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Large time behaviour of oscillatory nonlinear solute transport in porous media

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# Large time behaviour of oscillatory nonlinear solute transport in porous media

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## Key Words

convection, dispersion, Freundlich equation, homogenization, oscillation

## Abstract

Oscillations in flow occur under many different situations in natural porous media, due to tidal, daily or seasonal patterns. In this paper, we investigate how such oscillations in flow affect the transport of an initially sharp solute front, if the solute undergoes nonlinear sorption. By homogenization, we show that after many cycles, the transport converges to a zero convection, pure nonlinear diffusion problem. With numerical simulations, we show that this convergence may occur relatively fast (say 10 cycles). The implication of the diffusion like large time behaviour is that the transition zone continues to spread beyond the zone of convective oscillation.

## Introduction

The study of flow and transport in porous media, and in particular natural porous media such as soil and aquifers, has always been dominated by the assumption of steady state flow. This is quite understandable, as this assumption simplifies the mathematical analysis, and for many laboratory and field conditions, it is also quite justified. However, it cannot be ignored that for many other situations, flow is transient.

A special case of transient conditions is that of oscillating flow, where flow in one direction is compensated by a complete reversal. For conditions studied in soil science and other geosciences, for instance, seasonal fluctuations are often oscillatory. Examples are seasonal wetting and drying, although wetting and drying may occur at different time scales. Atmospheric forcing that has an oscillatory aspect is not limited to precipitation/evapotranspiration cycles, but also related with fluctuating air pressures (Neeper, 2001, Neeper and Stauffel, 2012, Jaeger and Kurzweg, 2003). In fact, oscillatory gas exchange for porous media has been investigated decades ago when Raats and Scotter (1968) considered flow that varies sinusoidally with time and investigated the dispersive behaviour due to such oscillations. The rate of dispersion can be described as a function of the Peclet number and the dimensionless amplitude of displacement, and this was experimentally tested by Scotter and Raats (1968) and elaborated numerically by Scotter and Raats (1969).

More recent is the work on fluctuating interfaces in shallow groundwater by Eeman et al. (2013, 2016) and Cirkel et al. (2015) and daily oscillating flow at the plant root surface (Espeleta et al., 2016). Also at drinking water wells, oscillating conditions may be part of management (Pauw et al., 2016) to keep filters open (free of iron oxide deposits) by periodically extracting and discharging water. In underground energy or chemical storage, oscillating conditions may be important, for instance seasonal underground heat storage. In the context of tracer dispersion in estuaries, Kay (1997) investigated oscillating flows due to tidal reversals.

Oscillating flow and transport has also been considered in chemical engineering. Though not considering a porous medium, Harvey et al. (2001), Reis et al. (2004) and Zheng and Mackley (2008) investigated mixing in a reactor with oscillatory flow. There is also earlier work for baffled tubes on mixing (Dickens et al., 1989) and heat transfer (Mackley and Stonestreet, 1995) for such flow conditions. Recently, Wang et al. (2017) considered mass transfer for a pulsed disc and doughnut (PDD) extraction column.

As both Neeper and Stauffel (2012) and Cirkel et al. (2015) observed, the combination of periodic flow of the fluid in the pores, on the long term leads to diffusion type of behaviour, that can be captured with an effective diffusion coefficient. This was also the key point of Cirkel et al. (2015), who combined oscillating flow with cation transport, for the case of nonlinear (Gapon type) cation exchange.

It is the scope of this paper, to reconsider the transport of a nonlinear adsorbing solute under an oscillating flow regime and to investigate the large time behaviour of the solute front and mixing behaviour.

## Problem statement

We consider a flow field describing an oscillating pore water velocity $V(t)$, with period $T$ and mean $\langle V \rangle = 0$. This flow field transports a reactive solute through an infinitely long and one dimensional column. Solute transport is given by the well-known convection-dispersion equation. In case of nonlinear adsorption of the solute subject to an initial step front, the transport is described by Convection-Dispersion-Reaction Problem (CDRP)

$$\frac{\partial \varphi(u)}{\partial t} + V(t)\frac{\partial u}{\partial x} = D(t)\frac{\partial^2 u}{\partial x^2} \quad x \in \mathbb{R}, \;\; t > 0, \tag{1}$$

$$u(x,0) = \begin{matrix} 1 & x < 0 \\ 0 & x > 0 \end{matrix}; \tag{2}$$

where $u \geq 0$ denotes a scaled solute concentration, the function $\varphi(u)$ is strictly increasing and describes the accumulated solute on a volumetric basis, $t$ is time, $x$ is position, and $D$ is the hydrodynamic dispersion coefficient (Bear, 1972). We assume sorption to be given by the Freundlich expression:

$$\varphi(u) = u + Au^p \quad A > 0, \ \ 0 < p < 1. \qquad (3)$$

Further, we ignore molecular diffusion, hence

$$D(t) = \alpha |V(t)| \ , \qquad (4)$$

with $\alpha > 0$ denoting the dispersivity. We rewrite (1) as

$$\frac{1}{|V(t)|}\frac{\partial \varphi(u)}{\partial t} + P(t)\frac{\partial u}{\partial x} = \alpha \frac{\partial^2 u}{\partial x^2}, \qquad (5)$$

where

$$P(t) = \begin{cases} 1 & in\ \{V > 0\}, \\ -1 & in\ \{V < 0\}. \end{cases} \qquad (6)$$

