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Groundwater residence time distributions in peatlands: Implications for peat decomposition and accumulation

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[1] Peat soils consist of poorly decomposed plant detritus, preserved by low decay rates, and deep peat deposits are globally significant stores in the carbon cycle. High water tables and low soil temperatures are commonly held to be the primary reasons for low peat decay rates. However, recent studies suggest a thermodynamic limit to peat decay, whereby the slow turnover of peat soil pore water may lead to high concentrations of phenols and dissolved inorganic carbon. In sufficient concentrations, these chemicals may slow or even halt microbial respiration, providing a negative feedback to peat decay. We document the analysis of a simple, one-dimensional theoretical model of peatland pore water residence time distributions (RTDs). The model suggests that broader, thicker peatlands may be more resilient to rapid decay caused by climate change because of slow pore water turnover in deep layers. Even shallow peat deposits may also be resilient to rapid decay if rainfall rates are low. However, the model suggests that even thick peatlands may be vulnerable to rapid decay under prolonged high rainfall rates, which may act to flush pore water with fresh rainwater. We also used the model to illustrate a particular limitation of the diplotelmic (i.e., acrotelm and catotelm) model of peatland structure. Model peatlands of contrasting hydraulic structure exhibited identical water tables but contrasting RTDs. These scenarios would be treated identically by diplotelmic models, although the thermodynamic limit suggests contrasting decay regimes. We therefore conclude that the diplotelmic model be discarded in favor of model schemes that consider continuous variation in peat properties and processes.

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1. Introduction

[2] Throughout the Holocene, peatlands in the maritime-temperate, boreal, and subarctic zones of the Northern Hemisphere have been persistent terrestrial sinks for atmospheric carbon dioxide (CO₂) while also acting as sources of methane (CH₄) [Frolking *et al.*, 2002; Korhola *et al.*, 2010]. Northern peat soils have been estimated to contain approximately one third of all global soil carbon [Gorham, 1991; Smith *et al.*, 2004]. The accumulation of peat over long timescales (10²–10³ years) reflects the fact that peatland plants have fixed carbon through photosynthesis at a slightly, yet consistently, greater rate than the combined rates of carbon release through plant respiration and depth-integrated soil (i.e., microbial) respiration. In particular, low decay rates in deep peat layers are commonly held to be the primary cause of the development of thick peat deposits [Clymo, 1984]. Most existing models cite a combination of low soil temperatures in deep peat layers and perennially saturated conditions, with water tables at or near the peatland surface for most of the year [Frolking *et al.*,

2002], as the primary causes of slow decomposition rates [Scanlon and Moore, 2000]. The slow diffusion of oxygen through water (approximately 10⁴ times slower than in air) [Crank, 1976] means that decomposition in the majority of northern peat profiles proceeds at slow, anaerobic rates, in the absence of oxygen, and depth to water table is seen as a strong predictor of peat decay rates [Strack *et al.*, 2004]. Similarly, multiple studies have observed strong increases in anaerobic decomposition rates with increases in soil temperature [Hogg *et al.*, 1992; Silvola *et al.*, 1996; Scanlon and Moore, 2000]. It is common, therefore, for models of peatland carbon stocks to represent peat decomposition as controlled largely by temperature and moisture regimes [e.g., Ise *et al.*, 2008].

[3] There has been concern that the peatland carbon store is a fragile one and may be vulnerable to lower water table positions and higher air temperatures over the next two centuries because of projected climate change [Roulet *et al.*, 1992; Moore *et al.*, 1998; Turunen, 2008; Yu *et al.*, 2009]. Indeed, a number of modeling [e.g., Ise *et al.*, 2008] and laboratory [e.g., Blodau *et al.*, 2004] studies have identified potential positive feedbacks, whereby a warmer and drier climate may lead to increased peat decomposition and release of CO₂ and CH₄ from peatlands, which may, in turn, exaggerate the global warming effect. However, recent research suggests that peatlands may have a “built-in”

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biogeochemical mechanism for resilience [e.g., *Beer et al.*, 2008], facilitated by long residence times of peatland groundwater.

[4] As decay proceeds, the resultant chemical end products of microbial decay may accumulate in deep peat pore water. For instance, *Beer and Blodau* [2007] and *Beer et al.* [2008] observed how CH₄ and dissolved inorganic carbon compounds (DICs) accumulated in deep pore water at their study site in Canada. Importantly, these end products of decay can, in sufficiently high concentrations, slow or even halt decay [*Beer and Blodau*, 2007], thereby providing a negative feedback to peat decomposition. The accumulation of DICs reduces the available Gibbs free energy [*Conrad*, 1999] to a level at which microbial decomposition becomes thermodynamically inhibited. Moreover, *Beer and Blodau* [2007] observed a prevalence of diffusive (as opposed to advective) pore water transport mechanisms in a temperate raised bog. Slow advective transport such as this leads to long groundwater residence times, thereby allowing decay-limiting end products to accumulate. More rapid groundwater movements would flush soil pores with fresh water and prevent these compounds from accumulating, thereby allowing potentially higher decay rates. Additionally, slow pore water turnover would also lead to the accumulation of phenolic compounds and a depletion of both terminal electron acceptors and the nutrients used in catabolic processes. All of these situations would act to reduce decay rates further [*Ivarson*, 1977; *Wickland and Neff*, 2008]. Given the potential importance of pore water turnover rates in determining decay rates, it follows that peat groundwater residence time distribution (RTD) and therefore peatland hydraulic structure (in the sense of *Baird et al.* [2008]) may be key determinants of peat decay regimes and therefore peatland vulnerability to human- or climate-mediated disturbances.

[5] Simple models of peatland development, such as those described by *Frolking et al.* [2001], *Hilbert et al.* [2000] and *Clymo* [1984, 1992], conceptualize peatlands as consisting of two functional layers, delineated by some metric of water table position: the upper “acrotelm,” above the lowest position of the water table and a few decimeters thick, where decay occurs aerobically at high rates, and the lower “catotelm,” below the water table and up to 10 m thick, where decay occurs anaerobically at much lower rates. First proposed formally by *Ingram* [1978], the so-called “diplotelmic model” is deeply ingrained into much of current thinking about peatland process and structure. Theoretical [*Belyea and Baird*, 2006] and observational [*Holden and Burt*, 2003] studies have identified a number of limitations to the diplotelmic model and have advocated the need for the peatland science community to adopt more flexible, cohort-based models of peatland development. However, this movement contrasts sharply with calls to maintain and expand the diplotelmic model via the inclusion of additional functional layers, such as the “mesotelm,” representing a transitional zone of peat structural collapse between the acrotelm and catotelm [*Clymo and Bryant*, 2008; see also *Clymo*, 1992; *Frolking et al.*, 2002], and the “pectotelm,” representing the live growing surface (R. S. Clymo, personal communication, 2009).

