

Unsaturated Transport with Linear Kinetic Sorption Under Unsteady Vertical Flow

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Abstract. We consider transport of a solute obeying linear kinetic sorption under unsteady flow conditions. The study relies on the vertical unsaturated flow model developed by Indelman *et al.* [*J. Contam. Hydrol.* **32** (1998), 77–97] to account for a cycle of infiltration and redistribution. One of the main features of this type of transport, as compared with the case of a continuous water infiltration, is the finite depth of solute penetration. In the infiltration stage an analytical solution that generalizes the previous results of Lassey [*Water Resour. Res.* **24** (1988), 343–350] and Severino and Indelman [*J. Contam. Hydrol.* **70** (2004), 89–115] is derived. This solution accounts for quite general initial solute distributions in both the mobile and immobile concentration. When the redistribution is also considered, two timescales become relevant, namely: (i) the desorption rate k^{-1} , and (ii) the water application time t_{ap} . In particular, we have assumed that the quantity $\varepsilon = (k t_{ap})^{-1}$ can be regarded as a small parameter so that a perturbation analytical solution is obtained. At field-scale the concentration is calculated by means of the column model of Dagan and Bresler [*Soil Sci. Soc. Am. J.* **43** (1979), 461–467], i.e. as ensemble average over an infinite series of randomly distributed and uncorrelated soil columns. It is shown that the heterogeneity of hydraulic properties produces an additional spreading of the plume. An unusual phenomenon of plume contraction is observed at long times of solute propagation during the drying period. The mean solute penetration depth is studied with special emphasis on the impact of the variability of the saturated conductivity upon attaining the maximum solute penetration depth.

Key words: linear kinetic sorption, unsaturated porous media, infiltration and redistribution, heterogeneity, stochastic modelling.

1. Introduction

Reliable and simple models for solute transport in unsaturated porous media (soils) are required for many application purposes such as the optimal management of agricultural practices, designing proper strategies to preserve soils or assessing groundwater pollution risks. Several models have

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been proposed to account for the complicated physical/chemical processes occurring in soils (e.g. Brusseau *et al.*, 1989). Although the wide variety of mathematical models available in the literature (for a comprehensive review, see Sardin *et al.*, 1991), finding analytical solutions is not an easy task. Even if numerical solutions can be achieved (e.g. Russo *et al.*, 1998), we believe that analytical solutions gain a better understanding of the importance of the different transport parameters and mathematical conditions, as well as study transport for conditions where numerical methods may not yield acceptably accurate or reliable results. Furthermore, analytical solutions will also serve as a benchmark for validating numerical codes.

Recently, Indelman *et al.* (1998) have addressed a typical problem of transport under unsteady flow conditions: solute transport during a cycle of infiltration and redistribution. Subsequently, Lessoff *et al.* (2002) have extended the results of Indelman *et al.* (1998) to the case of multiple infiltration-redistribution cycles. These solutions were applied at field scale by considering the soil as a collection of isolated columns whose parameters are modelled as random space functions with given probability distributions. In both studies the Authors have considered linear equilibrium sorption and decay.

The assumption of equilibrium conditions implies instantaneous solute partition between the dissolved (mobile) and sorbed (immobile) concentrations. Such conditions are applicable to those situations where the mass transfer rate from/toward each concentration is relatively high. However, there are many experimental evidences (e.g. Comegna *et al.*, 2001) showing that the time needed for solutes to sorb/desorb is relatively long, so that the transport is “kinetically controlled”. Even if an analytical solution for kinetically controlled transport valid for the infiltration has been recently derived by Severino and Indelman (2004), it is not possible to obtain a closed solution even for the redistribution.

The present paper aims to study solute transport with linear kinetic sorption during infiltration and redistribution, and is organized as follows. We make a preliminary review of the main results (Section 2.1) concerning water flow and linear equilibrium transport. In Section 2.2 we present an analytical solution valid for the infiltration which generalizes previous results of Lassey (1988) and Severino and Indelman (2004). Then, we solve transport in the redistribution by assuming that the desorption mass transfer is fast enough in order to seek a small perturbations analytical solution (Section 2.3). These solutions are subsequently averaged (Section 3) according to the methodology of the Dagan and Bresler (1979) column model to derive the mean concentration and solute advancement. The concluding remarks are reported in Section 4.

2. The Transport Model

We model transport during a cycle of infiltration and redistribution. One of the peculiarities of such a problem is that water flow (and therefore transport) is different whether considering infiltration or redistribution. In particular, water content and concentration at the end of the infiltration will constitute the initial condition for solving the redistribution. We introduce some assumptions which permit us to reduce the computational effort. One of these assumptions requires that gravity dominates the flow, i.e. the flow is essentially vertical. Assuming vertical flow greatly simplifies the computational aspect, and it was adopted in previous works (e.g. Dagan and Bresler, 1983; Indelman *et al.*, 1998; Lessoff *et al.*, 2002; Lessoff and Indelman, 2002; Severino and Indelman, 2004; Lessoff and Indelman, 2004). Although assuming vertical flow may lead to significant differences in terms of water content, it does not have a big impact upon solute transport as it has been recently shown by Lessoff and Indelman (2004). We also assume that the water table is deep enough so that it does not influence transport. To facilitate the discussion, we preliminarily review in the next subsection the main results of Indelman *et al.* (1998) concerning to water flow and linear equilibrium transport.

2.1. BACKGROUND MATERIAL

2.1.1. Water Flow

The infiltration stage originates from the application of a specific amount of water W (volume per area) at the soil surface during the time interval t_{ap} with constant rate $r = W/t_{ap}$. The redistribution stage starts after the infiltration of all the applied water W . In the gravitational regime the water content θ (L^3/L^3) and specific discharge q (L/T) satisfy

$$\frac{\partial \theta}{\partial t} + \frac{\partial q}{\partial z} = 0, \quad q = K(\theta), \quad K = K_s \left(\frac{\theta - \theta_r}{\theta_s - \theta_r} \right)^{1/\beta}, \quad (1)$$

where z (L) is the vertical coordinate pointing downwards from the soil surface $z=0$, q the specific discharge, and K (L/T) is the hydraulic conductivity. The third of (1) is the Brooks and Corey (1964) model for the hydraulic conductivity, being K_s (L/T) the conductivity at saturation, θ_s (L^3/L^3) and θ_r (L^3/L^3) the saturated and residual water contents, respectively, and β a constant power. Defining the parameter γ equal to 1 for $K_s < r$ and to r/K_s otherwise, the infiltration time t_i and the water influx q_0 (applied volume of water per area and time) are given by $t_i = (W/(\gamma K_s))$ and $q_0 = q|_{z=0} = \gamma K_s$. The redistribution stage corresponds to $q|_{z=0} = 0$.

The downward advancement of the wetting and drying front (and the corresponding water contents) is schematically represented in Figures 1a

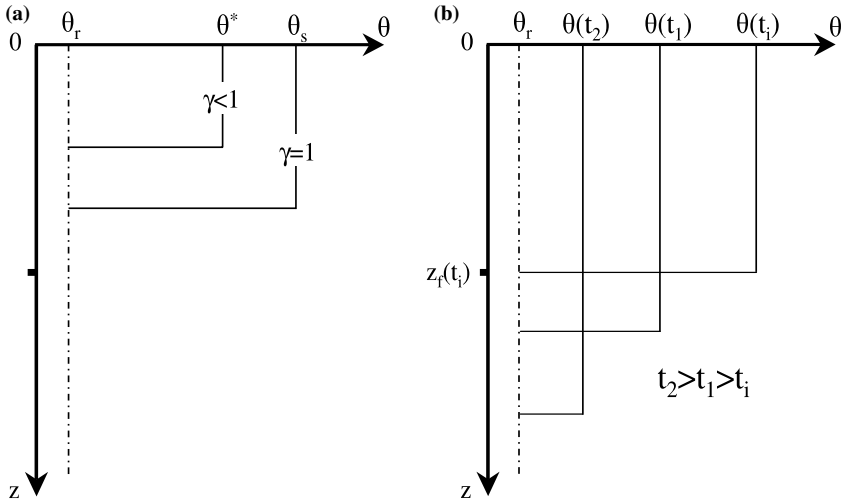


Figure 1. Definition sketch of the approximate local water content in the infiltration (a), and redistribution (b) stage.

and 1b, respectively. During the infiltration stage the flux q and the water content θ (see Figure 1a) are given by (Indelman *et al.*, 1998)

$$q(z, t) = \gamma K_s H[z_f(t) - z], \quad \theta(z, t) = \theta_r + (\theta^* - \theta_r) H[z_f(t) - z] \quad (2)$$

(H represents the Heaviside function). The wetting front $z_f = z_f(t)$ (L) advances at constant velocity dz_f/dt into the profile reaching the depth $z_f(t_i)$ at the end of infiltration. Starting from this time, a drying front develops (see Figure 1b), and it moves at a reduced velocity (deceleration is discussed in detail by Lessoff *et al.*, 2002). The flux and water content behind the drying front are obtained as (Indelman *et al.*, 1998)

$$q(z, t) = \frac{z K_s}{W} (\theta_s - \theta_r) \left[\frac{\gamma}{\Theta(t)} \right]^{1+\beta},$$

$$\theta(z, t) = \theta_r + (\theta^* - \theta_r) \Theta^{-\beta}(t) H[z_f(t) - z]. \quad (3)$$

