Through-migration of contaminants in aquitards and delayed releases into underlying water-supply aquifers

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ABSTRACT

Many aquitards are composed of over-bank silts that form relatively permeable aquitards in multi-aquifer floodplain or glaciofluvial or alluvial-fan deposits. Such aquitards may be sufficiently permeable to permit slow advective migration of contaminants downwards to underlying aquifers. In those cases where the underlying aquifer is used for groundwater supply, this will result in delayed release of these contaminants into the aquifer. The algorithm of Gimmi et al. (*2007)* with a mixing-cell boundary condition and finite-difference solution is used to predict advection-diffusion of contaminants through such an aquitard and discharge into the aquifer below. Applications of this algorithm include the estimation of nitrate in deep supply wells due to fertilizer application and rising concentrations of road salt in deep municipal wells.

1. INTRODUCTION

Over the past twenty years interest has grown in the effect of back diffusion of contaminants from aquitards on prolonging the duration of contamination within the adjacent aquifer. In this conceptual model, contaminants that have diffused from aquifers into aquitards will eventually diffuse back into the aquifer due to their thermal-kinetic energy that is the cause of molecular diffusion.

This concern was first identified by Mackay and Cherry (1989) as a constraint on the early removal of contaminants from sand-and-gravel (i.e., granular) aquifers by pump-and-treat remediation. Back diffusion of dissolved chlorinated solvents was later examined in detail by Liu and Ball (2002) using high-resolution coring at the controlled PCE-spill site at Dover Air Force Base, Delaware. They pointed out that molecular diffusion will dominate transport when the molecular Peclet number (Pe_m) at the grain scale is less than one, i.e.,

$$Pe_m = \frac{vd}{D} < 1\Lambda \;\; Eq[1]$$

where v is the average linear vertical groundwater velocity, d is the average grain size of the porous medium, and D is the effective molecular diffusion coefficient. This is likely to be the case in clay aquitards, i.e., aquicludes, that are not made effectively more permeable by through-going fractures propped open by sand or silt grains.

In essence, Liu and Ball confirmed the earlier explicit prediction by Mackay and Cherry for aquitards where advective transport of contaminants is minimal when compared with the diffusive flux that occurs in all directions. Chapman and Parker (2005) showed that back diffusion of TCE into an overlying aquifer at concentrations above drinking water MCLs (maxmimum contaminant level) might last for centuries. Most recently by Parker et al. (in press) has shown that thin (e.g., 20 cm) clay layers may eventually transmit contaminants by diffusion into an underlying aquifer and cause long-term contamination in that aquifer.

Remenda et al. (1996) considered the distribution of δ^{18}O in a thick unfractured aquitard in Saskatchewan and defined an advective-dispersive version of the Peclet number where diffusion is the dominant transport mechanism when:

$$Pe_T = \frac{v^2 T}{D_d} << 1\Lambda \;\; Eq[2]$$

where T is the total duration of the transport process (years) and D_d is the coefficient of hydrodynamic dispersion. When this condition of $Pe_T<<1$ is met, D_d is effectively equal to the coefficient of molecular diffusion.

This formulation of the Peclet number recognizes that aquitards may in fact transmit contaminants by advection when $Pe_T > 1$, which condition may well occur when the aquitards are not lacustrine or marine clays but rather are composed of overbank silts from adjacent stream channels. In this case, the vertical permeability of the silts only delays contaminant migration through the aquitard – assuming that sorptive retardation and/or biodegradation do not occur within the aquitard – before the contaminant exits the base of the aquitard and enters an underlying aquifer.

For contaminants that do not undergo sorption and/or biodegradation within these silts, their migration into the underlying aquifer may present a long-term hazard to deep groundwater-supply wells even where they are protected by thick silty aquitards. Contaminants that fit such a description would include chloride from road salt and other conservative anions that might include nitrate (i.e. assuming no biodegradation within the silts), as well as contaminants such as arsenic, chromium (VI) and selenium that might undergo redox reactions and become sorbed or co-precipitated.

