# Advective-diffusive controls on solute transport in a clay-rich aquitard: In situ experiment

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ABSTRACT
Solute transport in clay-rich aquitards is often assumed to be diffusion dominated; however, few *in situ* measurements of the Coefficient of Molecular Diffusion have been undertaken to date. In this study, an *in situ* experiment was undertaken to measure both the Coefficient of Diffusion and to demonstrate the transition from advection dominated to diffusion dominated transport within a clay aquitard.

The screen intake of a purpose-build well (78 mm ID) was completed at 13.6 m below ground surface and in direct contact with a thick clay-rich till, located in Saskatchewan, Canada. The standing water in the well was purged and the remaining well water was spiked with $^{2}H$ enriched 1M NaCl solution. The well was allowed to recover and water levels were measured, water samples collected and analyzed for $\delta^{2}H$ over the ensuing 1054 days of the experiment. On day 340, the well water was spiked with $^{18}O$ and the collected water samples were additionally analyzed for $\delta^{18}O$ for the remainder of the experiment. At the end of the experiment the water level approached static conditions. Based on the water level recovery and advective transport simulations the hydraulic conductivity of the aquitard was determined to be $1.7 \times 10^{-10}$ m/s, in good agreement with previously reported K values for this till.

Applying and comparing atomic mass calculations to a pure advective mixing/dilution process and advective-diffusive processes ($D_e = 5 \times 10^{-10}$ m$^2$/s, $n_e = 0.28$) showed that diffusion was the dominant transport mechanism at $u \leq 3.8 \times 10^{-9}$ m/s. This transition identifies the conditions from advection dominated (Pe > 1) to diffusion dominated (Pe < 1) transport.

RÉSUMÉ
Le transport des solutés dans les aquitards riche en argile est souvent supposé être dominé par la diffusion; pourtant, peu de mesures in-situ du coefficient de diffusion moléculaire ont été entreprises à ce jour. Dans cette étude, une expérience in-situ a été entreprise pour mesurer le coefficient de diffusion ainsi que pour démontrer la transition du transport dominé par l'advection à celui dominé par la diffusion au sein d'un aquitard d'argile.

La grille d'arrivée d'eau d'un puits spécialisé (78 mm ID) a été accomplie à une profondeur de 13.6 m de la surface du sol et en contact direct avec un till épais riche en argile, qui se trouve en Saskatchewan, Canada. L'eau stagnante dans le puits a été purgée et le reste de l'eau a été dopée avec solution de 1M NaCl enrichie en $^{2}H$. Le puits a été permis de se rétablir et les niveaux d'eau ont été mesurés, les échantillons d'eau recueillis et analysés pour $\delta^{2}H$ au cours des 1054 jours de l'expérience. Au jour 340, l'eau du puits a été dopée avec du $^{18}O$ et les échantillons d'eau recueillis ont été aussi analysés pour $\delta^{18}O$ pour le reste de l'expérience. À la fin de l'expérience le niveau d'eau s'est approché des conditions statiques. Basé sur la récupération du niveau d'eau ainsi que les simulations de transport advectif on a déterminé que la conductivité hydraulique de l'aquitard était $1.7 \times 10^{-10}$ m/s, en bon accord avec les valeurs de K reportées préalablement pour ce till.

L'application et la comparaison des calculs de masse atomiques à un processus de mélange/dilution advectif pur et aux processus advectifs-diffusifs ($D_e = 5 \times 10^{-10}$ m$^2$/s, $n_e = 0.28$) ont montré que la diffusion était le mécanisme dominant du transport à $u \leq 3.8 \times 10^{-9}$ m/s. Cette transition identifie les conditions de passage du régime de transport dominé par l'advection (Pe> 1) à celui dominé par la diffusion (Pe <1).

## 1 INTRODUCTION

Solute transport in clay-rich aquitards is often described as diffusion dominated. However, the hydrological conditions for this statement have, to the best of our knowledge, not been explored.

