

Plumes: Matrix Diffusion and Back Diffusion

1. DIFFUSION INTO AND OUT OF LOW PERMEABILITY ZONES

The subsurface environment typically has zones of different permeabilities, such as sand layers with embedded clay or silt lenses. A typical sequence of geological formations in valleys (where often cities are located due to the proximity to rivers) are weathered bedrocks (e.g., mudstones, limestones, sandstones, or igneous rocks) with low permeabilities followed by glacial sand and gravel deposits (which are very heterogeneous). These are topped by alluvial loam layers, which, to a large extent, may come from eroded soils amplified after the onset of agriculture. Thicknesses of these layers are highly variable (e.g., the top layer often has "windows" or is removed in urban areas for construction purposes). Glacial sand and gravel layers host valuable groundwater resources, which typically are used for drinking water production. Also, fractured sedimentary aquifers (limestones and sandstones) are important sources of drinking water; here groundwater flow occurs predominantly in the fractures while solute exchange with the rock matrix is by molecular diffusion. In both cases permeable units are surrounded by low permeability domains and the latter may store contaminants for very long time periods. After pollutant input stopped (application of pesticides ended or NAPL were removed), "back diffusion" out of the low permeability domain starts. An important feature of back diffusion is that concentrations are independent on compound and porous medium properties.

A typical example of contamination of low permeability domains are DNAPL spills in urban or industrialized areas. For example, DNAPLs would infiltrate into the ground(water) until they hit a low permeability layer (e.g., weathered mudstones or clays) and form pools. DNAPL constituents then diffuse continuously into the low permeability layer as long as the source exists (see Fig. 1.1).

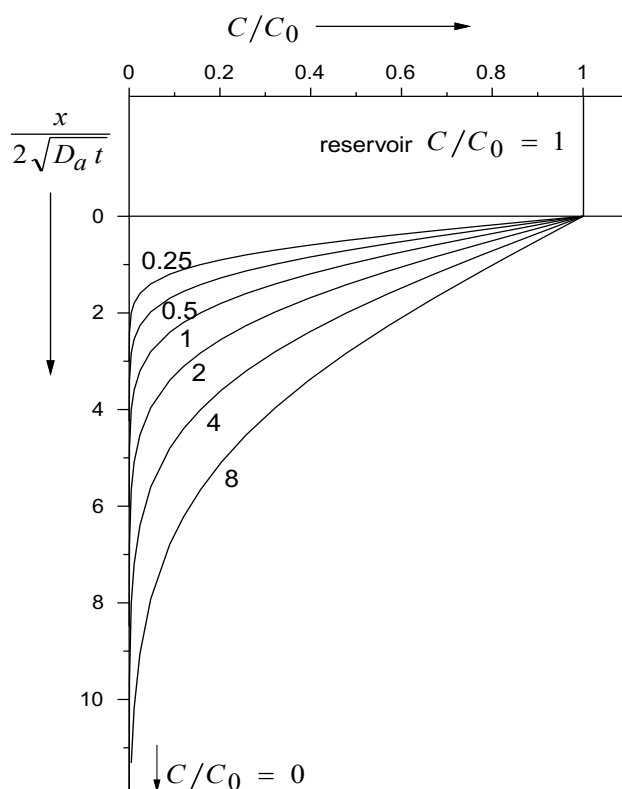


Fig. 1.1: Concentration profile during contaminant diffusion into a low permeability clay layer; normalized concentration vs. dimensionless distance calculated from the analytical solution for semi-infinite diffusion:

$$\frac{C}{C_0} = \operatorname{erfc}\left(\frac{z}{2\sqrt{D_a t}}\right)$$

Numbers on lines denote dimensionless time (i.e. arguments in the complimentary error function (erfc); "reservoir" may represent a landfill or any other long term contaminant source such as a DNAPL pool with constant concentrations at the top boundary.

After source removal by dissolution or active remediation (e.g., excavation of a landfill) back diffusion starts at the upper part of the low permeability zone and concentrations decrease, but at larger depth downward diffusion still continues as shown in Fig. 1.2. This causes hysteresis, which is frequently observed during remediation of contaminated sites. If the back diffusion time scale matches the exposure time (t_e) we still have significant contaminant mass in the low permeability zone. Since the porous medium is (semi-)infinite, back diffusion theoretically lasts for infinite times.

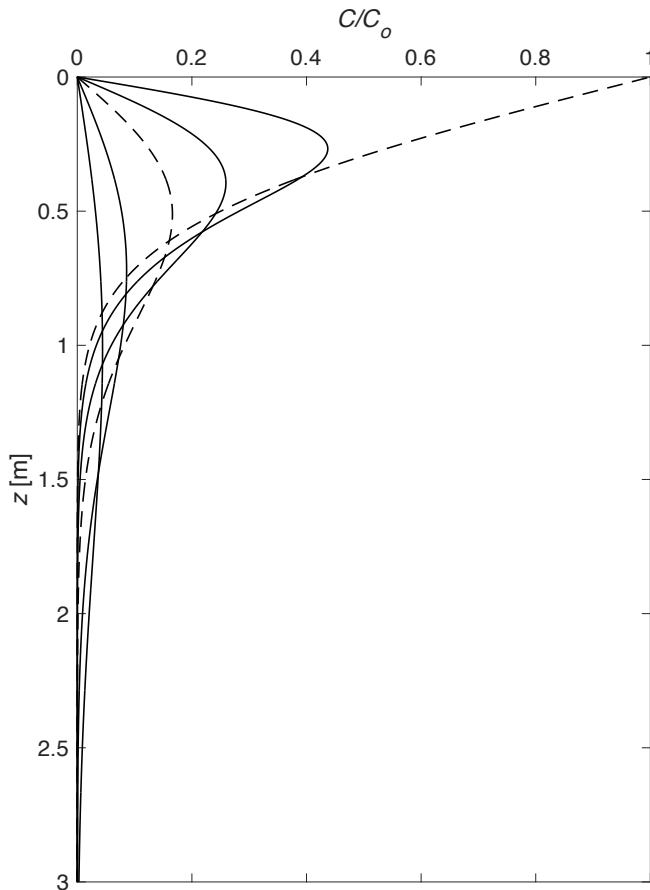


Fig. 1.2: Concentration profiles after 30 years of diffusion into a low permeability clay layer (dashed line) followed by back diffusion after 5, 15, 30 (dashed line) 100 and 200 years (apparent diffusion coefficient = $1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for TCE in weathered “Opalinuston” (Middle Jurassic mudstone) after Grathwohl, 1998).

The vertical concentration profiles for back diffusion may be calculated based on simple analytical solutions of the diffusion equation:

$$\frac{C}{C_0} = \operatorname{erfc}\left(\frac{z}{2\sqrt{D_a(t_e + t)}}\right) - \operatorname{erfc}\left(\frac{z}{2\sqrt{D_a t}}\right) \quad (1.1)$$

For practical purposes during remediation, the residual contaminant mass and fluxes out of the low permeability zone are more relevant. The mass in the porous medium (M_{te}) after exposure time (t_e) is:

$$M_{te} = 2 C_0 \alpha \sqrt{\frac{D_a t_e}{\pi}} \quad [\text{M L}^{-2}] \quad (1.2)$$

α denotes the rock capacity factor: $\varepsilon + K_d \rho$ (see also chap. 2). The solute mass (M_b) which left the porous medium during back diffusion is (Liedl, 1994, see Grathwohl, 1998):

$$M_b = 2 C_0 \alpha \sqrt{\frac{D_a t_e}{\pi}} \left(1 - \sqrt{1 + t_e/t} + \sqrt{t_e/t} \right) \text{ [M L}^{-2}\text{]} \quad (1.3)$$

This may be normalized to M_{te} (division by eq. 1.2):

$$\frac{M_b}{M_{te}} = 1 - \sqrt{t/t_e + 1} + \sqrt{t/t_e} \quad (1.4)$$

Now the relative mass during back diffusion is independent of the diffusion coefficient and sorption properties. It just depends on the ratio of the back diffusion time to the exposure time (t/t_e). For larger time periods this reduces further to:

$$\frac{M_b}{M_{te}} = 1 - \frac{1}{2} \sqrt{t_e/t}$$

and the relative mass left in the porous medium ($1 - M_b/M_{te}$) is: (1.5)

$$\frac{M}{M_{te}} = \frac{1}{2} \sqrt{t_e/t}$$

Ultimately eq. 1.4 becomes unity (= 1). As shown in Fig. 1.3 it takes about 30 times the exposure time to remove more than 90% of the initial mass just by back diffusion. Typically, DNAPL pools exist for decades and thus remediation times scale may easily amount to centuries to millennia.

