

# The effects of dual porosity on transport and retardation in peat: A laboratory experiment

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Rezanezhad, F., Price, J. S. and Craig, J. R. 2012. **The effects of dual porosity on transport and retardation in peat: A laboratory experiment.** *Can. J. Soil Sci.* **92**: 723–732. Peatlands cover up to half of the local landscape in the Athabasca oil sands region, and peat materials are commonly used in reclamation. The toxicity of oil sands process-affected water (OSPW) derived from the Athabasca oil sands is related to the elevated concentration of naphthenic acids (NAs) and sodium (Na). However, the transport and retardation of solutes through peat is significantly delayed by sorption and by diffusion into immobile water contained in the peat matrix. Approximately 94% of the 43.5 mg L<sup>-1</sup> of OSPW was sorbed by 1 kg of peat. For Na ~84% sorption occurred with 382 mg L<sup>-1</sup> kg<sup>-1</sup> of peat. The sorption and desorption of NAs and Na on peat fitted linear isotherms with distribution coefficients of 6.53 and 5.74 L kg<sup>-1</sup>, respectively. Solute breakthrough tests were performed for NaCl and the retardation due to sorption (*R*) of 1.73 was estimated for Na using a two-region (mobile and immobile) non-equilibrium transport model. However, the estimated mass transfer coefficient describing solute exchange between the mobile and immobile liquid regions indicated that part of retardation is attributed to solute exchange between the mobile and immobile phases. This was evident because Cl, a conservative solute (*R* = 1, no sorption), also exhibited characteristics of dual-porosity transport. Thus, the passage of the solute front was retarded by diffusion of solute into the immobile region and by solute exchange between the mobile and immobile phases, which occurs at a rate depending on the proportion of mobile/immobile pore spaces. In this study, we showed that the complex dual-porosity structure of the peat is the important factor in attenuating solute transport where the presence of immobile phase (dead-end pores) in the system contributes to the transport and sorption mechanism of solute into this porous medium.

**Key words:** Sorption, dual-porosity, peat, oil sands process-affected water, naphthenic acid, sodium

Rezanezhad, F., Price, J. S. et Craig, J. R. 2012. **Conséquences d'une porosité double sur le transport et la rétention dans la tourbe : une expérience.** *Can. J. Soil Sci.* **92**: 723–732. Les tourbières couvrent près de la moitié du relief local dans la région des sables bitumineux de l'Athabaska et on se sert couramment de tourbe pour restaurer les sols. La toxicité de l'eau employée pour traiter les sables bitumineux dérive de la concentration élevée d'acide naphthénique (AN) et de sodium (Na). Toutefois, la sorption et la diffusion des solutés dans l'eau immobilisée dans la matrice tourbeuse en retardent significativement le transport et la rétention. Ainsi un kilo de tourbe absorbe environ 94 % des 43,5 mg d'eau de traitement par litre, et environ 84 % des 382 mg de sodium par litre. La sorption et la désorption des NA et du Na par la tourbe suivent des isothermes linéaires aux constantes de distribution de 6,53 et 5,74 l/kg, respectivement. Les auteurs ont testé la percée des solutés avec du NaCl et ont estimé la rétention attribuable à la sorption (*R*) à 1,73 pour le Na, en recourant à un modèle de transport à deux zones (mobile et immobile), sans équilibre. Cependant, le coefficient de transfert de masse estimé, qui décrit l'échange des solutés entre la phase liquide mobile et la phase liquide immobile, révèle que la rétention résulte en partie de l'échange des solutés entre les deux phases. La chose paraît évidente, car le Cl, un soluté conservateur (*R* = 1, aucune sorption), reflète lui aussi les caractéristiques d'un transport par double porosité. Ainsi, le passage du soluté est retardé par la diffusion de ce dernier dans la zone immobile et par son échange de la phase mobile à la phase immobile, dont la rapidité dépend de la proportion de pores dans chaque phase. Avec leur étude, les auteurs démontrent que la structure à double porosité complexe de la tourbe est le principal facteur qui ralentit le transport des solutés quand l'existence d'une phase immobile (attribuable aux pores fermés) dans le système modifie les mécanismes de transport et de sorption des solutés dans un tel milieu poreux.

**Mots clés:** Sorption, porosité double, tourbe, eau de traitement des sables bitumineux, acide naphthénique, sodium

Peatlands are a dominant feature of the Athabasca oil sands region, located near Fort McMurray in north-eastern Alberta, Canada, comprising up to half of the local landscape (Chee and Vitt 1989). Oil sands mining disturbs large tracts of this landscape as the vegetation-soil layer must be removed to access the oil sands beneath. Processing oil sands in the Athabasca oil sands

region produces large volumes of wet tailings material including sand, silts and clays in suspension, soluble organic chemicals, ammonia, heavy metals, salts and oil sand process-affected water (OSPW). Tailings materials

**Abbreviations:** NA, naphthenic acid; OSPW, oil sands process-affected water

that have settled in ponds, or that are otherwise used in landscape reclamation, contain OSPW that may adversely affect the ecology of the system being reclaimed, including peatlands. Many of the current pressing problems of environmental concern in this region involve transport and retardation of OSPW contaminated with sodium (Na) and naphthenic acids (NAs) (Alberta Environmental Protection 1996), since they may be at concentrations toxic to aquatic plants and animals (Apostol et al. 2004; Trites and Bayley 2005). Therefore, current attempts to reclaim the mined landscape to peat-forming systems require knowledge of the transport, fate and impact of OSPW, especially in peat systems. Given the broad spatial coverage of peatlands (Vitt and Chee 1989), use of peat in artificial soil cover during reclamation (Shurniak and Barbour 2002) and the recent thrust to reclaim post-mined landscape to fen peatlands (Price et al. 2010), it is essential to determine the fate of OSPW in peat soils and this information can be used to evaluate and improve the post-mined landscape reclamation design.

Groundwater flow in peat directly influences how effectively solutes are removed or dispersed by chemical (Hill and Siegel 1991), physical (Price and Woo 1988; Ours et al. 1997), and microbiological processes (Todorova et al. 2005). Na and NAs are readily transported through porous geological media with little attenuation beyond mechanical dispersion (Gervais and Barker 2005). However, very little information is available in the literature on their movement into peat soils. Naphthenic acids (commonly referred to as naphthenic acids but strictly speaking are deprotonated naphthenate anions) are naturally occurring surfactants that are associated with the bitumen of the oil sands. NAs have been shown to be the principal acute toxicant in the OSPW (Alberta Environmental Protection 1996) and they can be highly toxic to aquatic plants and animals, because they disrupt respiration by altering the outer living membranes (Alberta Environment 2008). Naphthenic acids have been found to be strongly adsorbed by organic matter (Janfada et al. 2006), and subject to degradation by microbial action (Herman et al. 1994). Hadwin et al. (2005) and Rezanezhad et al. (2012) found that exposure to slightly higher than naturally occurring levels of naphthenic acids shifted the microbial community structure to one that is capable of metabolizing NAs. Thus, there may be some capacity for wetlands to remove NAs from process-affected water. Toor et al. (2007) reported that this metabolization was not affected by hydraulic residence time, but could not substantiate the mechanism that explains it. As with NAs, Na is also adsorbed by peat soils (Ho and McKay 2000). However, even the transport of non-reactive anions (e.g.,  $\text{Cl}^-$ ) through peat can be retarded as a consequence of its dual-porosity structure (Hoag and Price 1997; Ours et al. 1997).

