

**N and DOC losses
from an artificially
drained grassland on
organic soils**

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Nitrogen and dissolved organic carbon (DOC) losses from an artificially drained grassland on organic soils

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Abstract

Nitrate-nitrogen ($\text{NO}_3\text{-N}$) as well as dissolved organic carbon (DOC) and nitrogen (DON) concentrations and losses were studied for three respectively two years in a small catchment dominated by a degraded peatland used as intensive grassland. Concentrations in the shallow groundwater were spatially and temporally very variable with $\text{NO}_3\text{-N}$ being the most dynamic component ($7.3 \pm 12.5 \text{ mgL}^{-1}$). Average $\text{NO}_3\text{-N}$ concentrations of $10.3 \pm 5.4 \text{ mgL}^{-1}$ in the ditch draining the catchment and annual $\text{NO}_3\text{-N}$ losses of 19, 35 and 26 kg ha^{-1} confirmed drained peatlands as an important source of diffuse N pollution. The highest $\text{NO}_3\text{-N}$ losses occurred during the wettest year. Resulting from concentrations of $2.4 \pm 0.8 \text{ mgL}^{-1}$, DON added further 4.5 to 6.4 kg ha^{-1} to the N losses and thus formed a relevant component of the total N losses. Ditch DOC concentrations of $24.9 \pm 5.9 \text{ mgL}^{-1}$ resulted in DOC losses of 66 kg ha^{-1} in the wet year 2006/07 and 39 kg ha^{-1} in the dry year 2007/08. Both DOC and N concentrations were governed by hydrological conditions, but $\text{NO}_3\text{-N}$ reacted much faster and clearer on rising discharge rates than DOC which tended to be higher under dryer conditions. In the third year of the study, the superposition of a very wet summer and land use changes from grassland to arable land in a part of the catchment suggests that under re-wetting conditions with a high groundwater table in summer, $\text{NO}_3\text{-N}$ would diminish quickly, while DOC would remain on a similar level. Further intensification of the land use, on the other hand, would increase N losses to receiving water bodies.

1 Introduction

Worldwide, peatlands are a major store of organic carbon and nitrogen (Gorham, 1991). In the course of the intensification of agriculture, most of the peatlands in Western Europe as well as in Mecklenburg-Vorpommern (north-eastern Germany) have been drained. Nowadays, the majority of the peatlands in Germany is used as grassland (UBA, 2012). Lowering the groundwater table by drainage leads to deleterious

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lands has been suggested as a measure to both reduce diffuse pollution originating from degraded peatlands themselves and to clean nutrient-rich water from upstream areas (Davidsson et al., 2002; Trepel, 2010; Vikman et al., 2010). Especially strongly degraded peat seems to have a high denitrification and N retention potential when re-wetted (Cabezas et al., 2012; Davidsson et al., 2002), although other studies found ongoing mineralisation under these conditions (Olde Venterink et al., 2002). Besides combating diffuse pollution as required by legislative efforts, the monetisation of ecosystem services of peatlands comes increasingly into the focus of attention (Russi et al., 2013; Trepel, 2010). Both topics need baseline data for drained peatlands against which improvements by re-wetting measures can be evaluated.

Dissolved organic carbon (DOC) may play an important role in the carbon cycle of peatlands and beyond: DOC losses may form an important part of the carbon balance (Dinsmore et al., 2010; Rowson et al., 2010), act as a transport vector for organically bound substances (Rothwell et al., 2007), and influence biogeochemical cycling in and drinking water quality of the receiving water bodies (Chow et al., 2003). While the governing processes and influence factors for nitrate are quite well known, the effects of drainage and re-wetting on DOC and dissolved organic nitrogen (DON) losses are less clear. Several factors determining DOC concentrations in the porewater and the groundwater of peatlands such as the groundwater levels (Frank et al., 2013), the temperature (Koehler et al., 2009), the ionic strength (Evans et al., 2006) and the pH (Clark et al., 2005) have been proposed, but effects are sometimes confounding or interacting. For example, higher temperatures might cause a water table drawdown, subsequent sulphate release and thus both a change in the ionic strength and the pH (Clark et al., 2005). Furthermore, as in the case of nitrate, different processes govern DOC concentrations *within* and losses *from* the peatland. While DOC release and consumption are mainly controlled by biogeochemical processes, hydrology – particularly the water balance – becomes an important factor when comparing losses from different peatlands (Fraser et al., 2001; Gibson et al., 2009). Drainage has frequently found to increase DOC concentrations in peatlands due to increased microbial activity (Frank

et al., 2013). In contrast to these results, some boreal peatlands showed decreasing DOC concentrations after drainage (Åström et al., 2004).

Overall, most authors suggest re-wetting as an effective measure to reduce DOC concentrations and/or losses (Frank et al., 2013; Wallage et al., 2006). However, some studies found – sometimes temporary – increasing DOC concentrations or losses after re-wetting, especially for highly degraded peat soils (Kalbitz and Geyer, 2002). These field observations are supported by laboratory studies (Cabezas et al., 2013; Zak and Gelbrecht, 2007), so that at least some care should be taken when recommending re-wetting to reduce DOC concentrations. As most field studies on DOC focus on bogs and/or re-wetted sites (Austnes et al., 2010; Dinsmore et al., 2010; Dawson et al., 2002; Frank et al., 2013; Fraser et al., 2001; Gibson et al., 2009; Wallage et al., 2006), there is a distinct lack of baseline data for temperate lowland peatlands with fen peat under agricultural use. Even less is known on DON than on DOC although some studies suggest that DOC and DON do not necessarily follow the same dynamics (Kalbitz and Geyer, 2002).

In this study, we want to show how hydro-meteorological conditions influence the DOC, NO₃-N and DON concentrations in and losses from an artificially drained lowland catchment with organic soils. The catchment represents a situation typical for Central Europe – artificially drained intensive grassland – and thus provides so far lacking baseline data. Due to extreme weather conditions and land use changes from permanent grassland to arable land during the course of the study, we can estimate how the hydrochemical dynamics might develop under a changing hydrological regime or intensified agriculture.

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2 Material and methods

2.1 The study site

The study area is situated in the pleistocene lowlands of north-eastern Germany (10 km southeast of the city of Rostock). The landscape is characterised by gently sloping ground moraines and by peatlands in the river and stream valleys. Long-term mean annual precipitation, reference crop evapotranspiration, and temperature are 642 mm, 561 mm and 8.7 °C, respectively. The study site is a small (85 ha) catchment of a drainage ditch (Fig. 1). The catchment consists of intensive grasslands mainly on organic soils and arable land on mineral soils.

Due to a hydrogeologically complex setting, the peatland has developed as a combination of terrestrialization and percolation mires (Edom et al., 2010). The properties and depths of the organic soils are spatially highly variable, but they are all drained by ditches and occasional tile drains. Peat thickness varies between a few cm and 1.50 m. The peat is partially underlain by a confining layer of either calcareous or organic gyttja and partially overlies directly an aquifer of coarse sand. The soil organic carbon (SOC) content of the topsoil varies between 8 and 409 g kg⁻¹ (Tiemeyer et al., 2007). This is reflected by a variety of soil types such as Eutric and Sapric Histosols, Histic Gleysols and Histic Stagnosols (WRB classification; IUSS Working Group WRB, 2007). Nowadays, the hydrology of the peatland is heavily influenced by anthropogenic changes by tile drains and ditches, which partially incise into the mineral layers. After a particularly wet summer (2007), some of the ditches and drains were renovated (Fig. 1).

At the beginning of the study, the organic soils were used as grassland. The grassland is managed as an intensive meadow with four to five cuts per year. The average yield of grass is 330 dt ha⁻¹ a⁻¹ (fresh mass). The sward is regularly re-sown and mainly consists of ryegrass (*Lolium perenne* L.), common meadow-grass (*Poa pratensis* L.) and couchgrass (*Elymus repens* L.). In wetter parts, meadow foxtail (*Alopecurus pratensis* L.), reed canarygrass (*Phalaris arundinacea* L.) and Yorkshire fog (*Holcus*

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lanatus L.) are found as well. In spring 2007, a part of the grassland was ploughed and converted to arable land for corn (*Zea mays* L.) production (Fig. 1).