The purpose of this paper is to consider the time delay of these contaminants by silty aquitards and the likely concentrations exhibited by the contaminant in a supply well situated in the underlying aquifer. As Parker et al (in press) showed, contaminants that have diffused through a thin (20 cm thick) clay aquitard appear in the lower aquifer at concentrations that may cause the closing of deep groundwater supply wells. This same process occurs within silty aquitards that are common fluvial sediments in floodplains where they are caused by overbank flood events. We consider here the algorithm used by Gimmi et al. (2007) to simulate the diffusion of solutes through argillaceous rocks but generalised to allow advection through the one-dimensional porous medium with a bottom mixing cell (Gimmi and Flüher, 1998) that will represent the underlying aquifer.

2. ALGORITHM FOR ADVECTION & DIFFUSION ACROSS AN AQUITARD

Consider the advection-diffusion-reaction equation

$$\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \lambda C \Lambda \ Eq.[3] ,$$

on the domain $0 < z < L$ and $t > 0$, where

$D_d =$ coefficient of hydrodynamic dispersion
$v =$ average linear groundwater velocity
$\lambda =$ first-order reactive rate constant, which might be used to represent denitrification of fertilizer nitrate or some other appropriate transformation reaction.

Let the initial condition be

$$C(z,0) = g(z) , \ 0 < z < L .$$

Consider various boundary conditions as suggested by Eq. [3]. However, a reactive decay is included in the aquifer treatment boundary condition and a pulse type concentration specified boundary condition. A time dependent Dirichlet type boundary condition specifies the concentration on the boundary with reactive decay as

$$C(0,t) = C_0 e^{-\lambda_0 t} \text{ or } C(L,t) = C_L e^{-\lambda_L t} .$$

For zero reactive rates, the Dirichlet conditions reduce to

$$C(0,t) = C_0 \text{ or } C(L,t) = C_L .$$

A pulse type Dirichlet condition is specified by

$$C(0,t) = \begin{cases} C_{0\_1}, & t \le t^* \\ C_{0\_2} & t > t^* \end{cases} .$$

A no flow Neumann type boundary condition specifies zero concentration gradient on the boundary

$$\frac{\partial C}{\partial z}(0,t) = 0 \text{ or } \frac{\partial C}{\partial z}(L,t) = 0 .$$

A mixing-cell type boundary condition (Gimmi & Flüher, 1998) for Eq. [3] that includes reactive decay is modeled at the upper aquifer by

$$\frac{\partial C_m}{\partial t} = \rho(C_{in} - C_m) + \frac{D_d}{\zeta}\frac{\partial C}{\partial z}(0,t) - \lambda_0 C_m$$

or at the lower aquifer by

$$\frac{\partial C_m}{\partial t} = \rho(C_{in} - C_m) - \frac{D_d}{\zeta}\frac{\partial C}{\partial z}(L,t) - \lambda_L C_m$$

where

$\rho =$ flushing rate,
$\zeta =$ equivalent height of the aquifer or mixing cell.

3. CONTAMINANT MIGRATION IN THE AQUITARD

For the aquifer-aquitard system under consideration, the Peclet number may be estimated from soil cores obtained from the aquitard. Figure 1 shows the normalized concentrations of a contaminant in a soil core collected from a silty aquitard of ~10 m thickness.

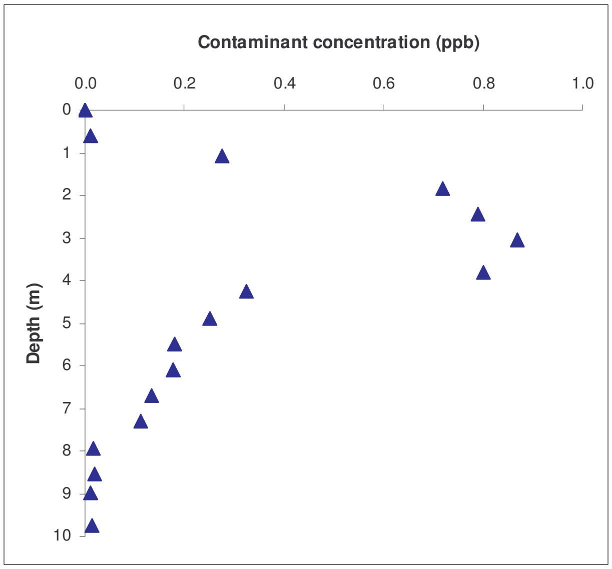

Figure 1: Contaminant concentrations shown versus depth for one of several cores through a silt aquitard.

