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Solute Migration from the Aquifer Matrix into a Solution Conduit and the Reverse

Li Guangquan
Department of Geophysics, Yunnan University, Kunming, Yunnan 650091, P. R. China, Tel: 011-86-13708762808

Malcolm S. Field[1]
U.S. Environmental Protection Agency, National Center for Environmental Assessment (8623P), 1200 Pennsylvania, Ave., N.W., Washington, D.C. 20460, USA

Abstract

A solution conduit has a permeable wall allowing for water exchange and solute transfer between the conduit and its surrounding aquifer matrix. In this paper, we use Laplace Transform to solve a one-dimensional equation constructed using the Euler approach to describe advective transport of solute in a conduit, a production-value problem. Both nonuniform cross-section of the conduit and nonuniform seepage at the conduit wall are considered in the solution. Physical analysis using the Lagrangian approach and a lumping method is performed to verify the solution. Two-way transfer between conduit water and matrix water is also investigated by using the solution for the production-value problem as a first-order approximation. The approximate solution agrees well with the exact solution if dimensionless travel time in the conduit is an order of magnitude smaller than unity. Our analytical solution is based on the assumption that the spatial and/or temporal heterogeneity in the wall solute flux is the dominant factor in the spreading of spring-breakthrough curves, and conduit dispersion is only a secondary mechanism. Such an approach can lead to better understanding of water exchange and solute transfer between conduits and aquifer matrix.

Keywords

conduit; advection; dilution; Laplace Transform; Lagrangian approach

Introduction

Karst is a geological feature characterized by sinking streams, sinkholes, solution conduits, and springs that are formed by dissolution of soluble rocks such as carbonates and evaporites. The dissolution of carbonate rocks is caused by surface recharge rich in carbon dioxide. Karst aquifers are an important resource because they provide drinking water to approximately one quarter of the world's population (Ford and Williams 1989). In Florida, USA, almost 90% of the population obtains drinking water from the karstic Floridan aquifer

[1] Corresponding Author Malcolm S. Field, Tel: (703) 347-8601, Fax: (703) 347-8692, field.malcolm@epa.gov.

(Johnston and Bush 1988). In some rural areas of Southwest China, groundwater from karst aquifers is the only water source available for drinking and irrigation.

Small pores and fissures in soluble rocks constitute the first and secondary porosities of karst aquifers, respectively (commonly denoted as aquifer matrix or just matrix), while a tertiary porosity consists of an interconnected system of solution conduits that typically results in preferential and turbulent flow (Shuster and White 1971; Kiraly 1998). Although the conduits only store a small quantity of water, they control transmission of water and pollutants. This is because hydraulic resistivity in large conduits is small, which allows for typically fast and turbulent flow in the conduits in contrast to a slower laminar flow occurring inside the pores and fissures of the matrix. As such, the equations for flow and transport in conduits are distinctively different from those in the aquifer matrix, which leads to a singularity in the mathematics (i.e., the equations and their solutions are discontinuous across the wall of a conduit). In addition, conduit systems are typically heterogeneous and anisotropic (i.e., conduits have certain orientations such that conduit flow is preferential in certain directions), which renders the dual-continuum model proposed by Bear et al. (1993) for fractures to be inapplicable to flow in solution conduits.

The key issue of karst hydrology is the significant variation of conduit cross-section and the complicated exchanges of water and solute between conduits and matrix. Numerical modeling of such feature and processes is very tedious, requiring significant efforts in development and computation. Previous studies such as MT3D adopted the far-field approach (like Fick's law). In this paper, we prefer the near-field approach because it is more reasonable from the physical perspective. The analytical solution we develop in this paper allows for a reduction of such in the development and computation efforts and can be integrated into numerical models for solute transport in the aquifer matrix.

One of the least understood subsurface processes is water exchange between conduits and the surrounding aquifer matrix. According to the traditional perspective, when a sinkhole or swallet drains a large quantity of water from various surface runoffs, the sinkhole head will rise abruptly with a consequent increase in pressure head that then forces some of the conduit water into the surrounding matrix where it becomes temporarily stored. Later, when the pressure difference between conduit water and matrix water is reversed, water will be slowly released back into the conduit (Rorabaugh 1964; Atkinson 1977; Li 2004; Kovács et al. 2005; Li et al. 2008; Birk and Hergarten 2010), causing the skewness or asymmetry in spring-discharge curves. Chemical evidence for reversible water exchange between different seasons has been documented by Martin and Dean (2001) and Mitrofan et al. (2015). Peterson and Wicks (2005) determined, however, bank storage to not be a dominant process because water exchange between the conduit water and the matrix is very limited when the rocks are telogenetic rather than eogenetic (Vacher and Mylroie 2002). Li and Field (2014) constructed a model that neglected bank storage and attributed the skewness in spring-discharge curves to the natural drop of water head after sinkhole flooding.