Next, we introduce as new time scale

$$\tau = \int_0^t |V(z)| dz, \qquad (7)$$

which is the total travelled distance of the fluid particle in time $t$. With $v(x,\tau) = v\big(x,\tau(t)\big) = u(x,t)$ and $P^*(\tau) = P^*\big(\tau(t)\big) = P(t)$, we find the transformed problem

$$\frac{\partial \varphi(v)}{\partial \tau} + P^*(\tau)\frac{\partial v}{\partial x} = \alpha \frac{\partial^2 v}{\partial x^2} \qquad x \in \mathbb{R}, \quad \tau > 0, \qquad (8)$$

$$v(x,0) = \begin{cases} 1 & x < 0, \\ 0 & x > 0. \end{cases} \qquad (9)$$

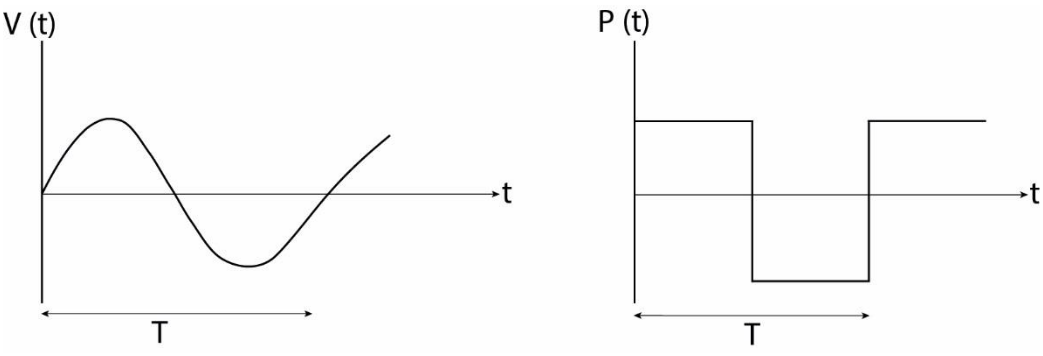


Figure 1: Illustration of the velocity as a function of time (Fig. 1a) and the function $P(t)$, with $T$ a characteristic time.

## Large time behaviour

We are interested in the large time behaviour of the solute front, i.e., the solute distribution in the column after many oscillations. Therefore, we introduce a second scaling

$$s := \frac{\tau}{\tau_{obs}} \quad \text{and} \quad y := \frac{x}{\sqrt{\alpha \tau_{obs}}}, \tag{10}$$

where

$$\tau_{obs} = NT^*, \quad \text{with} \quad T^* = \int_0^T |V(z)| dz, \tag{11}$$

is the travelled distance at the moment of observation. Note that $\tau_{obs}$ corresponds with $T_{obs} = NT$. We also introduce the parameter

$$\varepsilon = \frac{1}{N}, \tag{12}$$

which is small after many periods ($N$). Setting now $w(y,s) = w\left(\frac{x}{\sqrt{\alpha\tau_{obs}}}, \frac{\tau}{\tau_{obs}}\right) = v(x,\tau)$ and

$$\tilde{P}(z) := \sqrt{\frac{T^*}{\alpha}} P^*(zT^*), \tag{13}$$

we obtain the scaled (dimensionless) initial value problem (IVP)

$$\begin{aligned} &\frac{\partial \varphi(w)}{\partial s} + \varepsilon^{-\frac{1}{2}} \tilde{P}\left(\frac{s}{\varepsilon}\right) \frac{\partial w}{\partial y} = \frac{\partial^2 w}{\partial y^2} \qquad y \in \mathbb{R}, \quad s > 0, \\ &w(y,0) = \begin{matrix} 1 & y < 0, \\ 0 & y > 0. \end{matrix} \end{aligned} \tag{14}$$

We investigate the solution of problem (IVP) for many oscillations ($N \rightarrow \infty$) or small $\varepsilon$ ($\varepsilon \downarrow 0$), while considering $s$=O(1) (or $\tau$ =O($\tau_{obs}$). Before studying the nonlinear (reactive) case, it is instructive to first consider the linear (non-reactive) one.

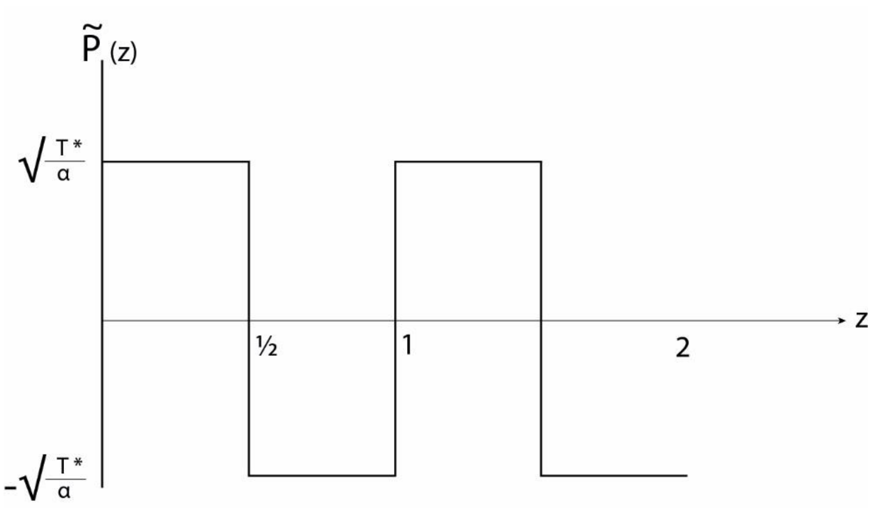


Figure 2: Illustration of the oscillation function $\tilde{P}(z)$, as defined in (13).

## Linear (non-reactive) case

For the linear case, $\varphi(w) = w$ and the solution is well-known in terms of the complementary error function (Appendix A).

Since $\tilde{P}$ is a 1-periodic function, we may consider $z = \frac{s}{\varepsilon} \in (0,1)$ and consider for any $s > 0$, $z = \frac{s}{\varepsilon} mod 1$. Introducing the function

$$g(z) = \int_0^z \tilde{P}(\xi) d\xi \tag{15}$$

the solution of the linear version of (14) can be written as

$$w_\varepsilon(y,s) = \frac{1}{2} erfc\left(\frac{y}{2\sqrt{s}} - \frac{\varepsilon^{1/2}}{2\sqrt{s}} g(z)\right). \tag{16}$$

Setting

$$w^0(y,s) = \frac{1}{2} erfc\left(\frac{y}{2\sqrt{s}}\right), \tag{17}$$

We observe that

$$w_\varepsilon(y,s) = w^0\left(\left(y - \varepsilon^{1/2} g(z)\right), s\right), \tag{18}$$

which can be expanded in terms of $\varepsilon$ to give

$$w_\varepsilon(y,s) = w^0(y,s) - \varepsilon^{1/2} g(z) \frac{\partial w^0}{\partial y} + \frac{1}{2} \varepsilon g^2(z) \frac{\partial^2 w^0}{\partial y^2} + O\left(\varepsilon^{3/2}\right). \tag{19}$$

Note that expansion (19) is of the form

$$w_\varepsilon(y,s) = w^0(y,s) + \varepsilon^{1/2} w^1(y,s,z) + \varepsilon w^2(y,s,z) + \cdots, \tag{20}$$

where the functions $w^i$ are 1-periodic with respect to $z$. It is a two scale expansion, i.e., in $\varepsilon$ and in $z = \frac{s}{\varepsilon}\big|_{mod 1}$. Such expansions are well-known in the theory of homogenization, see for instance Cioranescu and Donato (1999) and Hornung (1997).