The top of the aquitard is given by depth, z = 0. The bottom of the aquitard is approximately at 10 m depth.

Figure 2 shows the simulation domain with the mixing cell boundary condition with the initial concentration within the aquifer = 0 ppb.

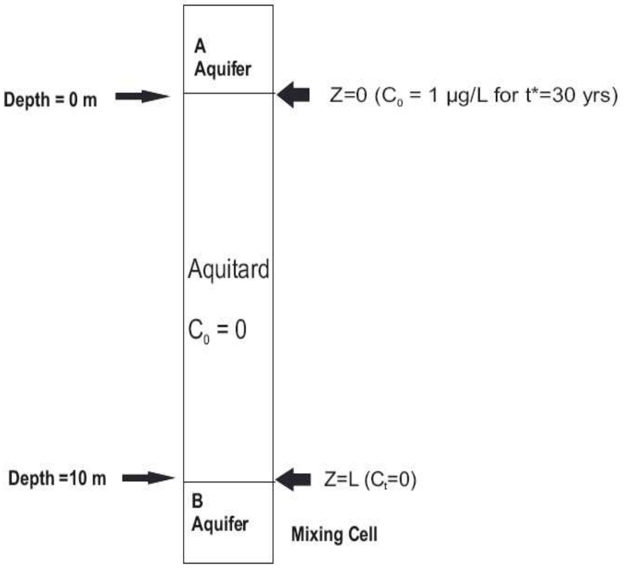

Figure 2: Schematic of simulation domain. By specifying the lower boundary as a mixing cell, the cell is equivalent to the lower or 'B' aquifer.

The best-fit simulation shown in Figure 3 to the model yields a vertical groundwater velocity of ~ 8 cm/yr for a 50-year simulation period, the first 30 years of which the upper boundary is at a concentration of 1 ppb after which it is reduced to 0.015 ppb. These conditions yield a Pe_T ~ 100, i.e., the Peclet number indicates that molecular diffusion is indeed negligible when compared with advection due to downward flow into the underlying aquifer. This condition is likely to be common when the underlying or B aquifer is pumped as a water supply.

Figure 4 is a schematic of the mixing-cell type boundary condition for this case. It assumes a 7 m thick lower (B) aquifer with a hydraulic conductivity of 3.4E-02 m/s and a porosity ~0.3. The flushing rate in the B aquifer is 4%/yr due to the low hydraulic gradient. This flushing rate would be accelerated by pumping.

Figure 5 illustrates that the lower aquifer is subject to a peak contamination at about 150 years of 0.13 ppb. That is, the lower aquifer becomes contaminated to a level of 13% of the 1 ppb loading in the upper aquifer that contaminated the aquitard. This delayed response is obviously a function of the aquitard thickness, i.e., 10 m. Thinner aquitards will clearly result in earlier breakthroughs to the lower aquifer. However, the principle established here is that the delayed release of contamination from the aquitard may be very far into the future for conservative contaminants like road salt and, in the absence of biodegradation, nitrate. By considering the C_0 input level in the upper aquifer, which is normalized to 1 ppb, it is possible to determine whether groundwater in the lower aquifer will exceed the MCL and at what time in the future. We are currently generalizing these scenarios to allow a broader interpretation of the problem that will produce nomograms relating lower aquifer contaminant levels with aquitard thicknesses and transport parameters.

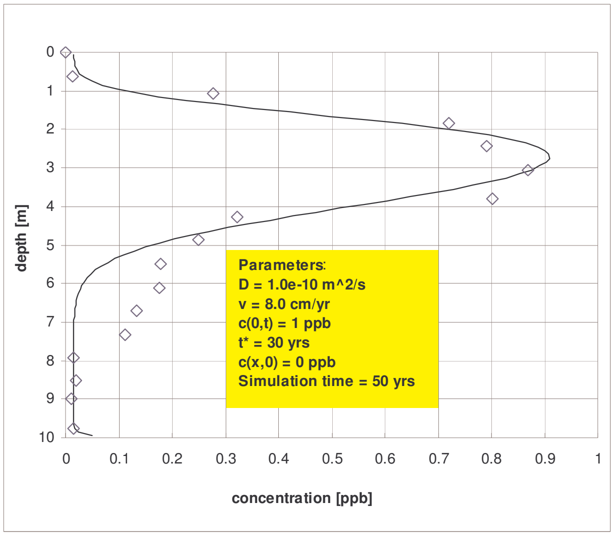

Figure 3: Matching of field core data for contaminant with the model for the specified conditions. The variable t is the duration of the 1 ppb input at the upper boundary (30 yrs) after which time it is reduced to 0.015 ppb. Total simulation time is 50 years.*