In a dual-porosity approach a “mobile region” is conceptualized as exhibiting relatively high velocity fluid

transport, while a second “immobile region” is conceptualized as exhibiting contrastingly low or zero-velocity fluid transport. Exchange of water and solute between the two regions may occur through diffusion (van Genuchten and Wierenga 1976). The total porosity of peat is approximately 90% (Boelter et al. 1968; Hobbs 1986), which includes a volume fraction of relatively large, interparticle pores that actively transmit water (mobile water phase), sometimes referred to as the “active porosity” [ $\sim 60\%$ , reported by Hoag and Price (1997) and Quinton et al. (2000)]. The remaining water is in the relatively small, closed and dead-end pores formed by the remains of plant cells and this water is immobile, referred to as “inactive porosity” (Hoag and Price 1997; Quinton et al. 2000). This complex dual porosity structure of the peat matrix affects solute transport.

Advection (through open and connected or active pores) and matrix diffusion (into closed pores) are typically assumed to be the dominant mechanisms controlling non-reactive solute transport in peat (Reeve et al. 2001). Solute passing through open and connected pores is abstracted through diffusion into closed pores (Loxham and Burghardt 1983; Price and Woo 1988; Viraraghavan and Ayyaswami 1989; Hoag and Price 1997). Adsorption of metals (e.g., Dumontet et al. 1990; Deiss et al. 2004) and organic pollutants (e.g., Zynter et al. 1989; Deiss et al. 2004) onto the peat surface also cause retardation. Furthermore, transport of contaminants through the peat may be impacted by ion exchange, ion exclusion, chemical and biological transformation, volatilization, dissolution and precipitation, biodegradation and dispersion (Tindall and Kunkel 1999). Cation exchange is also an important sorption mechanism for sodium and naphthenic acids on peat and involves electrostatic attraction between an inorganic/organic anion or cation and a charged site on the sorbent (Kyziol 2002; Janfada et al. 2006).

In this study, a series of laboratory experiments and model simulations were run to assess the effects of dual porosity on transport and retardation in peat. The main objectives were to improve our understanding of the transport, sorption mechanisms and the interaction of the NAs and Na with the peat matrix and to understand how the structure and properties of peat affects solute transport and retardation. The specific objectives were: (1) to characterize the soil water characteristic curve (water retention capacity and hydraulic conductivity relation) of a peat soil; (2) to determine the sorption and desorption properties of Na and NAs in peat; and (3) to evaluate how peat structure may govern solute movement and retardation.

## MATERIALS AND METHODS

### Physical and Hydraulic Properties of the Peat

Fen peat was obtained from the Athabasca oil sands region and shipped to the University of Waterloo for

laboratory experiments. The soil was moderately decomposed rich-fen sedge-peat (pH = 7.4), which is the dominant local peatland type in the oil sands region (Chee and Vitt 1989). The peat was highly disturbed by digging operations, consistent with its anticipated condition in a reclaimed peatlands (Price et al. 2010) currently under construction at the Suncor Energy Pilot Fen reclamation site (C. Daly, personal communication 2012). The peat was repacked in the laboratory and after the experiments the bulk density ( $\rho_b$ ) was determined gravimetrically based on an oven-dry mass basis for peat dried at 80°C for a period of a week, and the unit wet bulk volume (Gardner 1986). The reconstituted samples were assessed for their basic hydraulic properties including the hydraulic conductivity and water retention.

The hydraulic conductivity ( $K$ ) of the repacked peat was determined as a function of water content ( $\theta$ ) using the steady-state head control method (Klute and Dirksen 1986). The peat was packed in a column ( $\rho_b = 0.16 \text{ g cm}^{-3}$ ) of clear Lexan (15 cm high, 8 cm in diameter) and the hydraulic head of the water supply to the upper end of the system was controlled by a Marriott system and an outflow device was connected to the bottom of the column. Two short tensiometers (25 mm long, 5 mm in diameter, air entry value higher than 1 bar) were placed at 2 cm and 12 cm height to measure the hydraulic gradient between two points during the experiment. The whole column was placed on a balance to gravimetrically determine the mean water content of the peat, based on its volume and its dry weight (Gardner 1986). In this method, a steady state flow of the liquid phase was established in a soil sample at a constant water content and pressure. The volumetric flux density and the hydraulic gradient were measured, and the hydraulic conductivity was calculated from the flux density/gradient ratio (Darcy's law). The soil sample was progressively desaturated by elevating the gas-phase pressure in the sample above atmospheric pressure, using compressed air and a pressure regulator.

Water retention tests to determine the relationship between water content ( $\theta$ ) and pressure head ( $h$ ), used a pressure-plate apparatus with lower boundary porous ceramic plate (>60 kPa air entry pressure). One 6-cm diam., 3-cm high saturated peat sample of known mass ( $\rho_b = 0.157 \text{ g cm}^{-3}$ ) was placed in the apparatus on top of the porous plate. The sample was progressively desaturated by elevating the gas-phase pressure to a port on the side of the cell, ranging from 10 mbar to 2300 mbar. The moisture content was calculated using the measured volume of water removed from the sample at each increasing pressure step by weighing the sample at the end of each applied pressure.

The volume of the peat sample decreased continuously due to shrinkage during the hydraulic conductivity test as the sample desaturated. Under the high-pressure conditions, a small horizontal fracture in the peat developed caused by shear against the upper tensiometer cup. In the

water retention test, peat volume changes due to soil shrinkage were calculated from measurements of the sample diameter and height, and used in the determination of the sample volume for the water content measurements. Most of the volume changes occurred at high pressure conditions and the percentage of volume changes were ~6% at 400 mbar, ~13% at 1200–1500 mbar and ~16% at 2300 mbar.

### Sorption Batch Tests

Batch tests (Freeze and Cherry 1979; Pignatello 2000) were used to determine the equilibrium times for sorption of Na and NAs in the peat. A known mass of peat (~120 g) with initial water content of  $0.45 \text{ cm}^3 \text{ cm}^{-3}$  was placed into a 200-mL glass vials (sealed with a cap) with 120 mL of diluted OSPW (70% of original OSPW collected from Suncor Energy oil sands operation tailings ponds and 30% deionized water, representing the range of NAs and Na present in many reclaimed wetlands (C. Daly, personal communication, 2009) with initial concentration of  $382 \text{ mg L}^{-1}$  of Na and  $43.5 \text{ mg L}^{-1}$  of NAs. The samples were agitated on a constant mixer for 24 h. The solute was extracted from the paste by suction lysimeter after 1 h, 3 h, 6 h, 18 h, 24 h, 48 h, 3 d, 7 d and 14 d. The same procedures were used for six other samples with different concentrations as 100, 55, 30, 15, 5 and 1% of OSPW.

