



Invited research article

Structure of peat soils and implications for water storage, flow and solute transport: A review update for geochemists



Fereidoun Rezanezhad ^{a,*}, Jonathan S. Price ^b, William L. Quinton ^c, Bernd Lennartz ^d, Tatjana Milojevic ^a, Philippe Van Cappellen ^a

^a Ecohydrology Research Group, Water Institute and Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada

^b Department of Geography and Environmental Management, University of Waterloo, Waterloo, Canada

^c Cold Regions Research Centre, Wilfrid Laurier University, Waterloo, Canada

^d Faculty of Agricultural and Environmental Sciences, Rostock University, Rostock, Germany

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ABSTRACT

Global peatlands are a valuable but vulnerable resource. They represent a significant carbon and energy reservoir and play major roles in water and biogeochemical cycles. Peat soils are highly complex porous media with distinct characteristic physical and hydraulic properties. Pore sizes in undecomposed peat can exceed 5 mm, but significant shrinkage occurs during dewatering, compression and decomposition, reducing pore-sizes. The structure of peat soil consists of pores that are open and connected, dead-ended or isolated. The resulting dual-porosity nature of peat soils affects water flow and solute migration, which influence reactive transport processes and biogeochemical functions. Advective movement of aqueous and colloidal species is restricted to the hydrologically active (or mobile) fraction of the total porosity, i.e. the open and connected pores. Peat may attenuate solute migration through molecular diffusion into the closed and dead-end pores, and for reactive species, also through sorption and degradation reactions. Slow, diffusion-limited solute exchanges between the mobile and immobile regions may give rise to pore-scale chemical gradients and heterogeneous distributions of microbial habitats and activity in peat soils. While new information on the diversity and functionalities of peat microbial communities is rapidly accumulating, the significance of the geochemical and geomicrobial study on peat stands to benefit from a basic understanding of the physical structure of peat soils. In this paper, we review the current knowledge of key physical and hydraulic properties related to the structure of globally available peat soils and briefly discuss their implications for water storage, flow and the migration of solutes. This paper is intended to narrow the gap between the ecohydrological and biogeochemical research communities working on peat soils.

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1. Introduction

Peat forms through the accumulation of partially decomposed plant biomass in fens, bogs, salt marshes and some swamps in various parts of the world, including vast peatlands in boreal/taiga landscapes, as well as temperate and tropical locations (Canadian System of Soil Classification, CSSC, 1998). Peat deposits cover large areas of northern North America, northern Europe, western Siberia, Indonesia and south-east Asia; they occur as arctic and alpine tundra, taiga, boreal and sub-boreal bogs, fens and other peatlands, where *Sphagnum* mosses are often the dominant peat-forming species (Kuhry et al., 1993; Glaser et al., 2004a). Peatlands are transitional environments between terrestrial and aquatic ecosystems that provide essential hydrological, ecological and biogeochemical functions (Fraser et al., 2001a,b; Joosten and Clarke, 2002; Chapman et al., 2003; Mitra et al., 2005; Krueger et al., 2015). Although

peatlands only cover about 3% of the continents (IMCG, 2008), globally they store on the order of 10% of all freshwater and 30% of land-based organic carbon (300–450 PgC; Mitra et al., 2005; Limpens et al., 2008; Bragazza et al., 2013). There is growing interest in understanding and predicting how soil processes in peatlands respond to anthropogenic pressures, including land-use changes, resource extraction and global climate warming (Strack, 2008; Booth et al., 2012).

The ecology and biogeochemistry of peat soils are closely linked to the movement through and storage of water and reactive solutes (e.g., Ca, Mg, Fe, Na), which, in turn, depend on the chemical composition of the soil water (Hill and Siegel, 1991), microbiological and chemical processes (Todorova et al., 2005) and the physical characteristics of the porous matrix (Päivinen, 1973; Rycroft et al., 1975a,b; Price and Woo, 1988; Ours et al., 1997). The total porosity of peat soils often exceeds 80% (Boelter, 1968). Peat can have relatively large pores (Hayward and Clymo, 1982) that are highly irregular and interconnected (Quinton et al., 2009; Rezanezhad et al., 2010), as well as smaller open pores, dead-end pores and those that are closed or partially closed

* Corresponding author.

E-mail address: frezanez@uwaterloo.ca (F. Rezanezhad).

(Hoag and Price, 1997). Peat is thus a dual-porosity medium that includes a “mobile region” through which water, solutes and colloids move relatively easily, and an “immobile region” with negligible fluid flow velocity. Exchange of solutes between the two regions occurs primarily via molecular diffusion (van Genuchten and Wierenga, 1976). While advection through the open and connected (or active) pores, and matrix diffusion into and within closed pores are generally assumed to be the dominant mechanisms controlling solute transport in peat, only a relatively small number of studies have investigated the effects of the complex dual-porosity structure of peat on solute transport (e.g., Loxham and Burghardt, 1983; Price and Woo, 1988; Hoag and Price, 1997; Ours et al., 1997; Reeve et al., 2001; Rezanezhad et al., 2012b).

The hydraulic properties of peat strongly depend on the peatland vegetation and the degree of decomposition of the plant debris. Decomposition is mainly carried out by microorganisms that use soil organic compounds as energy substrates. The degree of decomposition and physical make-up of the peat varies with depth, age, plant community and, foremost, the drainage regime (Swanson and Grigal, 1989; Schoepfroster and Furbush, 1974). The degree of decomposition is commonly assessed using the 10 classes of humification of the von Post scale (von Post, 1922) where H1 refers to the least, H10 the most decomposed peat. The von Post classification is based on the visual inspection of extracted soil solutions and plant residues, and is therefore particularly useful in the field. Additional characterization methods have been developed to describe the degree of decomposition based on size fractions, density, and fiber content (Boelter, 1969; Lynn et al., 1974; Lishtvan and Kroll, 1975; Malterer et al., 1992) while increasingly, isotopic and spectroscopic approaches are used for assessing soil organic matter decomposition and the associated changes in molecular composition, functionality and reactivity (Moers et al., 1990; Baldock et al., 1997; Macko et al., 1991; Menot and Bums, 2001; Drexel et al., 2002; Grover and Baldock, 2013; Cao et al., 2014). Carbon/nitrogen ratios are also commonly used to assess relative states of decomposition of peat soils (Kuhry and Vitt, 1996; Bridgman et al., 1998).