Solutes in groundwater may originate from dissolution of soluble rocks, agricultural chemicals such as nitrate and phosphate, industrial inorganics such as mercury and lead, or organics such as BTEX and MTBE due to petroleum spills. Naturally-occurring solute

concentrations in losing streams and/or sinking streams may be lower than that in the aquifer matrix, because water in the matrix has experienced sufficient time and surface-area contact to facilitate the dissolution of minerals. During a drought season, water pressure in conduits is lower than that in the matrix, such that water discharges (one way) from the matrix into the conduits, which sustains the discharge of base-flow springs. In this sense, conduit flow during a drought season is relatively simple and relatively steady. During an ordinary season (humid weather with a small amount of precipitation), conduit water enters the aquifer matrix and then returns back to the conduit. Alternatively, matrix seepage enters the conduit and then returns back to the matrix (Ho and Gelhar 1973; Thibodeaux and Boyle 1987). For this scenario, water exchange and solute transfer exhibit a two-way mode. During a flood season (heavy rainfall), water that enters the subsurface via sinkholes and/or swallets often exhibit relatively high concentrations of contaminants from surface runoff, causing the (mathematical) boundary condition at the sinkholes and/or swallets to become significant when describing solute transport.

Mathematical modeling provides an effective approach for revealing the physical processes of solute transport and for parameterizing the relevant quantities. Currently, the most popular software available for simulating transport in a karst conduit is CXTFIT (Toride et al. 1995; Field and Pinsky 2000). The CXTFIT program is based on a two-region non-equilibrium model (Toride et al. 1993) that describes solute exchange between mobile- and immobile-flow regions. When applied to transport inside solution conduits the CXTFIT model is typically used to model the physical detention of solutes in immobile-flow regions, but mathematically is equivalent to simulating transport in a karst conduit with the matrix being treated as a sink/source. The basic idea was that when a highly-concentrated pollutant flows through a conduit, the matrix acts as a sink at that moment to temporarily absorb part of the pollutant. When the pollutant passed through the conduit, that portion of pollutant sequestered in the matrix will then be released back into the conduit and the matrix will behave like a source. The CXTFIT model can reproduce the typically observed strong skewness, gradual spreading, and long breakthrough curve tailing (Birk et al. 2005; Geyer et al. 2007; Göppert and Goldscheider 2008; Goldscheider 2008). Field and Leij (2014) substantially improved on the CXTFIT model when applied to solute transport in a conduit with their PHYSCHEM model, which allows for consideration of solute reactivity in conjunction with physical detention. Conceptually, four complexities in the application of CXTFIT to transport in a conduit are evident: (1) it is applicable to the boundary-value problem (i.e., prescribing a function of solute concentration with time at the sinkhole), the initial-value problem (i.e., prescribing a function of solute concentration with location in the conduit at a chosen zero moment), and the zero-order production problem (i.e., the solute released from matrix into the conduit is a constant), but was not designed for the production-value problem when production is transient or nonuniform in the conduit; (2) flow velocity is assumed to be a constant along the conduit; (3) dilution by clean waters from tributary conduits, fractures, and pores in the surrounding matrix is ignored; and (4) solute transfer between conduit and matrix is assumed to be passive (diffusive-like), based on the far-field approach, but, from the near-field point of view, solute transfer between conduit and matrix is advective and is driven by seepage flow between them.

Substantial progress in modeling has been achieved recently by the efforts of karst hydrologists. Birk et al. (2006) used a hybrid method (with MODFLOW and the Darcy–Weisbach equation to simulate matrix seepage and conduit flow, respectively) to model the discharge response and breakthrough curve at a spring. Recharge at the sinkhole was considered to be solute-free, while water released from the matrix was taken as rich in calcium. Both the water exchange and solute transfer between the conduit and matrix were assumed to be diffusive-like. A significant finding by Birk et al. (2006) was that a secondary valley appears following a major valley in the spring breakthrough curve (see figure 3 in Birk et al. (2006)). Li and Loper (2011) developed a model in which advection, dilution, and dispersion were all included, using an approximate solution for the initial-value problem that successfully simulated a dye-tracing experiment between Ames Sink and Indian Spring, northwest Florida. Later, Li (2011) used transform of variables to obtain the solution for the initial-value problem as well as the approximate solution for the boundary-value problem with that model.