To determine desorption of Na and NAs, inverse batch tests were performed. A known mass of peat (~120 g) and 120 mL of 65% OSPW with initial Na and NAs of  $344.1 \text{ mg L}^{-1}$  and  $33.9 \text{ mg L}^{-1}$ , respectively, were mixed into a 200-mL glass vial (sealed with a cap). The initial sampling was done after 24 h using a suction lysimeter to remove ~100 mL of solution for analysis, and then 100 mL of deionized water was added back to the container. This was repeated in eight steps of dilution and sampling. Both sorption and desorption depend on the initial moisture content of the peat. After the batch experiments were completed, the peats were dried at 80°C for a period of a week and the measured concentrations were adjusted on the basis of its oven-dry weight.

### Breakthrough Experiment

To determine the transport characteristics of Na in the peat soil, a breakthrough experiment in saturated peat was performed by introducing NaCl ( $1000 \text{ mg L}^{-1}$ ) in a column (6 cm height, 5.5 cm diameter) where the peat sample (83 g) was placed between two porous ceramic pressure-plates at the upper and lower ends of the column ( $\rho_b = 0.16 \text{ g cm}^{-3}$ ). The solute (NaCl) was introduced as a step-input of known initial concentration ( $C_i$ ) at a steady-state constant rate flux using a Marriott system (McCarthy 1934). The pore water velocity,  $v_m$ , ( $\text{L T}^{-1}$ ) was calculated using:

$$v_m = \frac{Q}{A\theta_m} \quad (1)$$

where  $Q$  is the volumetric discharge from the column ( $L^3 T^{-1}$ ),  $A$  is the cross-sectional area of the column ( $L^2$ ), and  $\theta_m$  is the mobile region volumetric water content (estimated from model calibration results). Na and Cl concentrations of effluent ( $C$ ) were measured frequently during the test. Solute breakthrough curves were plotted for Na and Cl in terms of relative concentration (effluent concentration/input solution concentration or  $C/C_i$ ) versus the number of pore volumes. Breakthrough curves were also generated using the testing apparatus without a peat sample (the "blank"), to determine the dispersion and delay in solute breakthrough caused by the "dead" spaces in the apparatus [inflow tubing ( $\sim 5\%$  of column volume) and pressure plates].

Traditionally, the correction for the extra-column effects is performed by conducting experiments where the column is replaced by a zero-dead-volume blank and subtracting this response from the composite breakthrough curve. This procedure (point-by-point) was used to eliminate the extra-column effects and obtain the true response of the adsorption column in previous literatures (e.g., Farooq et al. 2002; Guntuka 2006). In this study, once the time was measured for the blank apparatus, this blank response was then subtracted point-by-point from the composite response to account for extra-column contributions (Gritti et al. 2006; Rajendran et al. 2008). Since NAs analysis requires greater than 100 mL of solute and this would have unacceptably disturbed the experiment, only Na was monitored during the breakthrough experiment.

### Analytical Methods, Analysis of Water Samples

All water samples were analyzed for total NAs using Fourier Transform Infrared spectroscopy developed by Jivraj et al. (1995) and for total Na using Perkin Elmer model 3100 atomic absorption spectroscopy. Naphthenic acids standards (in methylene chloride) were prepared using Merrichem Refined NAs and a Perkin Elmer Spectrum RX 1 FT-IR System was used to obtain the spectrum for NAs standards and samples with the method detection limit  $2.5 \text{ mg L}^{-1}$ . The atomic absorption spectroscopy was calibrated using the standards 25, 50, 100 and  $500 \text{ mg L}^{-1}$  Na with a method detection limit of  $1 \text{ mg L}^{-1}$ . Chloride (Cl) concentrations were measured using an Orion Chloride Combination Electrode (VWR Cat. No. 14002-786). Chloride concentrations were calculated from a calibration curve constructed using standards of known concentration. Samples and standards were first diluted with 2% ionic strength adjusting solution ( $5 \text{ M Na NO}_3$ ).

### Model Simulations

The measured water retention  $\theta(h)$  and hydraulic conductivity  $K(\theta)$  peat characteristic curves were fitted using the RETC code (van Genuchten et al. 1991) with dual-porosity Mualem-van Genuchten models. RETC was run with the fitting parameters ( $\theta_r$ ,  $\theta_s$ ,  $K_s$ ,

$a$ ,  $n$ ,  $\Omega_2$ ,  $a_2$ ,  $n_2$ ); simultaneously fitting hydraulic conductivity and water retention data. The subscripts  $r$  and  $s$  refer to residual and saturated values,  $\Omega$  is the weighting factor (see Köhne et al. 2004) for the primary porosity,  $a$  and  $n$  are fitted parameters that determine the shape of the curves and  $\Omega_2$ ,  $a_2$  and  $n_2$  are the weighting factor and fitted parameters for the secondary (closed pore) porosity of the dual-porosity peat.

For fitting the breakthrough curves of observed Na and Cl effluent concentrations from the column experiment, the computer code CXTFIT (Toride et al. 1995) was used. This code uses a non-linear least squares method to fit the parameters of analytical solutions to the one-dimensional convection-dispersion equation. The options include one or two site sorption functions and two-region fractions of the pore space (mobile/immobile). Here, the CXTFIT code was used to estimate the transport properties of Athabasca peat by fitting the Na and Cl breakthrough experiment data. The primary intention was to determine the degree of influence of the secondary porosity through exchange of solute between mobile and immobile regions. This model assumes that the liquid phase is partitioned into mobile (flowing) and immobile (stagnant) regions. The assumptions lead to the following governing equations for aqueous concentration in the primary (mobile) and secondary (immobile) pore space (van Genuchten and Wagenet 1989):

$$\left(1 + \frac{f\rho_b K_{ads}}{\theta_m}\right) \frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial x^2} - v_m \frac{\partial c_m}{\partial x} - \frac{\alpha}{\theta_m} (c_m - c_{im}) - \left(\mu_{1,m} + \frac{f\rho_b K_{ads} \mu_{s,m}}{\theta_m}\right) c_m \quad (2)$$

$$\left(1 + \frac{(1-f)\rho_b K_{ads}}{\theta_{im}}\right) \frac{\partial c_{im}}{\partial t} = \frac{\alpha}{\theta_m} (c_m - c_{im}) - \left(\mu_{1,m} + \frac{(1-f)\rho_b K_{ads} \mu_{s,im}}{\theta_{im}}\right) c_{im} \quad (3)$$

