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Pore water velocity and ionic strength effects on DOC release from peat-sand mixtures: Results from laboratory and field experiments

Bärbel Tiemeyer [a],*, Nora Pfaffner [a,b,1], Stefan Frank [a,2], Klaus Kaiser [c], Sabine Fiedler [b]

[a] Thünen-Institute of Climate-Smart Agriculture, Bundesallee 50, 38116 Braunschweig, Germany
[b] Institute for Geography, Johannes Gutenberg University Mainz, Johann-Joachim-Becher-Weg 21, 55099 Mainz, Germany
[c] Soil Sciences, Martin Luther University Halle-Wittenberg, von-Seckendorff-Platz 3, 06120 Halle (Saale), Germany

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ABSTRACT

Organic soils are the most important source of dissolved organic carbon (DOC) in surface water. To date, most studies have focused on natural and re-wetted peatlands, but in Central Europe a large proportion of organic soils are drained and under agricultural use. Furthermore, measures such as deep ploughing or sand addition have been conducted to improve trafficability and have resulted in topsoil horizons consisting of a peat-sand mixture. Very little is known about DOC losses from such soils. Moreover, peat soils frequently feature both mobile zones, characterised by active water and solute transport, and immobile zones, which exchange solutes with the mobile zone by diffusion. Surprisingly, however, the effects of this dual porosity on DOC transport have not yet been explored. This study investigated the physicochemical controls on DOC concentrations in a peat-sand mixture by means of a saturated column experiment with undisturbed columns. The soil came from a former bog in northern Germany where peat layers remaining after peat extraction were mixed with the underlying mineral soil by ploughing. Three pumping rates and two levels of electrical conductivity (EC) were applied. The transport properties of the soil were obtained by analysing breakthrough curves of potassium bromide using the transport model STANMOD, which is based on the two-region non-equilibrium concept. The results of the column study were compared to DOC concentrations measured bi-weekly for two years at the field site from where the columns were taken. Despite a similar texture and soil organic carbon (SOC) content, the fraction of the mobile zone in the columns varied between 51% and 100% of total porosity. Thus even heavily degraded organic soils mixed with sand still showed a dual porosity comparable to degraded peat soils. Percolating the columns with the high EC solution caused low pH values, probably due to ion exchange and cation bridging. The combination of high EC and low pH greatly decreased DOC concentrations at the outlet of the columns. DOC concentrations decreased and fluxes increased as the pumping rates increased. Taking pore water velocity in the mobile zone into account could help to explain the differences between the columns. Overall, transport of DOC did not seem to be limited by production of DOC, but by rate-limited exchange processes. In contrast to the column experiment, field concentrations of DOC were much higher and were not related to pH, but increased with higher electrical conductivity. These higher concentrations could be explained by low pore water velocities and the slightly higher SOC content in the field. This first experiment on DOC transport in peat-sand mixtures taking the dual-porosity nature of organic soils into account clearly demonstrated the importance of pore water velocity and thus the residence time for DOC concentrations. While hydrochemical conditions are frequently addressed in laboratory studies, there is a need for improved understanding of their interaction with hydrology and soil-physical properties, especially when attempting to interpret DOC data on different spatial and temporal scales.

1. Introduction

Organic soils are the most important source of dissolved organic carbon (DOC) in surface water (Aitkenhead et al., 1999). Most studies investigating the release of DOC from organic soils have focused on natural and re-wetted peat soils (Clark et al., 2005; Evans et al., 2012; Koehler et al., 2009; Wallage et al., 2006), but the majority of organic soils in central Europe are drained for agriculture or forestry use (Lappalainen, 1996). While there have been a few studies on DOC

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* Corresponding author.
E-mail addresses: baerbel.tiemeyer@thuenen.de (B. Tiemeyer), npfaffn@uni-goettingen.de (N. Pfaffner), stefan.frank@lbeg.niedersachsen.de (S. Frank), klaus.kaiser@landw.uni-halle.de (K. Kaiser), s.fiedler@geo.uni-mainz.de (S. Fiedler).

[1] Present address: Department of Physical Geography, Institute of Geography, Georg-August University of Göttingen, Goldschmidtstrasse 5, 37077 Göttingen, Germany.

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

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concentrations in agricultural peatlands (Frank et al., 2014; Schwalm and Zeitz, 2015) and natural organo-mineral soils (Clark et al., 2011; Stutter et al., 2007a), there is very little information on DOC concentrations in organic soils that have been disturbed by being mixed with sand. There is only one single laboratory study on the effects on water quality of mixing peat with mineral soil, suggesting that the concentrations of several solutes, including DOC, increase as the remaining peat aggregates decrease in size (Ross and Malcolm, 1988). Measures such as deep ploughing or sand addition followed by normal ploughing have frequently been practised to improve trafficability, and have resulted in topsoil horizons consisting of a peat-sand mixture. For example, in north-western Germany, at least 17% of the organic soils used agriculturally have been subjected to sand mixing or application (Schulz and Waldeck, 2015). Similar measures have been implemented in Scandinavia (Sognnes et al., 2006) and The Netherlands (de Bakker, 1978). Biogeochemical data on such soils are scarce. Results on greenhouse gas emissions suggest drained peat-sand mixtures are still strong sources of carbon dioxide (Leiber-Sauheitl et al., 2014). Field data at the same study site showed high DOC concentrations irrespective of the soil organic carbon (SOC) content and the pH (Frank et al., 2017). However, to the best of the authors' knowledge, no attempts have been made besides the study by Ross and Malcolm (1988) to explain the effects of sand mixing on water quality.

After peat extraction, former bogs are frequently re-wetted to initiate new peat formation (Andersen et al., 2016; Gorham and Rochefort, 2003; Poschlod et al., 2007). Depending on the extraction depth, the local geohydrology, and the re-wetting method, formerly rain-fed sites may become influenced by groundwater or allochthonous surface water with higher nutrient contents and ionic strength (Graf and Rochefort, 2008; Malloy and Price, 2014). The effects of re-wetting on the peatland's biogeochemistry (e.g. Frank et al., 2014; Strack and Zuback, 2013) and biodiversity (e.g. Poschlod et al., 2007) need to be evaluated to define appropriate restoration goals, taking into account changes in hydrology and hydrochemistry compared to the pre-extraction conditions (Graf and Rochefort, 2008; Malloy and Price, 2014).

Ionic strength has frequently been suggested as an important driver of DOC concentrations in surface waters (Hruška et al., 2009), since a high ionic strength reduces the solubility of DOC (Kalbitz et al., 2000; Tipping and Hurley, 1988). However in field studies it is difficult to differentiate potential drivers of DOC concentrations such as water table depth (WTD) (Frank et al., 2014; Wallage et al., 2006), temperature (Koehler et al., 2009), ionic strength (Clark et al., 2011) and pH (Evans et al., 2012) because these factors may interact. For instance, high temperatures may cause lower WTD, which in turn induces lower pH and higher ionic strength due to sulphate formation (Clark et al., 2005). Moreover, different processes operate on different spatial and temporal scales and with different lag times, thus complicating the causal interpretation of DOC data (Clark et al., 2010).

Laboratory studies on DOC in organic soils are frequently run without percolation and/or with disturbed soil samples (Clark et al., 2011; Grybos et al., 2009; Münch et al., 2002). Therefore, the majority of studies do not address effects of flow velocity or non-equilibrium flow on DOC or other solutes. Non-equilibrium flow and transport can be caused by mobile and immobile zones within the soil (Jarvis, 2007). According to the concept of dual porosity, water only moves within the mobile zone while water in the immobile zone is stagnant, and solute exchange between the two domains only happens via diffusion (van Genuchten and Wierenga, 1976). In the context of DOC studies, Kalbitz et al. (2000) have already pointed out the discrepancies between laboratory and field results due to preferential flow being neglected in laboratory studies. There is little data on peat soils, but Forsmann and Kjaergaard (2014) showed that release rates of phosphorus under preferential flow conditions are less than those obtained in batch studies.