In order to get concentrations in overlying groundwater, the back diffusion fluxes are needed which are simply given by the time derivatives of eq. 1.5:

$$\frac{F}{M_{te}} = \frac{1}{4} \sqrt{t_e/t^3} \quad (1.6)$$

Now we get a relative decrease of the back diffusion flux which scales with $t^{-3/2}$ as shown in Fig. 1.4. Such real world data were observed in reactive tracer experiments on radionuclide transport in fractured rocks at the Grimsel test site in Switzerland (Heer and Haderman, 1994).

For the absolute fluxes we have to account for M_{te} (from eq. 1.2):

$$F = 2 C_0 \alpha \sqrt{\frac{D_a t_e}{\pi}} \frac{1}{4} \sqrt{t_e/t^3} = \frac{1}{2} C_0 \alpha t_e \sqrt{\frac{D_a}{\pi t^3}}$$

and the extended solution is (time derivatives of eqs. 1.3 or 1.4): (1.7)

$$F = 2 C_0 \alpha \sqrt{\frac{D_a t_e}{\pi}} \frac{1}{2} \left(\frac{1}{\sqrt{t/t_e}} - \frac{1}{\sqrt{t/t_e} + 1} \right) = C_0 \alpha \sqrt{\frac{D_a}{\pi t}} \left(1 - \frac{1}{\sqrt{1 + t_e/t}} \right)$$

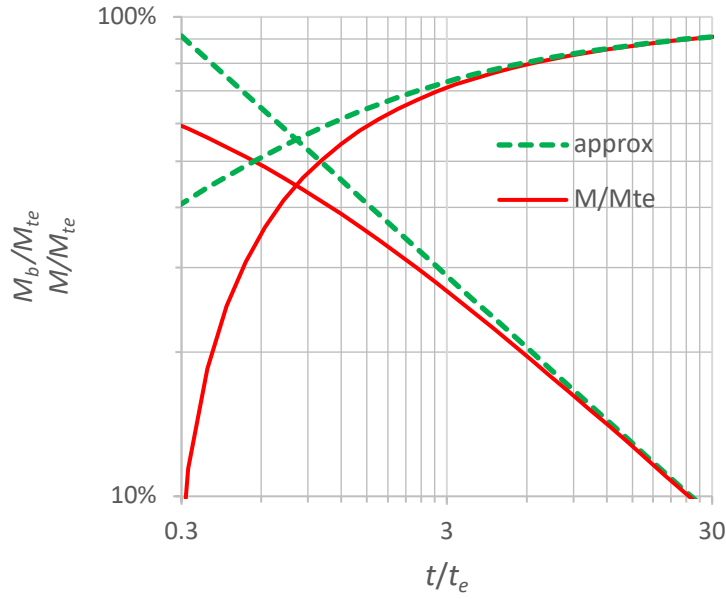


Fig. 1.3: Relative mass in the porous medium during back diffusion (M/M_{te} , descending lines) and relative mass which has left the low permeability domain (M_b/M_{te} , ascending lines) vs. t normalized to the exposure time t_e ; after $t/t_e = 10$ still 15% of the original solute are in the low permeability domain.

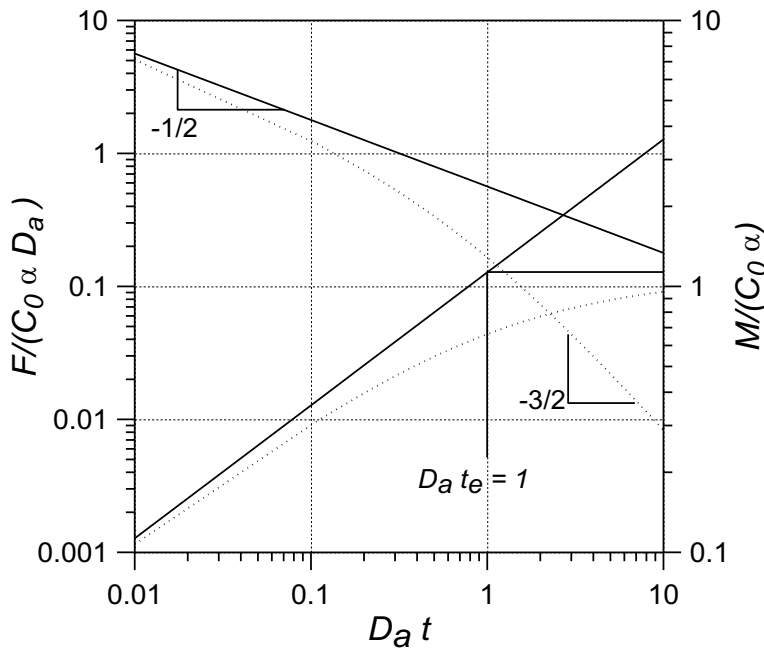


Fig. 1.4: Diffusive fluxes into (solid lines) and out (dotted lines) of a semi-infinite medium (descending lines) and total mass (ascending lines); from Grathwohl (1998).

2. TRANSPORT IN FRACTURED AQUIFERS WITH MATRIX DIFFUSION

2.1 BREAKTHROUGH CURVES AND RETARDATION FACTORS

Advective transport of a concentration front (constant source) in a fracture can be calculated with a simple analytical solution which accounts for retarded pore diffusion in the rock matrix (Rahman et al., 2004):

$$\frac{C}{C_o} = \operatorname{erfc} \left(\frac{R_{im} \varepsilon \sqrt{D_a} \frac{x}{v}}{b \sqrt{4 \left(t - \frac{x}{v} \right)}} \right) = \operatorname{erfc} \left(\frac{\sqrt{D_e \alpha} \frac{x}{v}}{2 b \sqrt{t - \frac{x}{v}}} \right) \quad (2.1)$$

R_{im} and ε denote the retardation factor and the porosity of the rock matrix (immobile phase). D_a is the apparent diffusion coefficient in the rock matrix; t , x and v denote time, distance along fracture and the flow velocity in the fracture (x/v is the travel time of water in the fracture). b is the half aperture of the fracture or the inverse of the surface to volume ratio of a channel (then the solution also applies to other geometries and cylindrical pores, see Rahman et al., 2004). R_{im} is given by $1 + K_d \rho / \varepsilon$ (ρ is the bulk density of the rock matrix ($= (1-\varepsilon) \rho_{solids}$)) and the product of $R_{im} \varepsilon$ is the rock capacity factor $\alpha = \varepsilon + K_d \rho$. D_a is the ratio of the effective diffusion coefficient (D_e) and α (or the ratio of the pore diffusion coefficient (D_p) and R_{im}):

$$D_a = \frac{D_e}{\alpha} = \frac{D_p}{R_{im}} = \frac{D_{aq} \varepsilon^m}{\varepsilon + K_d \rho} = \frac{D_{aq} \varepsilon^{m-1}}{1 + K_d \frac{\rho}{\varepsilon}} \approx \frac{D_e}{K_d \rho} = \frac{D_p}{K_d \frac{\rho}{\varepsilon}} \quad (2.2)$$

m is an empirical exponent (from Archies law) and often close to 2 (Boving and Grathwohl, 2001). D_e thus mostly depends on the matrix porosity (and not much on the compound); for conservative solutes α reduces to ε ($K_d = 0$).

