Effect of anisotropy on solute transport in degraded fen peat soils

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Abstract
Peat soils are heterogeneous, anisotropic porous media. Compared to mineral soils, there is still limited understanding of physical and solute transport properties of fen peat soils. In this study, we aimed to explore the effect of soil anisotropy on solute transport in degraded fen peat. Undisturbed soil cores, taken in vertical and horizontal direction, were collected from one drained and one restored fen peatland both in a comparable state of soil degradation. Saturated hydraulic conductivity ($K_s$) and chemical properties of peat were determined for all soil cores. Miscible displacement experiments were conducted under saturated steady state conditions using potassium bromide as a conservative tracer. The results showed that (1) the $K_s$ in vertical direction ($K_{sv}$) was significantly higher than that in horizontal direction ($K_{sh}$), indicating that $K_s$ of degraded fen peat behaves anisotropically; (2) pronounced preferential flow occurred in vertical direction with a higher immobile water fraction and a higher pore water velocity; (3) the 5% arrival time (a proxy for the strength of preferential flow) was affected by soil anisotropy as well as study site. A strong correlation was found between 5% arrival time and dispersivity, $K_s$ and mobile water fraction; (4) phosphate release was observed from drained peat only. The impact of soil heterogeneity on phosphate leaching was more pronounced than soil anisotropy. The soil core with the strongest preferential flow released the highest amount of phosphate. We conclude that soil anisotropy is crucial in peatland hydrology but additional research is required to fully understand anisotropy effects on solute transport.

KEYWORDS
5% arrival time, anisotropy, breakthrough curves, degraded fen peat, preferential flow

1 | INTRODUCTION

Peatlands cover only 3% of global land area, but store about 10% of global fresh water and play a major role in water purification (Rezanezhad et al., 2016; Xu, Morris, Liu, & Holden, 2018). More than 40% of European peatlands have been anthropogenically altered and are degraded because of drainage and climate change, losing their ecosystem functions as water storage and water filter (Joosten, 2009; Lennartz & Liu, 2019). Several studies have been conducted on hydro-physical (Holden, Chapman, & Labadz, 2004; Liu & Lennartz, 2019a) and solute transport properties (Liu, Forsmann, Kjaergaard, Saki, & Lennartz, 2017; McCarter, Rezanezhad, Gharedaghlo, Price, & Van Cappellen, 2019), as well as pore water chemistry (Tiemeyer, Pfaffner, Frank, Kaiser, & Fiedler, 2017; Zak & Gelbrecht, 2007) of degraded peat soils and their significant impact on carbon and nitrogen cycles could be demonstrated (Baird, Belyea, Comas, Lee, &
Slater, 2009; Limpens et al., 2008; Liu, Zak, Rezanezhad, & Lennartz, 2019). Water flow and solute transport in peat soils are controlled by soil physical properties (e.g. soil organic matter content, pore structure), but are also affected by pore water chemistry (Kettridge & Binley 2010; Ours, Siegel, & Glaser, 1997).

Compared with mineral soils, peat has some unique features such as a high organic matter content and a low bulk density (Eggelsmann et al., 1993). The total porosity of peat could be as high as almost 100 vol% (Paavilainen & Päivänen, 1995). Peat soils exhibit highly heterogeneous and anisotropic properties. For instance, the saturated hydraulic conductivity ($K_s$) may range over about two orders of magnitude for a specific peat soil (Cunliffe, Baird, & Holden, 2013; Liu & Lennartz, 2019a). The anisotropic behaviour of $K_s$ has been studied over the last two decades (Beckwith, Baird, & Heathwaite, 2003; Cunliffe et al., 2013; Gharedaghloo, Price, Rezanezhad, & Quinton, 2018; Kruse, Lennartz, & Leinweber, 2008; Lewis, Albertson, Xu, & Kiely, 2012; Liu, Janssen, & Lennartz, 2016; Morris, Baird, Eades, & Surridge, 2019; Rosa & Larocque, 2008). Gharedaghloo et al. (2018) investigated the pore structure of bogs and found that $K_s$ is isotropic locally at pore-scale, but becomes anisotropic after upscaling to core-scale because of the layered structure of the peat. Liu et al. (2016) conducted a dye tracer experiment for non-layered fens and the pore network indicated that the connected macropores are predominantly vertically or horizontally orientated depending on sampling site leading to an anisotropic $K_s$. In addition, the anisotropic nature of peat is highly affected by soil degradation (Liu et al., 2016). In more pristine peat, the dominant flow and transport direction depends on the peat forming process and how dying plants and decaying plant materials were deposited. With advancing peat degradation, the volume fraction of macropores and pore connectivity decrease significantly (Liu & Lennartz, 2019a, 2019b; Liu et al., 2016) resulting in a relative isotropic structure of highly degraded peat soils (Kechavarzi, Dawson, & Leeds-Harrison, 2010; Liu et al., 2016). In addition, cracks occur in peat soils in dry summers, which may increase macroporosity of peat soils (Holden, Burt, & Cox, 2001).