Based on scanning electron microscopic imaging and theoretical considerations, Loxham (1980) recognised early on the importance of immobile zones in peat for solute transport. Despite growing interest in DOC and nutrient release from organic soils, there have only been a few studies on the transport properties of organic soils. These studies have shown that pristine (Hoag and Price, 1997), moderately decomposed (Ours et al., 1997; Rezanezhad et al., 2012) and strongly degraded (Kleimeier et al., 2014) peat soils feature immobile zones. Some of these studies (Kleimeier et al., 2014; Rezanezhad et al., 2012) used re-packed peat material, which complicates the interpretation of results. No study has focused on the solute transport characteristics of peat-sand mixtures. To the best of the authors' knowledge, there has also been no study on the dual porosity of organic soils in conjunction with DOC transport, although it has been suggested that mean residence time, which is greatly affected by the extent of immobile zones, controls DOC concentrations (Limpens et al., 2008).

Here, we aim to improve our understanding of DOC dynamics in peat-sand mixtures using both laboratory and field data. By quantifying the transport properties of undisturbed columns collected at the field site with a bromide tracer test in the laboratory, we wish to take into account effects of the dual porosity nature of organic soils on DOC concentrations and fluxes. Furthermore, we want to test the impact of pore water velocity and ionic strength on DOC concentrations in these columns to improve the understanding of the dynamics of the DOC concentrations in the field. It was hypothesized that:

(1) due to the peat-derived organic material, peat-sand mixtures exhibit a dual porosity nature,
(2) higher pore water velocities, either induced by experimental boundary conditions or by a larger share of immobile regions, cause decreasing DOC concentrations,
(3) high ionic strength, i.e. high electrical conductivity, causes lower DOC release than low electrical conductivity,
(4) and experiments under controlled laboratory conditions provide reasonable estimates of DOC mobilisation under field conditions.

2. Material and methods

2.1. Study area

The "Großes Moor" study area is a former bog in north-western Germany. Mean annual precipitation and temperature are 663 mm and 8.5 °C respectively. At the study site, shallow peat (≈30 cm) remained after peat extraction. In parts of the study area, the remaining peat was mixed with the underlying sand by ploughing (≈30 cm), leading to a very heterogeneous soil. After several years of more intensive agricultural use, the study site became a nature conservation area in

Table 1

Basic soil properties of the soil columns and the upper horizon (0–30 cm) of the field sites (SOC, soil organic carbon; C/N ratio, carbon to nitrogen ratio; n.d. not determined). Sand, silt and clay fractions refer to the fine soil. Pore volume is only a useful parameter for samples of a defined volume. $C_{low}W_{29}$: sampling site with a low SOC content and a mean water table depth of 29 cm; $C_{low}W_{14}$: low SOC content and mean water table depth of 14 cm (Leiber-Sauheitl et al., 2014).

		Columns				Field	
Parameter	Unit	C1	C2	C3	C4	$C_{low}W_{29}$	$C_{low}W_{14}$
SOC	(g kg^{-1})	46.9	48.6	57.9	47.7	113.0	93.0
pH ($CaCl_2$)	–	n. d.	n. d.	n. d.	n. d.	4.5	4.5
C/N ratio	–	20	21	25	20	27	24
Bulk density	(g cm^{-3})	1.31	1.33	1.31	1.30	1.06	0.97
SOC stock (kg m^{-2} m^{-1})	55	59	65	56	107	81	
Porosity	–	0.45	0.47	0.47	0.47	0.59	0.59
Pore volume	ml	673	710	704	708	–	–
Coarse material	(g kg^{-1})	100	86	140	98	n. d.	n. d.
Sand	(g kg^{-1})	848	835	838	839	717	856
Silt	(g kg^{-1})	106	119	116	116	212	102
Clay	(g kg^{-1})	47	46	46	46	72	42

1980 and is now used as grassland with low-intensity sheep grazing. Details of the study site are given in Table 1 and in Leiber-Sauheitl et al. (2014), who measured greenhouse gas emissions.

2.2. Column experiment

Undisturbed soil columns 9.8 cm in diameter and 20 cm in length were taken from the area between the sites referred to as "$C_{low}W_{29}$" and "$C_{low}W_{14}$" in Leiber-Sauheitl et al. (2014). These sites have mean water table depths (WTD) of 29 cm and 14 cm respectively (July 2011 to June 2013) and a low SOC content due to ploughing. After removal of the sward and the first 5 cm of soil with a dense root system, the soil was pre-cut with a knife. The columns were then gently pushed into the soil until they were completely filled before finally being carefully dug out. Five columns were taken in total, of which one was used for a pre-experiment and four for the actual experiment.

Due to the heterogeneity of the study site, the mean SOC content at the field sites were slightly higher than those in the column samples, despite the samples being taken from the area between the two sites (<5 m apart). Accordingly, bulk density and porosity also differed between the columns and mean field conditions. In contrast, the four columns had similar properties, especially with regard to SOC and texture (Table 1).

The experiments were carried using a column system (emc GmbH, Erfurt, Germany). Briefly, four columns can be run in parallel, each fed by an individual percolation solution and placed onto a balance (Münch et al., 2002, Fig. S1). All the columns were fed by a peristaltic pump, and thus were subjected to the same flow regime. Filter plates (ecoTech Umwelt-Meßsysteme GmbH, Bonn, Germany) were placed at the top (outlet, 0.45 μm) and bottom (inlet, 0.2 mm) of the columns. The experiments can either be run in a closed circuit (e.g. for saturation of the columns) or samples can be taken according to a user-defined sampling scheme.

Two different percolation solutions and three pumping rates were used, and the study was concluded by a tracer experiment with potassium bromide (Table 2). A pre-experiment was performed with one additional column to test when quasi-constant DOC concentrations would be reached. On the basis of this pre-experiment, it was decided that each experimental step should correspond to the exchange of 10 pore volumes (PV). Due to minor differences in soil properties, the steps lasted 8.4 to 12.8 pore volumes during the actual experiment.

The experiment was conducted under saturated conditions. Prior to the actual experiment ("step 0"), the soil columns were saturated with the percolation solution. To ensure saturation, the pumps were switched off several times to allow water re-distribution, and finally saturation was determined by the constant weights of the supply flasks. During the whole experiment, theoretical pumping rates were corrected using the actual weight losses of the supply flasks.

During steps 1 to 3, the pumping rate was varied to test the effects of different pore water velocities (0.5, 0.1 and 1.05 ml min^{-1}). The maximum pumping rate was set to the saturated hydraulic conductivity measured at the field sites. During step 4, the pumping rate was again set to 0.5 ml min^{-1} to test for initial effects.

Two percolation solutions were selected to mimic the electrical conductivity of the soil solution sampled in the field and of a "hypothetical" groundwater (or surface water). For steps 0 to 4, two columns (referred to as "column pairs" below) were percolated with each percolation solution. As a proxy to natural conditions, a mixture of sodium chloride and calcium chloride was used (Table 3), and the pH of the percolation solutions was adjusted to pH 5.3 with hydrochloric acid. The percolation solutions of the two column pairs were exchanged in step 5 to test for effects caused by the heterogeneity of soil properties.

As the last step, a tracer experiment was conducted with potassium bromide. The percolation solutions were changed to the tracer solution (500 mg l^{-1} bromide). The columns were percolated with this solution until the EC of the effluent of the columns reached the EC of the tracer solution. Finally, the percolation solution was changed back to percolation solution B (PB) for all columns.

