon (C) and nitrogen (N) in peatlands is determined by the water table position. Under pristine conditions C and N fixation exceed gaseous and dissolved losses in these oxygen limited ecosystems (Hemond, 1983; Urban & Eisenreich, 1988; Limpens *et al.*, 2008; Blodau, 2002). Thus, peatlands are able to accumulate and store C and N over millennia and constitute an important part of the global C and N cycle (Gorham, 1991; Limpens *et al.*, 2006).

In many parts of Europe, peatlands have been drained during the last centuries for agriculture, forestry and peat extraction. Nowadays, nearly all peatlands in Germany are affected by drainage and mainly used as grassland (40%) and arable land (32%; Federal Environment Agency, 2013).

The exposure of previously anaerobically stored peat to oxygen is associated with an increase in the C and N mineralization (Bridgham *et al.*, 1998), greenhouse gas emissions (Schafer *et al.*, 2012; Flessa *et al.*, 1998; Berglund & Berglund, 2011) and concentrations of water soluble C and N (Holden *et al.*, 2004). Therefore, drainage turns these ecosystems from a net C and N sink to a source.

Compared to mineral soils, peatlands are characterized by high (20-50 mg $l^{-1}$) DOC pore water concentrations (Blodau, 2002). Under pristine conditions, DOC can contribute up to 10 % to the overall carbon losses (Limpens *et al.*, 2008). Drainage was shown to increase DOC concentration in peatlands (Wallage *et al.*, 2006; Banas & Gos, 2004; Glatzel *et al.*, 2003; Moore & Clarkson, 2007). Peat degradation under drainage and intensive land use shifts the quality of dissolved organic matter (DOM) towards aged and strongly microbiologically altered DOC (Kalbitz & Geyer, 2002) with a higher amount of aromatic moieties (Hoell *et al.*, 2009; Kalbitz, 2001). The quality of DOM determines its bioavailability (Kalbitz *et al.*, 2003) and its adsorption potential to the mineral phase or iron oxides (Kaiser *et al.*, 1996) and, consequently, DOM turnover and transport to surface waters (Fraser *et al.*, 2001; Stutter *et al.*, 2012).

Peat mineralization after drainage also releases nitrogen in the forms of ammonium, nitrate and DON (Venterink *et al.*, 2002). Ammonium generally increases after drainage whereas nitrification, which is strongly pH dependent (Dancer *et al.*, 1973), is restricted to less acidic peatlands (Holden *et al.*, 2004). The actual export, especially of nitrate from drained peatlands, depends on the flow pathways (Kieckbusch *et al.*, 2006) and denitrification during transport through water saturated, carbon-rich layers (van Beek *et al.*, 2004). Especially in drained minerotrophic peatlands, nitrate concentrations in ditches were found to exceed drinking water and general water quality limits (Tiemeyer *et al.*, 2007). High nitrate concentrations pose a strong risk of eutrophication for downstream water bodies.

Rewetting is a common strategy to revitalize peatlands after peat cutting. Frequently, the main objective of rewetting is nature conservation by restoring the flora and fauna typical for peatlands. Ideally, successful rewetting creates environmental conditions suitable for peat formation and C and N sequestration as well as for an improved water quality. Several factors determine whether rewetting leads to quasi natural soil solution concentrations. Firstly, the state of peat degradation determines the mobilisable DOC pool. This pool was found to be highest in degraded peat compared to less degraded peat as a result of a higher amount of redox sensitive substances as well as increased availability of decomposable organic matter (Zak & Gelbrecht, 2007). Secondly, stable high water levels are important to mimic biogeochemical conditions of pristine peatlands as pronounced water table fluctuations throughout the year can boost DOC concentration (Kalbitz *et al.*, 2002). Thirdly, time is an important factor to overcome the disturbance by drainage. Directly after rewetting, Worrall *et al.* (2007) measured increased DOC concentrations compared to drained sites. On the long run, Wallage *et al.* (2006; after up to 4 years) and Hoell *et al.* (2009; after 20 years) found lower DOC concentrations compared to drained sites.

Rewetting can also reduce dissolved nitrogen losses. This is particularly effective in the case of nitrate as rewetting inhibits nitrification and increases denitrification (Kieckbusch & Schrautzer, 2007). Under water-saturated conditions, the denitrification potential is controlled by the status of the peat degradation, the nitrate load and the temperature (Cabezas *et al.*, 2012). However, high net N mineralization rates can persist after rewetting (Venterink *et al.*, 2002) and can keep ammonium concentrations initially after rewetting above natural levels (Wind-Mulder *et al.*, 1996). High nutrient concentrations hamper the revitalization of typical bog vegetation, which usually requires nutrient-poor conditions.

The separate understanding of the cycling of DOC and dissolved N was improved over last decades, but many studies have either focused on dissolved C or on N. Kalbitz & Geyer (2002) found a different response of DOC and DON to peat degradation and highlighted knowledge gaps about the interaction between DOC and DON in peatlands and about DON in peatlands in general. However, nearly all of the studies on DOC have been conducted in boreal peatlands (Moore, 2003), blanket bogs (Wallage *et al.*, 2006) or fens (Hoell *et al.*, 2009; Kalbitz, 2001), which all differ hydrologically and climatically from raised bogs in the temperate zone. Therefore, it may be questionable whether these findings and the $CO_2$ emission factors for DOC losses summarized in IPCC (2013) are transferable to raised bogs in the temperate zone, especially under intensive grassland management.

In addition, only very few field studies have simultaneously observed drained, rewetted and natural conditions to determine whether and, if yes, how fast drainage effects on DOM are reversible and at what risk (Wallage *et al.*, 2006; Glatzel *et al.*, 2003) To fill these knowledge gaps, this study compares concentrations and quality of dissolved C and N and dissolved gases ($CO_2$, $CH_4$, and $N_2O$) along the peat profile in a peat bog complex under four land use types: a deep drained intensive grassland, an extensive grassland partially rewetted to shallow water levels for 8 years, a former peat extraction site fully rewetted for 10 years, and a near-natural bog site. We hypothesize (1) that increased C and N mineralization after drainage has increased concentrations of dissolved C and N species in the peat pore water, (2) that the degradation of the uppermost peat layers at the drained sites has altered the quality of released DOM (DOC to DON ratio and aromaticity) and (3) that 10 years of rewetting are too short to re-establish quasi natural DOM concentrations and quality in the peat pore water.

## 2.3 Materials & Methods

### 2.3.1 Site description

Our study was conducted in the “Ahlen-Falkenberger Moor” peat bog complex, which is located 20 km south of Cuxhaven and the North Sea (53°41´ N, 8°49´ E) in north-western Germany. The long term mean annual temperature and precipitation are 9.4 °C and 905 mm (period: 1971-2011; German Weather Service, 2012). The “Ahlen-Falkenberger Moor” is one of the largest (39 km²) peat bog complexes in northern Germany.

The peatland grew in a depression of Pleistocene sands, partly mixed with gravel and clay. The bog formation started on former fen areas approximately 4000 B.C. and afterwards directly on Pleistocene sand (Schneekloth, 1970).

Since the Middle Ages, small-scale peat-cutting was performed at the edges of the complex. Intense drainage started at the beginning of the 20th century. From 1939 to 1965 over 50 homesteads were established and land use was intensified (Ahrendt, 2012). Nowadays, the “Ahlen-Falkenberger Moor” peat bog complex is mainly used as grassland. Furthermore, from 1957 to 2002 industrial peat-cutting took place. These areas were rewetted after terminating peat extraction in 2002. A small area in the south-eastern part of the bog has never been drained (Fig. 2-1).

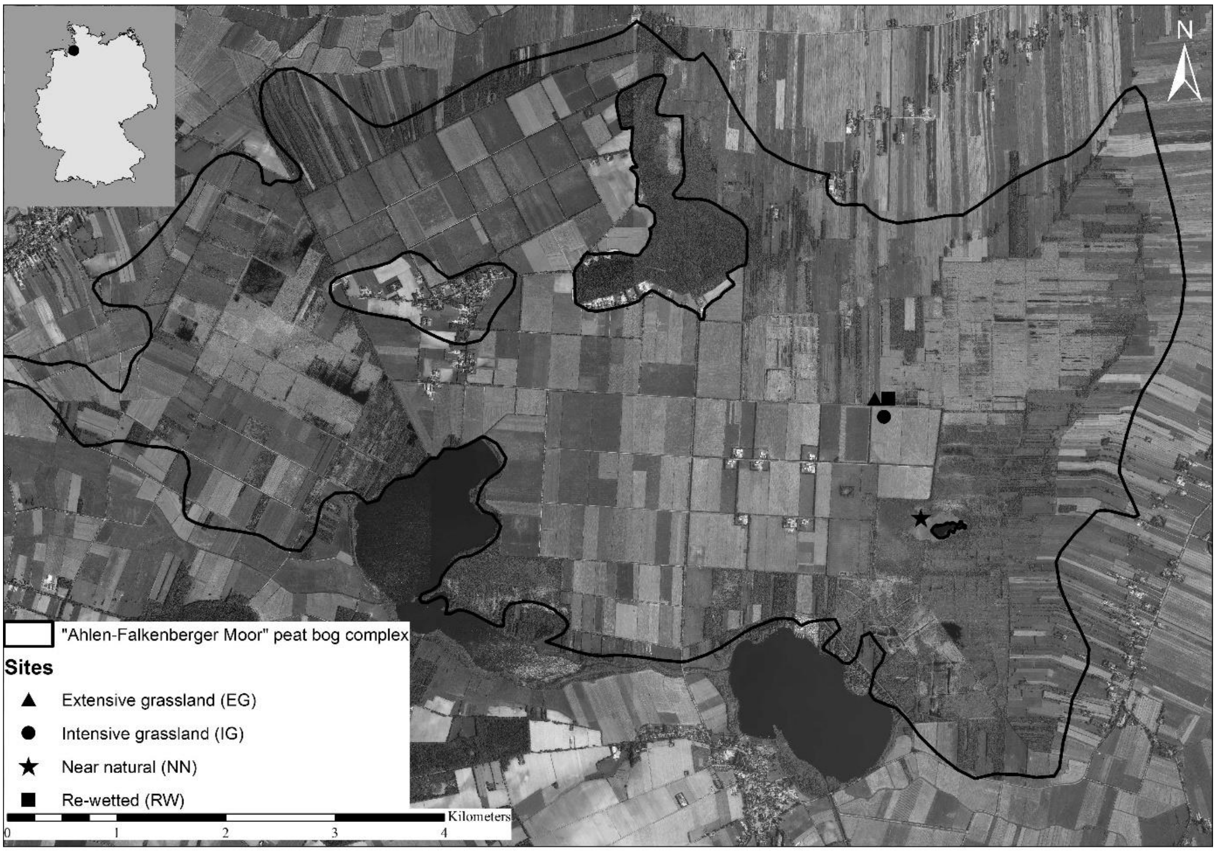

**Fig. 2- 1:** Location of the study sites within the “Ahlen-Falkenberger Moor” peat bog complex and location of the “Ahlen-Falkenberger Moor” peat bog complex within Germany (upper left) (BKG, 2013).

**Table 2- 1:** Plant species and species cover in brackets, water management, and agricultural management of the study sites.

| Site | Plant species cover | Water management | Fertilization | Mowing |
|---|---|---|---|---|
| *NN* | *Sphagnum fallax* H. Klinggr. (86 %)<br>*Eriophorum angustifolium* Honck. (10 %)<br>*Myrica gale* L. (10 %)<br>*Empetrum nigrum* L. (7 %)<br>*Vaccinium oxycoccos* L. (4 %)<br>*Sphagnum cuspidatum* Ehrh. (4 %)<br>*Rhynchospora alba* (L.) Vahl (3 %)<br>*Drosera rotundifolia L. (2 %)*<br>*Betula pubescens* Ehrh. (1 %) | None (possibly influenced by surrounding drainage) | None | None |
| *IG* | *Poa trivialis* L. (60 %)<br>*Poa pratensis* L. (30 %)<br>*Lolium perenne* L. (5 %)<br>*Phleum pratense* L. (3 %)<br>+ several species with a cover < 1 % | Drainage pipes<br>Drainage ditches | Cattle slurry (April, May, July, August) | 4 times (May, June, August, September) |
| *EG* | *Rhytidiadelphus squarrosus* (Hedw.) Warnst. (45 %)<br>*Juncus effusus* L. (40 %)<br>*Anthoxanthum odoratum* L. (15 %)<br>*Agrostis stolonifera* L. (5 %)<br>*Rumex acetosa* L. (5 %)<br>*Rumex acetosella* L. (5 %)<br>+ several species with a cover < 1 % | Drainage ditches (partly closed since 2003/2004) | None | Once (August) |
| *RW* | *Sphagnum* spp. (65 %)<br>*Eriophorum vaginatum* L. (55 %)<br>*Molinia caerulea* L. (12 %) | Polder,<br>water level regulation at the outlet (rewetted since 2002) | None | None |

Two drained and two wet study sites were chosen to represent the dominant land use forms (Fig. 2-1): an intensive grassland site (*IG*), an extensive grassland site (*EG*), a rewetted peat extraction site (*RW*) and a near-natural site (*NN*). The vegetation at *IG* mainly consists of two species of *Poaceae* (Table 2-1). At *EG* large patches of *Juncus effusus* L. dominate the vegetation besides mosses and various *Poaceae*. The vegetation at the wet sites (*RW* and *NN*) is composed of typical bog species (*Sphagnum* spp., *Eriophorum* spp.). Missing rarer species such as *Rhynchospora alba* (L.) Vahl or *Vaccinium oxycoccos* L. as well as the occurrence of *Molinia caerulea* L. at *RW* indicates that the transition towards an undisturbed bog has not yet been completed.

Agricultural use of the drained sites (*IG* and *EG*) has not been changed for more than 20 years. *IG* was cut 3 to 5 times per year depending on seasonal water table position and trafficability. *EG* was cut once a year for nature conservation purposes. Mineral fertilizers and cattle slurry were only applied at the *IG*. From 2007 to 2009 Beetz *et al.* (2013) reported an average application of 12 g N $m^{-2}$ $yr^{-1}$ by mineral fertilizer and 216 g C $m^{-2}$ $yr^{-1}$ by cattle slurry at *IG*. During our study period, only slurry was applied. In contrast, *EG* was not fertilized for at least 20 years.

The grassland is divided into rectangular units surrounded by drainage ditches with a depth of at least 1.5 m. To improve drainage and trafficability, PVC drainage pipes were additionally installed at the intensive grassland (drainage depth: 1 m, drainage spacing: 10 m). The shallower drainage ditches at *EG* have partly closed since 2003/2004 due to a lack of ditch maintenance. Thus, the water table at *EG* is higher than at *IG*. *RW* was actively rewetted in 2002 using polder technique. Dams were constructed around and within the former peat extraction area to create rectangular polder units. Vertically installed PVC pipes are used as outlets and determine the water table in the polder units. After rewetting, the upper parts of the degraded bog peat (15-55 cm) started to float and was re-vegetated by *Sphagnum* spp. *RW* is now characterized by floating peat layers with a thickness of 65 cm. There is no water management at *NN*, but the area may be slightly influenced by the neighbouring grassland (Fig. 2-1).

Prior to our investigations, greenhouse gas emissions were measured from 2007 to 2009 at the *IG*, *EG* and *NN* site (Beetz *et al.*, 2013).

### 2.3.2 Sampling and chemical analysis

Samples were taken between February 2012 and February 2013. Dialysis sampler (“peeper”; Hesslein, 1976) were used to sample soil solution in a high vertical resolution. This technique is often used to investigate redox-sensitive solutes in peat pore water (*e.g.* Zak *et al.*, 2004) and

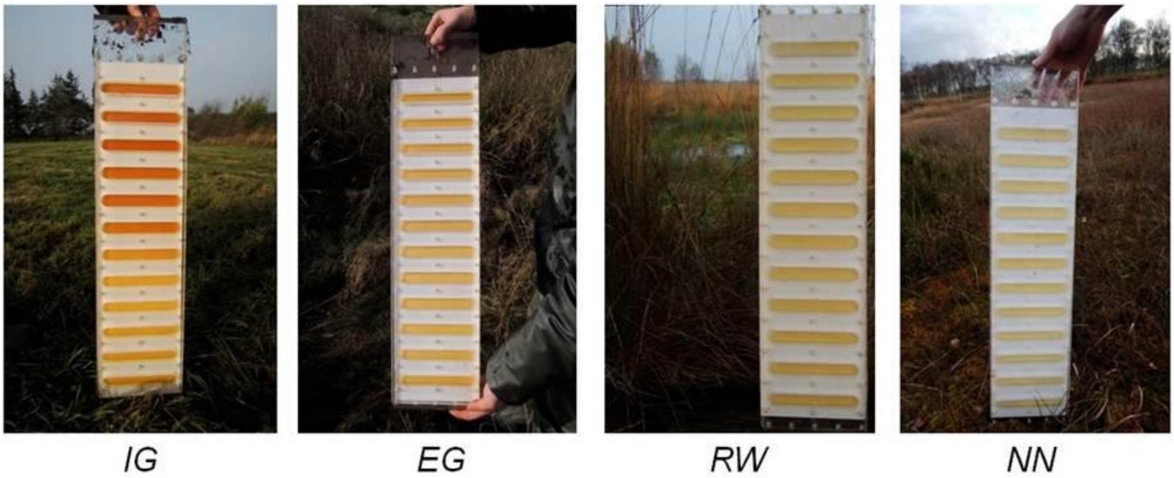

**Fig. 2- 2:** Pictures of peepers at drained (IG, EG) and wet (RW, NN) sites (sampling date: October 2012).

is based on the equilibration of solute concentrations in the soil solution and the de-ionised water in the peeper chambers, which are covered by a semi-permeable membrane. In our case, the soil solution between 10 and 65 cm below the surface was sampled. Each plexiglas peeper contained 12 chambers with 5 cm spacing and a chamber volume of 50 ml each (Fig. 2-2). Prior to field installation the chambers were filled with de-ionised water and covered with a 0.2 µm polysulfone membrane filter (HT-Tuffryn 200; Pall Gelman Laboratory). To avoid a disturbance of the natural redox conditions, oxygen from the chamber water needs to be displaced. Therefore, the peepers were placed in PVC vessels filled with de-ionised water and purged with $N_2$ for 2 days. The peepers were transported to the field sites in the same PVC vessels. For equilibration with the soil solution, the peepers were left in the field for approximately 4 weeks, leading to 14 dates of sampling within one year.

Three peepers were installed at each site. Each peeper was inserted into a slit which was cut with a specifically manufactured stainless steel spade. One of the three peepers was used for high resolution vertical profile sampling (each chamber). To account for changing peat properties with depth but to reduce sampling effort and costs, bulk samples (chambers 1 to 3: 10-22 cm, chambers 3-6: 25-37 cm and chambers 7-12: 39-65 cm) were collected from the other two peepers. After drawing the peepers from the peat, they were cleaned with de-ionised water and immediately emptied in the field. Between 10-15 ml aliquots were filled in PE-vials for the separate measurement of (1) DOC/UV-Vis absorption, (2) major ions and (3) total nitrogen (TN). The samples were cooled during transport. When measurements could not be performed within a few days, samples were stored at -18°C until analysis. No further sample preparation was made.

Between November 2012 and February 2013 (4 dates) samples were additionally analyzed for dissolved $CO_2$, $CH_4$ and $N_2O$. For these analyses 10 ml solution was filled in 20 ml air tight glass vials. The vials were flushed with $N_2$ prior to sampling and prepared with 1ml $ZnCl_2$ (50% w/v) to suppress microbial activity (Romero *et al.*, 1999).

The water table position during the sampling period was recorded using Mini-Divers (Schlumberger Water Services, Delft, Netherlands).

Peat samples were taken with a resolution of 5 cm using a peat corer and were oven dried (40 °C), sieved and ground prior to measurement. The peat soil organic carbon (SOC) and total nitrogen ($N_t$) content was measured on a LECO TrueMac CN (LECO Corporation, St. Joseph, Michigan, USA). Additionally, a soil profile was dug at each site to determine the soil type and to take samples for the determination of the bulk density (BD).

A DimaTOC 2000 (DIMATEC, Essen, Germany) was used to measure DOC concentration. DOC was calculated as the difference between total carbon (TC; measured via combustion at 850°C) and total inorganic carbon (TIC; measured via combustion at 165°C after acidification with $H_3PO_4$ - 40% w/v). DOC was measured in at least three replicates.

UV-Vis absorbance was measured on a Shimadzu-1800 spectrophotometer (Shimadzu Germany, Duisburg, Germany) between 200 and 700 nm in a 1 cm quartz glass cuvette. The UV-absorbance is often used to assess the quality of DOM. Appropriate wavelengths are shown in Grayson & Holden (2012). In our study, we chose a wavelength of 280 nm, because Chin *et al.* (1994) reported a strong correlation between $SUVA^{280}$ and aromaticity derived by $^{13}$C-NMR from fulvic acids. $SUVA^{280}$ was calculated as the absorbance at 280 nm divided by the corresponding DOC concentration and is given in $l\ mg^{-1}\ m^{-1}$. $SUVA^{280}$ was used as DOC quality indicator regarding aromaticity.

Total nitrogen (TN) of the water samples was determined with a Total Nitrogen Analyzer (TN-100; Mitsubishi, Kanagawa, Japan) by reduced pressure chemiluminescence detection. Concentrations of major ions ($NH_4^+$, $NO_3^-$, $SO_4^{2-}$ and $Cl^-$) were measured with an ion chromatograph 850 Professional (Metrohm, Filderstadt, Germany). Dissolved organic nitrogen (DON) was calculated as the difference between TN and the dissolved inorganic nitrogen species $NH_4$-N and $NO_3$-N.

Concentrations of $CO_2$, $CH_4$ and $N_2O$ were determined with a gas chromatograph 7890-A (Agilent Technologies, Loveland, USA) using the headspace method. Samples were shaken for 2 hours at 21°C prior to measurement to equilibrate headspace and solution. Concentration of dissolved $CO_2$, $CH_4$ and $N_2O$ were calculated according to Henry´s law using the solubilities of $CO_2$, $CH_4$ and $N_2O$ at 21°C given by Weiss & Price (1980), Weiss (1974) and Wilhelm *et al.* (1977) and taking into account headspace pressure and volume and the volume of the liquid phase.

Bulked samples were further analyzed for pH and electrical conductivity (WTW, Weilheim, Germany).

As the peeper technique is only applicable under soil moisture conditions near saturation, chambers above minimum water table were excluded for analysis during each of the 14 sampling periods. Additionally, depth profiles of chloride were used to identify upper chambers with insufficient contact between the membrane and the peat, which were characterized by considerably lower chloride concentrations compared to the mean profile concentrations. Only in April 2012 the impact of cattle slurry application on dissolved solutes at IG could be examined. These results were discussed separately and the data from this occasion were not included in the general data analysis.

## 2.4 Results & Discussion

### 2.4.1 Peat properties

At *NN* the vegetation (Table 2-1) and peat properties (Table 2-2) clearly indicate the pristine state of the upper peat layers. Additionally, Beetz *et al.* (2013) measured ongoing carbon accumulation. Thus, despite the surrounding drainage and increasing land use intensity over the last decades, the *NN* site may be used as a near-natural reference site.

The drained sites (*IG*, *EG*) are characterized by a strongly degraded amorphous peat layer with high von Post indices and narrowed C to N ratios at the soil surface (Table 2-2). Narrow C to N ratios may be caused by retention of N in these peat layers, possibly due to immobilization of N by microbes during peat decomposition (Wells & Williams, 1996). Despite differences in fertilizer application at *EG* and *IG* over the last decades, there is no difference in the C to N ratio or other basic peat properties. Basic peat properties clearly indicate peat mineralization, especially in the uppermost layer, which is supported by substantial gaseous C losses measured by Beetz *et al.* (2013). Additionally, elevated BD and slightly increased von Post indices at all peat layers compared to *NN* suggest that peat degradation by compaction and mineralization after drainage has reached deeper peat layers.

**Table 2- 2:** Soil properties (0-100 cm) of the study sites in the “Ahlen- Falkenberger” peat bog.

| **Depth (cm)** | **SOC (%)** | **$N_t$ (%)** | **C to N ratio** | **pH** | **BD (g $cm^{-3}$)** | **von Post** |
|---|---|---|---|---|---|---|
| *Near-natural site (NN): Ombric Fibric Histosol* , peat layer thickness: 440 cm* | | | | | | |
| 0-40 | 46.7 | 0.9 | 53 | 3.9 | n.d. | 1 |
| 40-50 | 46.1 | 0.9 | 60 | 4.0 | 0.05 | 1 |
| 50-100[a] | 49.3 | 1.8 | 28 | 5.0 | 0.04 | n.d. |
| *Intensive grassland site (IG): Ombric Fibric Histosol (Drainic)*, peat layer thickness: 330 cm* | | | | | | |
| 0-12 | 46.2 | 2.3 | 20 | 5.3 | 0.26 | 10 |
| 12-33 | 48.9 | 1.2 | 41 | 3.9 | 0.13 | 5 |
| 33-50 | 49.2 | 0.9 | 54 | 4.1 | 0.12 | 7 |
| 50-100 | 50.2 | 0.9 | 58 | 4.0 | 0.10 | 3 |
| *Extensive grassland site (EG): Ombric Fibric Histosol (Drainic)* , peat layer thickness: 340 cm* | | | | | | |
| 0-10 | 47.3 | 2.4 | 20 | 5.2 | 0.31 | 9 |
| 10-19 | 49.1 | 1.3 | 40 | 5.0 | 0.12 | 5 |
| 19-50 | 48.3 | 1.0 | 50 | 4.0 | 0.09 | 3 |
| 50-60 | 48.0 | 1.0 | 49 | 3.8 | 0.10 | 5 |
| 60-100 | 49.2 | 0.9 | 54 | 4.0 | 0.07 | 2 |
| *Rewetted site (RW): Ombric Floatic Hemic Histosol*, peat layer thickness: 260 cm* | | | | | | |
| 0-5 | 42.7 | 0.9 | 47 | n.d. | n.d. | 1 |
| 5-15 | 44.2 | 1.0 | 44 | n.d. | n.d. | 2 |
| 15-55 | 46.5 | 1.2 | 40 | n.d. | n.d. | 6 |
| 55-65[b] | 51.8 | 1.0 | 52 | n.d. | n.d. | 5 |

n.d. = not determined; BD = bulk density; SOC = content of soil organic carbon; $N_t$ = content of total nitrogen; C to N ratio = SOC to $N_t$ ratio

[*] IUSS Working Group WRB (2007) [a] limnic organic deposit [b] 65-100 open water body

The basic peat properties of both the floating degraded peat (15-55 cm horizon) and the peat at the bottom of the polder (data not shown) are comparable to the peat layers at drained sites

(IG and EG) below the uppermost degraded peat layer. On this peat *Sphagnum* spp. colonized and built up a 15 cm thick slightly decomposed peat layer since 2002. The basic properties of this newly formed layer are comparable to NN (Table 2-2).

### 2.4.2 Water table

Groundwater table dynamics are shown in Figure 2-3. Mean water table positions during the sampling period differed distinctly between drained sites (*IG*: 45 cm, *EG*: 28 cm) and wet sites (*RW*: -3 cm, *NN*: -1 cm). Positive values represent a water table below surface and negative values above soil surface. Similarly, the water table fluctuations during the sampling period had higher amplitudes at the drained sites (*IG*: 5 to 87 cm; *EG*: 2 to 62 cm) than at the wet sites (*RW*: -27 to 6 cm; *NN*: -10 to 5 cm).

