Solluble cases of the matrix diffusion equation

Pekka Kekäläinen

1 The matrix diffusion equation

Consider soluble tracer in fluid flow through a channel (length L, width w and aperture $2b$) in a porous medium (porosity ϵ).

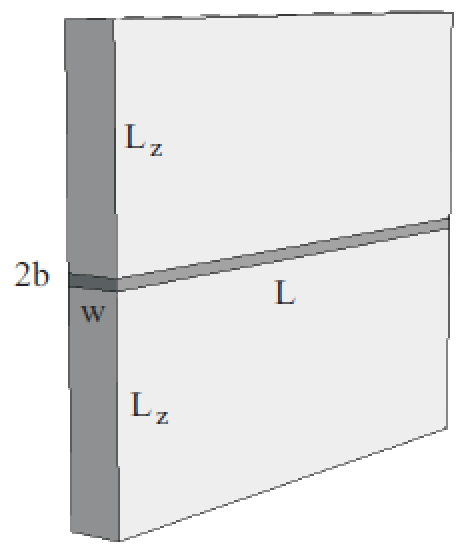


Figure 1: Schematic representation of the transport system of a fracture in a porous medium

If we only consider here advection and diffusion of the tracer in the flow channel, and its transverse diffusion in the matrix, its concentration in the flow channel, C, and the porous matrix, C_m, are governed by the equations

$$\begin{aligned} &\frac{\partial C_f}{\partial t}(x,t) + v\,\frac{\partial C_f}{\partial x}(x,t) - D_f\,\frac{\partial^2 C_f}{\partial x^2}(x,t) = \frac{\epsilon\,D}{b}\,\frac{\partial C_m}{\partial z}(x,0,t) \\ &\frac{\partial C_m}{\partial t}(x,z,t) - D\,\frac{\partial^2 C_m}{\partial z^2}(x,z,t) = 0 \end{aligned} \tag{1.1}$$

with the boundary and initial conditions,

$$\begin{aligned} &C_m(x,z,0) = 0 && C(x,0) = 0 \\ &C_m(x,0,t) = C(x,t) && C(0,t) = \frac{M_0}{2\,w\,v\,b}\,\delta(t) \\ &\frac{\partial C_m}{\partial z}(x,L_z,t) = 0. && \end{aligned} \tag{1.2}$$

Here D is the diffusion coefficient of the tracer in the matrix, v is the flow velocity in the channel, D_f is the diffusion coefficient of the tracer in the fluid. In the case of infinitely deep matrix the boundary condition at $z = L_z$ is replaced by the condition $\lim_{z\to\infty} C_m(x,z,t) = 0$.

Furthermore, if the cross sectional velocity profile is not constant, we have to take into account Taylor dispersion. This can be done by replacing the diffusion coefficient D_f with an effective diffusion coefficient,

$$D_{eff} = D_f \left(1 + K \cdot Pe^2\right), \tag{1.3}$$

where Pe is the Péclet number and K a constant depending on the geometry of the channel.

The diffusion equation for $C_m(x, z, t)$ can be solved by separation of variables. Substituting this solution in Eq. (1.1) gives us an integro-differential equation for C. With the substitution

$$\xi = \frac{x}{L}, \quad \tau = \frac{t\,v}{L}, \quad C(\xi, \tau) = \frac{2\,w\,b\,L}{M_0}\,C_f(x, t) \tag{1.4}$$

we obtain a dimensionless form of that equation,

$$\begin{aligned}
&\frac{\partial C}{\partial \tau}(\xi,\tau) + \frac{\partial C}{\partial \xi}(\xi,\tau) - \mu^2 \frac{\partial^2 C}{\partial \xi^2}(\xi,\tau) = -\lambda \int_0^\tau \Lambda(\tau-\sigma)\,\frac{\partial C}{\partial \sigma}(\xi,\sigma)\,d\sigma,\\
&C(\xi,0) = 0\\
&C(0,\tau) = \delta(\tau)
\end{aligned} \tag{1.5}$$