The degree of decomposition of peat generally increases with depth below the ground surface, while the geometric mean pore diameter and active porosity simultaneously decrease. For example in the Arctic tundra, the active porosity typically drops from values around 80% near the ground surface to <50% at depths of 0.5 m (Quinton et al., 2000). Over the same depth range, however, reductions in permeability of three or more orders of magnitude are not unusual (e.g., Boelter, 1965; Hoag and Price, 1995; Quinton et al., 2000; Beckwith et al., 2003a). The depth variations of porosity and pore-size distribution (McCarter, 2014), as well as the structural alignment of the peat fabric (Landva and Pheeney, 1980), affect water storage and flow in peat, including the partitioning of pore water between the mobile and immobile regions (Caron et al., 2015a). The low permeability and reduced active porosity of deeper, well-humified peat layers limit exchanges of water and solutes with surface waters and the atmosphere.

Climate change and human disturbances in high latitude regions are producing ecosystem changes with largely unknown consequences for the fluxes and storage of water, carbon and nutrients (Rowland et al., 2010). It has been shown that peatlands release substantial volumes of biogenic gases into the atmosphere, in response to changing climate, through plant shoots, slow diffusion across the peat surface, and episodically via ebullition (release of free-phase gas in the form of bubbles), and some of it is converted to carbon dioxide in the oxic portion of the peat (Rosenberry et al., 2003; Baird et al., 2004; Glaser et al., 2004b; Tokida et al., 2005; Strack et al., 2006; Rosenberry et al., 2006). Estimated volumes of gaseous-phase gas in peatlands range from 0 to nearly 20% of the peat volume (Rosenberry et al., 2006). This accumulation and release of trapped gases may affect the peat matrix and, thus alter hydraulic gradients and movement of water and solutes in peat (Kellner et al., 2004; Beckwith and Baird, 2001), which in turn can alter the composition and flux of greenhouse gases (Rosenberry et al.,

2006; Strack et al., 2005). In particular, there is a need to reduce the uncertainties associated with potential feedbacks to climate warming of organic matter degradation rates and greenhouse gas emissions in northern peatlands. A better understanding of belowground biogeochemical processes in peat soils must account for the unique transport and water-holding properties of these complex environments. In this paper, we review current knowledge on the structure of globally available peat soils and the resulting effects on flow and solute transport. Our review will, we hope, provide the geochemical community with an entry point to the literature on physical soil properties and processes that are relevant to the biogeochemical functioning of peat soils.

2. Physical properties

Peat soils are organic rich materials, usually containing ≥ 20 mass % C_{org} (Canadian System of Soil Classification, CSSC, 1998). The unique combination of physical properties of peat, including low bulk density, high total porosity, and the ability to swell and shrink upon wetting and drying (Table 1), means that concepts and methods used to describe the porous media properties of mineral soils may often be inadequate (Dettmann et al., 2014; Caron et al., 2015b). The total porosity of peat includes the relatively large, inter-particle pores that can actively transmit water, as well as relatively small, closed, and dead-end pores formed by the remains of plant cells (Hayward and Clymo, 1982; Kremer et al., 2004). Scanning electron microscopy of peat reveals (I) open and connected macropores, (II) closed or partially closed cells, and (III) dead-end or isolated pore spaces (Fig. 1). These micro-scale pore structures are responsible for the dual-porosity behavior observed at the scales of macroscopic peat samples (e.g., Hoag and Price, 1997; Ours et al., 1997; Rezanezhad et al., 2012a) and field observations (e.g., Hoag and Price, 1995; Baird, 1997): I comprises the “active porosity”, and II plus III comprise the immobile water fraction or “inactive porosity”. Undecomposed peat with high fiber content and a large active porosity yields as much as 80% of its saturated water content to drainage; the most decomposed peat samples release less than 10% of their water to drainage (Radforth and Brawner, 1977; Letts et al., 2000).

Peat decomposition reduces the proportion of large pores by breaking down plant debris into smaller fragments, thereby reducing the inter-particle pore spaces (Moore et al., 2005; Bragazza et al., 2008). Fig. 2 shows an example of decomposition and pore structure differences between Sphagnum peat layers collected at 5 and 55 cm cross-sectional depths where a higher decomposition and compression is observed at a depth of 55 cm. In the peatland-dominated zone of discontinuous permafrost, total porosity drops by about 10% between the ground surface and 35 cm depth, however, the active porosity decreases by as much as 40% over the same distance (Quinton et al., 2000). The water storage coefficient of peat and its saturated hydraulic conductivity similarly decrease rapidly with depth in the soil (see Section 3). Decomposition increases the mass of dry material per volume of peat and therefore the bulk density of peat increases with depth from <30 kg m⁻³ near the ground surface to >150 kg m⁻³ at a depth of 35 cm (Quinton et al., 2000). Nonetheless, because of the high organic matter content, even highly decomposed peat has a relatively low bulk density compared to mineral soils (Driessens, 1977).

Peat is a highly compressible material (Hobbs, 1986; Price and Schlotzhauer, 1999; Price et al., 2005). Peatland surfaces may therefore exhibit daily to seasonal vertical movement due to swelling and shrinking. The vertical movement of the ground surface is accompanied by changes in water storage, but also in the hydraulics, biogeochemistry and thermal properties (Waddington et al., 2010). The compressibility of peat is controlled by its physical properties, including the structure and arrangement of its pores (Kennedy and Price, 2005), factors that are largely controlled by the degree of decomposition (Price et al., 2005). Undecomposed peat near the ground surface has both elastic and plastic properties that enable it to expand and contract readily with wetting and drying. Decomposed peat at greater depths typically

Table 1

Some peat soil parameter ranges assembled from a variety of field and laboratory studies.