For steps 1 to 5, 60 samples (10 ml) were taken at each step. Sampling frequency decreased from 20 samples, i.e. one sample every 90 min, during the first PV of each step to two samples, i.e. one sample every 15 h, during the last three PVs. During the tracer experiment, samples were taken every 90 min at the beginning and after changing back to PB; at the end sampling frequency was reduced to one sample every 15 h. The excess solution was collected in two waste flasks. The two column pairs C1/C2 and C3/C4 each shared one waste flask. The flasks were changed daily and the solution was analysed for EC and pH. Four samples from each of the experimental steps 1 to 5 were chosen for the analysis of sulphate (SO_4^{2-}) and total iron (Fe_t). These samples were shaken and divided into two subsamples. One subsample was decanted before analysis of DOC, Fe_t and SO_4^{2-}, and the other subsample was acidified to pH 2 before measurement of DOC and $Fe_{t.}$

2.3. Field study

Borosilicate glass suction plates (ecoTech Umwelt-Meßsysteme GmbH, Bonn, Germany) were installed in triplicate at 15 cm depths at sites "$C_{low}W_{29}$" and "$C_{low}W_{14}$". These two sites differ in WTD, but only marginally so in SOC. Soil solutions were collected by applying suction according to tensiometer (T8, UMS GmbH, Munich, Germany) readings at the sampling depth. Samples were collected in dark glass bottles over two-week periods for two years (June 2011 to May 2013) as described in detail in Frank et al. (2017). At both sites, WTD was recorded using MiniDivers (Schlumberger Water Services, Delft, The Netherlands).

2.4. Analytical methods

Field solution samples were analysed for pH and EC immediately upon arrival at the laboratory (WTW, Weilheim, Germany). They were then filtered through 0.45 μm polyethersulfonate membrane filters (Pall Life Science, Port Washington, NY, USA). For the solutions obtained in the column experiment, filtering was not necessary due to the filter plate (0.45 μm) at the column outlet. DOC was measured with a DimaToc 2000 (DIMATEC, Essen, Germany). The system runs two columns and detectors, allowing for parallel determination of dissolved inorganic carbon (DIC, combustion at 165 °C after acidification with phosphoric acid) and total dissolved carbon (TDC, combustion at

Table 2
Experimental scheme. PR: pumping rate, PA: percolation solution A (electrical conductivity 1064 μS cm^{-1}, pH 5.3), PB: percolation solution B (electrical conductivity 94 μS cm^{-1}, pH 5.3).

	Step 0	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Pre-defined PR (ml min^{-1})	0.50	0.50	0.10	1.05	0.50	0.5	0.5
Actual PR (ml min^{-1})	n.d.	0.45 ± 0.04	0.13 ± 0.01	0.97 ± 0.03	0.46 ± 0.02	0.48 ± 0.02	0.47 ± 0.01
Column 1	——Percolation solution A——					PB	Tracer[a]
Column 2	——Percolation solution A——					PB	Tracer
Column 3	——Percolation solution B——					PA	Tracer
Column 4	——Percolation solution B——					PA	Tracer

[a] Potassium bromide.

Table 3
Chemical composition of the percolation solutions (n.d.: not determined).

	NaCl	$CaCl_2$	KBr	EC	pH
	[mg l^{-1}]			[μS cm^{-1}]	–
Percolation solution A (PA)	193	485	0	1064	5.3
Percolation solution B (PB)	15	38	0	94	5.3
Tracer solution	0	0	745	825	n.d.

850 °C). DOC is calculated as the difference between TDC and DIC. Each sample was measured in at least three replicates. Sulphate and bromide (Br^-) concentrations were measured with the 850 Professional (Metrohm, Filderstadt, Germany) ion chromatograph.

Total iron was measured at selected samples (n = 40) using inductively coupled plasma-optical emission spectroscopy (Ultima 2, Horiba Jobin-Yon S.A.S., Longjumeau, France). Total iron and DOC was additionally analysed for these selected samples acidified to pH 2.

After completing the column experiments, all soil of each column was oven-dried (60 °C) and weighed to determine bulk density. After sieving (<2 mm), the texture (sieve-pipette analysis) of the fine earth fraction was determined. Columns were assumed to be saturated during the experiment. This allowed the calculation of the pore volume PV and the porosity *f* of each column from the mass of the saturated soil ($m_{saturated}$), the mass of the dry soil (m_{dry}), the density of water (ρ_{H2O}) and the volume of the columns (V_{column}):

$$PV = \frac{m_{saturated} - m_{dry}}{\rho_{H_2O}} \tag{1}$$

$$f = \frac{PV}{V_{column}} \tag{2}$$

Finally, an aliquot of the soil samples was ground and total organic carbon (TOC) was determined with a LECO TrueMac CN analyser (LECO Corporation, ST. Joseph, Michigan, USA).

2.5. Modelling DOC baseline concentrations and tracer transport

The dependency of DOC concentrations on the percolated pore volumes (*PV*) was fitted for each column and each experimental step (Table 2) with an exponential model (Eq. (3)):

$$DOC(PV) = DOC_0 - a\left(1 - e^{-b\,PV}\right) \tag{3}$$

Fitting was performed with the non-linear least squares (*nls*) function in R (R Core Team, 2013). The baseline concentration (DOC_{base}) was then given by Eq. (4). The term "baseline" was preferred as although the concentrations reached quasi-constant values at the end of each step, the existence of immobile zones would prevent equilibrium, which could probably only be achieved under stagnant conditions (Münch et al., 2002).

$$DOC_{base} = DOC_0 - a \tag{4}$$

Tracer breakthrough was modelled with STANMOD software (Simunek et al., 1999), which solves the convective-dispersive transport equation, accounting for an immobile zone.

To model the breakthrough curve and for further analyses of DOC transport, it is crucial to differentiate between the pumping rate PR [ml d^{-1}] of the peristaltic pump (Fig. S1), the Darcy flux q [cm d^{-1}] and pore water velocity v [cm d^{-1}]:

$$q = \frac{PR}{A} \tag{5}$$

$$v = \frac{q}{\theta} \tag{6}$$

A [cm^2] is the cross-sectional area of the soil columns and θ [−] the volumetric water content. As the soil was completely saturated during the experiment, θ equalled the porosity *f* in this case.

In its dimensionless form, the solute transport in a dual porosity medium can be written as Eqs. (7) and (8) (van Genuchten and Wierenga, 1976), where β [−] is the fraction of the mobile zone and ω [−] the mass transfer coefficient between the two regions:

$$\beta R\frac{\partial C_m}{\partial T} + (1-\beta)R\frac{\partial C_{im}}{\partial T} = \frac{1}{Pe}\frac{\partial^2 C_{im}}{\partial X^2} - \frac{\partial C_m}{\partial X} \tag{7}$$

$$(1-\beta)R\frac{\partial C_{im}}{\partial T} = \omega(C - C_{im}) \tag{8}$$

The solute transfer rate α [d^{-1}] can be calculated according to Eq. (9), where L [cm] is the length of the soil column:

$$\alpha = \frac{\omega\, q}{L} \tag{9}$$

The subscripts "m" and "im" refer to the mobile and the immobile water fractions respectively. "Dimensionless" means that time T, concentration C and space coordinate X are given as relative values:

$$T = \frac{v\,t}{L} \tag{10}$$

$$C = \frac{c}{c_0} \tag{11}$$

$$X = \frac{z}{L} \tag{12}$$

where c_0 the applied tracer concentration [mg l^{-1}]. The Peclet number (Pe) is defined as:

$$Pe = \frac{v_m\, L}{D_m} \tag{13}$$

D_m is the hydrodynamic dispersion coefficient [cm^2 d^{-1}]. Finally, in the present experiment, the retardation coefficient R could be assumed to be 1 because there is no bromide sorption to soils. Therefore, the volumetric water content θ_m and the mean pore water velocity v_m in the mobile region as well as the mean residence time t_{res} are given by:

$$\theta_m = \beta f \tag{14}$$

$$v_m = \frac{q}{\theta_m} \tag{15}$$

$$t_{res} = \frac{\beta\, PV}{PR} \tag{16}$$

Input data for STANMOD are C, T (= exchanged pore volumes) and v. Fitted parameters are β, ω and D_m.