[6] While the acrotelm is generally assumed to have a much higher hydraulic conductivity K (dimensions of $L T^{-1}$)

and effective porosity s (dimensionless; defined as the volumetric proportion of a soil which is available to the flow of water, therefore excluding dead and closed pores) than the underlying catotelm [*Ingram*, 1978], the available literature indicates that K -depth relationships are highly variable between individual peatlands, in terms of both the absolute values of K and the shape of the relationship, bringing the utility of the diplotelmic model into question [see *Belyea and Baird*, 2006]. For example, *Chason and Siegel* [1986] observed no correlation between depth and K at a raised bog in Minnesota, while *Fraser et al.* [2001] found K to decrease strongly (four orders of magnitude variation in K in a 5 m deep profile) and nonlinearly with depth below the surface at a Canadian peatland. *Clymo* [2004], *Kneale* [1987], and *Waddington and Roulet* [1997] all found evidence of C-shaped profiles of K with depth at various European peatlands. While it is clear that strong, systematic variations in K with depth likely influence the RTD of peat groundwater, we are unaware of any studies that have determined down-core (within-site) variations in peatland pore water residence times. Moreover, we argue that if peat groundwater RTD exerts a strong control over decomposition rates, then it stands that decomposition is likely to vary in a continuous (and possibly complex), rather than dichotomous, manner with depth. Given the uncertainty associated with the shapes of depth profiles of K and s in peatlands, it is possible to imagine peatlands of contrasting hydraulic structures. Although such peatlands would likely possess contrasting groundwater RTD, they may still exhibit similar water table positions [cf. *Armstrong*, 1995]. In such a situation, the thermodynamic model of *Beer and Blodau* [2007] and *Beer et al.* [2008] suggests markedly different decay regimes between the imagined peatlands (a direct reflection of the different RTDs), yet the diplotelmic model, relying as it does solely upon water table position, would predict no difference in decay regimes.

[7] *Beer and Blodau* [2007] demonstrated that shallow peat layers at their study site in Canada exhibit shorter residence times than deep layers. Shallow layers are more readily flushed by rainwater and throughflow, leading to pore water chemistry more favorable to decay in these shallow depths. *Beer and Blodau* [2007] went on to suggest that deep peat layers may be thought of as partially closed systems, disconnected from rainwater inputs. A corollary of the thermodynamic mechanism, therefore, is that older, thicker peat deposits, in which deep pore water is highly disconnected from rainfall, may exhibit greater resilience to climate change than shallower peatlands, where pore water turnover is more rapid and decay rates are potentially higher.

[8] Building upon the insight of *Beer and Blodau* [2007] and *Beer et al.* [2008], we used a numerical modeling approach to examine the potential implications of peatland hydraulic structure for peat decomposition and accumulation. Specifically, we used a one-dimensional hydrological model to demonstrate how different depth profiles of K and s can lead to identical water table positions in a conceptual peatland yet markedly different groundwater RTDs, thereby illustrating a specific limitation of the diplotelmic model in relation to understanding the proposed thermodynamic limit to peat decay. We also used the model to examine the sensitivity of groundwater RTDs in an idealized raised bog to

the size and shape of the modeled bog, thereby representing peatlands at different stages of development. In this way we explored the issue of whether the resilience of individual peatlands to climate change may increase with peatland size via the thermodynamic limit to decay.

2. Model Description

[9] We constructed a model of an idealized raised bog that is hemielliptical in cross section [cf. *Ingram*, 1982] and in which K and s vary with depth. Our model is one-dimensional (vertical) and considers only properties and processes at the central axis of the bog (i.e., at the zenith of the hemiellipse). The model consists of two submodels, one representing the advective movements of groundwater solutes and the other representing chemical mixing of groundwater due to molecular diffusion. We do not consider processes in the unsaturated zone, so for the purposes of the current modeling exercise, the height of the peatland is taken to be equal to the height of the water table. We could have used a number of more sophisticated, spatially distributed models to compute the spatial distribution of pore water residence times in a peatland (e.g., *Modflow* [see *McDonald and Harbaugh*, 1984]). However, we believe that our simple, 1-D approach is sufficient to address our research questions. The aim of our study is to illustrate the potential importance of peatland hydraulic structure (including the gross dimensions of the peat aquifer) in determining pore water residence times and potentially, therefore, peat decomposition rates. As such, we required a model that is able to illustrate the general direction and approximate magnitude of the effects of a changing hydraulic structure upon pore water residence times. A more detailed model that is able to account for factors such as site-specific changes in topography and 2- or 3-D variations in peat properties is therefore not necessary at this early stage of research.

2.1. Advection Submodel

[10] *Ingram* [1982] discussed a conceptual raised bog that has a uniform distribution of K and meets the following

assumptions: (1) lateral extent L (dimensions of L) is constrained by two parallel streams of equal hydraulic head to which the bog drains, (2) vertical head gradients are negligible (i.e., the Dupuit-Forcheimer (D-F) approximation holds [cf. *McWhorter and Sunada*, 1977]), (3) the bog is immediately underlain by a flat, impermeable substrate, and (4) the bog is indefinitely long in the axis that is parallel to the two boundary streams. In this situation, *Ingram* [1982] showed that the following relationship may be taken to hold [see also *Childs and Youngs*, 1961]:

$$\frac{U}{K} = \frac{H^2}{L^2}, \quad (1)$$

where U is recharge ($L T^{-1}$), which for our purposes may be taken to be equivalent to net rainfall rate (total precipitation minus evapotranspiration and losses from the saturated zone to live surface biomass and the unsaturated zone), delivered at a constant rate, and H is hydraulic head (L) at the center of the bog, which given our adoption of the D-F approximation, may be taken as equal to be the height of the water table above the impermeable base (see Table 1 for a glossary of algebraic terms and their default values). Under steady state conditions (i.e., when all terms in equation (1) are constant), the rate of advective flow from the bog Q_{tot} ($L T^{-1}$) is equal to the net rainfall rate U .

[11] In a situation where K varies with depth, as required by our research questions, equation (1) does not hold. In order to overcome this problem, we may imagine a system in which the peat profile is divided by multiple hemiellipses that are equal in L but unequal in height z above the impermeable base (see Figure 1). This situation leads to multiple layers of peat; at the center of the bog the divisions between these layers are oriented horizontally. The ellipses represent divides between peat layers of uniform K and s , such that layer i possesses hydraulic conductivity K_i and effective porosity s_i . Along the central axis of our hemielliptical bog, each layer possesses identical thickness Δz in the vertical dimension (we assumed that $\Delta z = 1$ cm for all layers). The steady state rate of advective outflow may then

Table 1. Glossary of Algebraic Terms

Symbol	Quantity	Dimensions	Units	Default Value ^a
c	tracer concentration	$M L^{-3}$	$g\ cm^{-3}$	
c_0	initial tracer concentration	$M L^{-3}$	$g\ cm^{-3}$	0.001
D	free solution diffusivity of CO_2	$L^2 T^{-1}$	$cm^2\ yr^{-1}$	504.6
H	water table height above impermeable base	L	cm	749.5
i	layer number (index)			
j	layer number (index)			
J	tracer diffusive transport rate (vertical)	$M L^{-2} T^{-1}$	$g\ cm^{-2}\ yr^{-1}$	
K	hydraulic conductivity	$L T^{-1}$	$cm\ yr^{-1}$	1.67×10^4
L	peatland lateral extent	L	m	250
λ	tracer half-life	T	yr	
m	tracer mass	M	g	
n	number of layers below water table			
Q_i	rate of advective outflow from layer i	$L T^{-1}$	$cm\ yr^{-1}$	
Q_{tot}	total advective outflow rate from entire bog	$L T^{-1}$	$cm\ yr^{-1}$	
s	effective porosity			0.138
t	model time	T	yr	
U	net rainfall rate (total precipitation minus evapotranspiration)	$L T^{-1}$	$cm\ yr^{-1}$	15
z	height above impermeable base	L	cm	
Δz	layer thickness increment	L	cm	1

^aDefault values, where given, were assumed unless otherwise stated.