where

$$\Lambda(\tau) = \frac{2}{\kappa}\sum_{n=0}^{\infty} e^{-(\gamma_n^2/\kappa^2)\,\tau}, \qquad \gamma_n = (n+\tfrac{1}{2})\pi, \tag{1.6}$$

and the dimensionless parameters are

$$\lambda = \epsilon\,\frac{L}{b}\sqrt{\frac{D}{L\,v}}, \qquad \kappa = \frac{L_z}{L}\sqrt{\frac{L\,v}{D}}, \qquad \mu = \sqrt{\frac{D_{eff}}{L\,v}}. \tag{1.7}$$

For an infinitely deep matrix the function Λ is given by

$$\Lambda(\tau) = \frac{1}{\sqrt{\pi\,\tau}}. \tag{1.8}$$

2 No longitudinal diffusion or dispersion in the channel ($\mu = 0$)

Equation (1.5) can be solved using Laplace transformation. The solution can be expressed in the form

$$C(\xi,\tau) = \begin{cases} \dfrac{4}{(\lambda\xi)^2}\,\Psi\left((\tau-\xi)/(\lambda\xi)^2, \kappa/\lambda\xi\right); & \tau > \xi, \\ 0; \quad 0 \le \tau \le \xi, \end{cases} \tag{2.1}$$

where function Ψ can be given as a series expansion in terms of two basis functions, $f(x)$ and $g(x)$,

$$
\begin{aligned}
\Psi\left(\frac{\tau}{(\lambda\xi)^2},\frac{\kappa}{\lambda\xi}\right) &= f\left(\frac{4\tau}{(\lambda\xi)^2}\right)+\frac{4}{z_1^3}\,g'\left(\frac{4\tau}{(\lambda\xi z_1)^2}\right)\\
&+\sum_{N=2}^{\infty}\frac{(-1)^N}{z_N^2}\left(\sum_{k=1}^{\left[\frac{N}{2}\right]}\frac{1}{(2k)!}\binom{N-1}{N-2k}\left(\frac{4}{z_N}\right)^{2k}f^{(k)}\left(\frac{4\tau}{(\lambda\xi z_N)^2}\right)\right.\\
&\left.-\sum_{k=1}^{\left[\frac{N+1}{2}\right]}\frac{1}{(2k-1)!}\binom{N-1}{N-2k+1}\left(\frac{4}{z_N}\right)^{2k-1}g^{(k)}\left(\frac{4\tau}{(\lambda\xi z_N)^2}\right)\right)
\end{aligned}
\tag{2.2}
$$

with $z_n = (2n\kappa/\lambda\xi) + 1$ and

$$
f(x)=\frac{1}{\sqrt{\pi\,x^3}}\,e^{-\frac{1}{x}} \qquad g(x)=\frac{1}{\sqrt{\pi\,x}}\,e^{-\frac{1}{x}}. \tag{2.3}
$$

In the case of an infinitely deep matrix the solution is obtained from Eq. (2.1) by taking instead of Ψ only the first term in the expansion Eq. (2.2),

$$
C(\xi,\tau)=\begin{cases}\dfrac{\lambda\xi}{2\sqrt{\pi(\tau-\xi)^3}}\cdot e^{-\frac{(\lambda\xi)^2}{4(\tau-\xi)}}; & \tau>\xi,\\ 0; & 0\le\tau\le\xi,\end{cases} \tag{2.4}
$$

2.1 Breakthrough curve

We are interested in C at the end of the flow channel, $C(L, t)$, i.e. the breakthrough curve.