The oscillation of the peat at *NN* and *RW* buffered the amplitudes of the water table. Thus, even during dryer summer months, the water tables at these sites did not drop deeper than 6 cm below soil surface. In contrast, the drainage ditches (open at *IG* and partly closed at *EG*) and the active drainage pipes (at *IG*) led to low mean and minimum water table levels and fast water table

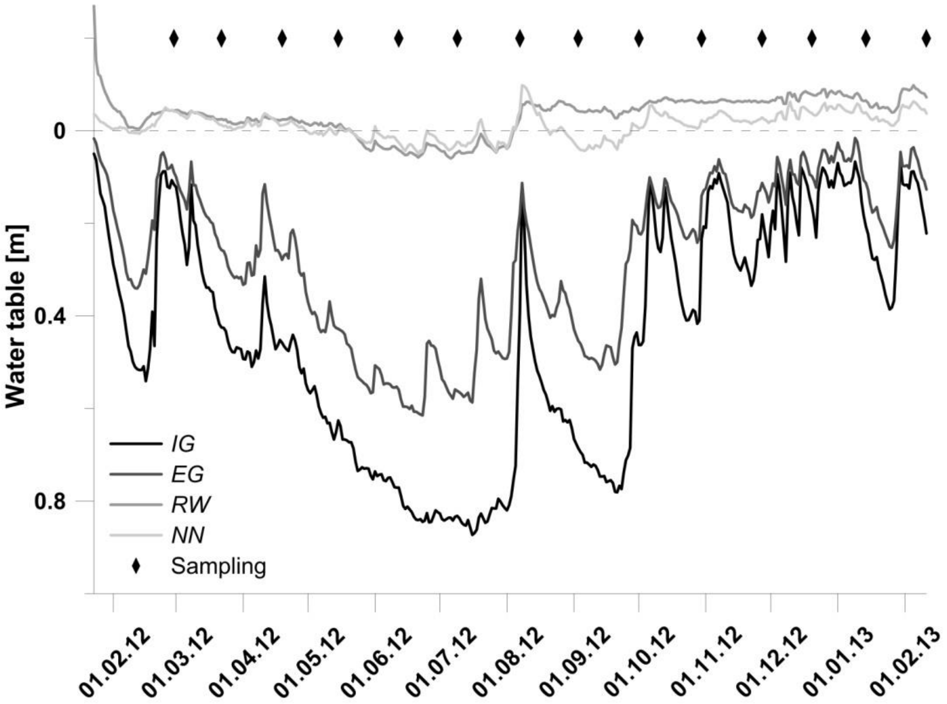

**Fig. 2- 3:** Groundwater table dynamics at the study sites during the complete sampling period (February 2012 - February 2013). The dashed line represents soil surface.

fluctuations. Rain events in summer months triggered a strong and fast rise in the water table at *IG* and *EG*. This can be explained by the physical properties of drained peat (Silins & Rothwell, 1998). Degraded peat has high bulk densities (Table 2-2) and thus a lower pore volume and a higher share of fine pores. Rain events therefore trigger a stronger rise of the water table per mm of rain (Edom, 2001). Furthermore, the rapid drawdown of the water table after rain event peaks at *IG* showed that the drainage system worked efficiently at this site. The daily water table drawdown at *IG* and *EG* during periods without precipitation was comparable in summer and winter despite higher transpiration rates of the vegetation in summer. Drainage management was the most important driver for the water table dynamics at drained sites (*IG, EG*). Deep water table positions during summer at the drained sites (*IG*, *EG*) led to deep oxygen penetration into the soil profile in contrast to the wet sites (*RW, NN*), which stayed anoxic (see Estop-Aragones *et al.*, 2012).

At the wet sites (*RW, NN*) all peeper chambers could be sampled throughout the whole sampling period. As mentioned before, pore water from the topsoil at *IG* and *EG* could not be sampled under dry conditions. We only used samples below the minimum water table level of each sampling period to ensure that the peeper chamber got sufficient contact with the soil solution during sampling periods. At *IG*, all peeper chambers could be used in 8 of the 14 sampling dates, chambers below 25 cm soil depth could be used in 8 of sampling dates and only chambers below 39 cm in 9 of sampling dates. At *EG* all chambers could be used in 9 of sampling dates, chambers below 25 cm in 12 of sampling dates and chambers below 39 in 12 of sampling dates. As mentioned earlier 10, 25 and 39 cm represent the upper boundary of the bulk samples. There is thus a lack of information due to sampling constraints for the upper soil solution of *IG* and *EG* during April to September. Differences between drained sites (*IG*, *EG*) and wet sites (*RW, NN*) are mainly driven by differences during moist periods of the investigation period.

### 2.4.3 Basic properties of the soil solution and concentrations of $SO_4^{2-}$ and $Cl^-$

The pH values around 4 at *IG*, *RW* and *NN* of the soil solution represent the acidic character of bogs (Table 2-3). The slight increase in pH values at *IG* may be caused by liming, cattle slurry and fertilizer application over the last decades.

A low electrical conductivity (EC) as at *NN* is typical for ombrotrophic peatlands. The EC values at *IG* and *EG* were elevated by 25 % and 145 % compared to *NN* due to an increased amount of solutes in the soil solution. This agrees with Wind-Mulder *et al.* (1996), who found increased EC associated with higher nutrient and $SO_4^{2-}$ concentrations in post-harvested and natural bogs in Canada. Electrical conductivity at *RW* was comparable to *NN* (Table 2-3), indicating near-natural conditions.

$SO_4^{2-}$ concentrations strongly differed between wet (*RW*, *NN*) and drained sites (*IG*, *EG*). Whereas $SO_4^{2-}$ concentrations were low (usually <1 mg $l^{-1}$) and without vertical pattern at the wet sites (Fig. 2-4a), concentrations at drained sites were21 (*IG*) and 9 (*EG*) times higher. $SO_4^{2-}$ concentrations were highest in summer. At *IG*, $SO_4^{2-}$ concentrations remained relatively high in colder and wetter periods, whereas at *EG*, $SO_4^{2-}$ concentrations drop sharply during winter months. At the drained sites (*IG*, *EG*), the topsoil patterns of $SO_4^{2-}$ concentration were partly masked by a lack of summer samples (Fig. 2-4a). Mean concentrations of $SO_4^{2-}$ tended to decrease below a depth of 40 and 55 cm at *EG* and *IG*, respectively, where peat layers were mostly water saturated and $SO_4^{2-}$ reducing processes were likely to occur. The vertical and temporal $SO_4^{2-}$ concentration patterns matched the water table dynamics and associated oxygen penetration at drained sites, which allowed oxidation of reduced sulphur compounds to $SO_4^{2-}$. In contrast, oxidation was suppressed at wet sites throughout the entire profile.

As mentioned before, $Cl^-$ was used to determine whether the peeper chambers got sufficient contact throughout the sampling interval. A vertical pattern was only found at *IG* (Fig. 2-4b). The constant depth profiles at our sites are in contrast to measurements by Beer & Blodau (2007) in an oligotrophic bog in Canada, who found a strong increase in the upper 65 cm. This latter profile pattern was mainly explained by diffusion. Thus in our case, different transport mechanisms such as advective transport have to be considered especially at the drained sites.

**Table 2- 3:** pH-Values, electrical conductivity (EC) and concentration of sulphate ($SO_4^{2-}$) and chloride ($Cl^-$) of the soil solution (means ± standard deviation).

| Site | pH | EC [µS $cm^{-1}$] | $SO_4^{2-}$ [mg $l^{-1}$] | $Cl^-$ [mg $l^{-1}$] |
|---|---|---|---|---|
| *NN* | 4.0 ± 0.2 | 83.2 ± 15.0 | 0.8 ± 0.8 | 12.7 ± 1.5 |
| *IG* | 4.6 ± 0.3 | 204.0 ± 71.5 | 16.7 ± 8.4 | 19.5 ± 9.4 |
| *EG* | 4.1 ± 0.2 | 104.1 ± 35.3 | 7.0 ± 6.2 | 9.7 ± 4.0 |
| *RW* | 4.1 ± 0.2 | 77.9 ± 11.6 | 0.5 ± 0.7 | 14.0 ± 2.4 |

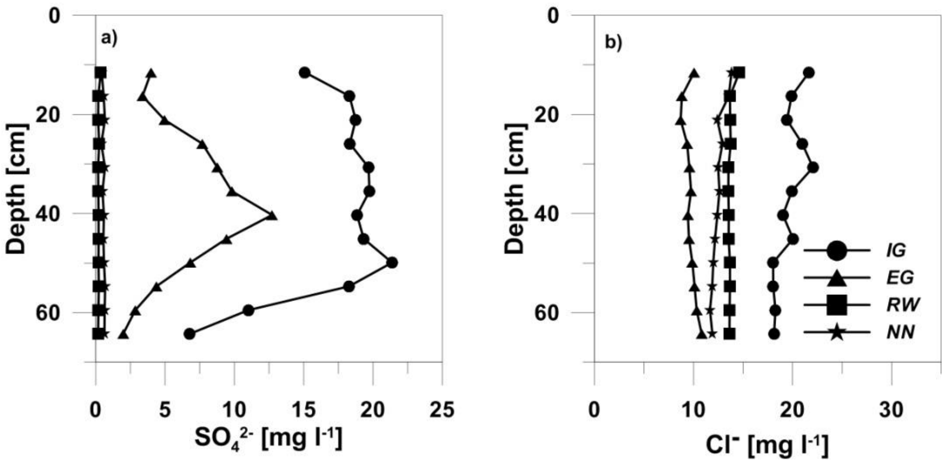

**Fig. 2- 4:** Vertical profiles of mean (a) sulphate and (b) chloride concentrations the study sites.

### 2.4.4 Carbon

**Dissolved organic carbon – quantities**

Mean dissolved organic carbon (DOC) concentrations were 195.8 ± 77.3 mg $l^{-1}$, 89.4 ± 31.4 mg $l^{-1}$, 38.8 ± 6.4 mg $l^{-1}$ and 48.6 ± 16.3 mg $l^{-1}$ at *IG*, *EG*, *RW* and *NN*, respectively. Mean DOC concentrations at the drained sites were increased by 84 % (*EG*) and 303 % (*IG*) compared to *NN*. At the drained sites DOC concentrations showed a higher spatial and temporal variability than the wet sites (Fig. 2-5a). Overall, DOC concentrations ranged from 14 to 490 mg $l^{-1}$. The mean DOC concentrations were negatively correlated with mean annual water table positions. Deep drainage has doubled DOC concentrations compared to shallow drainage. The DOC concentrations were fairly constant over depth at *EG*, *NN* and *RW*, but elevated in the upper 35 cm at *IG* (Fig. 2-5b). The vertical pattern at *IG* suggest that DOC was primarily produced in the uppermost peat layers (Mcknight *et al.*, 1985) and was diluted or partly consumed during advective transport to deeper horizons. DOC concentrations at the drained sites (*IG*, *EG*) exceeded those of *NN* in all depths. Near-natural DOC concentrations over the whole profile were found at *RW* after 10 years of rewetting.

DOC concentrations of the near-natural site (*NN*) were comparable to previous studies in natural temperate and boreal peatlands, which often found values of around 50 mg $l^{-1}$ (Moore, 2003; Blodau *et al.*, 2007), but quite high in comparison to natural blanket peatlands in the UK (*e.g.* Wallage *et al.* 2006).

Elevated DOC concentrations (≈ 70 mg $l^{-1}$) at drained bogs in Poland were reported by Banas & Gos (2004). Their results were comparable to our site *EG* and rather low compared to our deeply drained intensively used grassland site (*IG*). The only study with comparably high DOC concentrations (> 200 mg $l^{-1}$) was also conducted in a German raised bog (Glatzel *et al.*, 2006). In the studies summarized in IPCC (2013) DOC concentrations at drained sites were between 15 and 118% higher than at natural sites. In contrast, in our temperate raised bog, DOC concentrations were between 84 % (*EG*) and 303% (*IG*) higher at the drained sites than at the reference site *NN*. This corresponds to the upper end (*EG*) of or is by far higher (*IG*) than the relative DOC increase given by IPCC (2013). Assuming similar discharge sums after drainage (*IG* vs. *NN*), deeply drained, intensively used peatlands in the temperate climate constitute potential large sources of DOC. Most studies summarized in the IPCC (2013) guidelines originate from boreal peatlands, fens or blanked bogs which are all hydrologically and climatically different to raised bogs in temperate Central Europe. For the latter, the relative DOC concentration increase by drainage given by the IPCC (2013) default might underestimate the dissolved carbon loss.

The difference in DOC concentrations between *IG* and the other sites might even have been underestimated in our study due to sampling constraints for the uppermost peat layer at *IG* during dry summer periods when highest DOC concentrations are expected. Several factors (*e.g.* drainage, fertilizer application, changing plant and microbial communities) can contribute to the high DOC concentrations at the drained grassland sites (*IG*, *EG*). Drainage is obviously the most important factor, which determines the length of the period and the volume of peat under aerobic conditions. The enhanced ingress of oxygen during periods of low water tables (Estop-Aragones *et al.*, 2012) increases microbial activity as well as enzymatic activity (Freeman *et al.*, 1996), fostering the degradation of the uppermost peat layer in the short and the long run. This is supported by findings of Clark *et al.* (2009) who reported an increase of net DOC release during water table drawdown by a factor of 7 during incubation of peat cores at 20°C. Leiber-Sauheitl *et al.* (2014) found a strong linear increase of $CO_2$ emission from organic soils used as grassland with lower water table position. Thus it is likely that the amount of C exposed to oxygen in our case was the most important driver for DOC concentrations differences between *IG* and *EG*.

Peat degradation could additionally be primed by a higher amount of and more easily degradable roots and root exudates from *Poaceae* replacing the original bog vegetation at the drained sites (*IG*, *EG*). However, incubation experiments by Basiliko *et al.* (2012) showed that

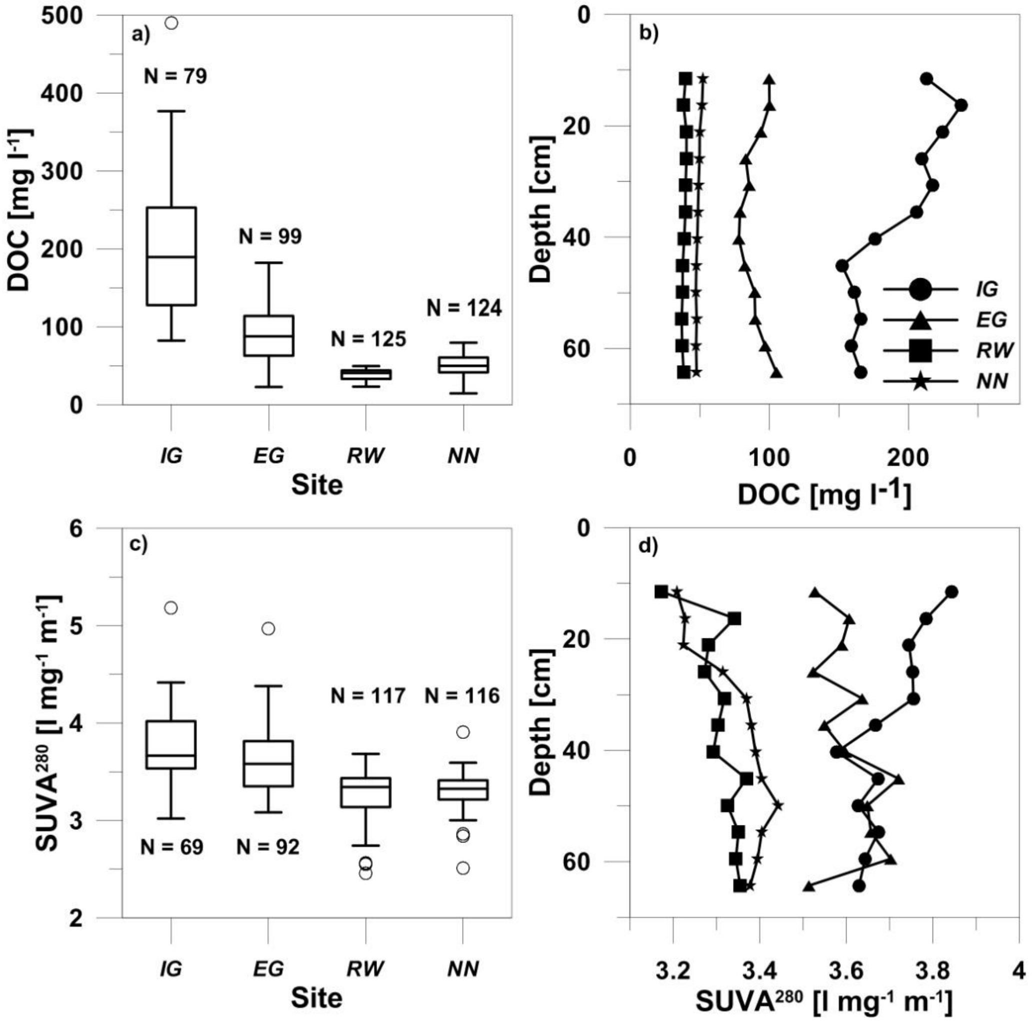

**Fig. 2- 5:** Left: concentrations of (a) DOC-concentrations and (c) SUVA$^{280}$ at the study sites in the bulk samples (central crossbars represent the median, the boxes the 75th and 25th percentile and the circles extreme values). Right: vertical profiles of mean (b) DOC concentrations and (d) SUVA$^{280}$ values.

the addition of root exudates only increased the net C release by 4 % compared to the microbial respiration in the control plot. The authors stated that the impact of root exudates on peat degradation ”priming” seems to be rather small under aerobic conditions. Additionally, above-ground net primary production was relatively similar at *IG* and *EG* so that it is unlikely that vegetation composition and potential differences in amount and quality of belowground carbon input can trigger a twofold difference in DOC concentration between *IG* and *EG.*

We also rule out a significant effect of slurry application and past fertilization on DOC concentration. Firstly, we could not measure a direct increase in DOC concentrations after slurry application at *IG* in April 2012 (Fig. 2-6). Secondly, the application of 216 g C m$^{-2}$ yr$^{-1}$ by slurry at *IG* (Beetz *et al.*, 2013) is less than 0.1 % of the SOC stock (53 kg C m$^{-2}$) of the upper 65 cm of the peat. Thirdly, the peat properties (Table 2-2) as well as the DOM quality (see chapter

3.4.2 and 3.6) were nearly identical at both grassland sites although *EG* did not receive any fertilizer or slurry during the last decades.

Comparable peat properties in *IG* and *EG* point to a similar land use history. Prior to drainage ditch closure at *EG* DOC concentrations may have been as high as at *IG*. Comparing *IG* and *EG* suggests that rewetting a grassland containing a highly degraded peat layer instead of a peat extraction site would also cause a reduction of the DOC concentrations. However, as long as the water table was not restored to the soil surface – a common problem in many rewetting projects – DOC concentrations will likely remain higher than at near-natural sites.

Mean DOC concentrations at *RW* were comparable to *NN* 10 years after rewetting. We found constant DOC concentrations over depth at *RW* even in the more degraded peat layer below 15 cm, which had been aerated during peat harvesting. The mobile DOC pool seems to be been exhausted as suggested by Glatzel *et al.* (2003) and Wallage *et al.* (2006) who found lower DOC concentrations in rewetted sites already after 3 to 4 years of rewetting. The re-colonisation with typical bog plants may have supported the transition to near-natural C cycling (see Laiho 2006). Rewetting by polder technique in former peat extraction areas proves to be a suitable

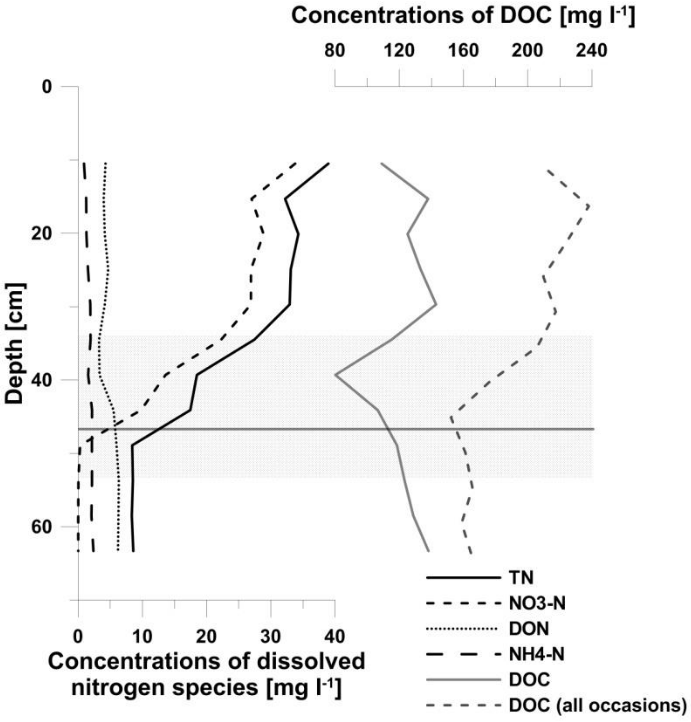

**Fig. 2- 6:** Vertical profiles of total nitrogen (TN), dissolved organic nitrogen (DON), $NO_3$-N, $NH_4$-N and dissolved organic carbon (DOC) concentrations after cattle slurry application in April 2012. DOC (all occasions) represent the mean vertical DOC concentrations during periods without slurry application. The horizontal line represents the mean water table position and the dotted area the amplitude of the water table fluctuation during the sampling interval.

method to re-establish permanently anoxic conditions and to reduce C mineralization and DOC production. Despite differences in land use history (IG, EG vs. RW) comparable peat properties between 15 and 60 cm (see section 3.1 & Table 2-2) suggest that the establishment of permanently wet condition and the removal of the uppermost highly degraded peat layer can reduce DOC concentration to near natural conditions on longer time scales. However, these results are not transferable to all rewetted peatlands, especially nutrient-rich or stronger degraded sites. Overall, we reject our hypothesis and conclude that 10 years of full rewetting have been long enough to re-establish near-natural DOC concentrations in a rewetted peat extraction site.

### Dissolved organic carbon – qualities

Mean SUVA$^{280}$ values were elevated by around 10% at the drained sites (*IG*: 3.8 ± 0.4 $l\ mg^{-1}\ m^{-1}$, *EG*: 3.6 ± 0.3 $l\ mg^{-1}\ m^{-1}$) compared to the wet sites (*RW* 3.3 ± 0.3 $l\ mg^{-1}\ m^{-1}$, *NN:* 3.3 ± 0.2 $l\ mg^{-1}\ m^{-1}$). SUVA$^{280}$ values ranged from 5.57 $l\ mg^{-1}\ m^{-1}$ to 2.46 $l\ mg^{-1}\ m^{-1}$ (Fig. 2-5c). Deeper drainage at *IG* has led to much higher DOC concentrations but no change in DOC quality compared to *EG*. Within the soil profile, SUVA$^{280}$ values were fairly constant at *EG*, *RW* and *NN*, and slightly elevated in the upper 35 cm at *IG* (Fig. 2-5d).

These results support our hypothesis that prolonged water table drawdown has led to a higher degree of aromaticity of DOC, which must have been mainly released from the highly degraded, intensely humified upper peat layer (high von Post indices and narrow C to N ratio at *IG* and *EG* compared to *NN*). DOC then percolates down the peat profile with only little (*IG*) or no alteration (*EG*) in aromaticity. As in our study, Hoell *et al.* (2009) measured higher SUVA$^{280}$ values in a drained grassland than in a rewetted fen. Kalbitz *et al.* (1999) showed as well that DOC sampled from degraded peat was enriched in aromatic moieties. The differences in SUVA$^{280}$ between drained sites and wet sites were slightly lower than those found by Kalbitz (2001) between fen areas of different land use history. This could be explained by the longer land use history (up to 200 years) and thus even stronger peat degradation compared to our study area (60 years).

The stable SUVA$^{280}$ profiles contrast with results for mineral soils under grassland where Don & Schulze (2008) found a decline in SUVA$^{280}$ by around 30% from 10 to 65 cm depth. This can be attributed to missing adsorption of aromatic DOC moieties in bog peat, which lacks a mineral phase or iron oxides. Thus, drainage of bogs with thick peat layers bears a great risk of additional DOC losses to subsurface of surface waters due to lacking retention capacities.

In contrast to our assumption, the DOC quality of *RW* and *NN* was comparable, which supports our findings for DOC concentrations that *RW* has reached a near-natural DOC status after 10 year of rewetting. Apparently, DOC production and turnover in the soil profile are governed by recent soil redox conditions rather than by the legacy of peat degradation during past drainage reflected in the soil properties of *RW* below 15 cm.

### Dissolved $CO_2$ and $CH_4$

Dissolved $CO_2$ was the dominant greenhouse gas during our winter period investigations, but no general difference was found between drained (*IG*, *EG*) and wet sites (*RW*, *NN*; Fig. 2-7). The mean concentrations of $CO_2$-C decreased in the order *NN*, *IG*, *RW* to *EG* with 16.8 ± 4.4 mg $l^{-1}$, 15.4 ± 5.0 mg $l^{-1}$, 10.4 ± 1.6 mg $l^{-1}$ and 7.8 ± 4.5 mg $l^{-1}$, respectively. Concentrations of dissolved $CO_2$-C tended to increase with depth at all sites.

In contrast, $CH_4$-C concentrations at the wet sites (*RW*: 4.4 ± 1.3 mg $l^{-1}$; *NN*: 3.0 ± 0.9 mg $l^{-1}$) were 11 to 22 times higher than at the drained sites (*IG*: 0.2 ± 0.4 mg $l^{-1}$; *EG*: 0.3 ± 0.5 mg $l^{-1}$). $CH_4$-C concentrations tended to increase with depth at all sites. While $CH_4$ was measured over the whole sampling depth at wet sites, it was only found at drained sites in water saturated zones below a depth of 40 cm (Fig. 2-7).

In general, the corresponding DOC concentrations were higher than the concentrations of dissolved $CO_2$-C and $CH_4$-C. Thus, DOC accounts for 74 % to 93 % of total dissolved carbon in the peat pore water at our sites. However, the soil solutions were enriched in dissolved $CH_4$-C and $CO_2$-C compared to equilibrium water concentration ($CO_2$-C: 0.33 mg $l^{-1}$; $CH_4$-C: 0.05 µg $l^{-1}$) at atmospheric pressure and at the average air temperature (2°C) during sampling between November 2012 and February 2013. At supersaturation of the soil solution $CH_4$-C and $CO_2$-C degas into the atmosphere at the water-air boundary. But $CH_4$ may not necessarily be released from the soil because methanotrophic processes dominate in the upper peat layers. Beetz *et al.* (2013) did not measure any $CH_4$ emissions in winter at the drained sites (*IG*, *EG*).

An accumulation of microbially produced $CO_2$ and $CH_4$ with depth was also found elsewhere (Clymo & Bryant, 2008; Blodau & Siems, 2012) and was attributed to low diffusion coefficients in water associated with a slow ongoing mineralization in deeper peat layers (Beer & Blodau, 2007).