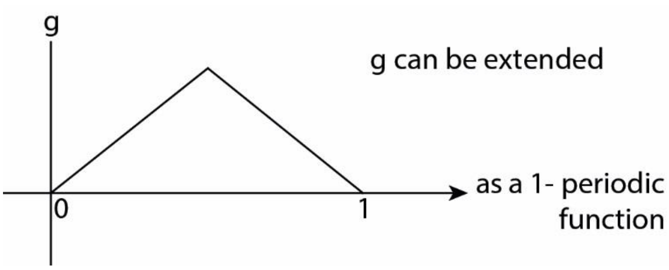


Figure 3: Illustration of the oscillatory function $g(z)$, defined in (15).

What is the interpretation of (16) in terms of the original variables $x$, $t$, and $u$? The backwards transformation gives

$$u(x,t) = \frac{1}{2} erfc\left(\frac{x}{2\sqrt{\alpha\tau(t)}} - \frac{1}{2}\sqrt{\frac{T^*}{\tau(t)}}\, g\left(\frac{\tau(t)}{T^*}\right)\right). \tag{21}$$

Hence, at each $t = NT$, we have

$$\tau(NT) = NT^* = N\int_0^T |V(\xi)|d\xi = \langle|V|\rangle NT, \tag{22}$$

$$g\left(\frac{\tau(NT)}{T^*} = N\right) = 0 \;, \tag{23}$$

and thus

$$u(x, NT) = \frac{1}{2} erfc\left(\frac{x}{2\sqrt{D_{eff}NT}}\right), \tag{24}$$

where $D_{eff} = \alpha\langle|V|\rangle$. (25)

This holds exactly after each period (for all $N \geq 1$. It holds approximately for $t \neq NT$, up to order $\sqrt{\varepsilon} = \sqrt{\frac{1}{N}}$. Note that expression (24) coincides with the solution of the linear diffusion problem:

(LD) $$\begin{aligned} \frac{\partial u}{\partial t} &= D_{eff}\frac{\partial^2 u}{\partial x^2} \quad x \in \mathbb{R}, t > 0, \\ u(x,0) &= \begin{matrix} 1 & x < 0, \\ 0 & x > 0. \end{matrix} \end{aligned} \tag{26}$$

at $t = NT$. Thus, at $t = NT$, the solution of (LD) coincides with the solution of the linear convection dispersion problem

$$\begin{aligned} \frac{\partial u}{\partial t} + V(t)\frac{\partial u}{\partial x} &= D(t)\frac{\partial^2 u}{\partial x^2} \quad x \in \mathbb{R},\ t > 0, \\ u(x,0) &= \begin{matrix} 1 & x < 0 \\ 0 & x > 0. \end{matrix} \end{aligned} \tag{27}$$

## Nonlinear reactive case

Based on the linear case, we apply a two scale expansion to the nonlinear equation (14), by substituting

$$w_\varepsilon(y,s) = w^0(y,s,z) + \varepsilon^{1/2}w^1(y,s,z) + \varepsilon w^2(y,s,z) + \cdots \tag{28}$$

where $(y,s) \in H = \{(y,s): y \in \mathbb{R}, s > 0\}$ and $z \in (0,1)$. The functions $w^i$ are constructed in such a way that they are 1-periodic in $z$ and that for each $\varepsilon > 0$

$$\lim_{s\downarrow 0} w_\varepsilon(y,s) = \begin{matrix} 1 & y < 0, \\ 0 & y > 0. \end{matrix} \tag{29}$$

Because $z = \frac{s}{\varepsilon}$, we have the following rule for differentiating with respect to s in the expansion:

$$\frac{\partial}{\partial s} \to \frac{\partial}{\partial s} + \frac{1}{\varepsilon}\frac{\partial}{\partial z}. \tag{30}$$

In expansion (B1) from Appendix B, we collect terms of the same order of $\varepsilon$.

At the order of $\varepsilon^{-1}$ we have

$$\frac{\partial}{\partial z}\varphi(w^0) = 0, \quad \text{with } (y,s) \in H,\ z \in (0,1), \tag{31}$$

which implies

$$w^0 = w^0(y,s) \tag{32}$$

only, as in the linear case. As we see later, $w^0$ is determined by higher order terms in the expansion. At the order $\varepsilon^{-1/2}$ we find the equation

$$\frac{\partial}{\partial z}(\varphi'(w^0)w^1) + \tilde{P}(z)\frac{\partial w^0}{\partial y} = 0 \qquad \text{with } (y,s) \in H,\ z \in (0,1). \tag{33}$$

Using (32), we have

$$\frac{\partial w^1}{\partial z} = -\tilde{P}(z)\frac{1}{\varphi'(w^0)}\frac{\partial w^0}{\partial y} \tag{34}$$

and since $\int_0^1 \tilde{P}(z)dz = 0$, (34) implies 1-periodicity of $w^1$ (as then, the left hand site when integrated is zero, implying $w^1(y,s,0) = w^1(y,s,1)$).

We will construct $w^0$ to satisfy the initial condition in (14). Now, choosing the functions $w^k$, such that

$$w^k = 0 \qquad \text{for } z = 0, \quad (y,s) \in \mathrm{H} \quad \text{and} \quad k = 1,2,\ldots, \tag{35}$$

ensures that expansion (28) satisfies initial condition (29). The unique 1-periodic solution of (34) and (35) is given by

$$w^1(y,s,z) = -g(z)\frac{1}{\varphi'(w^0)}\frac{\partial w^0}{\partial y}. \tag{36}$$

Note that this expression is identical to the second term in (19) for the linear case where $\varphi(w^0) = w^0$.