Tracer techniques provide useful tools to explore water flow and solute transport processes in soils (Leibundgut, Maloszewski, & Kulls, 2009). Various forms of tracers such as isotope $^{18}$O (Ronkanen & Kläve, 2007), salt (Baird & Gaffney, 2000; Hoag & Price, 1997; Liu et al., 2017; McCarter, Weber, & Price, 2018), fluorescence (Ramirez, Baird, & Coulthard, 2016) and dyes (Liu & Lennartz, 2015; Liu et al., 2016; Mooney, Holden, Ward, & Collins, 1999) have been applied onto peat in the field or laboratory. All tracer experiments verify that preferential flow is a common phenomenon in peat soils. The occurrence of preferential flow is in accordance with the dual porosity structure of peat (active porosity and dead-end pores; Rezanezhad et al., 2016). Undecomposed plant material (e.g. woody or phragmites structures) as well as biopores such as root channels may serve as preferential flow pathways in peat soils (Liu & Lennartz, 2015; Liu et al., 2016; Mooney et al., 1999). Recent studies indicated that pronounced preferential flow mainly occurs in highly degraded peat soils (Liu et al., 2017). In this study, we define preferential flow as all phenomena where water, solutes and colloids move along certain pathways, while bypassing a fraction of soil matrix (Hendrickx & Flury, 2001). In other words, the soil contains a fraction of dead-end pores and/or immobile water (Liu et al., 2017; Vanderborght & Vereecken, 2007).

The determination of solute transport properties and the identification of preferential flow also depend on the properties of applied tracers. Chloride as well as tritium tracers were retarded in less degraded peat soils (Liu et al., 2017; McCarter et al., 2018). The adsorption of chloride onto peat was found to be related to its concentration (e.g. >500 mg l$^{-1}$, McCarter et al., 2018) and the soil organic matter content (Sheppard, Long, Sanipelli, & Sohlenius, 2009). Although there are several studies on solute transport in peat soils (Hoag & Price, 1997; Liu et al., 2017; McCarter et al., 2018; Rezanezhad, Price, & Craig, 2012), to our knowledge, there is no discussion on the effect of soil anisotropy on solute transport and strength of preferential flow in degraded fen peat soils in the existing literature.

Preferential flow pathways may enhance contaminant (e.g. phosphate) transport to groundwater leading to eutrophication in adjacent water bodies (Forssmann & Kjærgaard, 2014; Ronkanen & Kläve, 2009). Macropores are likely the primary transport pathways for phosphorus (P) in soils (Geohring et al., 2001; Simard, Beauchemin, & Haygarth, 2000; Vidon & Cuadra, 2011). Previous studies also indicated the P accumulation along macropore flow pathways (Backnäs, Laine-Kaulio, & Kläve, 2012; Gächter, Ngatiah, & Stamm, 1998; Ronkanen & Kläve, 2009). The P adsorption/desorption behaviour was found to differ between soil material forming macropores (pore wall material) and the soil matrix (Hansen, Hansen, & Magid, 1999; Jensen, Hansen, & Magid, 2002). However, little is known about the effect of anisotropic soil structure on phosphate leaching in degraded fen peat. In this study, miscible displacement experiments were conducted on horizontally and vertically collected fen peat. The objectives of the study were to quantify the effect of peat anisotropy (i) on solute transport properties, (ii) the preferential flow phenomenon and (iii) on the release of phosphate from degraded fen peat.