According to eq. 2.1 the solute breakthrough starts for $t > x/v$ with a fast (initially almost linear) increase followed by slower and slower increase (“tailing”) and it takes almost 5 times longer to reach $C/C_o = 0.75$ compared to $C/C_o = 0.5$ (50% breakthrough) as illustrated in Fig. 2.1.

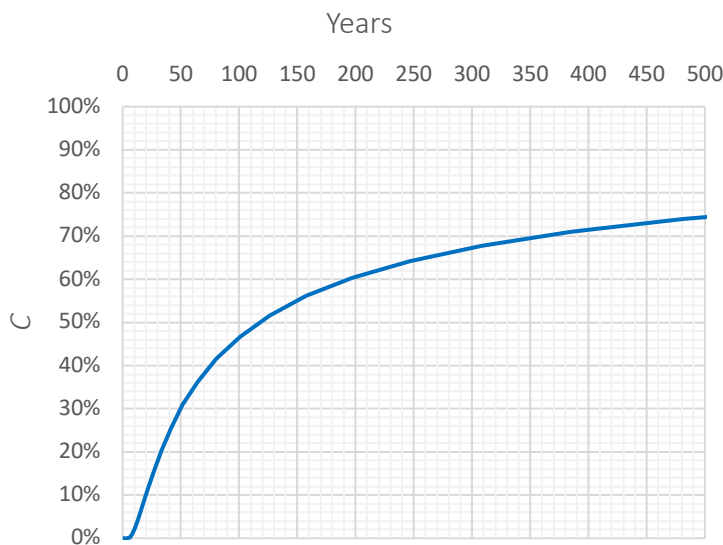


Fig. 2.1: Breakthrough of a solute in a fracture retarded by matrix diffusion (eq. 2.1); $K_d = 10$, $\varepsilon = 0.06$, $b = 1$ mm, $x/v = 100$ d, $x/v = 100$ d.

Retardation factor from boundary layers. In order to predict the advancement of a solute front propagating in a fracture retardation has to be considered. There are many ways to derive retardation factors in solute transport (R_m) – the most simple one is just based on mass balance considerations (see the appendix for other approaches). R_m then is the ratio of total solute mass in the system to mobile mass in the fracture. The total solute mass in the rock matrix may be calculated based on a boundary layer approach as shown in Fig. 2.2. The mobile mass is given by the solute concentration in the fracture (C_w) times the distance traveled in the fracture (x) and its half aperture (b). R_m thus becomes:

$$R_m = \frac{\text{total}}{\text{mobile}} = \frac{C_w b x + C_w x \alpha \sqrt{D_a t}}{C_w b x} = 1 + \frac{1}{b} \alpha \sqrt{D_a t} = 1 + \frac{1}{b} \sqrt{D_e \alpha t} \quad (2.3)$$

$x C_w \alpha \sqrt{D_a t}$ represents the solute mass in the matrix on one side of the fracture and $C_w b x$ is the mobile mass in the half aperture. C_w and x ($= v t / R_m$) are not exactly known, but drop out anyway. Thus, this approach can be used for different scenarios (without exact knowledge of x and C_w). The thickness of the boundary layer in the rock matrix is not exactly known and depends on the scenario, but may be approximated by the mean square displacement $\sqrt{D_a t}$ (e.g., representing half of the boundary concentration for an advancing front, see Fig. 1.1).

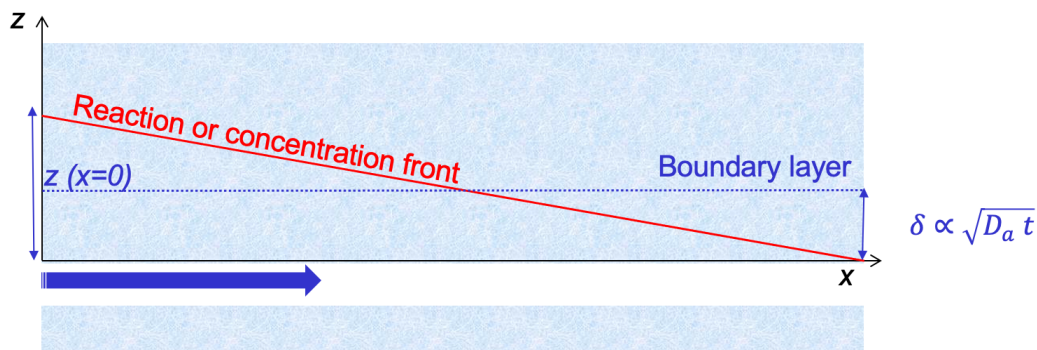


Fig. 2.2: Fracture and rock matrix illustrating a boundary layer representation of a sorbing or reactive solute concentration front

For strong retardation ($R_m \gg 1$) the second term in in eq. 2.3 becomes much larger than 1 and reduces to just the last term:

$$R_m = \frac{1}{b} \alpha \sqrt{D_a t} = \frac{1}{b} \sqrt{D_e \alpha t} \quad (2.4)$$

Alternatively, this solution can be derived from eq. 2.1 if a certain value for C/C_o is assumed as shown in Appendix 1 (e.g., $C/C_o = 0.478$ for an argument of erfc of 0.5, see Fig. 2.1). R_m increases with the square root of time and the larger the aperture the smaller R_m becomes.

2.2 BREAKTHROUGH FOLLOWED BY BACK DIFFUSION

In most cases, we don't have a continuous input of a solute, but only for a certain time period (exposure time t_e) before it stops. Rahman et al. (2004) derived an analytical solution for transport in a squared macropore (surface to volume ratio = 4/aperture) which can be applied to fractures (surface to volume ratio = 2/aperture), see also eq. 2.1:

$$\frac{C}{C_0} = \operatorname{erfc} \left(\frac{\sqrt{D_e \alpha} \frac{x}{v}}{2 b \sqrt{t - \frac{x}{v}}} \right) - \operatorname{erfc} \left(\frac{\sqrt{D_e \alpha} \frac{x}{v}}{2 b \sqrt{t - \frac{x}{v} - t_e}} \right) \quad (2.5)$$

One example of limited input of a solute followed by back diffusion from the rock matrix is the application of the pesticide atrazine on agricultural land, which stopped after about 33 years of application in 1991 (but we still find it in fractured aquifers). Figs. 2.3 compares the breakthrough of a tracer and atrazine and Fig. 2.4 illustrates transport behavior in space and time.