At the order $\varepsilon^0$, collection of the terms in the expansion (B1) of Appendix B leads to the equation

$$\frac{\partial}{\partial z}\left\{\varphi'(w^0)w^2 + \frac{1}{2}\varphi''(w^0)(w^1)^2 - \frac{1}{2}g^2\frac{\partial}{\partial y}\left(\frac{\partial w^0/\partial y}{\varphi'(w^0)}\right)\right\} = \frac{\partial^2 w^0}{\partial y^2} - \frac{\partial \varphi(w^0)}{\partial s}. \tag{37}$$

This is an equation for $w^2$. The function $w^2$, or the total bracketed term in (37), is 1-periodic in $z$ if and only if

$$\frac{\partial \varphi(w^0)}{\partial s} = \frac{\partial^2 w^0}{\partial y^2} \qquad \text{in H.} \tag{38a}$$

This nonlinear diffusion equation is solved subject to the initial condition

$$w^0(y,0) = \begin{matrix} 1 & y < 0, \\ 0 & y > 0. \end{matrix} \tag{38b}$$

The solution of (38) is a self-similar solution of the form

$$w^0(y,s) = f(\eta), \qquad \eta = y/\sqrt{s}, \tag{39}$$

where $f$ satisfies the boundary value problem

$$\frac{1}{2}\eta\frac{d\varphi(f)}{d\eta}+\frac{d^2f}{d\eta^2}=0 \qquad for-\infty<\eta<\infty, \qquad f(-\infty)=1, \quad f(+\infty)=0. \tag{39}$$

Problems of this kind received considerable attention in the mathematics literature. Some details and references are given in Appendix C.

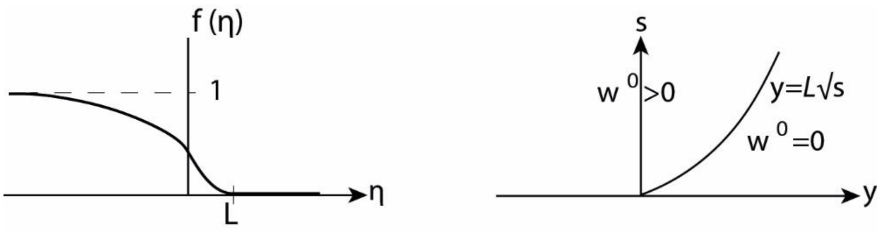


Figure 4: Sketch of solution of Problem (39). The solution has a front at $\eta=L>0$ and $f(\eta)=0$ for all $\eta\geq L$ in Figure 4a, and behaviour of corresponding $w^0(y,s)=f\left(\frac{y}{\sqrt{s}}\right)$ in the $(y,s)$-plane in Figure 4b.

Using (38a) and (36) in (37) and applying $w^2=0$ for $z=0$ and $(y,s)\in$H, we find (see Appendix B for the details)

$$w^2=\frac{1}{2}g^2\left\{\frac{1}{\left(\varphi'(w^0)\right)^2}\frac{\partial^2w^0}{\partial y^2}-2\frac{\varphi''(w^0)}{\left(\varphi'(w^0)\right)^3}\left(\frac{\partial w^0}{\partial y}\right)^2\right\}. \tag{40}$$

For the linear case ($\varphi(w^0)=w^0$), this is identical to the third term of (19).

Continuing the expansion would result in the fourth term $\varepsilon^{3/2}w^3$. However, here the procedure breaks down in the sense that it is not possible to find a function $w^3$ that is 1-periodic in $z$. This is explained in Appendix B. Therefore, we stop the expansion at order $\varepsilon^{3/2}$, and consider the approximation

$$w_\varepsilon(y,s)=w^0(y,s)+\varepsilon^{1/2}w^1(y,s,z)+\varepsilon w^2(y,s,z) \tag{41}$$

where $(y,s)\in$ H and $z=\frac{s}{\varepsilon}\big|_{mod1}$.

This expression satisfies the initial condition and approximates the solution up to O$(\varepsilon^{3/2})$. Since $w^1=w^2=0$ when $z=0,1$ we have in terms of the original variables $x$, $t$, and $u$

$$u(x,NT)=f\left(\frac{x}{\sqrt{D_{eff}NT}}\right)+\mathrm{O}(\varepsilon^{3/2}), \tag{42}$$

where $f$ is the solution of the boundary value problem (39). When $t\neq NT$, the presence of $w^1$ and $w^2$ gives

$$u(x,t)=f\left(\frac{x}{\sqrt{D_{eff}NT}}\right)+\mathrm{O}(\varepsilon^{1/2}). \tag{43}$$

It is of interest to investigate the behaviour of the functions $w^1$ and $w^2$ near the front $y=L\sqrt{s}$ of the lowest order approximation $w^0$. Since $w^1$ and $w^2$ are expressed in terms of $w^0$, and thus in terms of $f$, we need to consider the behaviour of $f(\eta)$ near $\eta=L$.

In Appendix D we show, by integrating (39), that

$$f(\eta) \sim C(L-\eta)^{\frac{1}{1-p}} \qquad \text{near } \eta = L, \tag{44}$$

where $C$ is a positive constant given by expression (D4).

Using (44) in expressions (36) and (40), it follows that (see again Appendix D)

$$w^1(y,x,z) \sim g(z)\frac{C}{\sqrt{s}}\left(L-\frac{y}{\sqrt{s}}\right)^{\frac{1}{1-p}} \tag{45}$$

and

$$w^2(y,x,z) \sim (g(z))^2\frac{C}{s}\left(L-\frac{y}{\sqrt{s}}\right)^{\frac{1}{1-p}} \tag{46}$$

for $s > 0$ and $y$ near $L\sqrt{s}$. Here $C$ is a generic positive constant.

Hence, all terms in approximation (41) vanish in a similar way near the front $y = L\sqrt{s}$ and $w^1$ and $w^2$ can be extended by $w^1 = w^2 = 0$ beyond $y = \sqrt{s}$ in a continuous way. With these extensions, the approximation truly holds for $(y, s) \in \mathrm{H}$.

