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Large time behaviour of oscillatory nonlinear solute transport in porous media

C.J. van Duijn\textsuperscript{a,b}, S.E.A.T.M. van der Zee\textsuperscript{c,d,}* 

\textsuperscript{a}Department of Earth Sciences, Utrecht University, P.O. Box 80.115, 3508 TC Utrecht, The Netherlands 
\textsuperscript{b}Department of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands 
\textsuperscript{c}Soil Physics and Land Management, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands 
\textsuperscript{d}School of Chemistry, Monash University, Melbourne, 3800 VIC, Australia

\textsuperscript{*}Corresponding author at: Soil Physics and Land Management, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands. E-mail addresses: C.J.v.Duijn@TUE.NL (C.J. van Duijn), Sjoerd.vanderZee@WUR.NL (S.E.A.T.M. van der Zee).

**Highlights**
- Oscillation for nonlinear reacting solute gives nonlinear reaction-diffusion problem.
- Mechanical dispersion coefficient involves the time averaged absolute discharge.
- Nonlinear reactions lead to a large time limit asymmetric, non-Gaussian mixing zone.

**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 and, disregarding molecular diffusion, mechanical dispersion. By homogenization, we show that after many cycles, the transport converges to a zero convection, pure nonlinear diffusion problem. The impact of the oscillatory flow requires an adjustment of the dispersion coefficient, where instead of the modulus of the particle velocity, we have to use its time averaged value. Physically, this agrees with a velocity defined by the distance travelled by particles in solution, divided by the time needed for that displacement. The nonlinearity of the sorption reaction is retained in the concentration distribution of the mixing zone, because in the large time limit, this distribution is not Gaussian but asymmetric. 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.

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**1. Introduction**

When studying flow and transport in natural porous media in field conditions or in packed columns in the laboratory, steady state flow is often assumed. However, there are many important cases where transient flow needs to be considered (Dagan et al., 1996, Dentz and Carrera, 2003).

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 Stauffer, 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. (2012, 2016) and Cirkel et al. (2015). At a small time scale, daily oscillations may occur at the plant root surface due to the day-night pattern of transpiration (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 from iron oxide deposits) by periodically extracting and discharging water. In underground energy or chemical storage, oscillating conditions may be important, for instance for seasonal underground heat storage and harvesting. In the context of tracer dispersion in estuaries, Kay (1997) investigated oscillating flows due to tidal reversals. Of interest is also the analysis by Pool et al. (2016), who considered oscillatory movement for an inert (conservative) solute. Their mathematical analysis, supported by numerical as well as experimental observations, revealed the impact of oscillations on the width of a mixing zone between two solutions with different concentrations. At large times, a symmetric, Gaussian, distribution of the concentration front developed and they provided expressions of e.g. the width of the concentration front which displaces as a function of time.

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 Neep and Stauffer (2012) 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. The latter speculated, based on an approximation of the governing equations, that the effective diffusion coefficient comprises a generalization of the so-called mechanical dispersion coefficient. Whereas in classical theory the mechanical dispersion coefficient equals the product of a formation factor (the dispersivity) and the absolute value of the pore water velocity, for oscillatory flow the time average of the absolute value of pore water velocity should be used. Therefore, for zero net displacement of a mixing zone, the velocity in the mechanical dispersion term is given by the travelled distance of particles in either direction divided by the time needed for this displacement.

With regard to the work by Cirkel et al. (2015), it is worthwhile to emphasize that nonlinear adsorption/desorption essentially differs from the nonreactive or linear sorption and transport behaviour. As Van Duijn and Knaapen (1991, 1992) and Van Der Zee (1991) showed, for appropriate initial and boundary conditions (steady flow), traveling wave behaviour is found, as nonlinear sorption counteracts dispersiveal spreading. For reversed conditions, sorption and dispersion enhance each other, leading to rapidly spreading fronts: rarefaction waves (RW). For oscillatory flow, Cirkel et al. (2015) showed that these types of waves are not observed after a number of oscillations.