2.6. Statistics

Differences between pH values and DOC concentrations as a result of the two percolation solutions and the column pairs were evaluated with linear mixed effects (*lme*) model from the R package "nlme" (Pinheiro et al., 2013). We followed the general recommendations of Zuur et al. (2009). The basic *lme* model treated the column pairs and percolation solutions as fixed effects, while flow rates were set as random effects. As pH values were measured in the waste flasks (and not for each individual column), we had to evaluate column pairs instead of individual columns. Due to heteroscedasticity, an appropriate variance structure was added to the basic model. The basic model and models with different variance structures were compared using the Akaike Information Criterion (AIC). When a model with a variance structure had a lower AIC than the basic model, both models were refit with the maximum likelihood (ML) method, and an ANOVA was conducted to decide whether to add the variance structure. The final model was then refitted with the restricted maximum likelihood (REML) method to report p-values. As the fixed effect was significant, the post-hoc Tukey test for general parametric models of the R package "multcomp" (Hothorn et al., 2008) was applied.

Differences of DOC and Fe concentrations between acidified and non-acidified samples were also tested with linear mixed effects models using the same procedure as described above except the post-hoc test. Flow rates and columns were used as random effects.

To evaluate the relationship between DOC concentration, pH, EC and water table depth of the samples from the field site, generalized least squares (*gls*) models were set up (the R-package "nlme", Pinheiro et al., 2013). Average values of all three suction plates were used. In addition to an appropriate variance structure, temporal autocorrelation was accounted for with an autoregressive model (AR) of the order 1. As in the case of the variance structure, the model including an autocorrelation term was compared to the basic model using an ANOVA.

For comparisons between the sites "$C_{low}W_{29}$" and "$C_{low}W_{14}$", a *gls* model with the fixed effect "site" was compared to a *gls* model using the mean of all data. This allowed taking into account autocorrelation and a variance structure as described above.

3. Results

3.1. Column experiment

3.1.1. Tracer experiment

Bromide breakthrough curves are shown in Fig. 1. Bromide concentrations rose quickly and reached 377 mg l^{-1} (C1), 310 mg l^{-1} (C2), 262 mg l^{-1} (C3) and 336 mg l^{-1} (C4) after the exchange of one pore volume. These great differences between the "fastest" (C1) and the "slowest" (C3) columns already indicated different fractions of the immobile zone. A comparable behaviour and only slight tailing could be observed for the decreasing branch of the breakthrough curves.

The earlier decrease in bromide concentrations in columns C3 and C4 was a result of an early exchange of the percolation solutions, but this did not preclude a good model fit. Data from C1, C2 and C4 were fit with the dual-porosity model, while no unambiguous parameter set could be found for C3. Therefore a single-porosity model (CDE) was used for C3, which agreed with the observed tracer concentrations of around 50% of the percolation solution's concentration at around 1 PV (Fig. 1). Overall, the model fit of STANMOD was very good ($0.970 < R^2 < 0.998$, RMSE: 0.13 to 1.64 mg l^{-1}). Fractions of the mobile zone (β) varied between 0.51 and 1. Therefore, the columns showed very different "active" zones and pore water velocities in the mobile zone (Table 4), despite having very similar basic soil properties (Table 1).

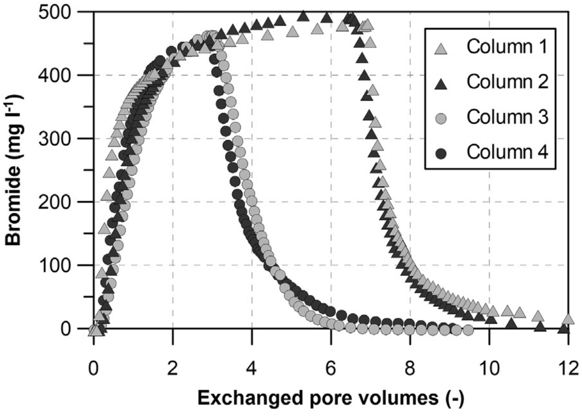

Fig. 1. Breakthrough curves of the bromide tracer.

3.1.2. Temporal variation in DOC concentrations

After the large initial peak and after each step change, DOC concentrations reached nearly constant values in all columns. An example is shown in Fig. 2. There were several single higher DOC concentrations in the effluent of some columns, possibly caused by the perturbation of the flow system at the step changes. The baseline concentrations of steps 1 and 4 were largely comparable (Fig. 4a and b). Furthermore, after changing from a percolation solution with high (PA) to low electrical conductivity (PB) and vice versa, DOC concentration levels quickly adjusted to the changed conditions.

3.1.3. Response to electrical conductivity and pH

The use of percolation solution with a high EC caused a strong (but reversible) and significant ($p < 0.001$) drop in pH in the effluent from both column pairs (Fig. 3a), which coincided with lower DOC concentrations (Fig. 3b, $p < 0.001$). The high variability of the DOC concentrations within each of the two EC classes (Fig. 3b) was caused by the different pore water velocities (Fig. 4a and b). The combination of high EC and low pH seemed to have supported iron flocculation as precipitates could be observed in the waste flasks (see also Section 3.1.5). Sulphate concentrations were always low (on average 0.5 ± 0.4 and 0.7 ± 0.7 mg l^{-1} for those steps run with percolation solutions A and B respectively).

3.1.4. Response to pore water velocity and fractions of the mobile zone

In all the columns, increased pumping rates decreased the DOC baseline concentrations (Fig. 4a and b), but increased the total DOC losses (Fig. 4c and d). At the same pumping rates, DOC_{base} differed greatly between the columns for both high and low EC conditions.

The arrows in Fig. 4a and b indicate whether there were higher DOC_{base} concentrations during step 1 or during step 4. There was no systematic difference between DOC_{base} of step 1 and step 4, indicating that there were no strong initial effects on DOC_{base} of step 1 and no systematic reduction of DOC release over the course of the experiment. In two cases, DOC_{base} was even slightly higher in step 4 than in step 1.

It was expected that the losses of DOC might reach a plateau at higher pumping rates as there should be no unlimited production, desorption or solution of DOC. However, no upper limit of DOC losses was observed, even at the highest pumping rates applied in this experiment (Fig. 4c and d).

Fig. 5 shows a nearly linear dependence of DOC_{base} on the mean residence time of the percolation solution. Taking the immobile region into account resulted in different "exchangeable" water volumes. Given similar total porosities and the same pumping rate, mobile water will be

Table 4
Darcy flux q, fitted parameters from STANMOD (β: fraction of the mobile zone, D_m: hydrodynamic dispersion coefficient, ω: mass transfer coefficient between the two regions), α: solute transfer rate, and characteristics of the mobile and immobile water fractions (θ_m: volumetric water content in the mobile region, θ_{im}: volumetric water content in the immobile region, and v_m: pore water velocity in the mobile zone during the tracer experiment).

	Unit	C1	C2	C3	C4
q	(cm d^{-1})	9.2	9.0	9.0	8.7
β	–	0.51	0.67	1.00	0.64
D_m	(cm^2 d^{-1})	173	60	89	91
ω	–	0.31	0.72	0	0.80
α	(d^{-1})	0.14	0.33	0	0.35
θ_m	–	0.23	0.32	0.47	0.30
θ_{im}	–	0.22	0.15	0	0.17
v_m	(cm d^{-1})	40.2	38.6	19.2	28.9

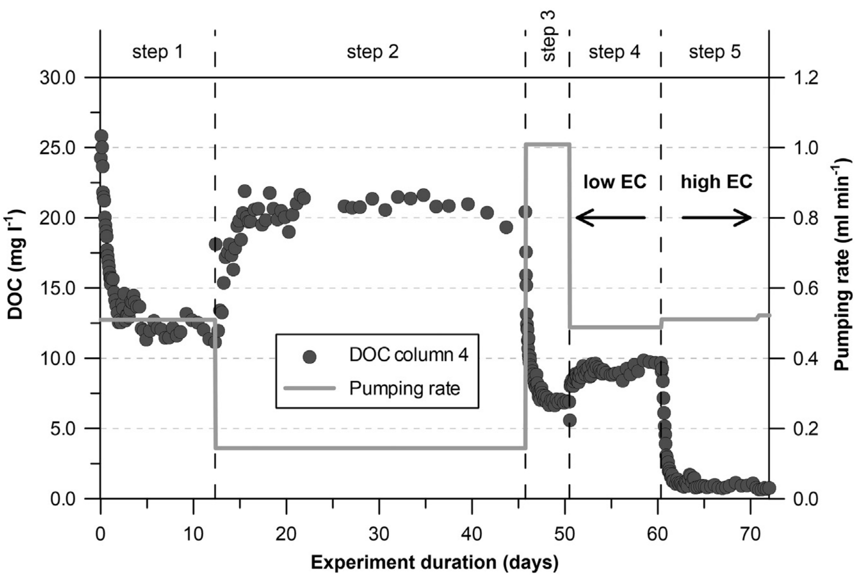

Fig. 2. Pumping rates and concentrations of dissolved organic carbon (DOC) in the effluent of column C4. The first three vertical hatched lines on the left indicate changes in the pumping rate and the one on the right the change from percolation solution B (low electrical conductivity (EC): 94 μS cm^{-1}) to percolation solution A (high electrical conductivity: 1064 μS cm^{-1}).

exchanged faster in a soil with immobile regions than in a soil without. This partially explains the variability between the columns, especially at low pumping rates and low EC.