In this study, we present an *in situ* method to observe the transition from advection dominated to diffusive dominated transport within a clay aquitard using a single well test and a conservative tracer.

The field testing system consisted of a purpose-built well completed 13.6 m below ground surface. The recovering formation water in the well was initially spiked with the conservative tracer $^{2}H$ and after 340 days of testing with $^{18}O$. Water level recovery and isotopic ratios ($\delta^{2}H$ and $\delta^{18}O$) in the collected samples were measured

until the water level returned to equilibrium conditions after approximately 1054 days.

The hydraulic conductivity and coefficient of molecular diffusion were determined by best-fitting the measured data (water level recovery and isotopic ratios) using numerical seepage and contaminant transport models. Because the diffusive transport of the tracer out of the well is opposed by advective transport into the well during well recovery, the onset of mass loss from the well with time can be used to define the transition for advective to diffusive dominated transport. The conditions at this transition can then be used to interpret the various components of the Péclet number.

## 2 MATERIALS AND METHODS

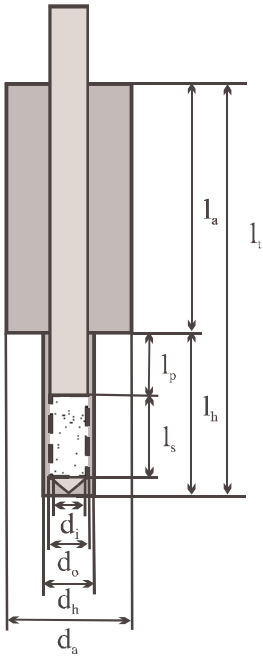
### 2.1 Description of Study Site

This study was carried out at the King Research Site in a thick two-layered aquitard system, located 140 km south of Saskatoon, Saskatchewan, Canada (51.05 N Lat., 106.5 W Long.). The aquitard system at this site consists of 80 m of uniform (geotechnically and geochemically), plastic, non-fractured clay-rich Battleford Formation till, unconformably overlying the Snakebite Member of the Cretaceous Bearpaw Formation (Christiansen 1971). The detailed hydrogeology at the research site is described by Shaw and Hendry (1998).

### 2.2 Instrumentation and Sampling

A purpose-build well was installed 13.6 m below ground surface into the till aquitard with the screen intake zone (0.47 m long, 78 mm ID) in direct contact with the formation (Figure 1). At the onset of the test, the well was filled with 2250 $cm^3$ of 1M NaCl solution enriched with $^2H$ ($C_i$ = +457 ‰ VSMOW; $H_i$ = 563.87 m asl) and recharge of formation water ($C_o$ = -163 ‰ VSMOW) into the well was allowed. The initial height of the water column in the well was 0.53 m. Static condition on site, based on adjacent monitoring wells, was estimated to occur at 10.5 m of standing water in the well. Water levels (WL) were measured, the water column mixed, and water samples collected (n = 48) and analyzed for $\delta^2H$ over the ensuing 1054 days of the experiment. On day 340, the water in the standpipe was spiked with $^{18}O$ ($C_o$ = -19.8 ‰ and $C_i$ = +14.9 ‰ VSMOW at H = 570.9 m asl). All water samples collected after this time (n = 19), were analyzed for both $\delta^2H$ and $\delta^{18}O$. At the end of the experiment the water level had reached 573.6 m asl, approaching static conditions at 574 m asl. (Figure 2).

The isotopic analyses were carried out on a mass spectrometer (Micromass Isoprime with Liquid Autosampler with Cr reduction in CF mode) at Environment Canada, Saskatoon, SK, Canada. The instrumental error for the isotope analyses was ±2 ‰ VSMOW.




$l_t$: total depth of well = 13.6 m
$l_a$: length of augered hole = 12.4 m
$l_h$: length of cored hole = 1.2 m
$l_p$: length of unscreened stand-pipe in cored hole = 1.0 m
$l_s$: length of screen = 0.47 m
$d_a$: diameter of augered hole = 160 mm
$d_h$: diameter of cored hole = 89 mm
$d_i$: inside diameter of screen = 78 mm
$d_o$: outside diameter of screen = 89 m m

Figure 1: Stylized construction of *in situ* advection-diffusion well.

