Influence of pore structure on solute transport in degraded and undegraded fen peat soils

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SUMMARY

In peat soils, decomposition and degradation reduce the proportion of large pores by breaking down plant debris into smaller fragments and infilling inter-particle pore spaces. This affects water flow and solute migration which, in turn, influence reactive transport processes and biogeochemical functions. In this study we conducted flow-through reactor experiments to investigate the interplay between pore structure and solute transport in samples of undegraded and degraded peat collected in Canada and Germany, respectively. The pore size distributions and transport parameters were characterised using the breakthrough curve and two-region non-equilibrium transport model analyses for a non-reactive solute. The results of transport characterisation showed a higher fraction of immobile pores in the degraded peat with higher diffusive exchanges of solutes between the mobile and immobile pores associated with the dual-porosity structure. The rates of steady-state potential nitrate reduction were compared with pore fractions and exchange coefficients to investigate the influence of pore structure on the rates of nitrate reduction. The results indicated that the degraded peat has potential to provide the necessary boundary conditions to support nitrate removal and serves as a favourable substrate for denitrification, due to the nature of its pore structure and its lower organic carbon content compared to undegraded peat.

KEY WORDS: dual-porosity structure, mobile and immobile pore fractions, nitrate reduction, peat decomposition and degradation, solute migration

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INTRODUCTION

Peat soils comprise partially decomposed and decayed organic soils with more than 65 % organic matter (Driessen 1978). They are formed under conditions of water saturation, acidity, nutrient deficiency and low oxygen availability (e.g. in wetlands), when the rate of accumulation exceeds the rate of decomposition. Peatlands are a major store of terrestrial organic carbon and nitrogen (Gorham 1991, Wang *et al*. 2016) and peat soils can lose carbon to the atmosphere *via* biological process during peat decomposition (Ise *et al*. 2008, Krüger *et al*. 2015). One of the important factors for the decomposability of organic soil carbon is its chemical composition, on account of the different activation energies (associated with variety in the quality of organic matter) which control the degree of decomposition and degradability (Lützow *et al*. 2006, Conant *et al*. 2011, Tfaily *et al*. 2014). Degree of decomposition is a key property of peat soils, and the most outstanding one when it comes to characterising and classifying peat soils, especially in relation to hydraulic properties and biogeochemical activities. The chemistry and quality of peat substrates can affect the rate of decomposition. For example, as new litter is decomposed, the remaining substrate becomes increasingly recalcitrant and more difficult for microbes to degrade, resulting in lower decomposition rates (Strack 2008). The formation of peat and the degree of decomposition and degradation are temperature dependent. Low temperatures reduce the rate of decomposition (e.g., in temperate, boreal and sub-arctic regions) and high temperatures increase the rate of decomposition (e.g., in humid tropical regions) (Page *et al*. 1999, Joosten & Clarke 2002).

Oxidation of the unsaturated peat layer (due to artificial drainage when the peatland is used for agriculture or forestry) increases the degradation rate of peat soils by promoting aerobic microbial decomposition. The peat degradation rate depends on the peat type, the density and thickness of peat layers, drainage depth, the rate of decomposition, climate, land use, and time since the peatland was drained (Stewart 1992). Peat degradation under drainage changes the quality of soil organic carbon (SOC) towards less active or labile fractions resulting in smaller pools of carbon that can be readily utilised by micro-organisms. As the denitrification process in

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soils is often limited by the availability of organic components, lower SOC in degraded peat leads to a low input of biomass carbon, a negative carbon budget and lower denitrification (Davidsson *et al*. 2002, Tiemeyer & Kahle 2014). Therefore, the rate of degradation or available SOC is an important factor for denitrification in soils. In the long term, however, most of the easily degradable organic matter (*i.e.*, SOC) may be consumed and a high denitrification would rely on the production of new organic matter or breakdown of more complex organic compounds.