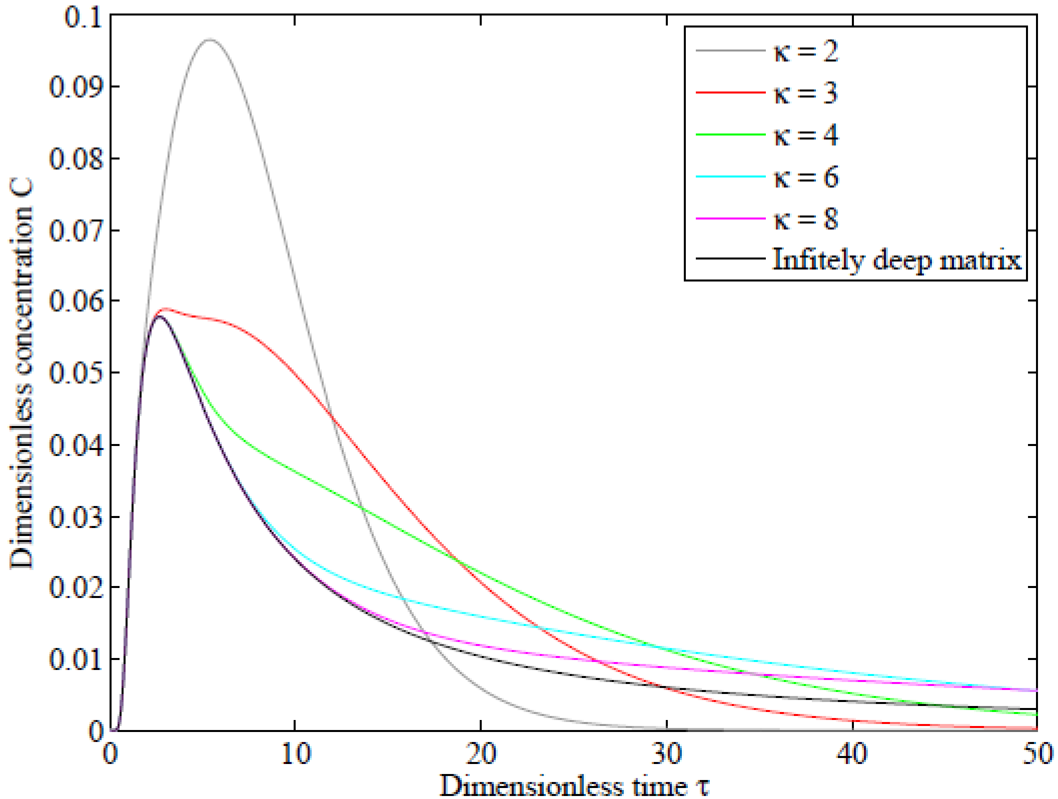


Figure 2: Breakthrough curves given by the matrix-diffusion equation for a porous matrix of finite depth with $\lambda = 4$ for $\kappa = 2, 3, 4, 6$, and 8, and for an infinitely deep matrix.