It is the scope of this paper, to reconsider the transport of a nonlinearly reacting (adsorbing/desorbing) solute under an oscillating flow regime and to investigate the large time behaviour of the solute front and mixing behaviour. In particular, we show that at large times, neither TW nor RW spreading is obtained. In fact, the front approaches a pure diffusion/dispersion type of spreading that is non-Gaussian due to the nonlinear reaction, and with an adjusted mechanical dispersion coefficient.

2. 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)

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

$$u(x,0) = \begin{cases} 1 & x < 0, \\ 0 & x > 0 \end{cases} \quad (2)$$

where $u \geq 0$ denotes a scaled solute concentration, the function $\phi(u)$ 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:

$$\phi(u) = \frac{u}{A} + u^p, \quad A > 0, \quad 0 < p < 1. \quad (3)$$

Further, we ignore molecular diffusion, hence

$$D(t) = \frac{\alpha}{|V(t)|}. \quad (4)$$

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

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

where $P(t)$ is a function given by $V(t)/|V(t)|$, i.e. (Fig. 1),

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

Next, we introduce as new time scale

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

which is the total travelled distance of the fluid particle in time $t$. With $v(x, \tau) = v(x, \tau(t)) = u(x, t)$ and $P'(\tau) = P'(\tau(t)) = P(t)$, we find the transformed problem

Fig. 1. Illustration of the velocity as a function of time and the function $P(t)$, where $T$ is the cycle period.
\[ \frac{\partial \rho(\nu)}{\partial \tau} + P(T) \frac{\partial \nu}{\partial x} = \frac{\partial^2 \nu}{\partial x^2} \quad x \in \mathbb{R}, \tau > 0, \] (8)

\[ \nu(x, 0) = \begin{cases} 1 & x < 0, \\ 0 & x > 0. \end{cases} \] (9)

### 3. 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 the second scaling

\[ s := \frac{\tau}{\tau_{\text{obs}}} \quad \text{and} \quad y := \frac{x}{\sqrt{2} \tau_{\text{obs}}}, \] (10)

here \( \tau_{\text{obs}} \) is the observation ‘time’

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

when \( N \) is the number of cycles and \( T \) the cycle period, see also Fig. 1. The length \( x \) is scaled by a diffusion length scale based on the observation ‘time’ \( \tau_{\text{obs}} \) multiplied by the dispersivity \( \alpha \) of the system. Note that \( \tau_{\text{obs}} \) corresponds to the real observation time \( \tau_{\text{obs}} = NT \). Thus, the problem has two time scales: the (small) cycle time \( T \) and the (large) observation time \( \tau_{\text{obs}} \).

We also introduce the parameter

\[ \varepsilon = \frac{1}{N}, \] (12)

which is small after many \( (N) \) cycles. Setting now \( w(y, s) = w(y, s; \frac{1}{\sqrt{\tau_{\text{obs}}}}) = \nu(x, \tau) \) and introducing for notational convenience

\[ \tilde{P}(z) := \frac{T}{\sqrt{2}} P(zT), \quad \text{for} \quad z > 0, \] (13)

see Fig. 2. We obtain the scaled (dimensionless) initial value problem (IVP)

\[ \frac{\partial \rho(w)}{\partial s} + \frac{\varepsilon}{\sqrt{2}} \frac{\partial \rho(w)}{\partial y} + \frac{\partial^2 \rho(w)}{\partial y^2} = 0 \quad y \in \mathbb{R}, s > 0, \] (14)

\[ w(y, 0) = \begin{cases} 1 & y < 0, \\ 0 & y > 0. \end{cases} \]

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

### 4. Linear (non-reactive) case

For the linear case, \( \rho(w) = w \) 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 \( z = \frac{\varepsilon}{N} \mod 1 \). Introducing the function

\[ g(z) = \int_0^z \tilde{P}(\zeta)d\zeta \] (15)

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

\[ w_r(y, s) = \frac{1}{2} \text{erfc} \left( \frac{y}{2\sqrt{s}} \frac{1}{\tau_{\text{obs}}} g(z) \right), \] (16)

setting

\[ w^0(y, s) = \frac{1}{2} \text{erfc} \left( \frac{y}{2\sqrt{s}} \frac{1}{\tau_{\text{obs}}} \right), \] (17)

we observe that

\[ w_r(y, s) = w^0(y - \varepsilon^{1/2} g(z), s), \] (18)

which can be expanded in terms of \( \varepsilon \) to give

\[ w_r(y, s) = w^0(y, s) - \varepsilon^{1/2} g(z) \frac{\partial w^0}{\partial y} + \frac{1}{2} \varepsilon g^2(z) \frac{\partial^2 w^0}{\partial y^2} + O(\varepsilon^{3/2}). \] (19)