### 2.3 Analytical Method

The hydraulic conductivity (K) of the formation was estimated using the Hvorslev (1951) method and introduced into the finite element seepage model SEEP/W (Krahn 2004) to simulate the water level response in the well. Two zones were identified in the model. A cylinder of radius r = 39 mm placed at the origin of the mesh, representing the well, was placed 13.6 m deep into a homogeneous halfspace, representing the formation. Initial head condition of 10.5 m was assigned to each node in the formation and the nodes in the well were assigned an initial head of 0.53 m. Constant head conditions of 10.5 m were assigned to the right hand side boundary. The formation was assigned a K between 1 and 3 x $10^{-10}$ m/s and a coefficient of compressibility of 2.5 x $10^{-5}$ kN/$m^2$.

Simulations of the advective-diffusive transport were performed by importing the results of the advective transport simulation into the contaminant transport program CTRAN/W (Krahn 2004). The formation was assigned the $\delta^2H$ background concentration $C_o$ = -163 ‰ VSMOW, and the well the initial concentration $C_i$ = +457 ‰ VSMOW. Calculations were carried out using effective diffusion coefficients $D_e$ ranging from 2 to 5 x $10^{-10}$ $m^2$/s and an effective porosity $n_e$ of 0.28.

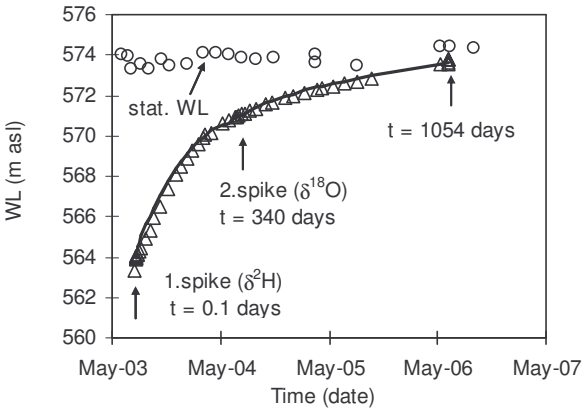



Figure 2: Measured (△) and simulated (—), using K = 1.7x10$^{-10}$ m/s, WL recovery in purpose-build well, and static WL in on site 12.7 m deep monitoring well (○). Spike introduction dates are indicated by arrows.

## 3 RESULTS

### 3.1 Water Level Recovery and Hydraulic Conductivity

The WL response was measured for 1054 days, starting on August 15, 2003 (Figure 2) with an initial WL of 563.87 m asl. After 1054 days of recovery the WL reached an elevation of 573.6 m asl, and approached steady state. Steady state was established at 574 m asl based on WLs measured in an adjacent, 12.7 m deep, monitoring well and averaged over 7 years. Heads measured in wells (data not shown) with screen intake zones at depths between 13.1 and 15.3 m bgs and located on site confirmed this equilibrium head condition.

A K of 1.9 x 10$^{-10}$ m/s was calculated from recovery data collected at early times (35-312 days) using the Hvorslev method (Hvorslev 1951). The K value for data collected for later times (292-746 days) was 2.1 x 10$^{-10}$ m s$^{-1}$. These values were in agreement with those measured in monitoring wells (K = 0.8 - 2.1 x 10$^{-10}$ m/s) placed on site at depths between 11.7 and 15.2 m bgs (Boldt-Leppin et al. 2008; in prep.). Shaw and Hendry (1998) reported an average K value of 4.5 x 10$^{-10}$ m/s, measured in 5 on site monitoring wells with screen intake zones between 8 and 15 m bgs. Vertical K values calculated from seasonal water level fluctuations measured in these same monitoring wells averaged 3.6 x 10$^{-10}$ m s$^{-1}$ (Boldt-Leppin and Hendry 2003). The numerical simulation of the WL response, superimposed on the measured data in Figure 2, resulted in a best fit using K = 1.7 x 10$^{-10}$ m/s.