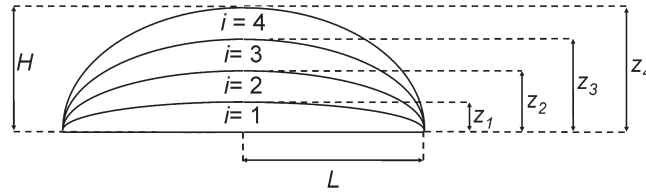


Figure 1. Cross-sectional schematic illustrating the multiple layers within the hydrological model. Even though layer height z_i differs between model layers, L is identical for all layers. In the illustrated example, the model consists of four layers. Note that this spatial arrangement of peat properties is consistent with *Belyea and Baird's* [2006] simultaneous initiation scenario.

be calculated for each layer individually and summed to give the total rate of outflow Q_{tot} for the entire bog. Given our adoption of the D-F approximation, all layers are subject to the same value of hydraulic head H regardless of their vertical position within the peat profile. The steady state rate of outflow Q_i (L T^{-1}) from any layer i is given by first calculating the rate of outflow for an entire bog with K_i (the first term on the right-hand side of equation (2)) and then correcting for the thickness of layer i as a proportion of the height of the water table (the second term on the right-hand side of equation (2)):

$$Q_i = \left(\frac{H^2 K_i}{L^2} \right) \left(\frac{\Delta z}{H} \right). \quad (2)$$

[12] Simplifying equation (2) and summing for all layers in the model gives the total steady state rate of outflow from the entire bog Q_{tot} in the case of vertically varying K :

$$Q_{\text{tot}} = \sum_{i=1}^n Q_i = \sum_{i=1}^n \frac{H K_i \Delta z}{L^2}, \quad (3)$$

where n peat layers are below the water table.

[13] In our finite difference model, each layer is represented by a single conceptual store. At the beginning of a simulation, groundwater is assumed to contain a conservative tracer at a uniform initial concentration c_0 (M L^{-3}). As model time progresses, the tracer drains at differential rates from each peat layer, depending on the rate of outflow from the layer Q_i and the layer's vertical position within the profile. Tracer in each layer also mixes with pore water in the layers immediately above and below, along a concentration gradient, because of molecular diffusion. We begin with a consideration of advective tracer movements only (i.e., we ignore diffusive transport for now). Pore water in the model's bottommost layer, $i = 1$, drains to the boundary at the rate Q_1 (see equation (2)), causing the layer to lose tracer at the rate $c_1 Q_1$ ($\text{M L}^{-2} \text{T}^{-1}$). In order to prevent a vertical head gradient from developing, this outflow must be replaced by water from the layer above, $i = 2$, at the same rate Q_1 . This input of water from farther up the peat profile also contains tracer, at the concentration c_2 , meaning that tracer is added to layer $i = 1$ at the rate $c_2 Q_1$ ($\text{M L}^{-2} \text{T}^{-1}$). In order to conserve mass, layer $i = 2$ must lose water and tracer at the same rates, Q_1 and $c_2 Q_1$, respectively. However, layer $i = 2$ also drains to the boundary, thereby losing additional water at the rate Q_2 (see equation (2)) as well as tracer at the rate $c_2 Q_2$. The total rates of loss of water and

tracer from layer $i = 2$ are therefore equal to $Q_1 + Q_2$ and $c_2 Q_1 + c_2 Q_2$, respectively. As with the bottom layer, layer $i = 2$ receives water and the tracer contained therein at the rates $Q_1 + Q_2$ and $c_3(Q_1 + Q_2)$, respectively, from the layer above, $i = 3$, which in turn loses those quantities at the same rates. Again, layer $i = 3$ also loses water and tracer to the boundary at the rates Q_3 and $c_3 Q_3$, respectively, meaning that the overall rates of loss of water and tracer from layer $i = 3$ are $Q_1 + Q_2 + Q_3$ and $c_3(Q_1 + Q_2 + Q_3)$, respectively. This iterative algorithm for calculating losses of water and tracer from each layer continues in a similar fashion upward through the profile. Formally, and assuming a unit cross-sectional area for a vertical column of peat at the center of our bog, the rate of change of tracer mass m_i (M) in layer i is given by

$$\frac{dm_i}{dt} = (c_{i+1} - c_i) \sum_{j=1}^i Q_j. \quad (4)$$

[14] Again assuming unit cross-sectional area for our column of peat, the rate of change of concentration of tracer in layer i may be given by dividing equation (4) by layer thickness Δz :

$$\frac{dc_i}{dt} = \frac{1}{\Delta z} (c_{i+1} - c_i) \sum_{j=1}^i Q_j. \quad (5)$$

[15] Rainfall containing a tracer concentration of zero is added to layer $i = n$ (the uppermost saturated layer) at the rate U . We assumed various distributions of K in our simulations (see section 2.4), but for all simulations, the initial water table height was equal to the calculated steady state water table height for that model configuration (i.e., water table position H did not change during a simulation; we ensured that $U = Q_{\text{tot}}$).

2.2. Diffusion Submodel

[16] Fick's law describes the one-dimensional flux of a solute along a concentration gradient within a fluid, assuming ideal mixing and infinite dilution:

$$J = -D \frac{dc}{dz}, \quad (6)$$

where J is diffusive flux of the solute ($\text{M L}^{-2} \text{T}^{-1}$), D is the free solution diffusion coefficient (or, for brevity, "diffusivity") of the solute ($\text{L}^2 \text{T}^{-1}$), c is solute concentration

($M L^{-3}$), and z is the distance over which diffusion occurs (L) [Crank, 1976]. For the situation where diffusion occurs within a porous medium (such as a soil profile), D should be reduced by a multiplier to reflect both the tortuosity of the pores and the fluidity of the solution [Shackelford and Daniel, 1991a]. The free solution value of D for CO_2 dissolved in water is approximately $504 \text{ cm}^2 \text{ yr}^{-1}$ [Crank, 1976], although this value should be reduced by a factor of between 2 and 50 in order to give a representative effective diffusivity in soils [Shackelford and Daniel, 1991a, 1991b; Freeze and Cherry, 1979].

[17] Archie's law is an empirically derived law in sedimentary geophysics that assumes that D may be reduced by multiplying by a factor of s^x , where x is a dimensionless exponent [cf. Archie, 1942]. This same assumption has also been made in peatland studies, in which the value of x has been assumed to be 2 [e.g., Fraser et al., 2001; Beer and Blodau, 2007]. We know of no direct assessment of Archie's law for the application of predicting effective diffusivity in peat as a function of porosity, although peat soils possess qualitatively different pore structures from the mineral soils and bedrock aquifers in which the law was originally developed. Particularly, Hoag and Price [1995, 1997] illustrated the confounding role of the so-called "dual porosity" of peat soils, where closed and disconnected pores may act to retard diffusive transport through peat soils by trapping solutes in dead-end pore spaces. Comas and Slater [2004] assessed Archie's law for electrical conductivity in peat soils. They found that the relationship was poorly suited to this application because of conduction across the surfaces of peat particles and the flocculation of organic matter as a result of their manipulated pore water chemistries. However, our application of Archie's law is quite different, and no such surface conductivity or flocculation effects are relevant to molecular diffusion. It is therefore unclear as to whether the law may be accurately applied to the molecular diffusion of solutes in peat pore water. However, recognizing the need in our model for effective diffusivity to be positively related to porosity and in the absence of a suitable alternative, we cautiously adopted Archie's law in our model. We know of no data which may be justifiably used to determine a value of x that is representative of peat; it was again with caution that we assumed $x = 2$, which enables comparison with studies by Fraser et al. [2001] and Beer and Blodau [2007], who also made the same assumption.