Note that expansion (19) is of the form

\[ w_r(y, s) = w^0(y, s) + \varepsilon^{1/2} w^1(y, s, z) + \varepsilon^{3/2} w^2(y, s, z) + \ldots, \] (20)

where the functions \( w^k \) are 1-periodic with respect to \( z \). It is a two scale expansion, i.e., in \( \varepsilon \) and in \( z = \frac{\varepsilon}{N} \mod 1 \). Such expansions are well-known in the theory of homogenization, see for instance Cioranescu and Donato (1999) and Hornung (1997). What is the interpretation of (16) in terms of the original variables \( x, t, \) and \( u \)? The backwards transformation gives

\[ u(x, t) = \frac{1}{2} \text{erfc} \left( \frac{x}{2\sqrt{\tau_{\text{obs}}}} \frac{1}{\tau_{\text{obs}}} \sqrt{T} \frac{\tau(t)}{\tau_{\text{obs}}} \right), \] (21)

Hence, at each \( t = NT \), we have

\[ \tau(NT) = NT = N \int_0^T |V(z)|dz = (|V|)NT, \] (22)

\[ g \left( \frac{\tau(NT)}{T} \right) = 0. \] (23)

and thus

\[ u(x, NT) = \frac{1}{2} \text{erfc} \left( \frac{x}{2\sqrt{D_{\text{eff}} NT}} \right). \] (24)
where $D_{\text{eff}} = \alpha |V|$, 

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

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

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

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 $\varepsilon^4$, collection of the terms in the expansion (B1) of Appendix B leads to the equation

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

This is an equation for $w^2$. The function $w^0$, or the total bracketed term in (37), is 1-periodic in $z$ if and only if

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

This nonlinear diffusion equation is solved subject to the initial condition

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

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

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

where $f$ satisfies the boundary value problem

$$\frac{1}{2} \frac{\partial f}{\partial \eta} + \frac{1}{2} \frac{d^2 f}{d \eta^2} = 0 \quad \text{for } -\infty < \eta < \infty, \quad (40)$$

$$f(-\infty) = 1, \quad f(+\infty) = 0. \quad (40)$$

See Fig. 4. Problems of this kind received considerable attention in the mathematics literature. Some details and references are given in Appendix C.

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)

$$w^2 = \frac{1}{2} \frac{\partial^2 w^0}{\partial y^2} \left\{ \frac{1}{\varphi'(w^0)} \frac{\partial \varphi^0}{\partial y} - 2 \frac{\varphi''(w^0)}{\varphi'(w^0)^2} \left( \frac{\partial \varphi^0}{\partial y} \right)^2 \right\}. \quad (41)$$

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

$$w_3(y, s) = w^0(y, s) + \varepsilon^{1/2} w^1(y, s, z) + \varepsilon w^2(y, s, z) \quad (42)$$

where $(y, s) \in H$ and $z = \frac{t \pi}{\sqrt{D_{\text{eff}} NT}}$.

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

$$u(x, NT) = f \left( \frac{x}{\sqrt{D_{\text{eff}} NT}} \right) + O(\varepsilon^{3/2}), \quad (43)$$

where $f$ is the solution of the boundary value problem (40). When $t \neq NT$, the presence of $w^1$ and $w^2$ gives

$$u(x, t) = f \left( \frac{x}{\sqrt{D_{\text{eff}} NT}} \right) + O(\varepsilon^{1/2}). \quad (44)$$
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 \( f(g) \) near \( g = L \).

In Appendix D we show, by integrating (40), that

\[
f(g) \sim C \frac{1}{g} \quad \text{near } g = L,
\]

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

Using (45) in expressions (36) and (41), it follows that (see again Appendix D)

\[
w_1(y, x, z) \sim g(z) \frac{C}{\sqrt{s}} \left( L - \frac{y}{\sqrt{s}} \right)^{1/2}
\]

and

\[
w_2(y, x, z) \sim \left( g(z) \right)^2 \frac{C}{s} \left( L - \frac{y}{\sqrt{s}} \right)^{-1/2}
\]

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

Hence, all terms in approximation (42) 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 \( (y, s) \in \mathbb{R} \).