where the subscripts  $m$  and  $im$  refer to the mobile and immobile liquid regions, respectively;  $x$  is distance down the column (L);  $t$  is time (T);  $c$  is concentration of solute ( $M L^{-3}$ );  $D_m$  is the hydrodynamic coefficient of dispersion of the solute in the soil solution in the mobile region ( $L^2 T^{-1}$ );  $K_{ads}$  is the distribution coefficient of the solute between the solid and the liquid phases ( $L^3 M^{-1}$ );  $\rho_b$  is the bulk density ( $M L^{-3}$ );  $\theta_m$  is the volumetric water content of the soil in the mobile region;  $\kappa$  is the volumetric water content in the mobile and immobile regions ( $\theta = \theta_m + \theta_{im}$ );  $v_m$  is the velocity of water through pores in the mobile region ( $LT^{-1}$ ;  $v_m = v\theta/\theta_m$ );  $f$  is the fraction of adsorption sites that equilibrate with the mobile liquid phase;  $\alpha$  is the first-order mass transfer coefficient ( $T^{-1}$ ) governing the rate of solute exchange between the mobile and immobile liquid regions; and  $\mu_{1,m}$ ,  $\mu_{1,im}$ ,  $\mu_{s,m}$ ,  $\mu_{s,im}$  are the first-order decay coefficients for the mobile and immobile liquid

and solid phases ( $T^{-1}$ ), respectively. Note that the immobile and mobile pore space in the transport model may not necessarily correspond to the dual porosity regions considered in the characteristic curves of the hydraulic model. The boundary conditions for the problem are a constant mass influx of  $v_m c_i$  at  $x=0$  (where  $c_i$  is the constant concentration of solute introduced onto the top of the column) and a zero gradient in concentration at infinity, i.e.,

$$\left( v_m c_m - D_m \frac{\partial c_m}{\partial x} \right) \Big|_{x=0} = v_m c_i \quad (4)$$

$$\frac{\partial c_m}{\partial x} \Big|_{x=\infty} = 0 \quad (5)$$

A uniform concentration distribution of  $c_m=0$  is applied as the initial condition. Equations 2 and 3 may be expressed in terms of dimensionless quantities, for a solute with negligible degradation ( $\mu_{l,m} = \mu_{l,im} = \mu_{s,m} = \mu_{s,im} = 0$ ), in the form:

$$\beta R \frac{\partial c_m}{\partial \tau} = \frac{1}{P} \frac{\partial^2 c_m}{\partial X^2} - \frac{\partial c_m}{\partial X} - w(c_m - c_{im}) \quad (6)$$

$$(1 - \beta)R \frac{\partial c_{im}}{\partial \tau} = w(c_m - c_{im}) \quad (7)$$

where the dimensionless variables  $X$  (distance),  $\tau$  (pore volume),  $P$  (Peclet number),  $R$  (retardation due to sorption),  $\beta$  (proportion of the pore space in the mobile phase), and  $w$  (dimensionless mass transfer (exchange) coefficient governing rate of solute exchange between the mobile and immobile liquid regions) are defined as:

$$X = \frac{x}{L}, \quad (8a)$$

$$\tau = \frac{vt}{L}, \quad (8b)$$

$$P = \frac{v_m L}{D_m}, \quad (8c)$$

$$R = 1 + \frac{\rho_b K_{ads}}{\theta}, \quad (8d)$$

$$\beta = \frac{\theta_m + f \rho_b K_{ads}}{\theta + \rho_b K_{ads}}, \quad (8e)$$

$$W = \frac{\alpha L}{\theta_m v_m}. \quad (8f)$$

The assumed initial and boundary conditions are, in dimensionless form:

$$c_m(X, 0) = c_{im}(X, 0) = 0 \text{ for all } X \quad (9a)$$

$$\left( P c_m - \frac{\partial c_m}{\partial X} \right) \Big|_{X=0} = P c_i \text{ for all } \tau \quad (9b)$$

$$\frac{\partial c_m}{\partial X} \Big|_{X=\infty} = 0 \text{ for all } \tau \quad (9c)$$

The analytical solution to above equations is given by van Genuchten and Wierenga (1976) and van Genuchten and Wagenet (1989).

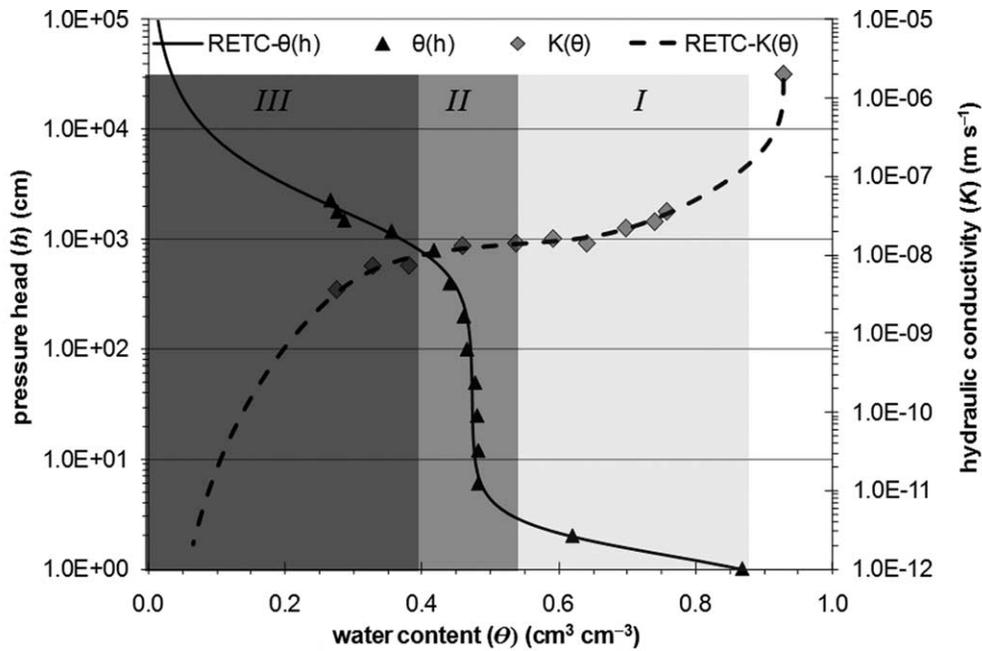
In this study, CXTFIT was used to estimate the four model parameters  $P$ ,  $R$ ,  $\beta$ ,  $w$  by fitting the breakthrough data (varied until the best fit between the observed and predicted was obtained) using a nonlinear least square optimization approach described in van Genuchten and Wagenet (1989) and Toride et al. (1995).

## RESULTS AND INTERPRETATION

### Physical and Hydraulic Properties of the Peat

Both  $\theta$  and  $K$  had a rapid initial decline (air entry pressure near zero) from saturation (Fig. 1), and levelled out between 0.45 and 0.5  $\text{cm}^3 \text{cm}^{-3}$  in the typical range of pressure expected for field conditions (e.g., Price and Whitehead 2001). Under greater suction pressures, the sample experienced a secondary drop in both  $\theta$  and  $K$ . The initial reduction in unsaturated hydraulic conductivity during drainage reflects the increase of air-filled pores in the sample that contribute to the obstruction of flow (Rezanezhad et al. 2009). The secondary drop is interpreted as drainage of closed and dead-end pores.