Until 2007, the arable land in the catchment was situated on mineral soils such as Luvisols and Cambisols, which are not artificially drained. The arable land is used for intensive conventional crop production dominated by winter wheat (*Triticum aestivum* L.), winter rape (*Brassica napus* L.), winter barley (*Hordeum vulgare* L.) and corn. At the grassland, nitrogen was solely applied as mineral fertiliser, while for the arable land, cattle slurry was used, too. Table 1 summarizes the field nitrogen budget comprising fertilisation, harvest and atmospheric deposition according to Behrendt (1996). Values for volatile losses and the nutrient contents of the mineral fertilisers, of the harvested crops and of the crop residues were taken from MELFF MV (2004). The amounts and dates of fertiliser application, the crop yields and the nutrient content of the organic fertiliser were provided by the farmer. Details of the budget calculation are described by Tiemeyer et al. (2006).

At the catchment outlet (Fig. 1), a sampling station measured the water level via a pressure sensor (UGT GmbH, Müncheberg, Germany) and collected, depending on the flow conditions, daily to weekly composite (3 h sampling interval) water samples with an automatic sampler (Teledyne Isco, Inc., Lincoln, NE). The discharge was measured weekly with an inductive flow meter (Flo-MateTM, Marsh-McBirney, Inc., Frederick, MD) to develop a rating curve. Air temperature, humidity, wind speed (UGT GmbH, Müncheberg, Germany) and precipitation (Seba Hydrometrie GmbH, Kaufbeuren, Germany) were recorded at a climate station in 1.5 km distance.

The dipwells used in this study are PVC pipes with an internal diameter of 5.2 cm, which are slotted and filtered with a nylon mesh at a depth of 0.5 to 1.5 m below ground. Twelve dipwells were installed in transects A and B on shallow organic soils and six dipwells in transect C on deep organic soils. Topsoil (0–30 cm) SOC content is $112 \pm 114 \text{ g kg}^{-1}$ (transect A), $211 \pm 116 \text{ g kg}^{-1}$ (transect B) and $368 \pm 39 \text{ g kg}^{-1}$ (transect C) (Tiemeyer et al., 2007). The dipwells were sampled weekly during the winter season (November to April), while the groundwater level was additionally measured fortnightly

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during summer (May to October) unless a dipwell (DW) fell dry. Groundwater samples were taken with a bailer after nearly emptying the DW and allowing the water level to recover. The bailer was rinsed with deionised water after each use. In addition to the groundwater samples and the samples at the catchment outlet, weekly grab samples were taken from the ditch adjacent to transect C (Fig. 1).

Details on the study site and the field methods can be found in Tiemeyer et al. (2007) who discussed the spatial variability of a number of ions (but neither of DOC nor DON) in the groundwater during the winter 2005/06. Here, we report on results from November 2005 to October 2008, and focus on nitrogen and DOC. To highlight the effects of extreme climatic conditions and land use change in the catchment, the results of the first year are also included in this study.

2.2 Laboratory methods

Nitrate (NO_3^-) and ammonium (NH_4^+) were analyzed by ion chromatography (Metrohm GmbH, Herisau, Switzerland) with chemical suppression for anion analysis. The electrical conductivity (EC) and the pH of the water samples were measured with the probes LF 196 and pH 196 (WTW, Weilheim, Germany). Unfortunately, EC and especially pH measurements are missing for a number of samples. Dissolved organic carbon (DOC) and total nitrogen (TN) were determined from filtered samples ($0.45 \mu\text{m}$ PET filter, Macharey-Nagel, Dühren, Germany) by combustion and infrared detection (DIMATOC©2000; Dimatec GmbH, Essen, Germany) and chemiluminescence detection (TN-100; Mitsubishi Chemical Corporation, Kanagawa, Japan), respectively. DON was calculated as the difference of TN and mineral N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$). DOC and TN concentrations were determined for ditch samples of the hydrological years 2006/2007 and 2007/08. Additionally, DOC in the groundwater from transect C was measured at selected ($n = 30$) samples from 2006/07 and at all samples from 2007/08.

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2.3 Statistics

All statistical analyses were carried out in R (R Core Team, 2013). To account for the residence time of the water and to identify additional explanatory parameters for the DOC, NO₃-N and DON concentrations, a cross-correlation analysis of the concentrations in the ditch and the average discharge over the last one to 90 days was conducted. The discharge was square-root-transformed before analysis to improve the linearity between the concentrations and the discharge.

During the study period, there was a relatively dry and a very wet period. Differences between these periods were evaluated with generalized least square (GLS) and linear mixed effects (LME) models from the nlme package (Pinheiro et al., 2013). Analyses were done separately for concentrations (c) of DOC, DON and NO₃-N. In a first step, a GLS model explaining the concentrations only by the fixed effect “period” was set up. Following the procedure outlined by Zuur et al. (2009), a suitable variance structure was added next. Different variance structures (varIdent, varPower and varExp) were tested. In the case of the concentrations in the groundwater, adding a random structure (i.e. using a LME model instead of a GLS model) with “dipwell” as a random factor was additionally tested. As a further step, a first order autocorrelation structure (corAR1) was added. The improvement of the model due to each addition was evaluated by the Akaike information criterion (AIC) and, after re-fitting the model with the maximum likelihood method, by an ANOVA between the first model and the model in question. Additionally, at each step, the residuals were visually checked for homogeneity. An example for the resulting model is given in Eq. (1).

$$\begin{aligned} \text{gls}(c \sim \text{period}, \text{weights} = \text{varIdent}(\text{form} = \sim 1|\text{period}), \text{cor} \\ = \text{corAR1}(\text{form} = \sim \text{date}|\text{period})) \end{aligned} \quad (1)$$

The final model was then tested against a reference model in which the fixed effect “period” was replaced by 1 which represents the mean of all data. If the Akaike information

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criterion (AIC) for the reference model was significantly higher, a significant difference between the two periods is assumed. For this final ANOVA, p values are reported.

Influence factors on the concentrations at the catchment outlet and in the groundwater were also analysed with GLS and LME models following the same general procedure starting with the most complex model including all meaningful interactions (Zuur et al., 2009). Next, the necessity of including the random factor “dipwell” (in the case of the groundwater concentrations) was evaluated followed by the choice of suitable variance and autocorrelation structures. Both a variance and an autocorrelation structure were necessary for nearly all model setups. Afterwards, the model structure was reduced stepwise depending on the AIC and the parameter significance: if an ANOVA indicated that the reduced model is not significantly worse than the full model, a parameter or a parameter interaction could be dropped. As GLS and LME models cannot deal with missing data, separate models had to be set up for the complete data set and those data with pH and EC measurements. To evaluate the explanatory power of the final models, the Nash–Sutcliffe coefficient (NSC) or “model efficiency” was calculated (Nash and Sutcliffe, 1970).

3 Results

3.1 Hydrology

Table 2 summarizes the hydrological conditions during the study period. While the first hydrological year (1 November 2005 to 31 October 2006) was fairly average, the following two years were unusual. Both years were warmer than average, and annual precipitation sums of 934 and 554 mm marked exceptionally wet and dry conditions. While the precipitation and the discharge were similar during the winter periods, the summer made the difference between the last two years. Given the long-term summer precipitation average of 372 mm, the summer of 2007 was extraordinary rainy with a precipitation of 551 mm. In contrast to other summers during which the ditch fell

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dry in May or June (Fig. 2), the summer discharge in 2007 (91 mm) was higher than that of dry winters (Tiemeyer et al., 2007). On an annual basis, to 24 to 32 % of the precipitation left the catchment as discharge. In the following, the 1 November 2005 to the 31 May 2007 is referred to as the “dry period”, and the remainder of the study period as the “wet period”. Technically, the summer of 2008 is dry again, but as both the ditch and the dipwells quickly dried out, there is nearly no data on this summer period.

