1 **Solute source depletion control of forward and back diffusion**
2 **through low-permeability zones**
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ABSTRACT

Solute diffusive exchange between low-permeability aquitards and high-permeability aquifers acts as a significant mediator of long-term contaminant fate. Aquifer contaminants diffuse into aquitards, but as contaminant sources are depleted, aquifer concentrations decline, triggering back diffusion from aquitards. The dynamics of the contaminant source depletion, or the source strength function, controls the timing of the transition of aquitards from sinks to sources. Here, we experimentally evaluate three archetypical transient source depletion models (step-change, linear, and exponential), and we use novel analytical solutions to accurately account for dynamic aquitard-aquifer diffusive transfer. Laboratory diffusion experiments were conducted using a well-controlled flow chamber to assess solute exchange between sand aquifer and kaolinite aquitard layers. Solute concentration profiles in the aquitard were measured in situ using electrical conductivity. Back diffusion was shown to begin earlier and produce larger mass flux for rapidly depleting sources. The analytical models showed very good correspondence with measured aquifer breakthrough curves and aquitard concentration profiles. The modeling approach links source dissolution and back diffusion, enabling assessment of human exposure risk and calculation of the back diffusion initiation time, as well as the resulting plume persistence.

Keywords: diffusion; tracer; back-diffusion; aquitard; groundwater

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1. Introduction

Storage and release of aquifer contaminants, including dissolved constituents of dense non-aqueous phase liquids (DNAPLs) from low-permeability zones is considered to be a critical limitation to contaminated site management (Cavanagh et al., 2014; Mackay and Cherry, 1989; Stroo et al., 2012; Stroo et al., 2003; Travis and Doty, 1990). In particular, the solute release process (back diffusion) from low-permeability zones leads to sustaining plume longevity with low-level contamination in the aquifer after the source zone has been isolated or remediated. Several field studies have demonstrated back diffusion from low-permeability zones as a significant contributor to plume persistence at contaminated sites (Ball et al., 1997; Chapman and Parker, 2005; Liu and Ball, 2002; Parker et al., 2004). Fundamental laboratory and modeling studies have been conducted to investigate back diffusion mechanisms and to develop predictive methods (Chapman et al., 2012; Sale et al., 2008b; Yang et al., 2015). In these studies, the aquifer concentration change that triggered a reversal from forward to back diffusion occurred instantaneously. However, aquifer concentrations in real source zones decrease gradually rather than instantaneously, because of aquifer and contaminant heterogeneity (Rao and Jawitz, 2003).

The dynamic behavior of source dissolution has been shown to be strongly influenced by the DNAPL architecture, with the pattern of concentration reduction with time referred to as source strength function, SSF (Chen and Jawitz, 2008; Chen and Jawitz, 2009; Christ et al., 2006; Falta et al., 2005a; Falta et al., 2005b; Fure et al., 2006; Jawitz et al., 2005; Parker and Park, 2004; Rao and Jawitz, 2003; Suchomel and Pennell, 2006). Plume persistence is thus affected both by SSF and back diffusion, and an important question is the relative contribution of these two factors. A recent modeling study addressed this question, finding that the persistence

of higher-solubility contaminant source zones is supported more from back diffusion than from dissolution, while both processes contribute to persistence of contaminants with lower solubility (Seyedabbasi et al., 2012). That study focused on source mass discharge but did not consider the evolution of aquitard contaminant concentration profiles during forward and back diffusion. The concentration profiles in aquitards represent the integrated history of the source zone, and these data may be used to infer information about the SSF (Chapman and Parker, 2005; Liu and Ball, 2002). Another modeling study investigated the influence of DNAPL source architecture on the risk of back diffusion in plume zones (Brown et al., 2012). Source zone dissolution was generated by a power law source depletion model, and the results suggested that the greatest back diffusion risk occurs from a constant SSF whereas less risk was expected with an increase in aquifer and contaminant heterogeneity. However, that study did not compare fluxes from back diffusion to those resulting from source dissolution dynamics, leaving a gap in understanding about the combined effects of SSFs on plume persistence.

In this study we extend the work of previous investigators by assessing the relative contributions to plume persistence of source dissolution dynamics (characterized by SSF) and back diffusion in controlled laboratory experiments where both breakthrough curves and aquitard solute concentration profiles were monitored. We implemented three archetypical transient source depletion patterns (step-change, linear, and exponential) in laboratory experiments in a two-dimensional flow chamber with high- and low-permeability layers representing an aquifer and aquitard, and with these data we validate analytical solutions for aquifer solute flux and aquitard concentrations. We also classify stages in plume evolution based on relative importance of dissolution and back diffusion, and provide guidance for the application of analytical solutions

to verify timing of back diffusion initiation and the magnitude of back diffusion flux from low-permeability layers, based on SSFs.