The secondary drop of the water retention curve shown in Fig. 1 suggests that fen peat is a dual-porosity porous medium (c.f. Hayward and Clymo 1982). The RETC code was used to fit the dual porosity Mualem-van Genuchten model (van Genuchten et al. 1991) to the measured characteristic curves. The residual and saturated water contents were fixed at 0.4 and 0.86  $\text{cm}^3 \text{cm}^{-3}$ , respectively, and the saturated hydraulic conductivity ( $K_s$ ) was fixed at  $1.98 \times 10^{-6} \text{ m h}^{-1}$ , which was directly interpreted from the drainage data. The remaining Mualem-Van Genuchten parameters estimated by RETC were  $a=0.5$ ,  $n=1.5$ ,  $\Omega_2=0.5$ ,  $a_2=1$ ,  $n_2=1.5$  (parameters were calibrated manually). The RETC-derived  $\theta(h)$  and  $K(\theta)$  curves fit the data well with 95% confidence intervals (see Fig. 1). With the dual porosity model fitted to the observed data, three hypotheses were assumed for the pore size distributions in peat samples (based on the model output; see below). These guiding hypotheses differentiate pore size distributions as: (I) open and connected macropores where most solute transport probably occurs, (II) closed or partially closed cell remains with more or less intact walls and (III) hyaline cells and dead-end or isolated pore spaces where solute transport is attenuated and retarded by diffusion into these spaces. The residual water content of 0.4  $\text{cm}^3 \text{cm}^{-3}$  was a surprise result as there was a significant fraction of water stored in the



I: open and connected II: closed or partially closed pores III: dead-end or isolated pores

**Fig. 1.** Unsaturated hydraulic conductivity versus water content and the water retention curves of the peat samples from measured data. RETC curves were estimated with RETC code using the dual porosity and Mualem-van Genuchten model parameters; simultaneous fitting of hydraulic conductivity  $K(\theta)$  and water retention  $\theta(h)$  data.

partially open pores that will empty at a lower pressure and may participate in the flow and transport.

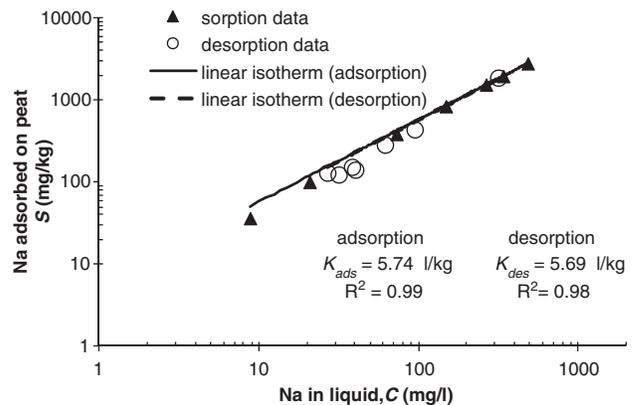
### Sorption Batch Tests

In addition to the hydraulic characteristics described above, the mobility of solutes in peat can be influenced by sorption. The batch tests showed rapid and significant sorption of Na and NAs to the peat. After adding OSPW, stable concentrations of Na and NAs were achieved within 1 h with no discernible trend and no significant difference occurring thereafter for the 2-wk duration of the experiment (dynamic results not shown). The amount of Na and NAs sorbed at equilibrium depended on the mass of peat available per volume of solution and solution concentration. The sorption rates computed from batch tests showed that 308 mg of Na in a  $382 \text{ mg L}^{-1}$  Na OSPW solution were sorbed in 1 kg of peat (80%). By comparison, NA sorption on peat was 41 of  $43.5 \text{ mg L}^{-1} \text{ kg}^{-1}$  peat in OSPW (94%). The amount of Na and NAs sorbed also depends on the concentration of the solution. It was found that the sorption behavior of Na and NAs (in Figs. 2 and 3) were well represented by a linear isotherm (e.g., Freeze and Cherry 1979):

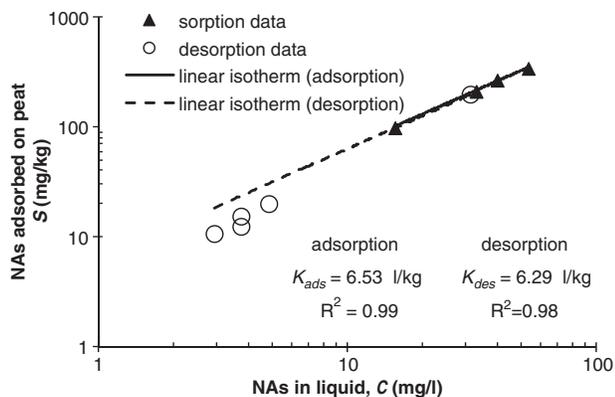
$$S = K_{ads} C \quad (10)$$

where  $S$  is the amount of a solute sorbed onto the solid phase ( $\text{mg kg}^{-1}$ ),  $C$  is the concentration of the solute in the aqueous phase ( $\text{mg L}^{-1}$ ), and  $K_{ads}$  is the sorption

distribution coefficient ( $\text{l kg}^{-1}$ ). The linear isotherms for Na and NAs showed an excellent fit to the measured sorption data ( $R^2 = 0.99$ ). These isotherms quantify the influence of liquid phase concentration on the extent of sorption on peat. As the distribution coefficient is related primarily to the capacity of the sorbent for the sorbate, higher  $K_{ads}$  for NAs than Na, 6.53 and  $5.74 \text{ l kg}^{-1}$ , respectively, in Figs. 2 and 3, shows a stronger sorption of the organic compound NAs to peat than Na, resulting in a higher percentage of NA sorption.



**Fig. 2.** Na sorption and desorption isotherms. The Na sorption on peat and desorption in the presence of fresh water are well represented by a linear relationship between sorbed Na ( $S$ ) and the aqueous Na ( $C$ ).



**Fig. 3.** Equilibrium sorption behaviour of NAs to peat generated from batch experiments. As with Na, NAs is also sorbed on peat and desorbed in the presence of fresh water with a linear partitioning of solutes between liquid phase ( $C$ ) and solid phase ( $S$ ).

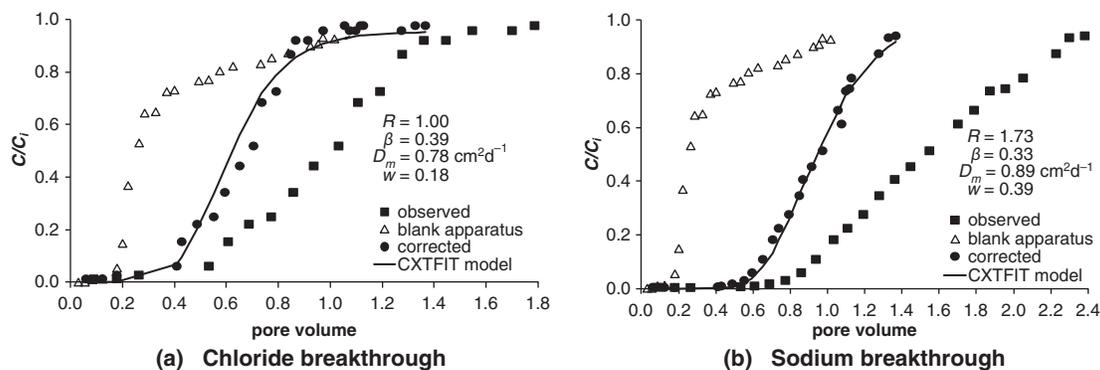
The desorption results of Na and NAs, tested by the inverse batch experiments are also depicted in Figs. 2 and 3. The Na and NAs sorbed on peat sample was removed after steps of dilution with deionized water. Desorption results were also fitted well by the same linear isotherm.