Whereas during winter the groundwater level was frequently near the ground surface, it dropped during dry spells deeper than 1.00 m even in the wettest places, demonstrating the heavy disturbance of the peatland. The wet summer 2007 had a lasting effect even on the groundwater table in the subsequent winter when the average water table depth (WTD) was, despite slightly less precipitation, higher and more homogenous in time than during the preceding winters (Fig. 4, Table 2). Thus, the wet summer might anticipate possible short-term effects of re-wetting.

Due to drainage, soil and topographical heterogeneity, there was a high spatial variability of the WTD with minimum and maximum averages over the whole study period of 0.27 m (DW 13) and 1.13 m (DW 4), respectively (Fig. 4). In summer 2008, dipwells quickly fell dry or had to be removed. Due to the spatially heterogeneous groundwater table dynamics, heterogeneous biogeochemical processes can be expected, especially as not only the mean WTD but also the amplitude differed even in the wetter winters as a result of heterogeneous soil properties. The ditch integrates all these responses together with groundwater flow from the non-drained part of the catchment (and, given the heterogeneous geological situation of the area, possibly also deeper groundwater).

3.2 DOC and nitrogen concentrations groundwater

An overview of the DOC and $\text{NO}_3\text{-N}$ concentrations is given in Table 3. The overall average (\pm standard deviation) DOC concentrations of all measurements in the dipwells was $50.6 \pm 15.2 \text{ mg L}^{-1}$. The spatial heterogeneity was relatively weak; in single dipwells, average DOC concentrations over the complete study period between 40.7 ± 11.7

NO₃-N concentrations of $44.1 \pm 19.7 \text{ mgL}^{-1}$ and $25.4 \pm 12.8 \text{ mgL}^{-1}$ in the first two winters decreased to 0.8 ± 1.2 and $1.5 \pm 2.2 \text{ mgL}^{-1}$ in the third winter (Fig. 4). As a result, the spatial heterogeneity (dipwell means: $0.2 \pm 0.1 \text{ mgL}^{-1}$ to $15.0 \pm 2.7 \text{ mgL}^{-1}$) was strongly reduced compared to the dry period. NH₄-N concentrations were still low (0.4 ± 0.7 mgL⁻¹).

The final LME model (NSC = 0.45) for the NO₃-N concentrations was also complex (Table 4). Besides the period, the depth to the groundwater table, the change of the groundwater table, and the nitrogen content of the peat were the most important parameters. Higher temperatures intensified these effects.

3.3 DOC and nitrogen concentrations in the ditch

Discharge, DOC and NO₃-N concentrations in the ditch are shown in Fig. 2, and an overview of the DOC, DON and NO₃-N concentrations is given in Table 5. DOC concentrations in the ditch ($24.9 \pm 5.9 \text{ mgL}^{-1}$) were much lower than in the groundwater ($50.6 \pm 15.2 \text{ mgL}^{-1}$). While DOC concentrations were slightly lower during the wet period than during the dry period (Table 3), this difference was only significant at a low level ($p = 0.049$). Visually, the DOC concentrations seem to be higher at the beginning of the discharge period and lower during discharge events. However, the instantaneous discharge was not included in the final model for the DOC concentrations in our catchment. To account for the residence time of the water, a cross-correlation analysis of the DOC, NO₃-N and DON concentrations in the ditch and the average discharge had been conducted. For the DOC concentrations, the maximum correlation coefficient was found for an average discharge over the last 70 days (Fig. 5). Accordingly, the average discharge over the last 70 days (Q_{70}) was the only significant parameter in the final GLS models for the full data set ($n = 237$) and the data set with EC measurements ($n = 224$). The NSC of these models was 0.48. No significant effects of the temperature, the instantaneous discharge or any interactions could be determined. The dataset including pH measurements was much smaller ($n = 88$), but had to be described by

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a more complicated GLS model (NSC = 0.54) including Q , Q_{70} , temperature, pH and EC as well as interaction between Q and EC as well as Q and pH. Removing the temperature (NSC = 0.51), the EC (NSC = 0.25) or the pH-value (NSC = 0.46) from the model would all reduce the NSC.

5 $\text{NO}_3\text{-N}$ concentrations in the ditch ($10.3 \pm 5.4 \text{ mg L}^{-1}$) were within the range of the concentrations in the dipwells. In contrast to the dipwells, average winter $\text{NO}_3\text{-N}$ concentrations in the ditch were increasing during the study period (Table 5). Therefore, the concentrations during the wet period ($11.7 \pm 4.2 \text{ mg L}^{-1}$) were significantly ($p = 0.016$) higher than during the dry period ($9.5 \pm 5.9 \text{ mg L}^{-1}$). There was a clear positive correlation between the discharge and the $\text{NO}_3\text{-N}$ concentrations (Fig. 2), while the maximum correlation coefficient (Fig. 5) was determined for an average discharge over of 13 days (Q_{13}). During summer, $\text{NO}_3\text{-N}$ concentrations were clearly lower than during winter in all years including the wet summer 2007 (Table 2). The concentration patterns of $\text{NO}_3\text{-N}$ and DOC strongly differed, resulting in a negative correlation between DOC and $\text{NO}_3\text{-N}$ concentrations, which suggest different transport mechanisms. $\text{NH}_4\text{-N}$ was not found at the catchment outlet.

The final GLS model for the full $\text{NO}_3\text{-N}$ dataset ($n = 361$) included Q_{13} and, with an opposite sign, the instantaneous discharge. When including EC into the analysis ($n = 240$), this parameter and its interaction with Q_{13} were significant according the procedure outlined by Zuur et al. (2009), but omitting them from the model did only reduce the NSC from 0.70 to 0.68. As in the case of DOC, the data set with pH-measurements was much smaller ($n = 91$) and resulted in a more complex model. However, omitting pH, temperature and EC did only reduce the NSC from 0.74 to 0.70.

25 DON concentrations in the ditch of $2.4 \pm 0.8 \text{ mg L}^{-1}$ were relatively low and less variable than DOC and $\text{NO}_3\text{-N}$ (Table 5), although concentrations during the wet period were significantly higher than during the dry period ($p = 0.0006$). The maximum correlation coefficient was found for the discharge at the date of the DON concentration measurement, but all correlation coefficients were very low (Fig. 5). Factors influencing the DON concentrations were difficult to determine; depending on the data sub-set, the

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discharge or the EC were identified as significant parameters, but the NSC was always only 0.05.

3.4 DOC and nitrogen losses

Seasonal losses of DOC, NO₃-N and DON are shown in Fig. 6. Annual DOC losses were 66 kg ha⁻¹ in the wet year 2006/07 and 39 kg ha⁻¹ in the dry year 2007/08. In 2006/07, the winter accounted for 65 % of the DOC losses, whereas in summer 2008 the ditch fell (and remained) dry from May onwards. Thus, in 2007/08, 98 % of the DOC losses occurred during winter.

Annual total N losses from the catchment amounted to 19 (without accounting for DON), 42 and 31 kg ha⁻¹. NO₃-N was thus the main component of the N losses. In both years with DON measurements DON accounted for around 15 % of the TN losses (Fig. 6). As the winter is the main discharge period (Table 2) and the NO₃-N concentrations were lower during the summer months (Table 5), 96 %, 75 % and 98 % of the NO₃-N losses took place during the winter months.