[18] Considering now only diffusive tracer movements between layers (i.e., ignoring for a moment the advective movements described by equations (5) and (6)), incorporating Archie's law, using the arithmetic mean of s between layers, and dividing by layer thickness Δz gives the rate of change of tracer concentration c_i in any layer i due to diffusive exchanges with the layers immediately above ($i + 1$) and below ($i - 1$):

$$\frac{dc_i}{dt} = \frac{D}{\Delta z} \left(\frac{s_{i-1} + s_i}{2} \right)^x \left(\frac{c_{i-1} - c_i}{\Delta z} \right) - \frac{D}{\Delta z} \left(\frac{s_i + s_{i+1}}{2} \right)^x \left(\frac{c_i - c_{i+1}}{\Delta z} \right). \quad (7)$$

[19] The sum of equations (5) and (7) accounts for both advective and diffusive tracer movements, giving

the overall rate of change of tracer concentration in any layer i :

$$\frac{dc_i}{dt} = \frac{D}{\Delta z} \left(\frac{s_{i-1} + s_i}{2} \right)^x \left(\frac{c_{i-1} - c_i}{\Delta z} \right) - \frac{D}{\Delta z} \left(\frac{s_i + s_{i+1}}{2} \right)^x \left(\frac{c_i - c_{i+1}}{\Delta z} \right) + \frac{1}{\Delta z} (c_{i+1} - c_i) \sum_{j=1}^i Q_j. \quad (8)$$

[20] Finally, substituting equation (2) for Q_j into equation (8) gives the rate of change of tracer concentration in layer i as a function of the hydraulic properties of that layer and all those below:

$$\frac{dc_i}{dt} = \frac{D}{\Delta z} \left(\frac{s_{i-1} + s_i}{2} \right)^x \left(\frac{c_{i-1} - c_i}{\Delta z} \right) - \frac{D}{\Delta z} \left(\frac{s_i + s_{i+1}}{2} \right)^x \left(\frac{c_i - c_{i+1}}{\Delta z} \right) + \frac{1}{\Delta z} (c_{i+1} - c_i) \sum_{j=1}^i \left(\frac{HK_j \Delta z}{L^2} \right). \quad (9)$$

[21] Equation (9) defines our model, although it is not readily analytically tractable. Therefore, we solved equation (9) using a numerical solution and, in doing so, calculated tracer half-life λ_i (T) for each layer i . We define λ_i as the length of time required for tracer concentration c_i in layer i to fall below half of the initial uniform concentration c_0 . We used λ_i as our primary measure of pore water residence time for each layer in our model. We recognize that our use of the term "residence time" in this way differs from that commonly used in the catchment hydrology literature (sometimes also referred to as "transit time"; see McGuire and McDonnell [2006] for a recent and comprehensive review). In addition, by the term "residence time distribution" or the abbreviation "RTD," we refer to the spatial (vertical) distribution of λ , rather than the aspatial, temporal recovery of tracer from a stream, as is common in catchment hydrology.

2.3. Bog Shape and Size

[22] For the case of uniform distributions of K [Chason and Siegel, 1986], equation (1) holds, and steady state water table height H is predicted simply by peatland lateral extent L and net rainfall rate U (Figure 2) [Ingram, 1982]. In order to address the question of whether peatland resilience increases with peatland size, we examined RTD for model peatlands of a range of sizes and shapes. Using Ingram's [1982] hydromorphic relationships for uniform K (equation (1)), we performed two sets of experiments. In the first set we held U constant and manipulated L ; while this generated different heights of groundwater mound under identical net rainfall rates, the linear relationship between L and H (Figure 2a) meant that these alterations led to identical hydraulic gradients (H/L) in the model peatland. In the second set of experiments we held L constant and manipulated U , which led to alterations in H and also the hydraulic gradient (Figure 2b). While Ingram's [1982] model has been shown to be oversimplified when considering long-term peatland developmental dynamics [Belyea and Baird, 2006], we adopted the assumptions inherent in equation (1) merely as a means of estimating drainage rates

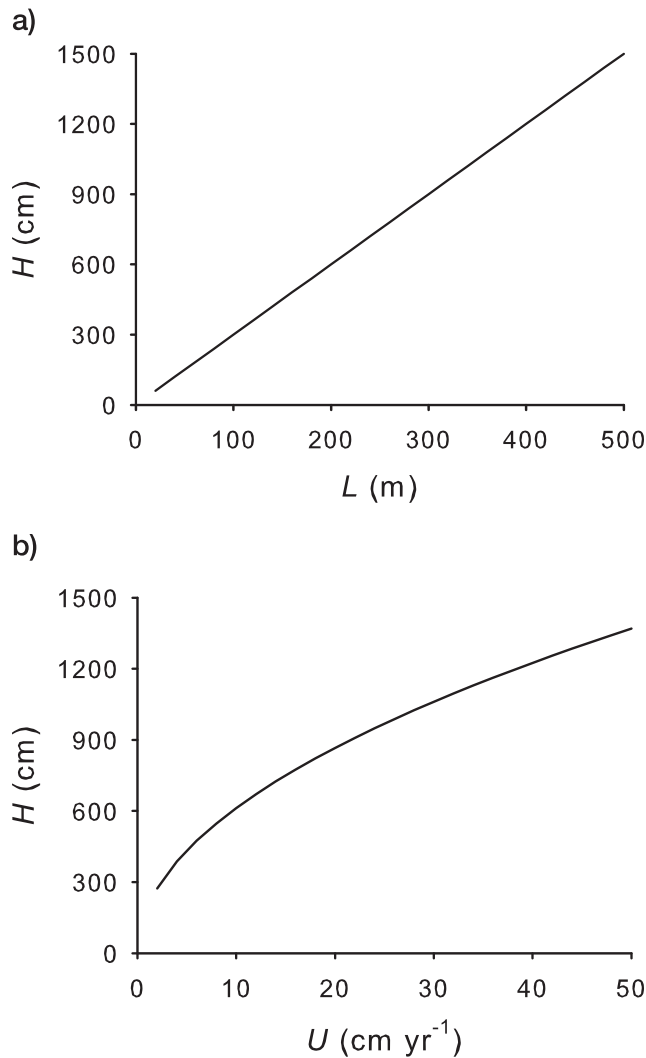


Figure 2. Relationships between (a) peatland lateral extent L and water table height H , assuming a net rainfall rate of $U = 15 \text{ cm yr}^{-1}$ and a uniform hydraulic conductivity of $K = 1.67 \times 10^4 \text{ cm yr}^{-1}$, and (b) net rainfall U and water table height H , assuming a constant $L = 250 \text{ m}$ [after Ingram, 1982].

and therefore advective transport rates (equations (4), (5), and (9)) from our idealized conceptual peatland.

