Heuristic numerical and analytical models of the hydrologic controls over vertical solute transport in a domed peat bog, Jura Mountains, Switzerland

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Abstract:

We report the results of numerical and analytical simulations to test the hypothesis that downward vertical flow of porewater from the crests of domed alpine and kettle bogs controls vertical porewater distributions of major solutes such as Ca and Mg. The domed Etang de la Gruère bog (EGr), Switzerland, characterized by a vertical downward gradient of 0·04 and stratified layers of peat, is chosen as a field site for the model calibration and evaluation. The middle 4-m section of the 6·5 m thick bog peat is heavily humified and has a hydraulic conductivity of $\sim 10^{-5\cdot6}$ cm s^{-1}. Above and below, peat is less humified with a hydraulic conductivity of $\sim 10^{-3}$ cm s^{-1}. Heuristic finite difference simulations, using Visual MODFLOW, of the bog hydraulics show that the higher conductivity peat at the bog base is critical to create the observed deep, local flow cells that substantively recharge porewater.

   Model results and Peclet number calculations show that before ~ 7000 ^{14}C yr BP diffusion of solutes from underlying mineral soils controlled the vertical distribution of porewater chemistry. From 7000 to ~ 1250 ^{14}C BP the porewater chemistry was probably controlled by both upward diffusion and downward advection, and after ~ 1250 ^{14}C yr BP porewater chemistry was probably controlled by downward advection. Concentrations of conservative major solutes in the porewaters of alpine, ombrotrophic bogs are the net effect of both downward vertical porewater movement and upward vertical diffusion, the magnitudes of which are delicately poised to the configuration of the bog water table over time and subsurface peat stratigraphy. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

Chemical diffusion and groundwater advection are the two major processes that move water and solutes vertically in peatland soils. The extent to which these processes control solute transport in peatlands depends both on the material properties of the peat and the evolving hydrogeologic setting of the wetland. In this paper, we heuristically explore the interplay between diffusion and advection on the vertical transport of solutes in raised bogs, a major wetland ecosystem type found in expansive circumboreal peatlands, in former glacial kettle lakes, and in other moraine and alpine depressions (Mitsch and Gosslink, 2000).

   Raised bogs are wetlands where peat soil accumulates to form a distinct dome-like shape, rising above surrounding mineral soils or other wetland landforms (Clymo, 1983; Ingram, 1983; Roulet, 1990; Siegel, 1981, 1983). Raised bogs are acidic environments that mostly obtain their water from precipitation. The acid

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conditions of raised bog surface waters evolve mostly from the dissociation of organic acids in porewater and *Sphagnum* (Shotyk, 1988; Steinmann and Shotyk, 1997a). Raised bogs are important repositories for long-term atmospheric data on anthropogenic change (Shotyk *et al.*, 1998), and their subsurface hydrology is an ideal setting to address the question: under what hydrologic conditions does chemical diffusion or advection control vertical solute transport in peat? Raised bogs are ideal settings to address this question because their morphology changes with time from relatively flat fens that are later covered by domed bog peat. Fens are circumneutral ecological communities that receive most of their solutes from groundwater discharge and first colonize most wetland settings. Fens gradually develop a groundwater mound which leads to downward advective flow of water in peat near the land surface, deflecting previous upward groundwater motion (McNamara *et al.*, 1992).

The Dupuit–Forcheimer approach, often used to model porewater flow in domed bogs (Armstrong, 1995; Hilbert *et al.*, 2000; Ingram, 1982; Winston, 1994), assumes that the groundwater flow is horizontal, the hydraulic gradient is equal to the slope of the water table, and the vertical hydraulic gradient is zero. However, this approach has been challenged as inexact because it does not incorporate downward recharge of porewater that theoretically occurs whenever the water table forms a mound, such as is found under raised bogs (e.g. Siegel, 1981, 1983). For example, field studies on the hydrogeology and geochemistry of large (several kilometre in diameter) raised bogs in the vast mire of the Glacial Lake Agassiz Peatlands, northern Minnesota, USA, have confirmed that porewater moves vertically downward and sometimes upward at bog crests, potentially flushing the bog peat columns within a decade under appropriate climatic conditions (Glaser *et al.*, 1997; Siegel *et al.*, 1995).

Knowing how dissolved solids, dissolved gases and trace metals move vertically through peat is important to understand the complexity of nutrient, carbon and other cycles and the controls over the ecological changes in wetlands (Glaser *et al.*, 1997; Price and Woo, 1990; Waddington and Roulet, 1997). Although vertical porewater flow clearly occurs under bogs in the Glacial Lake Agassiz Peatlands, similar studies are scant for the more common raised bogs found in alpine kettle lake settings in glaciated regions. McNamara *et al.* (1992) heuristically modelled the advective reversal from upward to downward flow under the crest of a raised bog (New York, USA) that evolved in a groundwater discharge zone. There, groundwater seeps continue to discharge from the steep proximate mineral soil outcrops that surround the bog, while under the bog, advective flow is downward deep into the peat.

We present the results of a study designed to extend the heuristic modelling approach developed by McNamara *et al.* (1992) to groundwater flow and solute transport at raised bogs not underlain by pervasive groundwater discharge zones. Instead we focus our study on raised bogs that formed in flatter areas under conditions where diffusive transport of solutes upward from mineral soils will first predominate, as opposed to advective transport. We specifically test the hypothesis that diffusive upward transport ultimately changes to net advective downward flux as the water table mounds in bogs grow, and that the time when this transition occurred in the history of the bog can be heuristically estimated, if not exactly determined. We further explore the manner by which changes in peat material properties may affect when the transition from diffusive to advective transport occurs.

Numerical and solute transport models may not accurately predict water and chemical mass movement in peatlands or any other hydrogeologic setting in detail, because of uncertainties in low flow velocities, evolving surface morphology and boundary conditions with time, and spatial distributions of material properties such as hydraulic conductivity (Schulze-Makuch *et al.*, 1999; Bredehoeft and Konikow, 1993; Konikow *et al.*, 1992; Oreskes *et al.*, 1994; Oreskes, 2000). Flow and transport models, however, have and are being extensively used to *heuristically* determine the fundamental controls over physical and chemical processes operating in hydrogeologic systems. These models, designed as learning tools rather than predictive devices, have led to new conceptual paradigms for the hydrogeology of many settings, notably wetlands (e.g. Winter, 1978; Siegel, 1993; Ingram, 1982; Reeve *et al.*, 2000).

STUDY AREA

We chose to heuristically model the hydrogeologic evolution and solute transport mechanisms at the Etang de la Gruère (EGr) bog, located near the crest of a glacially eroded anticline in the Jura Mountains, Switzerland (Figure 1) and for which there are excellent profiles of porewater chemical composition (Steinmann and Shotyk, 1997a; Shotyk, 1996). The bog is 1005 m above sea level, receives 1300 mm of precipitation each year and has an average annual temperature of 5·5 °C.

The bog is 22·5 ha, and is partially surrounded by a shallow artificial lake. The diameter of the bog is 300 m, and peat thickness increases from 2·5 m at the bog edge to 6·5 m at the bog centre (Joray, 1942; Steinmann and Shotyk, 1997a). The aspect ratio (the bog height divided by diameter) is 0·01, compared to 0·005 to 0·01 for large raised bogs with 1000 mm of precipitation per year (Hobbs, 1986).

The EGr bog overlies siliceous clay underlain by a calcareous, karstic plateau, eroded at the anticline crest. The siliceous clay sediments consist of ∼40% clay, ∼40% quartz, as well as small amounts of plagioclase, K-feldspar and carbonates (<5% each) (Steinmann and Shotyk, 1997b). The underlying sediments dip slightly from north to south (Joray, 1942) and the basal peat has been dated at 12 370 ± 50 ^{14}C yr BP, corresponding to ∼14 457 calibrated years BP (Shotyk et al., 1998).