4 Discussion

4.1 Controls on DOC and NO₃-N dynamics in the groundwater: effects of the changed hydrological conditions

Average DOC concentrations of $50.6 \pm 15.2 \text{ mgL}^{-1}$ are within the typical range of degraded peatlands; Fiedler et al. (2008) measured, for example, average DOC concentrations of 82 mgL^{-1} in the GW of a deeply drained fen also used as grassland. Kalbitz and Geyer (2002) found mainly lower DOC concentrations ($20\text{--}76 \text{ mgL}^{-1}$), but their soils did also have lower SOC contents than ours. In drained bog peats, higher DOC concentrations are common (Frank et al., 2013). The wet conditions from June 2007 to April 2008 – which are similar to those of recently re-wetted fens – had no clear effect

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on the groundwater DOC concentrations (Fig. 3). Generally, the effect of re-wetting on DOC concentrations is inconsistent and seems to depend on a number of factors such as the type and degradation status of the peat (Cabezas et al., 2013), the SOC content and the pH. While some authors found considerably higher DOC concentrations in re-wetted, highly degraded fens (Kalbitz and Geyer, 2002), others report significantly lower DOC concentrations after re-wetting (Fiedler et al., 2008; Frank et al., 2013; Wallage et al., 2006) or no change at all (Gibson et al., 2009).

Those dipwells with higher DOC concentrations in the wetter year were situated near the ditch (Fig. 3). Due to the drawdown effect of the ditch, the peat there is probably more degraded than in the centre of the field. Degraded peat is especially prone to high DOC losses under re-wetting conditions (Kalbitz and Geyer, 2002; Zak and Gelbrecht, 2007). Although the number of concentration measurements in 2006/07 is too limited to draw final conclusions, the observed minor changes both in the groundwater and in the ditch suggest that no large additional DOC losses would have to be expected under re-wetting conditions.

According to the results of the GLS model (Table 4), deep groundwater tables and strong changes of the WTD result in higher DOC concentrations. Furthermore, there is a negative relationship with the C : N ratio and the temperature. These results can be explained by higher mineralisation rates under these conditions and agree with results of other studies (e.g. Frank et al., 2013). The positive relationship with the groundwater table changes can be interpreted as a transport of DOC from the previously unsaturated zone towards the groundwater under conditions of a risen water table. Including the pH-value into the analysis yielded an even more complex (and possibly overdetermined) model with high DOC concentrations corresponding to low pH-values.

During the first two winters, $\text{NO}_3\text{-N}$ concentrations in some dipwells were extremely high (Fig. 4a), also compared to other studies. High $\text{NO}_3\text{-N}$ concentrations and losses can be explained by the intensive mineralisation of organic matter in drained peatlands (Hacin et al., 2001; Höper, 2002). At our study site, C : N ratios of 9–18 in 0–30 cm depth and additional fertiliser application create a favourable environment for nitro-

gen release. This is supported by the positive relationship between N concentrations of the peat and $\text{NO}_3\text{-N}$ concentrations in the dipwells (Table 4). Beetz and Glatzel (2013) measured net ecosystem exchange (NEE) at two grassland sites in our study area. Excluding harvest, they found gaseous $\text{CO}_2\text{-C}$ losses between around 4000 and 9000 $\text{kg ha}^{-1} \text{ a}^{-1}$. Assuming an average C : N ratio of 14 this corresponds to N mineralisation rates of around 300 to 650 $\text{kg ha}^{-1} \text{ a}^{-1}$. Thus, high $\text{NO}_3\text{-N}$ concentrations are hardly surprising.

Although the concentration levels differed strongly between the single dipwells, $\text{NO}_3\text{-N}$ concentrations generally rose with rising GW levels (Table 4), and the temporal patterns were similar between the dipwells. This can be explained by mineralisation during relatively dry periods and subsequent downward transport of $\text{NO}_3\text{-N}$ by rainfall events. Savard et al. (2007) showed in a dual-isotope study that winter nitrification can indeed be high. Snowmelt events tended to cause a dilution pattern (Tiemeyer et al., 2007), but significant snowmelt did occur only once during our study period.

While concentrations in the first two years were comparable, $\text{NO}_3\text{-N}$ concentrations were clearly lower during the third year of the study period which can be explained by different hydrological conditions. Although small concentration peaks still occurred in the third winter at rising GW levels – or, better after lower GW levels –, the wet summer 2007 had by then completely changed the $\text{NO}_3\text{-N}$ concentration dynamics towards lower and more homogenous values in the groundwater. The drop of the $\text{NO}_3\text{-N}$ concentrations was especially evident at the dip wells in transect C (deep peat), while some dipwells in transect A with a low SOC content were less affected (Fig. 4a). Due to the topography, these dipwells still showed low groundwater levels. The lowered $\text{NO}_3\text{-N}$ concentrations can be explained by denitrification during prolonged periods of high groundwater levels. A high denitrification potential is typical for degraded peatlands (Cabezas et al., 2012; Davidsson et al., 2002). In laboratory studies, $\text{NO}_3\text{-N}$ was found to be depleted within days to weeks (Cabezas et al., 2012; Corstanje and Reddy, 2004). Additionally, and probably more important, as the GW levels during the winter 2007/08 itself were not exceptionally high (Table 2), decreased mineralization during

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the preceding wet summer period may have led to lower $\text{NO}_3\text{-N}$ concentrations. Thus, the effect of the high groundwater table in summer is crucial for re-wetting projects, which should focus on wet conditions during summer when targeting nitrate retention.

Besides the wet summer, the variability of the groundwater table may play an important role for the $\text{NO}_3\text{-N}$ concentrations. The importance of fluctuating water levels for nitrogen mineralisation has been shown in laboratory studies (Corstanje and Reddy, 2004), but is difficult to quantify in the field. Compared to transects A and C, the water level fluctuations in transect B were relatively gentle (Fig. 4b), which resulted in clearly lower $\text{NO}_3\text{-N}$ peaks even in the first two years of the study period. In transect C, the groundwater table was less variable in the last year of the study period (Table 2), which in addition to the wet summer seemed to prevent mineralisation in times of lower water tables.

Overall, the LME model seems to summarise these observations (Table 4): the depth to the groundwater table, the change of the groundwater table, and the nitrogen content of the peat were the most important parameters. Interactions of the temperature with the N content of the soil and the groundwater table change probably indicate the enhanced mineralisation under warmer conditions.

4.2 Controls on DOC and N dynamics in the ditch: anthropogenic effects

DOC concentrations in the ditch (Table 5) were lower than in the groundwater, which is not surprising as the dipwells of transect C were installed in the part of the catchment with the highest SOC content (on average, 36.8 % in 0–30 cm and 45.2 % in 60–90 cm depth, Tiemeyer et al., 2007) and the deepest peat layer.

The average concentrations of 24.9 mg L^{-1} are quite high for a lowland peatland, especially given that only a part of the catchment is covered by organic soils. While in disturbed bogs sometimes much higher concentrations were measured (Frank et al., 2013), undisturbed sites clearly show lower DOC concentrations in the runoff water (Austnes et al., 2010; Dawson et al., 2002; Koehler et al., 2009). Kløve et al. (2010) measured comparable concentration in drainage pipes of agriculturally used peatlands.

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Data on comparable fen sites is largely missing. There is no clear effect of the dry or wet period on the DOC concentrations, which reflects the unchanged concentrations in the groundwater. Furthermore, the relatively high and – in the last year nearly undiluted – concentrations in the ditch strongly support the interpretation that the part of the catchment with organic soils is the main source of water for the ditch.

The highest concentrations were measured in the beginning of the study period, suggesting a flush of pore water enriched with DOC as soon as flow towards the ditch is initiated. In contrast to some other studies (Austnes et al., 2010) where DOC concentrations were found to increase with increasing discharge rates we could not find such a pattern in our catchment (Fig. 2). The reason for this difference can be found in the different hydrological processes resulting in discharge generation: while the catchment studied by Austnes et al. (2010) was covered by blanket peats with a fast response and highly conductive surface layers on sloped terrain, our site is essentially flat and dominated by tile and ditch drainage. Residence time is suggested as further controlling factor for DOC concentrations (Limpens et al., 2008), and indeed we found the best correlation of DOC to the average discharge over the last 60 to 80 days (Fig. 5). This is supported by the GLS model for the complete data set and the sub-set with EC measurements where Q_{70} was found as the only significant influence factor. This permits the interpretation that at higher discharge rates (and high groundwater level) over weeks the water has a shorter contact time with the peat, and less DOC is available for transport. If, in contrast, the water movement is slow, there will be a longer contact time with the peat, and thus an enrichment of the pore water with DOC. Additionally, times of slow water movement frequently coincide with aeration and increased mineralisation.