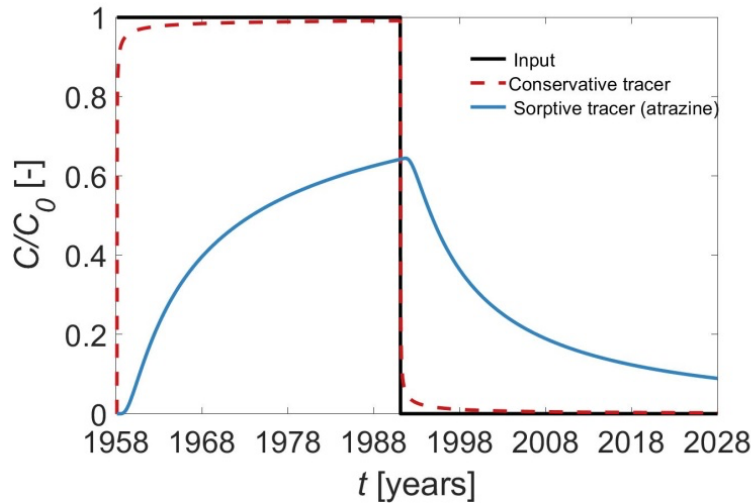


Fig. 2.3: Breakthrough curves of conservative (red) and sorbing tracer atrazine (blue) next to the fracture inlet (residence time of water: $x/v = 0.1$ year) calculated with eq. 2.5 for an input period from 1958-1991 (33 years, black line); aperture = 0.2 mm, $\epsilon = 1\%$, $v = 0.5 \text{ m d}^{-1}$, $K_d = 7 \text{ l kg}^{-1}$

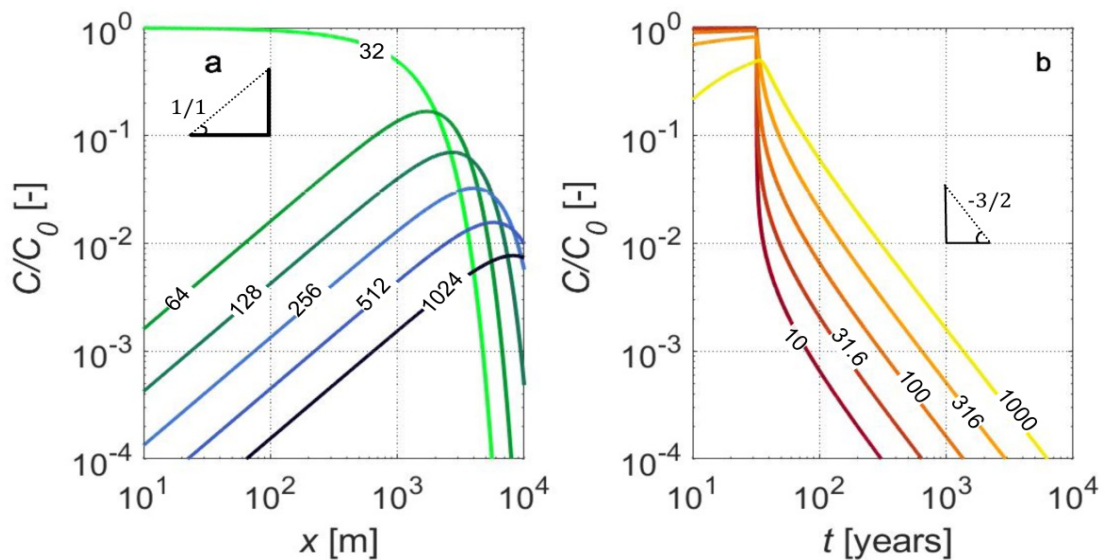


Fig. 2.4: Transport of a solute (top, no sorption) and atrazine (bottom) in a fracture with aperture of 1 mm (left, numbers: time in years) after 33 years of input and tailing concentrations after breakthrough (right, numbers: distance in meters); note the linear increase of concentrations with distance during back diffusion until the peak is reached (a). Since the peak concentration decreases linear with time and the distance traveled by the peak propagates with the square root of time the tailing concentrations (upstream) decrease with a slope of $t^{-3/2}$ (b); $K_d = 10 \text{ l kg}^{-1}$, hydraulic gradient 1‰, matrix porosity 3%.

2.3 APPROXIMATIONS FOR BACK-DIFFUSION

Approximations only apply for certain scales in time or space, but allow to get general insights on how concentrations in a fracture may develop. The approximation for the tailing part ($t > x/v$) of the analytical solution (eq. 2.5) is (for small arguments $\text{erfc}(\beta) = 1 - \beta \sqrt{2/\pi}$):

$$\frac{C}{C_o} = \frac{1}{b} \frac{x}{v} \sqrt{\frac{D_e \alpha}{\pi t}} \left(\frac{1}{\sqrt{1 - \frac{t_e}{t}}} - 1 \right) \quad (2.6)$$

and for $t \gg t_e$ the term in parenthesis goes to $t_e/(2t)$ and thus we get:

$$\frac{C}{C_o} = \frac{1}{b} \frac{x}{v} \sqrt{\frac{D_e \alpha}{\pi t}} \frac{t_e}{2t} = \frac{x}{2b} \frac{t_e}{v} \sqrt{\frac{D_e \alpha}{\pi t^3}} \quad (2.7)$$

In the long term, concentrations in the fracture drop with $t^{-3/2}$ compared with $t^{-1/2}$ for other diffusion phenomena. Concentrations decrease slower with increasing exposure time and the square root of sorption capacity. Increasing aperture and flow velocity in the fracture accelerate concentration decrease.

The distance X_{max} traveled by a certain “maximum” concentration may be estimated by introducing a retardation factor. For instance, for $R_m = 1 + 1/b \sqrt{\frac{4}{\pi} D_e \alpha t} \approx 1/b \sqrt{\frac{4}{\pi} D_e \alpha t}$ we get:

$$X_{max} = t \frac{v}{R_m} \approx \frac{b v t}{\sqrt{\frac{4}{\pi} D_e \alpha t}} = b v \sqrt{\frac{\pi t}{4 D_e \alpha}} \quad (2.8)$$

Inserting X_{max} (eq. 2.8) for x in eq. 2.6:

$$\frac{C_{max}}{C_o} = \frac{b v \sqrt{\frac{\pi t}{4 D_e \alpha}}}{b v} \sqrt{\frac{D_e \alpha}{\pi t}} \left(\frac{1}{\sqrt{1 - \frac{t_e}{t}}} - 1 \right) = \sqrt{\frac{1}{4}} \left(\frac{1}{\sqrt{1 - \frac{t_e}{t}}} - 1 \right) \quad (2.9a)$$

Inserting X_{max} (eq. 2.8) for x in the long term approximation (eq. 2.7) results in:

$$\frac{C_{max}}{C_o} = \frac{b v \sqrt{\frac{\pi t}{4 D_e \alpha}}}{2 b v} t_e \sqrt{\frac{D_e \alpha}{\pi t^3}} = \frac{t_e}{4 t} \quad (2.9b)$$

This simple approximation was also reported by Petrova et al. (2023) using a heuristic approach by “mapping” the analytical solution for the peak concentration. Since the peak decays linear with time (eq. 2.9b) but moves with the square root of time (eq. 2.8) the concentrations upstream of the peak decrease with $t^{-3/2}$. These approximations apply reasonably well for $t \gg t_e$. A better fit at early times is obtained by:

$$\frac{C_{max}}{C_o} = \frac{1}{1 + 4 \left(\frac{t}{t_e} - 1 \right)} \quad (2.9c)$$

which reduces to eq. 2.9b for long times (and = 1 for $t = t_e$; valid for $t / t_e \geq 1$). These simple equations (2.9a-c) for C_{max}/C_o have practical consequences since relative concentrations at any location are independent on flow fields, solute or rock properties and they will continue to drop

with time (e.g., always stay below the legal limit if this is larger than C_{max}). If t is twice t_e then C_{max}/C_o is 0.2 (eq. 2.9c), 0.233 (eq. 2.9a) or slightly underestimated by eq. 2.9b at 0.125. The “decay” of the peak concentration during back diffusion again thus is independent on the properties of the porous medium and solute as already observed for the relative mass in porous rock matrix in chap. 1:

$$\frac{M}{M_{te}} = \sqrt{1 + \frac{t}{t_e}} - \sqrt{\frac{t}{t_e}} \text{ and for } t \gg t_e \Rightarrow \frac{M}{M_{te}} = \sqrt{\frac{t_e}{4t}} \quad (2.10)$$

M_{te} is here the solute mass in the rock matrix after exposure time ($M_{te} = 2 C_o \sqrt{(D_e \alpha t_e)/\pi}$). M/M_{te} only depends on the ratio t/t_e . Back diffusion rates become independent on sorption and matrix diffusion if normalized to M_{te} .