In peat soils, higher decomposition and degradation rates lead to a reduced proportion of large pores through the breakdown of plant debris into smaller fragments and infilling of inter-particle pore spaces (Rezanezhad *et al*. 2016). Peat soil has a unique complex dual-porosity structure, with mobile-immobile pore fractions that influence advective water flow and solute transport through the open and connected (mobile) pores, and matrix diffusion into and within partially closed (immobile) pores (Hoag & Price 1997, Ours *et al*. 1997, Reeve *et al*. 2001, Rezanezhad *et al*. 2012a, 2012b, 2016). Therefore, in addition to the status of the nitrate load, we must consider moisture content, microbial activity and growth, temperature and state of peat degradation, all of which control the rate of denitrification (Cabezas *et al*. 2012). The complex pore structure of the peat may also influence the denitrification rate and nitrate removal efficiency. Rezanezhad *et al*. (2016) reviewed the key physical and hydraulic properties of peat soils and their implications for water storage and solute migration in peatlands, which is relevant for understanding the biogeochemical functioning of peat soils. They showed that an increase in the mobile (or active) fraction of the porosity accelerates the delivery of nitrate to the denitrifying microorganisms that couple the reduction of nitrate to the oxidation of organic compounds present in the peat.

Degraded peat has higher bulk density than undegraded peat and, thus, a lower porosity and higher number of small (immobile) pores (Frank *et al.* 2014). The differences in physical properties and pore size distribution between undegraded and degraded peat soils influence their denitrification activity. We hypothesised that, with the higher fraction of small pores in degraded peat, the diffusive solute exchanges between the mobile and immobile regions may increase the exchange rates and responses of microbial activity in degraded peat soils. To understand this unique property of peat, the main goal of our study was to investigate the reactive (nitrate) solute transformation properties of a degraded *versus* an undegraded peat soil by evaluating non-reactive (*i.e.*, bromide) solute breakthrough curves employing the concept of mobile and immobile pore water fractions. Furthermore, in order to understand the influence of pore structure on nitrate reduction activities, the different transport characteristics of degraded and undegraded peats (obtained by pore structure analyses) were compared with the reactive nitrate transformation processes.

METHODS

Field sites and peat soil sampling

Soil samples representing slightly decomposed “undegraded” peat were collected from the top peat layers at the *rare* Charitable Research Reserve, a forested riparian peatland located in Cambridge, Ontario, Canada. The soils of this site are characterised as fen peat and consist of incompletely decomposed organic matter with decomposition stage of H3 on the von Post classification scale (von Post 1922). The highly decomposed “degraded” peat samples were collected from the former floodplain of the Zarnow Brook (River Warnow catchment) in the Dummerstorf experimental site near to Rostock in Germany. This site was well-drained (water table at -40 cm) agricultural land and the peat had a fine aggregated structure with no recognisable plant residues, corresponding to a decomposition stage of H10 (fully decomposed, humified peat). Both undegraded and degraded peat samples were collected from the topsoil (0 to -30 cm). A 25 cm hand-pushed shuttle corer mounted with a Plexiglas ring of length 2 cm and inside diameter 4.2 cm was used to collect undisturbed peat samples by gently inserting the shuttle corer into the peat. After sampling, the peat cores were refrigerated and transported to the laboratory at the University of Waterloo (Canada), where they were used for analyses and flow-through reactor experiments (see below).

Physical and hydraulic properties of peat

Separate peat samples were collected from the undegraded and degraded field sites to determine physical and hydraulic properties including total porosity, bulk density and hydraulic conductivity. Total porosity (Φ) and bulk density (ρ_b) were determined gravimetrically from the saturated mass, the oven-dried (at 80 °C) mass and the original volume of the sample, following the method of Boelter (Gardner 1986). The saturated hydraulic conductivity (K_{sat}) was determined using the constant head method (Klute & Dirksen 1986). All the analyses of physical and hydraulic properties were conducted in triplicate for each of two undegraded and two degraded peat samples.