Only for the data sub-set with pH measurements, the pH-value, the temperature and the EC were included into the GLS model. Although removing these parameters from the model lead to a lower NSC, especially the interaction terms are difficult to interpret, and the model might be overdetermined.

In the ditch, there was a negative correlation between DOC and $\text{NO}_3\text{-N}$ concentrations. The different pattern can be explained as during periods of long residence time,

with the $\text{NO}_3\text{-N}$ concentrations, which reflects the hysteresis effects. As in the case of DOC, the data sub-set with pH measurements seems to be too small to allow plausible interpretations of the resulting complex model.

The $\text{NO}_3\text{-N}$ concentration patterns are strongly influenced by the presence of tile drains in the catchment, which directly discharge water into the ditches. First of all, ongoing drainage causes peat mineralisation and thus nitrogen mineralisation. Tile drain discharge is generally highest under high groundwater levels. These were those phases when during the first two years of the study period, $\text{NO}_3\text{-N}$ concentrations were highest. Thus, tile drainage may cause the water with high $\text{NO}_3\text{-N}$ concentrations to by-pass the deeper anaerobic peat layers, where denitrification could have happened. Due to the transit through saturated zones of peat depleted in oxygen, sometimes even in agriculturally used catchments especially under acidic soil conditions low concentrations of $\text{NO}_3\text{-N}$ were measured (Frank et al., 2013; Sapek et al., 2007; van Beek et al., 2007). Due to the tile drains which are previously found to carry high $\text{NO}_3\text{-N}$ concentrations (Roberts et al., 1986), the responsible processes do not fully work here. This interpretation is supported by lysimeter studies which also lack a prolonged transfer through the saturated zone. While Ross et al. (1995) measured, depending on the fertilisation level, $\text{NO}_3\text{-N}$ concentrations of 0–44 mg L^{-1} , Bergström and Johansson (1991) even found values $> 100 \text{ mg L}^{-1}$ in the lysimeter leachate.

During the last winter of the study period, there was a strong contrast between the $\text{NO}_3\text{-N}$ concentrations in the groundwater and the ditches, i.e. the catchment outlet and ditch directly adjacent to transect C. While the groundwater concentrations were diminished by the wet conditions in the preceding summer, the ditch concentrations were even higher (Fig. 4a). These results raise the question why the relationship between the ditch dynamics and the GW dynamics changed in the in the last year of the study (Fig. 7): there was still a close relationship between the average $\text{NO}_3\text{-N}$ concentrations in the GW and the $\text{NO}_3\text{-N}$ concentrations in the ditch, but the slope has strongly changed. This suggests that the processes in the part of the catchment where

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the dipwells are situated were still important for the catchment response, but that an additional source of $\text{NO}_3\text{-N}$ appeared during the last year of the study.

We suggest that there are two reasons for this observation: in the last year of the study period we observed – unintentionally – the effects of the superposition of changed hydrological conditions – which became apparent in the groundwater concentrations – and land use change, which determined the ditch concentration level and the change in the ditch-GW relationship: firstly, a part of the grassland was converted to arable land for corn production in spring 2007. Ploughing-up grassland can lead to a mobilisation of nitrate even from mineral soils (Sheperd et al., 2001). In an upland pasture on peat, nitrate losses were increased by around 70 % even three years after ploughing and reseeding (Roberts et al., 1986). Secondly, the summer of 2007 was exceptionally wet (Table 2), which caused farmers to renew the ditches and some of the tile-drains. This also affected the freshly ploughed arable land. Although we did not directly measure leaching from this “new” arable land, this combination seems a plausible explanation for the high $\text{NO}_3\text{-N}$ concentration in the ditch despite decreasing concentrations in the groundwater of the grassland.

DON concentrations were relatively low. Factors influencing the DON concentrations were difficult to determine; there is only a very slight effect of the discharge or EC. There was also no correlation between DOC and DON in the ditch water, supporting the assumption that different processes govern the release of DOC and DON (Kalbitz and Geyer, 2002).

4.3 DOC and nitrogen losses

Annual DOC losses from peat catchment as measured by Dawson et al. (2002), Gibson et al. (2009), Kløve et al. (2010) and Koehler et al. (2009) are considerably higher ($108\text{--}191 \text{ kg ha}^{-1}$) than our values (Fig. 6), but all these study focussed on upland areas with high discharge rates. Results from Fraser et al. (2001) are closer (83 kg ha^{-1}) to ours, but their system – a northern bog – is very different to our site. Data on agriculturally used lowland peatlands with fen peat is surprisingly scarce and we could find

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no data on comparable sites. Even if the DOC losses from our study site were not extraordinarily high, they could cause problems further downstream, i.e. for drinking water treatment. However, when comparing our DOC and N losses to other studies on peatlands, it has to be taken into account that only a part of the catchment is covered by organic soils.

We measured higher DOC losses in the wetter year (Fig. 6), but this was solely controlled by the discharge rates, not by the concentrations in the ditch or in the groundwater. As the groundwater concentrations remained largely unchanged by the extreme meteorological conditions, we would expect, at least in the short-term, similar DOC losses under re-wetting conditions, especially if more water was retained in the catchment.

At two grassland sites within the catchment, Beetz and Glatzel (2013) measured a net ecosystem exchange (NEE) between around 4000 and 9000 kg ha⁻¹. Thus, fluvial carbon losses of, on average, 53 kg ha⁻¹ do not play a large role for the total carbon budget of the catchment. Even assuming that the only origin of the DOC is the part of the catchment with organic soils, DOC only accounts for around 2 % of the gaseous carbon losses. These results seemingly contrast other studies where fluvial carbon losses form an important part of the carbon balance (Dinsmore et al., 2010). These near-natural catchments, however, have a significantly lower NEE resulting in a higher relative importance of the DOC losses. Moreover, they show higher discharge rates and thus higher DOC losses than our catchment.

Although it is widely known that NO₃-N can be released when peatlands are drained, there are surprisingly few studies actually providing numbers. The value (38 kg N ha⁻¹ a⁻¹) given by van Beek et al. (2007) for an experimental field in the Netherlands, however, is comparable to our results. Even under drained-conditions, nitrate losses even from agriculturally used peatlands are sometimes quite low as the water passes the permanently saturated part of the peat where optimal conditions for denitrification prevail (Kløve et al., 2010). However, in our case the tile-drains in parts of the catchment seem to cause an effective by-pass of the saturated zone. The su-

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perposition of hydrological and management effects are probably the reason why the wet conditions from June 2007 to April 2008 were not reflected by decreasing $\text{NO}_3\text{-N}$ losses from the catchment. Our values are lower than those of the lysimeter studies of Behrendt et al. (1996) and Roberts et al. (1986) who measured annual losses of more than $100 \text{ kg NO}_3\text{-N ha}^{-1}$. These higher values might be explained by the methodological differences and, in the case of Roberts et al. (1996), much higher precipitation. Lysimeter discharge and losses from Bergström and Johansson (1991) are, however, comparable to our results, while Ross et al. (1985) found clearly lower losses ($1\text{--}14 \text{ kg NO}_3\text{-N ha}^{-1} \text{ a}^{-1}$) from their lysimeters, but they neither report on discharge nor water table levels. In the regional context, the $\text{NO}_3\text{-N}$ losses are as high as or higher than losses from tile-drained arable land which is widely found to be important for N pollution (Tiemeyer et al., 2006).