The motivation for this paper is the need to develop a solution for one-way and two-way exchanges of water and solute between a conduit and the matrix when considering conduit cross section and seepage between the two while ignoring dispersion. Because solute migrating from the matrix into the conduit and from the conduit into the matrix are source and sink, respectively, the problem under investigation is essentially a production-value problem (PVP). The one-way exchange typically occurs during dry seasons, while the two-way exchange occurs during ordinary seasons as a result of the episodic variation of the conduit cross-section.

Our focus is advective transport (in a solution conduit) of solute released from the aquifer matrix during a drought or ordinary season. We only study the PVP in which the source of solute is from the matrix, is unsteady, and is nonuniform along the conduit. Solute transport originating from a sinkhole and/or swallet is a boundary-value problem, and transport with solute preexisting inside a conduit is an initial-value problem. This paper is an initial work that addresses the general PVP in karst conduits using an analytical approach.

Advective Transport in a Conduit

Basic Theoretical Concept

When head in a conduit exceeds that in the surrounding matrix, surface water draining from sinkholes and/or swallets can become partially emplaced into the surrounding matrix through the conduit wall and temporarily reside inside the matrix (Moore et al. 2009). This temporary recharge feeds a significant portion of spring discharge when the pressure gradient between conduit and the surrounding matrix is reversed after sinkhole flooding (Screaton et al. 2004; Martin et al. 2006; Li et al. 2008). A significant accompanying chemical reaction is that the water has a higher concentration of carbon dioxide, resulting in dissolution in the surrounding matrix. Previous karstification models assumed chemical reactions occur only at the conduit wall. Recently, Moore et al. (2009) described a conceptual model in which the boundary between conduit and matrix is not sharp, but instead is a fragile buffer zone where the megapore of a conduit transitions to the primary matrix far away and free from deposition. Chemical dissolution occurs preferentially in this

buffer zone, rather than only at the wall as assumed by most karstification models. This new conceptual model allows for a positive feedback between chemical dissolution and physical retention of water, and is well supported by observations of accelerated expansion of some conduits.

In our conceptual model (Figure 1), recharge entering the sinkhole and/or swallet is assumed to be steady and solute-free, and water in the conduit is initially considered solute-free. As a transient solute flux (product of solute mass and discharge) is released from the matrix into the conduit, the solute that is released through the permeable conduit wall is diluted by the solute-free recharge, and is transported downgradient in the conduit via advection.

Dispersion is intentionally neglected in our conceptual model because of the escalated difficulty in seeking an exact solution. The governing equation then degenerates to a first-order partial differential equation. For such an equation, traditional solution methods include the classic characteristic curve (Strauss 1992; Li and Liu 2014), and the parameterized characteristic curve (Holden and Risebro 2002; Li 2009).

Governing Equation

The essential features of mixing and transport in a conduit may be described using a relatively simple one-dimensional equation. Taking into consideration longitudinal dispersion in the conduit, solute-mass conservation yields

$$\begin{aligned} &2\pi a(z)\Delta z J(z,t) + \left[C(z,t)W(z) - D_c(z)\frac{\partial C(z,t)}{\partial z}\right]\pi a(z)^2 - \\ &\left[C(z+\Delta z,t)W(z+\Delta z) - D_c(z+\Delta z)\frac{\partial C(z+\Delta z,t)}{\partial z}\right]\pi a(z+\Delta z)^2 = \frac{\partial C(z,t)}{\partial t}\Delta z \pi a(z)^2, \end{aligned} \quad (1)$$

where C [M/L^3] is the solute concentration in the conduit, a [L] is the conduit radius, W [L/T] is the velocity of conduit flow averaged over the conduit cross section, D_c [L^2/T] is the coefficient of dispersion in the conduit, and Δz[L] is the length of a thin fluid disk within the conduit. The specific flux of solute at the wall J [M/(L^{2}T)] consists of two terms, advection and dispersion. The dispersive term is the solute-concentration gradient multiplied by the dispersion coefficient at the outside of the conduit, while the advective term is the solute concentration at the wall multiplied by the effective seepage q [L/T] that is defined as

$$q(z) = \frac{1}{2\pi a(z)}\frac{dQ(z)}{dz}, \quad (2)$$

where Q [L^3/T] is the volume flux of conduit water. Effective seepage q (Figure 1) can be transformed to the normal component of real seepage at the wall via a simple geometric relationship. The geometric relationship does not change the qualitative fact that if conduit flux Q increases downstream, matrix water must release into the conduit and the effective seepage must be positive, and vice versa.