### Breakthrough Experiment

The measured, blank, corrected and modelled two-region non-equilibrium transport breakthrough curves for chloride (Cl) and sodium (Na) normalized in terms of inflow concentration ( $C_i$ ) are shown in Fig. 4. Breakthrough curves are expressed in terms of pore volumes expunged, where the number of pore volumes of water passed through the medium in time  $t$  is equal to the volume  $Qt$  of water moved through the medium divided by the volume of water-filled pores  $(\theta_m + \theta_{im})V$  (Kirkham and Powers 1972). To evaluate the solute breakthrough for the sample, the effect of the blank system had to be subtracted out. The blank had a discharge rate of  $0.01 \text{ mL s}^{-1}$  ( $864 \text{ mL d}^{-1}$ ) and it took

approximately 13 min for a trace of the solute to be detected, and  $\sim 4 \text{ h}$  to reach  $C/C_i = 98\%$  (i.e., with no sample in it). Since the discharge rate for the blank apparatus and subsequent experiment (i.e., where sample was included) were different, the times for each measured solute concentration of the blank apparatus were normalized to the flow rate observed when the sample was present, by multiplying the times for the blank system by the ratio of blank discharge/sample discharge. The observed breakthrough data for Na and Cl through peat were then corrected by subtracting the observed time of detectable solute from time of blank apparatus at equivalent  $C/C_i$  (Fig. 4a, b).

For the conservative solute Cl, the centre of the solute front ( $C/C_i = 0.5$ ) was observed to occur at  $\sim 0.7$  pore volumes (Fig. 4a). This is not uncommon for relatively small test columns with reasonable Peclet numbers. Using a nonreactive solute, Scotter (1978) found that theoretical breakthrough curves, in finite domains and in the presence of large channels, indicated that a considerable amount of solute appeared in the effluent before one pore volume had leached through. The explanation for this is that when the mobile water region contains large pores, they fill with solute faster, so effluent appears at an earlier breakthrough time (less than one pore volume) and significant tailing occurs due to diffusion of solute into regions of immobile (stagnant) water (numerous pore volumes must pass before  $C/C_i = 1$ ). Therefore, the concept is that while the solute in the mobile phase (preferential paths) is transported via advection and dispersion due to water flow, solute is exchanged to/from the immobile via diffusion processes that are typically rate-limited. Thus, the dual-porosity nature of the peat affects the timing and shape of the breakthrough curve. For transport of reactive solutes such as Na, sorption of the solute to the solid phase is often the driving force that affects curve shape. As a result, the tracer does not reach the end of the column until sorption sites are filled, meaning a later breakthrough curve (shift to the right), as seen in Fig. 4b. This delay in the breakthrough curve means there is no more



**Fig. 4.** Chloride and sodium breakthrough curves where corrected data are fitted using the two-region non-equilibrium transport model in CXTFIT.

retardation for the quantity of tracer above the sorption capacity of the porous medium.

Transport parameters for individual corrected breakthrough curves of Na and Cl were determined using the two-region non-equilibrium transport model in CXTFIT. In the case of Cl, sorption and degradation are negligible, so the retardation factor,  $R$ , was fixed at 1.0 (i.e.,  $K_{ads}=0$ ), and the decay rates  $\mu_m$  and  $\mu_{im}$  were set to zero. The parameters  $P$ ,  $\beta$  and  $w$  were then optimised using CXTFIT's built in automatic calibration routine for the two-region non-equilibrium model of chloride transport governed by Eqs. 6 and 7. Here, the Peclet number,  $P$ , characterizes the relative impacts of advective and diffusive/dispersive transport. The parameters  $\beta$  and  $w$  characterize the influence of the secondary porosity in transport (e.g., in a single porosity medium,  $\beta=1$  and  $w=0$ ). The optimal parameter values for the Cl breakthrough curve are shown in Fig. 4a, leading to a coefficient of determination ( $R^2$ ) of 0.95 describing the fit of the model to observed data. The non-linear parameter estimation routine is also able to report 95% confidence intervals in the estimated parameters, here reported as ranges. The mobile region volumetric water content ( $\theta_m$ ) was calculated from the optimized  $\beta$  value ( $\beta=0.39\pm 0.030$  for Cl) and Eq. 8e ( $\beta=\theta_m/\theta$ , when  $K_{ads}=0$  for Cl) as  $0.33\pm 0.025\text{ cm}^3\text{ cm}^{-3}$ . Therefore, the immobile region volumetric water content ( $\theta_{im}$ ) can be estimated as  $\theta_{im}=\theta-\theta_m=0.53\pm 0.039\text{ cm}^3\text{ cm}^{-3}$ . This immobile water content,  $\theta_{im}$ , is higher than the estimated residual water content of the sample ( $\theta_r=0.4$ ), implying that there is a significant fraction of water ( $\theta_r-\theta_{im}=0.13\text{ cm}^3\text{ cm}^{-3}$ ) that is hydraulically active (i.e., will drain at standard pressures), but does not actively participate in advection through the peat. This leads to a conceptual model of three distinct pore spaces within the medium: an inactive zone of closed pores (zone I) that is hydraulically inactive (below the primary residual water content) and only participates in transport through diffusion. A second zone of residual dead end pores, zone II, will readily drain from the medium, but still does not act as an active pathway for advective transport, and also participates in transport only as an immobile storage area for solute. Zone III, lastly, is the active porosity consisting of open, connected pores, which provide channels for advective transport, at least at saturation. These zones are shown in Fig. 1 as interpreted from CXTFIT model output.

For Na, degradation was also assumed to be negligible, so  $\mu_m$  and  $\mu_{im}$  were fixed to zero, and  $P$ ,  $R$ ,  $\beta$  and  $w$  parameters were varied until the best fit between the observed and predicted concentration was obtained (see the parameters shown in Fig. 4b). The coefficient of determination for the regression of observed vs. predicted was  $R^2=0.98$ .

After fitting the corrected breakthrough curve data using CXTFIT, the dimensionless rate of solute exchange between the mobile and immobile liquid regions

( $w$ ) was estimated as  $0.18\pm 0.02$  and  $0.39\pm 0.07$  for Cl and Na, respectively, and the retardation due to sorption ( $R$ ) was estimated as  $1.73\pm 0.11$  for Na (Fig. 4a, b). These parameters suggest that the transport of NaCl was delayed partly due to sorption to the solid phase (only for Na) and partly due to solute exchange between the mobile and immobile phases [shown by the term  $w(c_m-c_{im})$  in Eqs. 6 and 5] for both Na and Cl. Hoag and Price (1997) and Ours et al. (1997) reported that peat soils are a dual-porosity medium and the retardation is attributed to diffusion of the flowing solute into the closed and dead-end pores of peat and defined it as matrix diffusion. It appears that this mechanism is also at play here; the observed delay of Na and Cl is likely controlled by both sorption to the organic matter (Na) and diffusion of solute into the closed and dead-end pores of the immobile region by solute exchange from the mobile region (Na and Cl).