Compared to theoretical losses between 300 and $650 \text{ kg ha}^{-1} \text{ a}^{-1}$ and an additional average field nitrogen budget of $81 \text{ kg ha}^{-1} \text{ a}^{-1}$ (Table 1), substantial amounts of mineral N have to be denitrified or immobilized within the peatland. Van Beek et al. (2007), for example, estimate an annual denitrification of 213 kg N ha^{-1} . Due to the high spatial variability it is difficult to assess how much $\text{NO}_3\text{-N}$ produced in the unsaturated zone is denitrified on its pathway to the ditches. Similarly, the might be input by groundwater flow or leaching to the deeper groundwater, which we cannot quantify.

Compared to DOC and $\text{NO}_3\text{-N}$, there is even less information on DON losses from lowland peatland catchments. In a near-natural blanked bog catchment, Adamson et al. (1998) measured DON losses in the same range (5.7 to $6.5 \text{ kg ha}^{-1} \text{ a}^{-1}$) as our values, but these are the result of much lower DON concentrations and higher discharge rates. As mineral nitrogen concentrations were very low in this study, DON formed 85% of the total nitrogen losses. Also in a catchment with high discharge rates, Kløve et al. (2010) measured average DON losses of $11 \text{ kg ha}^{-1} \text{ a}^{-1}$ from drained peat corresponding to 50% of the N losses. Results in our catchments were the other way round as in both years as DON losses accounted for around 15% of the TN losses. Nonetheless, DON may form a relevant component of the N balance of drained peat-

land catchments and even more so of re-wetted peatlands with decreased $\text{NO}_3\text{-N}$ concentrations. In addition, the controls on the DON concentration dynamics are not clear so that the topic seems to call for further attention.

5 Conclusions

5 We measured DOC and N concentrations in and losses from a grassland peatland under changing conditions. While the situation during the first 1.5 yr were typical for the region, the remainder of the study period saw a superposition of very wet conditions (in its effects, similar to re-wetting) and land use change. The results suggest that under re-wetting conditions, groundwater $\text{NO}_3\text{-N}$ concentrations would decrease very quickly, while DOC concentrations would remain on a similar level. Relatively, DOC losses did not constitute a major part of the carbon balance, but this is mainly because of the high NEE of a drained peatland, as the losses themselves are comparable to other studies. In this case, summer groundwater levels and groundwater table fluctuations decide on $\text{NO}_3\text{-N}$ concentrations in the subsequent winter. Further intensification of the land use, on the other hand, might increase the $\text{NO}_3\text{-N}$ losses to receiving waters. DON accounted for around 15% of the total N losses, but factors influencing DON concentrations deserve further study. In the light of the European Water Framework Directive, re-wetting peatlands is a valuable tool for reducing N losses to lowland rivers.

15
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Table 1. Management.

Period	N fertilisation grassland kg ha ⁻¹	N field balance grassland kg ha ⁻¹	N field balance catchment kg ha ⁻¹
2002/03	230	90	93
2003/04	230	90	100
2004/05	228	87	103
2005/06	184	54	92
2006/07	159	62	49
2007/08	240	102	54

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Table 2. Hydrological and meteorological conditions during the study period: precipitation (P), reference crop evapotranspiration (ET_c), discharge at the outlet (Q), mean and standard deviation water table depth (WTD), and temperature (T). Long-term averages: German Weather Service raster data 1990–2011. No groundwater level data is available for the summer 2008 (n.d. = not determined).

Period	P mm	ET_c mm	Q mm	WTD mean m	SD m	T °C
2005/06	701	507	165	0.74	0.18	8.9
Winter	289	68	158	0.51	0.18	1.7
Summer	413	439	17	0.98	0.19	16.0
2006/07	934	485	270	0.58	0.22	10.0
Winter	383	124	179	0.51	0.17	6.0
Summer	551	361	91	0.65	0.28	14.0
2007/08	554	515	180	n.d.	n.d.	9.0
Winter	346	99	177	0.37	0.10	4.0
Summer	208	416	4	n.d.	n.d.	13.9
Long-Term Mean	642	561	–	–	–	8.7
Winter	271	130	–	–	–	3.1
Summer	372	431	–	–	–	14.3

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Table 3. Dissolved organic carbon (DOC) and nitrate-nitrogen (NO₃-N) concentrations in the dipwells (n.d. = not determined).

Period	DOC			NO ₃ -N		
	mean ± std mgL ⁻¹	min mgL ⁻¹	max mgL ⁻¹	mean ± std mgL ⁻¹	min mgL ⁻¹	max mgL ⁻¹
2005/06	n.d.	n.d.	n.d.	8.8 ± 12.9	0	65.4
2006/07	46.8 ± 17.9	14.9	80.1	10.3 ± 15.4	0	79.4
2007/08	51.4 ± 14.6	21.4	88.5	2.4 ± 4.6	0	21.3

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Table 4. Coefficients of the GLS (DOC) and LME (NO₃-N) model for the DOC and the NO₃-N concentrations in the groundwater samples. WTD – water table depth, Δ WTD – change of the WTD within the last week, WTD₃₀ – average WTD of the last 30 days, T – air temperature, T_{30} – average air temperature of the last 30 days, dist – distance to the drainage ditch, N – nitrogen content of the topsoil, SOC – soil organic carbon content of the topsoil, CN – C : N ratio of the topsoil, period – wet or dry period.

Parameter	DOC		DOC (with pH)		NO ₃ -N	
	value	p	value	p	value	p
WTD	66.84	< 0.0001	176.81	< 0.0001	-11.03	< 0.0001
Δ WTD	63.28	0.0382	136.23	0.0009	-4.30	< 0.0001
WTD ₃₀			10.62	0.7850		
T	-0.30	0.3471	-0.94	0.0008	0.02	0.4634
T_{30}	5.65	0.0001	-18.75	0.0373		
dist			0.56	< 0.0001		
N	4.91	< 0.0001	8.93	< 0.0001	0.44	0.0001
SOC					-0.56	0.0012
CN	-13.62	< 0.0001	-25.22	< 0.0001		
pH			-14.71	0.0536		
period					6.48	< 0.0001
WTD : T_{30}	-10.08	0.0007	-51.05	< 0.0001		
Δ WTD : T	21.90	< 0.0001	15.40	< 0.0001	0.69	< 0.0001
Δ WTD : T_{30}	-35.49	0.0001	-59.46	< 0.0001		
WTD ₃₀ : T_{30}			36.33	0.0001		
T_{30} : pH			3.57	0.0066		
T : N					0.005	0.0003

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Table 5. Dissolved organic carbon (DOC), nitrate-nitrogen (NO₃-N) and dissolved organic nitrogen (DON) concentrations in the ditch (n.d. = not determined).

Period	DOC			NO ₃ -N			DON				
	mean ± std mgL ⁻¹	min mgL ⁻¹	max mgL ⁻¹	mean ± std mgL ⁻¹	min mgL ⁻¹	max mgL ⁻¹	mean ± std mgL ⁻¹	mgL ⁻¹	min mgL ⁻¹	max mgL ⁻¹	
2005/06	n.d.	n.d.	n.d.	8.1 ± 5.1	0	15.9	n.d.	n.d.	n.d.	n.d.	
Winter	n.d.	n.d.	n.d.	9.5 ± 4.6	0	15.9	n.d.	n.d.	n.d.	n.d.	
Summer	n.d.	n.d.	n.d.	2.5 ± 2.4	0	7.6	n.d.	n.d.	n.d.	n.d.	
2006/07	26.7 ± 6.6	15.1	47.7	9.6 ± 6.0	0	25.5	2.3 ± 0.7	0.7	6.2	6.2	
Winter	27.3 ± 6.7	15.4	39.4	10.9 ± 6.4	0	25.5	2.1 ± 0.6	0.7	3.8	3.8	
Summer	25.2 ± 6.2	15.1	47.7	6.9 ± 4.1	0	13.0	2.7 ± 0.8	1.5	6.2	6.2	
2007/08	22.6 ± 3.7	13.1	30.6	12.6 ± 4.4	0.2	21.2	2.6 ± 0.8	0.9	5.2	5.2	
Winter	22.5 ± 3.7	13.1	30.6	13.1 ± 3.7	5.6	21.2	2.6 ± 0.8	0.9	5.2	5.2	
Summer	24.4 ± 0.8	23.5	25.5	3.6 ± 3.1	0.2	9.1	1.9 ± 0.2	1.7	2.1	2.1	