The EGr peat is stratified into multiple layers of varying humification. Based on the *Von Post* (Landva et al., 1986; Von Post, 1922) peat classification system (a scale from H1 to H10, with nonhumified peat classified as H1 and completely humified peat as H10), a H8 peat unit peat lies between 130 and 420 cm depth. Below and above the H8 unit is less decomposed peat, at H3–H5 humification (Steinmann and Shotyk, 1997a).
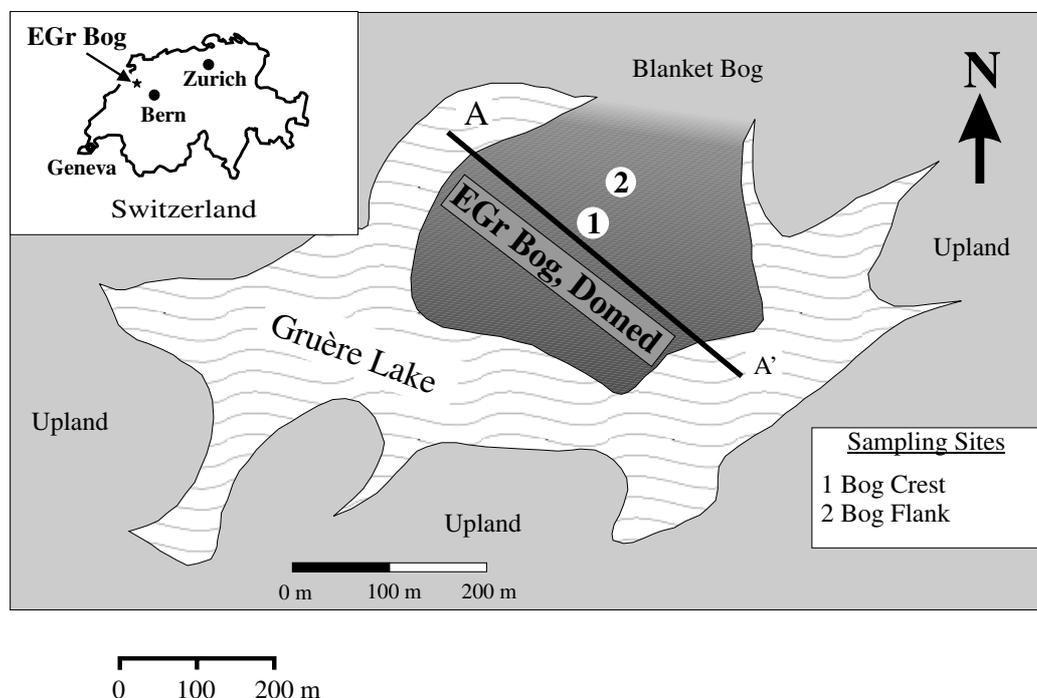
Figure 1. Map of Etang de la Gruère bog, with the locations of the three nested piezometers used for sampling and hydraulic head measurements. The bog crest is the location of sampling for geochemical profiles and age dating (Shotyk et al., 1998). Line A–A′ is the location of the numerical model cross-sections

METHODS

Field analysis

We needed representative, although not comprehensive, hydraulic information from the bog crest to constrain our heuristic models, and chose to use the approach established by others for qualitative calibration of bog hydrogeologic heuristic models (e.g. McNamara *et al*., 1992; Siegel *et al*., 1995). Four 50-cm long sections of peat were collected from the crest of the EGr bog at 20–70 cm (H4–H5), 200–250 cm (H8), 450–500 cm (H4) and 550–600 cm (H3) depths to obtain values for vertical hydraulic conductivity of the major stratigraphic zones in the peat. The cores were obtained with a 5-cm radius, semicircular, stainless steel, Belarus corer (Belokopytov and Beresnevich, 1955), and were wrapped in multiple layers of cellophane and stored in split PVC tubes at 4 °C. They remained wet in storage, and there was no indication of degassing or oxidation as would be shown by discoloration on the core edges.

One piezometer nest was installed at the EGr bog crest and another on the bog flank as a lateral control. The elevations of the piezometer nests were surveyed relative to the elevation of the surrounding lake. The piezometers were installed using the methods described by Chason and Siegel (1986) and consisted of 1·1-cm diameter casing and screen lengths of 5 to 10 cm. The piezometers were used to measure the vertical and horizontal hydraulic gradients and for field experiments to determine horizontal hydraulic conductivity. The water table was measured with a piezometer screened from the bog surface to 100-cm depth. Water levels in all of the piezometers were recorded 20 times between July 1, 1997 and August 31, 1998. Horizontal hydraulic conductivity was determined using slug and bail tests and the data were analysed using the Hvorslev method (Hvorslev, 1951). This method leads to qualitative, order-of-magnitude values for horizontal hydraulic conductivity because the parameter is measured only tens of centimetres from the casing (e.g. Butler and Healy, 1998) but the horizontal flow paths are hundreds of metres long.

Steinmann and Shotyk (1997a) used peepers to obtain detailed porewater profiles. These devices allow *in situ* chemical equilibration between deionized water and porewater across 0·2-μm filter paper, rather than extracting water from pore spaces directly.

Laboratory analysis

Vertical hydraulic conductivity was measured from falling-head tests on sealed peat cores in a Darcy apparatus (Freeze and Cherry,1979). Sections of core, 10–15 cm long, were set in a 12·5-cm diameter PVC tube using paraffin wax as described by Hoag and Price (1997). Water was run through the apparatus from the bottom upwards to force out trapped air. The peat was kept continually saturated, including during storage by refrigeration, to avoid shrinkage, a situation that might break the peat–wax seal. In contrast to the value for horizontal hydraulic conductivity, determined by slug tests, the laboratory tests for vertical hydraulic conductivity are more certain because the length of the peat sampled is a significant fraction of the total flow path length in the vertical peat column.

Batch experiments were used to obtain distribution coefficients for sorption of calcium and magnesium to the EGr peat. The results from batch experiments were fit to the Freundlich distribution that assumes an infinite sorption capacity of the solid matrix (Zheng and Bennett, 1995). The Freundlich distribution coefficient is defined as (Fetter, 1999):

$$C^* = KC^a \tag{1}$$

where C^* is the amount of solute sorbed onto the solid phase, C is the concentration of the solute in solution, and K, a are empirical constants found by fitting a line to a plot of C as a function of C^*. The distribution coefficient, K, is defined as the mass of solute on the solid phase per unit mass of solid phase divided by the concentration of solute in solution and has the units of *volume per mass* (e.g. ml g^{-1}).

A retardation coefficient, R, used as a sink term for removing solutes in advective–dispersive analytical models, is calculated as follows (Zheng and Bennett, 1995):

$$R = 1 + \frac{\rho_b}{n_e} aKC^{a-1} \tag{2}$$

where ρ_b is bulk density of the porous material, n_e is the effective porosity (from Hoag and Price, 1997), K and a are found empirically [Equation (1)], and C is the concentration of the dissolved concentration of the solute. The retardation coefficient equation is nonlinear because the Freundlich isotherm is a function of the dissolved concentrations.

The experimental method for the batch experiments was modified from Day *et al.* (1979). Peat samples were air dried for 36 to 48 h. The samples were ground to a powder using a mortar and pestle, mixed with 0·5 N hydrochloric acid and shaken with a wrist action shaker for 1 h. The solution was then filtered, and the soil was washed with 400 ml of deionized water and air dried.

Approximately 5 g of powdered sample was placed in a test tube, and topped to 20 ml with a solution containing varying amounts of magnesium (0–215 ppm) and calcium (0–2770 ppm). The test tubes were shaken for 48 h using a wrist action shaker. (Preliminary experiments showed that 48 h was ample time for equilibrium to be reached.) The solutions were then filtered with 0·45-μm filter paper and analysed using a direct current plasma spectrometer for magnesium and calcium. Distribution coefficients were measured for two different peat decomposition layers: 220–230 and 520–530 cm depth.

Analytical modelling

Solute transport in porewater is caused by chemical diffusion, fluid advection and/or mechanical dispersion (Freeze and Cherry,1979). The Ogata–Banks equation (Ogata and Banks, 1961) with retardation (Bedient *et al.*, 1994) in one direction is an analytical, solute transport equation:

$$\frac{C_i}{C_0} = \frac{1}{2}\text{erfc}\left(\frac{Rl - \overline{v}t}{2\sqrt{RD_l t}}\right) + \frac{1}{2}\exp\left(\frac{\overline{v}l}{D_l}\right)\text{erfc}\left(\frac{Rl + \overline{v}t}{2\sqrt{RD_l t}}\right) \qquad (3)$$

where C_i/C_0 is the relative concentration, l is the distance along the flow path, $\overline{v}$ is the average linear water velocity, D_l is the coefficient of dispersion, and erfc is the complementary error function. The retardation coefficient, R [Equation (2)], is set to unity for situations with no retardation.

If the average groundwater velocity is very slow, Equation (3) reduces to Fick's Second 'Law' of pure diffusion (Freeze and Cherry, 1979). In addition, at very low velocities, diffusion dominates dispersion, and the coefficient of dispersion is equal to the diffusion coefficient ($D_l = D^*$) (Freeze and Cherry, 1979).

Porewater data for Ca and Mg (Steinmann and Shotyk, 1997a) were compared to theoretical profiles of diffusion described by the Ogata–Banks equation [Equation (3)] with no advective velocity to test the hypothesis that diffusion controls solute transport in the bog. By holding t and D_l constant and changing the length term, a theoretical chemical diffusion profile was calculated. Values for t, 11 425 yr, and D^*, 10^{-10} m^2 s^{-1}, were used to model the expected amount of chemical diffusion upward in the peat column. The D^* value used is the average of the maximum and minimum chemical diffusion coefficients selected as representative values for a peatland setting (Cussler, 1997; Dominico and Schwartz, 1998; Freeze and Cherry, 1979).