Flow-through reactor experiment

To determine the solute transport characteristic, pore size distribution and dominant transport processes in the degraded and undegraded peat samples, the flow-through reactors (FTRs) technique (Pallud *et al*. 2007) was used. The reactors are designed to quantitatively assess solute transport and measure biogeochemical reaction rates in undisturbed soils/sediments, to yield kinetic parameters and information on reaction pathways that can be extrapolated to natural conditions (Pallud *et al*. 2006, 2007; Laverman *et al*. 2007, 2012; Geilert *et al*. 2014). To build a FTR, the front liner plate of the shuttle core used to sample the undisturbed peat core was removed and the reactor cell (Plexiglas ring filled with peat) was separated and sealed using two PVC plate caps and O-rings, and tightened using stainless steel screws (Figure 1). A polypropylene membrane filter (0.2 mm pore size, 50 mm diameter, Pall Life Sciences, Port Washington, NY, USA) and a fibreglass filter (1 mm pore size, 47 mm diameter, Pall Life Sciences) were placed on each side of the Plexiglas ring before the PVC plate caps were attached. The bottom cap had an inflow channel to supply input solution and the top cap had an outflow channel to recover the effluent. Both end caps had carved grooves to ensure uniform flow of the solution through the sample in the reactor. Two FTRs were prepared for each of the two degraded and undegraded peat samples. In what follows, FTRs I and II are referenced as containing undegraded, and FTRs III and IV degraded, peat samples. An input solution with non-limiting concentrations of nitrate (NO_3^-) and bromide (Br^-), containing KBr (0.37 mM) and KNO_3 (1.6 mM) in deoxygenated water, was continuously supplied to the reactors at a constant flow rate (1 ± 0.05 ml h^{-1}, n = 212) imposed by a peristaltic pump (Minipuls 3; Gilson, Middleton, WI, USA). The inflow solution was purged continuously with filtered argon gas to remove oxygen. Outflow samples (see Figure 1) were collected every 2 hours for the first 2 days, every 5 hours for the following 2 days, and then every 2 to 3 days for a total elapsed incubation time of 30 days. The experiments ran at room temperature (22 ± 2 °C).

Pore water and solid-phase geochemistry

The outflow water samples from the FTRs were filtered through a 0.2 μm membrane filter (Thermo Scientific Polysulfone filter) for analysis of NO_3^--N and Br^- using a Dionex ICS-5000 ion chromatograph equipped with a capillary IonPac® AS18 column (MDL= 0.75 and 0.42 μM for NO_3^--N and Br^-, respectively). 1 ml samples of the collected water were used to measure the dissolved total organic carbon (TOC) and total nitrogen (TN, including inorganic and organic compounds) concentrations. The TOC and TN concentrations were determined using a Shimadzu TOC-LCPH/CPN analyser following HCl addition (< pH 2) to degas dissolved inorganic carbon (MDL= 6 and 4.5 μM for TOC and TN, respectively). At the end of the experimental period, the FTRs were fully drained and the peat samples were homogenised, freeze-dried and the solid-phase total nitrogen and total organic carbon concentrations were measured on a CHNS Carbo Erba analyser (MDL: 0.1 %dry) without any pre-treatment of the freeze-dried samples. The solid-phase analyses were also conducted for the peat samples initially collected from each site. The