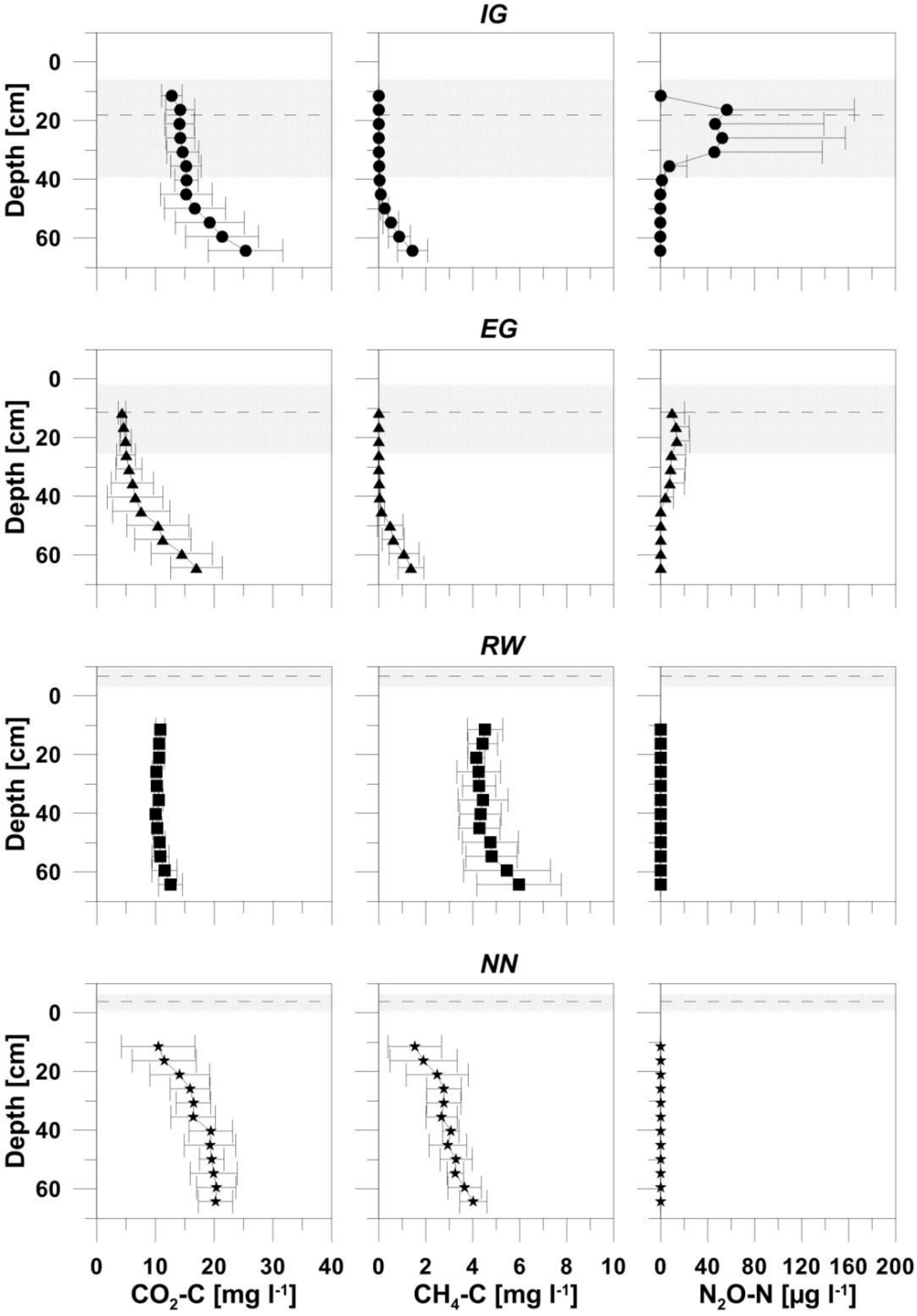

**Fig. 2- 7:** Concentrations of the dissolved gases $CO_2$-C (left), $CH_4$-C (centre) and $N_2O$-N (right; mean values per depth and standard deviation). The dashed lines represent the mean water table and the dotted area the amplitude of the water table fluctuation during the gas sampling period (November 2012 - February 2013).

$CH_4$ production is strictly related to anaerobic conditions. Under anaerobic conditions, methanogens are furthermore outcompeted for electron donors by $NO_3^-$ or $SO_4^{2-}$ reducing bacteria. Thus, during reduction of electron acceptors with higher standard redox potential, methanogenesis is fully (*e.g.* $NO_3^-$) or partly (*e.g.* $SO_4^{2-}$) suppressed (Achtnich *et al.*, 1995, Gauci *et al.*, 2004). The absence of oxygen or $NO_3^-$ and low (< 1 mg $l^{-1}$) $SO_4^{2-}$ concentrations offer suitable conditions for methanogenesis over the whole profile at *RW* and *NN*. Elevated net methane production can be expected at *RW* compared to *NN*, because $CH_4$-C concentrations exceed those at *NN*. Temporal water table draw down in summer months at the drained sites prohibits the methanogenesis during periods of high water tables in the winter months in the seasonally saturated peat layers at *IG* and *EG* above a depth of 40 cm and even below. This agrees with Knorr & Blodau (2009) who observed a delayed onset of methanogenesis in rewetted aerobic peat horizons by up to 50 days as long as other electron acceptors are replenished. Despite the higher water table at *EG* than at *IG*, the methane concentrations also suggest that C cycling is comparable at the two drained sites.

### 2.4.5 Nitrogen

#### Dissolved nitrogen

TN decreased in the order *IG* (11.9 ± 3.7 mg $l^{-1}$) > *EG* (5.2 ± 1.8 mg $l^{-1}$) > *RW* (2.2 ± 0.5 mg $l^{-1}$) ≈ *NN* (1.6 ± 0.4 mg $l^{-1}$). Overall, TN concentrations ranged from 0.9 to 21.4 mg $l^{-1}$.

At all sites DON was the dominant nitrogen species (Fig. 2-8), ranging on average from 55% to 88% of TN. Mean DON concentrations were 9.2 ± 3.2, 4.1 ± 1.3, 1.2 ± 0.4 and 1.4 ± 0.3 mg $l^{-1}$ at *IG, EG, RW* and *NN*, respectively and ranged from 0.6 to 19.88 mg $l^{-1}$. The depth profiles of DON were comparable to DOC and remained nearly constant at *EG, RW* and *NN*. At *IG*, DON values were higher in the top 30 cm (Fig. 2-8a).

$NH_4$-N was the dominant inorganic N species, ranging on average from 13% to 46% of TN. Mean $NH_4$-N concentration decreased in the order *IG* (2.3 ± 1.4 mg $l^{-1}$) > *RW* (1.0 ± 0.5 mg $l^{-1}$) ≈ *EG* (0.9 ± 0.7 mg $l^{-1}$) > *NN* (0.2 ± 0.3 mg $l^{-1}$) and ranged from detection limit to 9.14 mg $l^{-1}$. Comparing the concentrations in 10 cm and 65 cm depth, $NH_4$-N tended to increase at all sites with depth by a factor of 1.5 to 6 (Fig. 2-8b). At *NN* and *RW* the increase was nearly linear. In contrast, the vertical pattern at *IG* and *EG* showed the lowest $NH_4$-N concentration in upper aerated peat layer and increased linearly at a depth below the mean water table at each site (Fig. 2-8b).

$NO_3$-N was only present at drained sites (*IG, EG*). At *NN* and *RW,* no or only trace amounts of $NO_3$-N could be measured. Average $NO_3$-N concentrations were 0.5 ± 1.0 mg $l^{-1}$ at *IG* and 0.2 ± 0.4 mg $l^{-1}$ at *EG* and ranged from detection limit to 5.9 mg $l^{-1}$. Highest $NO_3$-N concentrations were found in 10 cm depth and decreased downwards to 40 cm depth (Fig. 2-8c). Below 40 cm depth, no $NO_3$-N could be detected.

Slurry application at *IG* in April 2012 led to a spike in nitrogen concentrations in the form of $NO_3$-N (Fig. 2-6). Compared to the colder and wetter periods of the year the $NO_3$-N concentrations were increased by a factor of approximately 37, but only in the soil solution above the mean water table. Surprisingly, concentrations of DON and $NH_4$-N were unaffected by the slurry application although considerable amounts of DON and $NH_4$-N had been added to the peat surface. The N profile (Fig. 2-6) can be explained by fast nitrification of applied N followed by strong denitrification in the soil profile around groundwater level (van Beek *et al.*, 2004) and N uptake by the vegetation.

In this study, the near-natural site (*NN*) showed the lowest concentration of all measured N species, reflecting the nitrogen-poor conditions of pristine bogs. As in our study, Bragazza & Limpens (2004) found DON being the dominant N species in six European bogs. DON concentrations measured during our study were comparable to DON concentrations reported by Moore *et al.* (2005) for an ombrotrophic bog in Canada. High DON concentrations are typical for peatlands, where anaerobic conditions constrain mineralization of organic nitrogen compounds. Under acidic waterlogged conditions $NH_4$-N is the main inorganic N compound, because nitrification rates are low due to low pH values and the absence of available oxygen. $NH_4$-N concentrations during our study were lower than reported by Hemond (1983) in an ombrotrophic bog in Massachusetts and comparable to ombrotrophic bogs in Canada (Wind-Mulder *et al.*, 1996). Despite low ammonification under water logged conditions, over longer time periods $NH_4$-N accumulates in deeper peat layers at *NN*.

In general, long-term agricultural peatland use associated with drainage has led to increased concentrations of all measured nitrogen compounds (*IG*, *EG* vs. *NN*). DON concentrations at drained grassland sites were in the range of agricultural fen areas in Germany (Kalbitz & Geyer, 2002), but exceeded concentrations in agriculturally used mineral soils (Siemens & Kaupenjohann, 2002). DON may be further mineralized to $NH_4$-N or $NO_3$-N in downstream ecosystems. Obviously, drained agricultural bogs bear similar risks of DON export as fens.

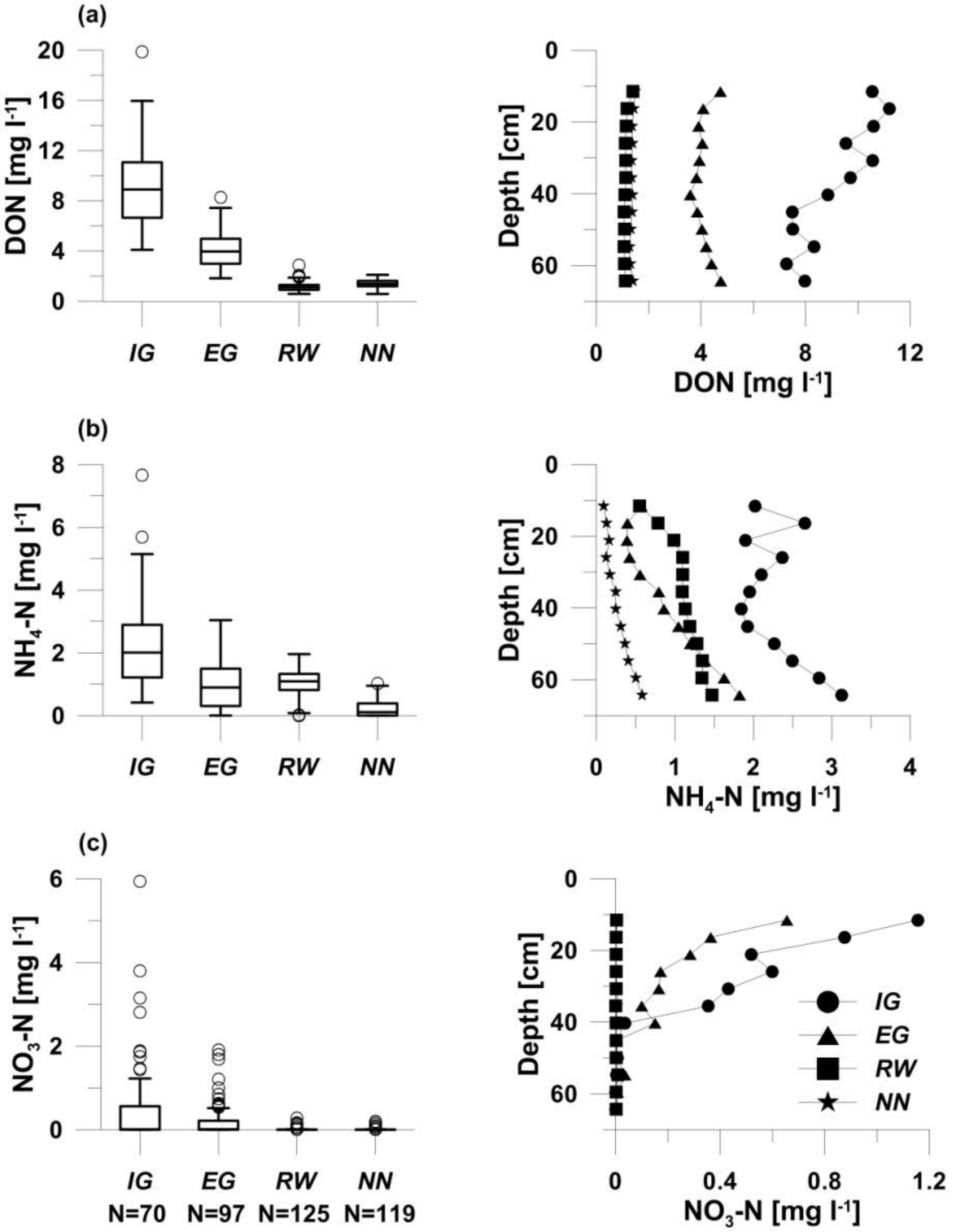

**Fig. 2- 8:** Left: concentrations of (a) DON, (b) $NH_4$-N and (c) $NO_3$-N at the study sites in the bulk samples (central crossbars represent the median, the boxes the 75th and 25th percentile and the circles extreme values). Right: vertical profiles of mean concentrations. Sampling date after cattle slurry application excluded (April 2012).

Nitrogen species at *IG* were on average about twice as high as at *EG*. DON to $NH_4$-N ratio was constantly at 5 to 1 at both sites despite the different fertilization history and not affected by slurry application. Only $NO_3$-N was elevated for a short period immediately after slurry application. This confirms our findings for DOC that fertilization only had a short and reversible impact on dissolved species and drainage depth governs both DOC and N species concentrations in the soil solution. Carbon to nitrogen ratio in the topsoil of both drained grassland sites (*IG*, *EG*) is 20 so that peat mineralization releases proportional amounts of N as DON, which is partially ammonified. Plant uptake remains slower than mineralization so that N species have accumulated in the soil solution. The concentration differences between *IG* and *EG* are likely attributed to lower N mineralization in the wetter *EG* site but can also result from higher N use efficiency of the vegetation or more effective nitrification and denitrification. The strong $NO_3$-N gradient with depth after fertilization (Fig. 2-6) and during periods without fertilization (Fig. 2-8c) additionally indicates a strong denitrification potential at our drained sites. The nitrification potential can be assumed to be lower at our grassland sites compared to a nutrient rich fen area used as grassland in North East Germany, where $NO_3$-N was the dominating inorganic N compound (Tiemeyer *et al.*, 2007).

After 10 year of rewetting, *RW* showed near-natural (*NN*) DON concentrations. This agrees with our findings for DOC. In contrast, $NH_4$-N concentration at *RW* exceeded those at *NN* by a factor of 4.5. Wind-Mulder *et al.* (1996) also showed that rewetted post-harvested bogs were characterized by elevated $NH_4$-N concentrations compared to intact bogs. The $NH_4$-N concentrations at *RW* doubled from 10 to 25 cm (Fig. 2-8b), indicating $NH_4$-N uptake or lower $NH_4$-N production in the upper newly formed peat layers. Higher $NH_4$-N concentrations were especially found in the more strongly degraded peat (15-65 cm). This agrees with Zak & Gelbrecht (2007) who showed increased $NH_4$-N release from degraded peat after rewetting. Thus, it can be assumed that the elevated $NH_4$-N concentrations are a memory effect of the former drainage and mineralization of this peat layer during harvesting and prior to rewetting.

**Dissolved $N_2O$**

$N_2O$ was only found at the drained sites (*IG*, *EG*) and ranged from 0 to 688 µg $l^{-1}$ at *IG* and 0 to 30 µg $l^{-1}$ at *EG*. $N_2O$ concentrations were highest in November and December 2012 in zones of water table fluctuation during the sampling period, in general above 40 cm depth, where no $CH_4$ was present (Fig. 2-7).

Due to water table fluctuations saturated and unsaturated conditions alternate in the upper peat layers at *IG* and *EG*. These alternations favour nitrification and denitrification and maintain zones of low oxygen content in soil ideal for $N_2O$ production. Figure 2-8 clearly indicates nitrate production within the unsaturated zone and strong nitrate consumption in zones of water table fluctuation (10 to 40 cm). Both processes produce $N_2O$ (Wrage *et al.*, 2001) and, indeed, Beetz *et al.* (2013) measured $N_2O$ emissions at *IG* and *EG* including the winter periods in 2008 and 2009. The production of $N_2O$ was restricted to periods directly after water table rise to the soil surface when nitrate is present. During longer periods of water saturation, $N_2O$ formation decreased, probably due to ceased nitrification and thus exhaustion of available nitrate or further denitrification to $N_2$.

### 2.4.6 DOC to DON ratios of soil solution

The DOC to DON ratios of drained (*IG*, *EG*) and wet sites (*RW*, *NN*) were clearly different. Drained sites were characterized by narrow and stable DOC to DON ratios (*IG*: 21.5 ± 1.9; *EG*: 21.9 ± 1.6) in contrast to the wet sites (*RW*: 35.4 ± 7.1; *NN*: 35.6 ± 4.9). A low DOC to DON ratio and elevated $SUVA^{280}$ values at *IG* and *EG* suggest an increased degradation level of the released DOM (Currie *et al.*, 1996, Austnes *et al.*, 2010). This supports our hypothesis that drainage alters the DOM quality.

At all sites, the DOC to DON ratio remained constant over depth (Fig. 2-9). Comparing the DOC to DON ratio with the C to N ratio of peat can help to identify the origin and turnover of DOC within the soil profile. At the wet sites, the DOC to DON ratio was lower than the C to N ratio of the peat in the uppermost and in the corresponding peat layer (Fig. 2-9). At *NN,* the corresponding C to N ratio of the transition zone between peat and limnic organic deposit (39-65 cm) equals the DOC to DON ratio in soil solution. DOM enriched in N compared to peat may result from N immobilization by microbes (Bowden, 1987), microbial N recycling (Broder *et al.*, 2012) of a small N pool (Urban & Eisenreich, 1988) and therefore from an increased input of the microbial biomass. Another possibility may be a predominant release of low-molecular-weight organic compounds, as indicated by lower $SUVA^{280}$ values (Chin *et al.*, 1994), from the peat to soil solution, which were enriched in N (Qualls & Haines, 1991).

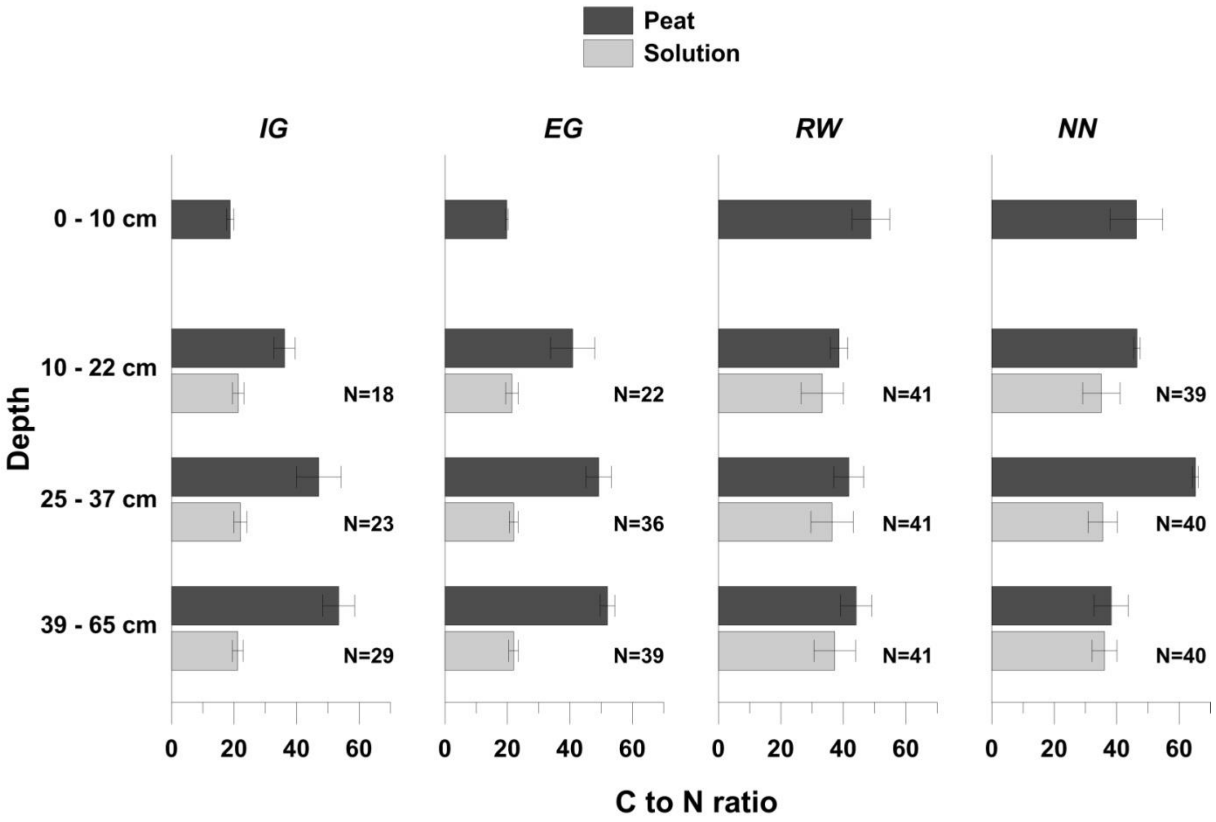

**Fig. 2- 9:** DOC to DON ratio of the soil solution and C to N ratio of the uppermost and the corresponding peat layers (n=3). Bulk solution means of 3 chambers (10-22 cm and 25-37 cm) and 6 chambers (39-65 cm) over the complete sampling period (February 2012 – February 2013).

At the drained sites (*IG*, *EG*), the DOC to DON ratio of the soil solution equals the C to N ratio of the strongly degraded upper peat layer in 0-10 cm depth (Fig. 2-9). Michalzik & Matzner (1999) also found concordance in C to N ratios of the solid phase and DOM in soil solution from a forest floor. They suggest a predominant release of DOM from the bulk soil organic matter rather than specific sources (*e.g.* microbial biomass). The similar DOC to DON ratios at *IG* and *EG* further suggest that at our sites, fertilizer and slurry application did not alter the DOM composition. This observation contrasts with Kalbitz & Geyer (2002) who attributed a stronger degradation of the uppermost peat layers associated with a shift in DOM quality to intensive use and long-time fertilisation. Obviously, the large mineralized peat pool at our site overrides fertilizer as nitrogen source for DOM and mineral N in the soil solution for most of the year. Furthermore, throughout the profile the DOC to DON ratio remained narrower than the C to N ratio of the corresponding peat layers (Fig. 2-9). This supports our interpretation of the SUVA$^{280}$ values that at the drained sites (*IG*, *EG*) DOM is produced in the degraded topsoil during peat degradation and percolates through the profile without microbial alteration. DOM in degraded peatlands is mainly built of recalcitrant humic substances (Zak *et al.*, 2004) which is not readily bioavailable (Kalbitz *et al.*, 2003). When this DOM is exported to ground- and surface waters the downstream photo-oxidation potential is altered as well, because degraded DOM with a higher aromatic content (*IG*, *EG*) may be more photo-labile (Köhler *et al.*, 2002) and be converted to $CO_2$ more easily.

## 2.5 Conclusion

This study is the first to analyse DOM and nitrogen concentrations in the soil solution of long-term drained, rewetted and near-natural peat in a raised bog complex in the temperate climate region. In contrast to other studies, peat degradation and DOM patterns were fully explained by drainage depth but not by contrasting fertilization history of drained bog grasslands. Compared to a near-natural site, artificial drainage of a temperate bog has strongly increased the concentrations of DOC and N species (DON, $NH_4$-N, $NO_3$-N). DOM and N quantities strongly raised with the groundwater table depth associated with grassland use intensity. The deeply drained intensive grassland (*IG*) has a much a higher risk of high DOC and DON losses to downstream water bodies than expected and described so far for other peatland types and climate zones. DOM was mainly released from the aerobic degraded topsoil and percolated through the profile without any clear sign of chemical alteration or physical retention.

After 10 years of rewetting a former peat extraction site, the soil solution has clearly reached quasi natural conditions (*RW* vs. *NN*). Elevated concentration of dissolved methane and $NH_4$-N in the degraded peat layer, which had formed the topsoil prior to rewetting, remained the only weak traces of former land use. Restoration by polder technique was successful because permanent anoxic condition have been re-established in the entire peat profile throughout the year. Partial rewetting also proved a successful step to reduce DOM and N concentrations in the soil solution of managed bog grasslands within less than 10 years.

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# 3 Publication no. 2

## Drivers of nitrogen and dissolved organic carbon (DOC) concentrations and losses from drained and re-wetted catchments in a temperate raised bog

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## 3.1 Abstract

Losses of dissolved organic carbon (DOC), dissolved organic (DON) and inorganic nitrogen (N) (ammonium [$NH_4$-N] and nitrate [$NO_3$-N]) vary widely between peatlands. There are very little data on the effects of drainage and re-wetting on DOC and in particular on total dissolved nitrogen (TDN) losses from raised bogs in temperate Europe. We measured DOC and N concentrations, discharge and environmental variables at a drained grassland and a re-wetted former peat extraction site in a raised bog in Germany over a period of two years. Together with previously published greenhouse gas fluxes, these data were used to estimate total carbon and nitrogen balances.

As mean concentrations of DOC, TDN, DON, $NH_4$-N and $NO_3$-N were primarily driven by water table depth (WTD), their concentrations and losses were both significantly higher at the grassland than at the re-wetted catchment. Temporal variability of losses was driven by differences in discharge. At the grassland, each solute showed an individual response to WTD or temperature. In contrast, at the re-wetted site all solutes behaved similarly and were negatively correlated with WTD, but positively with temperature over the preceding 14 days. The maximum DOC loss of > 500 kg C $ha^{-1}$ $yr^{-1}$ from the grassland is one of the highest values measured for peatlands in temperate climate regions, but still contributed less than 10% of the total carbon balance. DON accounted for 72-81% of the TDN loss in both catchments, representing the most important N source for downstream ecosystems.

## 3.2 Introduction

Peatlands are known to store huge amounts of carbon (C) and nitrogen (N) (Gorham, 1991; Limpens *et al.*, 2006), but drainage turns these originally anaerobic soils from sinks into sources (IPCC, 2014). Nearly all peatlands in Germany have been drained for agriculture, forestry or peat extraction and are now mainly used as grasslands (UBA, 2015). Greenhouse gas (GHG) emissions from drained peat grasslands are much higher than those from natural peatlands (IPCC, 2014) and are usually dominated by carbon dioxide ($CO_2$). While $CO_2$ fluxes from temperate raised bogs are relatively well studied (IPCC, 2014; Tiemeyer *et al.*, 2016), carbon losses via the aquatic pathway are less well quantified (Evans *et al.*, 2015).