The concentrations of solutes at the base of the analytical model, at 5·4 m depth, were assumed constant. The principle source of cations in the peat porewater is the underlying calcareous sediment. It is reasonable to assume that the Ca and Mg concentrations within 100 cm of the base of the peat (compared to ∼6 m total peat thickness) have been nearly constant since the bog formed. The rates at which Ca and Mg dissolve from granular carbonate minerals are comparable to the rates of solute transport from the base of the bog into the peat column, and are slow enough to maintain chemical equilibrium near the base of the bog (Langmuir, 1997).

Numerical modelling

Visual MODFLOW was used for the numerical modelling experiments, oriented for cross-sectional flow system analysis (e.g. Freeze and Witherspoon, 1967; Toth, 1963). Visual MODFLOW is a widely used Microsoft Windows based version of the US Geological Survey 3-D Finite Difference Groundwater Flow model, MODFLOW (Harbaugh and McDonald, 1988, 1996). The model of the EGr bog was run at steady state, two-dimensional with eight grid layers divided into four hydrogeologic units representing four stratigraphic

layers of different humification. The peat units were initially assigned vertical and horizontal hydraulic conductivity values based on the field and laboratory results to guide the heuristic modelling effort.

The modelled domain was 6·5 m thick at the centre and 2·5 m thick at the edges. The topography of the bog water table was adapted from Joray (1942) and from levelling the water table wells. The model had 34 columns evenly spaced over 300 m, except at the edges of the bog where the spacing was halved for better resolution (Figure 2; Tables I and II).

The top of the model was a constant head boundary, Dirichlet condition (Bear and Verruijt, 1987), reflecting a steady water table 30 cm below the topographic surface of the bog (Figure 2). The bottom and all sides of the model were considered no-flow boundaries, Neumann conditions (Bear and Verruijt, 1987) (Figure 2). Applying these types of boundary conditions is standard practice with respect to modelling steady-state hydrogeological conditions for wetland settings with pronounced water table mounds (e.g. Winter, 1978; McNamara *et al.*, 1992; Siegel, 1993) and with the absence of notable strong mass fluxes from the sides.
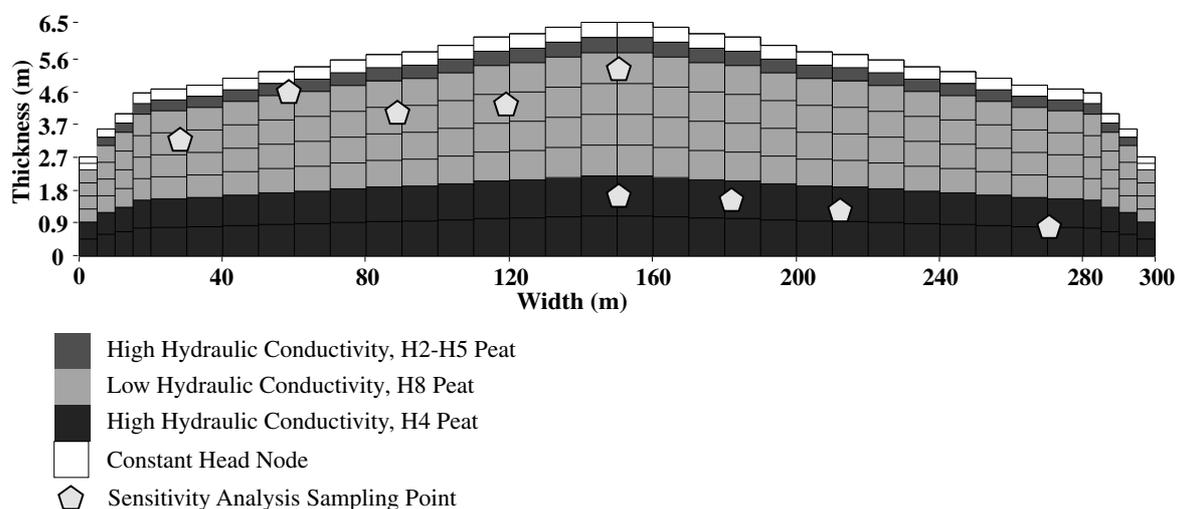
Figure 2. The grid network and simulated calibration wells used for the Visual MODFLOW simulations of the present day EGr bog. The bottom and sides of the model are no-flow boundaries, and the constant head layer across the top of the model represents the water table. The hydraulic conductivity units are described in Table II. The calibration wells are simulated wells placed throughout the model domain

Table I. Model input parameters for Visual MODFLOW. Descriptions of the hydraulic units are in Table II. (Note: measurements taken below the bog crest)

Model	A	B	C	D	E
Model age (^{14}C yr BP)	0	2000	4500	4250	7000
Model thickness (m)	6·5	5·5	4·5	3·5	3·0
Number of layers	11	9	8	7	7
Elevation of hydraulic unit 1 (m)	0·0–2·2	0·0–2·1	0·0–2·1	0·0–1·9	0·0–2·0
Elevation of hydraulic unit 2 (m)	2·2–5·5	2·1–4·0	2·1–3·5	1·9–2·5	2·0–2·0
Elevation of hydraulic unit 3 (m)	5·5–6·5	4·0–5·5	3·5–4·5	2·5–3·5	2·0–3·0
Depth to water table (m)	0·2	0·2	0·2	0·2	0·2
Model diameter (m)	300	300	300	300	300
Number of columns	32	32	32	30	30
Number of cells	352	288	256	210	210
Vertical gradient at crest (from 1 m below bog surface to 1 m above model base)	0·04	0·025	0·02	0·009	0·001

Table II. Description of hydraulic units used in numerical modelling with Visual MODFLOW

Hydraulic unit	1	2	3
Location in EGr bog	Bottom	Middle	Top
Calibrated horizontal hydraulic conductivity (cm s^{-1})	$10^{-4.5}$	$10^{-5.6}$	1
Calibrated vertical hydraulic conductivity (cm s^{-1})	$10^{-2.2}$	10^{-6}	10
Calibrated anisotropy ratio (K_h/K_v)	$10^{-3.3}$	2·3	0·1
Measured horizontal hydraulic conductivity (cm s^{-1})	$10^{-3.5}$	$10^{-5.6}$	Not measured
Measured vertical hydraulic conductivity (cm s^{-1})	$10^{-3.2}$	10^{-4}	10^{-2}
Measured anisotropy ratio (K_h/K_v)	0·5	0·02	Not applicable
Degree of decomposition (Von post scale)	H3–H4	H8	H1–H4

The numerical model results were fit to the average observed hydraulic head gradients at the bog crest and flank by varying horizontal and vertical hydraulic conductivity values. The average vertical hydraulic head distributions measured at the bog crest and flank remained almost the same, downward, throughout the field season. Vertical reversals of hydraulic head would be expected more at the bog–lake edge where transient flow reversals could occur as the lake rises or falls faster than the adjacent water table. However, the purpose of our research was to determine the hydraulic processes at the bog *crest*, the point of maximum accumulation of peat and focus of ombrotrophy. Therefore, while we do recognize potential boundary effects at the edge of the bog, calibration at this location is not emphasized in light of our objectives, similar to what was done by McNamara *et al*. (1992).

The dimensionless Peclet number was used to distinguish between the predominance of diffusive or advective mass transport (Remenda *et al*., 1996). The Peclet number, P_n, is (Freeze and Cherry, 1979):

$$P_n = \frac{\overline{v}d}{D^*} \tag{4}$$

where $\overline{v}$ is the average linear velocity, d is the average particle diameter, and D^* is the diffusion coefficient. Substituting Darcy's Law, solved for $\overline{v}$, into Equation (4) renders:

$$P_n = \frac{Kid}{n_e D^*} \tag{5}$$

where n_e is effective porosity, i is the vertical hydraulic gradient, and K is hydraulic conductivity.

If P_n is less than approximately 0·02, then solute transport is dominated by longitudinal diffusion, whereas if P_n is greater than 6, then solute transport is dominated by mechanical dispersion and advection (Fetter, 1999). If P_n is between 0·02 and 6, transitional conditions may occur (Fetter, 1999).

In Equation (5), the hydraulic conductivity, the average particle diameter, the effective porosity and the diffusion coefficient can be held constant. A numerical model can be used to heuristically calculate vertical hydraulic head gradients as the water table mound under the bog grows, and the result can then be applied to the Peclet number to assess if mass transport at any given time is dominated by diffusion or advection.