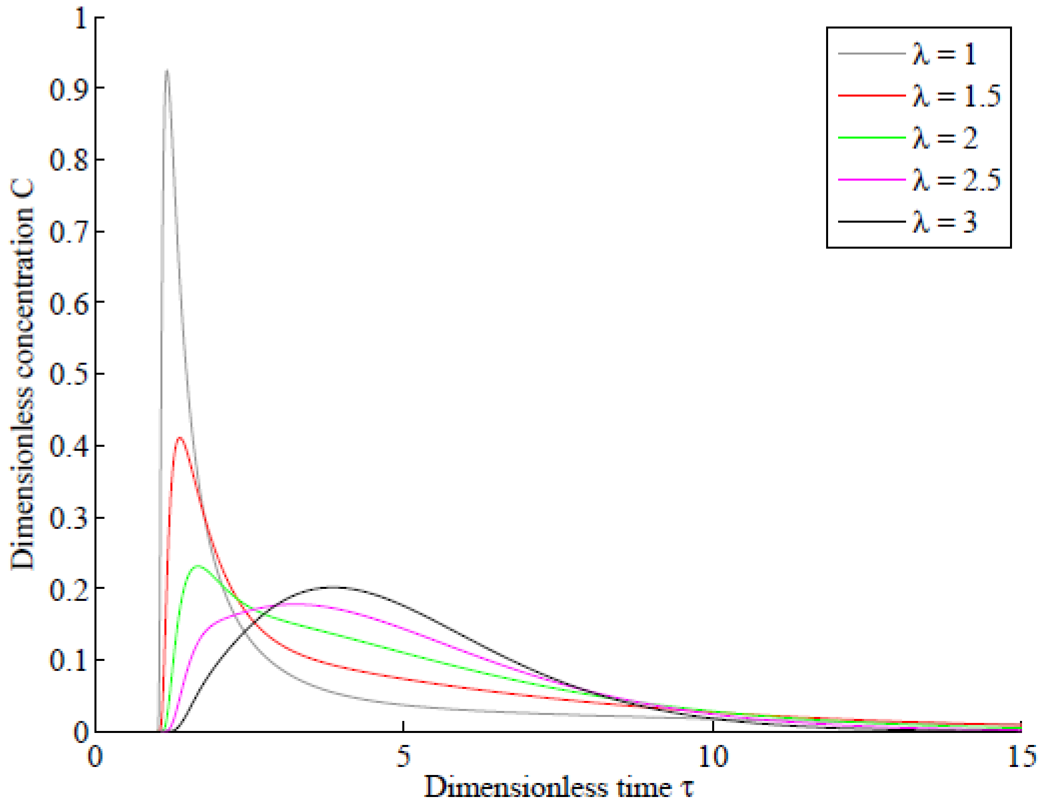


Figure 3: Breakthrough curves given by the matrix-diffusion equation for $\lambda = 1,\ 1.5,\ 2,\ 2.5$ and 3, with $\lambda\kappa = 4$.

The breakthrough curve takes in terms of the original variables the form

$$C(L,t) = \begin{cases} \dfrac{4M_0}{Q\,T}\,\Psi\left(\frac{t-t_0}{T}, \frac{L_z}{\sqrt{DT}}\right), & t > t_0 \\ 0, \quad 0 \le t \le t_0 \end{cases} \tag{2.5}$$

where

$$\begin{aligned} T &= \frac{4\epsilon^2 w^2 L^2 D}{Q^2}, \\ t_0 &= \frac{V}{Q}. \end{aligned} \tag{2.6}$$

Here $Q = 2\,w\,b\,v$ is the volumetric flow rate in the channel, and $V = 2\,w\,b\,L$ is its volume. Note that the aperture of the channel does not affect the shape of the breakthrough curve. This is true even in the case where the aperture of the channel varies.

2.2 Flow channel of varying aperture

Consider the case when the volumetric flow rate Q is constant but the aperture of the channel varies, ie $b = b(x)$ and $2\,w\,b(x)\,v(x) = Q$. The first equation in our model Eq. (1.1) is now given by

$$\frac{\partial C_f}{\partial t}(x,t) + v(x)\,\frac{\partial C_f}{\partial x}(x,t) = \frac{\epsilon\,D}{b(x)}\,\frac{\partial C_m}{\partial z}(x,0,t). \tag{2.7}$$

We can proceed in the same way as before. In this case we use the scaling

$$\xi = \frac{x}{L}, \quad \tau = \frac{t\,Q}{V}, \quad C(\xi, \tau) = \frac{V}{M_0}\,C_f(x, t), \tag{2.8}$$

and the dimensionless parameters are

$$\lambda = \frac{\epsilon}{\bar{b}}\sqrt{\frac{D\,V}{Q}} \quad \text{and} \quad \kappa = L_z\sqrt{\frac{Q}{D\,V}}, \tag{2.9}$$

where V is the volume of the channel,

$$V = 2\,w \int_0^L b(x)\,dx, \tag{2.10}$$

and $\bar{b}$ the average half aperture of the channel

$$\bar{b} = \frac{1}{L}\int_0^L b(x)\,dx = \frac{V}{2\,w\,L}. \tag{2.11}$$

The breakthrough curve $C_f(L, t)$ takes the same form as in the case of a channel with a constant aperture.