2  | MATERIALS AND METHODS

2.1  | Study sites and soil sampling

The two study sites are located at approximately 10 km south of the city of Rostock on either side of the Warnow River in Mecklenburg-Western Pomerania in Germany (site 1, 54°00’ N, 12°07’ E; site 2, 54°00’ N, 12°08’ E). The riparian fen peat soils at both sites have been artificially drained since the 19th century by ditches, which caused the mineralization of the organic matter predominantly of the upper few decimeters of soil horizons. The soil degradation process is accompanied by a loss of soil organic matter and an increase in soil bulk density. Both experimental sites have been under agricultural use mainly as grassland. Whereas site 1 is still subject to agricultural use, site 2 has been restored by blocking ditches and converted into a nature reserve (Ministry of the Environment Mecklenburg-Vorpommern, 2003) since the 1990s. The dominant botanical species forming the fen peat at both sites are sedge (Cyperaceae) and alder (Alnus). The fraction of wood-based material is approximately 30%.
For each of the two study sites, an area of 8 m × 8 m was selected for sampling. Eight sampling profiles (0.5 m × 0.5 m) were randomly chosen within the area and excavated down to a depth of 0.4 m. Two samples (one vertical and one horizontal) were taken from each pit at 0.4 to 0.5 m depth. For the horizontal samples, the pit was first deepened down to 0.6 m in order to take the sample exactly from the same depth as the vertical sample.

All 32 undisturbed soil cores (diameter of 8 cm, length of 5 cm) from both sites were collected by cutting the soil with a sharp knife in front of cylinder, which was slowly inserted into the soil in either horizontal or vertical direction. Cylinders were then removed from the soil by excavating a large soil block, from which the cylinders were carefully removed (Liu & Lennartz, 2019b). The soil cores were sealed on both ends with lids and tape before being neatly placed in a cool box and transported back to the laboratory.

2.2 | Hydro-physical properties

Before the determination of saturated hydraulic conductivity ($K_s$), all peat cores were slowly saturated upwards from the bottom with tap water; tap water was chosen because its electrical conductivity (EC, 650 µS cm$^{-1}$) is within the range of EC found for groundwater at the study sites (EC, 400–700 µS cm$^{-1}$). A previous study on samples from the same sites proved that the determination of $K_s$ was not sensitive to water salinity and EC variations (Gosch, Janssen, & Lennartz, 2018). A constant-head upward-flow method was used to measure $K_s$ in the laboratory at constant temperature of approximately 15°C (Supplemental Figure S1; Kruse et al., 2008; Liu et al., 2016). The chosen upward flow method allowed an exact adjustment of the hydraulic head and according flow rates. Low flow rates are desired to avoid internal erosion and gas bubble entrapment. The $K_s$ values have always been standardized to 10°C employing the equation provided by Klute (Klute 1965; see also Kruse et al., 2008).

Soil dry bulk density was determined by oven-drying the samples at 105°C for 24 h. After drying, the soil mass was related to the volume of the sample cylinder. The organic matter content was measured in the laboratory by the loss on ignition method (550°C; ISO 22476-3:2005). Soil particle density was determined following standard measurements ISO 17892-3:2004. Total porosity was estimated based on bulk density and particle density. Macroporosity was estimated by the differences between total porosity and volumetric water content at −60 cm H$_2$O pressure head assuming a contact angle of 0° for degraded fens (equivalent pore diameter of 50 µm; Liu & Lennartz, 2019a; Schindler, Behrendt, & Müller, 2003). Recently, a contact angle of 51.7° was reported for bogs by Gharedaghloo and Price (2019). However, differences in parent plant material as well as mineral content between bogs and fens do not allow to directly transfer the observations between peat types. The basic physical properties of the investigated peat are shown in Table 1.