3.1.5. Effects of iron flocculation

At low EC, DOC concentrations in the selected samples were slightly, but not significantly ($p = 0.053$) lower in non-acidified samples (mean value 18.2 mg l^{-1}, standard deviation 6.1 mg l^{-1}) than in acidified samples (19.4 ± 6.6 mg l^{-1}). The differences were much greater at high EC (1.4 ± 1.0 mg l^{-1} and 4.6 ± 2.1 mg l^{-1}, $p < 0.0001$). However, the great differences in DOC concentrations between the two percolation solutions remained valid despite the possible formation of Fe-DOC complexes. In contrast to DOC, concentrations of Fe_t were lower at low EC (non-acidified: 0.5 ± 0.2 mg l^{-1}, acidified: 1.2 ± 0.6 mg l^{-1}, difference significant at $p < 0.0001$) than at high EC (non-acidified: 1.4 ± 1.6 mg l^{-1}, acidified: 5.5 ± 2.2 mg l^{-1}, $p < 0.0001$). The effect of acidifying the samples was therefore even stronger for Fe than for DOC.

The ratio of DOC and iron concentrations respectively in the non-acidified samples to concentrations in the acidified samples was defined as the "recovery ratio". The recovery ratio of Fe depended greatly on the pore water velocity, while the recovery ratio of DOC depended on pore water velocity only when applying the high EC percolation solution (Fig. 6). Thus, Fe and DOC recovery were only correlated at high EC.

3.2. Field experiment

The mean DOC concentrations (±standard deviation) of the soil solution in the field were 139.1 ± 54.1 mg l^{-1} ($C_{low}W_{14}$) and 155.9 ± 43.9 mg l^{-1} ($C_{low}W_{29}$), respectively. DOC concentrations of the two sites did not differ significantly ($p > 0.05$). The mean EC of $C_{low}W_{14}$ (111 ± 28 μS cm^{-1}) and $C_{low}W_{29}$ (91 ± 25 μS cm^{-1}) did neither differ significantly ($p > 0.05$). However, mean water table depths ($C_{low}W_{14}$: 14 ± 14 cm and $C_{low}W_{29}$: 29 ± 13 cm, $p < 0.05$) and pH ($C_{low}W_{14}$: 5.8 ± 0.4 and $C_{low}W_{29}$: 4.8 ± 0.3, $p < 0.001$) both differed significantly between the two sites, but did not have an effect on the mean DOC concentrations.

On the basis of individual samples, there was no clear relationship between EC and pH in the soil solution of the field sites (Fig. 7a, $p > 0.05$ for both sites). Furthermore, there was also no correlation between pH and DOC (Fig. 7b, $p > 0.05$) or between WTD at the date of

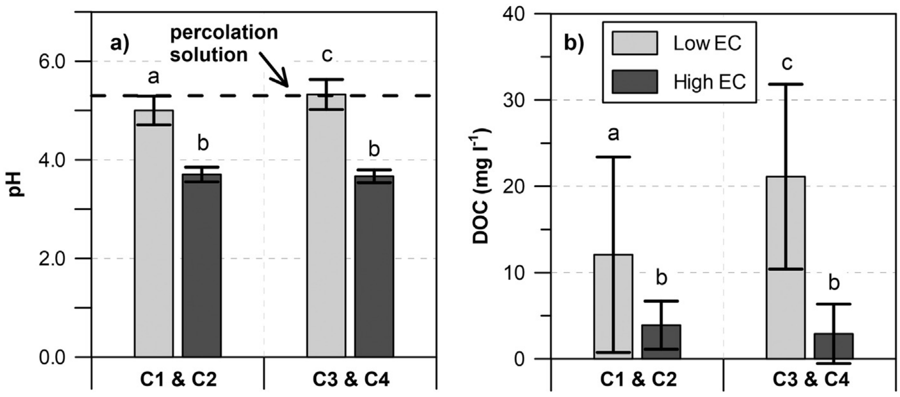

Fig. 3. a) pH values and b) concentrations of dissolved organic carbon (DOC) in the waste flasks. Columns C1 and C2 were percolated with the solution of high electrical conductivity (1064 μs cm^{-1}) during steps 1 to 4, and of low electrical conductivity (94 μS cm^{-1}) during step 5, while C3 and C4 started with low electrical conductivity. Error bars show the standard deviation, and letters indicate significant differences ($p < 0.001$).

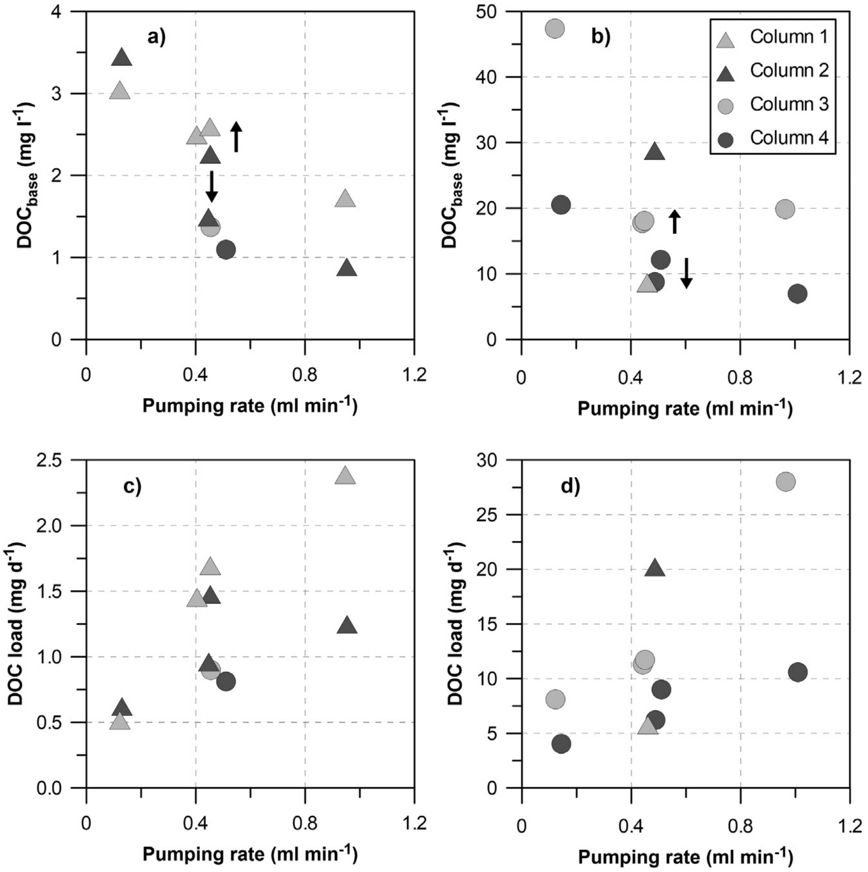

Fig. 4. Pumping rate and a) baseline concentrations of dissolved organic carbon (DOC_{base}) in the effluent of the columns percolated with the high electrical conductivity (EC) solution, b) and the low EC solution. Arrows indicate whether DOC_{base} concentrations are lower (downward arrow) or higher (upward arrow) during step 4 than during step 1 which where run under the same pumping rate. Pumping rate and DOC loads of the columns percolated with c) the high EC solution and d) the low EC solution.

sampling and DOC (Fig. 7d, $p > 0.05$). However, there was a clear positive correlation ($p < 0.001$) between DOC concentrations and EC (Fig. 7c). These results held true for samples taken under both saturated and unsaturated conditions.