Waterborne C is a mixture of various fractions including dissolved and particulate compounds as well as gases (Dawson *et al.*, 2004). In peatlands, dissolved organic carbon (DOC) has often been found to be the most important waterborne C fraction (Billett *et al.*, 2004; Dinsmore *et al.*, 2013). DOC losses may be > 300 kg $ha^{-1}$ $yr^{-1}$ (Dinsmore *et al.*, 2010; Rowson *et al.*, 2010), exceed soil to atmosphere fluxes (Billet *et al.*, 2004) and therefore constitute an important component of the C budget of peatlands. Thus, ignoring waterborne C losses may cause a misinterpretation of the real C source or sink strength.

The new IPCC Wetlands Supplement (IPCC, 2014) requires the inclusion of DOC losses from peatlands as off-site $CO_2$ emissions in national greenhouse gas inventories. The IPCC (2014) offers only one common DOC emission factor (EF) each for drained and re-wetted temperate peatlands, irrespective of peatland type and drainage depth. Furthermore, these EFs are mainly based on concentration differences, assuming no impact of drainage and land use on discharge. More field data on C concentrations and losses are therefore needed to differentiate between EFs for different peatland types (Evans *et al.*, 2015).

Waterborne N losses from German peatlands have been investigated thoroughly in the past (Kuntze & Eggelsmann, 1972; Tiemeyer *et al.*, 2007), but these studies mainly focused on dissolved inorganic nitrogen forms, primarily nitrate ($NO_3$-N), while dissolved organic nitrogen (DON) and ammonium ($NH_4$-N) were mostly neglected. This might be appropriate for drained eutrophic fens where N losses are dominated by inorganic N compounds, especially $NO_3$-N (Tiemeyer & Kahle, 2014). In contrast, DON is frequently the main N fraction in the soil solution of ombrotrophic peatlands (Frank *et al.*, 2014; McKenzie *et al.*, 2016). Ignoring DON losses may therefore cause an underestimation of the real N losses (Nieminen, 2004; Kløve *et al.*, 2010) and thus of the total eutrophication potential.

In most cases, long-term water table drawdown increases DOC, DON, $NH_4$-N or $NO_3$-N concentrations in peatland soil solutions (Wallage *et al.*, 2006; Daniels *et al.*, 2012; Frank *et al.*, 2014). This is caused by increased peat degradation under aerobic conditions (Updegraff *et al.*, 1995). The IPCC (2014) estimates a 49-118% increase in DOC concentration after drainage compared to natural areas. Depending on the effects of drainage on discharge, this may lead to a strong increase in DOC losses.

Re-wetting previously drained peatlands may initially increase DOC concentrations (Kalbitz *et al.*, 2002; Zak & Gelbrecht, 2007), but in the long run DOC concentrations are often reduced by re-wetting (Wallage *et al.*, 2006; Höll *et al.*, 2009), sometimes even to near-natural concentrations (Frank *et al.*, 2014). $NO_3$-N is strongly diminished by re-wetting (Kieckbusch & Schrautzer, 2007) due to denitrification under anaerobic conditions (Cabezas *et al.*, 2012). The effects of re-wetting on other N fractions are less clear; $NH_4$ concentrations sometimes experience a similar peak to DOC (Kieckbusch & Schrautzer, 2007; Zak & Gelbrecht, 2007), and information on DON is generally scarce.

The magnitude and dynamics of waterborne C and N losses depend on the interaction of peatland hydrology and biogeochemistry. Higher discharge sums generally coincide with higher DOC losses (Dawson *et al.*, 2004; Dinsmore *et al.*, 2013; Evans *et al.*, 2015). Single storm events can dominate the total DOC losses (Hinton *et al.*, 1997; Clark *et al.*, 2007) as the highest concentrations tend to concur with peak discharge rates (Koehler *et al.*, 2009), and this may also be the case for DON (Edokpa *et al.*, 2015). In blanket bogs, DOC concentrations are affected by changing flow paths and DOC sources from the temporarily unsaturated upper peat layer (acrotelm) during storm flows to water from the permanently saturated zone (catotelm) or the deeper groundwater (Clark *et al.*, 2007, Austnes *et al.*, 2010). Flow paths also control $NO_3$-N losses. A rapid export without passing through anaerobic peat layers, *e.g.* due to tile drains, has been found to cause high $NO_3$-N losses (Kieckbusch *et al.*, 2006; Tiemeyer & Kahle, 2014). As flow paths and discharge generation processes differ greatly between peatland types (Holden *et al.*, 2004), it is questionable whether results from blanket bogs or fens for example can be transferred to Atlantic raised bogs, especially if they have essentially become flat due to peat extraction and drainage. Furthermore, the impact of drainage and re-wetting on both discharge sums and peak flow rates is highly site specific (Holden *et al.*, 2004), and changes in hydrological processes are likely to affect DOC losses (Waddington *et al.*, 2008).

On larger spatial scales, rising temperatures as well as decreasing sulphate depositions have been linked to an increasing release of DOC from peatlands in the Northern Hemisphere (Freeman *et al.*, 2001; Monteith *et al.*, 2007). In a controlled plot experiment, acidification is clearly a cause of lower DOC concentrations (Evans *et al.*, 2012). Furthermore, Clark *et al.* (2005) highlight the importance of drought-induced acidification on DOC concentration patterns. The formation of sulphate during a drought led to a pH drop and an increase in ionic strength, reducing the solubility and release of DOC (Clark *et al.*, 2012). Due to an interaction of temperature-dependent microbial activity (Christ & David, 1996) and soil moisture effects, DOC concentrations often show a typical seasonality, with the highest values in summer months and the lowest in winter (Koehler *et al.*, 2009). Owing to the peatland-specific and scale-dependent (Clark *et al.*, 2010) interactions of all known drivers, no general consensus on the importance of these drivers on DOC and N concentrations and losses has yet been reached.

Until now, DOC and N have rarely been studied in conjunction and data on DON losses are particularly scarce for all peatland types, although this may be the most important fraction of TDN. Furthermore, most studies have been conducted in boreal peatlands or blanket bogs. The results on both C and N losses and their contributions to the C and N balance may not be transferable to temperate or more continental raised bogs since weather conditions, topography and discharge generation processes differ significantly.

The aim of our study was to reduce the knowledge gap on DOC and N losses from temperate raised bogs. We focused on the most common (intensive grassland) and the most discussed (rewetting) land use types of peatlands in the temperate zone. We therefore measured C and N concentrations and losses to answer the following research questions:

- How do dissolved C and N concentrations depend on land use?
- Which are the most important drivers of C and N concentrations?
- How much dissolved C and N are exported from the two land use systems?
- How much do waterborne C and N losses contribute to the total carbon and nitrogen budgets of these two systems?

## 3.3 Materials and methods

### 3.3.1 The study site

The Ahlen-Falkenberger Moor is a 39 km² large raised peat bog complex (53° 41´N, 8° 49´E) in north-western Germany (Lower Saxony, Fig. 3-1a). The long-term average temperature and precipitation are 9.4 °C and 905 mm respectively (German Weather Service, 2012).

Since cultivation began in the early 20th century, the bog has mainly been used as grassland of varying intensities (Ahrendt, 2012). Nowadays, intensive grassland is the dominant land use outside nature conservation areas. These grasslands consist of regular rectangular parcels of varying size (Fig. 3-1b). Each parcel is surrounded by drainage ditches at least 1.5 m deep. Ditch maintenance (*i.e.* cutting down vegetation inside the ditches) is performed regularly in the autumn to maintain fast drainage. In addition to the drainage ditch network, plastic drainage pipes were installed at a depth of one metre, spaced around 10 m apart. The topography is flat and therefore we did not observe any overland flow towards the ditches. As the regional groundwater head is lower than the water level in the peat, groundwater inflow is unlikely.

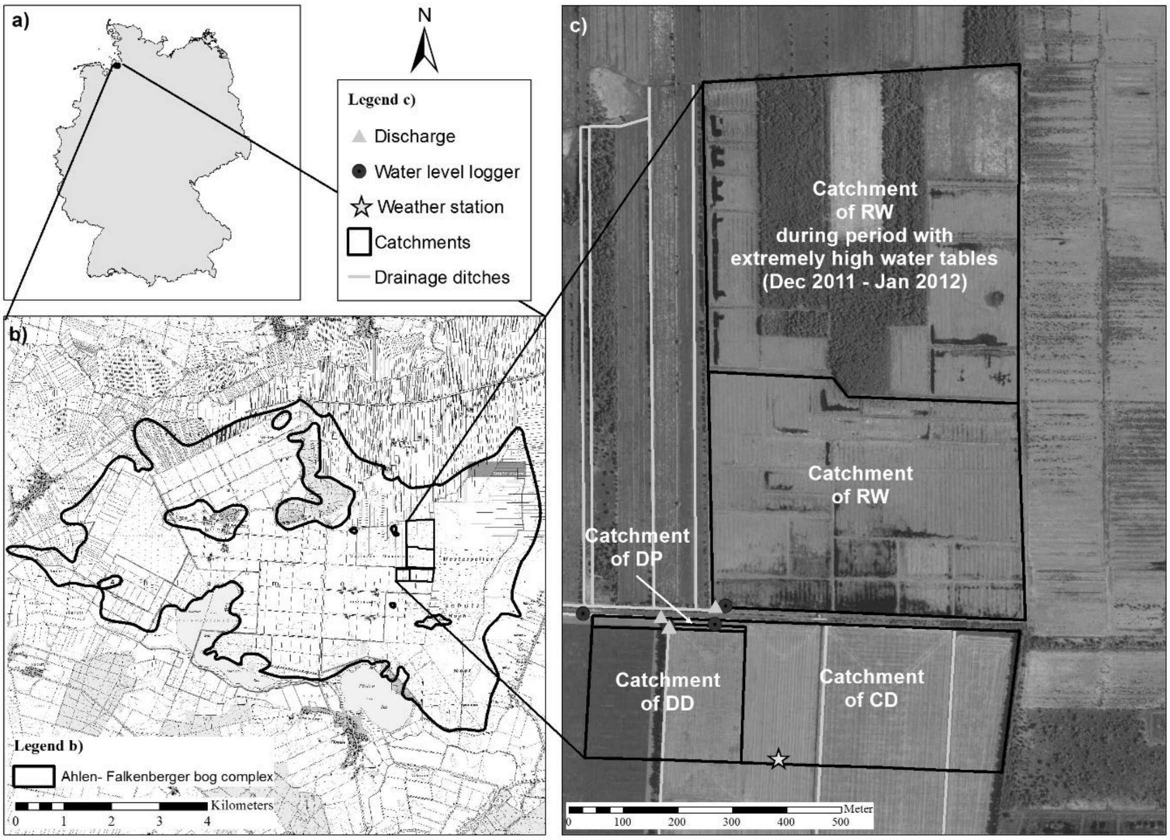

**Fig. 3- 1:** (a) Location of the study site in Germany, (b) location within the Ahlen-Falkenberger Moor bog complex (topographic map TK 1:25,000, Federal Agency for Cartography and Geodesy) and (c) the setup and catchments of the investigated drainage ditches and pipes. CD = collector ditch, DD = drainage ditch, DP = drainage pipe, and RW = re-wetted polder (aerial image: Federal Agency for Cartography and Geodesy).

The grassland mainly consisting of *Poa trivialis* L., *Holcus lanatus* L. and *Lolium perenne* L. is highly productive and cut up to five times per year. Fertiliser is applied three to seven times a year. Tiemeyer *et al.* (2016) estimate the N and C input *via* mineral fertiliser and cattle slurry to be around 22 g N $m^{-2}$ $yr^{-1}$ and 207 g C $m^{-2}$ $yr^{-1}$ respectively. Such intensive use is typical for peatlands in dairy farming regions. Peat layer thickness is about 330 cm. Weakly to medium decomposed *Sphagnum* and *Eriophorum* peat in deeper layers are covered by a strongly degraded peat horizon with a thickness of 15 cm. C contents increased from 46 to 50% and the C to N ratio from 20 to 50 in the degraded upper peat layer at 1 m depth (Frank *et al.*, 2014).

Industrial peat extraction took place in parts of the peatland from the 1950s until 2002. These areas were subsequently re-wetted (Fig. 3-1b). Rectangular polders varying in size were separated by peat dams to retain precipitation and ensure permanently waterlogged conditions. The water level in the polders is regulated by a vertical PVC pipe through which water starts to discharge at water levels higher than around 5 cm above ground surface. After 10 years of rewetting, the area was largely re-vegetated by *Sphagnum* spp., *Eriophorum vaginatum* L. and

*Molinia caerulea* L. (Moench), but some areas of open water still remained. Recent peat development was initiated on former medium degraded peat layers that had started to float after rewetting. Ten years after rewetting, up to 15 cm of almost undecomposed peat has accumulated. In the upper 65 cm of the peat, the C content ranges from 43% in the recently formed peat horizon to 52% in the deeper degraded peat, and the C to N ratio from 47 to 52 (Frank *et al.*, 2014).

We chose four sampling points for our study. Three nested points represented the grassland and one the re-wetted area (Fig. 3-1c). The samples from the drainage pipe (*DP*) characterised the water quality directly after leaving the peat profile. *DP* has a catchment of approximately 0.09 ha and discharges into the adjacent drainage ditch (*DD*) with a catchment size of approximately 6.8 ha. The *DD* is connected to a larger collector ditch (*CD*) with a catchment size of approximately 20 ha. At the re-wetted site (*RW,* 23 ha), water from the regulation pipe was sampled. In the winter of 2011/12, this PVC pipe became partially blocked by debris during a period of heavy rainfall, and the water table rose dramatically. Furthermore, the northern part of the re-wetted area also contributed water to the southern outlet when the water level rose above the level of an overflow between the two polders. This was taken into account for the discharge calculation for the period between 30.12.2011 and 31.01.2012 (33 days; Fig. 3-1c). All drainage water enters the lakes south of the bog (Fig. 3-1b).

### 3.3.2 Sampling and sample preparation

Grab samples were taken biweekly in 500 ml PE bottles from June 2011 to June 2013 (*DP*: *n*=43, *DD*, *CD*, *RW*: *n* = 51). Unfiltered samples were analysed for electrical conductivity (EC) and pH (WTW, Weilheim, Germany).

Samples were filtered using 0.45 µm PES membrane filters (Pall Life Science, Port Washington, NY, USA) within 48 h. Prior to filtration, a 20 mL aliquot was separated for POC measurements at the sampling points *DP* and *RW*. If measurements were not possible within three days, samples were stored frozen (-18 °C) until analysis. We did not observe any coagulation due to freezing.

### 3.3.3 Chemical analyses

DOC and POC concentrations were measured in at least three replicates with a DimaTOC 2000 (DIMATEC, Essen, Germany) using the subtraction method, *i.e.* the total inorganic carbon (TIC) concentration (measured *via* combustion at 165 °C after acidification with $H_3PO_3$ – 40%

w/v) was subtracted from the total carbon (TC) measured *via* combustion at 850 °C. The two analyses ran on parallel reactors and detectors.

TDN was measured on a Total Nitrogen Analyser (TN-100; Mitsubishi, Kanagawa, Japan) by reduced pressure chemiluminescence detection. Major ions ($NH_4^+$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$) were measured using an Ion Chromatograph 850 Professional (Methrom, Filderstadt, Germany). DON was calculated as the difference between TDN and dissolved inorganic nitrogen ($NH_4$-N plus $NO_3$-N).

### 3.3.4 Meteorological data

Air temperature, wind speed, humidity and solar radiation were measured by a weather station located at the grassland (Fig. 3-1c). Precipitation was calculated from four German Weather Service stations (Cuxhaven, Steinau, Freiberg/Elbe, Bremerhaven) surrounding the study site using inverse distance weighting. Precipitation data was corrected for measurement errors due to wind and evaporation according to Richter (1995). Grass reference evapotranspiration $ET_0$ was calculated according to Allen *et al.* (1998) using input data delivered by the local weather station.

### 3.3.5 Discharge and solute losses

Water table depths (WTD) at the grassland and at the re-wetted site, as well as water levels in the ditches, were measured with Mini-Divers (Schlumberger Water Services, Delft, The Netherlands) with a resolution of 15 minutes. Discharge was measured biweekly at *DD* and *CD* with an electromagnetic flow meter (Nautilus; OTT Hydromet, Kempten, Germany). Discharge at *DP* and *RW* was determined using a bucket and a stopwatch. During high flow conditions in the winter of 2011/12, discharge at *RW* was also measured using the flow meter. At each sampling point, discharge water-level rating curves were applied to calculate continuous discharge values. At *DD* and *CD*, the water levels in the ditches served as a reference, while at *DP* and *RW* WTD was used.

Different rating curves were applied for summer (May to October) and winter (November to April) conditions due to vegetation growth in the ditches during the growing season. Additionally, two more rating curves had to be applied. The first one (*RW*) was developed for a short period in the winter of 2011/12 where there were very high water tables at the re-wetted area after the PVC outlet tube was partially blocked. The second one was applied after drainage ditch maintenance in November 2012 when the water tables at *DD* and *CD* fell by 20 cm. $R^2$ of the rating curves varied between 0.98 and 0.91 at *CD*, 0.96 and 0.85 at *DD*, 0.88 and 0.62 at

*DP* and 0.99 and 0.82 at *RW*. Rating curves were not extrapolated beyond the maximum water table during discharge measurements. Thus, during some periods with high water tables, the maximum measured discharge was used, which led to an underestimation of the discharge during these periods, especially at *DD* and *CD*.

Annual losses (L) of DOC, POC, TDN, DON, $NH_4$-N and $NO_3$-N were calculated by Eq. 1 (method 5 of Walling & Webb, 1985), where K is a unit conversion factor, $c_i$ the instantaneous concentration, $Q_i$ the instantaneous discharge, Q the mean discharge of the period and n the number of measurements:

$$(1)\ L = \frac{K \sum_{i=1}^{n} c_i Q_i}{\sum_{i=1}^{n} Q_i} \overline{Q} \qquad [\text{kg ha}^{-1}\ \text{yr}^{-1}]$$

### 3.3.6 Estimation of average annual C and N budgets

Waterborne C and N losses from the grassland are given as the average value of the three sampling points (*CD*, *DD* and *DP*), while the sampling point *RW* was assumed to be representative for the re-wetted area.

From 2007 to 2011, greenhouse gas (GHG) emissions were measured at the intensive grassland (Beetz *et al.*, 2013; Tiemeyer *et al.*, 2016) and from 2007 to 2009 at the re-wetted area (Drösler *et al.*, 2013) using the same experimental and modelling approach of the closed chamber technique with transparent chambers for the measurement of net ecosystem exchange (NEE) of $CO_2$ and opaque chambers for methane ($CH_4$) and nitrous oxide ($N_2O$) respectively. The measurement methods and interpolation of annual budgets are described in detail by Beetz *et al.* (2013).

In addition to $CO_2$-C and $CH_4$-C, C fluxes by harvest and slurry application at the grassland site were taken into account (Tiemeyer *et al.*, 2016). All single C fluxes were combined to give the net ecosystem carbon balance (NECB). Positive flux values represent C losses from the peatland and negative fluxes C input to the peatland.

Measurement of gaseous N fluxes was restricted to $N_2O$-N (Drösler *et al.*, 2013; Tiemeyer *et al.*, 2016), while fluxes of $N_2$ as well as N input *via* wet and dry deposition were lacking. An average value of dry and wet deposition of 24 kg $ha^{-1}$ $yr^{-1}$ was taken from Hurkuck *et al.* (2014) measured in a comparable region. Data for N input and export *via* fertilisation and harvest are given by Tiemeyer *et al.* (2016). As for the C balance, all single N fluxes were combined to give the net ecosystem nitrogen balance (NENB). In addition to the NENB, the theoretical N release or N fixation ($N_{NEE}$) due to peat mineralisation or growth was estimated by dividing NEE by the C to N ratio of the uppermost peat layer. The difference between $N_{NEE}$ and NENB represents those N fluxes ($N_{Gap}$) not considered in the N balance, as well as uncertainties of the other terms.

WTDs at the grassland were slightly higher during our study period (-0.46 m) than during the GHG flux measurement period (-0.55 m). As this difference has mainly been caused by one very wet winter, and as land use at this site has not changed for decades, we still assumed our study period to be representative for the GHG measurement period.

At the re-wetted site, groundwater levels have been fairly constant at ground surface for the last five years, but the vegetation is still in succession and continues to re-colonise the polder, reflected by a shift in plant species composition and total vegetation cover. Therefore, the GHG measurements might not be entirely representative for our study period or even the complete polder, which is integrated by our measurements.

### 3.3.7 Statistics

Statistical differences between the concentrations at the different sampling points were evaluated using generalised least square models from the nlme package (Pinheiro *et al.*, 2013) in R (R-Core-Team, 2013). For each solute, a separate model was set up following the model selection procedure outlined by Zuur *et al.* (2009). In a first step, a model explaining the concentrations only by the fixed effect “sampling point” (*CD*, *DD*, *DP*, and *RW*) was set up (Eq. 2).

(2) GLS (concentration ~ sampling point)

Due to heteroscedasticity between the sampling points, a “within group” heteroscedasticity structure was added to the model (Eq. 3).

(3) GLS (concentration ~ sampling point, weights = varIdent(form=~1|sampling point))

To account for the temporal autocorrelation, for each sampling point a “within group” autoregression structure of order one was added (Eq. 4), where “numdate” is the number of days since the first sampling date.

(4) GLS (concentration ~ sampling point, weights = varIdent(form=~1|sampling point), cor = corAR1(form=~numdate|sampling point))

For each step, the Akaike information criterion (AIC) was used to decide whether the more complex model was better. In all cases, the model including the temporal autocorrelation structure provided the best fit. To assess whether the fixed effect “sampling point” had a significant impact, the full model (Eq. 4) was tested against a zero model (Eq. 5), where the fixed effect “sampling point” was replaced by 1, *i.e.* the mean of all data.

(5) GLS (concentration ~ 1, weights = varIdent(form=~1|sampling point), cor = corAR1(form=~numdate|sampling point))

Models (4) and (5) were compared using the AIC. If the model including the fixed effect “sampling point” has a significantly lower AIC, this fixed effect will have a significant impact. In these cases, the post-hoc Tukey test implemented for generalised linear models in the R package multcomp (Hothorn *et al.*, 2008) was applied to evaluate which sampling points were significantly different from one other.

Additionally, Spearman rank correlation was used to find the most important drivers of the measured concentrations as well as the relationships between the concentrations of different solutes.

## 3.4 Results

### 3.4.1 Meteorological conditions, discharge and water balances

Annual air temperatures were lower than the long-term average of 9.4 °C (Table 3-1). Whereas in the winter of 2011/12 only two weeks in February had extremely low air temperatures, mean air temperature fell below 0 °C more often in 2012/13 (Fig. S3-1). The annual precipitation sums (Table 3-1) were higher than the long-term average of 843 mm. During both periods (14.06.2011-13.06.2012 and 14.06.2012-13.06.2013), most of the precipitation fell in the summer, while the winter seasons differed: Whereas in 2011 more than 200 mm of precipitation was measured in December only, the winter of 2012/13 was comparably dry (158 mm). Most of the precipitation fell as rain and thus the maximum snow depth at the nearby climate station at Steinau was 9 cm and snow cover lasted 39 days over the whole study period.

**Table 3- 1:** Mean annual air temperature (T), precipitation (P), grass reference evapotranspiration ($ET_0$), water table depth (WTD) and discharge (Q) at the sampling points for the periods 2011/12 (14.06.11-13.06.12) and 2012/13 (14.06.12-13.06.13). $WB_{error}$ (water balance error) is defined as the ratio between ET + Q and P (positive values represent a surplus in P and vice versa).

| **Period** | **T** | **P** | **$ET_0$** | **WTD** | | **Q** | **$WB_{error}$** | **Q** | **$WB_{error}$** | **Q** | **$WB_{error}$** | **Q** | **$WB_{error}$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Grassland | Re-wetted polder | Collector ditch | | Drainage ditch | | Drainage pipe | | Re-wetted polder | |
| | °C | —— mm —— | | ———— m ———— | | mm | % | mm | % | mm | % | mm | % |
| 2011/12 | 9.1 | 940 | 541 | -0.48 | -0.01 | 405 | -1 | 345 | 6 | 335 | 7 | 394 | 1 |
| 2012/13 | 8.1 | 889 | 539 | -0.45 | 0.00 | 414 | -7 | 392 | -5 | 180 | 20 | 263 | 10 |

Discharge ranged from 180 to 414 mm yr$^{-1}$ (Table 3-1), corresponding to 20-47% of the annual precipitation during our study period. At all sampling points most of the discharge occurred in colder periods of the year. Low or no discharge was measured during the summer as high evapotranspiration rates exceeded precipitation.

During 2011/12 comparable discharge sums were measured at all sampling points (Table 3-1). This suggests that differences in land use (*DP*, *DD*, *CD* vs. *RW*) do not strongly impact the water balance components on an annual basis despite different vegetation cover, plant species composition and runoff generation processes – discharge at *RW* (polder) only occurred after a threshold value was exceeded. The water budgets at all sampling points were balanced during the first period despite the reference grass evapotranspiration ($ET_0$) being more appropriate for the drained grassland site than for the re-wetted site.

Despite lower precipitation during the second period (Table 3-1), discharge was higher in the ditches *DD* and *CD*. This may have been caused by drainage ditch maintenance in November 2012 reducing the water level by about 20 cm and thus increasing the gradient towards the ditches. As expected, discharge at *RW* was lower due to less precipitation during the second period. The reason for the lower discharge sum at *DP* was not entirely clear.

### 3.4.2 Solute concentrations

Concentrations of the C and N fractions as well as basic water properties are given in Table 3-2. At *DP* and *RW* DOC concentrations exceeded those of POC by a factor of 11 and 5 respectively. DOC was thus the most important C component irrespective of land use. Likewise, at all sampling points DON contributed most to TDN, followed by $NH_4$-N. $NO_3$-N was only found in the grassland ditches.

At the grassland, all C and N concentrations apart from $NO_3$-N decreased in the order of *DP* > *DD* > *CD* with increasing scale. This decrease ranged from 14% (DOC) to 33% ($NH_4$-N), but was not statistically significant ($p > 0.05$) due to the high temporal variability at all sampling points. Compared to *DP*, concentrations of $NO_3$-N and $SO_4^{2-}$ were two to three times higher ($p < 0.05$) in the ditch network, but in the case of $NO_3$-N were at a very low level (< 0.5 mg l$^{-1}$).