### Physical properties of the investigated peat soils, mean (SD), n = 8

| Study site | von post | Soil organic matter content wt% | Bulk density g cm$^{-3}$ | Particle density g cm$^{-3}$ | Total porosity vol% | Macroporosity* vol% | Total phosphate content mg g$^{-1}$ | Redox sensitive phosphate content mg g$^{-1}$ |
|------------|---------|-------------------------------|--------------------------|-----------------------------|-------------------|-------------------|-----------------------------|-----------------------------|
| Site 1     | H5      | 81.2 (3.0)                    | 0.19 (0.01)              | 1.56                        | 87.8 (0.6)       | 10.16 (0.03)     | 0.78 (0.06)                | 0.03 (0.004)                |
| Site 2     | H5      | 88.1 (0.7)                    | 0.19 (0.01)              | 1.51                        | 87.4 (0.1)       | 4.34 (0.01)      | 0.44 (0.03)                | 0.01 (0.005)                |

*Macroporosity was calculated by the difference between total porosity and volumetric soil water content at −60 cm H$_2$O pressure head.
The parameters were eventually chosen based on the obtained from the numerical inverse model are provided in the upper and lower boundaries of the three fitted parameter values as values (van Genuchten, Simunek, Leij, Toride, & Sejna, 2012). The several estimation trials were conducted with adjusting the initial set to 1.0, 0.5 and 0.2, respectively (Toride et al., 1999), and thereafter was fixed at the average pore water velocity (0.383 cm h$^{-1}$). During the optimization procedure, the parameters were calibrated using the nonlinear least-squares parameter optimization program CRXFIT (Toride et al., 1999) with $R$ fixed at 1. The parameter $v$ was fixed at the average pore water velocity (0.383 cm h$^{-1}$). During the optimization procedure, the parameters $D$, $\beta$, and $\omega$ were initially set to 1.0, 0.5 and 0.2, respectively (Toride et al., 1999), and thereafter several estimation trials were conducted with adjusting the initial values (van Genuchten, Simunek, Leij, Toride, & Sejna, 2012). The upper and lower boundaries of the three fitted parameter values as obtained from the numerical inverse model are provided in the Supplemental Table S1. The parameters were eventually chosen based on the highest coefficient of determination and lowest mean square error.

Additionally, the strength of preferential flow was estimated based on the 5% bromide mass arrival time, when 5% of the applied bromide has been recovered in the effluent (Knudby & Carrera, 2005; Koestel, Moey, & Jarvis, 2011; Koestel et al., 2013; Norgaard, Paradela, Moldrup, Katuwal, & de Jonge, 2018; Soares et al., 2015). The lower the 5% arrival time, the stronger the preferential flow with limited residence time (Koestel et al., 2011; Soares et al., 2015).

2.4 Chemical and statistical analysis

For all collected effluent samples, bromide concentrations were determined by ion chromatography employing a Metrohm 930 Compact IC Flex. Soluble reactive phosphorus concentration in the outflowing water from soil cores, in following denoted as soil leachate, was analysed after filtration with syringe filters (0.45 μm pore size) by using the molybdenum blue method (Cary 1E; Varian, Darmstadt, Germany) according to Murphy & Riley (1962). For the determination of total phosphorus (TP), dried peat (60°C, 48 h) was homogenized in a stainless-steel mill. The TP content of peat was determined as SRP after an acid digestion procedure (circa 10 mg dry sample + 2 ml 10 M H$_2$SO$_4$ + 4 ml 30% H$_2$O$_2$ + 20 ml deionized water at 160°C for 2 h). TP of sites 1 and 2 was 0.78 mg g$^{-1}$ and 0.44 mg g$^{-1}$, respectively ($n = 8$, 40–50 cm depth). To determine the amount of P, which can be mobilized under anoxic conditions by redox processes, 10 g of fresh (i.e. wet) peat were extracted with a 0.11 M bicarbonate-dithionite solution in accordance with Zak, Gelbrecht, Wagner, and Steinberg (2008). The dissolved P in the filtered extract solution (syringe filters; 0.45 μm pore size) was analysed with ICP-OES (Inductively coupled plasma–optical emission spectrometry).

A t-test was used to test the differences in $K_s$ (as log$_{10}$ $K_s$) of peat between horizontal and vertical directions and the differences in total phosphate between sites. The effect of sites and sampling direction on 5% arrival time was tested using a general linear model. All the statistical analyses were performed using R (R Core Team, 2015) and the level of significance was set to 0.05.