3 Longitudinal diffusion and Taylor dispersion ($\mu > 0$)

In this case we can express the solution of the equation Eq. (1.1) in the form

$$C(\xi,\tau) = \frac{\xi\, e^{\frac{\xi}{2\mu^2}}}{\mu\sqrt{\pi}} \int_0^\tau \frac{1}{z\sqrt{z}}\, e^{-\frac{\xi}{4\mu^2}\left(\frac{z}{\xi}+\frac{\xi}{z}\right)}\, K(z,\tau - z)\, dz, \tag{3.1}$$

where function K is given by

$$K(z,\tau) = \frac{4}{(\lambda z)^2}\, \Psi\left(\tau/(\lambda z)^2, \kappa/\lambda z\right). \tag{3.2}$$

In the case of an infinitely deep matrix, instead of Ψ we take only the first term in the expansion Eq. (2.2).

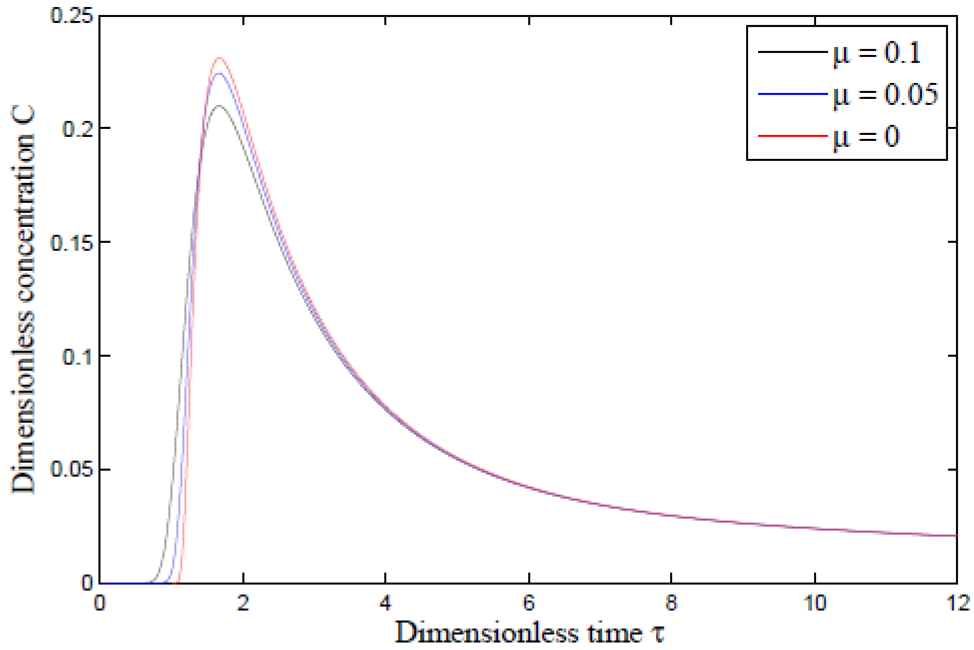


Figure 4: Breakthrough curves given by the matrix-diffusion equation for $\lambda = 2$ and $\kappa = 5$ without longitudinal diffusion ($\mu = 0$) and with longitudinal diffusion for $\mu = 0.1$ and 0.05.