**Table 3- 2:** Concentrations of DOC, POC, TDN, DON, $NH_4$-N, $NO_3$-N, $SO_4^{2-}$ and ratios of DOC to DON as well as pH value and electrical conductivity (EC) at the sampling points DP (drainage pipe), DD (drainage ditch), CD (collector ditch) and RW (re-wetted area). Values represent means ± standard deviation; n.d. = not determined. Different letters indicate significant differences between the sampling points ($p < 0.05$).

| **Sampling point** | **DOC** | **POC** | **TDN** | **DON** | **$NH_4$ -N** | **$NO_3$ -N** | **$SO_4^{2-}$** | **DOC/DON** | **pH** | **EC** |
|---|---|---|---|---|---|---|---|---|---|---|
| | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | mg $l^{-1}$ | - | - | µS $cm^{-1}$ |
| *DP* | $164.7^{b}$ ± 33.9 | $14.7^{a}$ ± 43.8 | $9.6^{b}$ ± 1.7 | $7.1^{b}$ ± 1.6 | $2.4^{b}$ ± 0.8 | $0.1^{ab}$ ± 0.2 | $5.3^{b}$ ± 3.1 | $23.4^{a}$ ± 2.1 | $4.4^{b}$ ± 0.1 | $190^{b}$ ± 23 |
| *DD* | $155.6^{b}$ ± 30.3 | n.d. | $9.2^{b}$ ± 2.3 | $6.6^{b}$ ± 1.2 | $2.4^{b}$ ± 1.7 | $0.3^{bc}$ ± 0.6 | $9.8^{c}$ ± 3.8 | $23.9^{a}$ ± 2.4 | $4.7^{c}$ ± 0.2 | $205^{b}$ ± 40 |
| *CD* | $142.4^{b}$ ± 27.9 | n.d. | $7.7^{b}$ ± 1.6 | $5.8^{b}$ ± 1.2 | $1.6^{ab}$ ± 0.8 | $0.3^{c}$ ± 0.5 | $10.0^{c}$ ± 4.5 | $24.7^{a}$ ± 2.6 | $4.8^{d}$ ± 0.2 | $187^{b}$ ± 26 |
| *RW* | $39.2^{a}$ ± 11.5 | $7.4^{a}$ ± 17.2 | $1.7^{a}$ ± 0.8 | $1.3^{a}$ ± 0.5 | $0.4^{a}$ ± 0.4 | $< 0.01^{a}$ | $0.5^{a}$ ± 0.4 | $32.0^{b}$ ± 5.2 | $4.0^{a}$ ± 0.1 | $74^{a}$ ± 12 |

The DOC to DON ratios showed no significant difference despite a slight increase with increasing scale (< 10% increase from *DP* to *CD*). While there was no difference in EC, pH values clearly increased with increasing scale.

The re-wetted area (*RW*) showed significantly ($p < 0.05$) lower concentrations of all measured solutes than the grassland sampling points (Table 3-2). Additionally, the higher DOC to DON ratios at *RW* compared to the drained grassland suggested differences in the degradation state of dissolved organic matter (DOM).

### 3.4.3 Temporal patterns of solute concentrations

At the grassland (*DP*, *DD*, *CD*) temporal patterns depended on the individual solute and not on the sampling points/scale. DOC concentrations were highest in late summer/early autumn and lowest during cold periods after heavy precipitation prior to sampling (Fig. 3-2). No general interactions between DOC and potential drivers valid for the whole study period could be found at any of the sampling points (Fig. 3-3). DOC concentration peaks in late summer/early autumn suggested interactions of temperature and hydrology. Figure 3-4a and b show the relationship between DOC and discharge separated by the long-term mean average temperature (> 9.4 °C). An increase in discharge was associated with an increase in DOC concentrations during warm

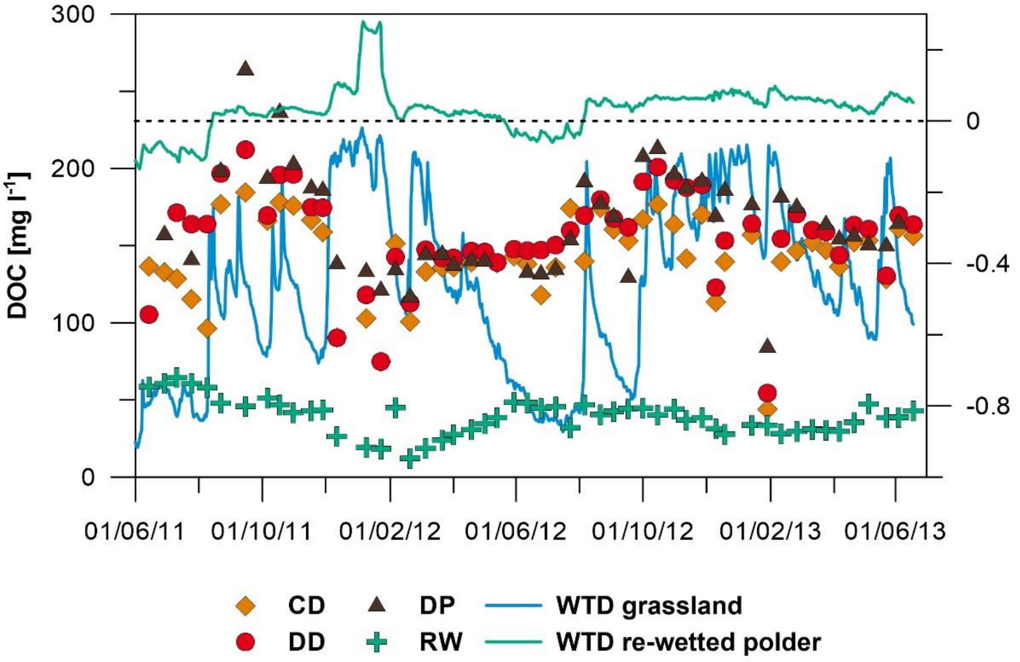

**Fig. 3- 2:** DOC concentrations at the sampling points and water table depths in the grassland and re-wetted area from June 2011 to June 2013. CD = collector ditch, DD = drainage ditch, DP = drainage pipe, and RW = re-wetted polder.

periods (Fig. 3-4a) and a decrease during cold periods (Fig. 3-4b). Thus, the lowest DOC concentrations coincided with maximum discharge values, suggesting a dilution of DOC. As in the case of DOC, the highest $SO_4^{2-}$ concentrations were found after the initial flush in autumn (Fig. S3-2).

At the grassland, DON showed the same pattern as DOC with highest values in late summer/autumn and lowest in winter (Fig. 3-5a). A strong correlation between DOC and DON ($0.87 \geq r \geq 0.79$) suggested close interlinkage and similar interactions of the factors temperature and discharge as typical for peatland catchments (Edokpa *et al.*, 2016). At *DP* and *DD* concentrations of $NH_4$-N were negatively correlated with hydrological parameters (*e.g.* WTD, Q; Fig. 3-3b-c).

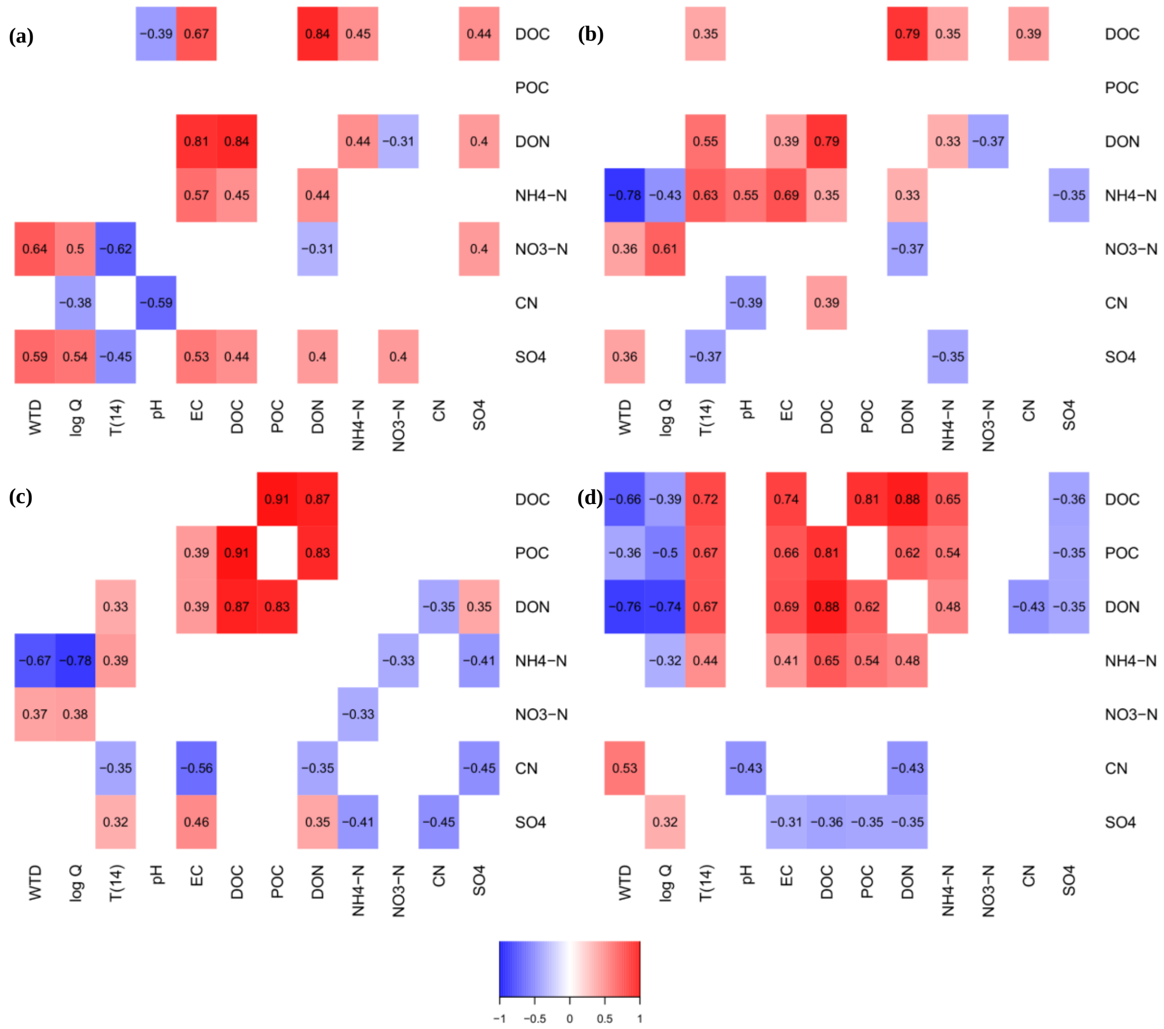

**Fig. 3- 3:** Spearman rank correlation matrix of weather data, solution properties and concentration of carbon and nitrogen species at (a) the collector ditch (CD), (b) the drainage ditch (DD), (c) the drainage pipe (DP) and (d) the re-wetted polder (RW). Only correlation coefficients > 0.3 are plotted, red colours represent positive correlations and blue colours negative correlations.

These relationships weakened on the largest scale (Fig. 3-3a) due to lower $NH_4$-N concentrations at *CD* during low flow conditions (Fig. 3-4c). In contrast, $NO_3$-N was found at *DD* and *CD* mainly during cold periods, and concentrations at these sampling points were positively correlated with discharge (Fig. 3-3a-b, Fig. 3-4d). Temporal dynamics of $NH_4$-N and $NO_3$-N concentrations are shown in the Fig. S3-3 and Fig. S3-4.

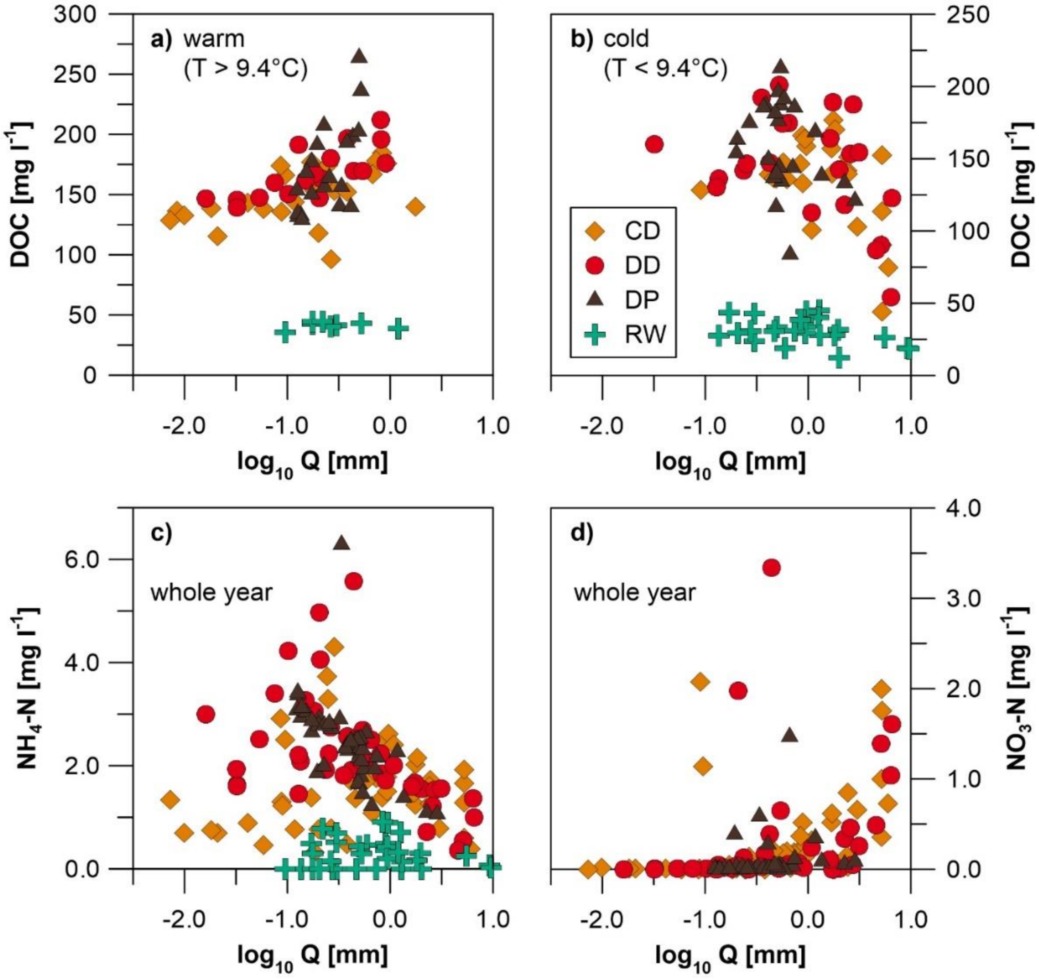

**Fig. 3- 4:** Relationship between $\log_{10}$ discharge (Q) and DOC separated by long-term mean annual air temperature (9.4 °C): (a) warm periods and (b) cold periods and between $\log_{10}$(Q) and (c) $NH_4$-N and (d) $NO_3$-N. CD = collector ditch, DD = drainage ditch, DP = drainage pipe and RW = re-wetted polder.

At the re-wetted area (*RW*), the concentration patterns of all compounds as well as EC were strongly and positively correlated to one other, as visualised by the red colour block in Fig. 3-3d. Overall, the temporal dynamics of solutes at *RW* were mainly driven by temperature (with a lag of 14 days) and WTD (Fig. 3-3d). In contrast to the grassland, highest DOC and DON concentrations were found during early summer (Fig. 3-2, Fig. 3-5a). The lowest concentrations were also measured after heavily rainfall, especially in winter 2011/12 (Fig. 3-2). Temporal patterns of $NH_4$-N differed between the years. Whereas maximum $NH_4$-N concentrations in

2011 occurred in the summer, in 2012 they were measured at the beginning and end of the growing season, while in between concentrations were below detection limit (shown in Fig. S3-3). Additionally, DOC to DON ratios showed a seasonal pattern, with the highest values measured in the summer and the lowest in late winter/early spring (Fig. 3-5b).

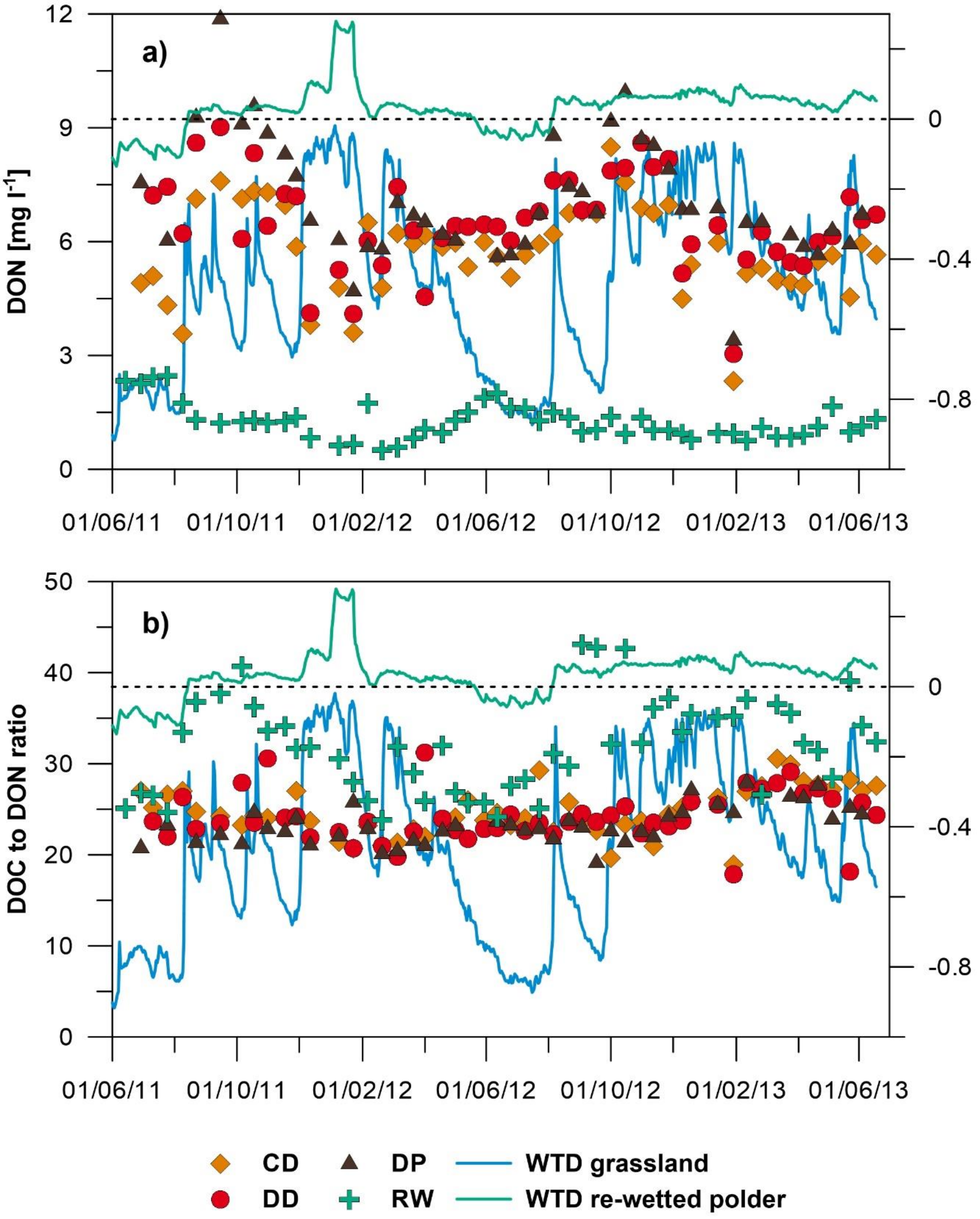

**Fig. 3- 5:** Concentrations of (a) DON and (b) DOC to DON ratios at the sampling points as well as water table depths in the grassland and re-wetted area from June 2011 to June 2013. CD = collector ditch, DD = drainage ditch, DP = drainage pipe and RW = re-wetted polder.

### 3.4.4 Losses of dissolved solutes

DOC losses from the grassland (*DP*, *DD*, and *CD*) ranged from 237 to 538 kg ha$^{-1}$ yr$^{-1}$ (Table 3-3) and thus showed considerable differences between both individual years and scales. Overall, DOC accounted for 96-99% of TOC losses from the drainage pipe (*DP)* and was thus the dominant organic carbon species. Losses from *DP* were lower than from *DD* and *CD* (Table 3-3), and the spatial variability was driven more by differences in discharge (Table 3-1) than by differences in DOC concentrations (Table 3-2).

**Table 3- 3:** Annual losses of total dissolved carbon (TOC), dissolved organic carbon (DOC), particular organic carbon (POC), dissolved organic nitrogen (DON), ammonium ($NH_4$-N), nitrate ($NO_3$-N) and total dissolved nitrogen (TDN) at the sampling points DP (drainage pipe), DD (drainage ditch), CD (collector ditch) and RW (re-wetted area) for the periods 2011/12 (14.06.11-13.06.12) and 2012/13 (14.06.12-13.06.13). n.d. = not determined.

| **Sampling point** | **Period** | **TOC** | **DOC** | **POC** | **TDN** | **DON** | **$NH_4$-N** | **$NO_3$-N** |
|---|---|---|---|---|---|---|---|---|
| | | **kg ha$^{-1}$ yr$^{-1}$** | | | | | | |
| *DP* | 2011/12 | 399 | 396 | 3 | 22.5 | 17.5 | 4.8 | 0.2 |
| | 2012/13 | 246 | 237 | 9 | 13.4 | 9.8 | 3.3 | 0.3 |
| *DD* | 2011/12 | n.d. | 420 | n.d. | 24.9 | 18.6 | 4.2 | 2.1 |
| | 2012/13 | n.d. | 517 | n.d. | 30.5 | 21.8 | 5.8 | 2.9 |
| *CD* | 2011/12 | n.d. | 462 | n.d. | 28.4 | 20.2 | 4.6 | 2.8 |
| | 2012/13 | n.d. | 538 | n.d. | 32.0 | 21.5 | 6.8 | 2.8 |
| *RW* | 2011/12 | 168 | 146 | 22 | 5.7 | 5.0 | 0.6 | 0.1 |
| | 2012/13 | 103 | 92 | 11 | 3.6 | 2.6 | 1.0 | < 0.1 |

DOC losses from the re-wetted polder (*RW*) for 2011/13 and 2012/13 were 146 and 92 kg ha$^{-1}$ yr$^{-1}$ (Table 3-3). POC export from this site accounted for just 22 and 11 kg ha$^{-1}$ yr$^{-1}$ or 11 and 13% of TOC losses respectively. Overall, DOC losses from the re-wetted polder were 61-83% lower than from the drained site.

TDN losses from the grassland ranged from 13.1 to 32.0 kg ha$^{-1}$ yr$^{-1}$ (Table 3-3). DON was the most dominant N fraction and accounted for 71-78% of total N losses, which is even higher than the value of 54% reported by Edokpa *et al.* (2016) for a disturbed peatland catchment. Next to DON, $NH_4$-N was the most abundant inorganic N compound (18-25%). The importance of $NO_3$-N to overall N losses increased with increasing catchment area, ranging from < 3% at *DP* and 10% at *CD*, which was caused by increased $NO_3$-N concentrations, especially during periods with high discharge (Fig. 3-4d).

TDN losses from *RW* ranged from 3.6 to 5.7 kg $ha^{-1}$ $yr^{-1}$ (Table 3-3). As in the case of the drained grassland, DON contributed most to TDN losses (72-87%), followed by $NH_4$-N (25-12%). Under acidic and permanently waterlogged conditions at *RW*, $NO_3$-N losses were negligible (< 2% of TDN). As in the case of DOC, N losses were 73-89% (TDN), 71-88% (DON) and 70-88% ($NH_4$-N) lower than at the grassland.

### 3.4.5 Contribution of dissolved C and N losses to overall C and N balance

Figure 3-6a shows the estimates of the average net ecosystem carbon balance (NECB). GHG measurements showed that intensive grassland is a strong source of carbon (Tiemeyer *et al.*, 2016). The high C losses were dominated by high $CO_2$ emissions due to peat mineralisation (NEE). Furthermore, biomass harvest contributed considerably to the NECB. TOC (DOC+POC) losses accounted for just 11% of the NEE or 8% of the NECB.

In contrast to the grassland, the re-wetted former peat extraction site is a carbon sink. NEE was the largest term in the C balance. The net C uptake was also visible in the newly formed upper peat layer in this area, which has reached a thickness of up to 15 cm after 10 years of re-wetting. After $CH_4$-C, TOC was the second largest loss term, but TOC losses counterbalanced just 6% of the C uptake by NEE.

Figure 3-6b shows the estimates of the average net ecosystem nitrogen balance (NENB). The highest measured N fluxes resulted from management activities. Beyond these fluxes, water-borne N losses represented the second largest N flux. Without accounting for N release during mineralisation, the N balance of the drained grassland is, on average, near zero, but highly variable. The net N release ($N_{NEE}$) estimated from the NEE was about 200 kg $ha^{-1}$ $yr^{-1}$. Thus, on average 193 kg N $ha^{-1}$ $yr^{-1}$ released during mineralisation of the peat was still unaccounted for in the N budget.

At the re-wetted area without management activities, waterborne N losses (primarily as DON) were the largest measured N fluxes. Under the assumption of 24 kg ha$^{-1}$ yr$^{-1}$ N deposition and an N “demand” of -50.4 kg ha$^{-1}$ yr$^{-1}$ ($N_{NEE}$) calculated from the NEE, there is a gap of -31 kg ha$^{-1}$ yr$^{-1}$ in the N balance.

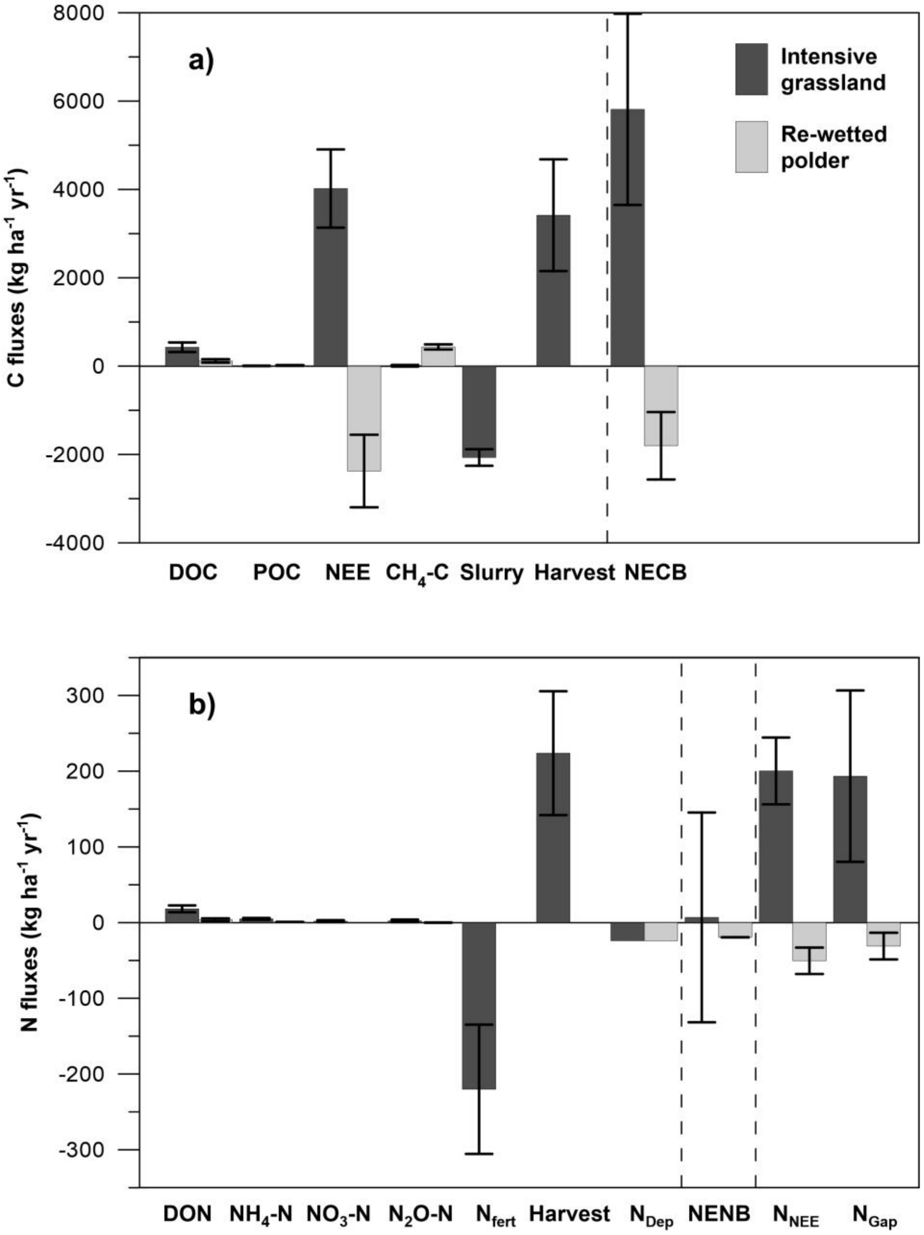

**Fig. 3- 6:** Carbon and nitrogen balances of the intensive grassland and the re-wetted polder: a) Carbon: dissolved organic carbon (DOC), particulate organic carbon (POC), net ecosystem exchange (NEE), methane ($CH_4$-C), carbon import via slurry application (Slurry), carbon export via harvest and net ecosystem carbon balance (NECB), b) nitrogen: dissolved organic nitrogen (DON), ammonium ($NH_4$-N), nitrate ($NO_3$-N), nitrous oxide ($N_2O$-N), nitrogen fertilisation ($N_{fert}$), nitrogen export via harvest, wet and dry deposition ($N_{Dep}$), net ecosystem nitrogen balance (NENB), estimated nitrogen release or uptake ($N_{NEE}$) and differences between NENB and $N_{NEE}$ ($N_{Gap}$).