The equation of the wetting/drying front as well as the expression of $\Theta(t)$ are given by

$$z_f(t) = \begin{cases} \frac{\gamma K_s t}{\theta^* - \theta_r}, & t \leq t_i \\ \frac{W \Theta^\beta(t)}{\theta^* - \theta_r}, & t > t_i \end{cases} \quad \Theta(t) = 1 + \frac{1}{\beta} \left(\frac{t}{t_i} - 1 \right). \quad (4)$$

2.1.2. Linear Equilibrium Transport

We define C^* (M/L^3) and C (M/L^3) as solute mass in the immobile and mobile phase per volume of solid, respectively. Assuming linear equilibrium sorption and neglecting pore-scale dispersion, transport equations are

$$\frac{\partial (RC)}{\partial t} + \frac{\partial (uC)}{\partial z} = 0, \quad C^* = \frac{K_d}{\theta} C, \quad (5)$$

where $R(\theta) = 1 + (K_d/\theta)$ represents the water content dependent retardation factor, and K_d is the dimensionless partitioning coefficient. The water pore velocity $u = q/\theta$ in (5) is derived from (2) and (3) depending if infiltration or redistribution is considered. The solution of (5) for any initial concentration distribution $C(z, 0) = \Psi(z)$ can be written as

$$C(z, t) = \frac{\bar{\theta}[z_r(t)]}{\bar{\theta}_r} \Psi[z - z_r(t)] \quad (6)$$

with the solute front $z_r(t)$ given as (Indelman *et al.*, 1998)

$$z_r(t) = \begin{cases} \frac{\gamma K_s t}{\bar{\theta}^*}, & t \leq t_i, \\ \frac{W}{\bar{\theta}}, & t > t_i \end{cases} \quad (7)$$

(we have set $\bar{\theta}_0 = \theta_0 + K_d$). In particular, for $K_d = 0$ Equation (7) defines the front $z_c(t)$ pertaining to a conservative solute. Since $z_f(t) > z_c(t) > z_r(t)$ at any t , we recover that the solute trails always behind the water front. Another interesting property of the solute propagation is the finite depth at large time, i.e.

$$z_r^\infty = \lim_{t \rightarrow \infty} z_r(t) = \frac{W}{\bar{\theta}_r} < z_c^\infty = \lim_{t \rightarrow \infty} z_c(t) = \frac{W}{\bar{\theta}_r}. \quad (8)$$

In fact, as the water content reduces because of the redistribution, the dissolved solute gets “confined” more and more in the irreducible water content θ_r (which is not moving). As a consequence, at large times the solute will be entirely in θ_r without moving anymore (provided that $\theta_r \neq 0$).

2.2. TRANSPORT WITH LINEAR KINETIC SORPTION

A widely used model for linear kinetic sorption is

$$\frac{1}{k} \frac{\partial C^*}{\partial t} = \frac{K_d}{\theta} C - C^* \quad (9)$$

(see e.g. Brusseau *et al.*, 1989; Weber *et al.*, 1991; Sardin *et al.*, 1991). Equation (9) states that the rate of change in time of the solute concentration stored in the immobile region is proportional to the difference between the mobile and immobile concentrations. For high desorption rate, i.e. for $k \rightarrow \infty$, the two concentrations mix instantaneously, and (9) “degenerates” into the linear equilibrium model (see the second of (5)). At the other extreme of zero mixing ($K_d = k = 0$) the immobile region is completely blocked off, and the solute behaves like a conservative one. In the intermediate times, the solute diffuses between the mobile and immobile regions until it reaches (asymptotically in time) equilibrium conditions (Lassey, 1988). Thus, from a physical point of view k represents a “measure” of how the model (9) will result close to the equilibrium.

With the neglect of pore-scale dispersion, transport is governed by the following system of equations

$$\frac{\partial C}{\partial t} + \frac{\partial (u C)}{\partial z} = - \frac{\partial C^*}{\partial t}, \quad (10a)$$

$$\frac{1}{k} \frac{\partial C^*}{\partial t} = \frac{K_d}{\theta} C - C^*, \quad (10b)$$

where the various variables have been already defined. Equations (10a) and (10b) are solved for an initial solute pulse distributed from $z=0$ to a given depth z_0 , i.e.

$$C(z, 0) = \frac{M_0}{z_0} H(z_0 - z), \quad C^*(z, 0) = \frac{M_0^*}{z_0} H(z_0 - z) \quad (11)$$

(being M_0 and M_0^* the initial specific mobile and immobile applied solute mass, respectively), and for zero solute flux at $z=0$. In the infiltration stage ($t \leq t_i$) systems (10a) and (10b) is analytically solvable. In particular, we need to distinguish whether the wetting front z_f has already reached z_0 ($z_f > z_0$), or not. In the latter case, at $z_f < z$ there is no advection, and therefore the solution is obtained by setting $u=0$ in (10a) and (10b) to have

$$C(z, t) = C(z, 0) \left\{ b(t) + \frac{M_r}{M_0} [1 - b(t)] \right\} H[z - z_f(t)], \quad (12)$$

$$C^*(z, t) = C^*(z, 0) \left\{ b(t) + \frac{M_r^*}{M_0^*} [1 - b(t)] \right\} H[z - z_f(t)] \quad (13)$$

with $b(t) = \exp[-k R(\theta_r) t]$, whereas $M_r = (M_0 + M_0^*) / R(\theta_r)$ and $M_r^* = M_r K_d / \theta_r$. At $z < z_f$ the two concentrations are obtained by solving (10a) and (10b) with $u \neq 0$. With the details reported in Appendix A, the mobile and immobile concentrations read as

$$C(z, t) = \frac{H[z - z_c(t)]}{z_0} \left[M_0 \exp\left(-\frac{kK_d t}{\theta^*}\right) + \Psi^{(m)}[z_c(t); 0] \right] + \frac{H[z_c(t) - z]}{z_0} \Psi^{(m)}(z; 0), \quad (14)$$

$$C^*(z, t) = \frac{M_0^*}{z_0} \exp(-kt) + \frac{H[z - z_c(t)]}{z_0} \Psi^{(s)}[z_c(t); 0] + \frac{H[z_c(t) - z]}{z_0} \Psi^{(s)}(z; 0) \quad (15)$$

with $z_0 > z_f(t) > z$. At $z_f(t) > z_0$ the two concentrations are:

$$C(z, t) = M_0 \exp\left(-\frac{kK_d t}{\theta^*}\right) \frac{H[z_0 - z + z_c(t)]}{z_0} H[z - z_c(t)] + \Upsilon^{(m)}(z, t), \quad (16)$$

$$C^*(z, t) = \exp(-kt) C^*(z, 0) + \Upsilon^{(s)}(z, t). \quad (17)$$

In (14)–(17) we have set

$$\begin{aligned} \Upsilon^{(j)}(z, t) = H[z - z_c(t)] & \left\{ \frac{H(z_0 - z)}{z_0} \Psi^{(j)}[z_c(t); 0] + \right. \\ & \left. + \frac{H[z_0 - z + z_c(t)]}{z_0} \Psi^{(j)}[z_c(t); z - z_0] \right\} \\ & + H[z_c(t) - z] \left[\frac{H(z - z_0)}{z_0} \Psi^{(j)}(z; z - z_0) + \right. \\ & \left. + \frac{H(z_0 - z)}{z_0} \Psi^{(j)}(z; 0) \right], \quad j = m, s, \quad (18) \end{aligned}$$

$$\Psi^{(m)}(a, b) = \frac{k}{u} \int_b^a dz \chi(z, t) \left\{ M_0 \frac{kK_d z}{u\theta^*} \tilde{I}[\zeta^2(z, t)] + M_0^* I_0[2\zeta(z, t)] \right\}, \quad (19)$$

$$\begin{aligned} \Psi^{(s)}(a, b) = \frac{kK_d}{u\theta^*} \int_b^a dz \chi(z, t) & \left\{ M_0 I_0[2\zeta(z, t)] + \frac{M_0^* k}{u} [z_c(t) - z] \right. \\ & \left. \times \tilde{I}[\zeta^2(z, t)] \right\}, \quad (20) \end{aligned}$$

$$\chi(z, t) = \exp\left\{ -\frac{k}{u} \left[z_c(t) - z + \frac{K_d z}{\theta^*} \right] \right\},$$

$$\zeta(z, t) = \frac{k}{u} \sqrt{\frac{K_d z}{\theta^*} [z_c(t) - z]}, \quad \tilde{I}(x) = \frac{I_1(2x)}{x} \quad (21)$$

(I_i represents the modified Bessel function of the first kind of i -order).

Transport beneath the front $z_f(t)$ (see Equations (12) and (13)) is regulated by the rate transfer k . At large kt , we have $b(t) \rightarrow 0$ and transport results “equilibrium dominated”. More complex is the pattern of concentrations behind the wetting front. The mobile concentration Cf for a solute

pulse initially distributed up to $z_0 = 0.05W/\theta_r$, for few values of the dimensionless time ($t' = t/t_{ap} = 0.25; 0.65; 1$), and two reaction rates ($k' = kt_i = 0.1$ and $k' = kt_i = 5$) is shown in Figure 2. Overall, the concentration is represented by: (i) a continuous distribution within $0 < z < z_c(t)$ (say tailing zone) which is addressed to kinematical effects, and (ii) a moving term $z_c(t) < z < z_c(t) + z_0$ (say advection zone) where the pulse is exponentially reduced with the growth of k and K_d , and it is further dispersed due to the kinetics (see Figure 2a). At increasing k' the solute is mainly located in the tailing zone (see Figure 2b) with a distribution approaching to a bell like shape as the time increases. In the limit case $kt \rightarrow \infty$, the mass is completely distributed within $z_r(t) < z < z_r(t) + z_0$ in the form of a new finite pulse.