2. Material and methods

2.1 Experimental method

2.1.1. Flow chamber boundary conditions

Three experiments were conducted in a well-controlled two-dimensional flow chamber to generate forward and back diffusion with three SSFs: (1) constant source with a step-change in strength, (2) linear source depletion, and (3) exponential source depletion. The flow chamber consisted of aluminum tubing frames ($28 \times 12 \times 1.2$ cm) and two glass sheets, similar to previous studies (Yang et al., 2014; Yang et al., 2015) and was filled with 20/30 mesh Accusand (4 cm) (Unimin Corp.) with an upper layer of kaolinite (7 cm) (Fluka) under saturated conditions (Fig. 1). Teflon tape was applied at the top of the clay layer to minimize evaporation. Steady-state flow was maintained with variable source concentrations delivered to an injection well using a syringe pump (Harvard Apparatus Syringe Infusion Pump 22) and outflow controlled using a piston pump (Fluid Metering Corp. “Q” Pump).

In each experiment bromide was displaced through the aquifer for a finite duration to facilitate forward diffusion to the aquitard, followed by different transitions to zero-concentration water flooding. After the loading periods in all experiments, water flushing was maintained without bromide for an additional 30 days to trigger back diffusion. In experiment I, a solution of 10 g/L of bromide was displaced for 7.5 d. In experiment II, for reproducing linear source depletion, bromide concentrations were reduced linearly from 10 to 0 g/L in 15 daily increments. In experiment III, a continuously stirred tank reactor (CSTR) was used to generate an

exponential SSF (Fig. 1). The effluent concentration, $C(t)$, from a CSTR is defined as (Schmidt, 1998)

$$C(t) = C_0 e^{\frac{-t}{V/Q}} \quad (1)$$

The CSTR volume (V) was maintained at 230 mL and the initial bromide concentration, C_0 , was 10 g/L. The effluent bromide concentration decreased from 10 to 0 g/L over 40 days. All experiments were conducted at a steady flow rate, $Q = 0.02$ mL/min. The experimental pore volume size was 40.3 mL and the estimated mean travel time from the inlet to the outlet of the flow chamber was 1.4 d. The timing and rate of the solute boundary condition transitions were designed such that an equal mass of bromide (2160 mg) was injected in each experiment.

2.1.2. In situ measurement of aquitard concentration

Bromide concentrations were measured in the kaolinite layer non-destructively by electrical conductivity analysis. Fourteen steel electrodes were installed in two columns of seven rows at 1 cm intervals on one side of the flow chamber (Fig. 1). The pore water electrical conductivity in the kaolinite was measured every 24 hours by connecting the electrodes in each row using a digital conductivity meter (Fisher Scientific). The conductivity of the flow chamber influent and effluent was also monitored continuously. Measured conductivities were converted to relative bromide concentration, $C_r(t)$,

$$C_r(t) = \frac{EC(t) - EC_i}{EC_0 - EC_i} \quad (2)$$

where $EC(t)$, EC_i , and EC_0 are the electrical conductivity at time t , without tracer, and with tracer at the injected concentration (C_0). Simple batch tests were conducted to determine bromide concentration in the kaolinite layer from the measured electrical conductivity (Fig. S1). These tests showed a linear relationship between measured electrical conductivity (approximate range

300 to 9000 $\mu\text{s/cm}$) and bromide concentration in kaolinite (0 to 10 g/L) with mean $R^2 = 0.99$ (Fig. S2).

2.2. Analytical solutions

In order to fill an important gap in understanding how the temporal pattern of contaminant source depletion in an aquifer controls accumulation in an aquitard and thus also controls how the contaminants are released back into the aquifer, we analyzed the experimental data with analytical solutions. The conceptual model began with more realistic source functions than the traditional step function. For simulating contaminant concentration distributions in low-permeability zones during forward and back diffusion, we adapted analytical solutions from the heat transport literature. For simulating breakthrough curves (BTCs), we developed analytical solutions for aquifer flux-average concentration.

2.2.1. Source strength functions

The relative concentration of dissolved DNAPL leaving the source zone can be expressed by a power law model (PLM) relating the source strength to the source mass (Parker and Park, 2004; Rao and Jawitz, 2003; Zhu and Sykes, 2004)

$$\frac{c(t)}{c_0} = \left[\frac{\int_t^\infty c(t)dt}{\int_0^\infty c(t)dt} \right]^\Gamma = \left[\frac{M(t)}{M_0} \right]^\Gamma \quad (3)$$

where C_0 is the initial contaminant concentration at the source zone control plane, M_0 is the initial source zone mass, and Γ is an empirical parameter that controls the shape of the concentration reduction curve and reflects the effects of heterogeneity in the flow field and DNAPL distribution.