The field data contrasted to the laboratory data in several aspects: First, there was no correlation between pH and EC or pH and DOC in the field data. Second, while there was a negative relationship between DOC and EC in the laboratory data (Fig. 3b), this relationship was clearly positive in the field. Third, DOC concentrations in the soil solution of the field site were much higher than those measured in the column effluents.

4. Discussion

4.1. Column study – interacting effects of electrical conductivity and pH

Percolating the columns with the high EC solution caused low pH values, and the combination of high EC and low pH greatly, but reversibly, decreased DOC concentrations at the outlet of the columns. Lower pH values can reduce the solubility of DOC due to lower charge density and a high degree of protonation of functional groups (Tipping and Hurley, 1988; Tipping and Woof, 1991). This can reduce desorption of

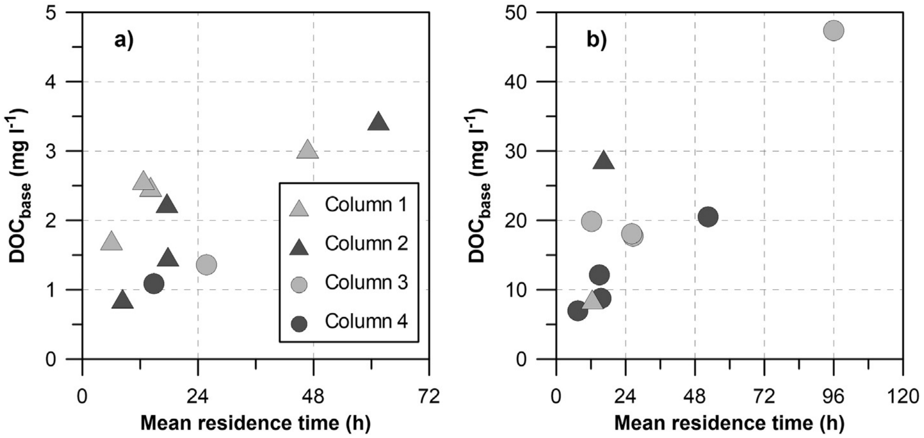

Fig. 5. Mean residence time and baseline concentrations of dissolved organic carbon (DOC_{base}) in the effluent of the columns percolated with a) the high electrical conductivity (EC) solution and b) the low EC solution respectively.

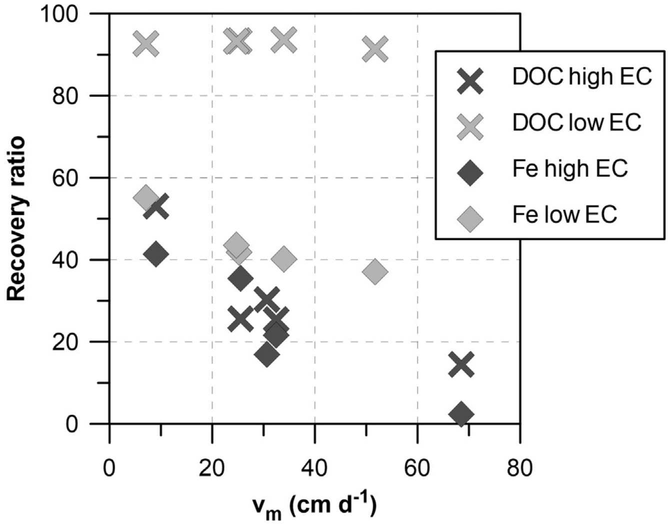

Fig. 6. Recovery ratio (ratio of concentrations in non-acidified samples to acidified samples) of total iron (Fe_t) and dissolved organic carbon (DOC) depending on pore water velocity in the mobile region (vm) and the electrical conductivity (EC) of the percolation solution.

dissolved organic matter (DOM) (Grybos et al., 2009), but also cause coagulation and subsequent precipitation of DOM (Tipping and Hurley, 1988). Nearly all laboratory studies on organic soil horizons reviewed by Kalbitz et al. (2000) showed that lowering the pH value generally decreases DOC release. The same effect was found in a field study on organic soils (Evans et al., 2012), and ecosystem recovery from acidification is proposed as a cause for rising DOC concentrations in surface waters (Evans et al., 2006). A high ionic strength might also reduce the charge density and thus decrease DOC release (Kalbitz et al., 2000; Tipping and Hurley, 1988). Therefore, ionic strength has also been put forward as a driver of long-term DOC concentration trends (Hruška et al., 2009).

As the higher EC percolation solution clearly but reversibly lowered both the pH and DOC concentrations of the effluent, it was not possible to distinguish clearly between the effects of EC and pH on DOC concentrations. A field study on acidification and alkalization of organic soils, however, suggests that acidity effects dominate the response of DOC concentrations as alkaline treatments showed increasing DOC concentrations despite increasing ionic strength (Evans et al., 2012; Oulehle et al., 2013). In our study, the drop in pH might be caused by the exchange of H^+ by Ca^{2+} ions. Exchangeable Fe^{2+} might also have been replaced by Ca^{2+} (Heron et al., 1994). This interpretation is supported by the higher Fe concentrations in the effluent of the high EC percolation solution (Fig. 6). Sulphate oxidation, which has been found to be responsible for reduced pH values in field studies (Clark et al., 2005; Knorr, 2013), cannot be the reason for the low pH since concentrations of SO_4^{2-} in the effluents were low and did not differ between the two treatments. The low SO_4^{2-} concentrations also ruled out FeS oxidation as the source of iron in the effluent.

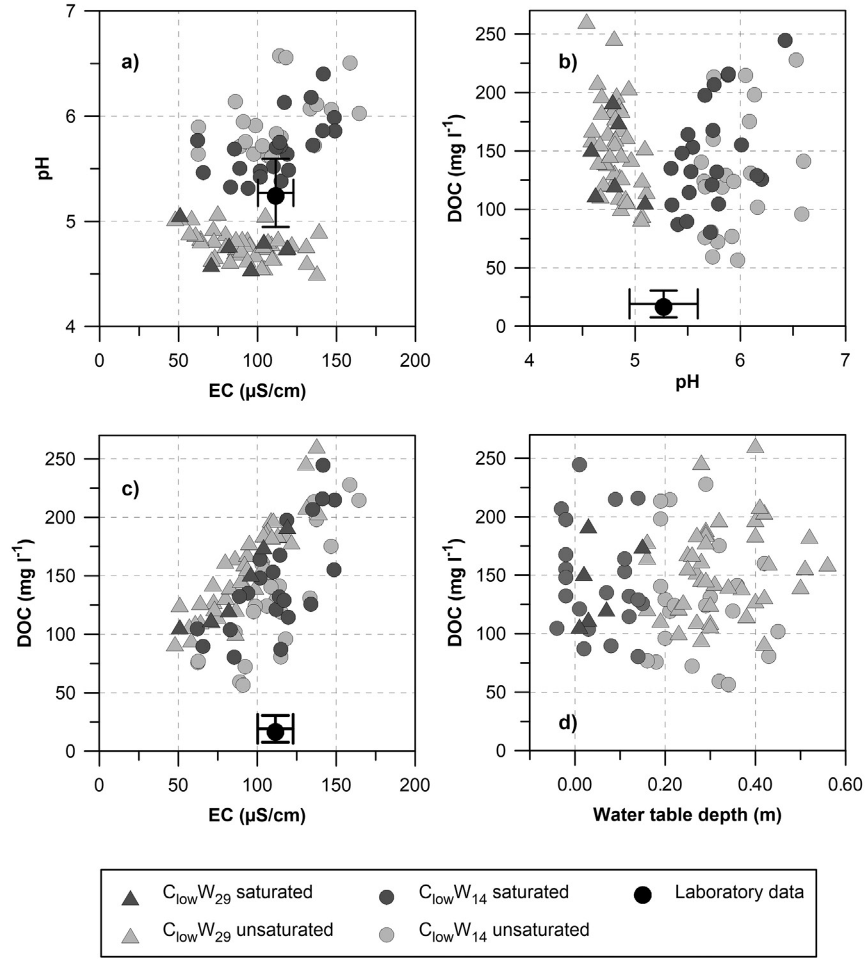

Fig. 7. Mean values of the three suction plates of a) Electrical conductivity (EC) and pH, b) concentrations of dissolved organic carbon (DOC) and pH, c) EC and DOC, and d) water table depth at the date of sampling and DOC in the soil solution at the field sites $C_{low}W_{29}$ (dry) and $C_{low}W_{14}$ (wet). Filled symbols refer to samples taken under saturated conditions at the sampling depth (15 cm). For comparison, the mean values ± standard deviations of all column effluent samples resulting from the percolation solution with low EC are shown.