[23] In the first set of experiments, we assumed five values of L , increasing in 100 m increments from 100 to 500 m, representing a broad range of peatlands, from small 10 ha kettle hole bogs at an early stage of development to extremely large (>50 ha) continental raised bogs. We also assumed constant values of $U = 15 \text{ cm yr}^{-1}$ and $K = 1.67 \times 10^4 \text{ cm yr}^{-1}$. This combination of parameters led to groundwater mounds with heights of $H = 300, 600, 900, 1200,$ and 1500 cm . In the second set of experiments with bog shape and size, we assumed a constant lateral extent of $L = 250 \text{ m}$ and net rainfall rates U between 2.4 and 60 cm yr^{-1} . The values of U , in combination with the other parameter values assumed, were chosen so as to give the same five heights of groundwater mound as those in the first set of experiments. While these values of U may initially seem low for peatlands,

it should be remembered that U is assumed to be net of evapotranspiration and represents the rate of addition of water to the saturated zone only [Ingram, 1982].

2.4. Hydraulic Structure

[24] We generated three depth profiles of hydraulic conductivity, each 750 cm deep, as inputs to our model. In the profiles, K was described as uniform, C-shaped, and exponentially increasing (upward) functions of elevation (Figure 3a), representing the most commonly observed distributions reported in the literature. We used a numerical optimization procedure (not reported here) to ensure that despite the different magnitudes and depth patterns of K between the three profiles, they gave the same steady state water table height of $H = 749.5 \text{ cm}$, according to our model (see equation (3)). Because of the identical water table positions, the diplotelmic model would predict identical decay regimes for the three profiles, yet any differences in RTD between the profiles would lead to different decay regimes according to the thermodynamic mechanism. It is apparent from equation (9)

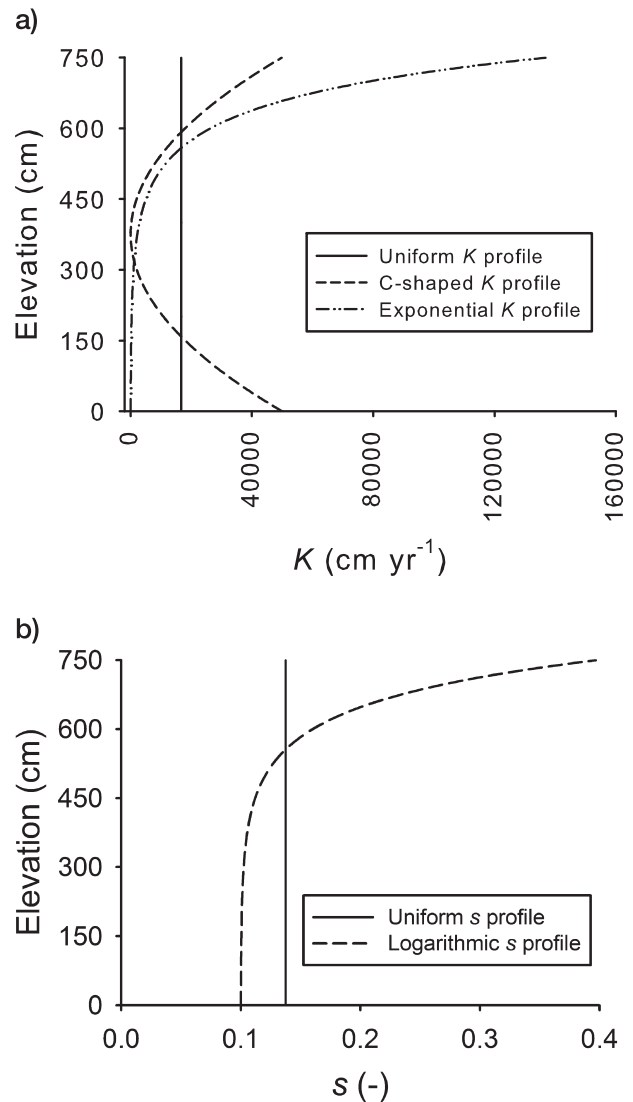


Figure 3. Assumed depth distributions of (a) hydraulic conductivity and (b) effective porosity.

that changes in tracer concentration, and so tracer residence time in any given layer, may be controlled by the relationship between K and s , rather than simply K . Thus, the three assumed K profiles were combined factorially with two depth profiles of s : uniform ($s = 0.138$ (3 significant figures)) and logarithmically increasing (upward) (Figure 3b) from a basal value of 0.1 to 0.4 at the surface [Vorob'ev, 1963; Siegel and Glaser, 1987]. The uniform default value of $s = 0.138$ used in all runs other than those three in which s was a function of height is equal to the depth-averaged s in the runs with variable s .

3. Results

[25] Figures 4 and 5 show that RTDs (and potentially, therefore, decay regimes) are controlled strongly by the

assumed K profile but only weakly by the assumed s profile. The uniform, C-shaped, and exponential K distributions gave rise to widely differing RTDs despite predicting identical water table elevations of 749.5 cm. The uniform K profiles exhibited mean pore water residence times of approximately $\log_{10}(\lambda) = 0.8-1.0$ year and near-symmetrical frequency distributions of $\log_{10}(\lambda)$ (Figure 4, top); the C-shaped K profiles (Figure 4, middle) exhibited similar mean residence times of approximately $\log_{10}(\lambda) = 0.8-1.05$ years but negatively skewed frequency distributions of $\log_{10}(\lambda)$; and the exponential K profiles (Figure 4, bottom) had much longer mean residence times of approximately $\log_{10}(\lambda) = 2.6-2.8$ years and highly negatively skewed frequency distributions of $\log_{10}(\lambda)$, reflecting the very low hydraulic conductivity at the base of the profile. The effects of variable s upon RTD were much less pronounced,