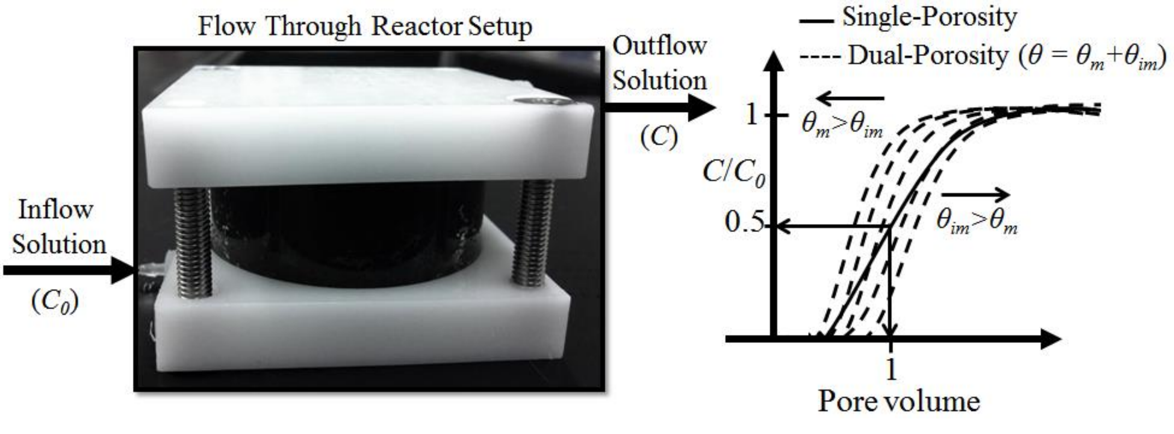

Figure 1. Schematic diagram of the flow-through reactor (FTR) experiment and breakthrough curves under single-porosity and dual-porosity (with mobile and immobile pore regions) conditions. Note that θ_m and θ_{im} are the volumetric pore mobile and immobile fractions, and subscripts '*m*' and '*im*' refer to the mobile and immobile regions.

precision and accuracy for all techniques was < 5 RSD% with respect to certified reference materials.

Breakthrough curves and transport characterisation

In peat soils with dual porosity (Loxham & Burghardt 1983, Price & Woo 1988, Hoag & Price 1997, Ours *et al*. 1997, Reeve *et al*. 2001, Rezanezhad *et al*. 2012a, 2012b, 2016) and a non-reactive solute (*e.g.*, Br^-), a considerable amount of solute appears in the effluent before one pore volume has been leached through (see Figure 1). The concept is that, while the solute is being transported by advection and dispersion due to water flow *via* pores that are open and connected (θ_m, mobile fraction), solute is also transferred to/from the partially closed pores (θ_{im}, immobile fraction) by diffusion processes that are typically rate-limited. Furthermore, the solute transport through peat is dominated by diffusional transport processes (between the immobile and mobile regions as well as within the mobile region) and, thus, the dual-porosity nature of the peat affects the timing and shape of the breakthrough curve (for more information about this concept, see Rezanezhad *et al*. 2012b and 2016).

The measured Br^- and NO_3^- concentrations (C) in the collected outflow pore water samples from each FTR were normalised to the inflow concentrations (C_0), then plotted against the number of pore volumes as Br^- and NO_3^- breakthrough curves. The number of pore volumes (P) was calculated by dividing the volume of water moved through the medium in time t (Qt; Q is the volumetric flow rate) by the volume of water-filled pores (ΦV; Φ is the porosity and V is the soil bulk volume) ($P = Qt/\Phi V$) (Kirkham & Powers 1972). The Br^- breakthrough curves were used to constrain the solute transport characteristics by calculating the transport parameters. The NO_3^- breakthrough curves were used to constrain steady-state nitrate reduction rates and the rates were calculated using the equation $(C_0 - C)Q/V$ once stable concentrations of NO_3^- were obtained in the FTR outflow solutions, according to previously published methodology (Pallud *et al.* 2007, Laverman *et al.* 2012).

The Br^- breakthrough curve for each undegraded and degraded peat reactor was fitted individually using the two-region non-equilibrium transport model in CXTFIT (Toride *et al*. 1995) and the solute transport parameters were extracted from the model simulation, which uses a non-linear least squares method to fit the parameters of analytical solutions with the option of a two-region fractionation of the pore space (mobile and immobile regions) (see van Genuchten & Wagenet 1989). This ‘two-region fractions’ model is called the ‘dual-porosity system model’, and assumes advective-reactive-dispersive transport in the mobile zone and diffusive-reactive exchange between mobile and immobile pores. The transport parameters calculated using this model included the volumetric pore mobile-immobile fractions (θ_m and θ_{im}, where the subscripts m and im refer to the mobile and immobile liquid regions), total porosity and volumetric water content ($\theta = \theta_m + \theta_{im}$), the first-order exchange coefficient (α), the proportion of pore space in the mobile phase (partitioning coefficient β), and the mass transfer (exchange) coefficient governing the rate of solute exchange between the mobile and immobile liquid regions (w). For a more detailed explanation of the model parameters for a dual-porosity medium, the reader is referred to Toride *et al*. (1995), Rezanezhad *et al*. (2012b) and Kleimeier *et al*. (2014).