The immobile concentration C^* contains the additional contribution (first term of (15) and (17)) showing how the initial immobile concentration is reduced because of the progressive release of material from the sorbed toward the moving concentration. Thus, for given time t , the quantity $\exp(-kt) C^*(z, 0)$ represents the concentration which is still left in the immobile phase, and it exponentially decreases with the growth of kt . It is worth to observe that a similar solution was previously obtained by Lassey (1988). However, he considered only the case where the initial solute is all applied in the mobile phase in the form of a Dirac pulse, whereas in our case we account for both general mixed initial solute masses and vertical distribution. Of course, when $M_0^* = 0$ and $z_0 \rightarrow 0$ we recover the solution provided by Lassey (1988). It is interesting to observe that during the infiltration stage the solute front is given by $z_c = z_c(t)$, suggesting that the solute advances like a conservative one. Thus, when linear kinetic sorption is accounted for the solute reaches higher depths as compared with those pertaining to the equilibrium transport (unless k is exceedingly high).

Turning to the general case of transport under infiltration and redistribution, we observe that two time scales, namely the inverse desorption rate k^{-1} and the application time t_{ap} , are relevant for our problem. Therefore, their ratio $\varepsilon = (kt_{ap})^{-1}$ is expected to play an important role. In particular, for rain/irrigation very prolonged as compared with k (or for sufficiently fast desorption rate as compared with the duration of water application) ε can be regarded as small parameter (i.e. $\varepsilon \ll 1$), and a perturbation solution is possible. This procedure will be applied in the next section. Before going on, we wish to emphasize that, although a numerical solution (free of the assumption of $\varepsilon \ll 1$) for such a problem may be achieved (see Severino and Indelman, 2004), the procedure becomes computationally heavy. Instead, we prefer to focus our attention on a particular case which still enables us to deal with solute transport with linear kinetics but in a simpler manner.

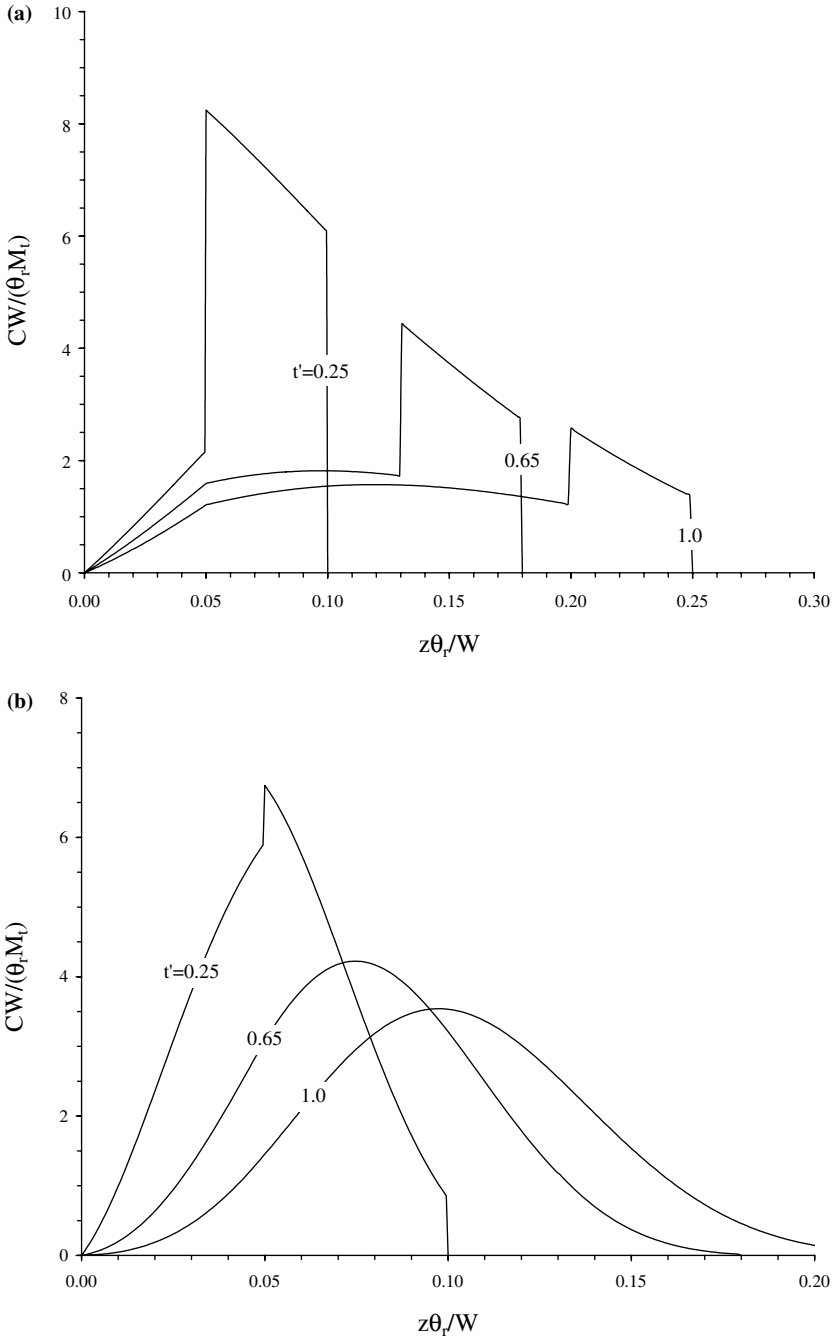


Figure 2. Concentration distribution along the depth for a finite pulse located at $z_0 = 0.05W/\theta_r$, for (a) $kt_i = 1.0$, and (b) $kt_i = 5.0$. The remaining parameters are $M_0 = M_0^* = M_t/2$, $\beta^{-1} = 4$, $\theta_s = 5\theta_r$, $K_d/\theta_r = 10$, $K_s = r$.

2.3. THE SMALL PERTURBATIONS SOLUTION

In this section we solve systems (10a) and (10b) by means of a perturbation approach. This is accomplished by adopting the procedure developed by Wallach (1998). However, unlike Wallach (1998) who considered steady state flow conditions, we apply the small perturbation approach to a cycle of infiltration and redistribution. In order to do this, we first rewrite (10a) and (10b) according to the dimensionless variables $\bar{t} = t/t_{\text{ap}}$, $\bar{C} = C/C^{(0)}$, $\bar{C}^* = C^*/C^{(0)}$ and $\bar{z} = z/L$ where $C^{(0)}$ is a suitable reference concentration (e.g. the initial concentration), whereas L is a length scale relevant for the specific problem. In doing this there is certain arbitrariness especially in selecting the reference length L . Such a choice strictly depends on the observation scale that one is dealing with. For example, at laboratory scale L usually represents the soil column height, while at larger (typically field or regional) scales L may represent a characteristic heterogeneity length (see Dagan, 1989). With such new variables equations (10a) and (10b) become

$$\frac{\partial C}{\partial t} + \frac{\partial (u_s C)}{\partial z} = -\frac{\partial C^*}{\partial t}, \quad (22a)$$

$$(k t_{\text{ap}})^{-1} \frac{\partial C^*}{\partial t} = \frac{K_d}{\theta} C - C^* \quad (22b)$$

(for simplicity, we have retained the over bar notation, and set $u_s = u t_{\text{ap}}/L$). Two main rate limited processes are clearly involved in the transport model (22a) and (22b): (i) the convection process characterized by t_{ap} , and (ii) the sorption kinetics determined by the rate k^{-1} . Of course, t_{ap} and k^{-1} may be close or greatly differ one from the other. In particular, if the rate of desorption is fast enough as compared with the rate of advection, we can drop down the term on the left-hand side of (22b). This is equivalent to assume that the transport is essentially at the equilibrium. In the remaining part of the present paper we shall adopt this assumption.

Assuming $\varepsilon = (k t_{\text{ap}})^{-1} \ll 1$ (but different from zero) makes systems (22a) and (22b) singular in the sense that the corresponding asymptotic expansion is not uniformly valid in the time domain. More precisely, a zone (hereafter termed as “boundary-layer”) is formed where the concentrations change very rapidly after being started at the initial conditions (11) to reach a completely different (and quite smooth) character. A uniformly valid (composite) solution is derived by the method of matched asymptotics (e.g. Cole, 1968), according to which the time domain is decomposed into two subregions: (i) the outer region (far from the boundary layer), and (ii) the inner region (inside the boundary layer). The composite solution is obtained by requiring that both the inner and the outer solution overlap in a common zone of existence. This represents a typical singular perturbation

problem encountered in various processes, like enzyme kinetics or the storing of energy in a plant through photosynthesis, and therefore we believe that our solution may also serve in other fields.