Physically, this result means that the front of the concentration profile with oscillatory velocity (i.e., with convection and dispersion/diffusion), merges with the front of the nonlinear diffusion equation without flow, at least up to O$(\varepsilon^{3/2})$. This was also suggested by Cirkel et al. (2015).

# Numerical approximation and results

To ascertain that the concentration fronts with oscillatory velocity converge towards that in the absence of convection, but with adjusted hydrodynamic dispersion coefficient, we simulated the solute transport. The development of the concentration front at a depth of 2 m, that starts as a Heavyside step concentration distribution at time t=0, was simulated using the software SWAP (Kroes et al., 2008). Whereas SWAP is intended for transient unsaturated flow and solute transport, we assumed that the 4 m long vertical soil column was water saturated and the flow rate was varied according to a sine function, alternately upward and downward. The discretization in depth was 0.002 m, the dispersivity is $\alpha$=0.005 m and time steps are adjusted by SWAP. Flow rate maximum values were 1 mm/d and other conditions were kept the same as Cirkel et al. (2015).

If we assume

$V(t) = V_{max}\sin(2\pi\frac{t}{T})$ and redefine $\psi = \frac{\varphi(u)}{A}, t := \frac{t}{T}, x := \frac{x}{L}, \delta := \frac{\alpha V_{max} T}{AL^2} = \frac{\alpha}{L}$, if we choose a characteristic length $L = \frac{V_{max}T}{A}$ =0.36/A. Then we obtain in a dimensionless setting $\tilde{P}(z) = \sqrt{\frac{T^*}{\delta}}P^*(zT^*) = \sqrt{\frac{T^*}{\delta}}P(z)$, which is 1 periodic. The amplitude can be determined for the chosen parameter values of the numerical approximations. For $V_{max}$ =0.36 m/y, $T$ =1 year, $\alpha$ =5x10$^{-3}$ m, we obtain an amplitude of $\tilde{P}$ equal to $\sqrt{\frac{T^*}{\delta}} = \sqrt{\frac{2}{\pi}\frac{\alpha}{L}}$ that varies in the simulations from about 2 to 5, depending on the used adsorption parameters. This amplitude is therefore O(1).

In Figure 5, we show the front as it develops with increasing number of flow cycles. Initially, the concentration front spreading is relatively fast, and it slows down as time proceeds. The case where convection is disregarded, except for accounting it in the calculation of an effective diffusion coefficient, similar as Scotter and Raats (1968) and Cirkel et al. (2015), appears to give results that increasingly converge with the oscillatory CDRP.

If indeed a nonlinear diffusion situation is approached, the concentration fronts should approach a single one if plotted as a function of a similarity variable as given by

$$\tilde{\zeta} = [x(u) - \langle x \rangle]/\sqrt{t} \qquad (47)$$

Figure 5b shows that this is indeed the case as already after a short time (1 cycle) the CDRP results practically overlap with those for 10 or more cycles. The agreement between pure diffusion and (oscillating) CDRP is excellent for $N \geq 10$.

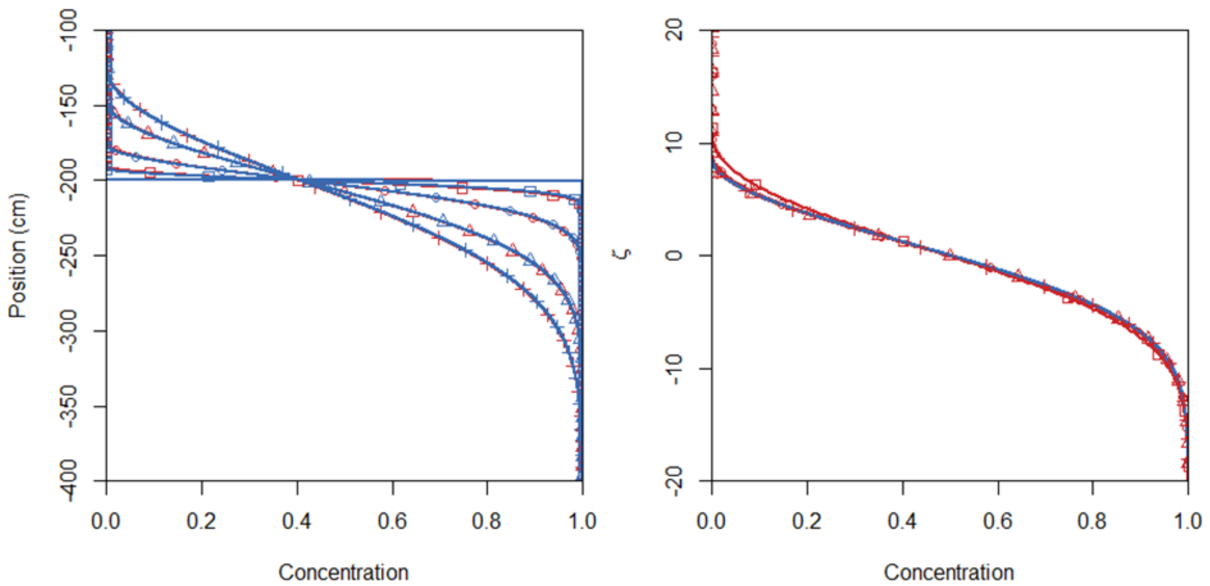


Figure 5: Concentration fronts at different number of cycles as a function of position (depth; left) and similarity variable (ζ; right; as defined in eq. 47). Red: solution for CDRP, Blue: solution for zero convection and corrected dispersivity. Number of periods: N=0 (only left; no marker), N=1 (□), N= 10 (o), 50 (Δ) and 100 (+).

An initial condition for the upper half of the domain of zero concentration is quite artificial and seldom realistic. Therefore, a second experiment was simulated where the initial concentration is slightly larger than zero (0.001 in the units of Figures 5 and 6). In that case, the non-Lipschitz continuity due to an infinite adsorption equation derivative, hence an infinite retardation of zero concentrations (Van Der Zee, 1990) does not occur. As Figure 6 shows, in that case the concentration spreading is slightly larger than for Figure 5, but changes are small for few cycles and diminish rapidly as the number N increases.