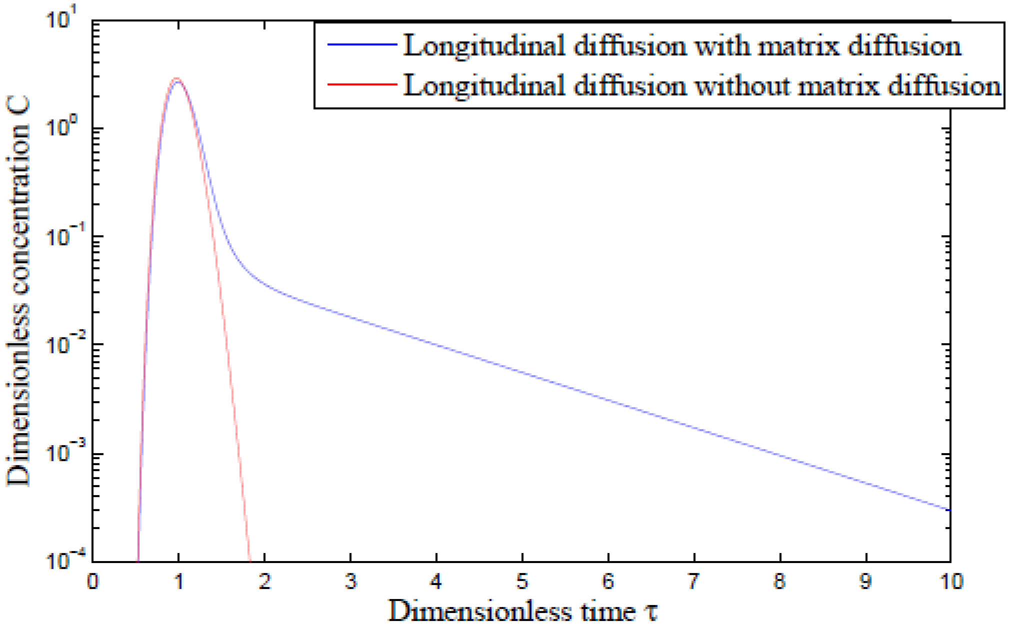


Figure 5: Breakthrough curves given by the advection-diffusion equation for $\mu = 0.1$, and by the matrix-diffusion equation for $\lambda = 0.1$, $\kappa = 2$, and $\mu = 0.1$.

4 General initial and boundary conditions ($\mu = 0$)

Consider the case when there is also an initial tracer distribution in the porous matrix and in the channel. Now we have the boundary and initial conditions

$$\begin{aligned} &C_m(x, z, 0) = C_0(x, z) \qquad && C(x, 0) = C_0(x, 0) \\ &C_m(x, 0, t) = C(x, t) && C(0, t) = C_1(t) \\ &\frac{\partial C_m}{\partial z}(x, L_z, t) = 0. \end{aligned} \tag{4.1}$$

with Eq. (1.1). Here C_0 is the initial tracer concentration in the matrix, and C_1 is the input concentration of tracer into the channel.

In the dimensionless setting the solution can be expressed in the form

$$\begin{aligned} C(\xi, \tau) = &\int_0^\tau \Phi(\xi, \tau - \sigma)\, c(\sigma)\, d\sigma + \int_0^\xi \Phi(\xi - \eta, \tau)\, F(\eta, 0)\, d\eta \\ &+ \frac{2\lambda}{\kappa} \int_0^\xi \left\{ \int_0^1 F(\eta, \zeta) \right. \\ &\times \left. \left(\sum_{n=0}^\infty \gamma_n \int_0^\tau e^{-(\gamma_n/\kappa)^2(\tau-\sigma)} \Phi(\xi - \eta, \sigma)\, d\sigma \, \sin \gamma_n \zeta \right) d\zeta \right\} d\eta, \end{aligned} \tag{4.2}$$

where F is the dimensionless form of the initial condition C_0, c is the dimensionless form of the boundary condition C_1, and Φ is the function C in Eq. (2.1),

$$\Phi(\xi,\tau) = \begin{cases} \frac{4}{(\lambda\xi)^2}\,\Psi\left((\tau-\xi)/(\lambda\xi)^2, \kappa/\lambda\xi\right); & \tau > \xi, \\ 0; & 0 \le \tau \le \xi. \end{cases} \tag{4.3}$$

5 Asymptotic behaviour of the breakthrough curve

The breakthrough curve of the matrix diffusion equation, Eq. (1.5) in the case of an infinitely deep matrix without longitudinal diffusion is given by

$$C(\tau) = \begin{cases} \frac{\lambda}{2\sqrt{\pi(\tau-1)^3}} \cdot e^{-\frac{\lambda^2}{4(\tau-1)}}; & \tau > 1, \\ 0; & 0 \le \tau \le 1, \end{cases} \tag{5.1}$$