3 RESULTS AND DISCUSSION

3.1 The anisotropy of saturated hydraulic conductivity

The obtained $K_s$ values of the investigated peat soils ranged over two orders of magnitude from 0.06 to 15.01 cm h$^{-1}$, which matches roughly the previous reported range of values from 0.6 to 71.8 cm h$^{-1}$ (Kruse et al., 2008; Liu & Lennartz, 2019a) of fen peat. The $K_s$ values differed significantly between the two sites ($p < .001$) although the peat of both sites is in a comparable degradation stage (e.g. bulk density, von Post humification and organic matter content are within the same range). The geometric mean value of $K_s$ of peat at site 1 is
2.25 cm h⁻¹, which is significantly higher than that of the peat from site 2 (geometric mean of $K_s = 0.23$ cm h⁻¹). The observed differences in $K_s$ are most likely related to the macroporosity (equivalent pore diameter of >50 μm; Schindler et al., 2003), which was found to be 0.13 ± 0.03 vol% (mean ± SD) for site 1 and 0.05 ± 0.01 vol% for site 2 (Table 1). The finding indicates that the $K_s$ of degraded peat is more sensitive to macroporosity rather than bulk density and von Post humification. The latter two properties did not differ between both sites (Table 1).

At both sites, significant differences were observed in $K_s$ between vertical ($K_{sv}$) and horizontal ($K_{sh}$) flow directions ($p < .01$), indicating that $K_s$ is anisotropic in the case of the two investigated sites (Figure 2). The anisotropy ratio (log_{10}[$K_{sh}/K_{sv}$]; Beckwith et al., 2003; Liu et al., 2016) of sites 1 and 2 are −0.80 and −0.41, respectively, suggesting that $K_{sv}$ was higher than $K_{sh}$. Previous studies on peat soils have reported that $K_{sh}$ could be greater than $K_{sv}$ (Beckwith et al., 2003; Cunliiffe et al., 2013; Lewis et al., 2012), whereas the opposite results ($K_{sv} > K_{sh}$) were also obtained (Kruse et al., 2008; Liu et al., 2016; Surridge, Baird, & Heathwaite, 2005). The anisotropy ratio found in this study is within the earlier reported range of values from −1.1 to 2.4 (Beckwith et al., 2003; Kruse et al., 2008; Liu et al., 2016). The hydraulic anisotropy of peat soils is related to the orientation of undecomposed plant materials (Chason & Siegel, 1986; Liu et al., 2016; Surridge et al., 2005). At both investigated sites, undecomposed wood branches (alder) were predominantly vertically orientated (Liu & Lennartz, 2015; Liu et al., 2016), facilitating water movement in vertical direction.

### 3.2 Breakthrough curves

The measured and corrected BTCs are presented in Figure 3. For all of the soil cores, the recovery of the applied tracer was greater than 95%, which is indicative for a negligible bromide adsorption (Kleimeier, Karsten, & Lennartz, 2014). All BTCs exhibited an early breakthrough with relative concentrations $C/C_0$ of 0.5 occurring at less than one pore volume. Four BTCs of vertically collected peat samples (S1V2, S2V3, S2V1 and S2V3) had a much earlier breakthrough and a longer tailing than the other eight BTCs, indicating a strong preferential flow (Liu et al., 2017; Rezanezhad et al., 2012).

In this study, both the CDE model (only $D$ was fitted; Supplemental Table S2) and the MIM model ($D$, $β$ and $ω$ were fitted) were employed to describe the measured BTCs (Table 2). The MIM model adequately described all BTCs with a higher fitting criterion of $R^2 > 0.99$ and smaller mean square error than those obtained with the CDE model (Supplemental Table S3), although for two BTCs the $R^2$ was above 0.99 using the CDE model. For most of the BTCs, the
errors between simulated and observed values are normally distributed (Supplemental Figure S3 and Table S4). The corrected Akaike information criterion (AICc; Burnham & Anderson, 2002; Supplemental Table S3) suggests that the MIM model did not over-fit the BTCs. The calibrated soil transport parameters of the MIM model, 95% confidence limits and the covariance matrix for fitted parameters of each sample are shown in Tables 2 and 3 and Supplemental Table S5, respectively. The covariance matrix suggests that the transport parameters were not highly correlated in the majority of the samples. The calibrated \( \beta \) ranged from 0.34 to 4.59 \( \text{cm}^2 \text{ h}^{-1} \) with a dispersivity (\( \lambda \)) ranging from 0.78 to 6.69 cm. The \( \beta \) value ranged from 0.48 to 0.94 indicating the presence of immobile water and preferential flow. The \( \omega \) parameter was found to vary from 0 to 1.70. The ranges of all the calibrated parameters (\( D, \beta \) and \( \omega \)) are within the span reported by Liu et al. (2017) for fen peat. The \( \beta \) values we found here generally smaller than those reported by Simhayov, Weber, and Price (2018), who estimated that the values of \( \beta \) was almost equal to one but with a great variance. One possible reason for the differences in parameter values may be that the fen peat soils in their study was less degraded (bulk density of 0.12 g cm\(^{-3}\)) compared to soils in this study (bulk density of 0.20 g cm\(^{-3}\)). Larger variability of calibrated parameters (e.g. \( \beta \) and \( v_m \)) were observed for vertical samples, which is consistent with the results from Liu et al. (2017). In their study, transport properties (vertically collected) varied considerably as determined on samples collected from one depth. However, in our study here the variability of \( D, \beta \) and \( \omega \) for the horizontal samples are