Properties	Parameters	References
Physical/Hydraulic	<ul style="list-style-type: none"> Bulk density: 0.02 - 0.254 g cm⁻³ Total porosity: 71 - 95.1% Specific yield: 0.048 - 0.45 Shrinkage: 18 - 34 mm (from initial thickness = 100 mm) Compression: 8 - 48 mm (from initial thickness = 100 mm) Saturated hydraulic conductivity (K_{sat}): $0.7 \times 10^{-5} - 1.3 \times 10^{-2}$ m s⁻¹ Unsaturated hydraulic conductivity (K_{usat}): $7.9 \times 10^{-7} - 1.2 \times 10^{-5}$ m s⁻¹ Pore diameter: 0.1 - 4.6 mm Adsorption-desorption partition coefficient: 1.33 - 5400 l g⁻¹ Diffusion coefficient: $10^{-7} - 10^{-9}$ m² s⁻¹ Dispersion coefficient: $0.3 \times 10^{-3} - 9.0 \times 10^{-7}$ m² s⁻¹ Mass transfer exchange coefficient: $4.4 \times 10^{-9} - 2.8 \times 10^{-5}$ s⁻¹ 	7, 8, 14, 18, 28, 32, 34, 35, 37, 48, 55, 57 21, 22, 35, 46, 47, 48 2, 3, 6, 27, 28, 36, 37, 42, 44, 48, 49 23, 24, 25, 37, 38, 39, 41, 42 1, 11, 12, 17, 30, 34, 43, 50, 58 9, 11, 16, 17, 19, 20, 32, 34, 40, 43, 45
(Bio) geochemical	<ul style="list-style-type: none"> Microbial biomass C: 10 - 1500 µg g⁻¹ Microbial biomass N: 5 - 75 µg g⁻¹ CO₂ production rates: 0 - 10 nmol cm⁻³ d⁻¹ CH₄ production rates: 0 - 2 nmol cm⁻³ d⁻¹ C/N: 5.5 - 26.8 Cation exchange capacity: 55-200 mEq per 100 g 	13, 33, 52, 54 4, 5, 10, 15, 31, 26, 29, 33, 51, 53, 54, 56, 59, 60, 61

¹Abat et al. (2012); ²Baird (1997); ³Beckwith et al. (2003a,b); ⁴Blodau and Moore (2003); ⁵Blodau et al. (2011); ⁶Boelter (1965); ⁷Boelter (1968); ⁸Boelter (1969); ⁹Boudreau et al. (2009); ¹⁰Bougon et al. (2009); ¹¹Deiss et al. (2004); ¹²Dumontet et al. (1990); ¹³Freeman et al. (1997); ¹⁴Hayward and Clymo (1982); ¹⁵Hill and Siegel (1991); ¹⁶Hoag and Price (1995); ¹⁷Hoag and Price (1997); ¹⁸Hobbs (1986); ¹⁹Jordan et al. (1997); ²⁰Keefe et al. (2004); ²¹Kellner and Halldin (2002); ²²Kennedy and Price (2005); ²³Kettridge and Binley (2008); ²⁴Kettridge and Baird (2010); ²⁵Kettridge and Binley (2011); ²⁶Koerselman et al. (1993); ²⁷Kruse et al. (2008); ²⁸Lewis et al. (2012); ²⁹Williams and Sparling (1988); ³⁰Lodenius et al. (1983); ³¹Moore and Dalva (1993); ³²Ours et al. (1997); ³³Preston et al. (2012); ³⁴Price and Woo (1988); ³⁵Price and Schlotzauer (1999); ³⁶Price et al. (2008); ³⁷Quinton et al. (2000); ³⁸Quinton et al. (2008); ³⁹Quinton et al. (2009); ⁴⁰Reeve et al. (2001); ⁴¹Rezanezhad et al. (2009); ⁴²Rezanezhad et al. (2010); ⁴³Rezanezhad et al. (2012a,b); ⁴⁴Robinson (2003); ⁴⁵Rycroft et al. (1975a,b); ⁴⁶Schothorst (1977); ⁴⁷Schothorst (1982); ⁴⁸Schwärzel et al. (2002); ⁴⁹Schwärzel et al. (2006); ⁵⁰Siegel and Glaser (2006); ⁵¹Tindal and Kunkel (1999); ⁵²Todorova et al. (2005); ⁵³Turetsky et al. (2000); ⁵⁴Tveit et al. (2013); ⁵⁵Verry and Boelter (1978); ⁵⁶Weiss et al. (2002); ⁵⁷Wellcock et al. (2011); ⁵⁸Zynter et al. (1989); ⁵⁹Bragazza et al., 2013; ⁶⁰Krueger et al., 2015; ⁶¹Ball et al., 1997.

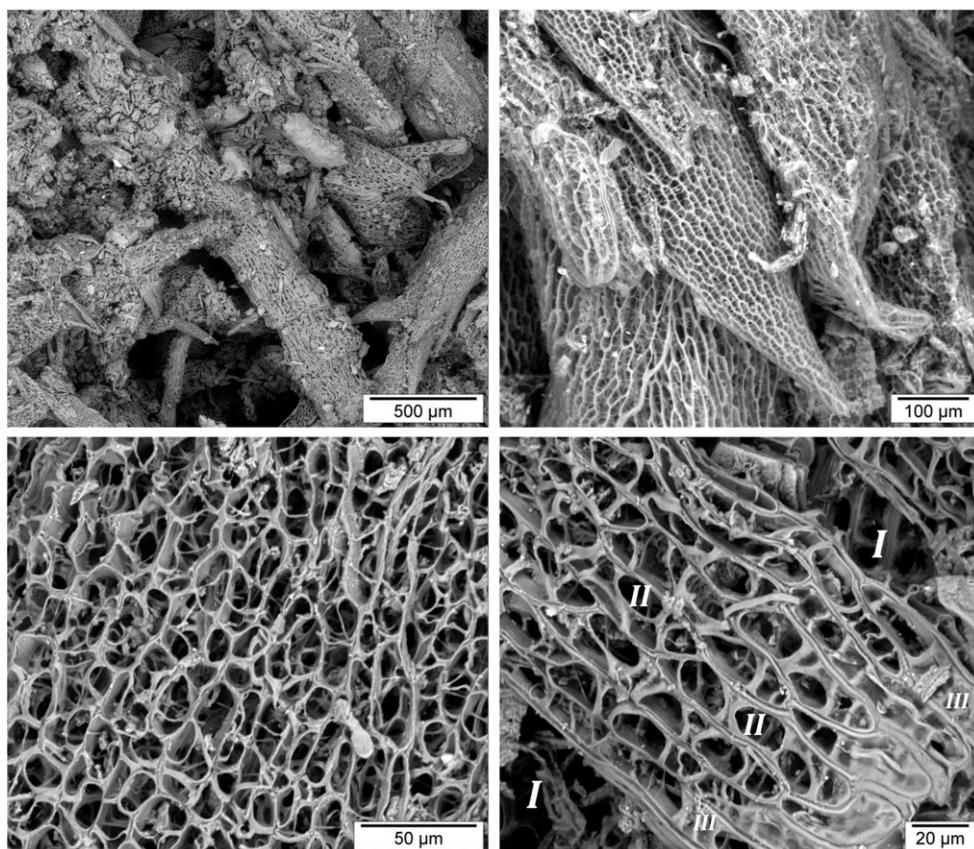


Fig. 1. Back-scattered electron (BSE) images of the pore structure of *Sphagnum* peat collected from a fen peatland located near Fort McMurray in northeastern Alberta, Canada. The micrographs obtained with a scanning electron microscope (SEM) at 10 kV. The images show differentiating pore size distributions: (I) open and connected macropores, (II) closed or partially closed cells, and (III) and dead-end or isolated pore spaces called hyaline cells.