Asymptotically this solution behaves as

$$C(\tau) \sim \frac{1}{\tau^{\frac{3}{2}}}, \quad \text{when} \quad \tau \to \infty. \tag{5.2}$$

For a matrix of finite depth we find the asymptotic behaviour using the Tauberian theory. The asymptotic behaviour of the breakthrough curve is of the form

$$C(\tau) \sim \frac{1}{\tau^{\frac{3}{4}}} \cdot e^{-a\tau + b\sqrt{\tau}}. \tag{5.3}$$

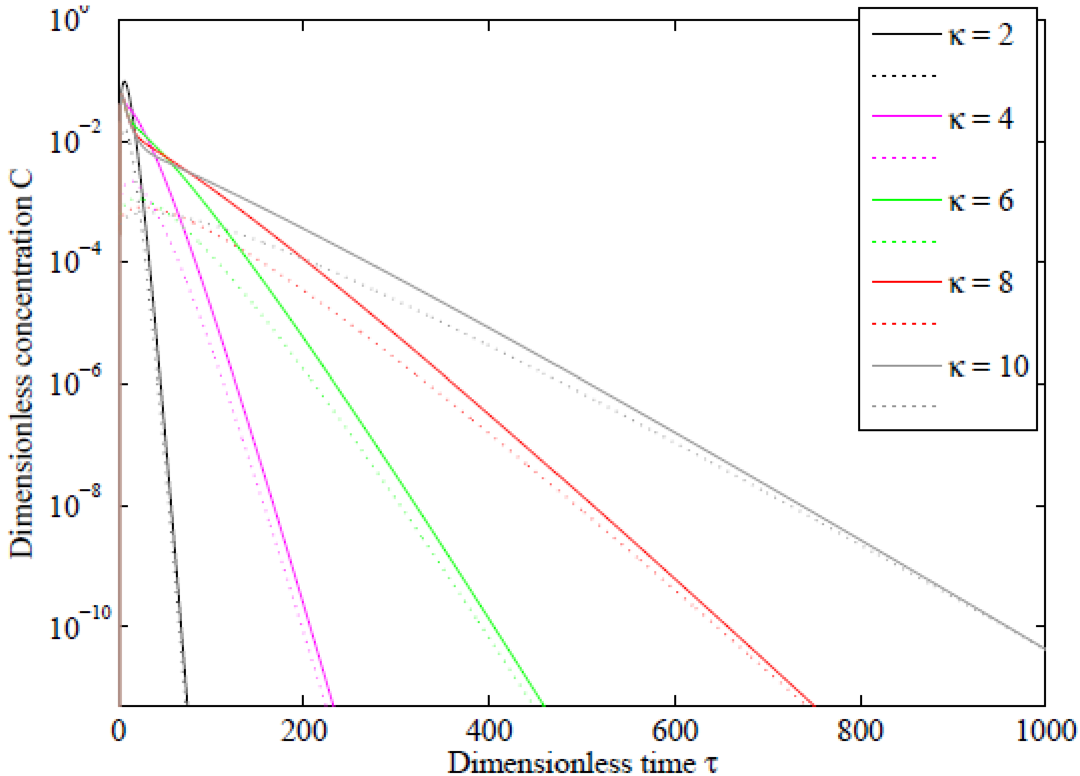


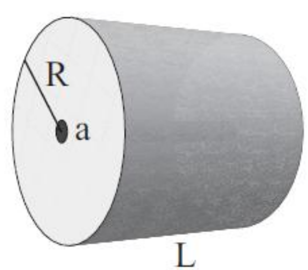
Figure 6: Breakthrough curves given by the matrix diffusion equation and their asymptotic limits (dotted curves) in a porous matrix of finite depth for $\lambda = 4$ and $\kappa = 2, 4, 6, 8$ and 10.