Inside the boundary layer the sorbed concentration C^* undergoes very rapid variations in time (i.e. $\partial C^*/\partial t \gg 1$), and because $\varepsilon \ll 1$ the left-hand side of (22b) can not be neglected. Therefore, inside the boundary layer the terms appearing on the right-hand side of (22b) balance with the left-hand side. Indeed, we introduce the new variable $\tau = t/\varepsilon$ in order to balance (22b), and expand the two concentrations as follows:

$$\tilde{C}(z, \tau) = \sum_n \varepsilon^n \tilde{C}_n(z, \tau), \quad \tilde{C}_n(z, \tau) = O(\varepsilon^n), \quad (23)$$

$$\tilde{C}^*(z, \tau) = \sum_n \varepsilon^n \tilde{C}_n^*(z, \tau), \quad \tilde{C}_n^*(z, \tau) = O(\varepsilon^n). \quad (24)$$

Substitution in (22a) and (22b) yields at the leading order

$$\frac{d}{d\tau} (\tilde{C}_0 + \tilde{C}_0^*) = 0, \quad (25a)$$

$$\frac{d\tilde{C}_0^*}{d\tau} = \frac{K_d}{\theta^*} \tilde{C}_0 - \tilde{C}_0^*. \quad (25b)$$

The higher-order terms can be obtained in a similar manner. At any rate, accounting for higher-order terms would represent only a technical complication with no further insights on the main features of the problem. For this reason, we shall limit our study to the leading order term, solely. Solving the above system leads to

$$\tilde{C}_0(z, \tau) = b(\tau) C(z, 0) + \frac{1-b(\tau)}{R(\theta^*)} C_t(z), \quad b(\tau) = \exp[-R(\theta^*)\tau] \quad (26)$$

being $C_t(z) = C(z, 0) + C^*(z, 0)$ the total initial concentration.

The outer solution is sought in the form of a perturbation expansion of C and C^* of the following type:

$$C(z, t) = \sum_n \varepsilon^n C_n(z, t), \quad C_n(z, t) = O(\varepsilon^n), \quad (27)$$

$$C^*(z, t) = \sum_n \varepsilon^n C_n^*(z, t), \quad C_n^*(z, t) = O(\varepsilon^n). \quad (28)$$

Substitution of (27) and (28) into (22a) and (22b) yields

$$\frac{\partial (RC_0)}{\partial t} + \frac{\partial (u_s C_0)}{\partial z} = 0. \quad (29)$$

It can be easily shown that the zero-order term C_0 satisfies Equation (5). In other words, the leading order term C_0 is the solution of the first-order equation (22a) which has been obtained by setting $\varepsilon = (kt_{\text{ap}})^{-1} = 0$ in (22b). In a general form the leading-order term writes as (see Equation (6))

$$C_0(z, t) = \frac{\bar{\theta}[z_r(t)]}{\bar{\theta}_r} \Psi[z - z_r(t)], \quad (30)$$

where Ψ remains at this stage unknown, and it will be determined later on by the method of asymptotic-matching.

In its simple and most intuitive form matching is achieved by requiring that (see, e.g., Cole, 1968) the outer limit of the inner solution be equal to the inner limit of the outer solution (30). Toward this goal, we consider an auxiliary region $\mu(\varepsilon)$ intermediate between the range of validity of the inner and outer solution where both the expansions are valid. To do this, we amplify the time t as follows

$$t_\mu = \frac{t}{\mu(\varepsilon)} \quad \text{with } \varepsilon \ll \mu(\varepsilon) \ll 1, \quad (31)$$

so that the above mentioned outer and inner limits (for fixed t_μ) write as

$$t = \mu(\varepsilon)t_\mu \rightarrow 0, \quad \tau = \frac{t}{\varepsilon} = \frac{\mu(\varepsilon)}{\varepsilon}t_\mu \rightarrow \infty \quad \text{for } \varepsilon \rightarrow 0. \quad (32)$$

With such variables, the matching requirements translate into

$$\lim_{t \rightarrow 0} C_0(z, t) = \lim_{\tau \rightarrow \infty} \tilde{C}_0(z, \tau). \quad (33)$$

By denoting as $C^{(\infty)}(z) = \lim_{\tau \rightarrow \infty} \tilde{C}_0(z, \tau)$, the unknown function Ψ is identified by virtue of (26), (30) and (33) as follows

$$C^{(\infty)}(z) = \lim_{t \rightarrow 0} C_0(z, t) = \Psi(z) = \frac{C_t(z)}{R(\theta^*)}. \quad (34)$$

The composite expansion is obtained by adding (26) and (30) and subtracting the common limit $C^{(\infty)}$, i.e.

$$C(z, t; \varepsilon) = \frac{\bar{\theta}[z_r(t)]}{\bar{\theta}_r} C^{(\infty)}[z - z_r(t)] + \tilde{C}_0(z, \tau) - C^{(\infty)}(z). \quad (35)$$

From (35) it follows that the advection coupled with pure retardation represents the dominant mechanism which influences solute transport, whereas the kinematical effect is felt only at the beginning.

Summarizing, the small perturbation approach basically leads to an equilibrium type solution. However, because of the presence of a boundary layer (whose thickness is equal to ε), an inner expansion is introduced. The boundary layer solution has the structure of a diffusive-type mechanism which permits on one hand to satisfy the initial condition and on the other hand to match the outer solution.

3. Stochastic Applications

In the previous sections we have considered transport with linear kinetic sorption under a cycle of infiltration and redistribution by regarding the soil as an homogeneous medium. In this case, our results are applicable at small (primarily laboratory) scales. At larger (typically field) scales one has to account for the complicated structure of the flow paths which significantly affects transport (e.g. Russo *et al.*, 1998). In this section we consider solute transport in large extent (and therefore heterogeneous) soils. In many practical situations (like assessing the soil pollution risk) we are interested into quantifying solute transport over depths much smaller than the characteristic horizontal length scale. However, unlike the laboratory scale, we have now to account for the horizontal variations of hydraulic properties which are quite irregular (e.g. Russo and Bouton, 1992; Russo *et al.*, 1997) and influence solute transport to a tremendous extent (e.g. Bresler and Dagan, 1979).

We have shown that the local concentration C (and similarly for C^*) depends upon several parameters like: hydraulic properties (K_s , θ_s , θ_r , β), reactive parameters (K_d , k), irrigation data (r , W), and the initially applied solute masses (M_0 , M_0^*), i.e.

$$C = C(z, t; K_s, \theta_s, \theta_r, \beta, K_d, k, r, W, M_0, M_0^*). \quad (36)$$

We can define the spatial mean concentration \bar{C} as ensemble average of (36) by regarding the various parameters as random variables and assuming ergodic conditions (Dagan and Bresler, 1979), i.e.

$$\bar{C}(z, t) \approx \langle C(z, t) \rangle = \int d\alpha C(z, t; \alpha) f(\alpha) \quad (37)$$

being $\langle \rangle$ the expectation operator and f the joint probability distribution of the parameters $(K_s, \theta_s, \theta_r, \beta, K_d, k, r, W, M_0, M_0^*) \equiv \alpha$. Generally, these parameters vary in the space and have a spatial correlation structure. Most of them (such as $\theta_s, \theta_r, \beta, K_d$) exhibit a small variability as compared with that of others, and therefore may be considered constant over the field (e.g. Indelman *et al.*, 1998; Lessoff and Indelman, 2002; Severino *et al.*, 2003). Toward simplifying the computations, we have focused on the effect of the heterogeneity of only one parameter, namely the saturated hydraulic conductivity K_s , since transport is highly sensitive to its variability (e.g. Dagan and Bresler, 1979; Mallants *et al.*, 1996; Lessoff and Indelman, 2002). Consequently, the joint probability distribution function appearing in (37) is replaced by the probability distribution function of K_s , i.e. $f(\alpha) \equiv f(K_s)$. Thus, the field scale concentration is calculated from (37) as

$$\begin{aligned} \langle C(z, t) \rangle = & \int_0^{W/t} dK_s C^i f(K_s) + \int_{W/t}^r dK_s C^r f(K_s) \\ & + \int_r^\infty dK_s C^r f(K_s) \quad t > t_{ap} \end{aligned} \quad (38)$$

being C^i and C^r the column scale mobile concentrations in the infiltration and redistribution derived in the previous sections. The mean concentration $\langle C(z, t) \rangle$ is expressed by the aid of three contributions whose physical meaning is straightforward. The first term accounts for transport in those columns which being under ponding ($r > K_s$) are at the infiltration. The second term of (38) represents the contribution of those columns that are still under ponding but at the redistribution, whereas the third term accounts for the columns where redistribution is taking place with no ponding ($K_s > r$). While at local scale the spreading of the pulse is due only to nonequilibrium effects (see Figures 2a and 2b), in the heterogeneous collection of columns there will also be a stochastic spreading of the plume due to the average upon all the columns.

3.1. ANALYSIS OF THE MEAN CONCENTRATION

We consider an initial solute pulse with a very thin layer which represents a quite realistic approximation in horizontally large extents soils (e.g. Indelman *et al.*, 1998; Lessoff *et al.*, 2002; Severino and Indelman, 2004; Lessoff and Indelman, 2004).