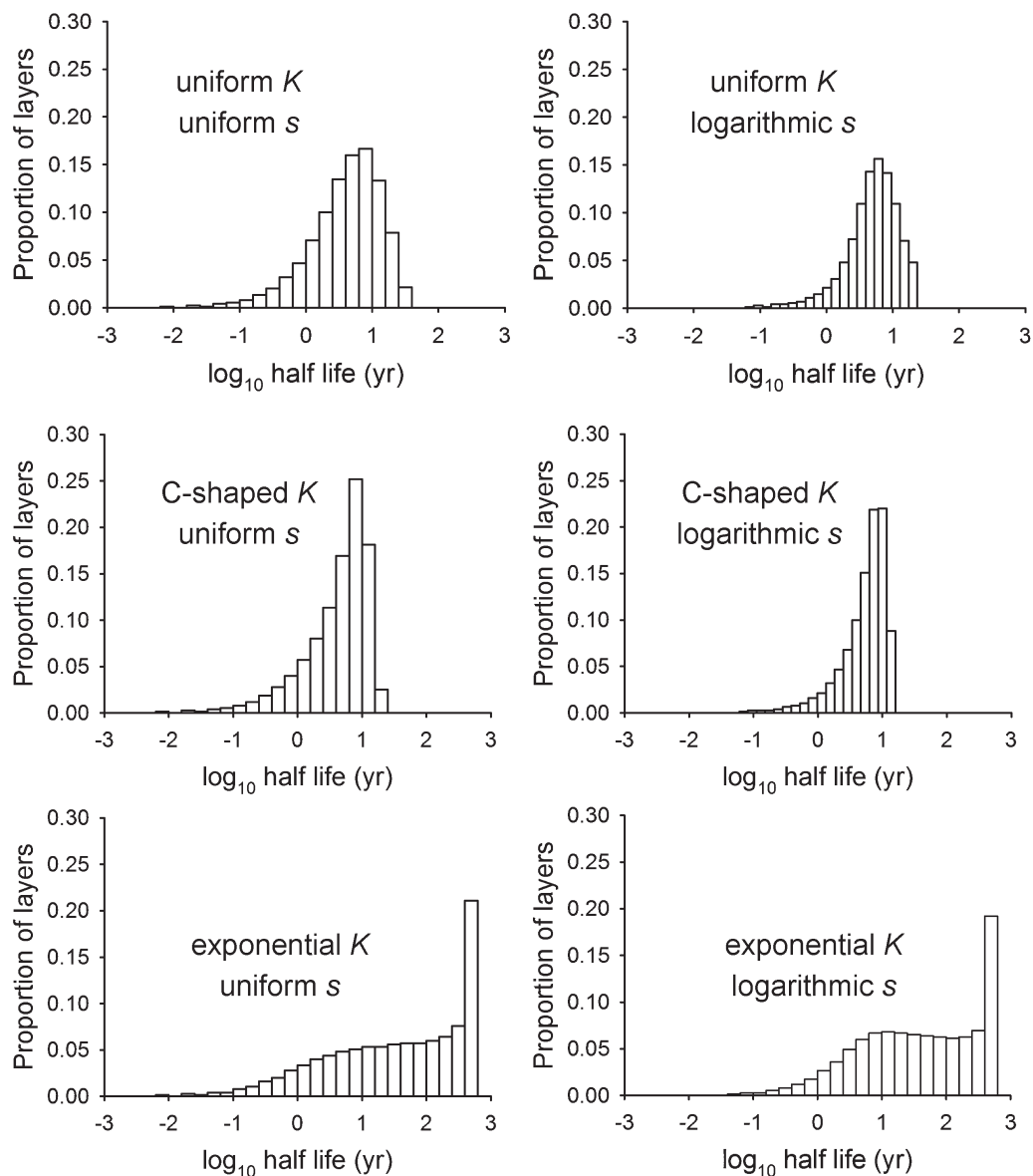


Figure 4. Frequency distributions of tracer half-life λ for uniform, C-shaped, and exponentially increasing (upward) distributions of K , while assuming uniform and logarithmically increasing (upward) distributions of s .

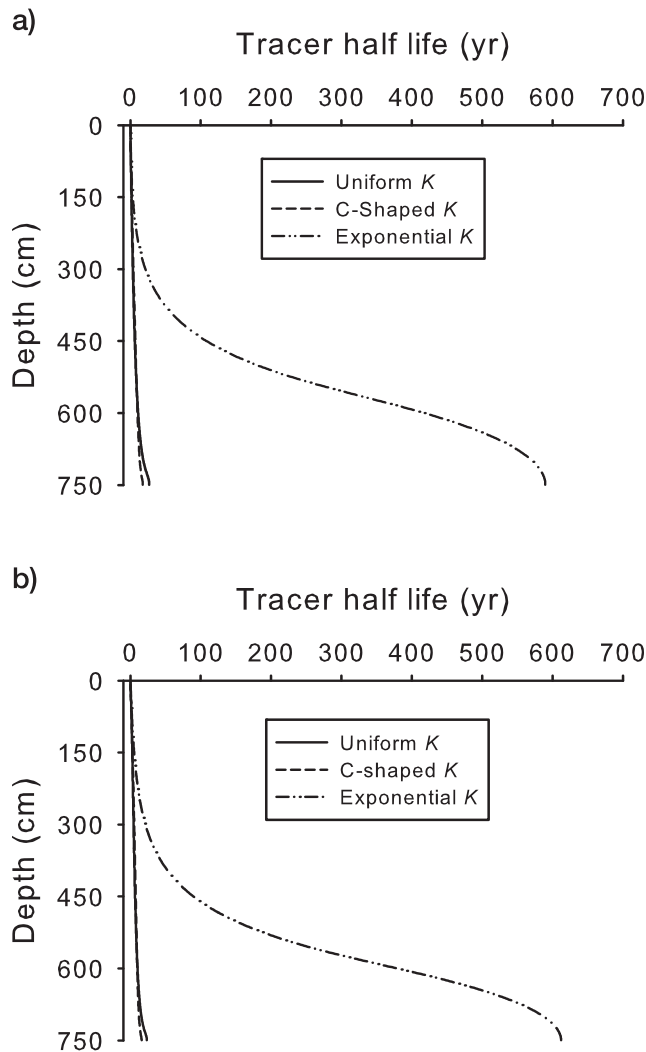


Figure 5. Depth distributions of tracer half-life λ for uniform, C-shaped, and exponentially increasing (upward) distributions of K , while assuming (a) uniform and (b) logarithmically increasing (upward) distributions of s .

although the logarithmic s profiles (Figure 4, right) all gave rise to slight increases in the largest values of λ compared to the uniform s profiles. Despite a factor of 3 difference in near-surface s ($s = 0.138$ in the uniform s profile, as opposed to $s = 0.4$ in the logarithmic s profile), the independent effects of variable s upon RTDs are very small. This is because λ in shallow layers is dominated by advection because of large hydraulic gradients, while in deep layers, where advection is limited by low hydraulic gradients and λ is controlled more strongly by diffusion (see equation (9)), s values are similar between runs (0.1 and 0.138). This finding suggests that the model is not sensitive to porosity in shallow layers but may be more sensitive to deeper porosity.

[26] Depth distributions of λ were similar for shallow peat layers between all model runs with $L = 250$ m, regardless of the surface value of K , but differed greatly between those same runs in midlevel and deep layers (Figure 5). High K values in the deepest peat layers (as in the C-shaped K profiles) caused only weak decreases in λ (relative to the uniform K profile), but very low K at depth (as in the exponential K pro-

files) caused more than an order of magnitude increase in λ in the deepest layers (again relative to the uniform K distribution; Figure 5). Very low K values at depth appear to increase the dominance of diffusive transport because of the further inhibition of advection, leading to an increasing disconnection of those deep layers from rainfall inputs of fresh water.

[27] All peatland sizes exhibited a sharp separation in λ at middepth, below which pore water residence times increased dramatically. This finding is consistent with Beer and Blodau's [2007] hypothesis that deep peat deposits represent a chemically semiclosed system. Increases in peatland lateral extent L led to pronounced increases in λ in deep layers (Figure 6a) because of a reduction in hydraulic gradient H/L at the bottom of the peat profile. However, λ in near-surface layers and the shapes of the λ -depth profiles