RESULTS

Characterisation of peat samples

Some physical, hydraulic and chemical properties of the degraded and undegraded peat samples used in the flow-through reactor experiments are shown in Table 1. The bulk density of the degraded peat was approximately double that of the undegraded peat (0.2 g cm^{-3} *versus* 0.09 g cm^{-3}) and total porosity values for the degraded and undegraded samples were measured as 61.4 Vol% and 85.1 Vol%, respectively. The saturated hydraulic conductivity of the degraded peat was much lower than that of the undegraded peat (1.09 m d^{-1} *versus* 41.8 m d^{-1}). These results clearly show the differences in pore structure between the degraded and undegraded peat samples. The undegraded peat had lower bulk density (and hence higher porosity) and higher saturated hydraulic conductivity, indicating larger pores and faster flow of water and solutes. Total organic carbon (TOC) was determined as 25.8 and 41.4 %dry (by weight) in the degraded and undegraded samples, respectively, when collected and 24.6 and 40.8 %dry at the end of the FTR experiment. These results show that the total organic carbon (C) content of the undegraded peat was higher than that of the highly degraded peat. The organic carbon content of both peat types was depleted by only ~ 1 %dry at end of the FTR experiments. Total nitrogen concentration was low in both degraded and undegraded peat samples, and increased by about 0.15 %dry in the undegraded peat and 0.95 %dry in the degraded peat by the end of the experiment because of continuous NO_3^- input to the FTRs (see Table 1). However, this increase in N content was not significant when compared to the high carbon content, leading to a significant difference in C/N quotient between the undegraded

Table 1. Physical, hydraulic and chemical properties of the undegraded and degraded peat samples used in the flow-through reactor experiments. All measurements and analyses of the initial samples were conducted in triplicate (mean ± SD, n = 3). The total organic carbon and nitrogen values for end-of-experiment samples are averaged between duplicate FTRs.

Peat samples	Bulk density (g cm^{-3})	Total porosity (%)	Saturated hydraulic conductivity (m d^{-1})	Total organic carbon (%dry)		Total nitrogen (%dry)	
				Initial	End*	Initial	End*
Undegraded	0.09 ± 0.01	85.1 ± 2.5	41.8 ± 3.2	41.4 ± 0.41	40.8 ± 1.12	1.17 ± 0.05	1.34 ± 0.17
Degraded	0.2 ± 0.01	61.4 ± 2.8	1.09 ± 0.1	25.8 ± 0.74	24.6 ± 0.49	1.34 ± 0.08	2.29 ± 0.10

*Average from two FTRs.

peat (30.44) and the degraded peat (10.74). The high C/N quotients observed for the undegraded samples were expected, as they contained fresh and poorly decomposed peat.

Solute transport characterisations and parameters

Breakthrough curves of the Br$^-$ concentrations measured in the effluent pore water from each FTR are illustrated in Figure 2. The volumetric flow rate (Q) was 1 ml h^{-1}, porosity (Φ) was 61.4 Vol% and 85.1 Vol% (Table 1) and the soil volume (V) was 27.7 cm^3. The early breakthrough of Br$^-$ in all FTRs, with C/C_0 = 0.5 occurring at less than one pore volume ($P \sim 0.60$ for undegraded peat and ~ 0.85 for degraded peat), reflects preferential flow through the connected macropores (Figure 2). Br$^-$ breakthrough happened earlier in the undegraded peat samples (FTR I and II curves shifted to the left side) indicating more advective flow in large active (or mobile) connected pores. Breakthrough happened later in the degraded peat samples (FTR III and IV) because of more diffusive flow in small inactive (or immobile) isolated pores (see below and Table 2). Hence, advective flow, matrix diffusion and dispersion along the flowpaths all contributed to the features of the observed Br$^-$ breakthrough curves.