For a continuous infiltration the mean concentration is calculated as

$$\langle C^i(z, t) \rangle = \int_0^{+\infty} dK_s C^i(z, t; K_s) f(K_s). \quad (39)$$

Substituting (16) (calculated for $\Phi \equiv \delta$) into (39) leads to the following expression of the mean concentration (see Appendix B for details)

$$\begin{aligned} \langle C^i \rangle = & H\left(\frac{rt}{\theta_s} - z\right) \frac{\theta_s}{t} \left[M_0 \exp\left(-\frac{kK_d}{\theta_s} t\right) f\left(\frac{z}{t}\theta_s\right) + \bar{P}\left(z; \frac{rt}{\theta_s}\right) \right] + H\left(\frac{rt}{\theta_r} - z\right) \\ & \times \left\{ H\left(z - \frac{rt}{\theta_s}\right) \left[M_0 f[K_t(z)] \frac{\partial K_t(z)}{\partial z} \bar{S} + \bar{Q}\left(z; \frac{rt}{\theta_r}\right) \right] \right. \\ & \left. + H\left(\frac{rt}{\theta_s} - z\right) \bar{Q}\left(\frac{rt}{\theta_s}; \frac{rt}{\theta_r}\right) \right\} \end{aligned} \quad (40)$$

with

$$\bar{P}(a; b) = \int_a^b d\lambda f\left(\lambda \frac{\theta_s}{t}\right) C_1\left(z, t; \lambda \frac{\theta_s}{t}\right) \quad \bar{S} = \exp\left(-\frac{zk}{r} K_d\right), \quad (41)$$

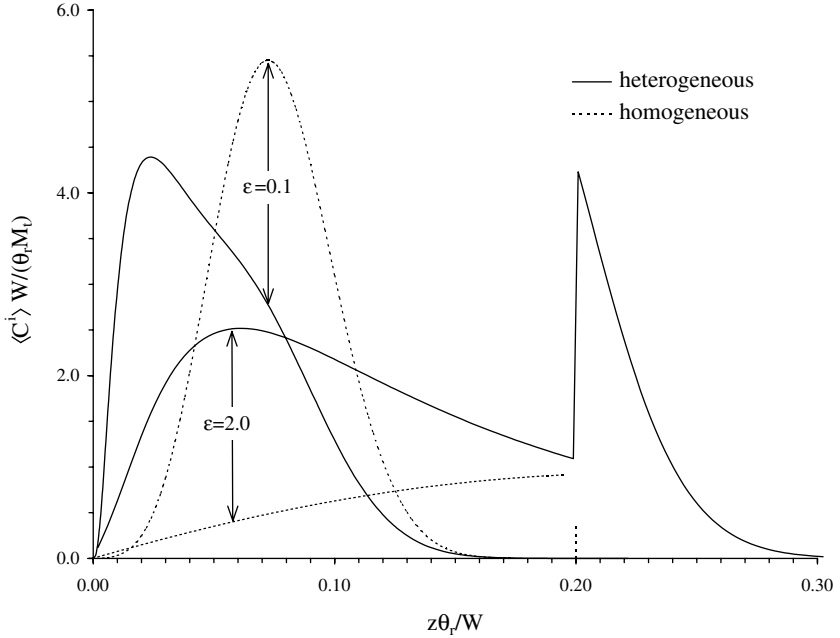


Figure 3. Mean concentration distribution along the depth at $t = t_{ap}$, and for $\varepsilon = 0.1$; 2.0. The remaining parameter values are: $M_0 = M_t$, $\beta^{-1} = 4$, $\theta_s = 5\theta_r$, $K_d/\theta_r = 10$, $\langle K_s \rangle = r$, $\xi = 1$. The vertical dashed line shows the location and the intensity of the delta-distributed solute.

$$\begin{aligned} \bar{Q}(a; b) &= \int_a^b d\lambda \frac{\partial K_t(\lambda)}{\partial \lambda} f[K_t(\lambda)] C_1(z, t; K_t(\lambda)), \\ C_1(z, t; K_s) &= \frac{k\theta^*}{\gamma K_s} \exp\left\{-\frac{k}{\gamma K_s} [\theta^*(z_c(t) - z) + K_d z]\right\} \\ &\quad \times \left\{M_0 \frac{kK_d}{\gamma K_s} z \tilde{I}_1[\zeta(z, t)] + M_0^* I_0[2\zeta(z, t)]\right\}, \end{aligned} \quad (42)$$

$$K_t(x) = r \left[\frac{(\theta_s - \theta_r) x}{r t - x \theta_r} \right]^{1/\beta} \quad (43)$$

(see also (21)). We have depicted in Figure 3 the mean concentration $\langle C^i \rangle W / (\theta_r M_t)$ (continuous line) versus $z\theta_r/W$ at $t = t_{ap}$, and for two characteristic values of ε (i.e. 0.1 and 2). Furthermore, throughout the paper we shall assume $\beta^{-1} = 4$ and $\theta_s = 5\theta_r$. These values are typical of sandy soils (see, e.g., Severino *et al.*, 2003), and have been adopted in extensive applications under various field conditions (e.g. Bresler and Dagan, 1981; Destouni and Cvetkovic, 1991; Dagan, 1993; Severino and Indelman, 2004; Lessoff and Indelman, 2004).

At the highest ε , we can clearly see that the variability of K_s makes $\langle C^i \rangle$ bimodal. The first peak (close to the top) is due to those columns with low saturated conductivities as compared with the mean value $\langle K_s \rangle = r$ (whereas the coefficient of variation ξ is equal to 1). Indeed, all these columns result under ponding with very low water velocities, and therefore the solute is mostly concentrated in the upper part of the soil surface. To the contrary, the second peak (much more pronounced with a spike-like shape) of Figure 3 represents the contribution of those columns whose saturated conductivity K_s is close to the mean $\langle K_s \rangle$. Thus, for such columns the local position of the solute pulse does not differ from the first of (7). For this reason at $z \approx r t_{\text{ap}} / \theta_s$ we observe a sudden raise representing the singularity term (see first term of (16)). Furthermore, since inside these columns water moves very quickly the solute is distributed also downstream the second peak. In order to appreciate how kinematical effects influence the concentration distribution, in Figure 3 we have also depicted the concentration profile (dashed lines) for the same set of parameters by regarding the soil as homogeneous, i.e. for $\xi = 0$. It is interesting to observe that for relatively slow kinetics ($\varepsilon = 2.0$) the reaction is completely overtaken by the medium heterogeneity. When kinetics is fast enough as compared with the application time t_{ap} (this is the case of $\varepsilon = 0.1$) the solute results at “quasi equilibrium” conditions in all the columns, and thus the kinetics becomes practically negligible. In such a case, solute transport is determined by: (i) the heterogeneity, and (ii) pure retardation. As a consequence, the solute is more concentrated at lower depths as compared with the previous case, since the solute distribution due to the linear equilibrium model is always located behind that corresponding to the conservative one (see (7)). The asymmetry shown by the continuous line is addressed exclusively to the medium heterogeneity. Unlike the previous case, the singularity term does not appear as its intensity is practically exhausted because of the relatively large reverse rate k . Furthermore, the linear sorption is now much more important as it can be easily seen by comparing the continuous (heterogeneous) with the dashed (homogeneous) line.

We consider now the mean concentration $\langle C \rangle$ as determined by a cycle of infiltration and redistribution. This is obtained by inserting into (38) the small perturbations expansion (35), i.e.

$$\begin{aligned} \langle C(z, t) \rangle = & \int dK_s f(K_s) \frac{\bar{\theta}[z_r(t)]}{\bar{\theta}_r} C^{(\infty)}[z - z_r(t)] + \\ & + \int dK_s f(K_s) [\tilde{C}_0(z, \tau) - C^{(\infty)}(z)]. \end{aligned} \quad (44)$$

Similarly to the column scale, the average concentration (44) is represented as sum of a pure equilibrium type component (first term on the right-hand side of (44)) and a kinetics-term which “adjusts” the first one in order to

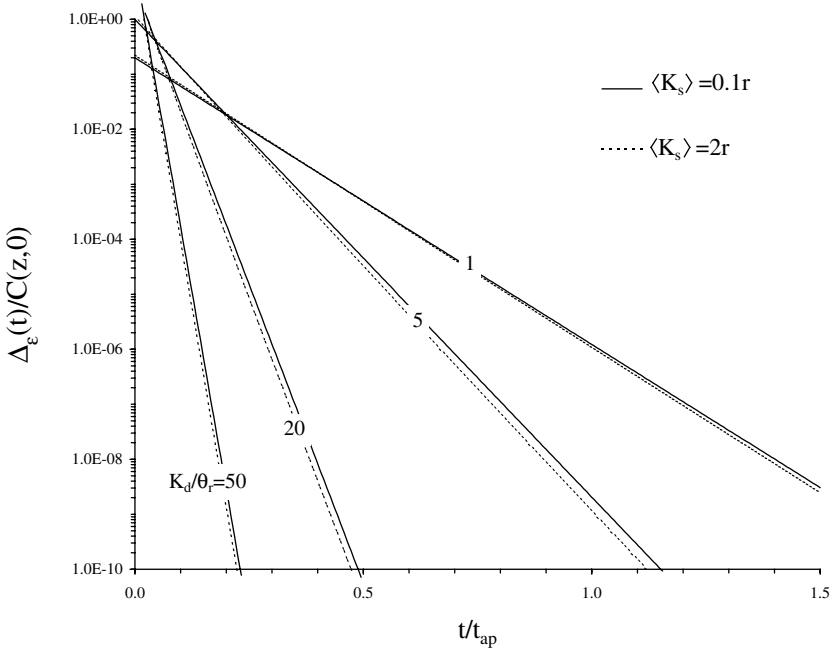


Figure 4. Deviation function $\Delta_\varepsilon(t)/C(z, 0)$ versus the dimensionless time t/t_{ap} , for $K_d/\theta_r = 1; 5; 20; 50$, and two mean saturated conductivities. The other parameter values are: $\varepsilon = 0.1$, $\beta^{-1} = 4$, $\theta_s = 5\theta_r$, $\xi = 1$.

match the initial condition. However, in this case the second term will also be affected by the stochastic spreading due to the heterogeneity of K_s . In order to show the transition from nonequilibrium to equilibrium conditions, we consider the second term on the right-hand side of (44), i.e.

$$\Delta_\varepsilon(z, t) = \int dK_s f(K_s) [\tilde{C}_0(z, \tau) - C^{(\infty)}(z)] \tag{45}$$

(for simplicity, we assume that all the initially applied mass is distributed in the mobile concentration, i.e. $C(z, 0) \equiv C_t(z, 0)$).