### TABLE 2  Values of calibrated parameters from MIM model

| Study sites | Direction of samples | Column | \( \beta \) | \( \omega \) | \( v_m \) cm h\(^{-1} \) | \( D_m \) cm\(^2\) h\(^{-1} \) | \( \lambda \) cm | \( R^2 \) | MSE |
|-------------|----------------------|--------|-------------|-------------|-----------------|-----------------|-----------|------|-----|
| Site 1      | Horizontal          | S1H1   | 0.83        | 0.00        | 0.46            | 1.25            | 2.69      | 0.995 | 0.0008 |
|             |                      | S1H2   | 0.94        | 0.00        | 0.41            | 1.36            | 3.34      | 0.995 | 0.0006 |
|             |                      | S1H3   | 0.88        | 0.00        | 0.43            | 1.62            | 3.73      | 0.997 | 0.0004 |
|             | Vertical            | S1V1   | 0.88        | 0.00        | 0.44            | 1.13            | 2.59      | 0.996 | 0.0006 |
|             |                      | S1V2   | 0.48        | 1.69        | 0.80            | 3.30            | 4.10      | 0.993 | 0.0008 |
|             |                      | S1V3   | 0.56        | 1.55        | 0.69            | 4.59            | 6.69      | 0.995 | 0.0005 |
| Site 2      | Horizontal          | S2H1   | 0.86        | 0.02        | 0.44            | 0.35            | 0.78      | 0.995 | 0.0009 |
|             |                      | S2H2   | 0.82        | 0.01        | 0.47            | 0.61            | 1.29      | 0.996 | 0.0007 |
|             |                      | S2H3   | 0.86        | 0.01        | 0.44            | 0.53            | 1.20      | 0.998 | 0.0004 |
|             | Vertical            | S2V1   | 0.83        | 0.03        | 0.46            | 1.92            | 4.15      | 0.986 | 0.0017 |
|             |                      | S2V2   | 0.87        | 0.00        | 0.44            | 0.73            | 1.65      | 0.991 | 0.0014 |
|             |                      | S2V3   | 0.52        | 0.14        | 0.74            | 2.52            | 3.42      | 0.982 | 0.0025 |

### TABLE 3  Upper and lower boundaries of the 95% confidence limits for fitted parameters (\( D, \beta \) and \( \omega \)) in mobile and immobile model

| Column | \( D \) (cm\(^2\) h\(^{-1} \)) | \( \beta \)  | \( \omega \)  |
|--------|---------------------------------|-------------|-------------|
|        | Lower                           | Upper       | Lower       | Upper       |
| S1H1   | 0.83                            | 1.23        | 0.77        | 0.88        |
| S1H2   | 1.04                            | 1.52        | 0.87        | 1.00        |
| S1H3   | 1.23                            | 1.64        | 0.83        | 0.93        |
| S1V1   | 0.83                            | 1.16        | 0.83        | 0.93        |
| S1V2   | 1.07                            | 2.07        | 0.33        | 0.62        |
| S1V3   | 2.02                            | 3.11        | 0.41        | 0.70        |
| S2H1   | 0.22                            | 0.38        | 0.82        | 0.91        |
| S2H2   | 0.40                            | 0.60        | 0.78        | 0.94        |
| S2H3   | 0.40                            | 0.53        | 0.83        | 0.89        |
| S2V1   | 0.58                            | 2.60        | 0.57        | 1.00        |
| S2V2   | 0.46                            | 0.81        | 0.80        | 0.93        |
| S2V3   | 0.20                            | 2.43        | 0.31        | 0.73        |
generally smaller than those reported by Liu et al. (2017) for highly degraded peat soils. The variability of calibrated parameter values among all samples is always greater for the vertical transport situation, which suggests that the spatial heterogeneity is greater in vertical direction than in horizontal direction. We take that as a hint that preferential flow is more likely to occur in vertical direction. In future studies, a range of velocities should be adjusted in flow-through experiments to derive definite conclusion.