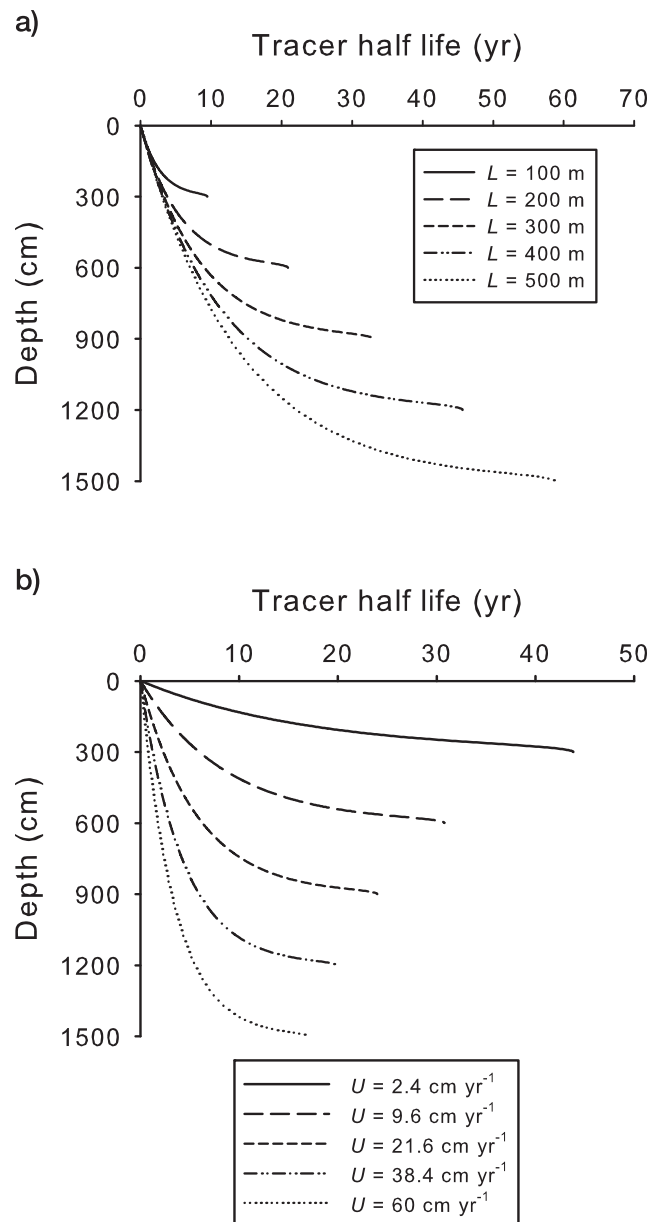


Figure 6. Depth distributions of tracer half-life λ in response to variations in (a) peatland lateral extent L and (b) net rainfall rate U .

are similar between those runs in which L was manipulated. Increases in L lead to proportional increases in H (Figure 2), meaning that the hydraulic gradient H/L , and therefore advective transport of tracer, at the top of the profile is identical between all simulations shown in Figure 6a, regardless of the assumed value of L . We recognize that this similarity of λ at the top of the model peatland between runs with varying L is partly an oddity of our groundwater drainage equation. However, alterations to the assumed net rainfall rate U (Figure 6b) allow us to examine the effects of bog size upon λ at the top of the model peatland without this model artifact. Like our manipulation of L , variations in U also had a pronounced effect on λ in deep peat layers (Figure 6b) but also led to markedly differently shaped depth distributions of λ . Increases in U from 2.4 to 60 cm yr⁻¹ caused a decrease in λ , from approximately 44 to 18 years at the base of the peat profile. However, increasing U led to thicker peat deposits (equation (1) and Figure 2b) and steeper hydraulic gradients at the top of the profile, which resulted in more rapid pore water turnover in middle and deep layers than in runs with low net rainfall rates (Figure 6b). That is, low net rainfall rates caused rapid increases in λ over short depth intervals near the surface, while higher net rainfall rates exhibited more gradual increases in λ with depth. High values of U caused the disconnection between pore water and fresh rainwater to occur deeper in the profile, suggesting that high net rainfall rates may increase the vulnerability of a peat deposit via rapid flushing of pore water. Our experiments offer partial support to our hypothesis that larger peatlands may possess greater stability in the face of climate change. For deeper layers, our evidence is unequivocal that broader peatlands exhibit longer pore water residence times, and so potentially lower decay rates, particularly at depth. However, any increases in net rainfall rate may lead to greater flushing, and so potentially higher decay rates, at all depths.

4. Discussion

[28] We know of few observational studies that can be used to validate our model directly and no studies that have estimated down-profile changes in peatland pore water residence time. All of our simulations suggested peatland pore water mean residence times of less than a year for the uppermost 100 cm or so of the modeled peat profile. These findings are broadly consistent with the results of *Aravena and Warner* [1992], who were able to identify seasonal patterns in pore water isotopic (¹⁸O and ²H) signatures, indicating mean pore water residence times of less than a year, to depths of 50–100 cm. Below this depth, mixing with older water meant that pore water isotopic concentrations were indistinguishable from the long-term rainfall average. Additionally, *Mazeika et al.* [2010], using ³H as a tracer, estimated that peatland pore water mean residence time at their site in Lithuania is on the order of decades. We take encouragement as to the reliability of our model from the broad similarity between this aspect of the model's behavior and the findings of *Aravena and Warner* [1992] and *Mazeika et al.* [2009].

[29] In the current study we have not attempted to assess the validity of the thermodynamic limit to decay as proposed by *Beer and Blodau* [2007]. Rather, we have assumed

that the mechanism represents a genuine negative feedback in peatland development (in the sense of *Belyea* [2009]) and examined the consequences for peat vulnerability when a detailed consideration is made of peatland groundwater hydrology. *Beer and Blodau* [2007] postulated that pore water DIC and methane concentrations on the order of 10 mmol L⁻¹ may represent a threshold, beyond which decomposition ceases. If such a threshold does, indeed, exist, then the depth at which it occurs in any given peatland would be an important factor in determining potential vulnerability to climate change. In turn, this threshold depth would seem to be controlled by the competing processes of (1) the production of the chemical end products of decay and (2) reductions in decay rates due to high concentrations of these end products, as well as interactions with (3) pore water RTDs. We have only considered the latter in our own modeling, so it is not possible for us to speculate on the depth at which such a threshold may occur (and therefore the depth of peat which may be vulnerable to decay) in any given peatland. However, the inclusion of mechanistic representations of the formation of decay end products and the associated reductions in decay rates within a model of RTDs such as ours represents a highly desirable future goal for this work and could eventually be used to inform models of long-term peat accumulation and peatland development [e.g., *Hilbert et al.*, 2000; *Frolking et al.*, 2001].

[30] Increases in lateral extent showed very clear increases in residence times of pore water in the deepest peat layers (Figure 6), offering partial support to our hypothesis that larger bogs become disconnected from rainwater inputs and thereby exhibit greater resilience to climate change via slow decay rates. However, the picture is complicated by the facts that increases in lateral extent led to little discernible change in mean residence times in surficial layers and that increases in net rainfall caused λ to decrease because of steeper hydraulic gradients and thus greater flushing by fresh rainwater. In layers at the top of the modeled peatland, tracer is lost rapidly because of advective drainage throughout the column and the direct dilution by rainwater. The linear relationship between H and L for a uniform K distribution (Figure 2; see equation (1)) means that the hydraulic gradient in our modeled peatland is controlled entirely by the ratio of U to K [*Ingram*, 1982] and does not decrease with increasing L . As such, the vulnerability of surficial peat layers, where residence times are shortest and concentrations of decay end products are lowest [*Beer and Blodau*, 2007], may be largely independent of peatland lateral extent, controlled instead by rainfall regime and small-scale topographical variations [*Nungesser*, 2003] and hydraulic properties [*Baird et al.*, 2009] of near-surface peat. Our results are consistent with the contention of *Beer and Blodau* [2007] that the deepest peat in large peatlands may be chemically disconnected from rainfall inputs because of slow pore water turnover, representing a partially closed system. It is interesting, indeed, that future increases in net rainfall rate in middle to high latitudes in the Northern Hemisphere, as predicted by the Intergovernmental Panel on Climate Change [*Meehl et al.*, 2007], may lead to increased vulnerability of shallow peat layers because of faster pore water turnover.