The time-dependent relative concentration at the control plane can be expressed (Brown et al., 2012; Falta et al., 2005b; Zhu and Sykes, 2004)

$$\frac{C(t)}{C_0} = \begin{cases} 1 & t < \frac{M_0}{J_0} \\ 0 & t \geq \frac{M_0}{J_0} \end{cases} \quad \Gamma = 0 \quad (4a)$$

$$\frac{C(t)}{C_0} = \exp\left(-\frac{J_0}{M_0} t\right) \quad \Gamma = 1 \quad (4b)$$

$$\frac{C(t)}{C_0} = \left[1 + \frac{J_0}{M_0} (\Gamma - 1)t\right]^{\frac{\Gamma}{1-\Gamma}} \quad \Gamma > 0, \Gamma \neq 1 \quad (4c)$$

where $J_0 = qAC_0$ is the initial discharge rate over a vertical plane of area A perpendicular to groundwater flow with Darcy velocity q . We consider three cases of (4) corresponding to $\Gamma = 0$, 0.5, and 1. Solutions for $\Gamma = 0$ and 1 are given above, and substituting $\Gamma = 0.5$ into (4c) yields a linear concentration decrease with time given by

$$\frac{C(t)}{C_0} = 1 - kt \quad \Gamma = 0.5 \quad (5)$$

where $k = \frac{J_0}{2M_0}$.

For the cases of $\Gamma = 0$, 0.5, and 1 examined here, analytical solutions for concentration profiles in a semi-infinite domain have been developed from Fick's second law (Eq. (S2)) (Carslaw and Jaeger, 1959; Crank, 1975). These solutions are shown below. Note that the solution for $\Gamma = 0$ is well known, while those for $\Gamma = 1$ and 0.5 are less widely applied for solute transport. All solutions consider initial condition $C(z > 0, t = 0) = 0$ in the low-permeability zone.

2.2.2. Source concentration step change ($\Gamma = 0$)

The analytical solution for the concentration distribution in a semi-infinite low-permeability zone subject to boundary condition $C(z = 0, t > 0) = C_0$ (i.e., forward diffusion) is expressed (Carslaw and Jaeger (1959):

$$\frac{C(z,t)}{C_0} = \text{erfc}(\zeta) \quad (6)$$

216 where $\zeta = \frac{z}{\sqrt{4D^*t}}$ and D^* is the effective diffusion coefficient, defined by Eq. (S3). For simulating
 217 back diffusion scenarios where the contaminant source is removed by remedial treatment or
 218 isolated by physical barriers, the solute concentration at the interface between high- and low-
 219 permeability layers is set to zero after loading duration T . The analytical solution for the
 220 concentration distribution in the semi-infinite low-permeability zone is obtained by superposition
 221 of the boundary conditions $C(z = 0, 0 < t \leq T) = C_0$ and $C(z = 0, t > T) = 0$ (Carslaw and Jaeger,
 222 1959):

$$223 \quad \frac{C(z,t)}{C_0} = \operatorname{erfc}(\zeta) - \operatorname{erfc}(\zeta') \text{ for } t > T \quad (7)$$

$$224 \quad \text{where } \zeta' = \frac{z}{\sqrt{4D^*(t-T)}}.$$

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226 2.2.3. Linear source depletion ($\Gamma = 0.5$)

227 The analytical solution for the concentration distribution in the semi-infinite low-
 228 permeability zone for $C(z = 0, t > 0) = C_0 - kt$, is (Crank, 1975)

$$229 \quad C = C_0 \operatorname{erfc}(\zeta) - kt \left[\operatorname{erfc}(\zeta) - \frac{2(\zeta)}{\sqrt{\pi}} \exp(-(\zeta)^2) + 2(\zeta)^2 \operatorname{erfc}(\zeta) \right] \quad (8)$$

230 Note that Eq. (8) is only valid for the time prior to zero concentration in the source zone.

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232 2.2.4. Exponential Source Depletion ($\Gamma = 1$)

233 The analytical solution for the concentration distribution in the semi-infinite low-
 234 permeability zone for $C(z = 0, t > 0) = C_0 \exp(-\beta t)$ is (Carslaw and Jaeger, 1959)

$$235 \quad C = \frac{1}{2} C_0 \exp(-\beta t) \left[\exp(-\theta) \operatorname{erfc}(\zeta - \sqrt{-\beta t}) + \exp(\theta) \operatorname{erfc}(\zeta + \sqrt{-\beta t}) \right] \quad (9)$$

236 where $\beta = \frac{J_0}{M_0}$ and $\theta = z\sqrt{\frac{-\beta}{D^*}}$. Comparison of the analytical solutions Eqs. (8) and (9) with a
 237 numerical solution to Fick's second law, Eq. (S5) is shown (Fig. S3) to provide identical results
 238 ($E = 1$).