### 3.2 Isotope Tracer Ratio

Each water sample was analyzed for its isotopic composition. The results, normalized to background, are plotted as function of time in Figure 3. The normalized isotopic ratio $C_n$ was defined as $[(C_t - C_b) / (C_i - C_b)]$, where $C_t$ represented the ratio measured at time t, $C_i$ the initial ratio, and $C_b$ the isotope ratio of the formation water. A 75% decrease of $\delta^2$H is observed in the first 100 days of the experiment, which is concurrent with the initial rapid increase of the WL (Figure 2). During the next 200 days of testing the $\delta^2$H decreased by 10%; decreasing a further 7% over the following 754 days ($C_n$ = 0.08) until approaching equilibrium conditions at the end of the experiment at 1054 days.

The ratio of $\delta^{18}$O, introduced as a tracer at 340 days, decreased by 50% during the remaining 754 days of the experiment (Figure 3). This was in agreement with the reduction of $\delta^2$H in the same timeframe.

Transport simulations carried out with K = 1.7 x 10$^{-10}$ m/s provide a good fit to the measured data for $n_e$ = 0.28 and coefficients of molecular diffusion of $D_e$ = 5 and 3 x 10$^{-10}$ m$^2$/s for $\delta^2$H and $\delta^{18}$O, respectively. These values are in agreement with $D_e$ values reported by Hendry and Wassenaar (1999). For a detailed inspection of the onset of diffusion dominated transport, numerical simulations were carried out for pure advective transport as well as advection-diffusion transport using $D_e$ values between 2 and 7 x 10$^{-10}$ m$^2$/s. Because of the similarities of both tracers, the results are only shown for $\delta^2$H (Figures 4 and 5), but are valid for either tracer.

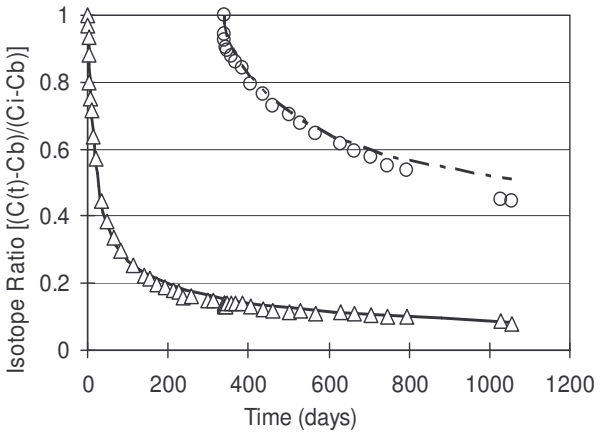



Figure 3: Measured and simulated isotope ratios normalized to background of $\delta^2$H (△) with $D_e$ = 5x10$^{-10}$ m$^2$/s (——) and $\delta^{18}$O (○) with $D_e$ = 3x10$^{-10}$ m$^2$/s (- — -), as function of time.

Numerical simulations, to predict the decrease in $\delta^2$H ratio over time, are plotted Figure 4. Three transport simulations were carried out: advective transport alone (only dilution of well water) and advective-diffusive transport for $D_e$ values of 2 and 5 x 10$^{-10}$ m$^2$/s. The results suggest that at about 250 days into the recovery process the decrease in concentration in the reservoir could not be accounted for by advective transport alone (dilution) as seen in the scale enhanced insert in Figure 4. By incorporating a diffusion coefficient into the transport model, the simulated traces approach the measured data with increasing $D_e$.