## 3.5 Discussion

### 3.5.1 Scale effect on C and N concentrations

Under average discharge velocities, the mean residence time between *DP* and *CD* was 30 minutes (distance ~30 m). The residence time of water from the drainage pipe furthest (> 700 m) from the sampling point *CD* was, on average, 12 hours. During this initial stage of export, no significant drop in DOC, DON or $NH_4$-N concentrations could be found, although the average concentrations at *CD* were 14% (DOC), 18% (DON) and 33% ($NH_4$-N) lower than at *DP*. This contrasts with findings by Daniels *et al.* (2012) who measured a much stronger (> 50%) decline in DOC and $NH_4$-N concentrations during the first 200 m in a stream. Similarly, Worrall *et al.* (2006) found that within a distance of 1 km, 32% of DOC released from peat was removed mainly due to mineralisation, but also due to mixing with water from other sources (Dawson *et al.*, 2004). However, an average residence time of 12 hours is fairly short for intense in-stream processing since Kalbitz *et al.* (2003) found just 10% of peatland DOC to be mineralised, even after 90 days of incubation.

Ammonium is the dominant form of inorganic nitrogen under acidic conditions. Furthermore, the nitrification potential of $NH_4$-N seems to be rather small. This was supported by only a small increase in $NO_3$-N with increasing scale. During low flow conditions in the summer and thus higher residence time in the drainage network, the differences in $NH_4$-N concentrations between sampling points increased (Fig. 3-4c, Fig. S3-2). Enhanced plant growth in the summer months at *CD* may have led to this finding, especially assuming that the reduction in DON concentrations was due to mineralisation.

Overall, our data suggest that during the initial stage of export DOC and DON were less readily mineralised or photo-oxidised than was found in the studies of Daniels at al. (2012) and Worrall *et al.* (2006). With increasing residence time and pH values further downstream, more DOC and DON may be mineralised and, in the case of $NH_4$-N, nitrified or taken up by plants.

In contrast to DOC, DON and $NH_4$-N, $SO_4^{2-}$ concentrations increased with increasing scale. This suggests a rapid oxidation of reduced sulphur compounds due to increasing oxygen availability in the ditches. Under aerobic conditions and pH values > 4, mineral sulphur is generally present as $SO_4^{2-}$ (Reddy & DeLaune, 2008). The pH value significantly increased from *DP* to *CD*, which may suggest a loss of $CO_2$ due to evasion as Frank *et al.* (2014) report a supersaturation of the soil solution with $CO_2$ at the same site.

At our site, all grassland sampling points had comparable concentrations, thus allowing a similar interpretation. Small ditches could be sampled to investigate concentration dynamics without the risk of fast in-stream processing altering solute concentrations, their pattern and therefore their interpretation.

### 3.5.2 Land use effect on water quality

Due to the vicinity of the chosen sites (Fig. 3-1), differences in water quality were only driven by differences in past and present land use and thus by differences in water table, soil properties and plant species composition. Land use showed a significant impact on all measured concentrations and parameters. Concentrations at the grassland were generally an order of magnitude higher than at the re-wetted polder (Table 3-2) and emphasised the risk that deep drainage of bogs combined with intensive agriculture poses for water quality. DOC concentrations measured at the grassland (154 ± 11 mg $l^{-1}$) were very high compared to values reported in literature so far for drained temperate peatlands (37.5-108 mg $l^{-1}$; IPCC, 2014). In comparison to other sites, higher temperatures and lower precipitation have probably led to both an enhanced formation of DOC and an accumulation in pore water due to longer residence times. Overall average DON concentrations of 6.5 mg $l^{-1}$ are in the range of or higher than those in nutrient-rich fen used for intensive agriculture in eastern Germany (2.5-8.5 mg $l^{-1}$; Kalbitz *et al.*, 2002; Tiemeyer & Kahle, 2014), whereas there is an absence of studies on bog sites with comparable land use intensity.

The much lower C and N concentrations at the re-wetted polder showed the benefit on downstream water quality of the establishment of permanently wet conditions as well as re-colonisation with typical bog vegetation. The peat formation clearly led to DOC, DON and $NH_4$-N concentrations typical for temperate peatlands (Adamson *et al.*, 1998; IPCC, 2014).

### 3.5.3 Drivers of solute concentrations

The effect of environmental drivers differed between the grassland and the re-wetted polder (Fig. 3-3, Fig. 3-4). Organic compounds (DOC and DON) in the grassland’s drainage network followed a pattern often described for mineral soils, where DOM accumulates during warmer and drier conditions in the unsaturated zone and is flushed by increasing discharge in late summer/early autumn (Kalbitz *et al.*, 2000). During colder periods, lower DOM production and higher discharge may have led to a dilution of DOM and hampered a clear correlation between DOM and discharge over the whole study period.

DOC to DON ratios remained more or less constant throughout the year. Average values of around 24 suggested that the upper degraded peat layer (C to N ratio: 21) was the main source over the whole year. This is supported by the findings of Frank *et al.* (2014) who show that DOM properties of the soil solution at the grassland the hydrological pathways remain fairly constant over the year. Therefore, even during low flow conditions, DOM produced in the degraded peat layer was exported. Due to the different hydrological dynamics, results from other hydrological and topographical settings cannot simply be transferred to flat sites with pipe drainage.

Inorganic N species at the grassland were directly related to hydrological parameters (WTD, discharge). Opposite patterns were found for $NH_4$-N and $NO_3$-N (Fig. 3-4c and d). The highest $NH_4$-N concentrations were measured during warm periods with deep water tables and low flows as a result of increased N mineralisation potential under aerobic conditions. Additionally, Frank *et al.* (2014) show that at the intensive grassland $NH_4$-N concentrations increase with depth as $NH_4$-N accumulates below rooting depth. Thus, during low flow conditions, water from deeper peat layers enriched in $NH_4$-N contributes most to the discharge. While nitrification is assumed to be low due to low pH values, $NO_3$-N nevertheless present in the unsaturated peat layers is fully denitrified in the saturated zone (Frank *et al.*, 2014). Thus, only in winter when high flow conditions and low temperatures hamper denitrification and plant uptake can a fast export of $NO_3$-N to the drainage network occur.

At the re-wetted area the correlation between concentrations and possible drivers was less complex than at the grassland site. The peat layer’s ability to float dampened water level fluctuations and ensured continuous water saturation. Generally, C and N compounds as well as DOM quality were either dependent on the air temperature of the preceding 14 days (T14) or on WTD (Fig. 3-3d). This suggests that two main processes were responsible for the temporal pattern. Firstly, microbial activity and therefore production of DOC, DON or $NH_4$-N is related to temperature (*e.g.* Gödde *et al.*, 1996). Thus, during warmer summer periods, the production and release of C and N compounds increases. Secondly, the correlation with WTD also suggests either dilution or accumulation. This could partly explain different decreases in DOC and DON concentration during the winter. A higher rise in the water table during the winter of 2011/12 (maximum water level: 0.28 m above surface) compared to the winter of 2012/13 (maximum water level: 0.10 m above surface) may therefore have led to a stronger dilution during the winter of 2011/12. However, the co-correlation between temperature and WTD hampered a clear differentiation between the effects of these two factors.

In the case of $NH_4$-N, uptake by plants also has to be taken into account. Especially during the summer of 2012, $NH_4$-N concentrations near zero suggested a higher N uptake by plants, which might balance a higher release due to conditions more suitable for $NH_4$-N formation.

The DOC to DON ratio at the outlet of the re-wetted area showed a clear seasonal pattern (Fig. 3-5b) and was positively correlated with WTD. One reason for this might be a higher residence time at lower WTD and thus a higher contribution of DOC from deeper and more degraded peat by diffusion. Direct baseflow did not occur because runoff formation is controlled by the height of the outlet tube. However, Frank *et al.* (2014) could not find depth-dependent DOC to DON ratios in the soil solution. Thus, the reason for these temporal dynamics is not entirely clear, but might be caused by the spatial heterogeneity within the polder.

### 3.5.4 Interactions of DOC with $SO_4^{2-}$, pH and EC

At the grassland, no general interaction between sulphate, pH, EC and DOC could be found (Fig. 3-3a-c). This contrasts with studies by Clark *et al.* (2005, 2012) who found that changes in $SO_4^{2-}$ concentrations influence EC and pH values, which in turn affect the solubility of DOC in the soil solution and the concentration level of DOC in surface water. In complete contrast, the concurrence of the highest DOC and sulphate concentrations at *CD* and *DD*, and at *CD* even a weak positive correlation, suggested a similar response by DOC and $SO_4^{2-}$ to warm and dry periods, favouring both DOC production and sulphate formation. Thus, hydrology seemed to be the more important driver for DOC concentrations, since $SO_4^{2-}$ and DOC concentrations peaked at high discharge following deep water tables in the summer. A lack of correlation between $SO_4^{2-}$ and pH and only a weak correlation between $SO_4^{2-}$ and EC suggested that high $SO_4^{2-}$ concentrations did not determine either pH or EC-dependent DOC release, as has been found in more natural and wetter peatlands (Clark *et al.*, 2005; Evans *et al.*, 2012). In our case, a lack of acidification during periods with the highest $SO_4^{2-}$ concentrations and suppression due to increased ionic strength might be outweighed by the increased DOC production under optimal conditions for peat degradation. When comparing the sampling points, even $SO_4^{2-}$ concentrations that were twice as high (*DD/CD* vs. *DP*) had no significant impact on DOC concentrations, as they might have been counteracted by slightly rising pH values probably caused by evasion of $CO_2$. Since the re-wetted area stayed water-saturated for nearly the entire study period, an interaction between changes in sulphate concentrations associated with changing pH values and EC due to water table drawdown was not detectable.

### 3.5.5 Losses of waterborne C and N

Waterborne C and N losses depend both on concentrations and on the amount of discharge. Discharge values at our sites were intermediate compared to blanket bogs (> 500 mm; Billett *et al.*, 2004; Clark *et al.*, 2007) or German fens (< 200 mm; Tiemeyer & Kahle, 2014).

The high DOC losses from the grassland (237 to 538 kg $ha^{-1}$ $yr^{-1}$) were mainly a result of extraordinarily high DOC concentrations. Our results suggested that deeply drained Atlantic bogs in temperate central Europe used as intensive grassland may export by far more DOC than abandoned fens or those in agricultural use (50 to 189 kg $ha^{-1}$ $yr^{-1}$; Hendriks *et al.*, 2007; Tiemeyer & Kahle, 2014) and even drained ombrotrophic peatlands in the UK (186-384 kg $ha^{-1}$ $y^{-1}$; Dinsmore *et al.*, 2010; Rowson *et al.*, 2010). The IPCC (2014) reports an average offsite $CO_2$ EF of 310 kg $ha^{-1}$ $yr^{-1}$ for DOC losses from temperate peatlands. Multiplying our DOC losses by the factor of 0.9 (percentage of DOC that will ultimately be mineralised to $CO_2$ (IPCC, 2014)), the EF of our site was about 213 to 484 kg $ha^{-1}$ $yr^{-1}$ and thus at the upper end or above the values given by the IPCC (2014).

DOC losses from the re-wetted polder (92 and 146 kg $ha^{-1}$ $yr^{-1}$) were both in the range of values reported for natural and semi-natural peatlands (53-360 kg $ha^{-1}$ $yr^{-1}$) in the temperate zone (IPCC, 2014), but even lower than those estimated by the precipitation or temperature-based regressions (170-200 kg $ha^{-1}$ $yr^{-1}$) of Evans *et al.* (2015). The difference between DOC losses from the grassland and the re-wetted polder was driven in our case by lower DOC concentrations (Table 3-2) under permanently wet conditions at the re-wetting area and not by differences in discharge (Table 3-1), especially during 2011/12 when discharge values were nearly the same.

If we assume that the DOC losses at a natural site in the same bog complex equalled the losses at the re-wetted site – which is supported by similar vegetation and thus probably evapotranspiration characteristics as well as similar DOC concentrations in the pore water (Frank *et al.*, 2014) – than drainage would have increased the quasi-natural DOC losses by 265%. This is considerably higher than the estimate of 60% given by both the IPCC (2014) and Evans *et al.* (2015) for drained temperate peatlands, which might underestimate the effect of drainage and intensive agriculture.

POC losses from the drainage pipe (grassland) and at the outlet of the re-wetted polder were of minor importance. In peatlands with higher precipitation and a steeper slope, POC losses were found to be more important for total waterborne C fluxes (Dawson *et al.*, 2002), but erosion is very unlikely to occur at our flat and permanently vegetated site.

Despite already being very high, total C losses *via* the aquatic pathway may still have been underestimated since dissolved $CO_2$ and $CH_4$ are found to account for up to 26% of dissolved C in soil solution at the re-wetted and drained area (Frank *et al.*, 2014).

Studies on nitrogen losses from agriculturally used bogs are extremely rare in literature. Comparable TDN losses (21.7 kg $ha^{-1}$ $yr^{-1}$) have been reported for a boreal bog in agricultural use (Kløve *et al.*, 2010), but are the result of lower concentrations and higher discharge. TDN losses in our study were also comparable to a drained grassland on nutrient-rich organic soils in north-eastern Germany (31-41 kg $ha^{-1}$ $yr^{-1}$; Tiemeyer & Kahle, 2014), but their study area is characterised by lower discharge and higher concentrations of inorganic N species, especially $NO_3$-N. Eggelsmann (1990) reviewed the effect of land use on N losses (not accounting for DON) from drained German peatlands with hydrological conditions comparable to our site. Intensification of land use increases N losses from 5 kg $ha^{-1}$ $yr^{-1}$ (undrained bogs) to 40 kg $ha^{-1}$ $yr^{-1}$ (bogs under agriculture). As in our study, Kløve *et al.* (2010) found that DON is the dominant N species. DON losses from drained grassland (9.8-21.8 kg $ha^{-1}$ $yr^{-1}$) are considerably higher than those reported for a near-natural UK blanket peatland (~ 6 kg $ha^{-1}$ $yr^{-1}$; Adamson *et al.*, 1998), a disturbed peatland (~ 8 kg $ha^{-1}$ $yr^{-1}$; Edokpa *et al.*, 2016) or a German fen also used as grassland (~ 7 kg $ha^{-1}$ $yr^{-1}$; Tiemeyer & Kahle, 2014).

In comparison to nutrient-rich and drained fens in temperate Europe, where $NO_3$-N losses of up to 38 kg $ha^{-1}$ $yr^{-1}$ dominate the waterborne N losses (Van Beek *et al.*, 2007; Tiemeyer & Kahle, 2014), mineral N losses at our drained bog site were fairly low ($NH_4$-N + $NO_3$-N < 10 kg $ha^{-1}$ $yr^{-1}$; Table 3-3). However, assuming that most of the exported DON from our site will be mineralised further downstream, such high DON losses (18.2 kg $ha^{-1}$ $yr^{-1}$) will negatively affect downstream water bodies in a similar way to the direct release of mineral N as $NO_3$-N.

TDN losses from the re-wetted polder were lower than those measured by Adamson *et al.* (1998) in a semi-natural UK blanked peatland (6.7-7.5 kg $ha^{-1}$ $yr^{-1}$) and at the lower end of values (3-21 kg $ha^{-1}$ $yr^{-1}$) reported by Koerselman & Verhoeven (1992) for natural peatlands. The dominance of DON and the low mineral N export ($NH_4$-N + $NO_3$-N < 1 kg $ha^{-1}$ $yr^{-1}$; Table 3-3) agree with values (0.4 to 6.7 kg $ha^{-1}$ $yr^{-1}$) from previous studies on semi-natural and natural peatlands summarised in Koerselman & Verhoeven (1992).

As in the case of DOC, differences between the re-wetted polder and grassland are driven by changes in N mineralisation due to differences in WTD and land use intensity, not by differences in discharge.

### 3.5.6 Contribution of waterborne C and N losses to the C and N balances

Figure 3-6a shows the C balance, but does not account for waterborne gaseous losses and methane emissions from ditches. The proportions of the single C fluxes measured at the deeply drained grassland (Fig. 3-6a) clearly show that the C balance was mainly driven by intense peat mineralisation leading to high $CO_2$ emissions and by the harvest of previously photosynthetically-bound C. Since peat mineralisation and thus $CO_2$ release are strongly dependent on WTD (Leiber-Sauheitl *et al.*, 2014), drainage of our site caused higher $CO_2$ emissions (Beetz *et al.*, 2013) than at only shallow drained peatlands (Dinsmore *et al.*, 2010). Despite being some of the highest DOC losses reported so far, DOC and POC were of minor importance for the NECB.

Carbon fixation at the re-wetted area exceeded losses *via* $CH_4$-C and TOC. Thus, the NECB clearly demonstrated successful re-establishment of C accumulation. This was mainly achieved by permanently wet conditions lowering the mineralisation potential and enabling *Sphagnum* growth. NEE at *RW* was about ten times higher than that reported for nutrient poor re-wetted temperate peatlands (-230 kg $ha^{-1}$ $yr^{-1}$, IPCC, 2014) and suggested that the site was still in succession and that NEE might decrease in the long run. The ratio of waterborne C losses to NEE was in a similar range as that at the grassland (6%), which agrees with a semi-natural grassland in the Netherlands also characterised by high $CO_2$ sequestration (NEE: -3110 kg $ha^{-1}$ $yr^{-1}$, Hendriks *et al.*, 2007). In contrast to these results, waterborne C losses from natural and semi-natural peatlands are often found to be a major component of the overall C balance (Nilsson *et al.*, 2008; Dinsmore *et al.*, 2010; Rowson *et al.*, 2010) and counterbalance 24% (Dinsmore *et al.*, 2010) or 36% (Worrall *et al.*, 2003) of NEE. This is mainly caused by lower NEE (-480 kg $ha^{-1}$ $yr^{-1}$ to -1360 kg $ha^{-1}$ $yr^{-1}$). Since DOC concentrations in the re-wetted area are already similar to a near-natural site in the bog complex (Frank *et al.*, 2014), it is unlikely that waterborne C losses will change greatly in future. Assuming a reduction of NEE to -230 kg $ha^{-1}$ $yr^{-1}$ in the long run, waterborne C losses from the re-wetted area may counterbalance up to approximately 50% of the NEE in future. Overall, the relative importance of waterborne C losses depends on NEE in many peatlands and seems to be higher for re-wetted or natural peatlands with a low NEE.

The drained grassland was a source of N as well (Fig. 3-6b). The NENB is dominated by management activities (harvest, fertilisation). Including the theoretical N release *via* peat mineralisation ($N_{NEE}$) left a gap of 193 kg N ha$^{-1}$ yr$^{-1}$. In our grassland, $NO_3$-N concentrations of > 30 mg l$^{-1}$ were measured in the soil solution after slurry application (Frank *et al.*, 2014). Therefore, we assume that the gap can be explained by denitrification, since up to 300 kg ha$^{-1}$ yr$^{-1}$ have been reported as potential denitrification rates in wetlands (Bowden, 1987) and peat soils have been found to have a higher denitrification capacity than mineral soils (Well *et al.*, 2005). Using $N_{NEE}$ as an equivalent to NEE, around 13% of the released N was exported as TDN, which is slightly higher than in the case of C.

Currently, the re-wetted area acts as an N sink (Fig. 3-6b). Waterborne N losses were the second largest N flux after atmospheric deposition, and the largest N export term. This underpins the importance of measuring aquatic N losses as thoroughly as possible when studying the N balance of (wet) peatlands. 10% of the nitrogen fixation estimated from the NEE ($N_{NEE}$) was lost as TDN. This fraction may increase with reduced NEE in future. Using a constant C to N ratio from the newly formed *Sphagnum* peat, up to -50 kg N ha$^{-1}$ yr$^{-1}$ ($N_{NEE}$) was needed to realise the measured NEE. Thus, an additional source of up to -31 kg N ha$^{-1}$ yr$^{-1}$ ($N_{Gap}$) was missing. N deposition rates of up to 43 kg N ha$^{-1}$ yr$^{-1}$ have been reported for a peatland in the Netherlands (Olde Venterink *et al.*, 2002), but the conditions are not fully comparable to our site. However, the vegetation at the re-wetted polder is still in succession. The high absolute values of NEE assumed for the re-wetted area may not be fully representative for our study period and may therefore account for the high $N_{Gap}$. A lower NEE during our study period would have led to a lower plant N demand for biomass production and would reduce the $N_{Gap}$. Alternatively, it has been shown that biological $N_2$ fixation by prokaryotes can take place in peatlands dominated by *Sphagnum* (Vile *et al.*, 2014). This process might serve as an additional source of N, especially during the earlier development stages of a peatland (Larmola *et al.*, 2014).

## 3.6 Conclusions

By conducting one of the first studies dealing with both waterborne C and N losses from temperate raised bogs under two important land use types (intensive grassland, re-wetting after peat extraction), we were able to show clearly that all measured solute concentrations were considerably higher in the grassland than in the re-wetted area. Since discharge in our study area was fairly independent of land use, each measure raising the groundwater table may help reduce DOC and N losses by lowering concentration levels.

We demonstrated that deeply drained bogs in temperate Europe used as intensive grassland lose up to 538 kg DOC $ha^{-1}$ annually or increase the quasi-natural values by more than 200%. Therefore, even recent reviews might underestimate the effects of drainage and intensive land use on DOC losses.

Our results also show the importance of DON losses for both land use types, for which data is presently missing (re-wetted bogs) or rare (grassland) in literature. If we assume a downstream mineralisation of 90% of DOC (IPCC, 2014), most of the DON will also be converted to $NH_4$-N or $NO_3$-N further downstream. Hence, we point out the importance of DON measurements at acidic bogs when investigating N losses to evaluate the full eutrophication potential of management decisions.

Even within one peatland complex, land use-specific hydrology clearly affected the temporal concentration patterns of the DOC and N fractions. Pond-like characteristics of the re-wetted peat extraction area resulted in a more straightforward relationship with the main factors of temperature and water table depth than at the pipe-drained grassland site. There, the interaction between these two drivers throughout the year caused an annual peak during rising water levels in the late summer.

High C sequestration at our re-wetted peat extraction site and high $CO_2$ emissions at our drained grassland site both resulted in just a ~ 8% contribution of DOC to the total C balance. At our re-wetted site, $CO_2$ uptake will probably decrease in future, resulting in a greater contribution of DOC to the overall C balance.

## 3.7 Acknowledgements

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## 3.9 Supplement

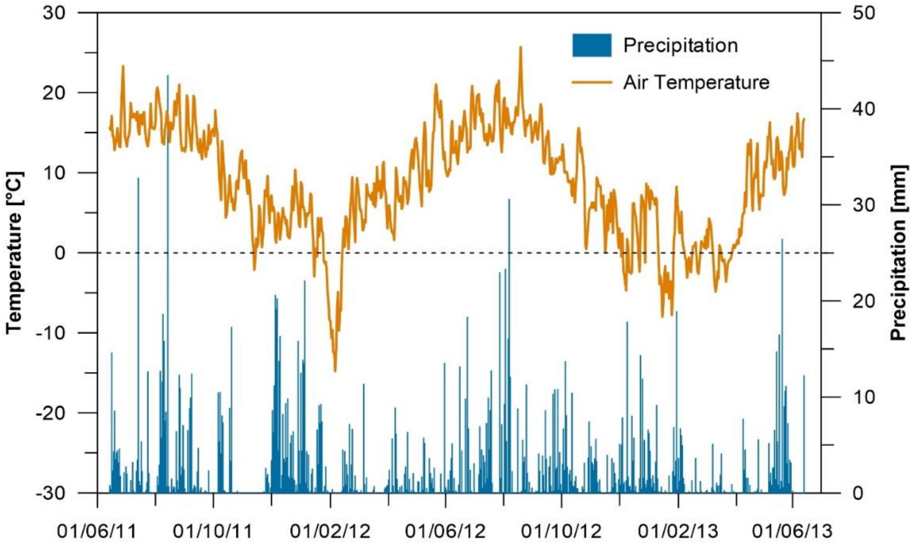

**Fig. S3- 1:** Figure of the daily precipitation sums and mean air temperature during the study period (June 2011 and June 2013).

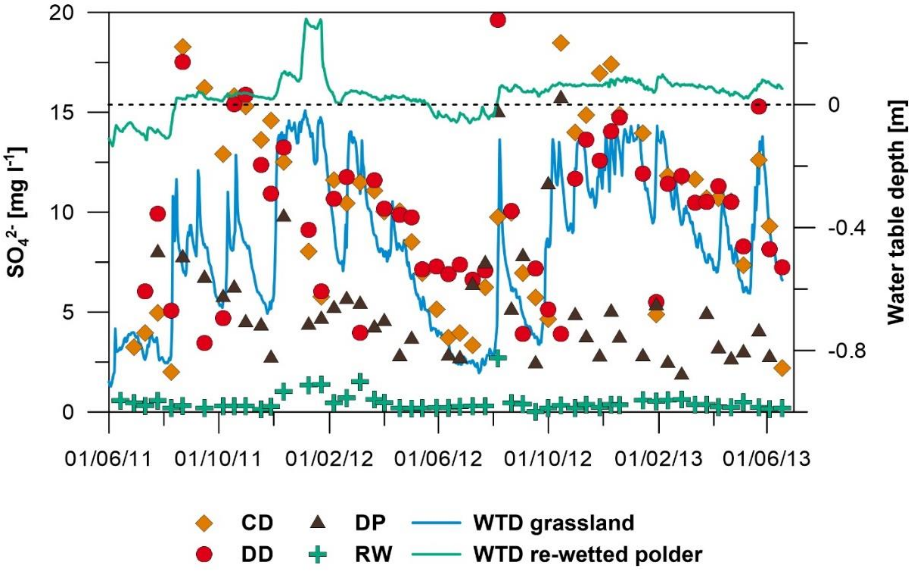

**Fig. S3- 2:** Figure of the temporal dynamics of sulphate ($SO_4^{2-}$) at the sampling points and water table depths in the grassland and re-wetted area from June 2011 to June 2013. CD = collector ditch, DD = drainage ditch, DP = drainage pipe and RW = re-wetted polder.