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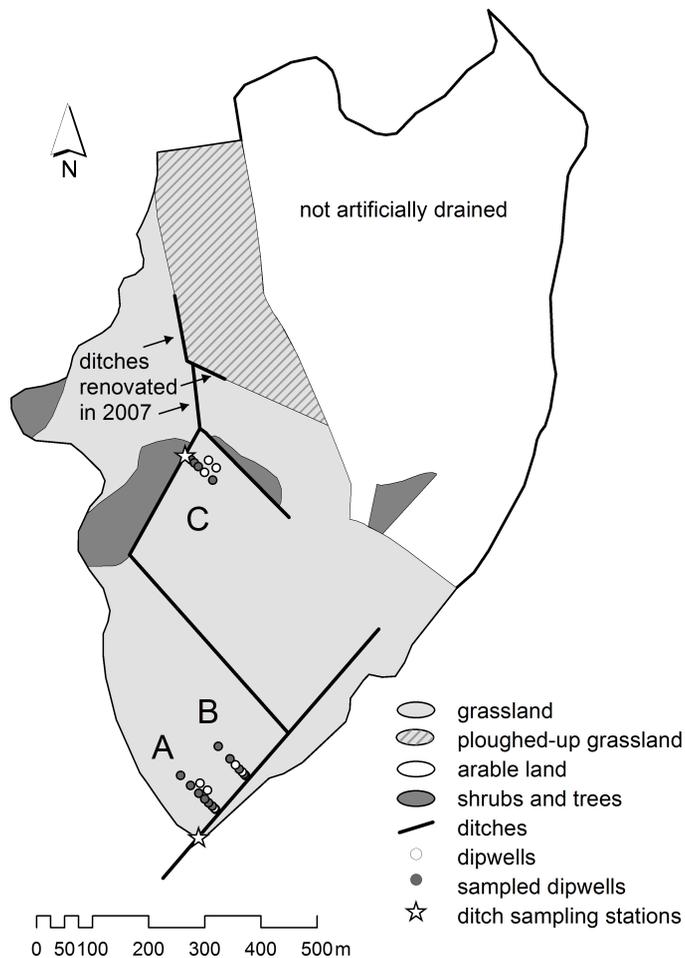


Fig. 1. The study area.

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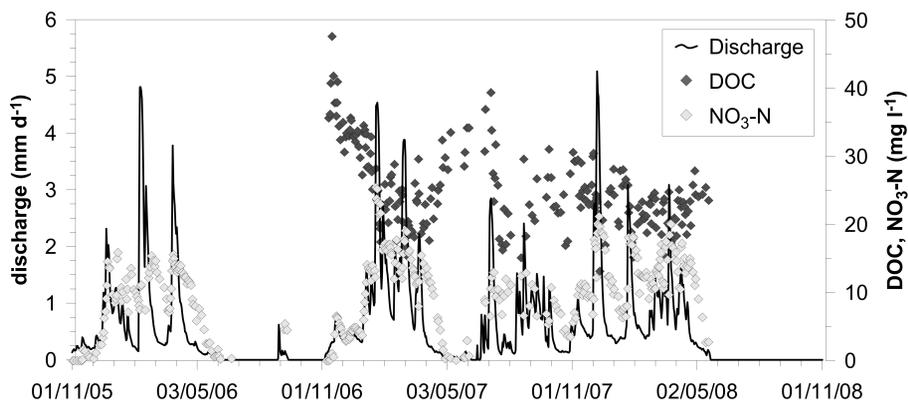


Fig. 2. Discharge (mm d^{-1}) and concentrations (mg L^{-1}) of dissolved organic carbon (DOC) and nitrate-nitrogen ($\text{NO}_3\text{-N}$) in the ditch.

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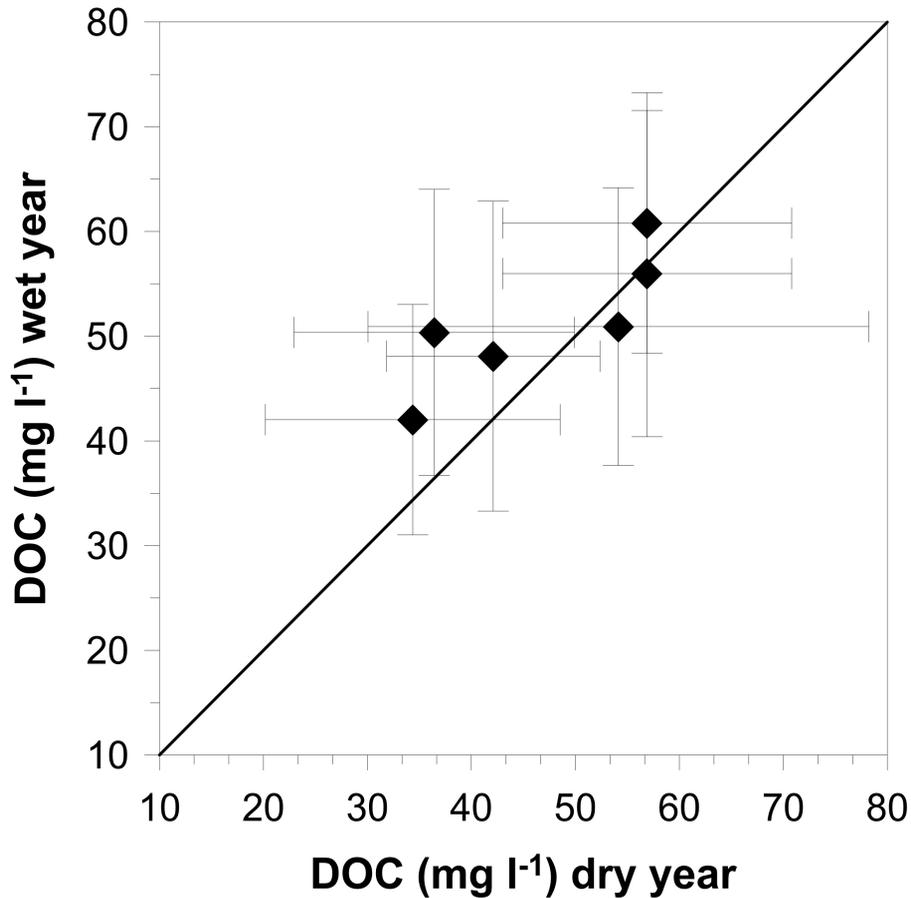


Fig. 3. Average (\pm standard deviation) DOC concentrations in the dry winter 2006/07 and in the wet winter 2007/08 in the dipwells of transect C.