The function $\Delta_\varepsilon(t)/C(z, 0)$ has been represented in Figure 4 versus the dimensionless time t/t_{ap} , and for several values of the rescaled linear partitioning equilibrium coefficient K_d/θ_r (the perturbation parameter is set equal to 0.1). As expected, in all the cases Δ_ε rapidly decreases with time t , since the transition due to the boundary layer is exhausted relatively quickly. In particular, given all the other parameters high values of K_d/θ_r favour a faster getting of the equilibrium conditions. Unlike the reactive parameters, the heterogeneity does not play an important role. In fact, assuming two significantly different (and quite representative of field scale applications) values of the mean conductivity (i.e. $\langle K_s \rangle = 0.1r, 2r$) does not imply relevant changes in the behavior of Δ_ε . Furthermore, preliminary

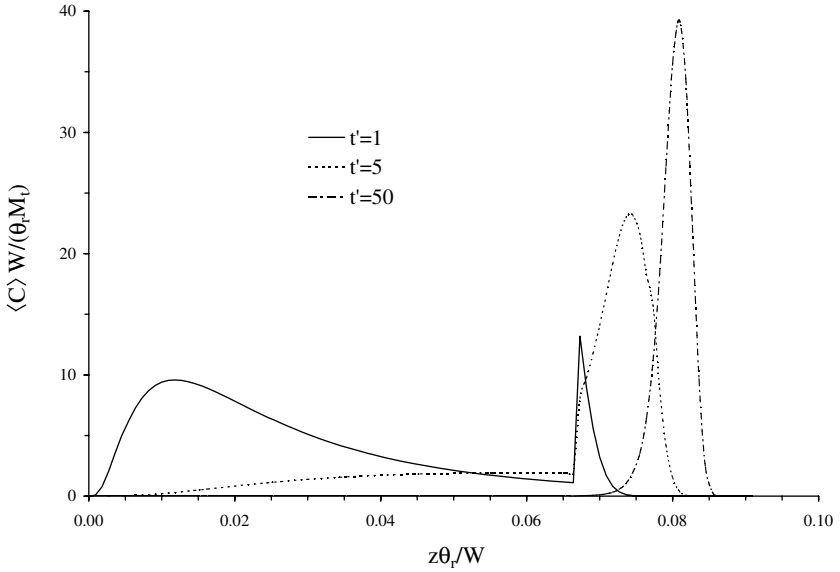


Figure 5. Mean concentration profile at the end of infiltration ($t' = 1$) and at two times after the water application has been halted ($t' = 5$ and 50). The remaining parameters are: $M_0 = M_t$, $\varepsilon = 0.1$, $\beta^{-1} = 4$, $\theta_s = 5\theta_r$, $K_d/\theta_r = 10$, $\langle K_s \rangle = r/2$, $\xi = 1$.

simulations have also shown that ξ does not impact (45). This suggests, unlike the results of Severino and Indelman (2004), that the applicability of the small perturbations solution can be assessed by measuring the reactive parameters solely, which since are normally carried out at laboratory scale (see, e.g., Comegna *et al.*, 2001), are much more accurate.

In Figure 5 we have depicted the mean concentration profile for different times $t' = t/t_{ap} = 1, 5, 50$ (the remaining parameter values are reported in the caption). At the end of infiltration ($t' = 1$) the bimodality of the distribution reflects the contribution of those columns with very-low conductivities (first peak), whereas the second peak is attributed to those columns whose conductivity is close to the mean value $\langle K_s \rangle$. During the redistribution ($t' > 1$) the solute in the low conductivity columns is strongly detained generating a pronounced spreading of the plume at $t' = 5$. At larger times ($t' = 50$) the plume compresses because in almost all the columns the solute approaches the maximum penetration depth $z_r^\infty = W/\bar{\theta}_r$. Thus, unlike the case of continuous water application, the finite depth of solute penetration implies the unusual phenomenon of “plume compression” after a preliminary expansion period.

To illustrate the transition due to the heterogeneity, we have shown in Figure 6 the mean concentration at the end of infiltration for increasing values of the coefficient of variation (i.e. $\xi = 0.2, 0.7, 4$), whereas the remaining parameters are the same as the previous case. At low ξ the

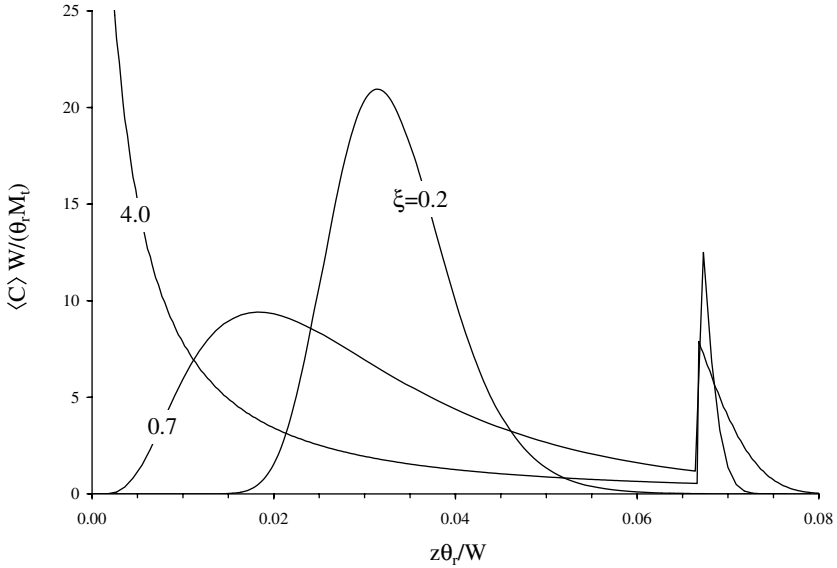


Figure 6. Mean concentration at the end of the water application ($t = t_{ap}$) for $\xi = 0.2; 0.7; 4.0$. The other parameters are: $M_0 = M_t$, $\varepsilon = 0.1$, $\beta^{-1} = 4$, $\theta_s = 5\theta_r$, $K_d/\theta_r = 10$, $\langle K_s \rangle = r/2$.

profile is practically symmetrical with a small skewness due to the average over the columns where water moves faster. As ξ increases the profile clearly becomes bimodal because of the effects of the columns with low conductivities (which strongly detain the solute at the top) and the contribution of the columns whose conductivities are closer to the mean value $\langle K_s \rangle$.

3.2. ANALYSIS OF THE MEAN SOLUTE PENETRATION

In order to assess the potential hazard of soil contamination, we have computed from (7) the mean value of the solute penetration depth, i.e.

$$\begin{aligned} \frac{\langle z_r(t) \rangle}{z_r^\infty} &= \frac{t W^{-1}}{1 + \theta_d} \int_0^{W/t} dK_s f(K_s) K_s + \int_{W/t}^r dK_s \frac{f(K_s) \bar{\Theta}_w^\beta(K_s)}{\theta_d + \bar{\Theta}_w^\beta(K_s)} + \\ &+ \int_r^\infty dK_s \frac{f(K_s) (K_s/r)^\beta}{\theta_d/\bar{\Theta}_w^\beta + (K_s/r)^\beta}, \end{aligned} \tag{46}$$

where

$$\theta_d = \frac{\theta_s - \theta_r}{\theta_r + K_d}, \quad \bar{\Theta}_w(K_s) = 1 + \frac{1}{\beta} \left(\frac{K_s}{W} t - 1 \right), \quad \Theta_w = 1 + \frac{1}{\beta} \left(\frac{t}{t_{ap}} - 1 \right). \tag{47}$$

The knowledge of solute penetration may provide useful information for instance on the accumulation of pesticides that very often causes the reduction of the soil fertility (for a wide exposition, see Page *et al.*, 1981). To obtain a simple expression for $\langle z_r(t) \rangle$ we have adopted the rectangular distribution of given mean $\langle K_s \rangle$ and coefficient of variation ξ (see Appendix C for the details). The mean penetration depth pertaining to a conservative solute is obtained from (46) after setting $K_d = 0$.

In Figures 7a and 7b we have represented $\langle z_r(t) \rangle / z_r^\infty$ versus the dimensionless time t/t_{ap} for $\xi = 0.5, 1, 2, 5$ and $\langle K_s \rangle = 0.1r, 2r$ (with $\theta_d = 0.3$). It is seen that despite the asymptotic value does not depend upon the heterogeneity (see (8)), this latter greatly influences attaining it. At small degree of heterogeneity (low ξ) the asymptotic limit is reached relatively soon since the medium practically behaves as an homogenous one, and therefore in almost every column the solute front $z_r(t)$ has reached the same depth. At higher ξ , z_r^∞ is attained quite slowly owing to the large variations from column to column of the local penetration depth. For relatively low conducting soils (Figure 7a) the solute travels small distances at the end of infiltration (i.e. at $t/t_{\text{ap}} = 1$). Although this is not completely surprising, it is important to note that the mean percolation depth at the end of the water application is not significantly sensitive to ξ , while unlike the previous case, for highly conducting soils (Figure 7b) the solute has covered significant depths. Furthermore, a simple comparison between case (a) and (b) shows that after a certain time (say $t > 1000 t_{\text{ap}}$) the mean conductivity $\langle K_s \rangle$ does not play a significant role as $\langle z_r \rangle$ is essentially determined by ξ .