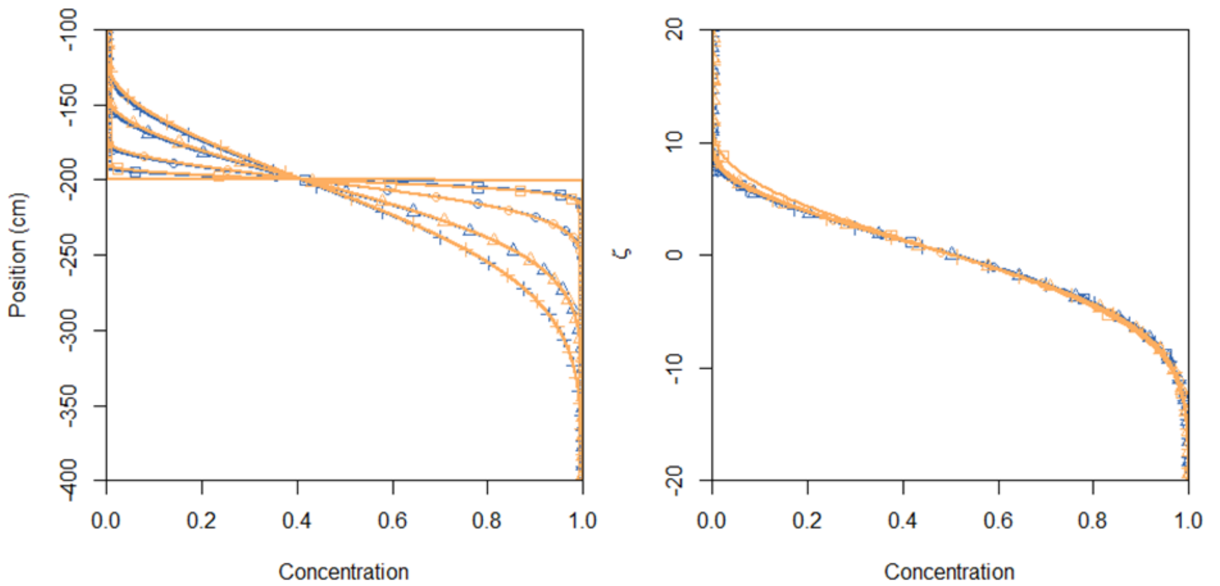


Figure 6: Concentration fronts as a function of position (left) and similarity variable (ζ, right) and for same times and markers as Figure 5, but for oscillating CDRP case initial concentration is 0.001 instead of 0 for position upward from -200 cm (orange). Blue lines and markers for the zero convection case and initial concentration of 0.

For both cases of Figure 5 and 6, we observe convergence to a pure nonlinear diffusion situation. As was commented on, the initial condition of a Heaviside concentration step front leads to higher order terms that do not disappear. Therefore, the simulations were done again for the case that the initial condition follows a steep but smooth errorfunction. The resulting concentration fronts after 10 cycles were indistinguishable from those in Figures 5 (not shown).

# Conclusion

In this paper, we analysed the long term behaviour of a solute front with oscillating flow, if that solute is subject to nonlinear (Freundlich) adsorption. Our mathematical analysis confirmed that the oscillating nonlinear convection-dispersion front converges to a nonlinear pure diffusion (i.e., zero convection) front, though with adjusted, enhanced dispersion coefficient according to Cirkel et al., (2015). This result supports conjectures made recently by Cirkel et al. (2015) and Neeper and Stauffer (2012) of the long term dominance of the diffusion process.

This result is of interest, as unidirectional flow (in the negative or positive directions for the current initial condition) would lead to either traveling wave (TW) or rarefaction wave (RW) behaviour (Van Duijn and Knabner, 1991, Van Der Zee, 1990). Both TW and RW behaviour essentially depend on convective transport. Although earlier a rapid convergence to a limiting analytical TW solution for unidirectional flow was observed (Bosma and Van Der Zee, 1993), this rate of convergence is apparently not fast enough to compensate for the spreading during the RW regime (with the flow rate in the opposite direction). By itself, this is plausible, because the analytical TW solutions are limiting solutions (for $t \to \infty$) (Bolt, 1982, Van Duijn and Knabner, 1991). But we may also conclude, that at large times, dispersional spreading dominates the oscillating case.

The oscillations for the present case were simplified to a sine function of flow velocity. Both Eeman et al. (2013) and Cirkel et al. (2015) also considered irregular fluctuations of flow velocity and direction, and this irregular behavior that is more in agreement with realistic situations could be captured well in the definition of the "effective diffusion coefficient".

The convergence of the oscillating case to pure diffusion implies that large time spreading occurs slower and slower, but does not stop. Accordingly, even if the fluctuations lead to a mean front that moves only over a small distance in the opposite directions, the concentration front at some time spreads over a much larger soil zone, than is involved in the fluctuations: front spreading continues unbounded.

As, in essence, for two situations with different nonlinear sorption (Gapon and Freundlich; Cirkel et al., 2015 and this paper) similar conclusions can be made, it could well be that for other nonlinear biogeochemical interactions (e.g. Monod kinetics, Janssen et al., 2006)) our conclusions remain valid. In that case, this work becomes of more general interest than the very different situations that have already been elaborated in this paper and cited work, e.g. of Neeper and Stauffer (2012) and Scotter and Raats (1968, 1969).


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# Appendixes

## Appendix A: Solution linear case

With $erfc(\eta) = \frac{2}{\sqrt{\pi}} \int_\eta^\infty e^{-p^2}\, dp$,

the solution for the linear case is

$$w_\varepsilon(y,s) = \frac{1}{2} erfc\left(\frac{y}{2\sqrt{s}} - \frac{\varepsilon^{-\frac{1}{2}} \int_0^s \tilde{P}\left(\frac{\xi}{\varepsilon}\right) d\xi}{2\sqrt{s}}\right). \qquad \text{(A1)}$$

Note: $\varepsilon^{-1/2}\int_0^s \tilde{P}\left(\frac{\xi}{\varepsilon}\right)d\xi = \varepsilon^{+1/2}\int_0^{s/\varepsilon}\tilde{P}(\chi)d\chi$.