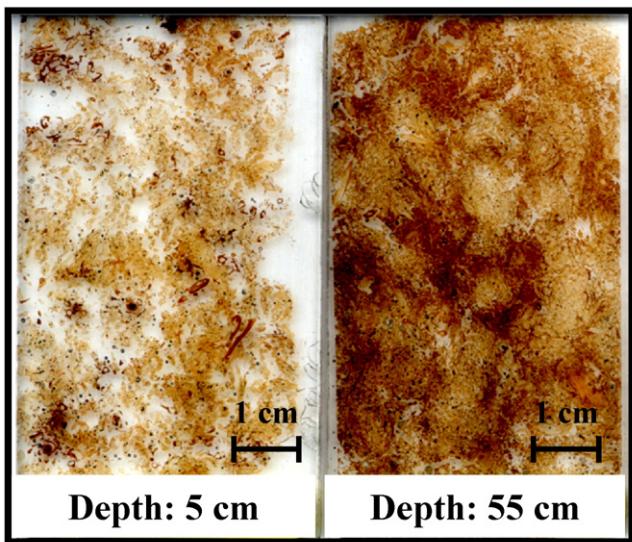


Fig. 2. Example of decomposition and pore structure differences between *Sphagnum* peat layers collected at 5 and 55 cm cross-sectional depths from a blanket bog peatland located in near Cape Race, Newfoundland, Canada. Higher decomposition and compression at a depth of 55 cm reduce the proportion of large pores by the breakdown of plant debris into smaller fragments and infilling of inter-particle pore spaces.

exhibits lower active porosity and compressibility. In addition, compression by the load of overlying materials causes the anisotropic deformation of the pores, which, together with the collapse of vascular plant debris, especially from sedges, results in the development of a horizontal laminar structure which becomes more pronounced with depth in the soil (Colley, 1950; Boelter, 1965). The latter may significantly reduce the vertical exchanges of water and solutes between the upper and lower parts of peat soils, while favoring horizontal flow through peatlands (Beckwith et al., 2003b). This structural arrangement of peat also entrains entrapped biogenic gas bubbles and controls ebullition, an important transport mechanism for methane, where the smaller range of porosities will enhance the relative importance of peat structure on gas entrapment (Rosenberry et al., 2003, 2006; Kettridge and Binley, 2011).

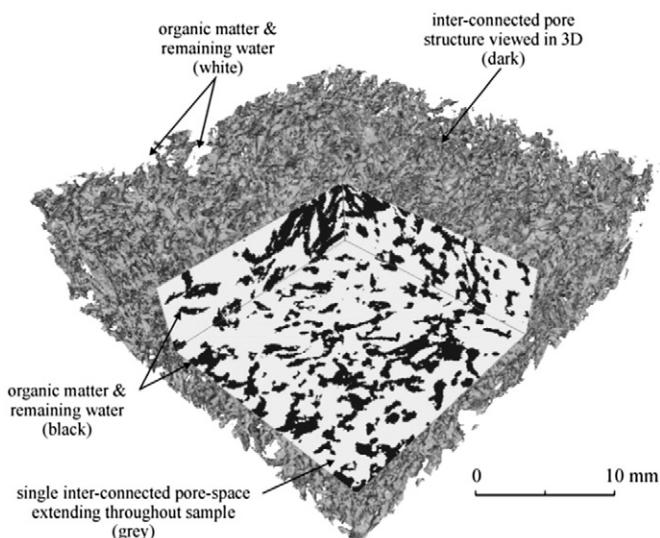


Fig. 3. 3D image of a near-surface *Sphagnum* peat sample at -40 cm soil water potential showing that the pore structure is dominated by a single, large and complex pore space with a volume and surface area 3 orders of magnitude greater than those of the next largest set of pores. Light areas represent the solid and liquid phases, and dark areas represent air-filled voids. Reproduced from Quinton et al. (2009).

Quinton et al. (2009) and Rezanezhad et al. (2009, 2010) used X-ray Computed Tomography (CT) to visualize the pore structure of *Sphagnum* peat at a spatial resolution of $45\ \mu\text{m}$. They found that the pore distribution in a near-surface sample of peat was dominated by a single, large highly connected and complex pore space with a volume and surface area 3 orders of magnitude greater than the next largest pore fraction (Fig. 3). This single pore space accounts for 94–99% of the total inter-particle pore volume and acts as a preferential flowpath by providing hydraulic connectivity, reduced tortuosity of connected pores, and reduced resistance to flow due to larger pore spaces (Baird and Waldron, 2003). The 3D CT images of air-filled pores in the *Sphagnum* peat samples also illustrate the large changes in the pore network as a function of soil depth (Fig. 4). In the deeper soil layers, pores are significantly smaller with less interconnection, which leads to more restricted flow and greater tortuosity.

3. Hydraulic properties

The flow and storage of water are intimately related to the physical properties of peat, and thus to the degree of decomposition and soil compression. The saturated hydraulic conductivity of peat typically drops by several orders of magnitude between the ground surface and a depth of 50 cm or more (Hoag and Price, 1995) and some studies report that layering of peat give more heterogeneity of hydraulic conductivity throughout the depth profile (e.g., Beckwith et al., 2003a). This decrease largely exceeds that expected from the reduction of the geometric mean pore diameter over the same depth interval, based on the relationships derived for mineral soils (Freeze and Cherry, 1979). Quinton et al. (2008) used image analysis of thin sections from different depths to directly measure the diameters and hydraulic radii of pores. From these data, they derived hydraulic conductivity values using the Hagen–Poiseuille and Kozeny–Carman equations. Their analysis yielded close agreement between computed and measured hydraulic conductivities, demonstrating that the hydraulic conductivity of water-saturated peat layers can, in principle, be predicted from a detailed characterization of the sizes plus shapes of the pores.