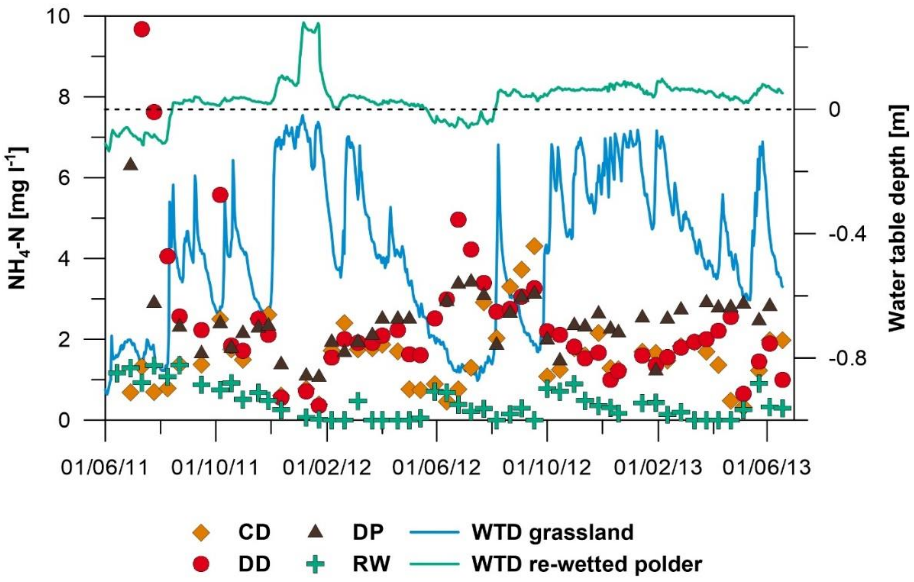

**Fig. S3- 3:** Figure of the temporal dynamics of ammonium-nitrogen ($NH_4$-N) at the sampling points and water table depths in the grassland and re-wetted area from June 2011 to June 2013. CD = collector ditch, DD = drainage ditch, DP = drainage pipe and RW = re-wetted polder.

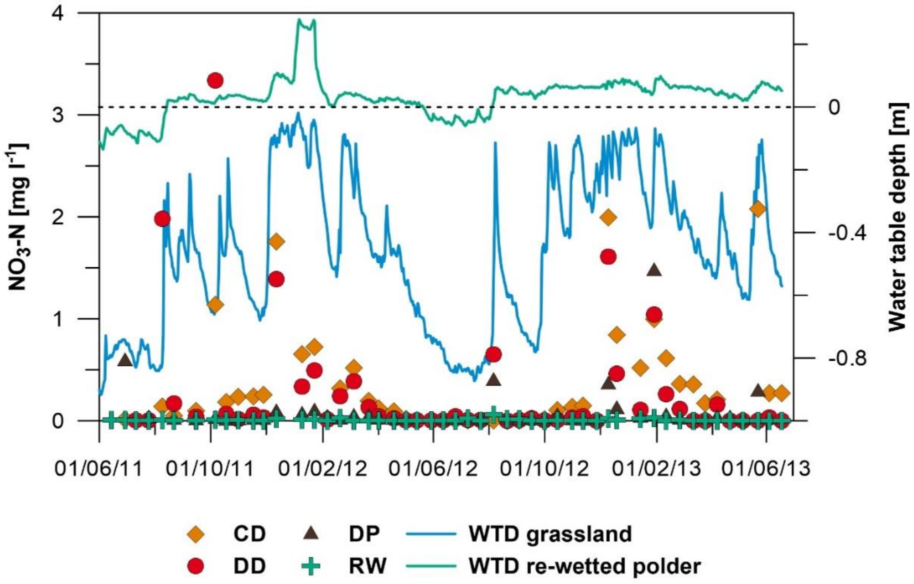

**Fig. S3- 4:** Figure of the temporal dynamics of nitrate-nitrogen ($NO_3$-N) at the sampling points and water table depths in the grassland and re-wetted area from June 2011 to June 2013. CD = collector ditch, DD = drainage ditch, DP = drainage pipe and RW = re-wetted polder.

# 4 Publication no. 3

## Past cultivation practice of a disturbed peatland determines quality and temporal dynamics but not mean concentration of dissolved organic carbon

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M. Bechtold: Hydrological modelling, comments to improve the manuscript

A. Lücke: $^{13}C$ and $^{15}N$ measurements, comments to improve the manuscript

R. Bol: $^{13}C$ and $^{15}N$ measurements, comments to improve the manuscript

## 4.1 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 also analysed for dissolved organic nitrogen (DON), $\delta^{13}C_{DOM}$ and $\delta^{15}N_{DOM}$.

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 kg DOC $ha^{-1}$ $yr^{-1}$.

## 4.2 Introduction

Soil solution and surface waters of peatlands are characterised by high concentrations of dissolved organic carbon (DOC) (Evans *et al.*, 2015). High DOC concentrations in rivers draining catchments with a high coverage of organic soils (Aitkenhead *et al.*, 1999) show that this carbon pool is mobile and significantly impacts aquatic systems. In natural peatlands, the export of 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 of these peatlands from a sink to a source or *vice versa*. Drainage usually increases DOC concentrations and losses (Evans *et al.*, 2015).

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 *et al.*, 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 & 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 & Geyer, 2002; Frank *et al.*, 2014) and an enrichment of $\delta^{13}C$ (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. For example, sulfate formed under dry conditions will alter pH and ionic strength, resulting in a suppression of DOC release (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 & Waldeck, 2015) 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 carbon dioxide ($CO_2$) 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 & Malcolm, 1988), while it does not reduce $CO_2$ emissions in the field (Leiber-Sauheitl *et al.*, 2014). However, 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.

## 4.3 Study site

The study was conducted on the “Grosses Moor” [Large Bog], a bog-fen complex covering 60 km² near Gifhorn (Germany; 52°34`N, 10° 39`E, see Fig. 4-1). Long-term mean annual temperature and precipitation were 9.6 °C and 656 mm (1982-2011). Peatland formation started in a Pleistocene depression approximately 8,000 years ago on gravelly, medium to coarse sand (Schneekloth & Schneider, 1971). The peat thickness reached 5 to 7 m in the centre of the bog.

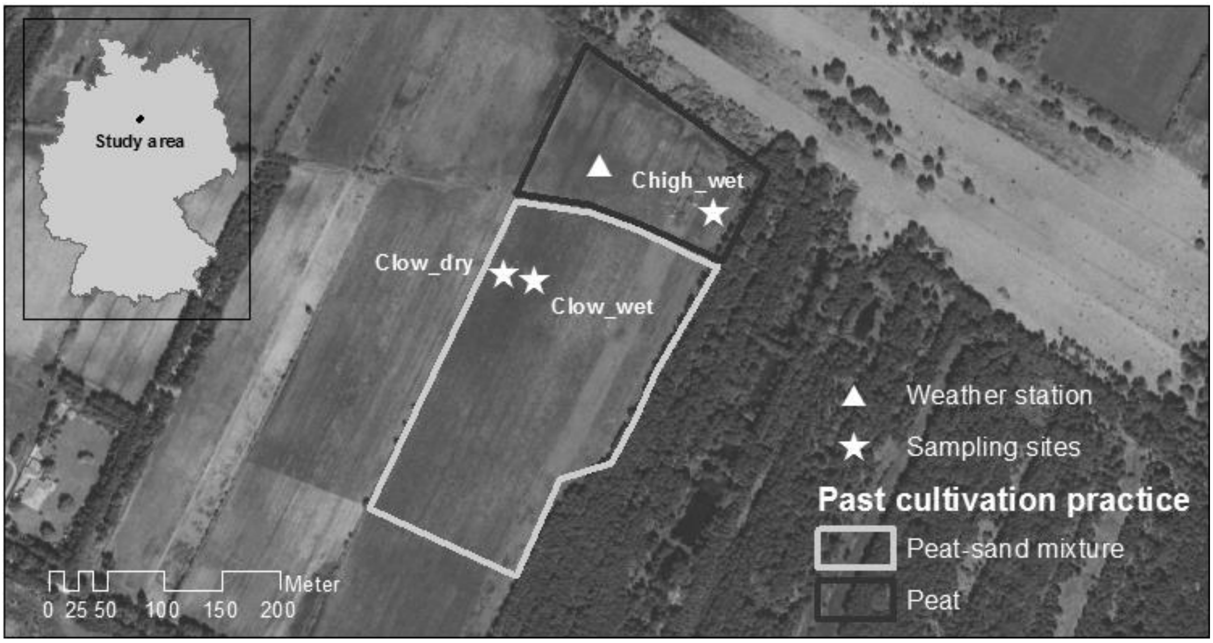

**Fig. 4- 1:** Map of the study area and sampling sites (aerial image: Federal Agency for Cartography and Geodesy).

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 & Schneider, 1971). Recent vegetation largely lacks original bog species and 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.

This study site (Fig. 4-1) is part of a nature conservation area which was established in 1984 and covers about 2,700 ha of the peatland. Since then, it has been managed as low-intensity grassland without fertilisation, and ditches have been partially closed to raise WTD. The study site is mulched in autumn and also grazed by sheep between one and 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 different cultivation practices after peat extraction. 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 deep ploughing. 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 $C_{low}$_dry and $C_{low}$_wet have a relatively low SOC content compared to $C_{high}$_wet while “dry” and “wet” refer to the mean annual water table depth (Table 4-1). Greenhouse gas fluxes were measured at directly adjacent plots (Leiber-Sauheitl *et al.*, 2014).

In the SOC-rich layer, C concentrations ranged from around 10% at sites with a peat-sand mixture as topsoil ($C_{low}$_dry and $C_{low}$_wet) to around 48% at the site with a residual peat profile ($C_{high}$_wet) (Table 4-1). Mean WTD ranged from -0.16 to -0.31 m below the surface (Table 4-2). Differences in peat properties and water table position are reflected by the vegetation composition (Table 4-2), which is characterised by a higher percentage of moss cover at $C_{high}$_wet compared to the grass-dominated sites $C_{low}$_dry and $C_{low}$_wet.

**Table 4- 1:** Soil properties of the sampling sites (Leiber-Sauheitl *et al.*, 2014, amended). Soil type according to IUSS Working Group WRB (2007), BD = bulk density, SOC = soil organic carbon, $N_t$ = total nitrogen, C:N = SOC to $N_t$ ratio, n.d. = not determined.

| **Depth (cm)** | **SOC (%)** | **$N_t$ (%)** | **C:N** | **pH** | **BD (g $cm^{-3}$)** | **SOC stock (kg $m^2$)** |
|---|---|---|---|---|---|---|
| *$C_{low}$_dry: Histic Gleysol* | | | | | | |
| 0-30 | 11.3 | 0.42 | 27 | 4.5 | 1.06 | 36 |
| > 30 | 0.6 | 0.02 | 24 | 4.7 | 1.65 | n.d. |
| *$C_{low}$_wet: Histic Gleysol* | | | | | | |
| 0-32 | 9.3 | 0.39 | 24 | 4.5 | 0.97 | 29 |
| > 32 | 0.4 | 0.02 | 21 | 4.7 | 1.91 | n.d. |
| *$C_{high}$_wet: Histic Gleysol* | | | | | | |
| 0-30 | 47.9 | 1.73 | 28 | 3.8 | 0.29 | 41 |
| 30-34 | 12.9 | 0.44 | 29 | 4.3 | 1.00 | 5 |
| > 34 | 2.7 | 0.12 | 23 | 4.6 | 1.75 | n.d. |

**Table 4- 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)** |
|---|---|---|---|
| *$C_{low}$_dry* | *Poa pratensis* L.<br>*Agrostis stolonifera* L.<br>*Poa trivialis* L.<br>*Holcus mollis* L.<br>*Ranunculus repens* L.<br>*Agrostis capillaris* L. | 2011: 3 cuts, one mulching<br>2012: two cuts | -0.31 ± 0.13 |
| *$C_{low}$_wet* | *Carex leporina* L.<br>*Ranunculus repens* L.<br>*Agrostis stolonifera* L. | 2011: 3 cuts, one mulching<br>2012: two cuts | -0.19 ± 0.14 |
| *$C_{high}$_wet* | *Carex nigra* (L.) Reichard<br>*Aulacomnium palustre* (Hedw.) Schwägr.<br>*Sphagnum fallax* H. Klinggr.<br>*Drepanocladus fluitans*<br>*Molinia caerulea* (L.) Moench<br>*Sphagnum cuspidatum* Ehrh. ex Hoffm.<br>*Festuca ovina* L. | 2011: one cut, one mulching<br>2012: two cuts | -0.16 ± 0.15 |

## 4.4 Methods

### 4.4.1 Field measurements and sample collection

Air temperature (2 m), soil temperature (2, 5, 10, 20, 50 cm below surface), global radiation, albedo, wind speed and precipitation were measured at a weather station adjacent to the study site (Fig. 4-1). All meteorological and hydrological data were logged at 15 min intervals. Precipitation was corrected for measurement errors (Richter, 1995). The grass reference evapotranspiration $ET_0$ was calculated from the weather station data 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. Suction plates (borosilicate glass, 80 mm diameter, ecoTech, Bonn, Germany) were installed at three depths (15, 30 and 60 cm) in three replicates. To minimise disturbance of the natural water flow path, suction during each sampling interval was applied according to the soil tension 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.

### 4.4.2 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 (Nt) 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 (08/29/2011, 09/12/2011, 09/26/2011, 03/12/2012, 03/26/2012, 04/13/2012, 08/14/2012, 08/27/2012, 09/10/2012, 09/25/2012, 10/08/2012, 10/22/2012), covering a broad range of hydrological conditions and temperatures, were chosen for further analysis.

Dissolved organic nitrogen (DON) was determined from these selected samples as the difference between total nitrogen (TN) and mineral nitrogen (nitrate and ammonium). TN 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). Nitrate concentrations were negligible (< 0.9 mg $l^{-1}$).

DOM stable carbon and nitrogen isotope compositions were determined for these selected solution samples. Prior to measurement the solution samples were freeze-dried and the remaining dry matter was used for analysis. Since nitrate concentrations in the solutions were negligible, they did not bias (contaminate) $\delta^{15}N$ isotope measurements. Samples were smoothly homogenised with a spatula prior to analysis. Soil and vegetation (plant) 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 the sample were determined by peak integration 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 $\delta = (R_{sample}/R_{standard} - 1) * 1000$, with $R_{sample}$ and $R_{standard}$ as isotope ratios ($^{13}C/^{12}C$ or $^{15}N/^{14}N$) of samples and standards, respectively, and reported against VPDB ($\delta^{13}C$) and air ($\delta^{15}N$). Besides calibration standards, additional laboratory standard materials were inserted between samples to monitor the instrument's performance. The overall precision of replicate analyses of samples was generally <0.1 ‰ for $\delta^{13}C$ and $\delta^{15}N$.

### 4.4.3 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. A soil hydrological model (Hydrus 1D) was set up to overcome these limitations and to obtain a continuous and consistent time series of soil water tension at the measurement depths. For this purpose, the model was calibrated on the measured tensiometer data while prescribing precipitation, potential evapotranspiration and measured WTDs. Soil hydraulic parameters were additionally constrained by laboratory experiments using the evaporation method (Dettmann *et al.*, 2014). Due to the lack of flux and water content data, the site models were calibrated with tension data only, thus achieved fits for soil water tension were good (RMSE of 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.

### 4.4.4 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.

Linear mixed effects (LME) models and general least squares (GLS) were set up using 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 DOC concentrations.

Model building was conducted in accordance with Zuur *et al.* (2009). First, an LME model was set up to evaluate 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.

(1) LME (DOC ~ sampling site, random = 1|suction plate, weights = varPower(form=~1|sampling site), correlation=corAR1(0.6, form=~date|suction plate))

This full model was tested against a “zero” model (Eq. 2) to assess 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:

(2) LME (DOC ~1, random = 1|suction plate, weights = varPower(form=~1|sampling site), correlation=corAR1(0.6, form=~date|suction plate))

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 generalised 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 encompassed soil temperatures, pH values, modelled water fluxes, modelled water-filled pore space (WFPS) and WTD. The 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 procedure was conducted separately for each site and depth.

Model building for each site and depth 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):

(3) GLS ($DOC_{mean}$ ~ WTD*ST*FLUX*WFPS*pH, weights = varPower(form=~ WTD), correlation=corAR1(0.6, form=~date))

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

## 4.5 Results

### 4.5.1 Hydro-meteorological conditions

Mean air temperatures and precipitation sums during the periods 1 July 2011 to 31 May 2012 and 1 July 2012 to 31 May 2013 were 9.4 °C and 8.1 °C and 675 mm and 738 mm respectively. Annual grass reference evapotranspiration sums ($ET_0$) 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 greatest 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 average water-filled pore space (WFPS) at 15 cm depth but not at 30 cm depth (Table 4-3). 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%). Modelled median Darcian flow velocities at 15 cm depth at the sites with the peat-sand mixture ($C_{low}$_wet: 0.26 cm $d^{-1}$, $C_{low}$_dry: 0.23 cm $d^{-1}$) were more than twice as high as at the peat site ($C_{high}$_wet: 0.09 cm $d^{-1}$).

### 4.5.2 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. 4-2). DOC concentrations ranged from 95 to 449 mg $l^{-1}$ at $C_{low}$_dry, 59 to 230 mg $l^{-1}$ $C_{low}$_wet and 80 to 400 mg $l^{-1}$ at $C_{high}$_wet (Fig. 4-2). 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.

DOC concentrations depended on sampling depth at all three sites (Fig. 4-3). 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, but were both significantly ($p < 0.05$) higher than in the sand (132 mg $l^{-1}$).

Basic properties of the soil solution (Table 4-3) indicated that EC followed the pattern of the DOC concentrations. There was therefore a positive correlation between DOC and EC for each suction plate (data not shown). This suggests that DOC determined EC as an important solute of the soil solution. The pH values showed clear differences between the three sampling 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 4-3).

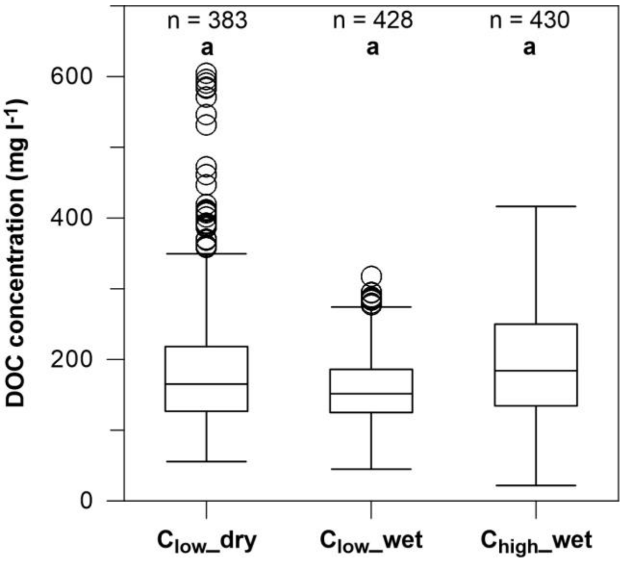

**Fig. 4- 2:** Boxplots of dissolved organic carbon (DOC) concentrations at the sampling sites summarising all depths (15, 30 and 60 cm). Central crossbars represent the median, the boxes the 75th and 25th percentiles and the circles extreme values; n: number of samples. Letters indicate significant differences between the sites.

**Table 4- 3:** Basic properties of the soil solution (pH; EC: electrical conductivity) of the complete sample set. Concentrations of dissolved organic nitrogen (DON), nitrate ($NO_3$-N) and ammonium ($NH_4$-N) of selected samples as well as the modelled water-filled pore space (WFPS) at all three depths (means ± standard deviation), n.d.: not determined.

| **Sampling site/depth** | **pH** | **EC (µS cm$^{-1}$)** | **DON (mg l$^{-1}$)** | **$NO_3$-N (mg l$^{-1}$)** | **$NH_4$-N (mg l$^{-1}$)** | **WFPS (%)** |
|---|---|---|---|---|---|---|
| ***C$_{low}$_dry*** | | | | | | |
| *15 cm* | 4.8 ± 0.3 | 91 ± 25 | n.d. | n.d. | n.d. | 95.2 ± 2.9 |
| *30 cm* | 5.1 ± 0.2 | 144 ± 50 | n.d. | n.d. | n.d. | 98.3 ± 2.7 |
| *60 cm* | 5.5 ± 0.2 | 104 ± 24 | n.d. | n.d. | n.d. | 100.0 ± 0.0 |
| ***C$_{low}$_wet*** | | | | | | |
| *15 cm* | 5.8 ± 0.4 | 111 ± 28 | 6.3 ± 1.9 | 0.0 ± 0.0 | 0.2 ± 0.3 | 96.3 ± 3.8 |
| *30 cm* | 6.1 ± 0.3 | 141 ± 34 | 7.2 ± 2.3 | 0.1 ± 0.2 | 0.4 ± 0.5 | 98.2 ± 3.1 |
| *60 cm* | 6.0 ± 0.3 | 141 ± 26 | 5.7 ± 0.7 | 0.0 ± 0.0 | 0.4 ± 0.1 | 100.0 ± 0.0 |
| ***C$_{high}$_wet*** | | | | | | |
| *15 cm* | 3.8 ± 0.1 | 142 ± 28 | 4.9 ± 1.7 | 0.0 ± 0.0 | 0.1 ± 0.2 | 97.9 ± 3.4 |
| *30 cm* | 4.4 ± 0.2 | 140 ± 14 | 6.1 ± 0.8 | 0.0 ± 0.0 | 0.1 ± 0.2 | 99.3 ± 1.6 |
| *60 cm* | 5.6 ± 0.4 | 121 ± 7 | 3.2 ± 0.5 | 0.0 ± 0.0 | 0.0 ± 0.0 | 100.0 ± 0.0 |

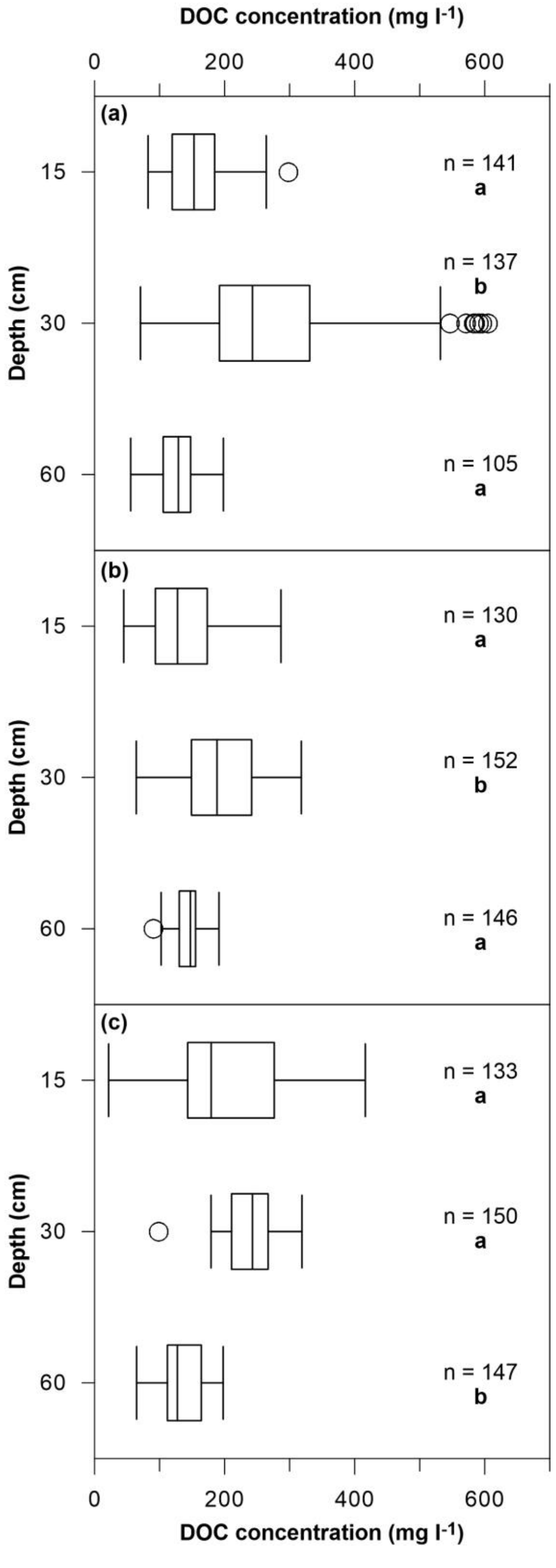

**Fig. 4- 3:** Boxplots of dissolved organic carbon (DOC) concentrations at the sampling sites: a) $C_{low}$_dry, b) $C_{low}$_wet and c) $C_{high}$_wet per depth. Central crossbars represent the median, the boxes the 75th and 25th percentile and the circles extreme values; n: number of samples. Letters indicate significant differences between sampling depths.

### 4.5.3 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. 4-4a). At $C_{low}$_wet and $C_{high}$_wet this was the case at 15 cm (Fig. 4-4b and 4c). 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. 4-4a and 4b). 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 there were no clear seasonal dynamics at 30 cm depth, DOC concentrations tended to be higher during colder periods.

At all sites, the DOC concentrations showed a delayed response to environmental conditions. In the peat-sand mixtures, DOC concentration increased with soil temperature, with lag times of 90 to 127 days (Table S4-1). 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 4-4). 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 4-4). This was usually the case, with a lag of 31 to 125 days. 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 4-4). pH values only had an impact on DOC concentrations in a few cases.

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 where, in contrast to the peat-sand mixtures, shallow WTD with lag times of 19 to 38 days increased DOC concentrations. Temperature was less important than at the peat-sand mixture sites, as indicated by lower significance levels (Table 4-4). 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).