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240 2.2.5. Aquitard diffusive flux

241 The diffusive flux out of the low-permeability zone can be expressed by Fick's first law
 242 (Eq. (S1)). For the three boundary conditions examined, Eqs. (7), (8), and (9) respectively are
 243 substituted into Eq. (S1) and differentiated. The diffusive flux from the low-permeability zone at
 244 $z = 0$ is then expressed for a step-change in source concentration ($\Gamma = 0$):

$$245 \quad j_B(z = 0, t) = C_0 \eta \sqrt{\frac{D^*}{\pi}} \left(\frac{1}{\sqrt{t}} - \frac{1}{\sqrt{t-T}} \right) \text{ for } t > T \quad (10)$$

246 for linear source depletion ($\Gamma = 0.5$):

$$247 \quad j_B(z = 0, t) = \eta D^* \frac{(C_0 + 2kt)}{\sqrt{\pi D^* t}} \quad (11)$$

248 and for exponential source depletion ($\Gamma = 1.0$):

$$249 \quad j_B(z = 0, t) = C_0 \eta D^* \exp(-\beta t) \left[i \sqrt{\frac{\beta}{D^*}} \operatorname{erf}(i\sqrt{\beta t}) + \frac{\exp(\beta t)}{\sqrt{\pi D^* t}} \right] \quad (12)$$

250 where i is the imaginary unit and η is porosity. Note that Eq. (11), similar to Eq. (8), is also
 251 limited to only the time prior to zero concentration in the source zone.

252 The aquifer flux-average concentration, C_f , is expressed in terms of the back-diffusion
 253 flux, j_B , from the interfacial area between the low- and high-permeability zones, A_i , and the flow
 254 through the high-permeability zone, Q_h .

$$255 \quad C_f = \frac{j_B A_i}{Q_h} \quad (13)$$

The input parameters for bromide diffusion in the kaolinite layer were obtained from literature sources (Yang et al., 2014; Yang et al., 2015): molecular diffusion coefficient $D = 1.7 \times 10^{-4} \text{ m}^2/\text{d}$, retardation factor $R = 1$, tortuosity $\tau = 0.2$, and porosity $\eta = 0.6$. The effective diffusion coefficient was calculated using Eq. (S3).

2.2.6. Dimensionless diffusion length

The dimensionless diffusion length, Z_D (range $[0, \infty]$), illustrates the transferability of relatively simple models among physical systems, and assists in determining potential errors from applying semi-infinite analytical solutions to finite domains (Yang et al., 2015). The solute diffusion length scale (L_d) is an important component of the concentration profile equations

$$L_{d,in} = \sqrt{4D^*t} \quad (14)$$

$$L_{d,out} = \sqrt{4D^*(t - T)} \text{ for } t > T \quad (15)$$

where the subscripts in and out indicate respectively solute loading and unloading after the source is exhausted. For aquitards with finite thickness (L), the relative diffusion length (Z_D) is

$$Z_D = \frac{L_d}{L} \quad (16)$$

Low Z_D values indicate that the solute has not penetrated close to the full thickness of a finite aquitard, and simple semi-infinite analytical solutions may be applied. However, errors from applying semi-infinite analytical solutions to finite domains may increase with high Z_D values, which are indicative of a long solute diffusion distance relative to the finite aquitard thickness.

2.3. Goodness of fit

The coefficient of efficiency, E (Legates and McCabe, 1999; Nash and Sutcliffe, 1970), was used for evaluating the goodness of fit between the measured and calculated values. The

coefficient of efficiency ranges from negative infinity to 1 with higher values indicating better agreement:

$$E = 1.0 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (17)$$

where P is the calculated data, O is the measured data and $\bar{O}$ is the measured mean.

3. Results and discussion

3.1. Source strength functions

Bromide concentrations in the flow chamber influent that were generated to correspond to the three SSFs are shown in Fig. 2 along with corresponding PLM fits for $\Gamma = 0, 0.5$, and 1.0 using Eqs. (4a), (5), (4b). In these measured and simulated data, $t = 0$ was the bromide arrival time at the flow chamber inlet. The PLM accurately described the source dynamics with high E values of $0.99, 0.97$, and 0.99 . The PLM simulations for $\Gamma = 0.5$ and 1.0 are equivalent to Eqs. (5) and (4b) with $k = 666.6$ and $\beta = 0.13$.