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Equation (2) represents water-mass conservation, and Equation (1) is solute-mass conservation from the Euler perspective (i.e. study of problems using a fixed space). The first term on the left side of Equation (1) represents the solute flux from the matrix into the conduit, which is the production term. The second and third terms on the left side represent the solute fluxes at z and $z + \Delta z$, respectively. The right side represents the change of solute within the fluid disk in the conduit, with respect to time.

Noting that Δz is a small quantity of the first order, Equation (1) can be simplified to:

$$2\pi a(z)\Delta z J(z,t) - \Delta z \frac{\partial}{\partial z}\left\{\left[C(z,t)W(z) - D_c(z)\frac{\partial C(z,t)}{\partial z}\right]\pi a(z)^2\right\} = \frac{\partial C(z,t)}{\partial t}\Delta z \pi a(z)^2 . \quad (3)$$

Dividing the above equation by $\pi\Delta z$ yields

$$a(z)^2\frac{\partial C}{\partial t} + \frac{\partial}{\partial z}\left[(WC - D_c\frac{\partial C}{\partial z})a(z)^2\right] = 2Ja(z) . \quad (4)$$

The conduit domain is $0 \le z \le L$. The initial condition is $C(z,0) = 0$ (no solute pre-existing inside the conduit). The boundary condition is $C(0,t) = 0$ for $t \ge 0$ (solute-free sinkhole recharge). Equation (4) differs from the traditional advection-dispersion equation in that it incorporates the specific fluxes of solute J and water q.

Analytical Solution without Conduit Dispersion

If conduit dispersion is ignored, Equation (4) simplifies to

$$a(z)^2\frac{\partial C}{\partial t} + \frac{\partial}{\partial z}\left[W(z)Ca(z)^2\right] = 2J(z,t)a(z) . \quad (5)$$

This governing equation with a zero initial condition and a zero boundary condition, is solved using Laplace Transforms in the Appendix. The solution is

$$C(z,t) = \begin{cases} \dfrac{1}{W(z)a(z)^2}\displaystyle\int_0^z 2a(z^*)J(z^*, t - T_{z^*z})dz^* & t \ge \displaystyle\int_0^z \frac{dz}{W(z)} \\ \dfrac{1}{W(z)a(z)^2}\displaystyle\int_{z_C^*}^z 2a(z^*)J(z^*, t - T_{z^*z})dz^* & t < \displaystyle\int_0^z \frac{dz}{W(z)} \end{cases} , \quad (6)$$

where

$$T_{z^*z} = \int_{z^*}^z \frac{dz}{W(z)} \quad (7)$$

is the travel time from z^* to z, and z_C^* is defined by

$$t = \int_{z_C^*}^{z} \frac{dz}{W(z)}. \quad (8)$$

If the definition of specific solute flux is extended to negative time (i.e., $J(z, t < 0) = 0$), then the above solution can be summarized as follows

$$C(z,t) = \frac{1}{W(z)a(z)^2} \int_0^z 2a(z^*)J(z^*, t - T_{z^*z})dz^*. \quad (9)$$

This solution allows for consideration of a nonuniform radius of the conduit and nonuniform seepage at the wall.

Physical Analysis

A physical analysis of advective transport of a solute released from the matrix into a conduit is examined to verify the analytical solution. As shown in Figure 2, a solute pulse is released from the matrix at location z^*, with a length Δz^* and a release duration Δt. This pulse will evolve into a parcel with a length Δz_p. The contribution of this parcel to the average concentration at z can be obtained by mass conservation of the solute

$$\Delta C(z,t) = \frac{2\pi a(z^*)J(z^*, t - T_{z^*z})\Delta z^* \Delta t}{\pi a^2(z)\Delta z_p}. \quad (10)$$