Note, that eq. 2.8 gives not exactly the peak location, for which Petrova et al. (2023) report following empirical relationship:

$$X_{max} \approx \frac{b v \left(t - \frac{t_e}{\pi} \right)}{\sqrt{\frac{D_e \alpha t}{2}}} = b v \left(1 - \frac{t_e}{t \pi} \right) \sqrt{\frac{2 t}{D_e \alpha}} \quad (2.11a)$$

Realizing that t_e/t is proportional to the concentration ratio ($C_{max}/C_o = t_e/(4t)$) allows to express eq. 2.11a as a function of the relative peak concentration which for small C_{max}/C_o (< 0.1) or for $t \gg t_e$ allows a simple approximation:

$$X_{max} = b v \left(1 - \frac{4 C_{max}}{\pi C_o} \right) \sqrt{\frac{2 t}{D_e \alpha}} \approx b v \sqrt{\frac{2 t}{D_e \alpha}} \quad (2.11b)$$

This would correspond to a slightly different retardation factor compared to the one used in eq. 2.8 ($R_m \approx 1/b \sqrt{\frac{1}{2} D_e \alpha t}$). An improved approximation for small values of X_{max} is possible using a simple correction term (in parenthesis under the square root):

$$X_{max} = b v \sqrt{\frac{2 t \left(1 - \left(\frac{t_e}{t} \right)^2 \right)}{D_e \alpha}} \quad (2.11c)$$

Note, eqs 2.11a-c are empirical and based on “trial and error”, fits with the analytical solution are shown in Fig. 2.6.

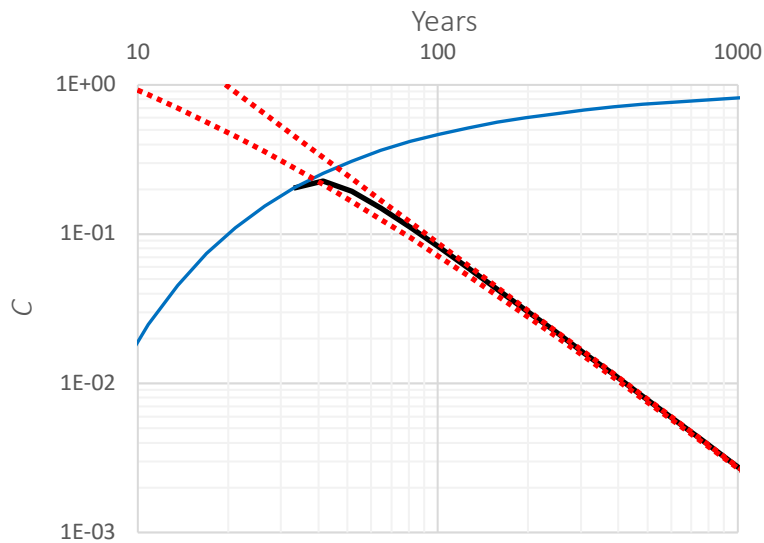


Fig. 2.5: Comparison of analytical solution and long term approximations in red (30 years exposure time); blue: breakthrough of the solute for continuous input, black: decrease after input stopped, red: approximations (eqs. 2.6 and 2.7; $K_d = 10$, $\varepsilon = 0.06$, $b = 1$ mm, $x/v = 100$ d).

Nonlinear sorption. In back diffusion the mass of the contaminant in the rock matrix drops with the square root of time (eq. 2.10.), while the aqueous concentration in the fracture drops even more rapidly (eqs. 2.7, 2.9, Fig. 2.5). If concentrations change a lot, e.g., during extended tailing, nonlinear sorption may become relevant. Since exponents of Freundlich sorption isotherms are typically below one, K_d values increase with decreasing concentrations; the ratio of K_d values scales with the ratio of the concentrations (e.g., low/high) to the exponent $(1/n-1)$, where $1/n$ here denotes the Freundlich exponent; for example, if the concentration drops by a factor of 10, K_d increases by a factor of 2 for $1/n = 0.7$.

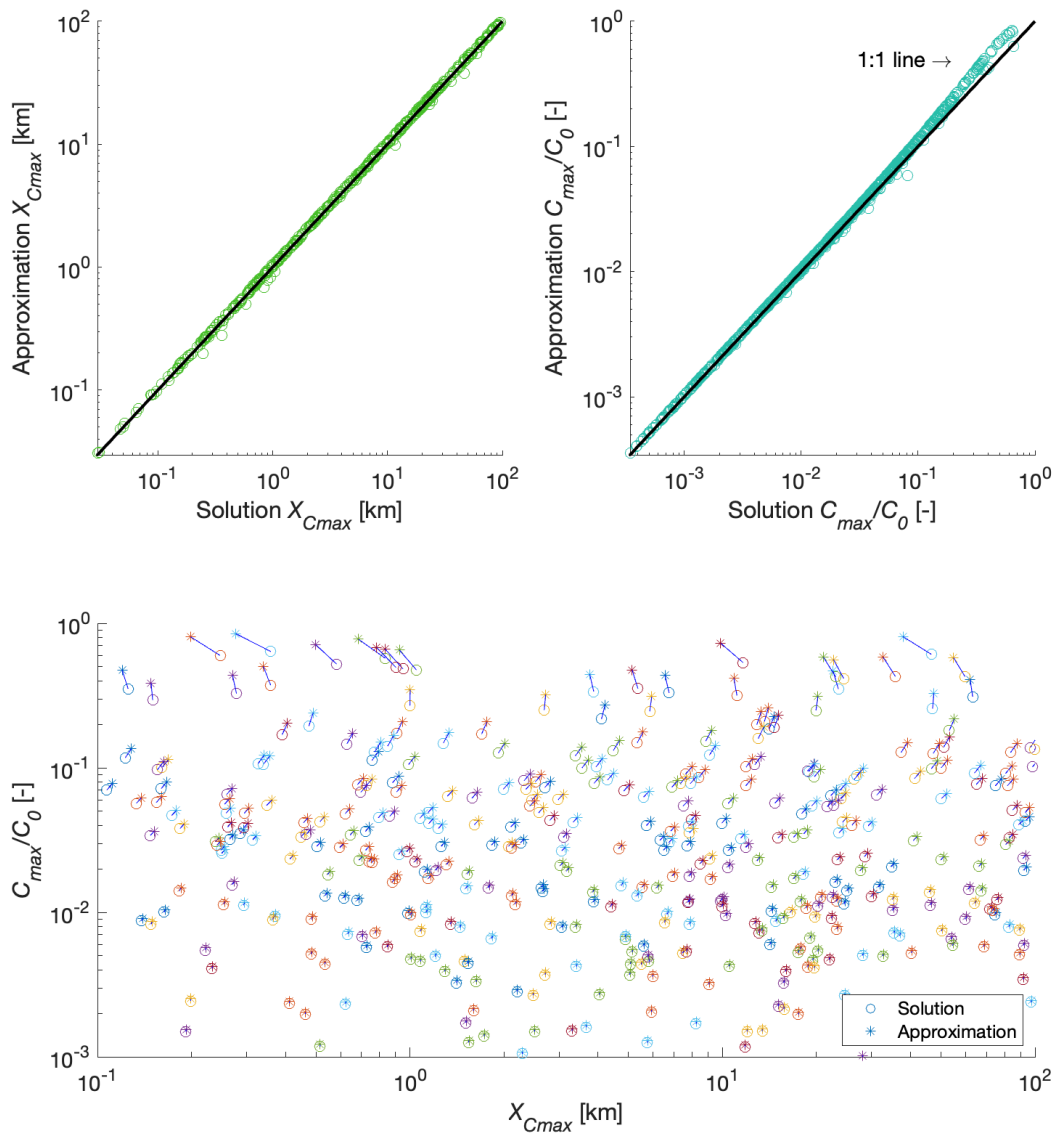


Fig. 2.6: Match of approximations of relative peak concentrations (eq. 2.9c) and peak travel distance (eq. 2.11c) for 500 random parameter combinations of aperture, porosity, total time, plume duration, aqueous diffusion coefficient, and distribution coefficient; bottom: relative concentration vs. the travel distance of the peak derived analytically (circles) and approximated (stars); symbols are connected via a blue line to clarify corresponding results (adapted from Petrova et al., 2023 but with different