4. Conclusions

In the present paper we have studied solute transport with linear kinetic sorption during infiltration and redistribution. In the infiltration stage, and under quite general initial conditions, we have derived a closed form solution which generalizes the previous results of Lassey (1988) and Severino and Indelman (2004). Owing to the complexity of the problem, an exact analytical solution valid for the redistribution is not achievable. In order to obtain a simple solution, we have assumed that the rate transfer (k^{-1}) is large compared with the application time (t_{ap}), i.e. $\varepsilon = (k t_{\text{ap}})^{-1} \ll 1$. Under such an assumption, we have derived a perturbation analytical solution. At column scale the solute concentration (unlike the equilibrium transport when the solute is distributed at the front) is gradually distributed along the depth. Such a distribution becomes steeper and steeper as the reaction rate k increases. In the limit case of $k \rightarrow \infty$, the profile approaches a new distribution located at a smaller depth in accordance with the linear equilibrium model.

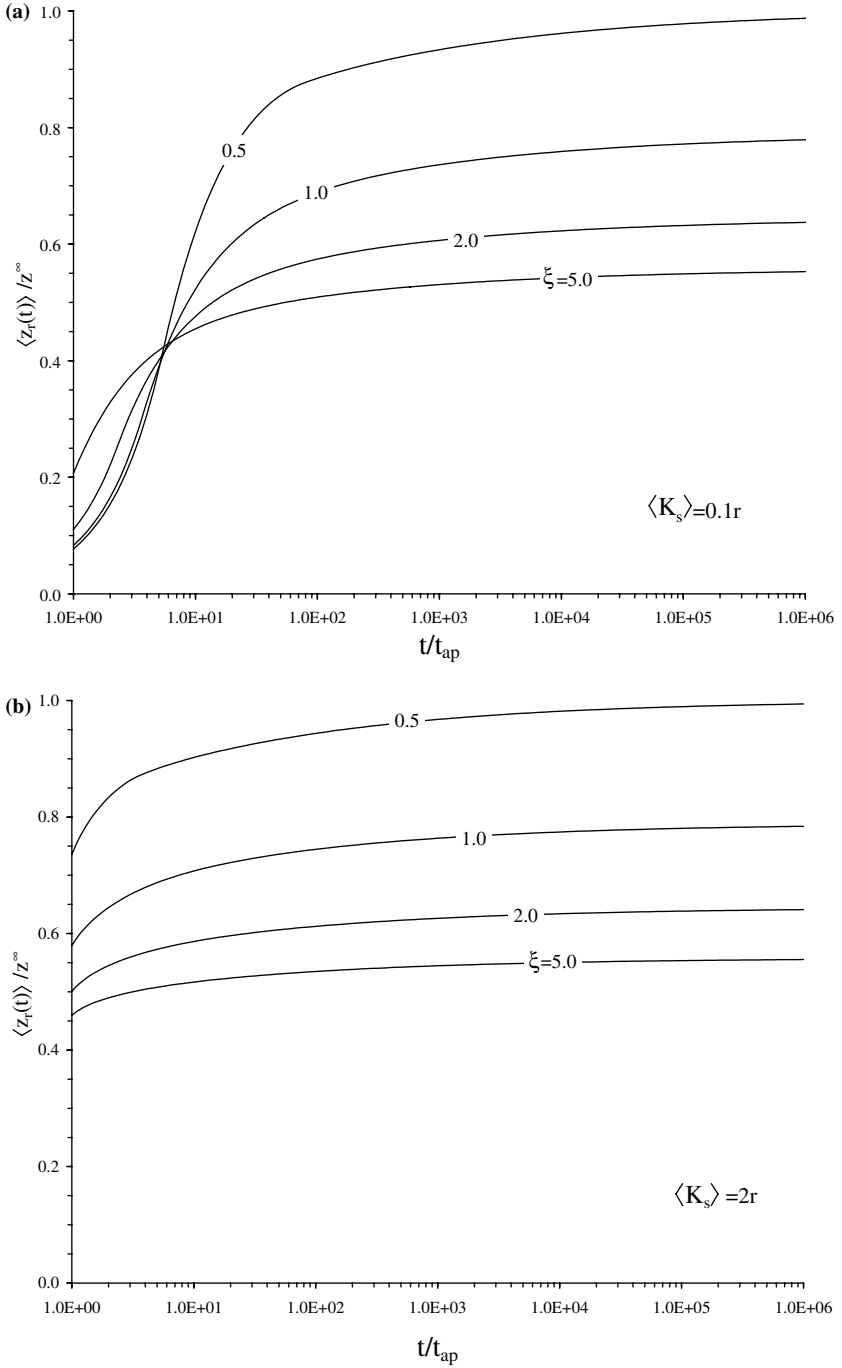


Figure 7. Location of the mean solute front over the time t/t_{ap} for (a) $\langle K_s \rangle = 0.1r$, and (b) $\langle K_s \rangle = 2r$. The remaining parameter values are $\theta_d = 0.3$, $\beta^{-1} = 4$, $\theta_s = 5\theta_r$.

These solutions are further applied to derive the mean concentration by means of the column model of Dagan and Bresler (1979). It is shown that the accuracy of our perturbation approach is not affected by the stochastic spreading due to the averaging procedure. Another remarkable feature of transport during the infiltration-redistribution cycle is the finite depth of solute penetration. This property was first found for equilibrium transport, and is shown to be also valid for linear kinetic sorption when $\varepsilon \ll 1$. The rate of approaching to the asymptotic value z_r^∞ of the solute penetration depth greatly depends upon the hydraulic/chemical parameters.

Due to their simplicity, our analytical results may be used to quantify the impact of transient flow coupled with the heterogeneity of hydraulic/chemical parameters upon the prediction of soil and groundwater pollution.

Appendix A. Derivation of the Analytical Solution for the Infiltration Stage

The system of Equation (10a) and (10b) for the infiltration is given by

$$\begin{aligned} \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} &= - \frac{\partial C^*}{\partial t}, \\ \frac{\partial C^*}{\partial t} &= k \left(\frac{K_d}{\theta^*} C - C^* \right), \end{aligned} \quad (\text{A1})$$

where $u = W/(\theta^* t_i)$. We solve (A1) for zero solute flux at the soil surface, i.e. $C(0, t) = 0$, and given initial concentrations

$$C(z, 0) = M_0 \Phi(z), \quad C^*(z, 0) = M_0^* \Phi(z)$$

being $\Phi(z)$ (L^{-1}) a known function with given support $[0, z_0]$ and accounting for the mass distribution along the depth.

We first apply p -Laplace transform to (A1) over the time t to yield the following initial value problem

$$\begin{aligned} p \bar{C} - M_0 \Phi(z) + u \frac{d\bar{C}}{dz} &= -p \bar{C}^* + M_0^* \Phi(z) & \bar{C}(0, p) &= 0 \\ p \bar{C}^* - M_0^* \Phi(z) &= k \left(\frac{K_d}{\theta^*} \bar{C} - \bar{C}^* \right) \end{aligned} \quad (\text{A2})$$

and further application of q -Laplace transform to (A2) over z provides the expressions of the double Laplace transforms of concentrations:

$$\begin{aligned} \widehat{\bar{C}}(q, p) &= \frac{1}{u} \left(M_0 + \frac{M_0^* k}{k+p} \right) \left\{ q + \frac{p}{u} \left[1 + \frac{k K_d}{\theta^* (k+p)} \right] \right\}^{-1} \widehat{\Phi}(q), \\ \widehat{\bar{C}^*}(q, p) &= \frac{k K_d}{\theta^*} \frac{\widehat{\bar{C}}(q, p)}{k+p} + M_0^* \frac{\widehat{\Phi}(q)}{k+p}. \end{aligned} \quad (\text{A3})$$

To facilitate successive derivations, it is convenient to rewrite the first of (A3) as follows:

$$\widehat{C}(q, p) = \frac{\widehat{f}_1(q, p)}{u} \left(M_0 + \frac{k M_0^*}{k+p} \right) \widehat{\Phi}(q), \quad (\text{A4})$$

where

$$\widehat{f}_1(q, p) = \left\{ q + \frac{p}{u} \left[1 + \frac{k K_d}{\theta^* (k+p)} \right] \right\}^{-1}.$$

A.1. MOBILE CONCENTRATION

The inverse q -Laplace transform of $\widehat{f}_1(q, p)$ is obtained as follows

$$\bar{f}_1(z, p) = \exp \left[-\frac{z}{u} \left(p + \frac{k K_d}{\theta^*} \right) \right] \exp \left(\frac{k^2 K_d z}{u \theta^*} \frac{1}{p+k} \right),$$

so that application of convolution yields

$$\bar{C}(z, p) = \frac{M_0}{u} \int_0^z dz' \bar{f}_1(z', p) \Phi(z-z') + \frac{k M_0^*}{u} \int_0^z dz' \frac{\bar{f}_1(z', p)}{k+p} \Phi(z-z'). \quad (\text{A5})$$

Inversion of $\bar{f}_1(z, p)$ and $\bar{f}_1(z, p)/(k+p)$ is obtained by means of standard techniques and is reported below

$$\begin{aligned} L^{-1}[\bar{f}_1(z, p)] &= u \exp \left(-\frac{k K_d}{\theta^*} t \right) \delta[z - z_c(t)] \\ &\quad + \frac{k^2 K_d z}{u \theta^*} \chi(z, t) \tilde{I}[\zeta^2(z, t)] H[z_c(t) - z], \\ L^{-1} \left[\frac{\bar{f}_1(z, p)}{k+p} \right] &= \chi(z, t) I_0[2\zeta(z, t)] H[z_c(t) - z], \end{aligned}$$

where $\chi(z, t)$, $\zeta(z, t)$, \tilde{I} , and I_0 have been defined in (21). Thus, the mobile concentration reads as

$$\begin{aligned} C(z, t) &= H[z_c(t) - z] \int_0^z dz' \Phi(z-z') \eta(z', t) \\ &\quad + H[z - z_c(t)] \int_0^{z_c(t)} dz' \Phi(z-z') \eta(z', t) \\ &\quad + M_0 \exp \left(-\frac{k K_d t}{\theta^*} \right) \Phi[z - z_c(t)] H[z - z_c(t)], \end{aligned} \quad (\text{A6})$$

in which $\eta(z, t)$ is the integrand appearing in (19), i.e.

$$\eta(z, t) = \frac{k}{u} \chi(z, t) \left\{ M_0 \frac{k K_d z}{u \theta^*} \tilde{I}[\zeta^2(z, t)] + M_0^* I_0[2\zeta(z, t)] \right\}.$$

In particular, when $z_f < z_0$ we have $\Phi(z) = z_0^{-1}$ and Equation (A6) leads to (14), whereas for $z_f > z_0$ the initial condition results $\Phi(z) = H(z_0 - z)/z_0$ and (A6) yields (16).