3.2. Aquitard concentration profiles during forward and back diffusion

Simulated and measured concentration profiles in the 0.06 m kaolinite layer are shown in Fig. 3 for the three experiments with $\Gamma = 0.0, 0.5$, and 1.0 . For experiment I ($\Gamma = 0$), the measured bromide concentrations during 5 PVs of solute loading into the aquitard (forward diffusion) are well described by Eq. (6), with mean $E = 0.97$ (Fig. 3(a)). The bromide penetration distance in the kaolinite increased over time during constant source loading ($C = C_0$), resulting in a continuously negative aquitard-aquifer concentration gradient (Fig. 4), as shown by Yang et al. (2015).

Measured bromide concentration profiles during 15 PVs of water flooding ($C = 0$) that followed the solute loading period are shown in Fig. 3(b), along with profiles calculated using

Eq. (7). These profiles showed characteristic shapes of zero concentration at the aquifer-aquitard interface, increasing with depth in the aquitard to a peak and then decreasing again with depth. The instantaneous concentration change in the high-permeability layer reversed the concentration gradient (Fig. 4(a)), which triggered bromide back diffusion from kaolinite to the sand layer. The calculated bromide concentration profiles in the kaolinite layer matched the measured data well with mean $E = 0.89$ (range 0.76 to 0.95), for PVs = 6.3, 8.3, 11.7, and 20.3.

For experiment II ($\Gamma = 0.5$), solute loading for 10 PVs into the aquitard is shown in Fig. 3(c). The profiles calculated using Eq. (8) show good correspondence to the measured data for PVs = 2, 5.3, 8, and 10, with mean $E = 0.91$. Note that Eq. (8) is only valid for the time prior to zero concentration in the source zone (10 PVs (15 d) in experiment II). Early in the loading time (less than 5.3 PVs), the bromide concentration profiles in the kaolinite layer showed similar patterns to those for $\Gamma = 0$ (Fig. 3(a)) with a negative concentration gradient (Fig. 4(a)). However, decreasing concentration at the aquifer-aquitard interface during linear source depletion resulted in the initial negative concentration gradient (forward diffusion) reversing and becoming increasingly positive (back diffusion) starting at 5.3 PVs (Fig. 3(c) and 4(a)).

For experiment III ($\Gamma = 1.0$), the aquitard bromide concentration profiles calculated using Eq. (9) showed good agreement (mean $E = 0.85$) with data measured during 27 PVs of exponential source depletion (Fig. 3(d)). The profile shapes are similar to those in Fig. 3(c), with the bromide concentration at the aquifer-aquitard interface decreasing with time due to the decreasing source concentration. The negative concentration gradient was maintained during the first 4.7 PVs, indicating forward diffusion. The rate that the bromide concentration at the interface decreased was more rapid than for $\Gamma = 0.5$ (5.3 PVs), resulting in an earlier back diffusion initiation time.

In all experiments, E gradually decreased with experiment duration as a result of underestimation of the concentrations at penetration depths greater than 0.04 m. This discrepancy results from application of semi-infinite analytical solutions to finite domains with diffusion lengths greater than the thickness of the low-permeability layer (Yang et al., 2015). The threshold for accurate application of semi-infinite analytical solutions to finite domains with minimal errors is relative diffusion length $Z_D < 0.7$ which corresponds to approximately 8 PVs in these experiments (Yang et al., 2015).

3.3. Plume tailing behavior

The measured and simulated bromide effluent concentrations based on SSFs with $\Gamma = 0$, 0.5, and 1.0 are shown in Fig. 5. Note that the calculated BTCs were shifted by the estimated mean travel time from the flow chamber inlet to the outlet ($\delta t = 1$ PV). The three SSFs generated different back diffusion and BTC tailing responses (Fig. 5(a)). Adapting the three-stage framework of Sale et al. (2008a), we generalize by classifying plume behavior based on dissolution and diffusion timeframes: initial stage 1 of source dissolution and forward diffusion, followed by stage 2 with continued dissolution but decreased aquifer concentrations resulting in back diffusion, and a final stage 3 where dissolution is not significant but back diffusion continues.