Substituting $\Delta z_p = W(z)\Delta t$ into this equation yields

$$\Delta C(z,t) = \frac{2a(z^*)J(z^*, t - T_{z^*z})}{a^2(z)W(z)}\Delta z^*. \quad (11)$$

If t is so large (i.e., $t \geq \int_0^z \frac{dz}{W(z)}$) such that all the contribution of solute at z comes from upstream only (i.e., $z^* = 0 \rightarrow z$), then we can lump and integrate Equation (11) to get the average concentration

$$C(z,t) = \int_{z^*=0}^{z} dC = \frac{2}{a^2(z)W(z)} \int_0^z J(z^*, t - T_{z^*z})a(z^*)dz^*. \quad (12)$$

If t is small (i.e.,$t < \int_0^z \frac{dz}{W(z)}$), there is a z_C^* that satisfies Equation (8) and all the contribution comes from $z^* = z_C^* \to z$

$$C(z,t) = \int_{z^* = z_C^*}^{z} dC = \frac{2}{a^2(z)W(z)} \int_{z_C^*}^{z} J(z^*, t - T_{z^* z}) a(z^*) dz^* . \quad (13)$$

The solution from the physical analysis is the same as that from the Laplace Transform in the preceding section. For a non-cylindrical conduit, the solution can be expressed as

$$C(z,t) = \frac{1}{A(z)W(z)} \int_{\max(0,\ z_C^*)}^{z} J(z^*, t - T_{z^* z}) \Gamma(z^*) dz^*, \quad (14)$$

where $\Gamma(z)$ and $A(z)$ are the circumference and cross-sectional area of the conduit at location z, respectively.

Two-Way Transfer of Solute between Conduit and Matrix

Approximate Solution for Two-Way Solute Transfer

The key quantity of advective transport in this paper is the specific flux of solute at the wall, $J(z, t)$. In terms of seepage from the matrix into the conduit (one-way) the concentration just inside the matrix, $C_m(z,t)$, may be known *a priori*, and thus by neglecting dispersive flux,

$$J(z,t) = C_m(z,t) q(z,t) . \quad (15)$$

At the scale of conduit length, conduit water enters the matrix at the upstream end and eventually returns back into the conduit at the downstream end (e.g., Li 2009). In this case, water travels a significant distance inside the matrix. As such, variations in conduit cross section can also induce a local (small-scale) two-way water exchange between conduit and matrix. In this instance, fluid mechanics states that where the conduit is wide, flow velocity is slow and conduit pressure is large if the conduit is pipe full, thus generating small-scale seepage starting from the wide conduit, through the conduit wall, and back into the narrow conduit (e.g., Ho and Gelhar 1973; Thibodeaux and Boyle 1987). Water travels a much shorter distance in the matrix than in the first case.

For two-way water exchange between conduit and matrix (Figure 3), the solute concentration at the wall where water seeps from the matrix into the conduit, is

$$J(z,t) = C_m(z,t) q(z,t), \text{ for } q(z,t) \geq 0. \quad (16)$$

At locations where water is forced into the matrix from the conduit due to varying conduit cross sections along its length and the resulting small-scale flow in the subsurface the specific solute flux at the wall may be approximated by using the solute concentration averaged over the conduit cross section

$$J(z,t) \approx C(z,t)q(z,t), \text{ for } q(z,t) < 0. \quad (17)$$

For two-way transfer of solute between conduit and matrix, substituting Equation (17) into Equation (14) makes the solution an implicit function of solute concentration in the conduit.

To solve Equation (17) the conduit is discretized along the downstream direction into several segments. Considering the qualitatively-periodical feature of increasing and decreasing conduit diameters along the conduit length, each segment has two parts (one part has seepage entering the conduit from the matrix, followed by the other part having water being forced into the matrix from the conduit). Initially, the solute concentration in the first segment must be determined. The first-order approximation of the solute concentration is obtained by setting the specific solute flux from the second part of that segment into the matrix to zero (i.e., $J = 0$, called the first approximation of J). We can then use the one-way solution to get the first-order approximation of the solute concentration within that segment that is then used to get the second-order approximation of J. This J will be entered into the (one-way) solution to obtain the solute concentration (of conduit water) at the second order.