In general, samples that were taken in vertical direction had a lower $\beta$, but higher $v_m$, $\omega$ and $D_m$ values than those of horizontal samples. Differences in solute transport properties between horizontal and vertical samples are more important than effects that are related to sampling sites. As mentioned above, four vertical samples from both sites (cores S1V2, S1V3, S2V1 and S2V3; Table 1) exhibit a pronounced preferential flow. The average value of $\beta$, as an indicator of the amount of mobile water, of these four soil cores was $0.60 \pm 0.16$ (mean $\pm$ SD), which was significantly lower (stronger preferential transport) than that for the other eight soil cores with $0.87 \pm 0.04$ ($p < .001$). As a consequence, these four vertical cores had a significantly higher pore water velocity of the mobile zone ($v_m = v/\beta$) than other soil cores ($p < .001$). The immobile water fraction of the mentioned four vertical cores was approximately $0.36 \text{ cm}^3 \text{ cm}^{-3}$; this soil water volume was not participating in the convective transport of bromide.

For most soil cores, a low mass transfer coefficient ($\omega \approx 0$) was observed. In the MIM model, a small $\omega$ value ($\omega < 0$) indicates that the immobile soil water region does not participate in transport and is not accessible for solutes (Raddiffe & Simunek, 2010). However, almost all $\beta$ values are $<0.9$, which indicates that the tested peat soil is a dual porosity medium. Minor immobile water fractions ($\beta > 0.9$) may result from isolated pores or unavoidable experimental and calculation errors.

### 3.3 Strength of preferential flow

The 5% arrival time of bromide mass ranged from 6.15 to 10.28 h. Significant differences in 5% arrival time were observed between sites ($P = 0.0095$; general linear model) and between soil sampling directions ($P = 0.024$). A significantly lower 5% bromide mass arrival time was observed for the samples from drained site (average of 7.58 h) than those from the restored site (average of 9.46 h). Moreover, a later 5% bromide mass arrival time was observed for horizontal samples (9.29 h) than for vertical samples (7.75 h). Thus, the strength of preferential flow is orientation-dependent and associated with land management. Given that no significant differences were observed in soil physical properties between sites and between orientations (e.g., bulk density or von post humification), the 5% tracer mass arrival time or preferential flow, respectively, is not predictable using physical properties of peat only.

The 5% arrival time has a strong negative linear relationship with dispersivity ($R^2 = 0.83$, $p < .001$; Figure 4a), moderate positive linear relationship with $\beta$ ($R^2 = 0.39$, $p < .05$; Figure 4b) and moderate negative linear relationship with $\log_{10}K_s$ ($R^2 = 0.51$, $p < 0.01$; Figure 4c). These relationships generally point out that the assumption of the MIM is correct and that high dispersivity values and a large fraction of immobile water are in accordance with pronounced preferential transport situations. The dispersivity may affect the values of 5% arrival time, however, it is hard to distinguish the effect of dispersivity on 5% arrival time when preferential flow occurs. For instance, in several soil cores (e.g. S1V2, S1V3 and S2V3), the larger immobile water fraction suggests that pronounced preferential flow occurred although the soil dispersivity is high. Previous studies (e.g. Koestel et al., 2011; Soares et al., 2015) have proved that 5% arrival time is the best indicator for the strength of preferential flow when preferential flow occurred. In this study, the corrected BTCs indicate that (strong/weak) preferential flow occurred in all soil cores. Therefore, the 5% arrival time was used to evaluate the BTCs. The results obtained here for peat soils for the first time are in consistence with observations made for mineral soils (Paradelo et al., 2013; Shaw, West, Raddiffe, & Bosch, 2000; Soares et al., 2015; Vervoort, Raddiffe, & West, 1999). The occurrence of significant preferential flow in samples, which exhibit higher $K_s$ and lower $\beta$ values, suggests that a few macropores are active in solute transport and these macropores...
Phosphate concentration (approximately 2 mg P l⁻¹) drained peat soils. For most soil cores from the drained site, a high P release rate from artificially peatland results in a high TP contents of the investigated peat soils (Table 1). This is also reflected in a high P release rate from artificially fertilized and ongoing soil organic matter mineralization of drained peatland (site 1) to avoid eutrophication of surface waters. The strong preferential flow in vertical direction may enhance P release to surface or ground water.