approximations: $\frac{C_{max}}{C_0} = \frac{1}{1+4\left(\frac{t}{t_e}-1\right)}$ and $X_{max} = b v \sqrt{\frac{2 t \left(1-\left(\frac{t}{t_e}\right)^2\right)}{D_e \alpha}}$); good agreement for medium distances (1 – 10 km) and low concentrations (< 30% C_0).

2.4 REVOLATILISATION ACROSS THE CAPILLARY FRINGE

Theoretically, groundwater contamination could result from the diffusion of volatile contaminants from the unsaturated zone across the capillary fringe (although in most cases it will DNAPL infiltration into the aquifer) which downgradient from the source zone could lead to back diffusion. Transfer of volatile compounds across the capillary fringe in principle follows the same initial and boundary conditions as in the case of pool dissolution (i.e., constant C_o at the groundwater table - calculated from the vapor phase concentration using the Henry's law constant - and semi-infinite diffusion into the groundwater, see Fig. 2.7) and a chemical boundary layer (Z_s) can be introduced to estimate the contaminant fluxes across the capillary fringe:

$$Z_s = \sqrt{D_t t_c \frac{4}{\pi}} = \sqrt{(D_p + \alpha_t v_a) \frac{x}{v_a} \frac{4}{\pi}}$$

if dispersion dominates (2.12)

$$Z_s = \sqrt{\alpha_t x \frac{4}{\pi}} \approx \sqrt{\alpha_t x}$$

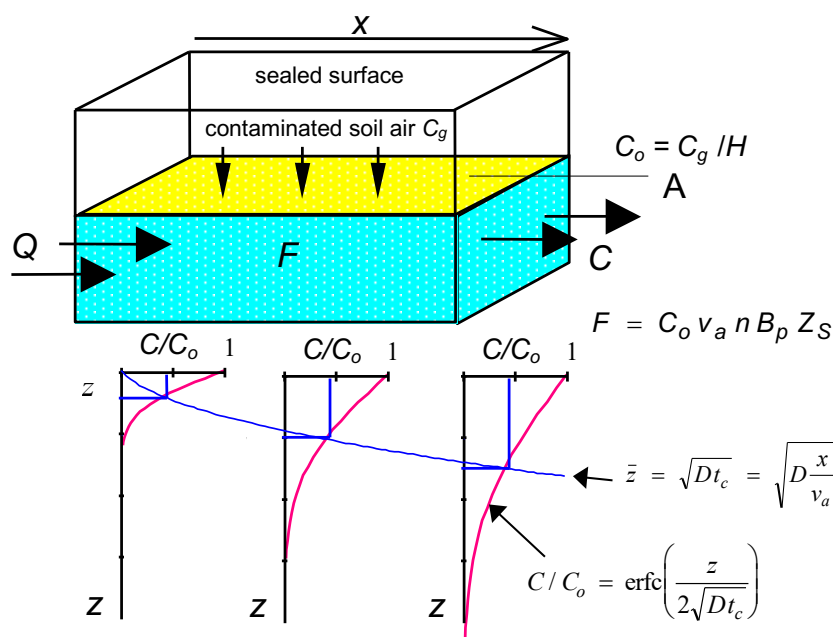


Fig. 2.6. Scheme of diffusion/dispersion of volatile organic compounds across the capillary fringe (analogous to the dissolution kinetics of pools: semi-infinite diffusion)

Downstream of the contaminated zone, volatile compounds may diffuse back into the unsaturated as shown in Fig. 2.7 for an idealized (no groundwater recharge). Note, like in the back diffusion examples the relative mass in groundwater downstream of the source zone is independent on dispersivity or diffusion coefficients (input and output processes are the same and cancel out). As outlined above, the penetration depth (i.e. Z_s) of volatile contaminants is usually very small and therefore fast volatilization may be expected. This scenario may be treated analogously to the case

of semi-infinite diffusion into a thick clay layer, followed by back diffusion of the contaminant (e.g. resulting from decontamination of the overlying aquifer). The decrease of the contaminant mass (or concentration) in the groundwater normalized to the mass diffused into the aquifer in the contaminated area is:

$$M'(x_a) = \sqrt{1 + \frac{x_a}{L_c}} - \sqrt{\frac{x_a}{L_c}} \tag{2.13}$$

x_a denotes the distance downstream of the contaminated zone (where back diffusion occurs). L_c is the length of the contaminated zone. In this case again pseudo-hysteresis is observed: it takes more time (longer distance) to remove the contaminant from the groundwater than to diffuse in (or longer distances are needed for back diffusion in comparison to the length of the contaminated zone). This is only valid at small scales where groundwater recharge plays no role.

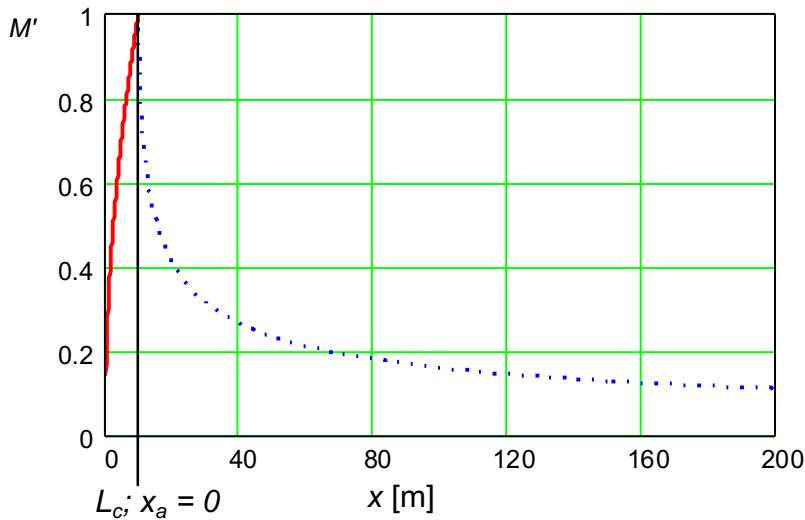


Fig. 2.7. Increase of normalized mass of contaminant (M') during flow past the contaminated zone of length $L_c = 10$ m (solid line) followed by contaminant diffusion out of the groundwater (dashed line).