In addition to pore size and shape, the hydraulic conductivity of unsaturated peat depends on the fraction of the active porosity occupied by gas (Beckwith et al., 2003a). However, given the large and complex porosity of peat, storage and transmission properties are greatly altered upon drainage, therefore limiting the extent to which the properties of unsaturated peat can be inferred from those determined under saturated conditions (Price et al., 2008). According to Rezanezhad et al. (2010), water flow through unsaturated peat depends on the fractal nature of the pore distribution patterns, which can be quantitatively described by the fractal dimension of the soil-pore microstructure. The same authors also found that pore interfaces are rough and exhibit fractal geometry at length scales below the pore size. Little is presently known about the effect of pore surface roughness on flow rates through peat.

The relationship between soil water content and relative humidity, or water potential, is shown schematically in Fig. 5 for both drying and wetting of a *Sphagnum* peat. The shape of the soil water retention curve reveals the presence of different pools of water. Starting from fully saturated conditions, suction initially drains water from the open and connected pores, that is, from the active porosity (seen as the first rapid decline in water content in Fig. 5). With increasing suction (i.e. increasingly negative pressure values) the peat experiences a second drop in water content, which is interpreted as the drainage of partially closed pores that include hyaline cells (see Fig. 1). Further increasing the suction ultimately mobilizes water from closed pores that were formerly hydraulically inactive. The corresponding pressure (or water potential) matches the air-entry pressure (or air-entry potential) of hyaline cells. At the latter potential, the concave meniscus expands inwards towards the centre of the cell until the meniscus breaks, thereby allowing the

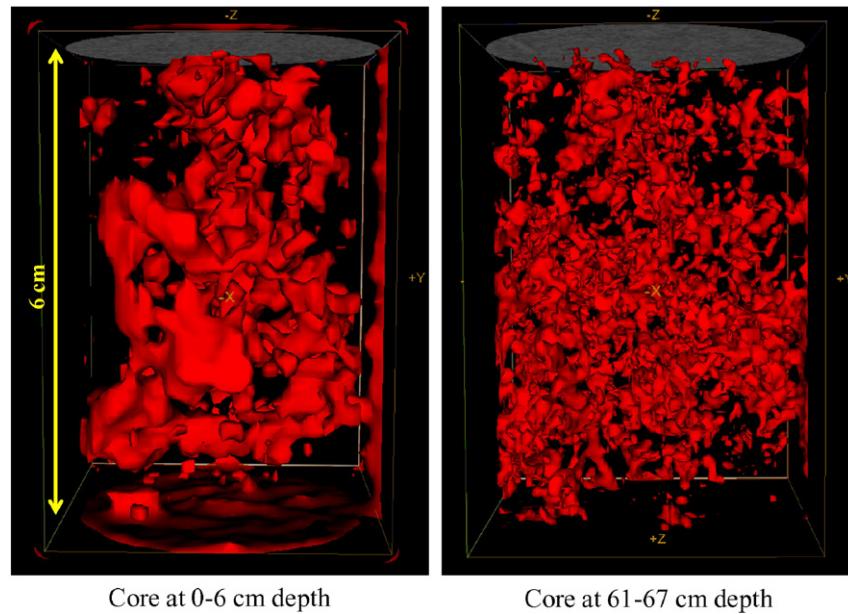


Fig. 4. 3D isosurface image visualization of the air-filled pores (taken by X-ray Computed Tomography) for two *Sphagnum* peat core sections extracted from the 2 different depth intervals and at the constant pressure head (-40 cm). Pores are significantly smaller with less interconnection in the deeper layer, which leads to more restricted flow. Red colored areas in the images show the air-filled pores. Modified from figure 5 in Rezanezhad et al. (2010).

entry of air into the hyaline cell (Hayward and Clymo, 1982; Lewis, 1988). In live *Sphagnum* mosses the hyaline cells, which are adjacent to the photosynthesizing cells, play a vital role in maintaining water availability for the photochemical machinery (Hayward and Clymo, 1982; Lewis, 1988).

Peat soils are both heterogeneous and anisotropic porous media. The individual and combined effects of heterogeneity and anisotropy of hydraulic conductivity strongly affect water movement in peat soils (Beckwith et al., 2003b). Beckwith et al. (2003a) determined horizontal and vertical saturated hydraulic conductivities (K_h and K_v) on 400 samples from 20 cores collected in the Humberhead Peatlands, England. In close to 80% of the samples they observed that K_h exceeds K_v , with the mean anisotropy, expressed as the ratio K_h/K_v , equal to 3.55. Whittington and Price (2013) found K_h/K_v of 1.8 in ~90% of their samples from *Sphagnum* dominated bogs and poor fens. Depending on the peat-forming plant community and its specific accumulation

pattern, preferred pore orientation acquired during the peat-forming process (Section 2), in addition to the layering of plant debris and root material within the peat matrix, explains the anisotropic character of most peat soils (Kruse et al., 2008). While the K_h and K_v values reported by Beckwith et al. (2003a) generally decrease with depth, the observed trends are irregular due to the alternation of peat layers with high and low K values. If layering occurs at a scale smaller than the sample size, the measured difference between K_h and K_v may in part reflect the heterogeneity of the peat, rather than only the anisotropy of the pore structure. Peat degradation, resulting for example from artificial drainage, can cause a loss of the preferred pore orientation and, hence, a decrease in anisotropy (Chason and Siegel, 1986; Beckwith et al., 2003a).