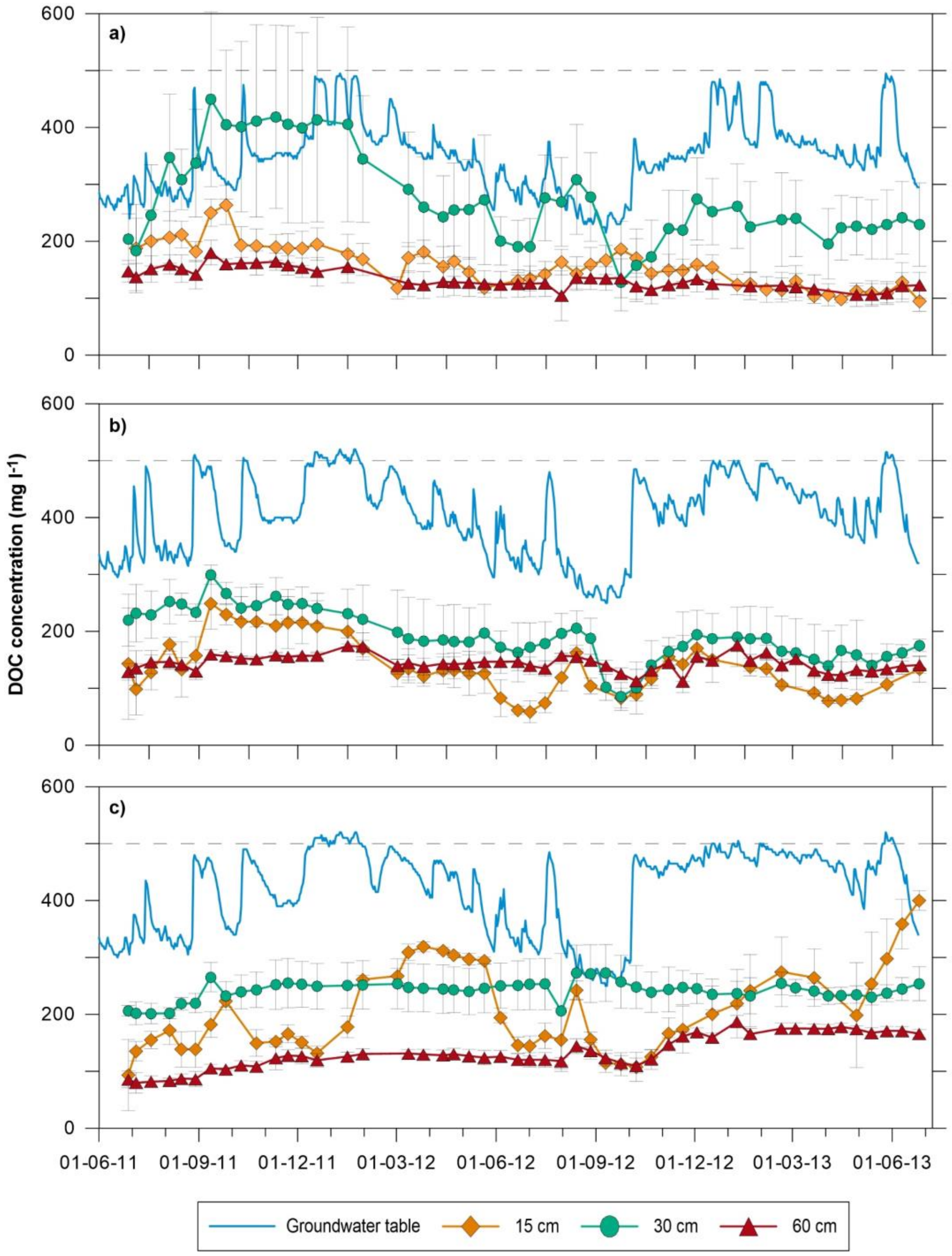

**Fig. 4- 4:** Temporal pattern of the dissolved organic carbon (DOC) concentrations of the soil solution at three depths (15, 30 and 60 cm) and water table dynamics over the study period (28.06.2011 - 26.06.2013) at the sampling sites: a) $C_{low}$_dry, b) $C_{low}$_wet and c) $C_{high}$_wet. Horizontal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

**Table 4- 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 = modelled water-filled pore space; Flux = modelled water flux (upward flux: positive values, infiltration: negative values); ST:Flux = interaction of soil temperature and modelled water flux.

| Depth | ST | WTD | WFPS | Flux | pH | ST:Flux |
|---|---|---|---|---|---|---|
| ***$C_{low}$_dry*** | | | | | | |
| *15 cm* | ↑*** | ↓** | | | | |
| *30 cm* | ↑*** | | | ↓** | | ↑** |
| *60 cm* | ↑*** | | | | ↑* | |
| ***$C_{low}$_wet*** | | | | | | |
| *15 cm* | ↑*** | | | ↓** | | ↑*** |
| *30 cm* | | | ↑*** | | ↑* | |
| *60 cm* | ↑* | | | ↓** | | |
| ***$C_{high}$_wet*** | | | | | | |
| *15 cm* | ↓* | ↑** | | | | |
| *30 cm* | ↑** | ↑* | ↓*** | | | |
| *60 cm* | | ↑*** | | ↓* | ↓*** | |

### 4.5.4 DOM properties

To evaluate possible source pools of DOM and differences in DOM cycling between $C_{low}$_wet and $C_{high}$_wet, the solution's DOC:DON ratio, $\delta^{13}C_{DOM}$ and $\delta^{15}N_{DOM}$ were compared with those obtained in the peat, the underlying sand and the present vegetation (Table 4-5 and Fig. S4-1).

The C:N ratio, $\delta^{13}C$ and $\delta^{15}N$ values of the peat-sand mixture at $C_{low}$_wet and the peat layer at $C_{high}$_wet did not differ significantly (Table 4-5). The underlying sand was also fairly homogenous (Table 4-5). The strongest differences between the two sites were found for the vegetation, especially regarding the lower $\delta^{15}N$ values of not only the mosses, but of the herbaceous vegetation as well at site $C_{high}$_wet. This coincided with wider C:N ratios in the vegetation at this site. At both sites, the $\delta^{15}N$ values were higher for the SOC-rich layer compared to the subsoil and vegetation compartments.

**Table 4- 5:** Isotopic signatures ($\delta^{13}C$ vs. VPDB and $\delta^{15}N$ 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 ($\delta^{13}C_{DOM}$ vs. VPDB and $\delta^{15}N_{DOM}$ 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 ± standard deviation).

| | | ***$C_{low}$_wet*** | | | ***$C_{high}$_wet*** | |
|---|---|---|---|---|---|---|
| **Pools** | **C:N** | **$\delta^{13}C$** | **$\delta^{15}N$** | **C:N** | **$\delta^{13}C$** | **$\delta^{15}N$** |
| *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*[1] | 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** | **$\delta^{13}C_{DOM}$** | **$\delta^{15}N_{DOM}$** | **DOC:DON** | **$\delta^{13}C_{DOM}$** | **$\delta^{15}N_{DOM}$** |
| *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 |

[1] peat-sand mixture at $C_{low}$_wet and peat layer at $C_{high}$_wet

Average DOC concentrations of the samples chosen for DOM quality analyses at 15, 30 and 60 cm at $C_{low}$_wet (139, 174, 139 mg $l^{-1}$) and $C_{high}$_wet (196, 252, 120 mg $l^{-1}$) were comparable to average DOC concentrations of these sites (Fig. 4-2).

DOM in the soil solution at the peat-sand mixture site ($C_{low}$_wet) was characterised by a narrower DOC:DON ratio compared to the peat site $C_{high}$_wet (Fig. 4-5). 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 4-3) of the sample subset at $C_{low}$_wet compared to $C_{high}$_wet contributed to the narrower DOC:DON ratios.

The isotopic signatures of DOM from the two sites were also clearly different (Fig. 4-5). DOM at $C_{low}$_wet was consistently higher in $\delta^{15}N_{DOM}$ by on average 1.5 ‰ and lower in $\delta^{13}C_{DOM}$ by on average 1.1 ‰ when compared to DOM from the peat site $C_{high}$_wet.

Within and across the sites, DOC:DON ratios were positively related to $\delta^{13}C_{DOM}$ (Fig. 4-5a). This effect was stronger for the peat-sand mixture than for the peat site. Across the sites, there was also a negative relationship between DOC:DON ratios and $\delta^{15}N_{DOM}$ (Fig. 4-5b). However, within a single site or depth this was either not the case ($C_{high}$_wet) or went against expectations (*i.e.* $C_{low}$_wet).

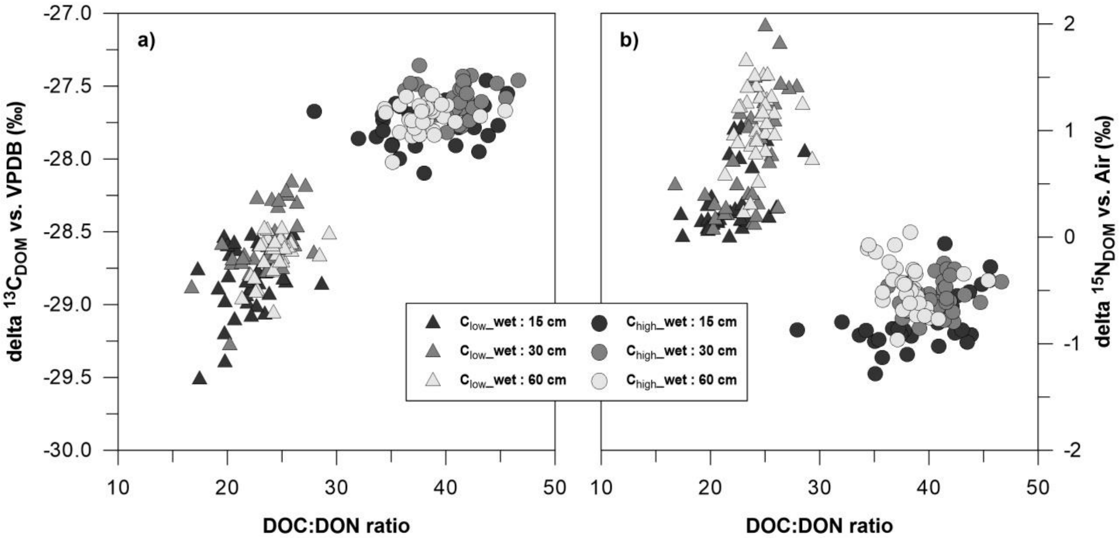

**Fig. 4- 5:** Relationship between the ratio of dissolved organic carbon (DOC) to dissolved organic nitrogen (DON) and the isotopic signature of $\delta^{13}C_{DOM}$ and $\delta^{15}N_{DOM}$ of DOM in the soil solution at all depths from the sampling sites $C_{low}$_wet and $C_{high}$_wet.

The DOC:DON ratio and $\delta^{13}C_{DOM}$ of soil solution were comparable to the C:N ratio and $\delta^{13}C$ of the peat and, in the case of $\delta^{13}C$, to the herbaceous vegetation at the peat-sand mixture site $C_{low}$_wet (Table 4-5). The $\delta^{15}N_{DOM}$ values at 30 and 60 cm depth were intermediate between $\delta^{15}N$ values of the peat and the vegetation. At 15 cm depth, average $\delta^{15}N_{DOM}$ values were lower than all investigated pools (Table 4-5). At the peat site $C_{high}$_wet, the DOC:DON ratios and the $\delta^{15}N_{DOM}$ values were intermediate between the values of vegetation and peat, but the $\delta^{13}C_{DOM}$ values were consistently higher than all the investigated pools except herbaceous vegetation (Table 4-5).

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

## 4.6 Discussion

### 4.6.1 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.

Similarly, Leiber-Sauheitl *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 $C_{high}$_wet was four times higher than at $C_{low}$_dry and $C_{low}$_wet, the SOC stock was only 1.2 to 1.6 times higher due to a negative correlation between bulk density and C content (Table 4-1). A study by Kalbitz *et al.* (2002) showed a clear dependency of DOC concentration on the SOC content of the remaining peat, which might be caused by an interaction with land use, recent land use change and WTD.

At this study site, a difference of 12 cm in mean WTD ($C_{low}$_wet vs. $C_{low}$_dry) did not cause significant differences in DOC concentration levels (Fig. 4-2). This was somewhat surprising since there was a clear effect of WTD on $CO_2$ emissions and thus microbial activity at this site, as measured by Leiber-Sauheitl *et al.* (2014). In previous field studies, differences in mean WTD of 5 to 17 cm are 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 under drained conditions by Chow *et al.* (2006) do not establish the impact of soil water content on DOC concentrations. Furthermore, the lysimeter study of Schwalm & Zeitz (2015) also 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 differences between $C_{low}$_dry and $C_{low}$_wet. Surprisingly, pH values (Table 4-3) did not have any obvious impact on DOC concentrations.

The distribution of DOC concentrations with depth (Fig. 4-3) 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 & 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 found 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 & 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 (including all sites) average DOC concentrations at 60 cm (134 and 135 mg $l^{-1}$), total annual DOC losses of 100 to 297 kg $ha^{-1}$ $yr^{-1}$ 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.* (2015) 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.

### 4.6.2 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 4-4), 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 trend 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 re-dissolution of DOC may occur. Such effects are already known from re-wetting projects, where DOC concentrations increase after raising the water table (Zak *et al.*, 2007). The pronounced DOC concentration dynamics at 15 cm depth suggest that frequent changes in the redox conditions 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. This could possibly be caused by a shift in pore size distribution and a higher contribution of macropores at the peat-sand mixture sites, 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 & 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.

### 4.6.3 DOM properties in relation to peat cultivation practice

DOM properties were only analysed for the two wet sites ($C_{low}$_wet and $C_{high}$_wet). The chosen subsamples for DOM quality measurements were considered to be a representative subset, 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 4-5). Measured $\delta^{13}C$ and $\delta^{15}N$ 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 $\delta^{13}C$ and $\delta^{15}N$ values of different species were highly variable, as previously described by Ménot and Burns (2001), while the $\delta^{13}C$ 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, $\delta^{15}N$ in the vegetation or a lack of possible end members ($\delta^{13}C$ vs. $\delta^{13}C_{DOM}$ at $C_{high}$_wet) (Table 4-5).

Nevertheless, the data suggest different shares of the source pools to DOM at $C_{low}$_wet and $C_{high}$_wet. At $C_{high}$_wet, the intermediate DOC:DON ratio and $\delta^{15}N_{DOM}$ value in soil solution compared to peat and mosses (Table 4-5) indicate a mix of plant and peat-derived DOM. DOM in peatlands is 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 $\delta^{15}N_{DOM}$ 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 tracer experiment over a period of four years.

In contrast, at the peat-sand mixture site ($C_{low}$_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, $\delta^{13}C_{DOM}$ and $\delta^{15}N_{DOM}$) clearly differed between the two sites (Fig. 4-5, Table 4-5) 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 $\delta^{15}N$ depleted mosses) may be responsible for the differences; 2) DOM properties also possibly being altered by degradation (Kalbitz *et al.*, 2003), thus higher $\delta^{15}N_{DOM}$ values at $C_{low}$_wet could also indicate enhanced microbial DON alteration by microbes (Högberg, 1997). Furthermore, the positive correlation between DOC:DON ratios and $\delta^{13}C_{DOM}$ (Fig. 4-5) suggests a change in DOM quality during decomposition at each site, as both parameters indicate stronger degradation (Kalbitz & Geyer, 2002), possibly due to a higher contribution of hydrophobic compounds (Kalbitz *et al.*, 2003). The steeper slope at $C_{low}$_wet may therefore indicate a more pronounced accumulation of hydrophobic compounds during biodegradation of DOM at the peat-sand mixture site.

## 4.7 Conclusions

The organic soils investigated in this study were characterised by:

(i) much higher DOC concentrations (> 150 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 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) 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, in addition to high $CO_2$ emissions (Leiber-Sauheitl *et al.*, 2014), mixing peat with sand is not beneficial in terms of water quality.

## 4.8 Acknowledgements

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## 4.10 Supplement

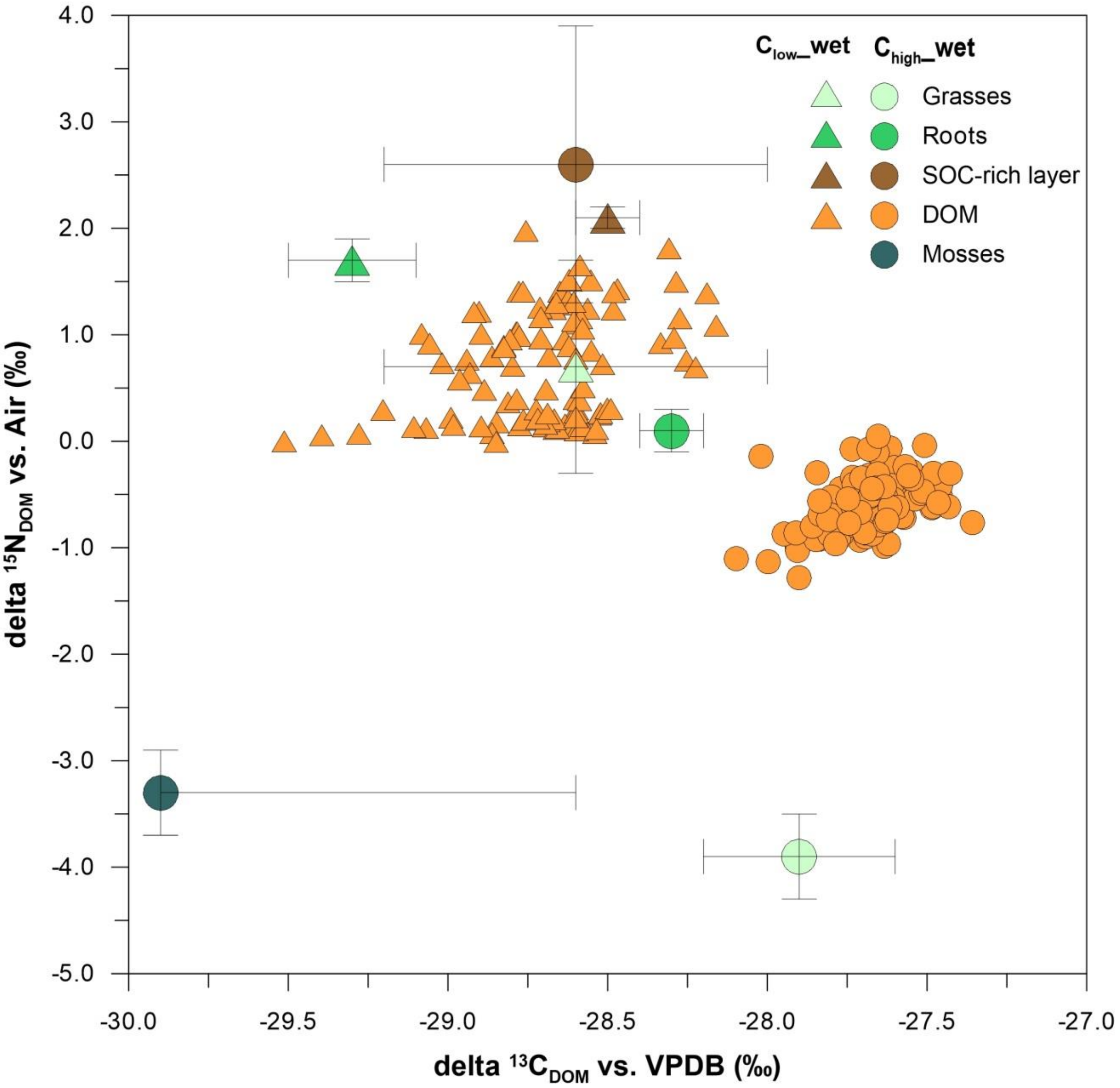

**Fig. S4- 1:** Mean isotopic signatures ($\delta^{13}$C vs. VPDB and $\delta^{15}$N vs. air; n=3) ± standard deviation of the solid compartments at the sample sites (vegetation and SOC-rich layer) as well as the isotopic signatures ($\delta^{13}C_{DOM}$ vs. VPDB and $\delta^{15}N_{DOM}$ vs. air) of dissolved organic matter (DOM) in the soil solution (all depths) from the two sample sites differing in soil organic carbon content.

**Table S4- 1:** Time lag (in days) of explanatory variables for DOC concentrations determined by a GLS model. ST = soil temperature; WTD = water table depth; WFPS = modelled water filled pore space; Flux = modelled water flux; ST:Flux = Interaction of soil temperature and modelled water flux.

| Depth | ST | WTD | WFPS | Flux | pH | ST:Flux |
|---|---|---|---|---|---|---|
| ***$C_{low}$_dry*** | | | | | | |
| *15 cm* | 90 | 34 | | | | |
| *30 cm* | 117 | | | 125 | | 117:125 |
| *60 cm* | 98 | | | | 0 | |
| ***$C_{low}$_wet*** | | | | | | |
| *15 cm* | 127 | | | 136 | | 127:136 |
| *30 cm* | | | 15 | | 0 | |
| *60 cm* | 116 | | | 31 | | |
| ***$C_{high}$_wet*** | | | | | | |
| *15 cm* | 66 | 19 | | | | |
| *30 cm* | 121 | 38 | 1 | | | |
| *60 cm* | | 17 | | 48 | 0 | |

# 5 Summarizing conclusions

This thesis deals with the impact of various factors (land use, water table depth and peat disturbance) on the cycling and losses of dissolved C and N species. This work helps to calculate more accurate C and N balances for disturbed peatlands by adding knowledge about waterborne losses to the existing data on gas exchange fluxes. This is advantageous in terms of climate feedback prediction as well as in estimating the eutrophication potential from bogs with varying land uses.

## 5.1 Land use effects on dissolved C and N

Within one single peat bog complex, soil solution concentrations and losses of C and N species were found to be determined by land use intensity and water table depth. The permanently wet areas (near-natural and re-wetted) could distinctively be separated from drained areas (grasslands). This separation is based on the general difference in C and N cycling (quantity: *e.g.* mineralization potential; quality: *e.g.* pathways of peat degradation) of aerobic and anaerobic environments. The absolute increase of soluble C and N species in soil solution after drainage depends on the typical water table depth for a given land use. Hence, deep drainage for intensive grassland usage showed the highest concentrations of all measured C and N species in soil solution.

Regarding DOC, this is important for the prediction of off-site $CO_2$ emissions, as the impact of drainage on DOC concentration changes is considered by a simple value without differentiation and does not depend on land use intensity (Evans *et al.*, 2015; IPCC, 2014). Thus, future work should further investigate the drainage impact on DOC concentration changes in relation to land use intensities. Furthermore, research on land use intensity impacts on DOC concentrations should be conducted within one peatland complex. This thesis showed that observations can be very different for comparable land use intensities, which is probably related to effects of past cultivation and hence peat properties (*e.g.* strongly degraded shallow peat vs. weakly to medium degraded deep peat). Similarly, a strong effect of peat properties was also suggested for German fens by Schwalm and Zeitz (2015), where DOC concentrations were more related to locations (peatlands) than to management.

C and N losses are generally affected by solute concentration levels as well as discharge sums, which both strongly vary with land use. In this thesis, the different land use types were characterized by different solute concentration levels and comparable discharge sums. Hence, measures dealing with the reduction of waterborne C and N losses should focus on the reduction of solute concentrations in the long run.

## 5.2 Drivers for temporal patterns of dissolved C and N

Temporal patterns of measured dissolved C and N species were in all cases either related to temperature, as a proxy for biological activity, to hydrological parameters (water table depth, discharge or flow direction), *e.g.* as a proxy for relocation within the soil profile or the catchment), or to both. The direction and strength of the relation, and their interaction were catchment-, site- and solute-specific. It is important to consider possible time lags of single drivers on solute concentration. The patterns were often found to be delayed, *e.g.* due to relocation processes, which are controlled by flow paths and peat properties (*e.g.* saturated and unsaturated conductivity). At the catchment scale, patterns of dissolved C and N species were controlled by hydrology (permanently saturated vs. alternating saturation), and at the plot scale, by peat disturbance (*e.g.* physical peat properties). Hence, even within a peatland with varying land use types, or even within one single land use type, temporal patterns may differ. In addition, the dependencies of solute concentrations on given drivers may change with increasing spatial scale due to in-stream solute processing. Thus, the location of the sampling point should be representative for a given target (*e.g.* land use) and scale. Furthermore, a regular and frequent temporal monitoring of chemical and hydrological variables is required to fully understand the cycling, in particular of DOC, in peatlands.

Furthermore, results of this thesis indicated that DOC concentrations from drained and disturbed peatlands are less affected by sulfate concentration or pH value changes. This suggests a higher importance of environmental conditions that affect production (*e.g.* drainage state and aeration) and less influence of environmental conditions that affect the solubility of DOC. Monteith *et al.* (2007) showed that the observed increase in DOC concentrations on the Northern Hemisphere might be caused by *e.g.* a reduced sulfate deposition and associated pH shifts. However, DOC concentration changes due to reduced sulfate deposition may be different for highly disturbed peatlands in Germany compared to more natural peatlands. Therefore, long time series of DOC data are needed for these environments.

## 5.3 Contribution of waterborne C and N losses to C and N balances of peatlands

A full balance, including all possible fluxes, is required to fully assess the C and N source or sink potential of peatlands. Input and output fluxes may occur via the land-atmosphere or the land-aquatic pathway. In agriculturally-used peatlands, management may also induce substantial C and N fluxes. C and N balances in this thesis were calculated for peatlands which are not in a state of an equilibrium. These transition states increase the importance of land-atmosphere, *e.g.* $CO_2$ emissions due to peat mineralization and enhanced $CO_2$ fixation by photosynthesis after re-wetting, and management fluxes (at the grassland site) in relation to land-aquatic fluxes. Hence, the contribution of waterborne C and N fluxes are of minor importance (around 8%). Regarding drained grassland areas, this may last as long as the land use continues. With respect to re-wetting, assuming that land-atmosphere fluxes converge to more natural values, the contribution of waterborne C fluxes to the C balance may increase in the long run. Further, at the re-wetted site, waterborne N, in particular DON, fluxes were the second largest flux beyond wet and dry deposition. Based on the importance of transition effects, it is emphasized here that projects evaluating the effects on climate mitigation and N cycling after re-wetting should cover a longer period of time (> 10 years) to receive a robust C or N balance, with respect to single flux contributions and their development over time.

Finally, it should be noted that given balances in this thesis did also not account for all possible pathways. $CO_2$ and $CH_4$ evasion from drainage water was not monitored. In soil solution, dissolved $CO_2$ and $CH_4$ contributed up to 26% to total dissolved carbon. Information about $CO_2$ and $CH_4$ evasion from the drainage network in German bogs with varying land uses is lacking and should be considered when assessing the full contribution of waterborne C species to the total C balance.

## 5.4 Implications for water protection

Results of this thesis provide implications for peatland management in terms of water protection. A high loss of both soluble C and N should be avoided, as DOC and soluble N species (*e.g.* nitrate) are known to negatively affect groundwater quality as well as trophy state and light availability in surface water bodies.

Deeply-drained highly-productive grassland areas are the worst case for water quality. Although nitrate is of minor importance in the drainage water of acidic bogs, DON losses (~ 20 kg

N $ha^{-1}$ $yr^{-1}$) were found to be in the range of inorganic N fluxes (*e.g.* nitrate) reported for less acidic peatlands (Tiemeyer & Kahle, 2014). Assuming a mineralization of up to 90% like for DOC (IPCC, 2014), additional amounts of inorganic N could negatively affect adjacent water bodies.

Partial re-wetting that is associated with an extensive grassland usage is a common peatland management practice. This management practice does not avoid oxygen penetration into the peat layer, as water tables are not shallow throughout the year. Thus, principles of C and N cycling in the soil solution are not altered when comparing with intensively used grassland areas. The uppermost peat layer still serves as main source of DOM, and DOM is further more microbially altered compared to natural areas. The main benefit is the considerable reduction of dissolved C and N concentrations compared to intensively-used grassland areas, due to a decreased peat degradation associated with reduced greenhouse gas (GHG) emissions (Beetz *et al.,* 2013). Furthermore, a dilution of peat C and N by mixing shallow peat layers with underlying sand may not be beneficial in terms of water quality, as observed DOC and DON concentrations were not lower for such a peat-sand mixture layer. In accordance to these findings, results from Leiber-Sauheitl *et al.* (2014) showed that peat-sand mixing is, in addition, no suitable climate mitigation measure, as GHG emissions did not decrease after peat-sand mixing.

A successful re-wetting of former peat extraction areas, with water saturated conditions throughout the year and a return of bog typical vegetation species (*e.g. Sphagnum* spp.), reduces concentrations of C and N species in soil solution to natural levels. This is achieved by establishing a C and N cycling related to natural areas under anaerobic conditions. As a consequence of the former disturbance, elevated ammonium concentrations may still occur, possibly delaying the return of the full vegetation spectrum typically found in near-natural areas.

At all study sites of this thesis, which covered a broad range of land use types typical for Lower Saxony, DON was the most important N species in soil solution. Thus, further research should account for DON when investigating the N cycling and waterborne N losses from acidic peatlands.

## 5.5 References

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