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

6. Numerical approximation and results

In this section, we provide numerical simulations of concentration fronts that are subject to velocity oscillations. Our aim is to show that these fronts at large times converge to the front that is calculated for the case of nonlinear ad/desorption, in the absence of flow (hence, no convection and no oscillations), provided that the latter front has a dispersion coefficient given by expression (25). The close agreement between these fronts supports the statements made at the end of the previous section.

We simulated solute transport to determine the development of the concentration front at a depth of 2 m, that starts as a Heaviside step concentration distribution at time \( t = 0 \), 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 (expression 4) 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).

We assume $V(t) = V_{\text{max}}\sin(2\pi t)$ and redefine $\psi = \frac{t}{V_{\text{max}}}$. $u = \frac{q}{\delta}$ if we choose a characteristic length $L = \frac{V_{\text{max}}}{q} = 0.36/A$. Then we obtain in a dimensionless setting $\hat{p}(z;\tau) = \sqrt{\frac{C}{L}} p(z;\tau) = \sqrt{\frac{C}{L}} p(z)$, which is 1 periodic. The amplitude can be determined for the chosen parameter values of the numerical approximations. For $V_{\text{max}} = 0.36$ m/y, $T = 1$ year, $\alpha = 5 \times 10^{-3}$ m, we obtain an amplitude of $\hat{P}$ equal to $\sqrt{\frac{C}{L}} = \sqrt{\frac{C}{L}}$ that varies in the simulations from about 2 to 5, depending on the used adsorption parameters. This amplitude is therefore $O(1)$.

In Fig. 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 with expression (25), similar as Scatter and Raats (1968) and Cirkel et al. (2015), appears to give results that increasingly converge with the oscillatory CDRP.

Fig. 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 $N \gg 10$. We emphasize that the initial condition follows a steep but smooth error function. The resulting concentration fronts after 10 cycles are indistinguishable from those in Fig. 5 (not shown).

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 Figs. 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 Fig. 6 shows, in that case the concentration spreading is slightly larger than for Fig. 5, but changes are small for few cycles and diminish rapidly as the number $N$ increases.

For both cases of Figs. 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 error function. The resulting concentration fronts after 10 cycles were indistinguishable from those in Fig. 5 (not shown).

7. 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 Neepoer 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, dispersionsal spreading dominates the oscillating case.

The oscillations for the present case were simplified to a sine function of flow velocity. Both Eeman et al. (2012) and Cirkel et al. (2015) also considered irregular fluctuations of flow velocity and direction, and this irregular behaviour 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, Jansen et al., 2006) our conclusions remain valid. In that case, this work becomes of more general interest than the different situations that have already been elaborated in this paper and cited work, e.g. of Neuper and Stauffer (2012) and Scort and Raats (1968, 1969).

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Appendix A. Solution linear case

With $\text{erfc}(y) = \frac{1}{\sqrt{\pi}} \int_y^\infty e^{-t^2} dt$, the solution of the linear case is

$$w_c(z) = \frac{1}{2} \text{erfc} \left( \frac{y}{2\sqrt{s}} \right)$$

Note: $e^{-y^2/2} \int_0^y \text{erfc}(u) du = e^{-y^2/2} \int_0^y \text{erfc}(u) du$.