As a starting point for the heuristic Peclet calculation for modern conditions a vertical diffusion coefficient of 10^{-10} m^2 s^{-1} (Freeze and Cherry, 1979) and an effective porosity of 0·25 (Hoag and Price, 1997) were used and an average pore diameter of 1 mm was used, based on data obtained from similar peat soil types (Yamaguchi *et al*., 1985). For the Peclet calculation a vertical hydraulic conductivity of $10^{-5.3}$ cm s^{-1} and a vertical hydraulic gradient calculated from the numerical cross-sectional model, calibrated by changing the estimated values for vertical and horizontal hydraulic conductivities in each hydrologic unit, were used. Then, the profile of the bog water table was changed to reflect the growth of the bog. The water table configuration was based on the age of the peat, determined by radiogenic dating (Shotyk *et al*., 1998). It was assumed that the width of the bog was effectively the same over time and that the shape of the water table mound historically was simply an increasingly subdued replicate of the modern setting.

Sensitivity analysis investigated the effects of varying the hydraulic conductivity on the modelled hydraulic head of the EGr bog. After the modelled head values at the piezometer locations were matched, the hydraulic head was noted at nine sampling points in the numerical model domain (Figure 2). The hydraulic head data for each sampling point was set arbitrarily to the computed head value at that location. Horizontal and vertical hydraulic conductivity values for each hydraulic unit were then varied individually, and a measurement of sensitivity of the simulated hydraulic head to hydraulic conductivity was calculated using the following equation (Anderson and Woessner, 1992; Zheng and Bennett, 1995):

$$X_i = RMS_{i,changed} - RMS_{original} \tag{6}$$

where X_i is the measure of sensitivity as a result of a change in parameter i, $RMS_{i,changed}$ and $RMS_{original}$ are the root-mean-squared error of the hydraulic head for the perturbed and original model respectively. The root-mean-squared error for a given model perturbation, i, is (Anderson and Woessner, 1992):

$$RMS = \sqrt{1/n \sum_{i}^{n} (h_m - h_s)_i^2} \tag{7}$$

where n is the number of samples, and $h_m - h_s$ is the difference between the perturbed and original hydraulic heads at the sampling points.

RESULTS

Peat properties

Upon extraction, the 20 to 70 cm depth core roughly consisted of two sections: a light brown, loose *Sphagnum*, H4 peat section from 20 to 40 cm depth, and a dark brown to black layer, H5, with wood material from 40 to 70 cm depth. The second core, from 200 to 250 cm depth, had no noticeable stratigraphic breaks, was black, and H8 peat. The third core, from 450 to 500 cm depth, was in two sections: *Carex* dominated, H4 peat from 450 to 480 cm depth, and slightly broken up *Sphagnum* and *Carex*, H4 peat to the end of the core. The fourth core, from 550 to 600 cm depth, had H3 peat and a gradual transition to light brown moss in the bottom 20 cm.

Hydraulic gradients

The gradients at the bog crest (Figure 3) and on the bog flank (not shown) were, on average, 0·04 downwards. The average vertical head gradient at the crest of the EGr bog is downward (Figure 3a), although seasonally, vertical head gradients change (Figure 3b). The hydraulic gradient at the bog flank is downward through most of the measurement period and fluctuated less than at the bog crest.

Hydraulic properties

The geometric mean of the horizontal hydraulic conductivity ($n = 7$) from the centre well-humified peat section, 1·0 to 4·3 m depth, is $10^{-5.6}$ cm s^{-1}, the minimum is $10^{-6.5}$ cm s^{-1} and the maximum is $10^{-4.5}$ cm s^{-1}. The horizontal hydraulic conductivity of the underlying less humified layer, 5·5 to 6·5 m depth, is $10^{-3.5}$ cm s^{-1} ($n = 1$). From the falling head tests, the vertical hydraulic conductivity was measured as 10^{-2} cm s^{-1} at 0·5 m depth, 10^{-4} cm s^{-1} at 2·5 m depth, and $10^{-3.2}$ cm s^{-1} at 4·6 m depth. The weighted average of the vertical hydraulic conductivity is $10^{-3.8}$ cm s^{-1}. Figure 4 displays the horizontal, vertical hydraulic conductivity values, and those predicted from peat bulk density with depth.

a)
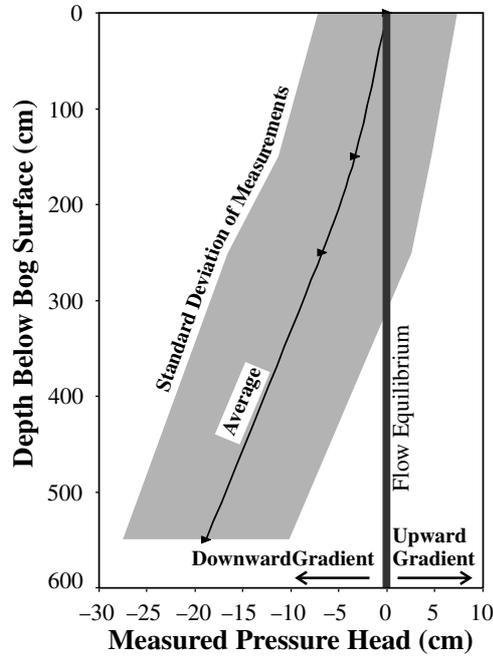
b)
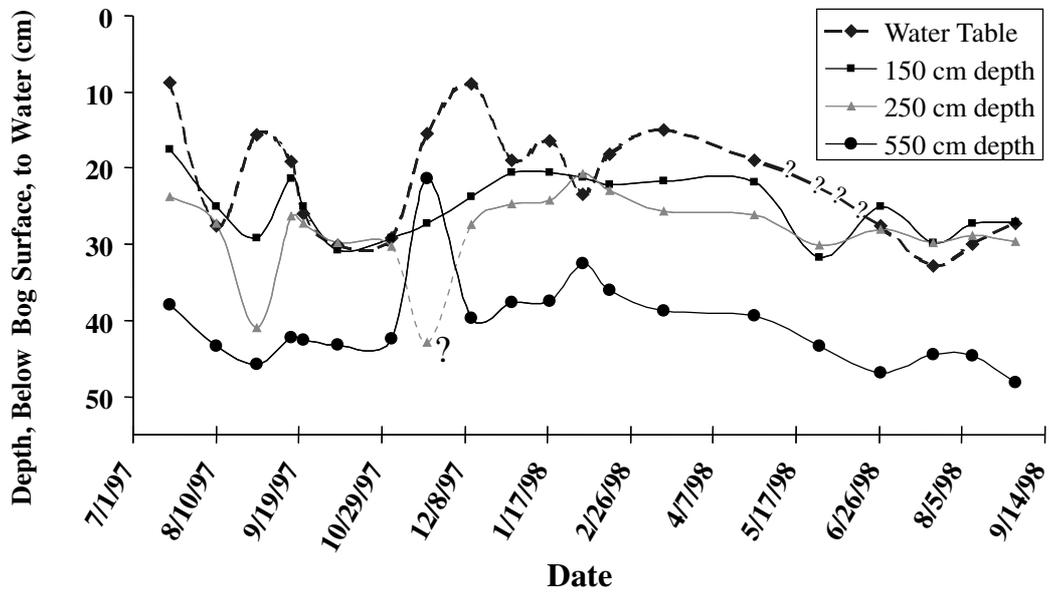
Figure 3. Hydraulic head measurements at the bog crest (a) with depth and (b) through time. The hydraulic head measurements were made with piezometers inserted to depths of 150, 250 and 550 cm. The water table was measured with a PVC tube that was fully slotted from a depth of 0 to 100 cm below the land surface. Part (a) shows the general trend of the vertical hydraulic head is downwards, with an average hydraulic gradient of 0·04
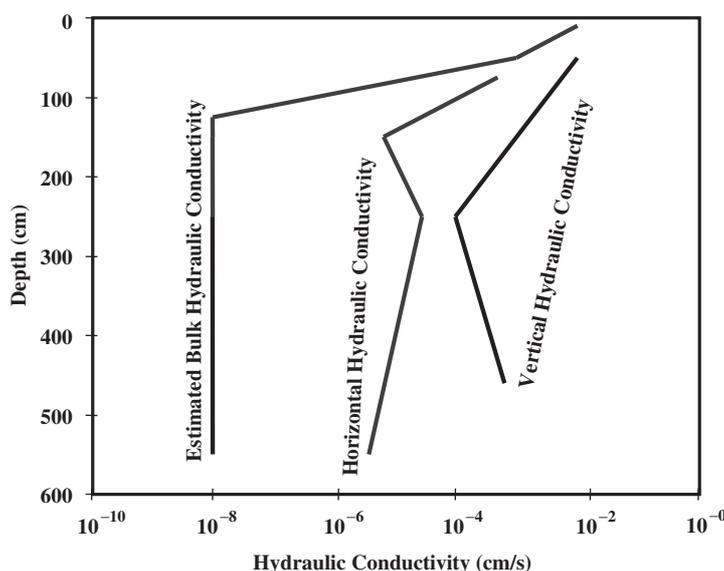
Figure 4. Summary of hydraulic conductivity values with depth. Values for vertical hydraulic conductivity were found from variable head tests, horizontal hydraulic conductivity from Darcy experiments, and estimated hydraulic conductivity based on bulk density (Steinmann and Shotyk, 1997a)

Adsorption experiments

The sorption data was fit to the nonlinear Freundlich sorption isotherm using Sigma Plot, a scientific graphing program. The distribution coefficients at 220 to 230 cm depth were 0·0025 and 0·016 ml g^{-1} for Mg and Ca respectively. The distribution coefficients at 520 to 530 cm depth were 0·0003 and 0·019 ml g^{-1} for Mg and Ca respectively. The retardation coefficients for Ca and Mg at both depths ranged from 1·0 to 5·3 for dissolved solute concentrations of 20 to 0·0001 ppm.