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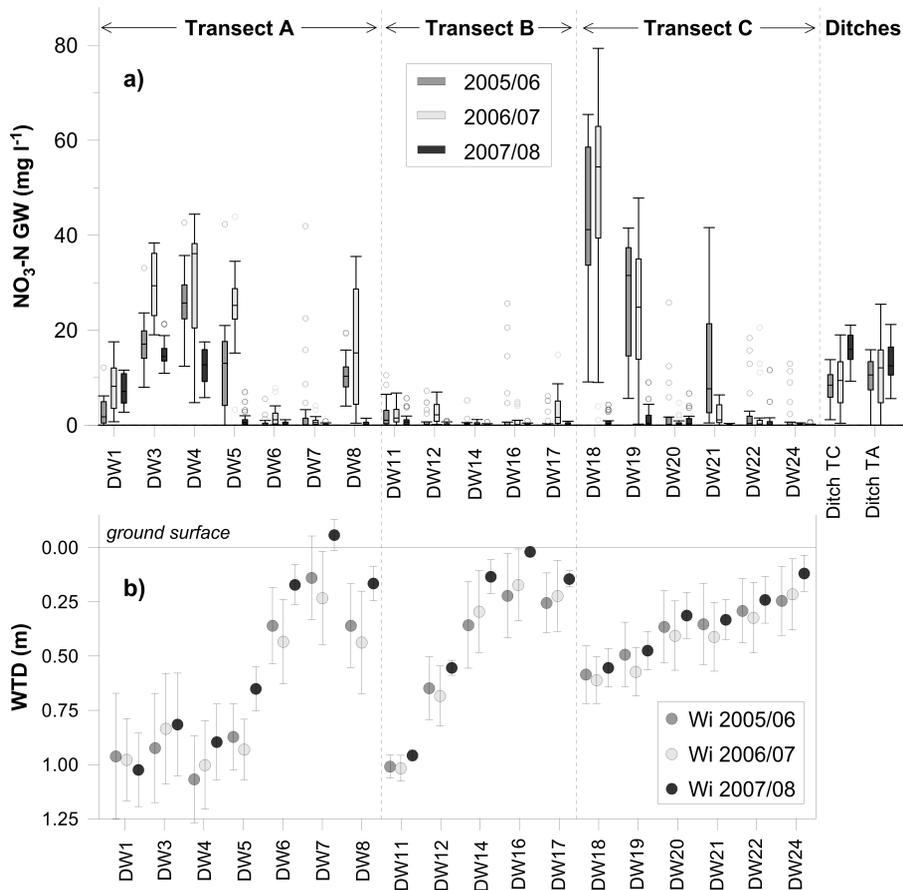


Fig. 4. (a) Spatial and temporal variability of nitrate-nitrogen (NO₃-N) concentrations in the dipwells; **(b)** Mean and standard deviation of the water table depth (WTD) during winter. Only sampled dipwells are shown.

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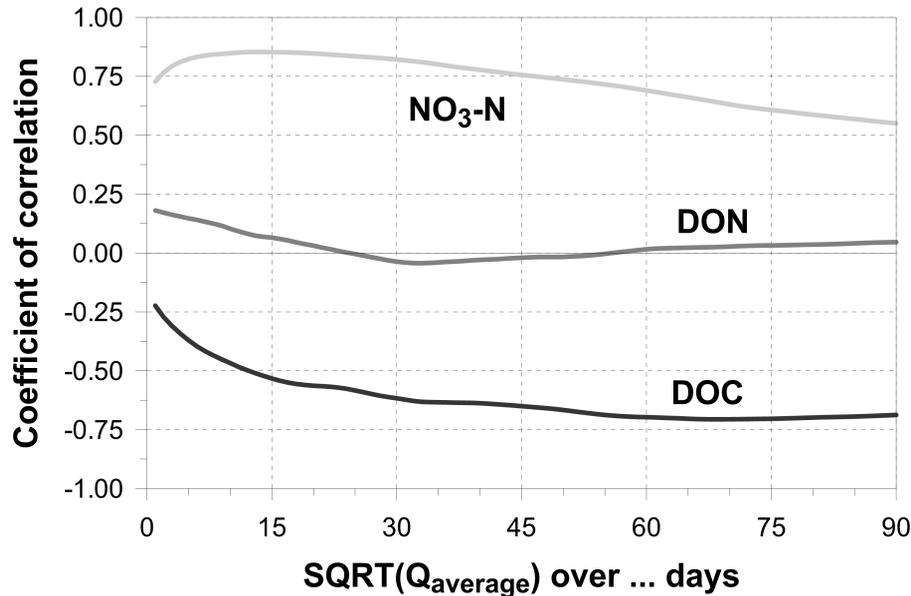


Fig. 5. Cross-correlation between the square root of the average discharge Q_{average} in the ditch and the concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and nitrate-nitrogen ($\text{NO}_3\text{-N}$).

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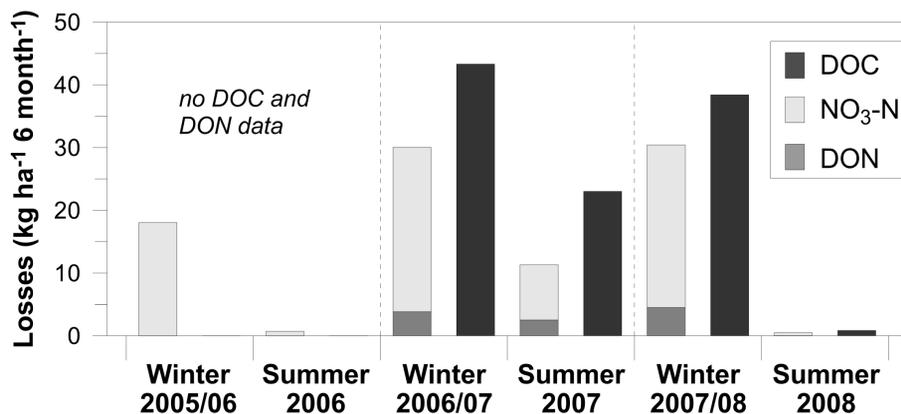


Fig. 6. Seasonal losses of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and nitrate-nitrogen (NO₃-N).

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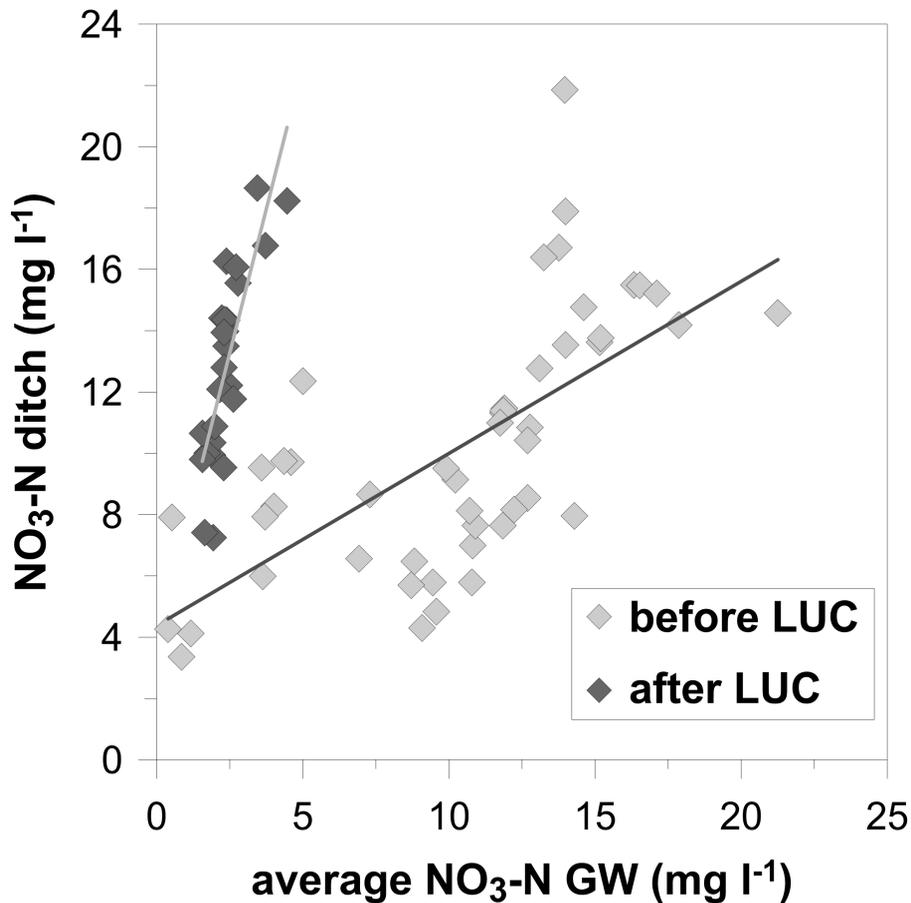


Fig. 7. Relationship between the average nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations in the dipwells and the $\text{NO}_3\text{-N}$ concentrations in the ditch before and after land use change (LUC). $\text{NO}_3\text{-N}$ concentrations of the ditch are 10 day-means starting at the date of dipwell sampling.