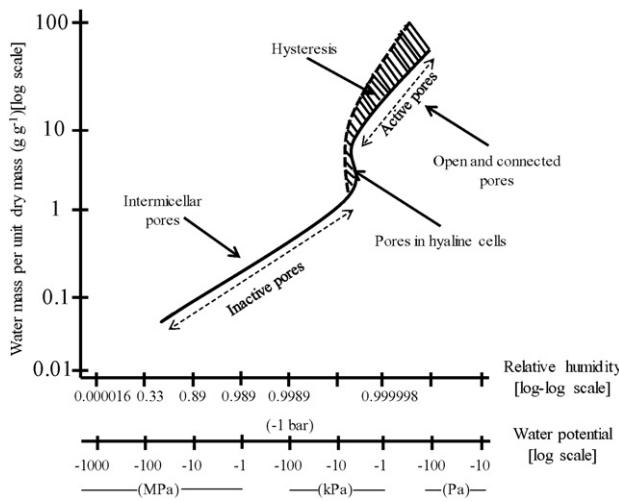


Fig. 5. Water retention curve during drying and wetting of a *Sphagnum* illustrating the presence of multiple pore water pools and water retention mechanisms. See text for detailed discussion. Drawn using values in Table 2 in Hayward and Clymo (1982).

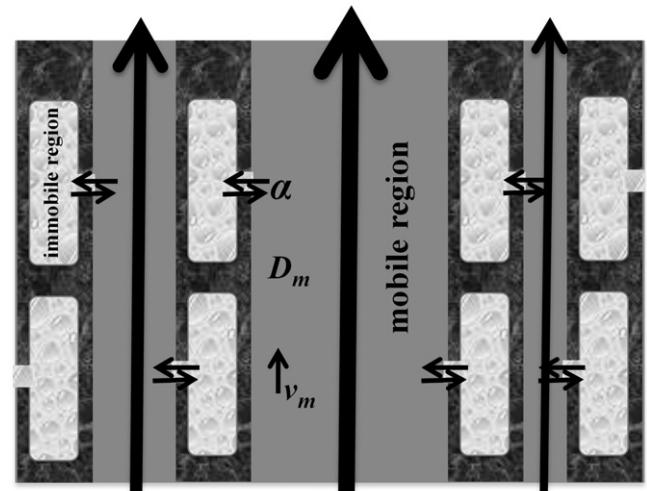


Fig. 6. Dual-porosity concept of peat soil including a "mobile region" with advective flow and an "immobile region" that exchanges solutes with the mobile region via diffusion. Symbols: D_m : dispersion coefficient in the mobile region; v_m : advective pore water velocity in the mobile region; α : first-order mass transfer coefficient governing the rate of solute exchange between the mobile and immobile pore water regions. Note that the figure assumes an upward hydraulic gradient.

4. Solute transport

In this section, we focus on the linkages between solute transport and the dual-porosity structure of water-saturated peat, and discuss some of the biogeochemical implications. We fully recognize that (1) coupled hydrological and biogeochemical processes in the unsaturated part of peat soils play a critical role in controlling soil-atmosphere-vegetation interactions, and (2) the macroscopic migration of solutes through saturated peat also strongly depends on the predominance of sorption sites associated with soil organic matter and the activity of anaerobic microbial communities. An example of the latter effects on solute migration is provided by naphthenic acids (NAs), a group of natural toxic compounds that occurs in crude oils and oil sand deposits (Clemente and Fedorak, 2005). In addition to matrix diffusion, the spreading of NAs in peat soils is strongly attenuated by the high capacity of peat organic matter to chemically bind NAs (Janfada et al., 2006), and the ability of resident microbial communities exposed to NAs to develop the capability to biodegrade these contaminants (Herman et al., 1994). Because the organic functional groups of peat can adsorb both polar (hydrophilic) and non-polar (hydrophobic) compounds, there is much interest in using peat to remediate a wide variety of (co-)pollutants including, among others, metal ions (Brown et al., 2000; Rezanezhad et al., 2012a,b; Caron et al., 2015a), mercury (Drexel et al., 2002), pesticides (Coppola et al., 2011), solvents (Kao et al., 2001), petroleum hydrocarbons and polycyclic aromatic hydrocarbons (Kalmykova et al., 2014).

In reaction-transport calculations, the representation of dual-porosity is usually based on the conceptual model shown in Fig. 6, where the rate of exchange of a given solute between the mobile and immobile regions is accounted for by a linear mass transfer term, which assumes that the rate is linearly proportional to the concentration difference between the two regions (for a more detailed explanation of the parameters shown in Fig. 6, the reader is referred to van Genuchten and Wierenga, 1976). Values of the first-order exchange coefficient can be experimentally determined from the breakthrough curves of conservative tracers, as illustrated in Fig. 7 for a peat collected from a forested riparian wetland area in Hamilton, Canada with a total porosity of 85%, divided nearly equally between the mobile (45%) and immobile phase (40%). Breakthrough curves are displayed by plotting the outflow concentration (C) normalized to the inflow concentration (C_0) against the number of pore volumes of flow through the reactor. For a single porosity medium, the centre of mass of the tracer breakthrough curve (i.e. $C/C_0 = 0.5$) should occur at 1 pore volume. The early breakthrough of chloride (Cl^-) in the peat, with $C/C_0 = 0.5$

occurring around 0.7 pore volumes, reflects the preferential flow through the connected macropores (Fig. 7). Fitting of the observed Cl^- breakthrough curve to a one-dimensional, dual-porosity, advection-dispersion model yields an exchange coefficient (α) of $3.8 \times 10^{-8} \text{ s}^{-1}$, and a longitudinal dispersion coefficient (D_m) of $10.1 \text{ cm}^2 \text{ s}^{-1}$. (Note: the linear flow velocity calculated directly from the imposed volumetric flow rate is $2.6 \times 10^{-3} \text{ cm s}^{-1}$.)

The transport regimes of single porosity media are often described using the Péclet number, Pe , which compares the rates of advective and diffusive (or dispersive) transport over a characteristic length scale. For dual-porosity media, van Genuchten and Wagenet (1989) propose the following definition of the Péclet number:

$$Pe = \frac{(\theta - \theta_{im})v_m^2}{\alpha D_m} \quad (1)$$

where θ and θ_{im} are the total and immobile volumetric water contents, respectively, $D_m (\text{L}^2 \text{ T}^{-1})$ is the dispersion coefficient of the solute in the mobile pore water region, $\alpha (\text{T}^{-1})$ is the first-order mass transfer coefficient governing the rate of solute exchange between the mobile and immobile liquid regions, and $v_m (\text{L} \text{ T}^{-1})$ is the linear pore water velocity in the mobile region. Values of Pe calculated with Eq. (1) vary from ≤ 1 , when solute transport is dominated by diffusional transport processes (between the immobile and mobile regions as well as within the mobile region), to ≥ 10 when solute movement is controlled primarily by flow through the hydraulically connected pore spaces.