For experiment I ($\Gamma = 0$), after loading concluded (6 PVs), the bromide concentration sharply decreased but with persistent tailing supported by the diffusive source in the low-permeability layer (Fig. 5(b)). The BTC tail simulated using Eq. (10) based on bromide diffusive flux out of the clay at $z = 0$ showed good agreement ($E = 0.98$) with the measured flux-averaged concentrations during the experiment period. The instantaneous change of the boundary

concentration from $C(z = 0, 0 < t \leq T) = C_0$ to $C(z = 0, t > T) = 0$ resulted in only two stages (stages 1 and 3) because there was effectively no time during which concentrations gradually decreased. After 15 PVs, the calculated BTC tailing concentrations were slightly underestimated. This discrepancy is likely related to applying semi-infinite analytical solutions to the relatively thin low-permeability zones used in these experiments, as noted above (Yang et al., 2015). Extending the analytical solution using the method of images to account for a finite aquitard (Eq. (S4)) (Yang et al., 2015) showed a slightly better fit ($E = 0.99$) for the BTC tail than without image sources (Eq. (10)) (Fig. 5(b)).

For experiment II ($\Gamma = 0.5$), all three stages proposed here were observed during the experiment period (Fig. 5(c)). In stage 1, the bromide effluent concentration gradually decreased as a result of linear source depletion during the first 6.3 PVs of loading (5.3 PVs of injection (Fig. 3(c)) plus estimated 1 PV mean travel time). Therefore, the decrease in concentration expected from linear source depletion was partially offset after 6.3 PVs by back diffusion from the low-permeability layer (stage 2). After dissolution was complete (11 PVs), the bromide concentration sharply decreased for a few PVs, followed by tailing behavior supported by back diffusion similar to experiment I (stage 3). In order to investigate the relative contributions of source dissolution and back diffusion to the plume behavior, the simulated BTC was calculated based on only source dissolution (Eq. (5)) for stage 1, superposition of source dissolution (Eq. (5)) and the flux-average concentration resulting from back diffusion (Eq. (11)) for stage 2, and only the back diffusion flux-average concentration (Eq. (10)) for stage 3. Note that since Eq. (11) is not valid after the source is exhausted, stage 3 was simulated using Eq. (10) by matching the calculated profile at 10 PVs in Fig. 3(c) using Eq. (7). The measured and simulated BTC concentrations showed good agreement for both stage 2 ($E = 0.98$) and 3 ($E = 0.98$).

For experiment III ($\Gamma = 1.0$), the gradual decrease in bromide effluent concentration after approximately 5 PVs of solute loading was controlled by the source loading function and was maintained due to the long source loading time (27 PVs) (Fig. 5(a)). Based on the concentration gradient reversal observed at 5.7 PVs in Fig. 3(d), back diffusion from the low-permeability zone also contributed to mass flux after this time. The relative contributions to the tailing behavior from back diffusion flux and dissolution for $\Gamma = 1$ are illustrated in Fig. 5(d). The measured effluent bromide concentrations are compared to the simulated influent (source dissolution from the SSF, Eq. (4b)) and effluent (source dissolution superposed with the flux-average concentration resulting from back diffusion (Eq. (12))). After stage 2 began with back diffusion initiation (5.7 PVs), the measured effluent bromide concentrations were higher than expected based solely on the SSF, and this discrepancy increased with time. The simulated values from dissolution coupled with back diffusion (Eqs. (4b) and (12)) showed good agreement with the measured data ($E = 0.98$).

In all experiments, the calculated BTC tail concentrations were slightly underestimated after 15 PVs (Fig. 5). As noted above, the use of finite-domain solutions would reduce these discrepancies (Yang et al., 2015). In addition, back diffusion began at approximately 5 PVs (without δt) but showed different trends. For experiment I, calculated diffusive flux out of the low-permeability layer was initially very high due to the instantaneous change of the boundary concentration from $C(z = 0, 0 < t \leq T) = C_0$ to $C(z = 0, t > T) = 0$. But as the concentration gradient decreased, back diffusion flux decreased relatively rapidly (Fig. 4). On the other hand, back diffusive flux for experiment III was initially very low because the concentration gradient reversed only gradually at approximately 4.7 PVs (Fig. 3(d)). For experiment II, the trend in back diffusive flux was initially similar to experiment III. But after the source was exhausted (10

PVs), the flux trend dramatically reverted to a shape similar to experiment I. After 15 PVs, the back diffusion flux for all cases showed similar slightly decreasing trends.

3.4. Aquifer-aquitard concentration gradient

The driving force for solute forward and back diffusion is the concentration gradient at the aquifer-aquitard interface. Here we examine how SSF affects the magnitude of this gradient, which controls back diffusion magnitude and duration, as well as the timing of back diffusion onset. The aquifer-aquitard concentration gradient during forward diffusion is shown in Fig. 6(a) as a function of the diffusion length scale, L_d , with a constant source concentration boundary ($\Gamma = 0$) (Eq. (6)). The commencement of solute loading produces a large (negative) gradient from the aquifer to the aquitard, and as forward diffusion progresses, the absolute value of the gradient sharply decreases until approximately $L_{d(in)} = 0.4$ m, after which gradient slowly approaches zero (i.e., the solute concentrations in the aquifer and the aquitard close to the interface are similar). This result indicates that most of the contaminant mass that is stored in aquitards during forward diffusion occurs within $L_{d(in)} \leq 0.4$ m.