In a cylindrically symmetric case the asymptotic behaviour is of the same form as for a matrix of finite depth. In the case of an infinitely deep matrix the asymptotic behaviour is different:

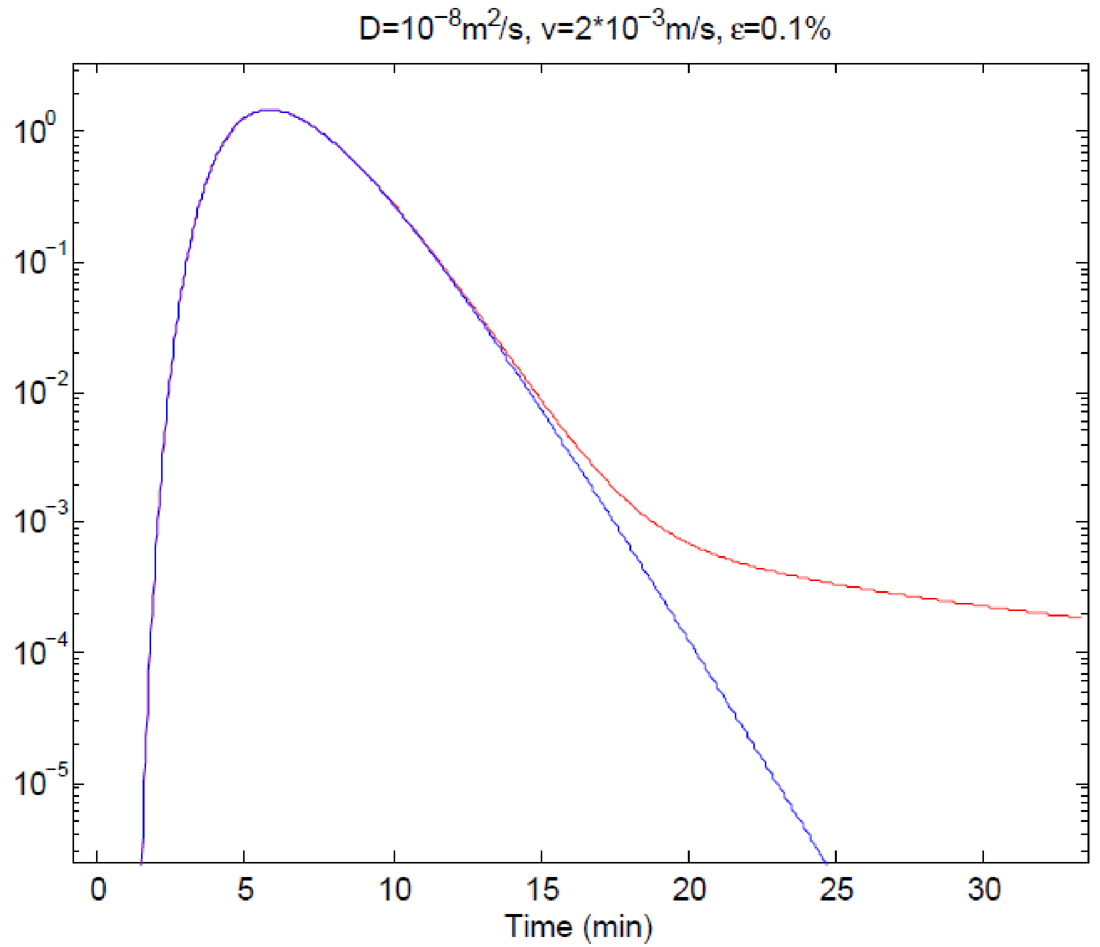
$$C(\tau) \sim \frac{1}{\tau(\log\tau)^2}. \tag{5.4}$$

6 Modelling experiments

Experimental setup is usually cylindrically symmetric, but it can be approximated by a one-dimensional model. This can be done, if κ/λ is large, for a matrix whose depth L_z is small compared to the radius of the channel. Furthermore, in experiments on rock matrix, longitudinal diffusion (and dispersion) dominates over matrix diffusion. The effect of matrix diffusion can be seen in the tail of the breakthrough curve.



Laboratory experiment, gas phase (cf. Voutilainen):



In-situ experiment, water phase (cf. Voutilainen):