Analytical modelling

Figure 5 summarizes the results of the analytical 1-D model for solute transport by chemical diffusion with and without retardation.

Numerical modelling

The flow net from the calibrated numerical flow model for the modern bog is shown in Figure 6a. The values of vertical and horizontal hydraulic conductivity observed and used in the calibrated model are in Table II. The calibrated values of the horizontal hydraulic conductivity of the bottom layer, $10^{-4·5}$ cm s^{-1}, and the vertical hydraulic conductivity of the middle layer, 10^{-6} cm s^{-1}, were smaller than the observed, $10^{-3·5}$ and 10^{-4} cm s^{-1} respectively. The calibrated values of the vertical hydraulic conductivity of the bottom hydraulic unit, $10^{-2·2}$ cm s^{-1}, and the top hydraulic unit, 10 cm s^{-1}, are larger than the observed, $10^{-3·2}$ and 10^{-2} cm s^{-1} respectively. The calibrated and observed vertical hydraulic conductivities of the horizontal hydraulic conductivity of the middle hydraulic unit are the same, $10^{-5·6}$ cm s^{-1}, and the horizontal hydraulic conductivity of the top layer was not measured. In our sensitivity analysis, we varied the horizontal and vertical hydraulic conductivity of individual hydraulic units by factors of 5 and 10. The results of the sensitivity analysis are presented in Figure 7.

The EGr bog was then modelled to evaluate changes in vertical hydraulic gradient with growth of the EGr dome. In addition to the modern scenario, heuristic models were run for bogs with a thickness of 5·5, 4·5, 3·5 and 3·0 m, corresponding to approximate ages of 2000, 4500, 6250 and 7000 ^{14}C yr BP (Figure 6). As
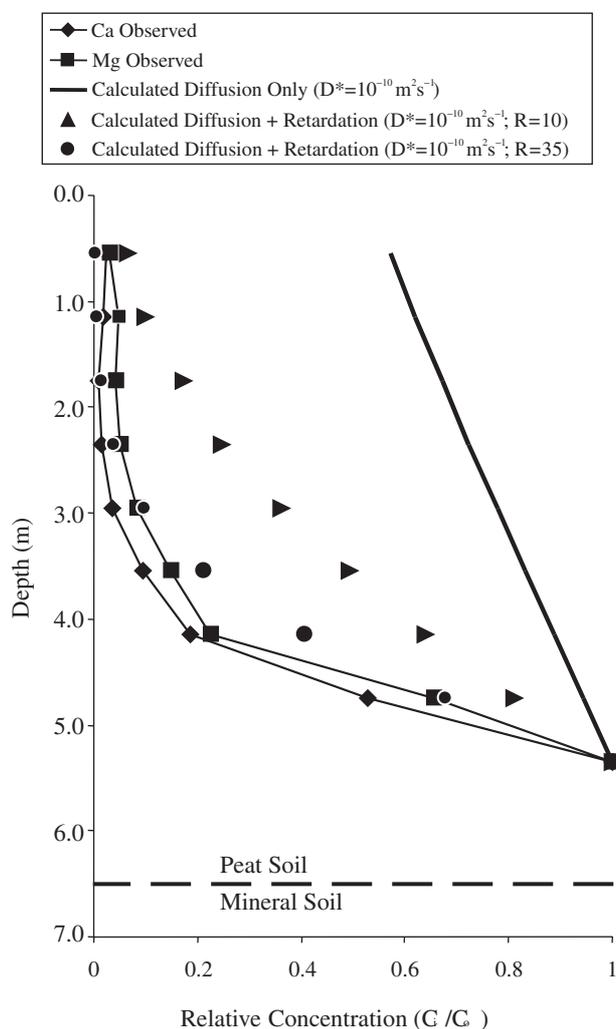
Figure 5. Measured porewater concentrations of Ca and Mg versus analytically modelled diffusion profiles (Ogata–Banks equation with and without retardation). The ordinate value for concentration is equal to the concentration at depth, C_i, divided by the concentration at the base of the profile, C_0. The C_i for Ca and Mg is 798·3 and 101·6 µM respectively. The results show that a retardation factor of 35 is needed for the analytical results to match the measured porewater profiles

the thickness of the bog decreased from 6·5 to 3·0 m, the vertical gradients decreased from 0·04 to 0·001 (Table I; Figure 6).

INTERPRETATION

The EGr bog has a groundwater mound that rises approximately 4·0 m above the surrounding lake. The measured downward hydraulic gradients in it are consistent with what is expected for lake–groundwater interaction when such a mound is present (Winter, 1978). Although the head gradient is generally downward at the bog crest, the gradient does seasonally change. These short-term changes in the vertical hydraulic gradients at the EGr bog crest are consistent with the hypothesis of episodic methane build-up and ebullition from the peat causing overpressuring in the centre of the peat column (Romanowicz *et al.*, 1993; Glaser *et al.*,
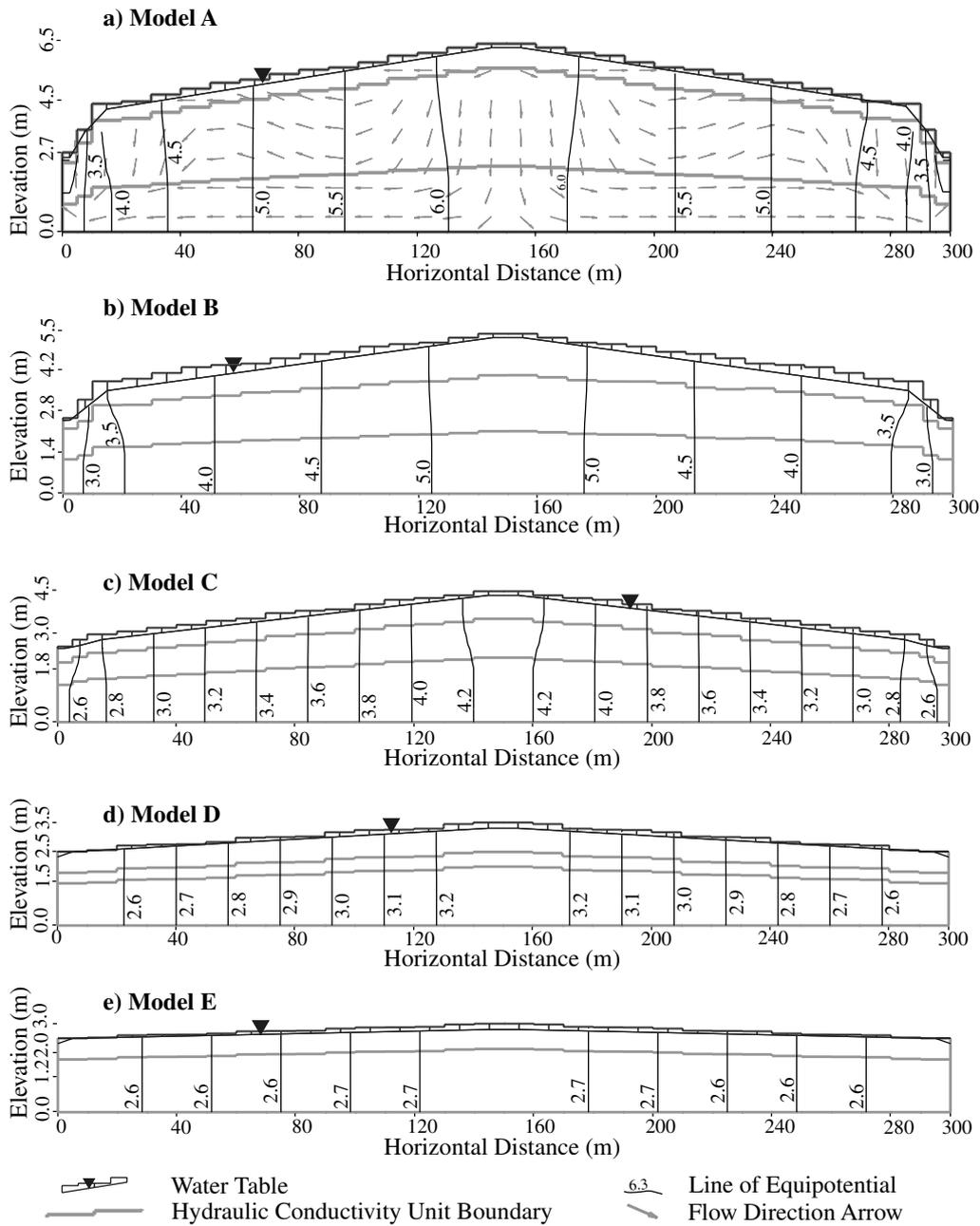
Figure 6. Flownet output of the Visual MODLFLOW models demonstrating the decrease in vertical hydraulic gradient with a decrease in the thickness of the EGr model dome. In the models, all of the hydraulic conductivity values were held constant but the thickness of the hydraulic units was varied. The resultant vertical gradients at the bog crest are 0·036, 0·025, 0·019, 0·0091 and 0·001 for models (a), (b), (c), (d) and (e) respectively. The model input parameters are tabulated in Tables I and II