3. REACTIVE DIFFUSION

Similar to transport of solutes in fractured systems as discussed above, reactions in the rock matrix may be handled based on a simple electron donor/acceptor balance, such as the mass of electron acceptor (e.g., O_2 , nitrate) which has entered the fracture after time t versus the loss of electron donor (e.g., organic matter, Fe^{2+} , sulfur) from the rock matrix:

$$\begin{aligned} F_{EA} t &= M_{ED} \\ C_{EA} b w v t &= C_{ED} \gamma w x_r z_r \end{aligned} \quad (3.1)$$

F_{EA} and M_{ED} denote the advective flux of the electron acceptor (EA) and the mass of electron donor (ED) lost from the matrix. C_{EA} and C_{ED} are the volumetric molar concentrations of the electron acceptor and donor in the fracture water and the rock matrix and γ accounts for the stoichiometry (mol EA consumed per mol ED). w , x_r , z_r , v and b denote fracture width (which drops out) and reactive distance, the average depth of electron donor depletion (location of the reaction front, see Fig. 2.2) in the matrix, the flow velocity in the fracture and the half fracture aperture, respectively. $1/b$ corresponds the surface to volume ratio of the fracture ($w x / w x b$). Thus Eq. 3.1 may be expressed as:

$$\frac{x_r}{v} = \frac{C_{EA} b t}{C_{ED} \gamma z_r} \quad (3.2)$$

x_r/v is the residence time of the water in the fracture until the electron acceptor is completely depleted ("reactive" residence time). The depth of electron donor depletion in the rock matrix at $x = 0$ is (see Fig. 2.2):

$$z(x = 0) = \sqrt{2 D_a t} \quad (3.3)$$

If we assume a boundary layer (average depth of donor depletion) as shown in Fig. 2.2, then the thickness of that layer (δ) is only half of $z(x = 0)$. D_a is an apparent diffusion coefficient which accounts for retardation of the electron donor depletion front ("oxidation front") in the matrix:

$$D_a = \frac{D_e C_{EA}}{C_{ED} \gamma} \quad (3.4)$$

D_e is the effective diffusion coefficient which accounts for matrix porosity and tortuosity of the pores. The term $C_{ED} \gamma / C_{EA}$ may be interpreted as capacity factor similar to sorption ($\approx K_d \rho$), thus eq. 3.2 becomes:

$$\frac{x_r}{v} = b \frac{2 C_{EA} t}{C_{ED} \gamma \sqrt{2 \frac{D_e C_{EA}}{C_{ED} \gamma} t}} = b \sqrt{\frac{C_{EA} 2 t}{C_{ED} \gamma D_e}} \quad (3.5a)$$

Thus, the residence time of the electron acceptor needed to be balanced by the consumption of an electron donor in the rock matrix increases with the square root of time and the acceptor/donor ratio and decreases with increasing diffusion coefficient in the matrix. This is equal to the analytical solution published by Sidborn and Neretnieks (2007), see Appendix. This approach assumes that the reaction (oxidation) front is located in the rock matrix where the solid electron donor (e.g. Fe^{2+} -bearing minerals) is consumed. Such reactions are often catalyzed by microorganisms; if these can't access to rock matrix, e.g., because of small pore sizes in dense

rocks, reactions are limited to the fracture surface (e.g., in biofilms), then C_{EA} in the definition of the apparent diffusion coefficient (eq. 3.4) has to be replaced by the solubility of the electron donor C_{EDaq} , which changes the picture:

$$\frac{x_r}{v} = b \frac{2 C_{EA} t}{C_{EDsolid} \gamma \sqrt{2 \frac{D_e C_{EDaq}}{C_{EDsolid}} t}} = b \sqrt{\left(\frac{C_{EA}}{\gamma}\right)^2 \frac{2 t}{D_e C_{EDaq} C_{EDsolid}}} \quad (3.5b)$$

Since C_{EDaq} is much smaller than C_{EA} , z becomes much smaller as well and x_r/v gets much longer. This illustrates that the reaction scenario chosen is decisive for the estimation the propagation of reaction fronts and large differences arise depending on where and how reactions occur. These scenarios (reaction in the matrix or in the fracture) represent the largest uncertainty, followed by the aperture with and the matrix porosity. Therefore, it is crucial to understand the biogeochemistry of the system, since differences in reactive distances easily are more than an order of magnitude (see Fig. 3.1). For a more in-depth discussion of this see Petrova et al. (2022) and Osenbrück et al. (2022).

Based on the above, one can easily derive a retardation factor based on the ratio of the distance traveled by the water in the fracture to the distance of a reactive compound:

$$R_m = \frac{v t}{b v \sqrt{\frac{2 t C_{EA}}{D_e C_{ED} \gamma}}} = \frac{1}{b} \sqrt{\frac{D_e C_{ED} \gamma}{2 C_{EA}}} t \quad (3.6)$$

The appendix shows how the same approach may be used to describe sorption of a solute in the rock matrix.

Reactive distance in a fracture and the “cubic law”. From eq. 3.5a we may define a reactive distance:

$$x_r = b v \sqrt{\frac{C_{EA} 2 t}{C_{ED} \gamma D_e}} \quad (3.7)$$

The velocity in a fracture is (from the “cubic law”):

$$v = \frac{b^2 g}{3 \mu} i \quad (3.8)$$

Where μ denotes the kinematic viscosity ($= \eta/\rho = 1.3 \times 10^{-6} \text{ [m}^2 \text{ s}^{-1}]$ at $10 \text{ }^\circ\text{C}$), g is the gravitational constant (9.80665 m s^{-2}) and i the hydraulic gradient (typically around 0.001 [-]). With that equation 3.7 becomes:

$$x_r = \frac{b^3 g}{3 \mu} i \sqrt{\frac{C_{EA} 2 t}{C_{ED} \gamma D_e}} \quad (3.9a)$$

or (based on eq. 3.5b)

$$x_r = \frac{b^3 g}{3 \mu} i \sqrt{\left(\frac{C_{EA}}{\gamma}\right)^2 \frac{2 t}{D_e C_{EDaq} C_{EDsolid}}} \quad (3.9b)$$

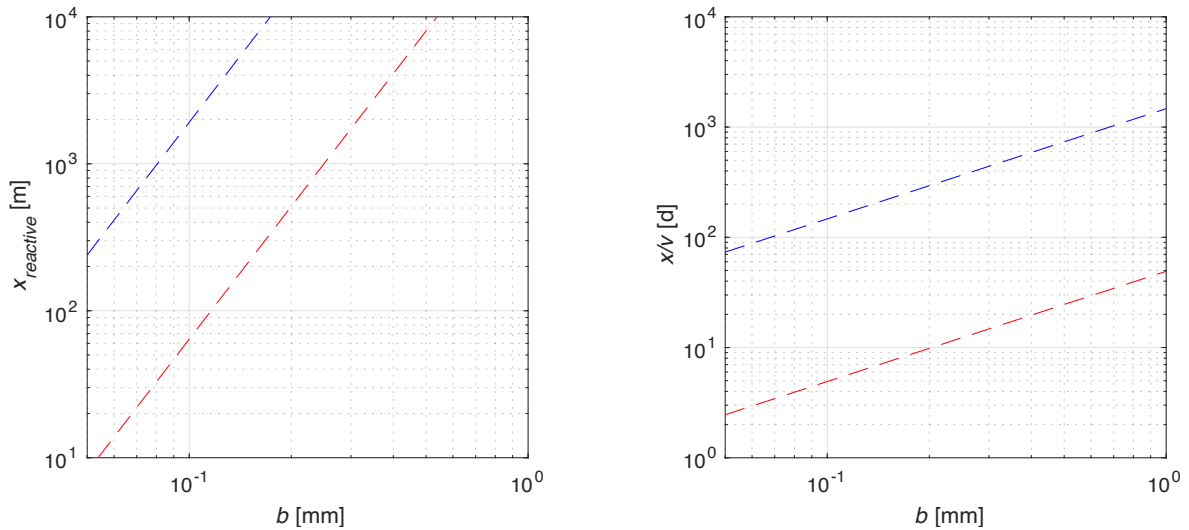


Fig. 3.1: Reactive distance and residence time (x/v) needed for denitrification (nitrate 1 mol m^{-3}) in fractures vs. half aperture (b) after 30 years for reaction only in the fracture (blue) and additionally in the matrix (red); hydraulic gradient $i = 0.003$, matrix porosity 3%; 1% Fe^{2+} bearing mineral ($\gamma = 1/5$).