A similar analysis for back diffusion is illustrated in Fig. 6(b) where the gradient is shown as a function of $L_{d(out)}$ for different values of $L_{d(in)}$ using Eq. (7). The instantaneous change of the boundary concentration from $C(z = 0, 0 < t \leq T) = C_0$ to $C(z = 0, t > T) = 0$ generates a large positive gradient that then sharply decreases. The diffusion length scale during back diffusion ($L_{d(out)}$) required for the gradient to approach zero increases with $L_{d(in)}$ (a larger effective diffusion coefficient or a longer loading time). This result illustrates the control of longer solute loading times on larger and longer-duration back diffusive flux.

The aquifer-aquitard concentration gradient during forward and back diffusion with linear source depletion ($\Gamma = 0.5$) (Eq. (8)) is shown in Fig. 6(c). The peak gradient driving back diffusion decreases as $L_{d(in)}$ increases because the discrepancy in solute concentration between aquifer and aquitard decreases as the solute loading time increases for the linear SSF. Thus, for $\Gamma = 0.5$, back diffusive flux decreases with increased loading time, contrary to the result for $\Gamma = 0$ (Fig. 6(b)). Back diffusion begins at approximately $0.7L_{d(in)}$. For example, for experiment II $L_{d(in)} = 0.046$ m and back diffusion started at $L_d = 0.032$ m $= 0.7L_{d(in)}$ (Fig. 4(a)). The three stages for plume behavior are also illustrated in Fig. 6(c). For $L_{d(in)} = [0.1, 0.5, 0.9, 1.3]$ m, stage 1 (dissolution and forward diffusion) occurred until approximately $0.7L_{d(in)} = [0.07, 0.36, 0.64, 0.92]$ m, the remaining portion (0.3) of $L_{d(in)}$ was stage 2 (dissolution and back diffusion), while stage 3 (back diffusion only) occurred after $L_{d(in)}$.

A similar analysis for the gradient change during forward and back diffusion with exponential source depletion ($\Gamma = 1$) is illustrated in Fig. 6(d). For exponential SSF, dissolution continues indefinitely and $L_{d(in)}$ was thus operationally defined as the time required for reduction to $C/C_0 = 0.001$. Exponential depletion reduced source concentrations faster than linear depletion at early times, and back diffusion initiation times were therefore earlier for the former: approximately $0.35L_{d(in)}$, ($L_d = [0.035, 0.18, 0.31, 0.46]$ m for the $L_{d(in)}$ values shown in Fig. 6(d)). For example, in the third experiment, the time required for bromide to reduce to $C/C_0 = 0.001$ was 53 d ($L_{d(in)} = 0.086$ m) and back diffusion began at 7 d ($L_d = 0.031$ m $= 0.35L_{d(in)}$). In Fig. 6(d), plume behavior stages 1 and 2 were observed: the relatively-short duration stage 1 ($0.35L_{d(in)}$) and long-duration stage 2 (the rest of L_d). The peak back diffusion gradient also decreases as $L_{d(in)}$ increases, similar to Fig. 6(c).

This gradient analysis illustrates how back diffusion risk varies based on SSF. Among SSFs used in this study, the plume behavior caused by instantaneous concentration change ($\Gamma = 0$) results in the greatest risk of back diffusion with high flux at early times during stage 3 after the source is exhausted. For exponential depletion ($\Gamma = 1$), early reduction in aquifer source zone mass results in lower initial back diffusive flux from the aquitard. As the source zone reduction rate increases, stage 2 (initiation of back diffusion) occurs earlier. The finding of reduced back diffusion risk as Γ increases is consistent with previous work (Brown et al., 2012). The magnitude of back diffusion flux increases with increased contaminant loading time for $\Gamma = 0$, but decreases with increased loading time for $\Gamma > 0$.

However, to assess the total effect on groundwater quality, the back diffusion flux must be considered in concert with source dissolution. During stage 1 (source dissolution with no contribution from back diffusion), the order of exposure risk, based on highest flux-averaged concentration in the aquifer, for the three SSFs is $\Gamma = 0 > 0.5 > 1$ (Fig. 5(a)). During stage 2 (source dissolution and back diffusion), this order is reversed, with the most-gradual source dissolution SSF ($\Gamma = 1$) leading to higher aquifer concentrations over an extended time (Fig. 5(a)). Thus, while $\Gamma = 1$ results in the lowest back diffusion flux (Fig. 6(d)), it would be misleading to conclude that this SSF is associated with the lowest risk. Simulated effluent concentrations for $\Gamma = 1$ (based on experiment III) using Eqs. (4b) and (12) show that this SSF maintains the highest aquifer concentrations until approximately 53 PVs (Fig. 7). It is only after this point, in the final stages of plume evolution that the order of highest aquifer concentrations reverses again to $\Gamma = 0 > 0.5 > 1$.