1997). However, during this project, no measurements of methane or other gases were made, so this hypothesis needs to be further tested. In any case, in general, vertical head gradients are almost always downward and sufficient to drive advective flow.
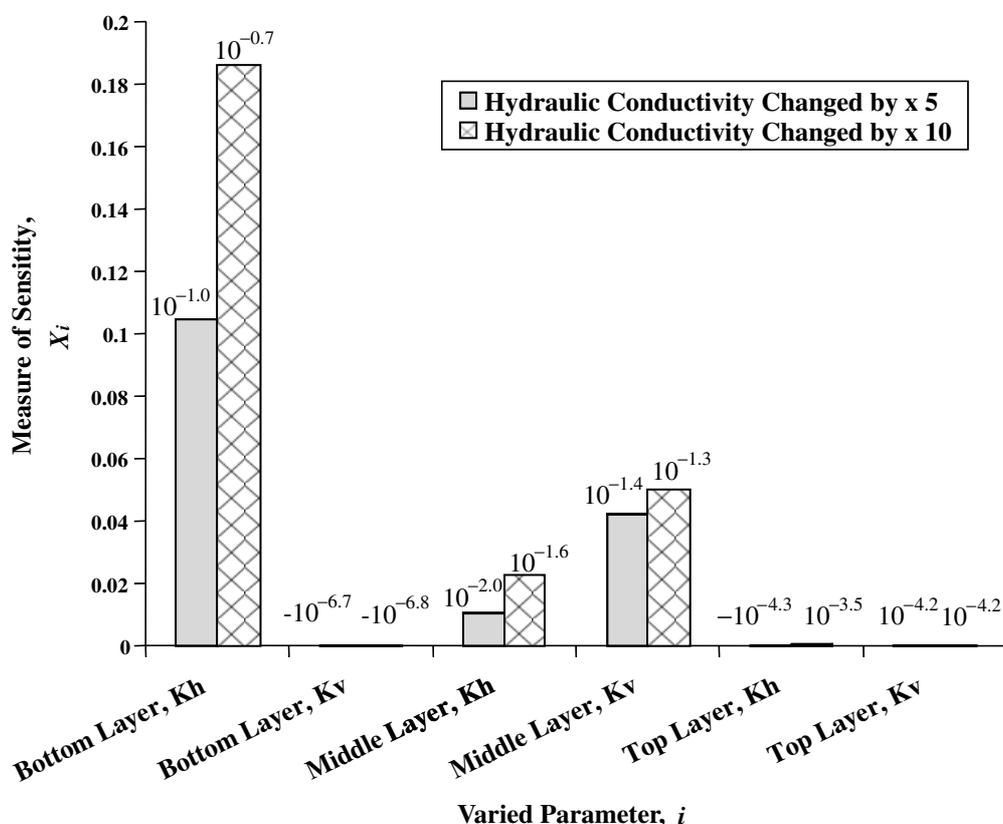
Figure 7. Sensitivity analysis of the EGr bog numerical model, shown as a graph of changes in the sensitivity of the calculated heads to changes in material properties of the peat. The figure indicates that the model is most sensitive to the horizontal hydraulic conductivity of the bottom layer, followed by both the vertical and horizontal hydraulic conductivity of the middle layer

The field values for horizontal hydraulic conductivity of EGr peat are similar to that found elsewhere, in the range of 10^{-4} to 10^{-3} cm s^{-1} (Chason and Siegel, 1986). However, the anisotropy ratio (horizontal hydraulic conductivity divided by vertical hydraulic conductivity) <1 (Figure 4) is unusual. The majority of porous materials, including those in wetlands, have anisotropy ratios greater than unity (e.g. Chason and Siegel, 1986; Freeze and Cherry, 1979).

There are two possible explanations for the inverse anisotropy in the EGr bog. First, the vertical hydraulic conductivity experiments may have failed due to poor seals between the peat and the surrounding paraffin wax. However, bubbles or other fluids were not seen moving through the wax seal during the experiments; therefore a failed seal is not plausible. Second, the peat profile from the surface to a depth of 420 cm contains significant remains of *Eriophorum* (Joray, 1942), a grass with a decay resistant base and long, fine fibres. These stalks and fibres are preserved in their original, upright orientation, probably creating secondary pathways that pipe water in the vertical direction. When the EGr bog cores were split, the vertical orientation of this plant macrofossil was readily apparent.

The porewater of the EGr bog has decreasing concentrations of major solutes from the base of the peat profile to the surface (Figure 5). Considering the hydrogeologic isolation of the dome from the surrounding topography, the only major source of high concentrations of solutes in the porewater is the underlying sediments. The three possible modes of upward transport for solutes are diffusion, upward advection driven by an upward porewater flow, and/or transverse dispersion driven by a horizontal flow (Reeve *et al.*, 2000).

The analytical models (Figure 5) show that the solutes, given the age of the lower peat sediments, simply could not have migrated upward by diffusion. The modelled diffusion profiles in all cases show more diffusion (i.e. the profile rises higher in the peat profile from the mineral soil base) than shown by the profiles of the measured solute concentrations. All measured solute profiles plot *below* plausible theoretical diffusion profiles, even the analytical one-dimensional model with a maximum plausible retardation factor of 10.

Hoag and Price (1997) found that the maximum retardation factor for base cations in well-humified peat is 7·3, indicating that our analytic model results (with a retardation factor of 35) are not a plausible representation of solute transport in the EGr bog. Finally, the retardation factors for Ca and Mg from the batch experiments range from approximately 1 to 5·3, thereby confirming that a retardation factor of 35 is unrealistic.

Reeve *et al.* (2000) show that horizontal flow, given sufficient time and distance, can create extensive transverse dispersion. The result of this process in the EGr bog would be increased upward movement of solutes into the peat profile from the mineral soil. However, the results of our study show that the upward movement of solutes is less than predicted, with or without dispersion from horizontal flow. The occurrence of transverse dispersion is difficult to estimate, but it will lead to an underestimation of the downward vertical flow.

Porewater solutes did not diffuse high into the peat profile because downward advection of pore water prevented it. The measured downward gradient at the bog crest is 4% (0·04). Assuming an effective porosity of 0·25 and using the weighted average of the measured vertical hydraulic conductivity values ($10^{-3 \cdot 8}$ cm s^{-1}), the average linear velocity is ~2 cm day^{-1} downwards.

The Visual MODFLOW simulation shows that flow paths originate at the bog crest, move downward, and then return to the bog flanks. These results are similar to those by Freeze and Witherspoon (1967) who prepared numerical models of regional groundwater flow in mineral soils including a buried layer of high hydraulic conductivity. Reeve *et al.* (2000) recently found that sand and gravel layers below large peatlands, such as the Glacial Lake Agassiz Peatlands, similarly influence the groundwater flow cells at a much larger scale. The model results and sensitivity analysis further show that groundwater flow in the bog peat is most sensitive to the horizontal hydraulic conductivity of the bottom layer, followed by the horizontal and vertical hydraulic conductivities of the middle layer (Figure 7). The hydraulic head did not change significantly when changes in other model parameters, including the depth of the lake or even the absence/presence of the lake, were made.