The pore water velocity ( $v_m$ ) of  $1.32\text{ cm d}^{-1}$  was calculated using Eq. 1 based on the sample discharge rate ( $Q$ ) of  $10.4\text{ mL d}^{-1}$ , cross-sectional area ( $A$ ) of  $23.7\text{ cm}^2$ , and the mobile region volumetric water content ( $\theta_m$ ) of  $\sim 0.33\text{ cm}^3\text{ cm}^{-3}$ . The fitted values of Peclet number were  $10.1\pm 0.31$  and  $8.9\pm 0.24$  for Cl and Na, respectively. Because the two Peclet numbers were independently determined from the unique Na and Cl breakthrough curves, the difference in value is likely a combination of data error, issues with the subtraction of the blank, and some interdependency between the fit parameters. However, the fact that the ranges of predicted fit values overlap suggests that the corresponding dispersion coefficient is reasonably well approximated. The Peclet number of roughly 10 in this relatively short column is likely the cause of the early breakthrough of Cl in less than one pore volume, i.e., there is some impact of both preferential flow and boundary effects.

## CONCLUSIONS

This research examined the transport and sorption characteristics of sodium, and the sorption characteristics of naphthenic acids in a peat soil. The complex dual-porosity structure of the peat was found to be an important factor in attenuating solute transport where the presence of an immobile phase (partially closed and dead-end pores) in the system contributes to the delayed transport of solute through this type of porous media. The findings are useful for understanding and predicting solute transport and retardation in peat.

The RETC software was used to fit the water retention and hydraulic conductivity experimental data using dual-porosity and Mualem-van Genuchten models, and the RETC curves fitted the data well. Batch tests showed no significant difference for either Na or NAs sorption after 1 h versus 2 wk, which thus were concluded to participate in near equilibrium sorption to the peat soil. The sorbed Na and NAs also depended on the concentration of the solution, where the lower initial

concentrations resulted in lower sorption by a proportion equivalent to the slope of the linear isotherm. NAs and Na sorbed on peat were desorbed in the presence of fresh water at a similar rate. The two-region (mobile and immobile) non-equilibrium transport model parameters estimation of Na and Cl effluent concentrations from breakthrough tests showed that solute retardation occurred. This retardation was partly attributed to sorption to the organic matter and partly to diffusion of the flowing solute from the mobile water region to closed and dead-end pore spaces in the peat matrix. Thus, the transport nonequilibrium is caused by slow diffusion between mobile and immobile water regions and the presence of solute in an immobile region depends on solute diffusion from the mobile to the immobile region.

The information gathered from these laboratory experiments will be useful for understanding the transport of contaminants in constructed or natural peatland settings. This study suggests that the complex dual-porosity structure of peat is an important factor that attenuates transport of solutes in groundwater.

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**Alberta Environment. 2008.** Guideline for wetland establishment on reclaimed oil sands leases. 2nd ed. Prepared by M. L. Harris of Lorax Environmental for the Wetlands and Aquatics Subgroup of the Reclamation Working Group of the Cumulative Environmental Management Association, Fort McMurray, AB. December 2007.

**Alberta Environmental Protection. 1996.** Fort McMurray–Athabasca subregional integrated resource plan. Alberta Environmental Protection, Edmonton, AB.

**Apostol, K. G., Zwiazek, J. J. and MacKinnon, M. D. 2004.** Naphthenic acids affect plant water conductance but do not alter shoot  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations in jack pine (*Pinus banksiana*) seedlings. *Plant Soil* **263**: 183–190.

**Boelter, D. H. 1968.** Important physical properties of peat materials. Proceedings of the 3rd International Peat Congress, Quebec, QC. pp. 150–154.

**Chee, W. L. and Vitt, D. H. 1989.** The vegetation, surface water chemistry and peat chemistry of moderate-rich fens in central Alberta, Canada. *Wetlands* **9**: 227–261.

**Deiss, J., Byers, C., Clover, D., Amore, D., Love, A., Menzies, M. A., Powell, J. and Walter, T. M. 2004.** Transport of lead and diesel fuel through a peat soil near Juneau, AK: a pilot study. *J. Contam. Hydrol.* **74**: 1–18.

**Dumontet, S., Levesque, M. and Mathur, S. P. 1990.** Limited downward migration of pollutant metals (Cu, Zn, Ni, and Pb) in acidic virgin peat soils near a smelter. *Water Air Soil Pollut.* **49**: 329–342.

**Farooq, S., Qinglin, H. and Karimi, I. 2002.** Identification of transport mechanism in adsorbent micropores from column dynamics. *Ind. Eng. Chem. Res.* **41**: 1098–1106.

**Freeze, R. A. and Cherry, J. A. 1979.** *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ. 604 pp.

**Gardner, W. H. 1986.** Water content. Pages 493–544 in A. Klute, ed. *Methods of soil analysis: Physical and mineralogical methods*. Agronomy Series 9 (Part 1). SSSA, Madison, WI.

**Gervais, F. and Barker, J. 2005.** Fate and transport of naphthenic acids in groundwater. Bringing groundwater quality to the watershed scale (Proc. GQ 2004, 4th Internat. Groundwater Quality Conference). International Association of Hydrological Sciences, Rennes, France. Publ. 297, pp. 305–310.

**Gritti, F., Felinger, A. and Guiochon, G. 2006.** Influence of the errors made in the measurement of the extra-column volume on the accuracies of estimates of the column efficiency and the mass transfer kinetics parameters. *J. Chromatogr. A* **1136**: 57–72.

**Guntuka, S. 2006.** Perovskite-based adsorption process for high temperature gas separation. Master's thesis, National University of Singapore.

**Hadwin, A. M., Del Rio, L. F., Pinto, L. J., Painter, M., Routledge, R. and Moore, M. M. 2005.** Microbial communities in wetlands of the Athabasca oil sands: genetic and metabolic characterization. *FEMS Microbiol. Ecol.* **55**: 68–78.

**Hayward, P. M. and Clymo, R. S. 1982.** Profiles of water content and pore size in *Sphagnum* peat, and their relation to peat bog ecology. *Proc. R. Soc. Lond. Series B* **215**: 299–325.

**Herman, D. C., Fedorak, P. M., MacKinnon, M. and Costerton, J. W. 1994.** Biodegradation of naphthenic acids by microbial populations indigenous to oil sands tailings. *Can. J. Microbiol.* **40**: 467–477.