## Appendix B : Details of expansion

In this appendix, we provide some details that were omitted in the main text. Substituting (28) into (14) leads to the expansion:

$$\left(\frac{\partial}{\partial s}+\frac{1}{\varepsilon}\frac{\partial}{\partial z}\right)\left\{\varphi(w^0)+\varphi'(w^0)\left(\varepsilon^{\frac{1}{2}}w^1+\varepsilon w^2+\varepsilon^{\frac{3}{2}}w^3\dots\right)+\frac{1}{2}\varphi''(w^0)\left(\varepsilon^{\frac{1}{2}}w^1+\varepsilon w^2+\cdots\right)^2+\frac{1}{3!}\varphi'''(w^0)\left(\varepsilon^{1/2}w^1+\cdots\right)^3+\cdots\right\}+\varepsilon^{-1/2}\tilde{P}(z)\frac{\partial}{\partial y}\left(w^0+\varepsilon^{1/2}w^1+\varepsilon w^2+\cdots\right)=\frac{\partial^2}{\partial y^2}\left(w^0+\varepsilon^{1/2}w^1+\varepsilon w^2\dots\right) \tag{B1}$$

Collection of terms at order $\varepsilon^0$, gives for $w^2$:

$$\frac{\partial w^0}{\partial s}+\frac{\partial}{\partial z}\left(\varphi'(w^0)w^2+\frac{1}{2}\varphi''(w^0)(w^1)^2\right)+\tilde{P}(z)\frac{\partial w^1}{\partial y}=\frac{\partial^2 w^0}{\partial y^2} \tag{B2}$$

since

$$\tilde{P}(z)\frac{\partial w^1}{\partial y}=-\tilde{P}(z)g(z)\frac{\partial}{\partial y}\left(\frac{\frac{\partial w^0}{\partial y}}{\varphi'(w^0)}\right)=-\frac{1}{2}\frac{dg^2}{dz}\frac{\partial}{\partial y}\left(\frac{\partial w^0/\partial y}{\varphi'(w^0)}\right)$$

(B2) can be rewritten as (37).

Using (38a) and (36) in (37) and applying $w^2=0$ for $z=0$ and $(y,s)\in$H, we obtain:

$$w^2=\frac{1}{2}g^2\frac{1}{\varphi'(w^0)}\frac{\partial}{\partial y}\left(\frac{\partial w^0/\partial y}{\varphi'(w^0)}\right)-\frac{1}{2}\frac{\varphi''(w^0)}{\varphi'(w^0)}(w^1)^2=\frac{1}{2}g^2\left\{\frac{1}{\varphi'(w^0)}\frac{\partial}{\partial y}\left(\frac{\partial w^0/\partial y}{\varphi'(w^0)}\right)-\frac{\varphi''(w^0)}{\left(\varphi'(w^0)\right)^3}\left(\frac{\partial w^0}{\partial y}\right)^2\right\} \tag{B3}$$

which leads to (40).

A problem arises for $\varepsilon$ of order $^3/_2$. From the expansion (B1), we deduce for $w^3$

$$\frac{\partial}{\partial s}(\varphi'(w^0)w^1)+\frac{\partial}{\partial z}\left\{\varphi'(w^0)w^3+\varphi''(w^1)w^1w^2+\frac{1}{3!}\varphi'''(w^0)(w^1)^3\right\}+\tilde{P}(z)\frac{\partial w^2}{\partial y}=\frac{\partial^2 w^1}{\partial y^2} \tag{B4}$$

Writing $w^2(y,s,z)=\left(g(z)\right)^2\chi(y,s)$ we have $\hat{P}(z)w^2=\frac{1}{3}\frac{d}{dz}(g(z))^3\chi(y,s)$.

Hence, we get for (B4)

$$\frac{\partial}{\partial z}\left\{\varphi'(w^0)w^3+\varphi''(w^0)w^1w^2+\frac{1}{3!}\varphi'''(w^0)(w^1)^3+\frac{1}{3}(g(z))^3\chi(y,s)\right\}=\frac{\partial^2 w^1}{\partial y^2}-\frac{\partial}{\partial s}(\varphi'(w^0)w^1) \tag{B5}$$

note that $w^1$, $w^2$, and $g$ are 1-periodic in $z$. To solve (B5) for $w^3$, being 1-periodic in $z$ as well, requires

$$C(y,s):=\int_0^1\left\{\frac{\partial^2 w^1}{\partial y^2}-\frac{\partial}{\partial s}(\varphi'(w^0)w^1)\right\}dz=0\quad\forall\,(y,s)\in\mathrm{H}. \tag{B6}$$

However, with (36) and $\langle g\rangle=\int_0^1 g(z)dz>0$, we find

$$\frac{1}{\langle g\rangle}C(y,s)=\frac{\partial^2 w^0}{\partial s\partial y}-\frac{\partial^2}{\partial y^2}\left(\frac{1}{\varphi'(w^0)}\frac{\partial w^0}{\partial y}\right)=\frac{\partial}{\partial y}\left\{\frac{\partial w^0}{\partial s}-\frac{1}{\varphi'(w^0)}\frac{\partial^2 w^0}{\partial y^2}+\frac{\varphi''(w^0)}{\left(\varphi'(w^0)\right)^2}\left(\frac{\partial w^0}{\partial y}\right)^2\right\}$$

$$=\frac{\partial}{\partial y}\left\{\frac{\varphi''(w^0)}{\left(\varphi'(w^0)\right)^2}\left(\frac{\partial w^0}{\partial y}\right)^2\right\}=0, \tag{B7}$$

only if $\varphi''(w^0) = 0$, which is the linear or non-reactive case.

Therefore, we stop the expansion at the order $\varepsilon^{3/2}$.