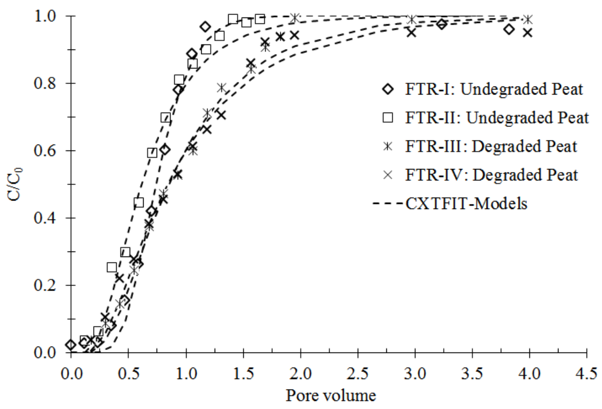

Figure 2. Normalised bromide breakthrough curves (in duplicate for undegraded and degraded peat samples) to constrain the transport characteristics and solute transport parameters using the two-region non-equilibrium transport model in CXTFIT.

The individual Br$^-$ breakthrough curves fitted using the dual-porosity system model in CXTFIT are also shown in Figure 2. The model parameters (see Methods) were varied until the best fit between the measured and predicted breakthrough curves was obtained. Thus, the optimal model parameter values of β, w and the dispersion coefficient (D_m) were determined for each undegraded and degraded FTR (Table 2). The optimised β values were used to calculate the volumetric water content of mobile and immobile regions (or the fractions of mobile and immobile pores) using the equations $\beta = \theta_m / \theta$ and $\theta_{im} = \theta - \theta_m$ ($\theta = 0.61$ for degraded peat and $\theta = 0.85$ for undegraded peat); assuming no adsorption (retardation due to sorption $R = 1$, no sorption) between the solid and the liquid phases for conservative Br$^-$ transport in peat. The exchange coefficient (α) was calculated from the optimised w values using the equation $\alpha = wq/l$, where q is the linear flow velocity calculated directly from the imposed volumetric flow rate (= 0.017 m d^{-1}) and l is the height of the FTR cell (2 cm) (see Table 2). The immobile pore fraction (θ_{im}) was higher in degraded than in undegraded peat (Table 2), as again indicated by the later breakthrough curves for degraded FTRs (Figure 2). The results for transport parameters (Table 2) showed that the exchange coefficient (α) was also higher in degraded peat.

Nitrate transformation

Nitrate breakthrough curves (*i.e.*, the NO$_3^-$ outflow concentration as a function of pore volume) that were used to constrain steady-state potential nitrate

Table 2. The estimated model parameter values of the partitioning coefficient (β), dispersion coefficient (D_m) and mass transfer exchange coefficient (w) for four Br^- breakthrough curves of undegraded and degraded peat samples determined by the two-region, non-equilibrium transport model in CXTFIT. The values of mobile pore fraction (θ_m), immobile pore fraction (θ_{im}) and first-order mass transfer coefficient governing the rate of solute exchange between the mobile and immobile pore water regions (α) are calculated using equations $\beta = \theta_m/\theta$ and $\theta_{im} = \theta - \theta_m$ and $\alpha = wq/l$. As an indication of the best fit, the root mean squared error (RMSE) values are given.

Peat samples	*RMSE*	β	θ_m	θ_{im}	w	α (d^{-1})	D_m ($m^2\ d^{-1}$)
FTR-I-Undegraded peat	0.98	0.55	0.4675	0.3825	0.88	0.76120	0.00037
FTR-II-Undegraded peat	0.97	0.57	0.4845	0.3655	0.75	0.64875	0.00089
FTR-III-Degraded peat	0.98	0.24	0.1560	0.4940	3.13	2.70745	0.00104
FTR-IV-Degraded peat	0.98	0.21	0.1365	0.5135	4.09	3.53785	0.00123