A.2. IMMOBILE CONCENTRATION

Using the function $\widehat{f}_1(q, p)$, the double Laplace transform of the immobile concentration results from (A3) as follows:

$$\widehat{C}^*(q, p) = \frac{M_0^* \widehat{\Phi}(q)}{p+k} + \frac{k K_d}{u \theta^*} \left[M_0 \frac{\widehat{f}_1(q, p)}{p+k} + M_0^* k \frac{\widehat{f}_1(q, p)}{(p+k)^2} \right] \widehat{\Phi}(q).$$

By applying the inverse q -Laplace transform yields:

$$\begin{aligned} \overline{C}^*(z, p) &= \frac{M_0^* \Phi(z)}{p+k} + \frac{k K_d}{u \theta^*} \int_0^z dz' \left[M_0 \frac{\overline{f}_1(z', p)}{p+k} + M_0^* k \frac{\overline{f}_1(z', p)}{(p+k)^2} \right] \\ &\quad \times \Phi(z-z'), \end{aligned} \quad (\text{A7})$$

where the inverse of Laplace transform of the second term between brackets appearing on the right-hand side of (A7) is

$$L^{-1} \left[\frac{\overline{f}_1(z, p)}{(p+k)^2} \right] = \frac{z_c(t) - z}{u} \chi(z, t) \tilde{I}[\zeta^2(z, t)] H[z_c(t) - z].$$

Summarizing, the immobile concentration writes as

$$\begin{aligned} C^*(z, t) &= \exp(-kt) C^*(z, 0) + H[z_c(t) - z] \int_0^z dz' \Phi(z-z') \eta^*(z', t) + \\ &\quad + H[z - z_c(t)] \int_0^{z_c(t)} dz' \Phi(z-z') \eta^*(z', t), \end{aligned} \quad (\text{A8})$$

where η^* is given by

$$\eta^*(z, t) = \frac{k K_d}{u \theta^*} \chi(z, t) \left\{ M_0 I_0[2\zeta(z, t)] + \frac{M_0^* k}{u} [z_c(t) - z] \tilde{I}[\zeta^2(z, t)] \right\}.$$

Similarly to the mobile concentration, for $z_f < z_0$ we recover from (A8) Equation (15), whereas for $z_f > z_0$ yields Equation (17).

Appendix B. Derivation of the Mean Concentration (40)

In order to calculate the mean concentration (39) for an initially applied Dirac pulse, we first recall that the local concentration C^i is derived from (16) after letting $z_0 \rightarrow 0$, i.e.

$$C^i(z, t; K_s) = M_0 \exp\left(-\frac{k K_d t}{\theta^*}\right) \delta[z - z_c(t)] + C_1(z, t; K_s) H[z_c(t) - z] \quad (\text{B1})$$

with C_1 given by (43). It is convenient to split $\langle C^i \rangle$ as

$$\langle C^i(z, t) \rangle = \langle C^{(1)} \rangle + \langle C^{(2)} \rangle,$$

where we have set

$$\begin{aligned} \langle C^{(1)} \rangle &= \int_0^r dK_s f(K_s) C^i(z, t; K_s), \\ \langle C^{(2)} \rangle &= \int_r^{+\infty} dK_s f(K_s) C^i(z, t; K_s). \end{aligned} \quad (\text{B2})$$

We proceed to calculate the two contributions separately. For the first of (B2) $\gamma = 1$ (see Section 2.1), and therefore $z_c(t) = K_s t / \theta_s$ (from the first of (7) with $K_d = 0$). By introducing the new variable $\lambda = K_s t / \theta_s$ yields

$$\begin{aligned} \langle C^{(1)} \rangle &= \frac{\theta_s}{t} \int_0^{rt/\theta_s} d\lambda f\left(\lambda \frac{\theta_s}{t}\right) \\ &\quad \times \left[M_0 \exp\left(-\frac{k K_d}{\theta_s} t\right) \delta(z - \lambda) + H(\lambda - z) C_1\left(z, t; \lambda \frac{\theta_s}{t}\right) \right]. \end{aligned} \quad (\text{B3})$$

We apply the same procedure to the second term of (B2) with $z_c(t) = rt / (\theta_r + \Delta\gamma^\beta)$, and $\gamma = r/K_s$. Indeed, we introduce the new variable $\lambda = rt / (\theta_r + \Delta\gamma^\beta)$ and substitute in $\langle C^{(2)} \rangle$ to have

$$\begin{aligned} \langle C^{(2)} \rangle &= \int_{rt/\theta_s}^{rt/\theta_r} d\lambda f[K_t(\lambda)] \frac{\partial K_t(\lambda)}{\partial \lambda} \\ &\quad \times \left[\exp\left(-\frac{\lambda k}{r} K_d\right) \delta(z - \lambda) + H(\lambda - z) C_1(z, t; K_t(\lambda)) \right], \end{aligned} \quad (\text{B4})$$

where $K_t(x)$ has been defined in (43). By carrying out the integrations and summing (B3) and (B4) leads to (40).

Appendix C. Mean Solute Penetration Depth

The mean solute penetration depth (46) is derived by adopting a uniform distribution f_r of given mean $\langle K_s \rangle$ and coefficient of variation ξ . By skipping the algebraic derivations, (46) writes as

$$\begin{aligned}
\frac{\langle z_r(t) \rangle}{z_r^\infty} &= \frac{t f_r}{2W(1+\theta_d)} H\left(\frac{W}{t} - K_a\right) \left\{ H\left(\frac{W}{t} - K_b\right) [K_b^2 - H(K_a)K_a^2] \right. \\
&\quad + H\left(K_b - \frac{W}{t}\right) \left[\left(\frac{W}{t}\right)^2 - H(K_a)K_a^2 \right] \left. \right\} + \frac{W}{t} f_r H\left(K_b - \frac{W}{t}\right) \\
&\quad \times H(r - K_a) \left\{ H(K_b - r) \left[H\left(K_a - \frac{W}{t}\right) \bar{\Lambda}_{(1/\beta)}(K_a, r) \right. \right. \\
&\quad + H\left(\frac{W}{t} - K_a\right) \bar{\Lambda}_{(1/\beta)}\left(\frac{W}{t}, r\right) \left. \right] + H(r - K_b) \left[H\left(K_a - \frac{W}{t}\right) \right. \\
&\quad \times \bar{\Lambda}_{(1/\beta)}(K_a, K_b) + H\left(\frac{W}{t} - K_a\right) \bar{\Lambda}_{(1/\beta)}\left(\frac{W}{t}, K_b\right) \left. \right] \left. \right\} \\
&\quad + r \beta^{-1} f_r H(K_b - r) [H(K_a - r) \Lambda_{(1/\beta)}(K_a, K_b) \\
&\quad + H(r - K_a) \Lambda_{(1/\beta)}(r, K_b)]. \tag{C1}
\end{aligned}$$

In (C1) we have set

$$\begin{aligned}
\bar{\Lambda}_{(1/\beta)}(x, y) &= \int_{\Theta(x)}^{\Theta(y)} d\lambda \frac{\lambda^{1/\beta}}{\theta_d + \lambda}, \quad \Theta(\kappa) = \bar{\Theta}_w^\beta(\kappa), \\
K_{a,b} &= (1 \mp \sqrt{3} \xi) \langle K_s \rangle, \tag{C2}
\end{aligned}$$

whereas $\Lambda_{(1/\beta)}(x, y)$ is obtained from the first of (C2) after replacing θ_d with θ_d/Θ_w^β and $\Theta(\kappa)$ with $(\kappa/r)^\beta$ (the remaining quantities were already defined in (47)). Since $\beta^{-1} = 2 \div 4$ (see, e.g., Indelman *et al.*, 1998) the integral appearing in (C2) is easily evaluated for integer values of β^{-1} , i.e. for $\beta^{-1} \equiv n = 2, 3, 4$, yielding

$$\begin{aligned}
\bar{\Lambda}_{(n)}(\bar{x}, \bar{y}) &= \int_{\bar{x}}^{\bar{y}} d\lambda \frac{\lambda^n}{\theta_d + \lambda} = \frac{(\bar{y}^n - \bar{x}^n)}{n} + (-\theta_d)^n \ln\left(\frac{\bar{y} + \theta_d}{\bar{x} + \theta_d}\right) \\
&\quad + \sum_{j=1}^{n-1} (-\theta_d)^j \frac{(\bar{y}^{n-j} - \bar{x}^{n-j})}{n-j}.
\end{aligned}$$

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