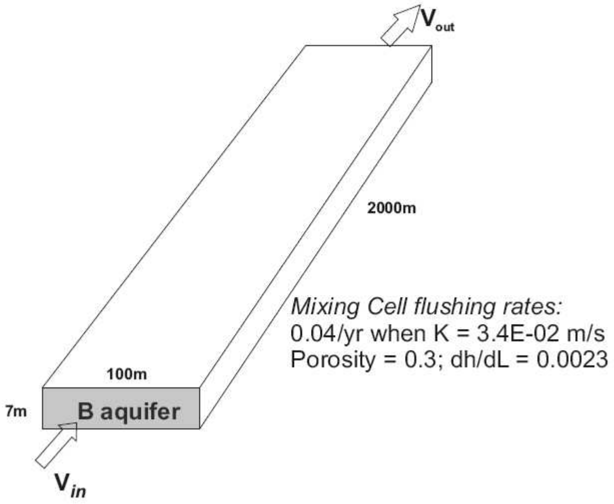

Figure 4: Schematic of mixing cell in the B aquifer.

Figure 6 presents the cumulative flux reaching the lower aquitard over the simulation period of 400 years. It assumes the transport parameters present in the earlier figures. At the end of 400 years the contaminant concentration is still climbing.

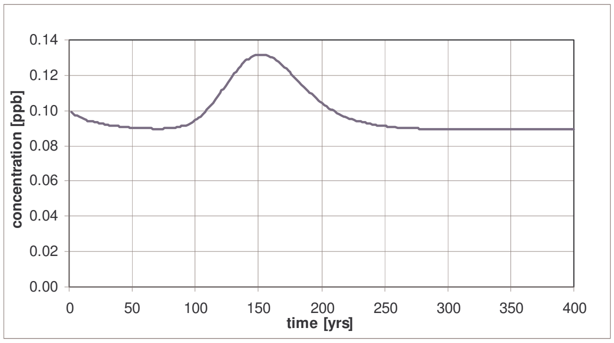

Figure 5: Concentration in the lower aquifer. Total simulation time is 400 years.

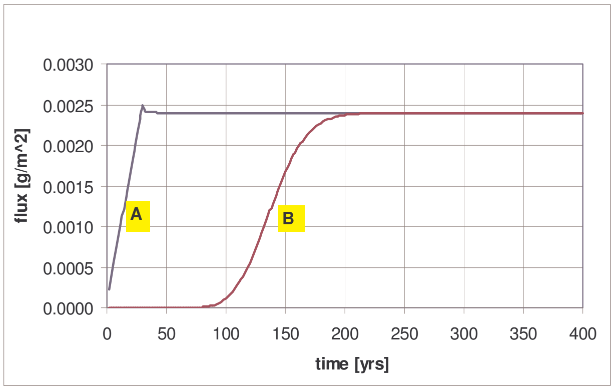

Figure 6: the cumulative fluxes from the upper (A) aquifer into the aquitard and from the aquitard to the lower (B) aquifer over the 400 yr simulation time. The 'knob' shown at t=30 yrs is the result of back diffusion from the aquitard into the upper aquifer when the input concentration of 1 ppb is reduced to 0.015 ppb.

4. CONCLUSIONS

By matching the contaminant concentrations in the aquitard to the numerical model based on the Gimmi algorithm, it has been shown that contaminant migration in the aquitard in question is caused only by slow advection and not by diffusion. In the case considered, advection dominates diffusion. By considering the lower aquifer to be a mixing cell and using appropriate initial and boundary conditions, the migration of contaminants through the aquitard and into the lower aquifer was simulated. Rather than 'back-diffusion' causing delayed contaminant release in the upper aquifer, a case of considerable concern in itself but not a new one, this study addresses the issue of 'through-migration' in the delayed contamination of deep aquifers being used for water supply and contaminated by overlying aquitards.

5. REFERENCES

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