Total mass transport in the bog hydrogeologic setting is, of course, still dominated by horizontal flow. Flow lines that originate at the bog crest travel down to the bottom high hydraulic conductivity layer, laterally to the edge of the model, and then upwards to the constant head boundary representing the lake. Flow paths that originate on the bog flanks travel downward slightly, move nearly parallel to the bog surface, and at the bog edge the water is discharged to the lake edge due to the change in slope of the bog surface near the lake.

The modern Peclet number defining the condition of vertical solute transport at the bog crest is 8·0, based on present day values for the vertical downward gradient. Holding the bog peat material properties constant, the Peclet number equation reduces to a function of the vertical hydraulic gradient, controlled by the doming of the bog, and a constant based on the physical properties of the peat [Equation (5)].

Reducing the value for the hydraulic gradient from 0·04 to <0·001 would theoretically result in pure diffusive solute transport. At EGr, the modelled vertical hydraulic gradient of 0·001 was heuristically calculated for a bog only 3·0 m thick, 7000 ^{14}C yr BP. Therefore, before 7000 ^{14}C yr BP, the porewater chemistry of the EGr bog was controlled purely by upward diffusion. From 7000 to ~1250 ^{14}C yr BP the porewater chemistry was controlled by both upward diffusion and downward advection. For the past ~1250 ^{14}C yr, solute transport in the EGr bog has been dominated by downward advection (Figure 8).

Uncertainties

There is obviously uncertainty in the parameters used for the analytical, numerical and Peclet number modelling. We chose parameters that we felt were most plausible for the hydrogeologic setting of the bog.
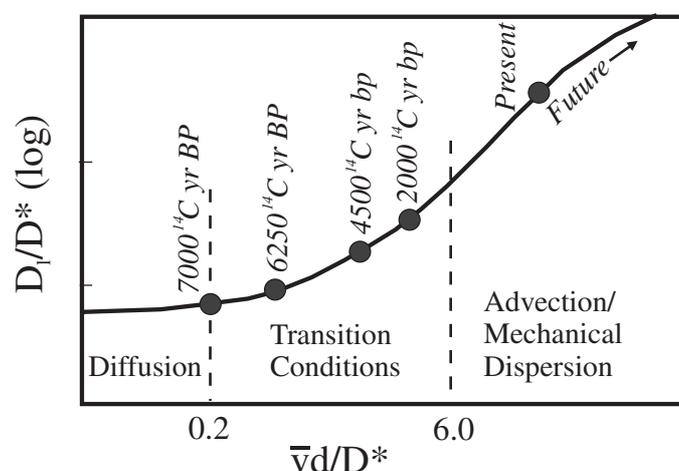
Figure 8. The Peclet number combined with the results of the variable thickness models. The theoretical Peclet number analysis shows the change from diffusion to advective controlled transport of porewater solutes through time. The basal peat of the EGr bog is 12 000 ^{14}C yr old

For example, our assumed value for D^* is consistent with the value commonly used in solute transport calculations (e.g. Freeze and Cherry, 1979) in like environments, and our assumed value and method of measurement for hydraulic conductivity is consistent with practice (e.g. Chason and Siegel, 1986).

For the Peclet number analysis, we assumed that the calibrated vertical hydraulic conductivity of the modern hydrogeologic numerical flow model was the most appropriate one to use. We calibrated to the observed head distributions by varying hydraulic conductivity; the boundary conditions of the bog margins, water table and lower no-flow boundary were fixed at steady state, and only the hydraulic conductivity was used to make the calibration as is typical in doing heuristic (or even transient) models (Anderson and Woesner, 1992). We then optimized the modern Peclet number to ensure that advective flow occurs in the peat profile today, based on modern field data, and that diffusion controlled solute transport when the bog initially domed 10 000 years ago, which is heuristically sensible from first principles, given a nearly flat water table.

It is clear that when the bog first formed, the upward diffusive flow of solutes was the dominant transport mechanism because there was no to minimal groundwater mounding that would drive recharge downward. It is also clear that modern downward advection of ground water now inhibits upward diffusion; otherwise, the measured solute profiles would match diffusion profiles. The fundamental question remains: what combination of hydraulic properties can lead to downward advection today? We attempt to resolve this issue by testing the sensitivity of changing the parameters in the Peclet number to obtain values greater than 6·0, indicating advection is the dominant transport process. Of the material properties used to calculate the Peclet number, the widest potential range in values are for the coefficient of dispersion which can span two orders of magnitude and for the vertical hydraulic conductivity. For example, assuming the lowest plausible value for vertical hydraulic conductivity, 10^{-7} cm s^{-1}, to obtain a Peclet number greater than 6·0 the diffusion coefficient would have to be $10^{-11·5}$ m^2 s^{-1}, smaller than the minimum plausible, 10^{-11} m^2 s^{-1} (Freeze and Cherry, 1979). Inversely, assuming the diffusion coefficient has a maximum plausible value of 10^{-9} m^2 s^{-1}, the vertical hydraulic conductivity must be $10^{-4·5}$ cm s^{-1} for advection to be the dominant solute transport process. Without detailed field experiments, such as mini-aquifer testing and tracer tests in the bog, it is not possible to constrain the uncertainty and variability of the Peclet number more, although the combination of values used must have a value greater than 6 to advect recharge downward today in the bog. Our sensitivity testing, although constrained in part by the difficulty of obtaining important material parameters for peat, does suggest that we have captured the essence of the evolution of the bog's solute transport history, if not the details in specific timing.

There are uncertainties in the Visual MODFLOW simulations. The lateral peat stratigraphy is not well constrained, but plausibly continuous and horizontal given the heuristic approach used in this study. The age of the peat at the EGr bog crest is well known (Shotyk *et al.*, 1998), but there is, as is usual in wetlands, limited information (i.e. Joray, 1942) on the palaeomorphology and growth rates at the bog flanks and edges. We assumed as a first approximation, based on changes in vegetation, that bog growth started out as a flatter 'fen-type' peatland and then domed.

CONCLUSIONS

Vertical porewater flow is an important process often overlooked by wetland scientists. Our research shows that vertical flow can and does influence the porewater chemistry of the EGr bog, and by extension, probably other isolated domed bogs as well. Using only the Dupuit–Forcheimer assumptions to calculate porewater movement and mass transport will invariably lead to errors in the chemical mass flux of bog systems at other than temporally short time scales. For example, prediction of the shape and size of raised bogs based only on the horizontal flow of water (Ingram, 1982; Winston, 1994) may be problematic where there is a significant component of vertical flow.

Our measured vertical profiles of porewater chemistry at the EGr bog plot lower than that calculated by analytical models incorporating pure vertical diffusive transport. Today at the crest of the EGr bog, porewater clearly moves downward and deep through the peat profile and hydraulic measurements suggest that the rate of movement is on the order of $\sim$2 cm day^{-1}.

Heuristic numerical modelling experiments of porewater flow at the EGr bog show that the high hydraulic conductivity layer at the bottom of the EGr bog is critical to form recharge flow cells extending to the base of the bog. Coupling the numerical model with Peclet number analysis shows that current solute transport in the bog is both advective and diffusive, although prior to 7000 ^{14}C yr before present, solute transport was controlled only by vertical diffusion (Figure 8). These results compare well to those of Reeves *et al.* (2000) for the larger Glacial Lake Agassiz Peatlands, where a higher permeability layer in mineral soils below the base of the peat column creates deep, vertical, groundwater flow cells. The hydrodynamics of porewater flow in these two very different peatland settings lead to the conclusion that the presence or absence of a higher permeability layer in or below a domed peat bog is a crucial factor to create conditions for deep vertical flow of porewater and advection of solutes in peat.

REFERENCES

Anderson MP, Woessner WW. 1992. *Applied Groundwater Modeling*. Harcourt Brace Jovanovich: San Diego; 381.
Armstrong AC. 1995. Hydrological model of peat-mound form with vertically varying hydraulic conductivity. *Earth Surface Processes and Landforms* **20**: 473–477.
Bear J, Verruijt A. 1987. *Modeling Groundwater Flow and Pollution*. D. Reidel: Dordrecht; 414.
Bedient PB, Rifai HS, Newell CJ. 1994. *Ground Water Contamination; Transport and Remediation*. Prentice Hall: Englewood Cliffs, NJ; 541.
Belokopytov IE, Beresnevich VV. 1955. Giktorf's peat borers. *Torfyanaya Promyshlennost* **8**: 9–10 (in Russian).
Bredehoeft JD, Konikow LF. 1993. Groundwater models: validate or invalidate. *Ground Water* **31**: 178–179.
Butler JJ, Healey JM. 1998. Relationship between pumping-test and slug-test parameters: scale effect or artifact? *Ground Water* **36**: 305–313.
Chason DB, Siegel DI. 1986. Hydraulic conductivity and related physical properties of peat, Lost River Peatland, Northern Minnesota. *Soil Science* **142**: 91–99.
Clymo RS. 1983. Peat. In *Ecosystems of the World, Vol. 4A, Mires: Swamp, Bog, Fen and Moore, General Studies*, Gore AJP (ed.). Elsevier: New York; 159–224.