## Appendix C: Solution problem (18)

Setting $h = \varphi(f)$ and $f = \varphi^{-1}(h) = \Lambda(h)$ in (39) results in the transformed equation

$$\frac{1}{2}\eta\frac{dh}{d\eta} + \frac{d^2\Lambda(h)}{d\eta^2} = 0 \text{ for } -\infty < \eta < \infty, \quad \text{(C1a)}$$

with

$$h(-\infty) = \varphi(1) \qquad h(+\infty) = \varphi(0) = 0 \quad \text{(C1b)}$$

Nonlinear diffusion problems as (C1) were studied by Atkinson and Peletier (1974) and Van Duijn and Peletier (1977) and Philip (1960). The function

$$D(h) := \Lambda'(h) \qquad h \geq 0 \quad \text{(C2)}$$

acts as a nonlinear diffusion function. It has been shown that fronts exist if $D(h)$ decays sufficiently fast to zero as $h \downarrow 0$. In particular if

$$\frac{D(h)}{h} \in L^1(0,\delta) \text{ for some } \delta>0 \quad \text{(C3)}$$

then there exists $0 < L < \infty$ such that

$$h(\eta) \begin{cases} > 0, \text{ strictly decreasing for } \eta < L \\ = 0 \text{ for } \eta \geq L \end{cases} \quad \text{(C4)}$$

Similar behaviour holds for the original variable $f(\eta)$.This behaviour is sketched in Figure 4.

**Example** Freundlich adsorption gives $\varphi(f) = f + Af^p$, with $A > 0, 0 < p < 1, f \geq 0$. Thus for small $f$ (since $p < 1$) we have approximately $\varphi(f) \sim Af^p$, and $\Lambda(h) \sim A^{-\frac{1}{p}}h^{\frac{1}{p}}$.

Hence, $D(h) \sim \frac{1}{p}A^{-\frac{1}{p}}h^{\frac{1}{p}-1}$ and $\frac{D(h)}{h} \sim \frac{1}{p}A^{-\frac{1}{p}}h^{\frac{1}{p}-2}$

is integrable near $h = 0$ since $p < 1$. Therefore, Freundlich adsorption leads to fronts as in (C4). In terms of the original variables ($x$ and $t$) the front is located at $\frac{x}{\sqrt{\alpha\tau_{obs}}} = L\sqrt{\frac{\tau}{\tau_{obs}}}$ and with (7) we have $x = L\sqrt{\alpha\int_0^t |V(\zeta)| d\zeta}$. After $N$ periods we have

$$x = L\sqrt{\alpha\int_0^{NT} |V(\zeta)| d\zeta} = L\sqrt{D_{eff}}.\sqrt{NT} \quad \text{(C6)}$$

where $D_{eff} = \alpha\langle|V|\rangle$ denotes the effective dispersion coefficient.

If $w^0$ has a front at $y = L\sqrt{s}$ in the sense that $w^0(y,s) = 0$ for $s > 0$ and $y \geq L\sqrt{s}$, then the same holds for the first approximation $w^1$, by virtue of (36). In fact, this holds for $w^2$ as well.

## Appendix D: Behaviour near front

Near the front, we have $\Lambda(h) = A^{-\frac{1}{p}}h^{\frac{1}{p}}$, giving for h the equation, see (C1a),

$$\frac{1}{2}\eta h + A^{-\frac{1}{p}}\frac{d^2h^{\frac{1}{p}}}{d\eta^2} = 0 \tag{D1}$$

Integrating, this equation from $\eta < L$ to $\eta = L$, and using $\frac{dh^{\frac{1}{p}}}{d\eta}(\eta) \to 0$ as $\eta \to L$ (vanishing flux at the front), gives

$$\frac{1}{2}\eta h(\eta) + \frac{1}{2}\int_{\eta}^{L} h(s)ds + A^{-\frac{1}{p}}\frac{dh^{\frac{1}{p}}}{d\eta}(\eta) = 0.$$

Dividing this equation by $h(\eta)$ yields

$$\frac{A^{1\frac{1}{p}}}{1-p}\frac{dh^{\frac{1}{p}-1}}{d\eta}(\eta) = -\frac{1}{2}\eta - \frac{1}{2}\frac{1}{h(\eta)}\int_{\eta}^{L} h(s)ds. \tag{D2}$$

Using the monotonicity of $h$ gives

$$0 < \frac{1}{h(\eta)}\int_{\eta}^{L} h(s)ds < L - \eta.$$

Applying this in (D2) leads to

$$\lim_{\eta\to L} h^{\frac{1}{p}-1} = -\frac{L}{2}(1-p)A^{\frac{1}{p}},$$

In terms of $f(\eta)$ this implies

$$f(\eta) \sim C(L-\eta)^{\frac{1}{1-p}} \qquad \text{near } \eta = L, \tag{D3}$$

where

$$C = \left(\frac{1}{2}(1-p)A\right)^{\frac{1}{1-p}} \tag{D4}$$

For $w^1$, see expression (36) and using $w^0 = f$, we need to investigate the behaviour of

$$\frac{1}{\varphi\prime(f)}\frac{1}{\sqrt{s}}\frac{df}{d\eta} \qquad \text{near } \eta = L, \tag{D5}$$

and for $w^2$, see expression (40), the behaviour of

$$\frac{1}{(\varphi\prime(f)^2}\frac{1}{s}\frac{d^2f}{d\eta^2} - 2\frac{\varphi"(f)}{(\varphi\prime(f))^2}\frac{1}{s}\left(\frac{df}{d\eta}\right)^2 \qquad \text{near } \eta = L. \tag{D6}$$

Using $\varphi(f) = Af^p$, we have, using (D3),

$$\varphi'(f) = Apf^{p-1} \sim C(L-\eta)^{-1}, \tag{D7}$$

$$\varphi"(f) = Ap(p-1)f^{p-2} \sim C(L-\eta)^{\frac{p-2}{1-p}}, \tag{D8}$$

near $\eta = L$. Here, and below, $C > 0$ is a generic constant that we do not explicit any further.

Using (D3) and the equation for $f$ (or $h$), it is possible to show that

$$\frac{df}{d\eta} \sim C(L-\eta)^{\frac{p}{1-p}} \text{ and } \frac{d^2f}{d\eta^2} \sim C(L-\eta)^{\frac{2p-1}{1-p}} \qquad \text{(D9)}$$

near $\eta = L$.

Finally, we combine (D7)-(D9) in (D5) and (D6) to obtain approximations (45) and (46).

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