4. Conclusions

This study demonstrated the effects of source depletion dynamics for $\Gamma = 0, 0.5$, and 1.0 with both laboratory experiments and analytical solutions. We used experimental results from a nonreactive solute, bromide, to validate the analytical solutions, but the conclusions derived from the tracer results are expected to be applicable to other solutes, including dissolved constituents of DNAPLs. The effective diffusion coefficient, D^* , Eq. (S3), which includes retardation effects (R or K_d) caused by the partitioning of contaminants between solution phase and aquifer and aquitard materials, directly incorporates these processes in the solutions for concentration profiles in aquitards, aquitard-aquifer concentration gradient, and plume tailing behavior in aquifers.

The analytical solutions with coupled source depletion models predicted aquitard concentration profiles and flux-averaged aquifer concentrations, and defined the stages of plume evolution and the characteristic dimensionless times of transitions between stages. The solutions were successfully validated with high coefficients of efficiency (mean $E = 0.91$). We defined three types of plume tailing behavior caused by the combined effects of source depletion and back diffusion. We used the experimental results and modeling framework to assess which SSFs correspond to the highest aquifer concentrations during each plume stage.

Previous studies have mainly employed instantaneous or step changes in concentration boundary condition for diffusion modeling in low-permeability zones (Chapman and Parker, 2005; Parker et al., 2004; Yang et al., 2015). However, theoretical considerations and laboratory experiments suggest that real heterogeneous sites converge to exponential source depletion (Chen and Jawitz, 2009). Similarly, an empirical investigation of BTCs at 23 contaminated sites indicated that exponential source depletion ($\Gamma > 0.5$) showed better fits with the field data (Newell et al., 2006). Hence, the results shown here for $\Gamma = 0.5$ and 1 will be of use for assessing

back diffusion risks under more realistic scenarios where source depletion is gradual and not instantaneous.

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Figures

Fig. 1. Conceptual illustration (a) of DNAPL source and plume zones where the dissolved contaminant plume (shaded area) is crossing the source zone control plane, and schematic of laboratory experimental apparatus (b), with a CSTR as a model of DNAPL source zone dissolution dynamics, and a flow chamber as a model of plume transport through an aquifer with an adjacent aquitard.

Fig. 2. Measured (markers) and simulated (lines) source depletion dynamics for $\Gamma = 0, 0.5$, and 1.0 . Agreement with measured data is provided based on the coefficient of efficiency, E .

Fig. 3. Measured and simulated bromide concentration profiles in the 0.06 m kaolinite layer during (a) forward and (b) back diffusion for experiment I ($\Gamma = 0$), (c) experiment II ($\Gamma = 0.5$), and (d) experiment III ($\Gamma = 1$). Simulations are from Eqs. (6), (7), (8), and (9) and are labeled in pore volumes (PVs). Agreement with measured data is provided based on the coefficient of efficiency, E . Insets are the aquifer input boundary conditions representing three SSFs.

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Fig. 4. Gradient (a) of the concentration profile and diffusive flux (b) out of kaolinite as a function of PVs and L_d for three experiments.

Fig. 5. Measured (markers) and simulated (lines) breakthrough curves for bromide in experiments I ($\Gamma = 0$), II ($\Gamma = 0.5$), and III ($\Gamma = 1$). (a) Measured BTC tail for experiment I compared to simulations with (Eq. (S4)) and without (Eq. (10)) image sources. Measured and simulated concentrations for influent (Eqs. (5) and (4b)) and effluent for experiments II (b) and III (c). Correspondence with measured data is reported based on efficiency, E and δt indicates the estimated mean travel time from the source zone to the monitoring location.

Fig. 6. Aquifer-aquitard concentration gradient as a function of diffusion length scale L_d for forward diffusion and back diffusion with $\Gamma = 0$ (a and b, Eqs. (6) and (7)), $\Gamma = 0.5$ (c, Eq. (8)), and $\Gamma = 1$ (d, Eq. (9)). All gradients were calculated using concentration profiles in aquitard between $z = 0$ and 0.001 m.

Fig. 7. Extended-duration simulated breakthrough curves for experiments I ($\Gamma = 0$), II ($\Gamma = 0.5$), and III ($\Gamma = 1$).