Cussler EL. 1997. *Diffusion; Mass Transfer in Fluid Systems*. 2nd edn. Cambridge University Press: Cambridge; 580.

Day JH, Rennie PJ, Stanek W, Taymond GP (eds). 1979. *Peat Testing Manual. Technical Memo No. 125*, National Research Council of Canada: Ottawa; 194.

Dominco PA, Schwartz FW. 1998. *Physical and Chemical Hydrogeology*, 2nd edn. Wiley: New York; 506.

Fetter CW. 1999. *Contaminant Hydrogeology*, 2nd edn. Prentice Hall: Englewood Cliffs, NJ; 500.

Freeze RA, Cherry JA. 1979. *Groundwater*. Prentice Hall: Englewood Cliffs, NJ; 604.

Freeze RA, Witherspoon PA. 1967. Theoretical analysis of regional groundwater flow: 2. Effect of water-table configuration and subsurface permeability variation. *Water Resources Research* **3**: 623–634.

Glaser PH, Siegel DI, Romanowicz EA, Shen YP. 1997. Regional linkages between raised bogs and the climate, groundwater, and landscape of north-western Minnesota. *Journal of Ecology* **85**: 3–16.

Harbaugh AW, McDonald MG. 1988. *A modular three-dimensional finite-difference ground-water flow model*. US Geological Survey techniques of water-resources investigations, book 6, chap. A1. *Open-File Report 83-875*, USGS: Reston; 586 pp.

Harbaugh AW, McDonald MG. 1996. *User's Documentation for MODFLOW-96, an update to the US Geological Survey modular finite-difference ground-water flow model. Open-File Report 96-485*, USGS: Reston; 56 pp.

Hilbert DW, Roulet N, Moore T. 2000. Modelling and analysis of peatlands as dynamical systems. *Journal of Ecology* **88**: 230–242.

Hoag RS, Price JS. 1997. The effects of matrix diffusion on solute transport and retardation in undisturbed peat in laboratory columns. *Journal of Contaminant Hydrology* **28**: 193–205.

Hobbs NB. 1986. Mire morphology and the properties and behaviour of some British and foreign peats. *Quarterly Journal of Engineering Geology, London* **19**: 7–80.

Hvorslev MJ. 1951. Time lag and soil permeability in ground-water observations. *Bulletin No. 36, Waterways Experiment Station, Corps of Engineers*, US Army: Vicksburg; 50.

Ingram HAP. 1982. Size and shape in raised mire ecosystems: a geophysical model. *Nature* **297**: 300–303.

Ingram HAP. 1983. In *Hydrology, in Ecosystems of the World, Vol. 4A, Mires: Swamp, Bog, Fen and Moor, General Studies*, Gore AJP (ed.). Elsevier: New York; 67–158.

Joray M. 1942. L'Etang de la Gruyère: Etude pollenanalytique et stratigraphique de la tourbière. *Nat. Levé Géobot. de la Suisse* **25**: 1–117 (in French).

Konikow LF, Bredehoeft JD, Hassanizadeh SM. 1992. Groundwater models cannot be validated. *Advances in Water Resources* **15**: 75–83.

Landva AO, Korpijaakko EO, Pheeney PE. 1986. Notes on the original *Von Post* peat and peatland classification system. Paper presented at *Advances in Peatlands Engineering*, NRC of Canada, Ottawa, Canada, August 25–26, 1986.

Langmuir D. 1997. *Aqueous Environmental Geochemisty*. Prentice-Hall: Upper Saddle River, NJ; 600.

McNamara JP, Siegel DI, Galser PH, Beck RM. 1992. Hydrogeologic controls on peatland development in the Malloryville Wetland, New York (USA). *Journal of Hydrology* **140**: 279–296.

Mitsch WJ, Gosselink JG. 2000. *Wetlands*. 3rd edn. Wiley: New York; 920.

Ogata A, Banks RB. 1961. *A solution of the differential equation of longitudinal dispersion in porous media. Professional Paper 411-A*, USGS: Washington, DC; 7.

Oreskes N. 2000. Why predict? Historical perspectives on prediction in earth science. In *Prediction; Science, Decision Making, and the Future of Nature*. Sarewitz D, Pielke Jr RA, Byerly Jr R, (eds). Island Press: Washington, DC; 23–40.

Oreskes N, Shrader-Frechette K, Belitz K. 1994. Verification, validation, and confirmation of numerical models in the earth sciences. *Science* **263**: 641–646.

Price JS, Woo M. 1990. Studies of a subarctic coastal marsh. III. Modelling the subsurface water fluxes and chloride distribution. *Journal of Hydrology* **120**: 1–13.

Reeve AS, Siegel DI, Glaser PH. 2000. Simulating vertical flow in large peatlands. *Journal of Hydrology* **227**: 207–217.

Remenda VH, van der Kamp G, Cherry JA. 1996. Use of vertical profiles of $\delta^{18}O$ to constrain estimates of hydraulic conductivity in a thick, unfractured aquitard. *Journal of Water Resources Research* **32**: 2979–2987.

Romanowicz EA, Siegel DI, Glaser PH. 1993. Hydraulic reversals and episodic methane emissions during drought cycles in mires. *Geology* **21**: 231–234.

Roulet NT. 1990. Hydrology of a headwater basin wetland: groundwater discharge and wetland maintenance. *Hydrological Processes* **4**: 387–400.

Shotyk W. 1988. Review of the inorganic geochemistry of peats and peatland waters. *Earth Science Reviews* **25**: 95–176.

Shotyk W. 1996. Peat bog archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environmental Reviews* **4**: 149–183.

Shotyk W, Weiss D, Appleby PG, Cheburkin AK, Frei R, Gloor M, Kramers JD, Reese S, Van Der Knaap WO. 1998. History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland. *Science* **281**: 1635–1640.

Shulze-Makuch D, Carlson DA, Cherkauer DS, Malik P. 1999. Scale dependency of hydraulic conductivity in heterogeneous media. *Ground Water* **37**: 904–919.

Siegel DI. 1981. *Hydrogeologic setting of the glacial Lake Aggasiz peatlands, northern Minnesota. Water-Resources Investigations 81-24*, USGS: Reston; 34.

Siegel DI. 1983. Ground water and the evolution of patterned mires, glacial Lake Agassiz peatlands, northern Minnesota. *Journal of Ecology* **71**: 913–921.

Siegel DI 1993. Ground water hydrology. In *The Patterned Peatlands of Northern Minnesota*, Wright Jr HE (ed.). University of Minnesota Press: Minneapolis; 163–173.

Siegel DI, Reeve AS, Glaser PH, Romanowicz EA. 1995. Climate driven flushing of pore water in peatlands. *Nature* **374**: 531–533.

Steinmann P, Shotyk W. 1997a. Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two *Sphagnum* peat bogs, Jura Mountains, Switzerland. *Geochimica et Cosmochimica Acta* **61**: 1143–1163.

Steinmann P, Shotyk W. 1997b. Geochemistry, mineralogy, and geochemical mass balance on major elements in two peat bog profiles (Jura Mountains, Switzerland). *Chemical Geology*. **138**: 25–53.

Toth J. 1963. A theoretical analysis of groundwater flow in small drainage basins. *Journal of Geophysical Research* **68**: 4795–4812.

Von Post L. 1922. Sveriges Geologiska Undersøknings torvinventering och några av dess hittils vunna resultat (Geological survey of Sweden peat inventory and some preliminary results). *Svenska Mosskulturførreningens Tidsskrift* **36**: 1–27 (in Swedish).

Waddington JM, Roulet NT. 1997. Groundwater flow and dissolved carbon movement in a boreal peatland. *Journal of Hydrology* **191**: 122–138.

Winston RB. 1994. Models of the geomorphology, hydrology, and development of domed peat bodies. *GSA Bulletin* **106**: 1594–1604.

Winter TC. 1978. Numerical simulation of steady state three-dimensional groundwater flow near lakes. *Water Resources Research* **14**: 245–254.

Yamaguchi H, Ohira Y, Kogure K. 1985. Volume change characteristics of undisturbed fibrous peat. *Soils and Foundations* **25**: 119–134.

Zheng C, Bennett GD. 1995. *Applied Contaminant Transport Modeling; Theory and Practice*. Van Nostrand Reinhold: New York; 440.