[31] Our model clearly highlights a specific limitation of the diplotelmic model of peatland structure. While the three assumed K profiles gave rise to contrasting RTDs and depth

distributions of λ , they did so despite exhibiting identical water table positions. In this situation, diplotelmic models of peatland development [e.g., *Clymo*, 1984, 1992; *Hilbert et al.*, 2000; *Frolking et al.*, 2001] would treat the three model configurations identically by assuming that the same decay rate applied throughout the entire profile below the water table. In contrast, the thermodynamic limit to decay suggests large differences in decay regimes between the six model profiles shown in Figure 3 because of qualitative differences in their predicted RTDs (Figures 4 and 5).

[32] We recognize that our model's prediction of longer pore water residence times in deep layers than in those near the surface, in all simulations, reflects, in part, our assumption of an entirely impermeable substrate. That is, by not allowing tracer-rich water to drain through the model's lower boundary, that tracer is effectively "trapped" in deep layers, whereas tracer in the model's upper layers is replaced much more rapidly by fresh rainwater. A number of studies have indicated the possibility of strong vertical exchanges of water between peatlands and their underlying substrates, evidenced by apparent reversals in regional groundwater flow patterns [e.g., *Glaser et al.*, 1996]. The strong upward movement of mineral-rich groundwater into a peatland or downward movement of DIC-rich water out of a peatland would act to reduce the concentrations of decay end products in peat pore water and could substantially increase decay rates according to the thermodynamic limit proposed by *Beer and Blodau* [2007] and *Beer et al.* [2008]. However, the general applicability of the kind of vertical flow observed by *Glaser et al.* [1996] is not clear. Furthermore, in many cases the fine lacustrine sediments which commonly underlie northern peatlands, while not necessarily impermeable, are often several orders of magnitude less permeable than the overlying peat, in which case vertical hydraulic gradients may be assumed to be negligible [*Reeve et al.*, 2000]. Another of our assumptions, that of a constant delivery of rainfall, likely causes residence times in near-surface layers to be longer than they would be under a more realistic, temporally variable rainfall regime. The fluctuations of the water table and of the peat surface itself [*Strack et al.*, 2004] would likely act to flush shallow layers more rapidly. However, the shallowest layers in which such a mechanism would operate seem likely, nonetheless, to possess DIC contents well below the 10 mmol L⁻¹ that has been proposed to halt decay [*Beer and Blodau*, 2007].

[33] Along with decomposition being thermodynamically limited by the in situ accumulation of its own chemical end products, there are a number of other possible mechanisms through which peat decomposition may be self-limiting. The in situ buildup of methane bubbles [*Waddington et al.*, 2009] as a by-product of decay has been shown to greatly reduce peat hydraulic conductivity [*Baird and Gaffney*, 1995], which would, in turn, increase groundwater residence times and further promote the buildup of DIC, methane, and phenolic substances. Also, the decay of peat fibers will lead to a reduction in peat structural integrity, which in combination with sufficient loading, will encourage compression of peat [*Clymo*, 1978; *Price et al.*, 2005] and a reduction in hydraulic conductivity [*Whittington et al.*, 2007], again leading, in turn, to longer residence times. Any reduction in K due to collapse would be accompanied by a reduction in s , although the control of s upon

RTD and down-core variations in λ is second order and almost negligible in comparison to K . Equation (9) suggests that both K and s would control pore water RTD, although this is not born out in Figure 5. It appears that increases in s act only weakly to reduce residence times in deep layers, through the influence of s^2 on diffusivity (equations (7)–(9)). As such, increases in s seem to have little overall effect on the depth distribution of λ , although the key question remains as to the validity of Archie's law (reflected in equations (7)–(9)) in peat soils. The lack of model sensitivity to s is likely also partially explained by the fact that K varied by several orders of magnitude within a given profile, whereas s varied by less than a factor of 3 (Figure 3b).

[34] Our assumption of decreasing s with depth (Figure 3b) is based partly on the assumption that the proportion of dead and closed pore spaces increases with depth, reflecting the so-called "dual porosity" of peat soils [*Hoag and Price*, 1995, 1997]. Closed pores are, by definition, unavailable to flow and therefore do not contribute to calculations of effective porosity. However, the immobile water that they contain will likely exhibit a chemistry less suitable for microbial decay than in the open pores. Dead and closed pores will have a much slower turnover of pore water than those open pores represented by s , meaning that dead pores may "trap" decay-limiting chemicals as decay progresses. Situations in which a low effective porosity represents a high proportion of dead and closed pore spaces (as opposed to a reduction in total porosity, such as in highly compressed peat) may therefore experience higher concentrations of decay end products in the total soil volume, and so lower decay rates, than soils with greater effective porosity. This mechanism is represented in part by our adoption of Archie's law, but in a black box manner. Our model would therefore likely be improved by a consideration of the dual-porosity structure of peat soils and a more mechanistic description of down-core changes in effective diffusivity. We suggest that future measurements of depth profiles of K and s in peatlands should also be accompanied by measurements of total porosity or some other estimate of the degree of the interconnectedness of pore spaces [cf. *Carey et al.*, 2007; *Quinton et al.*, 2009], with the eventual goal of developing predictive empirical relationships between K , s , and effective diffusivity in peat soils.

5. Conclusions

[35] The concept of dual porosity in peats [*Hoag and Price*, 1995, 1997] appears to be important to the thermodynamic limit proposed by *Beer and Blodau* [2007] and *Beer et al.* [2008] because of its influence on pore water RTDs. We therefore suggest that future measurements of effective porosity in peat soils should be accompanied by measurements of total porosity for the same samples; the difference between the terms gives the volumetric proportion of dead and closed pores. While our own results suggested that peat porosity exerts little control over peatland pore water RTDs, caution must be adopted because the accuracy and applicability of Archie's law to peat soils is not clear.

[36] Taking an alternative approach to the modeling presented here, it may be possible to estimate the vertical distribution of pore water residence times in peatlands directly, at least in shallow peat layers, by calculating lag times between

concentrations of stable liquid isotopes (such as ^2H and ^{18}O) in rainwater and pore water [Aravena and Warner, 1992]. Such an approach could be used to validate the model results presented here but would also provide further insight into the importance of microtopography and precipitation in determining near-surface RTDs for peatland pore water.

[37] Low basal hydraulic conductivity and disconnection from precipitation reduce the vulnerability of deep peat layers in thick deposits. However, somewhat counterintuitively, increases in future net rainfall may lead to increased peat vulnerability in northern peatlands, at least at shallow depths, because of more rapid flushing of pore water. More work is clearly required to resolve the potentially competing effects of more rapid pore water flushing and higher water tables upon peat vulnerability in shallow layers.

[38] Finally, our work adds weight to the growing argument that peat profiles are not well represented by classification into the discrete layers “acrotelm” and “catotelm” [e.g., Holden and Burt, 2003; Belyea and Baird, 2006]. Recent calls for the adoption of two further conceptual layers will only serve to add more unnecessary classifications to an already confusing nomenclature. We agree with the assertion of Belyea and Baird [2006] that the diplotelmic model should be discarded in favor of model schemes which offer greater flexibility.

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