reduction rates are shown in Figure 3. In all undegraded and degraded FTRs, a complete reduction of NO_3^- was observed in the first 5 pore volumes (~ 4 days after starting the experiment). In undegraded FTRs (I and II) the NO_3^- reduction then decreased and reached a steady-state condition after ~ 25 pore volumes (~ 20 days after starting the experiment). In the degraded peat FTRs (III and IV), the high reduction of NO_3^- concentrations continued throughout the 30-day experiment. From the difference between the inflow and final outflow NO_3^- concentrations, a steady-state rate of NO_3^- reduction (during stabilised conditions) was calculated using the equation: $(C_0 - C)Q/V$, where the C_0 was the NO_3^- concentration in the input solution (= 1.6 mM), Q was the volumetric flow rate (= 1 ml h^{-1}) and V was the volume of soil in the reactor (= 27.7 cm^3). The degraded peat samples exhibited a higher potential NO_3^- reduction rate than undegraded peat samples (0.056 ± 0.0003 μmol cm^{-3} h^{-1} on average for degraded peat FTRs III and IV *versus* 0.028 ± 0.007 μmol cm^{-3} h^{-1} on average for undegraded peat FTRs I and II). Thus, the potential NO_3^- reduction rates were approximately doubled in degraded peat samples and remained high for the entire 30-day period of this experiment.

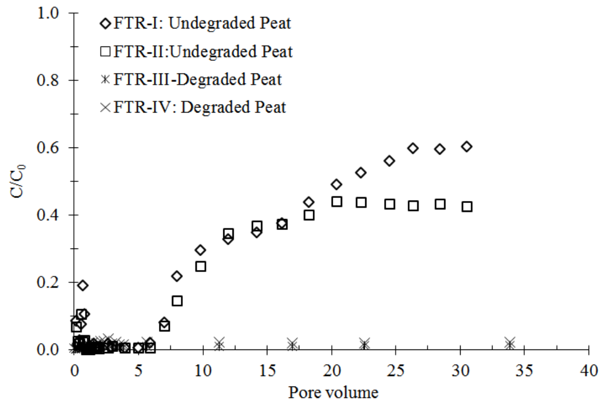

Figure 3. Normalised nitrate breakthrough curves (in duplicate for undegraded and degraded peat samples) to constrain steady-state potential nitrate reduction rates.

DISCUSSION

In this research, our motivation was to compare solute transport properties between two specific types of fen peat soil (degraded and undegraded) collected from contrasting peatlands in Germany and Canada, as part of a collaborative project between the Universities of Rostock and Waterloo. The degraded and undegraded fen peats selected had different pore structures associated with degradation processes, one resulting from effectively lowering the water table and the other reflecting natural conditions. The experimental and modelling results showed that the higher exchange coefficient values in the degraded peat can be explained by a greater number and volume of immobile pores, which increases the common interface surface area between mobile and immobile pores enabling more diffusive exchange between the two pore regions. Enhanced diffusive exchange between the two transport domains (mobile and immobile fractions) in degraded peat results in buffering of the responses of microbial communities, which affects biogeochemical activities such as nitrate reduction. The higher potential for NO_3^- reduction in degraded peat is in line with the results for transport characteristics of mobile and immobile pore fractions, the partitioning coefficients and the diffusive exchange coefficient rates (Figure 3 and Table 2), which show a link between potential NO_3^-

reduction rates and the pore structure and size distributions in undegraded and degraded peats. The higher immobile pore fraction in degraded *versus* undegraded peat (average FTR values ~ 0.5 and 0.14, respectively) implies a higher interface surface area between mobile and immobile pores in which the diffusive-reactive exchange of NO_3^- between pore domains enhances NO_3^- reduction. The first-order mass transfer coefficient (α) governing the rate of NO_3^- exchange between mobile and immobile pore water regions was also greater in the degraded than in the undegraded peat samples (average of FTRs 3.1 d^{-1} and 0.71 d^{-1}, respectively; see Table 2). Therefore, the greater physical accessibility of immobile pores in the degraded peat samples results in enhanced NO_3^- reduction, demonstrating that immobile water fractions in the peat are acting as hotspots for denitrification processes and creating more efficient and favourable conditions for nitrate removal.