Lower DOC concentrations due to high concentrations of both Na^+ and Ca^{2+} have been found by Münch et al. (2002). In addition to the effects of pH and ionic strength on the solubility of DOC, Ca^{2+} bridges might contribute to both DOC complexation and retention by soil organic matter (SOM) and iron oxides (Reemtsma et al., 1999; Tipping and Ohnstad, 1984).

The iron flocculation appeared to have happened in the waste flasks, not in the columns themselves. Thus, it cannot be ruled out that some of the drop in pH also occurred in the waste flasks due to re-oxidation of Fe^{2+}, which is similar to processes at groundwater-stream interfaces (Knorr, 2013). Although the precipitation of Fe-DOC complexes did decrease the DOC concentrations in the waste flasks during steps run with high EC percolation solutions, this does not fully explain the difference in DOC concentrations between the two treatments. However, the recovery ratio of both DOC and Fe decreased at high EC at higher pore water velocities, possibly because of reduced dilution of DOC concentrations with large water fluxes and consequently increased total DOC fluxes.

4.2. Column study – effects of non-equilibrium flow and transport

As expected, high pore water velocities in the mobile region reduced DOC concentrations (Fig. 4 and b, Fig. 5). DOC losses increased at higher pore water velocities, but did not reach an upper limit, i.e. did not level out asymptotically (Fig. 4c and d).

The mobile region dominated the pore space of the four columns ($\beta = 0.71 \pm 0.18$, Table 4). The organic matter of the studied sandy soils originates from peat. Although the remaining organic material has little resemblance to peat anymore, there was still a relatively high and variable extent of immobile pore regions ($0 \leq \theta_{im} < 0.22$). The extent of the immobile pore region was more similar to degraded peat soils than to intact peat soils: Hoag and Price (1997) found for pristine peat that the immobile zone dominated the pore space ($0.16 < \beta < 0.43$, $0.50 < \theta_{im} < 0.63$). Similar results were found for decomposed peat ($\beta = 0.39$ and $\theta_{im} = 0.53$, Rezanezhad et al., 2012), while for earthified degraded peat, β decreased from 0.60 to 0.19 while θ_{im} increased from 0.28 to 0.56 due to consolidation and microbial clogging during the course of the experiment (Kleimeier et al., 2014). Based on these limited data from literature, both the extent and the share of the immobile zone in "true" organic soils appear to decrease with increasing degradation and decreasing SOC content. Intact cell remains forming dead-end or closed pores are an important contribution to the immobile pore region of peat soils (Hoag and Price, 1997; Rezanezhad et al., 2016). Therefore, it is plausible that a strong breakdown of the original plant material changes the share and extent of the immobile zone. Non-equilibrium water flow and solute transport is an ubiquitous phenomenon in soils due to e.g. formation of aggregates, biopores or water repellence and does not only depend on soil properties themselves, but also on initial and boundary conditions (Jarvis, 2007). Unstructured sandy mineral soils low in SOC tend to be dominated by the mobile zone (Jarvis, 2007) provided that they do not become water repellent (Doerr et al., 2000). Nevertheless, as the extent of the immobile region in the columns in the present experiment was relatively high, the organic fraction seemed to be the key for the development of such transport characteristics. This was similar to finger flow in sandy soils, where SOM-induced water repellence is thought to cause non-equilibrium flow (Doerr et al., 2000).

However, we only carried out the tracer experiment at one level of electric conductivity (820 $\mu S\ cm^{-1}$). Several studies found that high EC increases the hydraulic conductivity of peat soils and attributed this to a 'dilation' of the pores (Comas and Slater, 2004; Kettridge and Binley, 2010; Ours et al., 1997). Pore dilation (or constriction) is interconnected with EC effects on DOC concentrations as the increased pore size is thought to be caused by coagulation of the humic acids (Ours et al., 1997). Although there are - to our best knowledge - no studies on the effect of EC on the transport properties of peat soils, EC might also have a 'physical' effect on the transport of DOC. However, in our case with a relatively low SOC content and thus a relatively rigid matrix, we assume the dilation effect to be weaker than for the relatively undisturbed peat used by e.g. Kettridge and Binley (2010) and Ours et al. (1997). Furthermore, Ours et al. (1997) observed decolouration of the percolation solution during the course of the experiment, while the DOC concentrations in our experiment did not decrease from step 1 to step 4 (Fig. 4).

While pH and EC jointly determined the DOC concentration levels, pore water velocity and in particular the residence time modulated these concentrations by factors of 2 to 4. A similar pattern was found in a column study with mineral soils (Münch et al., 2002), while there is an absence of data on organic soils. As expected, high pore water velocities in the mobile zone and thus decreased residence times reduced DOC concentrations and partially explained the differences between columns. Shorter contact time of the percolating water with the soil matrix and less time for exchange processes seem to be crucial as such concentration patterns (Fig. 4a and b) are typical for rate-limited processes (Münch et al., 2002; Stutter et al., 2007b; Wehrer and Totsche, 2005). The solute exchange rate α increases with increasing porewater velocity (Eq. (9)). As micropores or immobile zones might be key zones for the production of DOM in peat soils (Stutter et al., 2007b), higher DOC concentrations might be assumed for columns with a higher fraction of the immobile region. However, this was not the case in our study, as, for example C3 (single porosity, $\beta = 1$) showed higher DOC concentrations than C4 ($\beta = 0.64$) (Fig. 4b). Therefore, the stronger non-equilibrium caused by the increased pore water velocity in columns with a higher fraction of the immobile region seemed to be more important in the present case.

It was also notable that there was no upper limit in DOC losses (Fig. 4c and d), i.e. although higher pore water velocities and increased fractions of the immobile zone decreased DOC concentrations, this did not result in lower or constant DOC loads. Reasons might be the higher concentration gradients between the immobile region and the mobile region at higher pore water velocities and relatively high solute exchange rates compared to other studies (Kleimeier et al., 2014). This is particularly likely given that the lower recovery ratio at high EC and high v_m indicated even higher "true" DOC fluxes during these steps. Therefore, transport of DOC did not seem to be limited by production of DOC, but by rate-limited exchange processes.

4.3. Differences between the column and the field study

The results of the field study contrasted considerably with the laboratory experiment in several respects: a) there was no correlation between pH and EC or pH and DOC, although pH displayed a wider range under field conditions than in the two laboratory treatments, b) correlations between DOC and EC were positive instead of negative and c) the DOC concentrations in the field were much higher than those measured in the column effluents. Furthermore, no iron flocculation was observed in the solutions sampled in the field. These "contradictions" clearly show the limitations of transferring laboratory results to the field without taking hydrological conditions and soil-physical properties into account.