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:

$$\left( \frac{\partial}{\partial s} + \frac{1}{e} \frac{\partial}{\partial z} \right) \left( \varphi'(w^0) \varphi''(w^0) + \frac{1}{2} \varphi''(w^0) + \frac{1}{2} \varphi''(w^0) \varphi''(w^0) + \frac{1}{2} \varphi''(w^0) \varphi''(w^0) + \ldots \right)$$

$$= \frac{1}{2} \varphi''(w^0) \left( \varphi''(w^0) + \varphi''(w^0) \varphi''(w^0) + \varphi''(w^0) \varphi''(w^0) + \ldots \right)$$

$$+ e^{-1/2} \varphi'(z) \varphi''(w^0) \varphi''(w^0) + e^{-1/2} \varphi'(z) \varphi''(w^0) \varphi''(w^0) + e^{-1/2} \varphi'(z) \varphi''(w^0) \varphi''(w^0) + \ldots$$

$$= \frac{\partial^2}{\partial z^2} \left( \varphi''(w^0) + \varphi''(w^0) \varphi''(w^0) + \varphi''(w^0) \varphi''(w^0) + \ldots \right)$$

(B1)

Collection of terms at order $\varepsilon^*\psi_1$, gives for $w^2$:

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

(B2)

since

$$\frac{\partial \varphi^0}{\partial z} \frac{\partial \varphi^0}{\partial z} = - \frac{\partial \varphi^0}{\partial z} \frac{\partial \varphi^0}{\partial z} - \frac{1}{2} \frac{\partial \varphi^0}{\partial z} \left( \frac{\partial \varphi^0}{\partial z} \right)^2$$

(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:

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

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

(B3)

which leads to (41).

A problem arises for $\varepsilon$ of order $3/2$. From the expansion (B1), we deduce for $w^3$

$$\frac{\partial}{\partial z} \left( \varphi'(w^0)^3 \right) + \frac{\partial^2}{\partial z^2} \left( \varphi'(w^0)^3 \right) - \frac{1}{2} \frac{\partial \varphi^0}{\partial z} \left( \frac{\partial \varphi^0}{\partial z} \right)^2 = \varphi''(w^0) \left( \varphi'(w^0)^3 \right)$$

Writing $w^2(y, s, z) = \frac{1}{2} \frac{d}{dz} \left( \varphi'(w^0)^3 \right)$ and $w^3 = \frac{1}{3} \frac{d}{dz} \left( \varphi'(w^0)^3 \right)$, we have $\frac{\partial}{\partial z} w^3 = \frac{1}{2} \frac{d}{dz} \left( \varphi'(w^0)^3 \right)$

$$\varphi''(w^0) \left( \varphi'(w^0)^3 \right) = \frac{\varphi''(w^0)}{(\varphi''(w^0))^2} \left( \frac{\partial \varphi^0}{\partial z} \right)^2$$

(B4)

$$\frac{\partial}{\partial z} \left( \varphi'(w^0)^3 \right) = \frac{\varphi''(w^0)}{(\varphi''(w^0))^2} \left( \frac{\partial \varphi^0}{\partial z} \right)^2$$

(B5)

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

$$C(y, s) := \int_0^1 \left( \frac{\partial \varphi^0}{\partial z} \right)^2 \frac{\partial \varphi^0}{\partial z} \left( \varphi'(w^0)^3 \right) dz = 0 \quad \forall (y, s) \in H.$$  

(B6)

However, with (36) and $g = \int_0^1 \varphi'(w^0) dz > 0$, we find

$$\frac{1}{g} C(y, s) = \frac{\varphi''(w^0)}{(\varphi''(w^0))^2} \left( \varphi''(w^0) \left( \varphi'(w^0)^3 \right) \right)$$

$$= \frac{\partial}{\partial z} \left( \varphi''(w^0) \left( \varphi'(w^0)^3 \right) \right)$$

(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 $h = \phi(f)$ and $f = \phi^{-1}(h) = \Lambda(h)$ in (40) results in the transformed equation

$$\frac{1}{h} \frac{dh}{d\eta} + \frac{d^2 \Lambda(h)}{d\eta^2} = 0$$

for $-\infty < \eta < \infty$.