Furthermore, the results of this study showed that the difference in degree of decomposition (H3 *versus* H10) and organic carbon content (~ 41 % *versus* 25 %) between the undegraded and degraded peats strongly influenced the potential rate of nitrate reduction. As both undegraded and degraded peat samples showed high NO_3^- reduction rates in the first 5 pore volumes (see Figure 3), this high rate of nitrate reduction can be explained by significantly higher dissolved pore water TOC concentrations leached from the undegraded peat (~ 80 mM) relative to the degraded peat (~ 20 mM) (Figure 4). Even the dissolved TOC concentration was low in the degraded peat, but the rates of exchange between mobile and immobile pores were higher than in the undegraded peat, which enhanced NO_3^- reduction. These findings emphasise the importance, for NO_3^- reduction rate in peat soils, of both available soil organic matter and an operational exchange between mobile and immobile pores. The degraded peat samples also showed lower dissolved pore water TN (~ 0.3 mM) than the undegraded peat (~ 0.5 mM) in the first 5 pore volumes. The TN concentrations in undegraded peat then increased (to ~ 0.7 mM), suggesting that TN release is dependent on NO_3^- reduction activity (Figure 4), whereas high NO_3^- reduction continued in the degraded peat and the effluents of FTRs III and IV remained low in TN leachate for the full 30 days of the experiment.

The comparative analyses of the undegraded and degraded peat samples showed that the different pore size distributions and structures associated with their different stages of degradation had an effect on solute transport processes. The fractions of immobile pores and the diffusive exchange coefficient between mobile and immobile pores in the degraded peat were found to be higher than in the undegraded peat samples. The higher diffusive exchange between the two transport domains in degraded peat influenced the transport of reactive solute (nitrate), such that a higher capacity for nitrate reduction was observed. A greater immobile pore fraction implies a greater interface surface area and diffusive exchange between the two pore regions, which is expected to buffer the responses of microbial activity and enhance the nitrate reduction rate. Thus, the degree of peat degradation influences the transport and reduction of nitrate, and the reduction rate is found to be higher in the degraded peat than in less degraded peat as a result of the higher fraction of immobile pores as well as the greater ease with which nitrate is exchanged between mobile and immobile pore water regions.

In summary, even if it has lower organic carbon content than less-degraded peat, the highly degraded peat has, by nature, unique physical pore structure

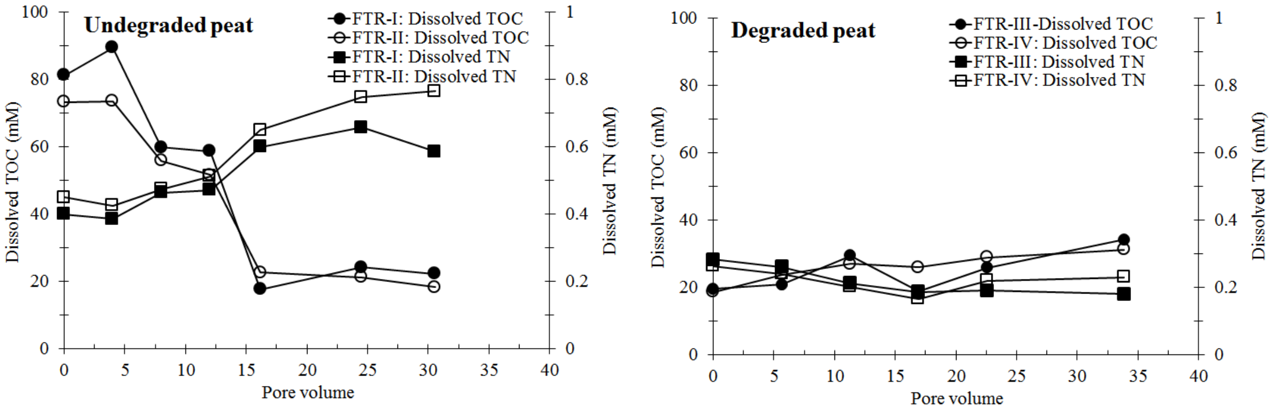

Figure 4. Dissolved total organic carbon (TOC) and total nitrogen (TN) concentrations in pore water samples from the effluents of FTRs with (left) undegraded (FTRs I and II) and (right) degraded (FTRs III and IV) peat samples.

properties that provide the necessary boundary and suitable conditions to enhance the efficiency of nitrate removal. Thus, more information on the type, degradation rate and physical and hydraulic properties of peat soils used in peatland reconstruction, as well as on management practices, will improve our understanding of how the physical changes and heterogeneity of the peat structure affects solute transport and biogeochemical activity.

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