For both mineral and organic soils, there is a clear correlation between pH and DOC concentration in the majority of laboratory experiments (e.g. Grybos et al., 2009; Kennedy et al., 1996 and other results summarized by Kalbitz et al. (2000). Clark et al. (2006), however, could not find a direct relationship between pH and DOC in peat samples subjected to a temporary drought, but a strong suppression of DOC concentrations compared to concentrations estimated for the absence of sulphate induced acidification. In many cases, a clear correlation between pH and DOC cannot be found in the field (Kalbitz et al., 2000). The study by Evans et al. (2012) showed that decreasing pH values cause lower DOC concentrations in organic soils, however that experiment was based on pH manipulation, while in the present study the temporal and spatial variability in pH was not controlled.

Several studies have shown that higher ionic strength (which is approximated by EC) reduces DOC concentrations (Clark et al., 2011; Hruška et al., 2009; Münch et al., 2002). The field values of EC never reached the values of the "artificial groundwater" used in the laboratory study (Fig. 7). Therefore, the field concentrations of cations might be too low to cause coagulation and bridging, but there might be a turning point at which a higher ionic strength would start to decrease DOC concentrations under field conditions as well. Furthermore, DOC also contributes to the EC. Thus the field EC might be determined by DOC concentrations and not vice versa.

In the following section, possible reasons for the different DOC concentration levels in the laboratory and the field will be discussed. Unfortunately, the lower SOC content of the soil columns compared to the field sites (Table 1) complicate the comparison between field and laboratory data. The low SOC content of the columns could explain the lower DOC concentrations in the laboratory study. However, at the "Großes Moor", even a SOC content as high as 479 g kg^{-1} did not result in higher DOC concentrations than those at sites $C_{low}W_{29}$ and $C_{low}W_{14}$ (Frank et al., 2017). Therefore, it is assumed that differences in SOC are not the only explanation for the differences in DOC concentrations between the field and the soil columns.

Overall, the high DOC concentrations in the field were remarkable since clear decreases in DOC concentrations with decreasing SOM were assumed for degrading peatlands. For example, Kalbitz and Geyer (2002) measured average DOC concentrations of 60 mg l^{-1} in a topsoil a with SOC content (87 g kg^{-1}) comparable to our field site. However, as a former fen, their site is influenced by the inflow of groundwater of probably higher ionic strength. One additional explanation for the high DOC concentrations might be that the physical disturbance (mixing with the underlying sand) overrides the influence of the relatively low SOM content. Ross and Malcolm (1988) showed that DOC concentrations are higher the smaller the peat aggregates in a sand matrix become.

While there were no clear differences in DOC concentrations under saturated and unsaturated conditions in the field (Fig. 7d), the existence of drier and warmer periods might have increased the production of DOC, which could have been produced in and leached from the top few centimetres of the soil. This is also supported by Frank et al. (2017), who found DOC concentrations to increase with soil temperature with a lag time of three to four month. Indeed Stutter et al. (2007a) explain similar differences between laboratory cores and field data by the superimposition of biological and physico-chemical processes. While there was generally a strong relationship between temperature and DOC in their study, long residence times and limited dilution of the soil solution during dry and warm periods might have been further reasons for higher DOC concentrations in the field. However, in our case, there was no clear instantaneous effect of WTD (Fig. 7d) or temperature at the date of sampling (data not shown) on DOC concentrations. This is a rather uncommon observation as previous research found lower WTD both increase and decrease DOC concentrations. During periods of low groundwater levels, increased microbial activity might enhance decomposition (Glatzel et al., 2006; Hribljan et al., 2014). Furthermore, missing dilution and enrichment of DOC due to high evapotranspiration rates during warm periods are frequently offered as an explanation for higher DOC concentrations at low WTD (Glatzel et al., 2006; Stutter et al., 2007a). In other cases, increased sulphate formation caused acidification and thus a suppression of DOC release (Clark et al., 2005, 2006). In our case, the rather small differences in mean WTD depth might have been superimposed by soil properties or climatic factors: Frank et al. (2017) discussed the DOC concentrations at different sites and different soil depth of our study area in detail and found that in many cases rather the flow direction, i.e. infiltrating conditions, than the WTD depth itself determined the DOC concentrations. However, as in the case of temperature, DOC reacts with long lag-times on these drivers.

In addition to the possible production of DOC in the top few centimetres of the soil, flow rates and hydrological dynamics in the field are the most plausible drivers for DOC concentrations. Frank et al. (2017) modelled soil hydrological processes at the field site with Hydrus 1D and estimated mean (1.6 cm d^{-1}) and median fluxes (0.23 and 0.26 cm d^{-1}) for sites $C_{low}W_{14}$ and $C_{low}W_{29}$ respectively. Not accounting for immobile regions, these fluxes roughly corresponds to pumping rates of 0.01 to 0.1 ml min^{-1}. In view of the non-linear relationship between pumping rates and DOC concentrations at low EC (Fig. 4b), field DOC concentrations of around 150 mg l^{-1} (average of all field samples) do not seem implausible. Furthermore, due to the lower water fluxes in the field compared to the column study, field conditions might allow for nearly unlimited diffusional exchange between different flow domains in contrast to the clearly rate-limitation in the laboratory. However, this analysis is restricted to average field conditions. Non-equilibrium conditions and, depending on weather conditions, high water fluxes might also occur in the field.

Our results illustrate that the seemingly contrasting DOC concentrations in the field and in the laboratory study can be explained by different hydrological regimes. This is even more likely as the real residence time will be increased by frequently changing flow directions (infiltration vs. upward flow), which could cause temporal accumulation of DOC in the pore water. Therefore, it is suspected that hydrological conditions in the field were the main reason for the higher DOC concentrations.

5. Conclusions

Even peat-sand mixtures with a relatively low SOC content clearly exhibit a dual porosity pore space comparable to that of degraded "true" peat soils. These soil physical properties influence pore water velocity in the mobile zone and thus solute transport. As expected, DOC concentrations decreased with increasing pore water velocity, and the extent of the mobile region could help explain differences between single soil columns. High pore water velocities induced shorter contact times of the percolating water with the soil matrix and less time for exchange processes. While micropores or immobile zones might be key zones for the production of DOM in organic soils, the stronger non-equilibrium caused by the increased pore water velocity in columns with a higher fraction of the immobile region seemed to be crucial for the resulting concentration patterns in the present study. Overall, transport of DOC does not seem to be limited by production of DOC, but by rate-limited exchange processes, especially under high pore water velocities.

As hypothesized, a high ionic strength (i.e. high EC) caused lower DOC release than percolation with a low EC solution. However, it was not possible to differentiate clearly between the EC effect and the influence of low pH values on DOC concentrations as the pH was strongly but reversibly lowered by the high EC solution. Future studies should try to disentangle the effects of EC and pH. The low pH values were probably caused by ion exchange and cation bridging. Under field conditions, there was no clear pH effect, while high DOC concentrations coincided with higher EC. This could be explained by the relatively low EC in the field: due to much lower cation concentrations, the turning point at which increasing EC would reduce DOC solubility had probably not been reached. Furthermore, DOC itself might have contributed to the EC of the soil solution.

The present results also showed that hydrological conditions and soil-physical properties need to be taken into account when transferring laboratory results to the field, as seemingly opposite effects can occur. Understanding the hydrological conditions, however, can help solve apparent contradictions between laboratory and field results: the low flow velocities in the field can explain – in addition to the higher SOC content in the field – the much higher DOC concentrations than those in the laboratory. With a good understanding of both chemical and soil physical effects, experiments under controlled laboratory conditions can indeed offer reasonable estimates of DOC mobilisation under field conditions.

Overall, our results demonstrate that more attention should be paid to experiments that address the interaction between hydrochemical conditions and soil hydrology. While hydrochemical conditions are frequently the focus of laboratory studies, soil hydrology beyond soil moisture is rarely addressed. This should be given greater consideration, however, especially when attempting to interpret DOC data from different spatial and temporal scales. Finally, the high DOC concentrations in the field show that soils with peat-sand mixtures not only emit considerable amounts of CO_2 (Leiber-Sauheitl et al., 2014), but are also strong sources of DOC.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.geoderma.2017.02.024.

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