**Hill, B. M. and Siegel, D. I. 1991.** Groundwater flow and the metal content of peat. *J. Hydrol.* **123**: 211–224.

**Ho, Y. S. and McKay, G. 2000.** The kinetics of sorption of divalent metal ions onto *Sphagnum* moss peat. *Water Res.* **34**: 735–742.

**Hoag, R. S. and Price, J. S. 1997.** The effects of matrix diffusion on solute transport and retardation in undisturbed peat in laboratory columns. *J. Contam. Hydrol.* **28**: 193–205.

**Hobbs, N. B. 1986.** Mire morphology and the properties and behaviour of some British and foreign peats. *Q. J. Eng. Geol.* **19**: 7–80.

**Janfada, A., Headley, J. V., Peru, K. M. and Barbour, S. L. 2006.** A laboratory evaluation of the sorption of oil sands naphthenic acids on organic rich soils. *J. Environ. Sci. Health Part A* **41**: 985–997.

**Jivraj, M. N., MacKinnon, M. and Fung, B. 1995.** Naphthenic acids extraction and quantitative analyses with FT-IR

- spectroscopy. Syncrude analytical methods manual. 4th ed. Syncrude Canada Ltd. Research Department, Edmonton, AB.
- Kirkham, D. and Powers, W. L. 1972.** Advanced soil physics. Wiley-Interscience, New York, NY.
- Klute, A. and Dirksen, C. 1986.** Hydraulic conductivity and diffusivity: laboratory methods. Pages 687–734 in A. Klute, ed. Methods of soil analysis. SSSA, Madison, WI.
- Köhne, J. M., Mohanty, B. P., Simunek, J. and Gerke, H. H. 2004.** Numerical evaluation of a second-order water transfer term for variably saturated dual-permeability models. Water Resour. Res. **40**: W07409.
- Kyziol, J. 2002.** Effect of physical properties and cation exchange capacity on sorption of heavy metals onto peats. Pol. J. Environ. Stud. **11**: 713–718.
- Loxham, M. and Burghardt, M. 1983.** Peat as a barrier to the spread of micro-contaminants to the groundwater. Pages 337–349 in C. H. Fuschman and S. A. Spigarelli, eds. Proc. Int. Symp. on Peat Utilization, Bemidji State University, Bemidji, MN.
- McCarthy, E. L. 1934.** Mariotte's bottle. Science **80**: 100.
- Ours, D. P., Siegel, D. I. and Glaser, P. H. 1997.** Chemical dilation and the dual porosity of humified bog peat. J. Hydrol. **196**: 348–360.
- Pignatello, J. J. 2000.** The measurement and interpretation of sorption and desorption rates for organic compounds in soil media. Adv. Agron. **69**: 1–73.
- Price, J. S. and Whitehead, G. 2001.** Developing hydrological thresholds for *Sphagnum* recolonization on an abandoned cutover bog. Wetlands **21**: 32–42.
- Price, J. S., McLaren, R. G. and Rudolph, D. L. 2010.** Landscape restoration after oil sands mining: conceptual design and hydrological modelling for fen reconstruction. Int. J. Mining Reclamat. Environ. **24**: 109–123.
- Price, J. S. and Woo, M. K. 1988.** Wetlands as waste repositories? Solute transport in peat. Proc. Nat. Student Conference on Northern Studies, 1986 Nov. 18–19, Association of Canadian Universities for Northern Studies, Ottawa, ON. pp. 392–395.
- Quinton, W. L., Gray, D. M. and Marsh, P. 2000.** Subsurface drainage from hummock-covered hillslope in the Arctic tundra. J. Hydrol. **237**: 113–125.
- Rajendran, A., Kariwala, V. and Farooq, S. 2008.** Correction procedures for extra-column effects in dynamic column breakthrough experiments. Chem. Eng. Sci. **63**: 2696–2706.
- Reeve, A. S., Siegel, D. I. and Glaser, P. H. 2001.** Simulating dispersive mixing in large peatlands. J. Hydrol. **242**: 103–114.
- Rezanezhad, F., Quinton, W. L., Price, J. S., Elrick, D., Elliot, T. and Heck, R. 2009.** Examining the effect of pore size distribution and shape on flow through unsaturated peat using computed tomography. Hydrol. Earth Syst. Sci. **13**: 1993–2002.
- Rezanezhad, F., Andersen, R., Pouliot, R., Price, J. S., Rochefort, L. and Graf, M. D. 2012.** How fen vegetation structure affects the transport of oil sands process-affected waters. Wetlands **32**: 557–570.
- Scotter, D. R. 1978.** Preferential solute movement through larger soil voids. I. Some computations using simple theory. Aust. J. Soil Res. **16**: 257.
- Shurniak, R. E. and Barbour, S. L. 2002.** Modeling of water movement within reclamation covers on oilsands mining overburden piles. American Society of Mining and Reclamation, 3134 Montavesta Rd., Lexington KY.
- Tindal, J. A. and Kunkel, J. R. 1999.** Unsaturated zone hydrology for scientists and engineers. Prentice Hall, Upper Saddle River, NJ. 624 pp.
- Todorova, S. G., Siegeland, D. I. and Costello, A. M. 2005.** Microbial Fe(III) reduction in a minerotrophic wetland – geochemical controls and involvement in organic matter decomposition. Appl. Geochem. **20**: 1120–1130.
- Toor, N., Liber, K., MacKinnon, M. and Fedorak, P. 2007.** The role and effectiveness of wetlands for mitigation of oil sands process affected waters CEMA Progress Report 2007 Nov. 01.
- Toride, N., Leij, F. J. and van Genuchten, M. Th. 1995.** The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.0, Research Report No. 137, U. S. Salinity Laboratory, USDA, ARS, Riverside, CA.
- Trites, M. and Bayley, S. E. 2005.** Effects of salinity on vegetation and organic matter accumulation in natural and oil sands wetlands. Final Report CEMA Reclamation Working Group Grant 2005-0018.
- van Genuchten, M. T. and Wierenga, P. J. 1976.** Mass-transfer studies in sorbing porous-media: 1. Analytical solutions. Soil Sci. Soc. Am. J. **40**: 473–480.
- van Genuchten, M. Th. and Wagenet, R. J. 1989.** Two-site/two-region models for pesticide transport and degradation: theoretical development and analytical solutions. Soil Sci. Soc. Am. J. **53**: 1303–1310.
- van Genuchten, M. T., Leij, F. and Yates, S. R. 1991.** The RETC code for quantifying the hydraulic functions of unsaturated soils. In R. S. Kerr, ed. Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency Ada, OK.
- Viraraghavan, T. and Ayyaswami, A. 1989.** Batch studies on septic tank effluent treatment using peat. Can. J. Civ. Eng. **16**: 157–161.
- Vitt, D. H. and Chee, W. L. 1986.** The vegetation, surface water chemistry and peat chemistry of moderate-rich fens in central Alberta, Canada. Wetlands **9**: 227–261.
- Zynter, R., Biswas, N. and Bewtra, J. K. 1989.** Adsorption and desorption of perchloroethylene in soils, peat moss, and granular activated carbon. Can. J. Civil Eng. **16**: 786–806.