For the conditions of the Cl^- breakthrough experiment, Eq. (1) yields an intermediate value of ~ 8 . Hence, matrix diffusion, advective flow and dispersion along the flowpaths all contribute to the features of the observed Cl^- tracer breakthrough curve. Groundwater flow velocities in peatlands are typically in the range $10^{-1}\text{--}10^{-7} \text{ cm s}^{-1}$ between acrotelm and catotelm (Fraser et al., 2001a,b; Holden, 2005; Kellner, 2007), that is, much slower than the flow velocity imposed in the reactor experiment of Fig. 7. The corresponding Pe values are therefore significantly smaller than the experimental value of ~ 8 reported here. In general, we can thus expect diffusional transport and, in particular, diffusion-limited mass transfer between the mobile and immobile pore water regions, to have a strong impact on solute transport and the associated biogeochemical processes.

In the same experiment where the Cl^- breakthrough curve was measured, the inflow solution also contained sulfate (SO_4^{2-}) (Fig. 8). Initially, the SO_4^{2-} breakthrough curve closely resembles that of Cl^- , with outflow SO_4^{2-} concentrations approaching inflow values after about 3 pore volumes. As for Cl^- , the early breakthrough of SO_4^{2-} is due to

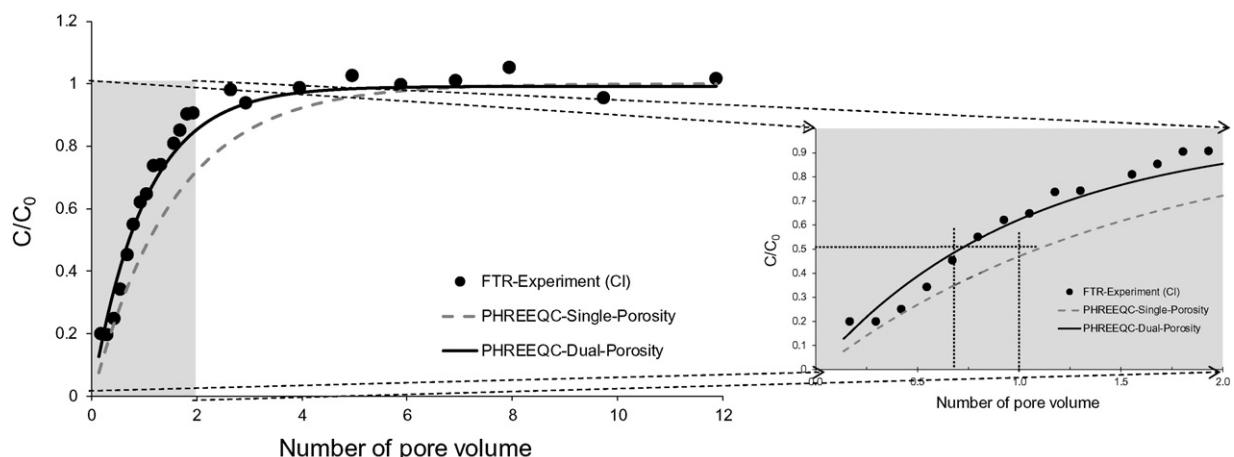


Fig. 7. Measured outflow Cl^- concentrations (C) normalized against inflow concentration (C_0) in a flow through reactor (FTR) experiment containing a natural peat soil collected from a forested riparian wetland area. The data are fitted using the single porosity and dual-porosity models available in the software package PHREEQC (Parkhurst and Appelo, 1999). The optimal parameter values for the Cl^- breakthrough curve fitted by the dual-porosity model are: $10.1 \text{ cm}^2 \text{ s}^{-1}$, $3.8 \times 10^{-8} \text{ s}^{-1}$, 0.45 and 0.4 for the dispersion coefficient, exchange coefficient, and fractions of mobile phase and immobile phases, respectively. A coefficient of determination (R^2) of 0.95 describes the fit of the model to the observed data.

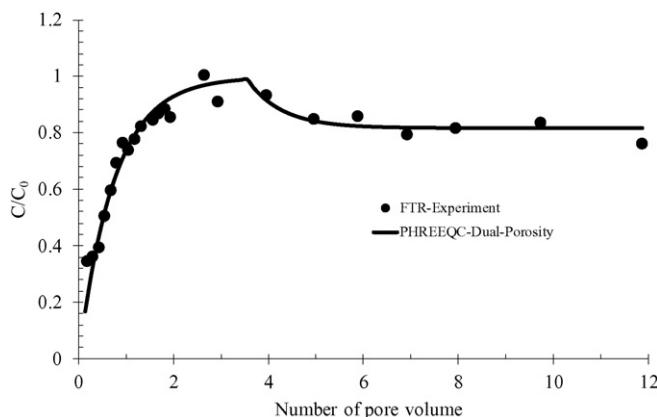


Fig. 8. Measured outflow SO_4^{2-} concentration normalized against inflow concentration (C_0) in the same flow through reactor experiment as Fig. 7. The final C/C_0 values are <1 because of microbial sulfate reduction within the peat. The data are fitted with the PHREEQC dual-porosity model and a Monod-type kinetic expression for sulfate reduction, using the same transport parameters as for the conservative tracer Cl^- . See text for further details.

preferential flow through the macropores. Afterwards, however, the outflow SO_4^{2-} concentration drops before stabilizing at a constant value below the inflow concentration. The decrease in the outflow SO_4^{2-} concentration reflects the delayed, diffusion-controlled supply of SO_4^{2-} to the immobile region of the pore structure where it is consumed by sulfate reducing bacteria. From the difference between the inflow and final outflow SO_4^{2-} concentrations, a steady state rate of sulfate reduction of $9.3 \text{ nmol cm}^{-3} \text{ h}^{-1}$ is calculated. (Note: for details on the use of the flow-through reactors to measure biogeochemical reaction rates, see Pallud et al., 2007 and Laverman et al., 2012). By incorporating a Monod-type rate law describing sulfate reduction in the immobile phase to the one-dimensional, dual-porosity, advection-dispersion model, the entire breakthrough curve of SO_4^{2-} can be fitted using the same exchange and dispersion coefficients as for Cl^- (Fig. 8). Thus, the breakthrough curves of both the unreactive (Cl^-) and reactive (SO_4^{2-}) solutes carry the imprint of the dual-porosity transport properties of peat.