To more precisely define the transition from advection to diffusion dominated transport, a mass balance approach was applied. For each data set, the measured and simulated mass loss or gain of $^2$H in the well water was calculated at each time step in the recovering process (Figure 5). As expected, in the case of only advective flow

no mass was lost or gained in the accumulating volume of the well water (horizontal solid line). The change of concentration over time is solely the result of dilution. However, the measured data (triangles) show a mass loss starting at about 250 days, evident by the decrease in relative mass. The onset of mass loss defined the time at which transport behaviour transitions from advection dominated (Pe>1) to diffusion dominated (Pe<1) transport, where Pe is the dimensionless Péclet number, defined in the general form by $Pe = u \bullet L/D_e$. with L representing the "characteristic" hydraulic length (Fetter 1999).

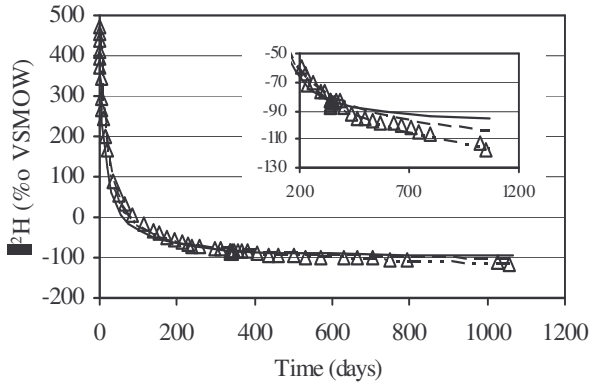



Figure 4: $\delta^2$H ratio in ADW; (Δ) measured; (——) dilution by advection only; (---) dilution by advection including diffusion for $D_e = 2x10^{-10}$ m$^2$/s and (-- — --) for $D_e = 5x10^{-10}$ m$^2$/s.

The results of the numerical simulations including diffusive transport for $D_e$ values of 2 and 5 x $10^{-10}$ m$^2$/s (dashed lines) confirm the onset of diffusive dominance at 250 days as the two lines begin to separate into sloping and horizontal lines. A good fit to the measured data was achieved for $D_e = 5 \times 10^{-10}$ m$^2$/s.

In geological media the threshold between advective and diffusive mass transport dominance is defined by Pe equal to 1 (Freeze and Cherry 1979). In this experiment the transformation of the dominant transport mode occurred at 250 days (Figure 5, vertical dashed line).

At this time, the linear ground water velocity, u, plotted for the entire recovery process (Figure 5, right hand scale) equals 3.8 x $10^{-9}$ m/s at the screen intake zone. This suggests that in the studied aquitard system, diffusion is the dominant transport mechanism (Pe = 1) if u < 3.8 x $10^{-9}$ m/s. Based on the definition of the Péclet number in Fetter (1999), L was calculated as 0.037 m with $D_e = 5 \times 10^{-10}$ m$^2$/s.

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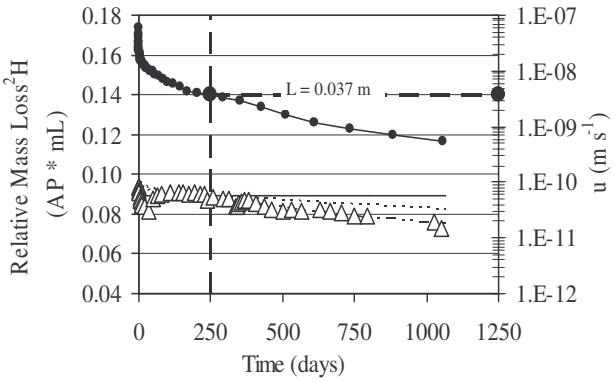


Figure 5: Relative mass loss of $^2$H with time in advection-diffusion well: measured (Δ), pure dilution by advection (——), dilution by advection plus diffusion with $D_e = 2x10^{-10}$ m$^2$/s (---) and $D_e = 5x10^{-10}$ m$^2$/s (-- — --).'Linear ground water velocity u (—•—) at the screen intake zone. The horizontal line (•----•) represents u calculated for Pe = 1 and $D_e = 5x10^{-10}$ m$^2$/s. L is the "characteristic" hydraulic length.

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