There was no significant difference in the amount of released P between samples from the vertical and horizontal direction. A negative but statistically not significant correlation was observed between the mass of released P and 5% arrival time (Pearson’s correlation coefficient of 0.76; p = .07). The very high P release rate as observed for one sample may be related to the P accumulation in preferential flow pathways. In cases where P content is high in the topsoil because of agricultural usage, it may be transported and enriched along preferential pathways (Backnäs et al., 2012; Gächter et al., 1998; Ronkanen & Kleve, 2009) and the preferential transport tracks enhanced P leaching (Backnäs et al., 2012; Fuchs, Fox, Storm, Penn, & Brown, 2009; Gächter et al., 1998). In summary, the findings of this study provide evidence that solute transport and the release of P are mainly related to soil heterogeneity and the effect of anisotropy needs more detailed consideration.

FIGURE 5 Effluent phosphate concentrations of peat soils in horizontal and vertical directions from drained peatland (site 1)

are, likewise, ensuring the water conductance under staturated condition (Goncalves, Leij, & Schaap, 2001).

Overall, solute transport in peat soils was affected by the structure of peat. The effect of soil anisotropy on solute transport properties is not as clear as on Ks. The transport parameters and the lower 5% arrival time of vertical samples suggest that preferential flow is more likely to occur in vertical directions. It is more likely to encounter preferential transport situations in locations where Ks is high. In cases where Ks values are greater in horizontal than in vertical direction (Beckwith et al., 2003; Lewis et al., 2012), preferential flow can, likewise, be stronger in horizontal direction.

3.4 Phosphate leaching

Fertilization and ongoing soil organic matter mineralization of drained peatland results in a high P release rate from artificially drained peat soils. For most soil cores from the drained site, a high phosphate concentration (approximately 2 mg P l⁻¹; Figure 5) was observed in the leachate. The high P leaching concentrations are in consistent with recent studies by Parvage, Ulén, & Kirchmann (2015) and Riddle et al. (2018), who observed a range of phosphate concentrations in the effluent from 0.36 to 10.3 mg P l⁻¹ for organic soils. For the studied fen peat, the redox sensitive P accounts for only <4% of total P, which is a small fraction if compared to values reported in other studies (>15%; Forsmann & Kjaergaard, 2014). We assume that other more loosely bound P fractions (e.g. water-extractable P) dominated the released P of 3–18 mg during the relatively short experimental period of 3 days. The observed P concentrations in leachate from the drained and degraded peatland were 1000 times higher than the suggested threshold concentration of P (0.01 mg l⁻¹) to avoid 4 CONCLUSIONS

The effects of soil anisotropy on water flow and solute transport in degraded fen peat soils were explored. We assume that the more abundant vertically orientated macropores lead to a significantly higher Ks in the vertical than in the horizontal direction, whereas the solute transport properties as derived from breakthrough curves (BTCs) are moderately affected by soil anisotropy. It is likely that the macroporous structure that facilitates water conductance also (rapidly) convey dissolved compounds. The great variance of leached amount of phosphate indicate that phosphate transport is more determined by soil heterogeneity than anisotropy. In this study, the solute transport behaviour was investigated on samples that were either taken in horizontal or vertical direction. Both sample groups have their own heterogeneity, which may have overwritten the anisotropy effect. In future studies, an approach should be developed that allows for transport tests in various directions on the same sample. It should be likewise noted that soil anisotropy as well as preferential flow and compound release are scale-dependent and related to the degree of water saturation.

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DATA AVAILABILITY STATEMENT
Data available on request from the authors.

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