The close link between microbial activity and solute transport in peat soils is further illustrated by the results in Fig. 9, which shows potential rates of nitrate reduction measured in the laboratory using flow-through reactors containing homogenized mixtures of peat and quartz sand. In these experiments, input solutions with non-limiting concentrations of nitrate were continuously supplied to the reactors. (Note: the reactors are the same as those used in the Cl^- and SO_4^{2-} breakthrough experiments described above.) As can be seen, the

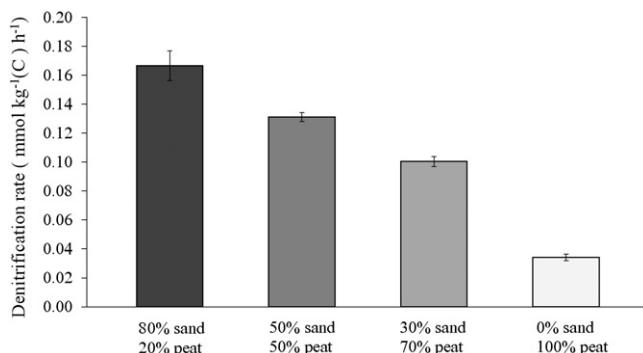


Fig. 9. Potential nitrate reduction rates measured in flow-through reactors packed with mixtures of peat and quartz sand. Note that the rates are expressed per unit mass organic carbon. The only source of organic carbon in the reactors is the peat. The description of the reactor system and their use to determine reaction rates can be found in Pallud et al. (2007).

specific rates of nitrate reduction expressed per unit mass organic carbon (or per unit mass peat) increase systematically with increasing percentage of sand. The admixture of sand to the peat artificially increases the mobile (or active) fraction of the porosity, hence accelerating the delivery of nitrate to the denitrifying microorganisms that couple the reduction of nitrate to the oxidation of organic compounds present in the peat.

The ability of peat to act as a multi-purpose sorbent and long-term source of electron donors forms the basis for incorporating peat in reactive barriers and constructed wetlands (Kao et al., 2001; Nwaishi et al., 2015). The degradation of the peat in these engineered systems, however, may cause changes in the pore structure and hydraulic properties over time which, in turn, may affect their performance as shown by Kleimeier et al. (2014). These authors investigated the feasibility of using wetlands constructed on peat soils for the treatment of nitrate-rich agricultural effluents. In laboratory mesocosms, they observed that flushing with nitrate-containing water caused the immobile pore water fraction of the peat to increase from 40 to 80% over a period of two years, as a consequence of physical consolidation and denitrifying activity causing pore clogging. The accompanying decreases in hydraulic conductivity and the fraction of mobile pore water would ultimately compromise the operation of the constructed wetlands and their ability to remove nitrate.

Pore-scale mass transfer limitations of microbially mediated reactions in peat are expected to be fairly common, because soil microorganisms preferentially reside in organic-rich micro-niches (Cleveland et al., 2004), which in peat soils tend to be associated with the immobile region of the porous structure. In the example of Fig. 9, the metabolic activity of the nitrate reducing community is modulated by the supply from the active porosity of an essential substrate (i.e. the terminal electron acceptor, nitrate). Conversely, microbial activity can be limited by the removal of reaction products to the active porosity as, for example, in the case of methanogenesis. In a series of long-term column experiments with water-saturated, anaerobic peat-sand mixtures, Blodau et al. (2011) showed that the build-up of dissolved methane (CH_4) and dissolved inorganic carbon (DIC) ultimately reduces the thermodynamic driving force of acetoclastic methanogenesis to the point where the process stops. Based on their experiments, Blodau et al. were able to calculate the minimum Gibbs energy yield required for the methanogens to remain active, about 25 kJ per mole CH_4 produced. The slow, pore-scale diffusion of CH_4 and DIC from methanic microniches into the active porosity may therefore represent a key rate-controlling process for the production of methane in peatlands.

Diffusional solute exchanges between the mobile and immobile domains of the porosity can generate steep chemical gradients at the soil aggregate scale (Pallud et al., 2010a,b). These gradients in turn support the coexistence of closely associated microhabitats, and thus help explain the high genetic and functional diversity of microbial populations found in soils in general, and peat soils in particular (Dechesne et al., 2007; Kuesel et al., 2008; Lin et al., 2012; Sun et al., 2014; Nunes et al., 2015). The slow diffusive exchanges associated with the dual-porosity nature of peat are also expected to buffer the responses of microbial communities in peat soils to changes in hydrology and land use. The newest molecular tools, including metagenomic profiling and proteomics, offer the possibility to directly document microbial responses to external forcing (Nunes et al., 2015). The challenges ahead, however, will be to map out the spatial and temporal distributions of chemical conditions and microorganisms within the dual-porosity structure of peat, and to determine how chemical heterogeneity, microbial activity and community structure at the microscale translate into the biogeochemical functioning of peatlands at the field and ecosystem scales.

5. Concluding remarks

Peat exhibits unique dual-porosity properties owing to mobile and immobile regions within the pores, with far-reaching implications for

water flow regulation, contaminant transport and remediation, greenhouse gas production and the cycling of carbon and nutrients. Increasingly detailed knowledge on the porous structure of peat is becoming available, including quantitative data on size, geometry, connectivity, surface roughness and anisotropy of the pore spaces. Additional studies are required, however, to predictively relate this structural information to the material properties, hydraulic conductivity, pore-scale transport processes and biogeochemical reactivity of peat soils. For instance, the change in peat structure during wetting and drying influences the heterogeneous distributions of microbial habitats and activity in peat soil and plays a crucial role in emission and sequestration of CO₂ and CH₄ fluxes in peatlands. Furthermore, most information on the porous structure of peat has been obtained on relatively small samples, which raises the question about their representativeness and applicability at larger scales. In particular, our understanding of how the spatial and temporal heterogeneity of the porous structure of peat affects solute transport and biogeochemical activity at the landscape scale remains fairly limited. Thus, future research should focus on multi-scale studies that integrate the acquisition of physical, hydraulic, chemical and microbial data in the laboratory, with field-based information on hydrology, pore water geochemistry, microbial diversity and functions, and biogeochemical rates and fluxes.

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