Box 3: Example for reduction and denitrification capacity (not necessarily representative)

Below we discuss some hypothetical scenarios for the oxidation of pyrite and denitrification. Often reaction pathways and location of bioactive zones (matrix vs. fracture surface) are not clear, and thus reaction distances (location of oxidation and denitrification fronts) are uncertain.

Pyrite oxidation: The oxidation of 1 mol of FeS_2 consumes 3.5 mol O_2 (mainly for the production of sulfate), γ thus is 3.5. Assuming an oxygen concentration of 8 mg l^{-1} ($1/4 \text{ mol O}_2 \text{ per m}^3$) in recharge water and a pyrite content in the rock from 0.3 – 3 mass-% resulting in 7.5 – 75 kg pyrite per m^3 of rock (rock bulk density 2500 kg m^{-3}) or 62 - 620 mol m^{-3} ($\text{FeS}_2 = 119.98 \text{ g mol}^{-1}$) leads to $C_{EA}/(C_{ED} \gamma)$ in a range of 0.001 - 0.0001.

Nitrate reduction: Here we may assume that 1 mol of nitrate consumes 5 mol Fe^{2+} (to produce 5 mol iron hydroxide: $\text{Fe}(\text{OH})_3$), γ thus is 1/5. Nitrate in groundwater may range from 30 mg l^{-1} to 300 mg/l (ca. $0.5 - 5 \text{ mol m}^{-3}$; $\text{NO}_3 = 62 \text{ g mol}^{-1}$) and pyrite in the rock from 0.3 – 3 mass-% or 62 - 620 mol m^{-3} Fe as above. $C_{EA}/(C_{ED} \gamma)$ in this case is in a range of 0.004 - 0.4. At 1% pyrite (25 kg m^{-3} ; 208 mol m^{-3}) and $62 \text{ mg l}^{-1} \text{ NO}_3^-$ (1 mol m^{-3}), $C_{EA}/(C_{ED} \gamma)$ is around 0.024 meaning that 42 m^3 of nitrate containing water would be needed per m^3 of rock to consume the Fe^{2+} .

$C_{EA}/(C_{ED} \gamma)$ is about 10 times smaller in the O_2 than in the nitrate scenario and thus the nitrate reaction distance is around 3 times ($\sqrt{10}$) longer than for O_2 . Since O_2 in recharge water occurred at least 100 times longer than nitrate pollution, the O_2 oxidation zone still would be longer than the denitrification zone. For the case of Fe^{2+} does not react in the matrix (small pores exclude bacteria) but has first to diffuse into the fracture to react with the nitrate, then C_{EDaq} would be only around $5.6 \times 10^{-3} \text{ mol m}^{-3}$ (from the solubility product of siderite) and the denitrification distance would increase significantly (approx. factor of 30, see eq. 3.9b, Fig. 3.1).

For more information on such scenarios see Osenbrück et al. (2022) and Petrova et al. (2022).

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APPENDIX

Retardation factor from concentration front in the fracture: Breakthrough of solute in a fracture at a transport distance x maybe defined for a certain relative concentration C/C_0 ; if this is close to 0.5 then the argument of erfc is 0.5 (= 0.478). For $t \gg x/v$ in eq. 2.1 we get:

$$\frac{\sqrt{D_e \alpha} \frac{x}{v}}{2 b \sqrt{t}} = 0.5 \quad (\text{A1})$$

The distance the solute front traveled thus is:

$$x = b v \sqrt{\frac{t}{D_e \alpha}} \quad (\text{A2})$$

This distance traveled of the “retarded” compound increases with velocity and aperture width and with the square root of time, it decreases with the square root of the effective diffusion coefficient and the capacity factor (increasing sorption). The retardation factor of the solute in the fracture may be defined as the ratio of the distance traveled by conservative tracer with no matrix diffusion (e.g., particles in the fracture water: $v t$) and the retarded solute:

$$R_m = \frac{v t}{b v \sqrt{\frac{t}{D_e \alpha}}} = \frac{1}{b} \sqrt{D_e \alpha t} \quad (\text{A3})$$

which is the same as eq. 2.4 (but neglects the solute mass in the fracture: $1 + \dots$).

This retardation factor may also be derived based on a flux balance for sorption of a solute in the rock matrix:

$$\begin{aligned} F_{half\ fracture} t &= M_{matrix} \\ C_w v b w t &= (C_s \rho + C_w \varepsilon) w x z \\ C_w v b t &= (K_d C_w \rho + C_w \varepsilon) x z \\ v b t &= (K_d \rho + \varepsilon) x z = \alpha x z \end{aligned} \quad (\text{A4})$$

C_w and C_s denote the solute concentration in the water (fracture and pore water) and the concentration in the solids (C_s multiplied by the bulk density ρ of the rock matrix denotes the volumetric concentration in the rock). z is the diffusion distance given by $\sqrt{D_a t}$. D_a is the apparent diffusion coefficient in the rock matrix, i.e., the ratio of the effective diffusion coefficient (D_e) and rock capacity factor ($\alpha = \varepsilon + K_d \rho$) and thus we get:

$$\frac{x}{v} = \frac{b t}{(\varepsilon + K_d \rho) z} = \frac{b t}{\alpha \sqrt{D_a t}} = b \sqrt{\frac{t}{D_e \alpha}} \quad (\text{A5})$$

The distance traveled by the solute front (retarded by matrix diffusion) increases with velocity and aperture width and with the square root of time; it decreases with the square root of the effective diffusion coefficient and the capacity factor. x/v denotes here the residence time of the reactive solute until it “vanishes” (no longitudinal dispersion). The retardation factor R may be obtained by calculating the ratio of velocity of the water (v) in the fracture to the retarded velocity

(x/t) of the solute (this may also be interpreted as the ratio of the total mass in the matrix to mobile mass in fracture):

$$R_m = \frac{v}{\frac{v}{t} b \sqrt{\frac{t}{D_e \alpha}}} = b \sqrt{D_e \alpha t} \quad (\text{A6})$$

To account for the mass of solute in the fracture we have to add 1 to the right-hand side:

$$R_m = 1 + \frac{1}{b} \sqrt{D_e \alpha t} \quad (\text{A7})$$

Travel time of a reaction front. Eq. 4.5 is equal to the analytical solution (A9) published by Sidborn and Neretnieks (2007) for reactive transport (also compare to A5):

$$z(t, x) = \sqrt{2 D_e \frac{C_{EA}}{C_{ED}} t - \frac{D_e x}{v b}} \quad (\text{A8})$$

z is the location of the reaction front in the rock matrix. For $z = 0$ we get the end of the plume:

$$\begin{aligned} \frac{D_e x}{v b} &= \sqrt{2 D_e \frac{C_{EA}}{C_{ED}} t} \\ \frac{x}{v} &= b \sqrt{\frac{2 C_{EA}}{D_e C_{ED}} t} \end{aligned} \quad (\text{A9})$$

x/v denotes the residence time of the solute needed until it is depleted in the fracture (same as eq. 4.5). Eq. A9 may be interpreted as a flux balance (diffusion flux into matrix vs. advective flux of the electron acceptor):

$$\frac{D_e}{\sqrt{2 D_e \frac{C_{EA}}{C_{ED}} t}} x w C_{EA} = b v w C_{EA} \quad (\text{A10})$$

w denotes the width of the fracture and drops out ($x w$ and $b w$: area of fracture surface and of half aperture, resp.).