(C1a)

with

$$h(-\infty) = \phi(1), \quad h(+\infty) = \phi(0).$$

(C1b)
Nonlinear diffusion problems as (C1) were studied by Atkinson and Peletier (1974) and Van Duijn and Peletier (1977) and Philip (1960). The function
\[ D(h) := \Lambda(h) \quad h \geq 0 \] (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
\[ \frac{D(h)}{h} \in L^1(0, \delta) \quad \text{for some } \delta > 0 \] (C3)
then there exists \( 0 < L < \infty \) such that
\[ h(\eta) \begin{cases} \geq 0, \text{strictly decreasing for } \eta < L \\ = 0 \text{ for } \eta > L \end{cases} \] (C4)

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

**Example**
Freudlich 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 \( \Lambda(h) \sim A \frac{h^p}{h^{p-1}} \).

Hence, \( D(h) \sim \frac{1}{p}A \frac{h^{p-1}}{h^p} \) and \( \frac{D(h)}{h} \sim \frac{1}{p}A \frac{h^{p-2}}{h^{p-1}} \) is integrable near \( h = 0 \) since \( p < 1 \). Therefore, Freudlich adsorption leads to fronts as in (C4). In terms of the original variables (\( \tau \) and \( x \)) the front is located at \( \frac{\phi}{\sqrt{\phi}} = L \sqrt{\frac{x}{\tau}} \) and with (7) we have \( x = L \sqrt{\int_0^{NT} |\varphi(\tau)| \, d\tau} \).

After \( N \) periods we have
\[ x = L \sqrt{\int_0^{NT} |\varphi(\tau)| \, d\tau} = L \sqrt{D_{eff} \cdot \sqrt{NT}} \] (C5)

where \( D_{eff} = \alpha |\varphi| \) denotes the effective dispersion coefficient.

If \( w^p \) has a front at \( y = L \sqrt{\phi} \) in the sense that \( w^p(y, s) = 0 \) for \( s > 0 \) and \( y > L \sqrt{\phi} \), 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 \( \Lambda(h) = A \frac{h^p}{h^{p-1}} \), giving for \( h \) the equation, see (C1a),
\[ \frac{1}{2} \frac{\partial h}{\partial \eta} + A \frac{h^p}{h^{p-1}} \frac{\partial^2 h}{\partial \eta^2} = 0 \] (D1)

Integrating, this equation from \( \eta < L \) to \( \eta = L \), and using \( \frac{\partial h}{\partial \eta} \to 0 \) as \( \eta \to L \) (vanishing flux at the front), gives
\[ \frac{1}{2} \frac{\partial h}{\partial \eta} + \frac{1}{2} \int_0^L h(s) \, ds + A \left( \frac{1}{p} \frac{h^p}{h^{p-1}} \right) \left( \eta \right) = 0. \]

Dividing this equation by \( h(\eta) \) yields
\[ \frac{A \frac{h^p}{h^{p-1}}}{1 - p} \frac{dh}{d\eta} (\eta) = \frac{1}{2} \frac{1}{h(\eta)} \int_\eta^L h(s) \, ds. \] (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
\[ \lim_{\eta \to 0} h(\eta) = -\frac{L}{2} (1 - p) A h^p \]

In terms of \( f(\eta) \) this implies
\[ f(\eta) \sim C (L - \eta)^{\frac{p-1}{2}} \quad \text{near } \eta = L, \] (D3)

where
\[ C = \left( \frac{1}{2} \right)^{\frac{1}{2}} (1 - p) A \] (D4)

For \( w^1 \), see expression (36) and using \( w^p = f \), we need to investigate the behaviour of
\[ \frac{1}{\varphi(f)} \frac{1}{\sqrt{\frac{d\eta}{f}}} \quad \text{near } \eta = L, \] (D5)

and for \( w^2 \), see expression (41), the behaviour of
\[ \frac{1}{\varphi(f)} \frac{1}{\sqrt{\frac{d\eta}{f}}} - 2 \frac{\varphi(f)}{\varphi(f)^2} \frac{1}{\sqrt{\frac{d\eta}{f}}} \quad \text{near } \eta = L. \] (D6)

Using \( \varphi(f) = Af^p \), we have, using (D3),
\[ \varphi(f) = Af^{p-1} \sim C (L - \eta)^{-1}, \] (D7)

\[ \varphi(f) = Ap(p - 1)f^{p-2} \sim C (L - \eta)^{-2}, \] (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
\[ \frac{df}{d\eta} \sim C (L - \eta)^{\frac{p-1}{2}} \text{ and } \frac{df}{d\eta} \sim C (L - \eta)^{-\frac{p-1}{2}} \] (D9)

near \( \eta = L \).

Finally, we combine (D7)–(D9) in (D5) and (D6) to obtain approximations (46) and (47).

References