The specific solute flux J in the whole first segment then becomes known. For the second segment, J is prescribed for the first part, whereas J is unknown for the second part. Similar to that described above, J is temporarily set to zero for the second part of the second conduit segment (as a first-order approximation). Then the solute concentration within the second segment can be computed using Equations (12) and (13). The computation must start from $z = 0$ through to the downstream end of the second segment. Further recursion can be applied to obtain a more accurate J. These steps are repeated from the first segment and on through the most downstream end of the conduit. This technique uses recursion and that once J is known (whether one-way or two-way), the concentrations of conservative solutes in the conduit can be obtained using the solution for the PVP. If only production within a segment was computed, we would have to consider the additional contribution from its upstream (which is a boundary-value problem (BVP)). By computation of all the production (upstream to the conduit entrance), we avoid the BVP and fully utilize the solution for the PVP.

This solution approach is based on the assumption that the specific solute flux through the wall is decoupled (i.e., determined by the solute concentration in the conduit when $q < 0$ and the solute concentration in the matrix when $q > 0$). This assumption, although reasonable, makes the solute flux nonlinear with respect to q. For this reason, transport in a conduit with two-way transfer of solute between a conduit and the matrix is very complex. The complexity increases when the solute flux from the matrix into the conduit is coupled with the earlier migration of solute from the conduit into the matrix (e.g., small-scale water

exchange between conduit and matrix due to varying conduit diameters), which would necessitate determination of the time of solute retention *a priori*.

A Simple Model for Two-Way Solute Transfer

A simple model for two-way solute transfer may be developed for a conduit of uniform radius that consists of just two segments. The upper segment has a solute-carrying seepage from the matrix into the conduit, while the lower segments exhibit seepage from the conduit into the matrix. As a first-order approximation, solute flux from the lower segment into the matrix is intentionally ignored. This could occur as illustrated in Figure 4. In terms of pumping well, some matrix water in the upstream end can be drawn indirectly into a pumping well via the conduit.

The solute flux at the conduit wall is

$$J(z,t)=\begin{cases} C_m q & 0 \le z < \lambda/2 \\ 0 & \lambda/2 \le z < \lambda \end{cases}, \quad (18)$$

where λ is the conduit length under investigation (Figure 4). In addition

$$C_m=\begin{cases} C_m^0 & 0 \le t < t_S \\ 0 & t_S \le t \end{cases}. \quad (19)$$

The first-order approximation of Equation (19) is

$$C(z,t) = \frac{2}{aW_0}\int_0^{\lambda/2} J(z^*, t - T_{z^*z})dz^*, \quad (20)$$

where W_0 is the flow velocity at the conduit end, and the definition of the specific solute flux is extended to negative time, i.e.,$J(z, t < 0) = 0$. The travel time, Tc, in the upper or lower segment is

$$T_C = \int_0^{\lambda/2} \frac{dz}{W_0 + \frac{W_{\lambda/2} - W_0}{\lambda/2}z} = \frac{a}{2q}\ln\left(1 + \frac{\lambda q}{aW_0}\right). \quad (21)$$

The travel time from z^* (at the wall of the upper segment) to the conduit exit is

$$T_{z^*\lambda} = 2T_C - \frac{a}{2q}\ln\left(1 + \frac{2q}{aW_0}z^*\right), \quad (22)$$

so that the critical position (where the fluid particle in the upper segment will arrive at time *t*) is

$$z_C^* = \frac{aW_0}{2q}\left(e^{\frac{2q}{a}\left(2T_C - t\right)} - 1\right). \quad (23)$$

For $t < T_C$, the solute particle (from the upper segment) will not yet have reached the conduit exit, and for $t > 2T_C + t_S$, all the solute particles have passed the exit. Therefore, for these two extremes, the solute concentration at the conduit exit is zero. The non-trivial solution can be sorted into two families, Family I for $t_S > T_C$ and Family II for $t_S \le T_C$. Substituting Equations (18) and (19) into Equation (20) yields

$$\frac{C(\lambda, t)}{C_m^0} = \begin{cases} e^{\frac{2q}{a}T_C} - e^{\frac{2q}{a}\left(2T_C - t\right)} & T_C < t \le 2T_C \\ e^{\frac{2q}{a}T_C} - 1 & 2T_C < t \le T_C + t_S \\ e^{\frac{2q}{a}\left(2T_C + t_S - t\right)} - 1 & T_C + t_S < t \le 2T_C + t_S \end{cases}, \quad (24)$$

for Family I and, similarly,

$$\frac{C(\lambda, t)}{C_m^0} = \begin{cases} e^{\frac{2q}{a}T_C} - e^{\frac{2q}{a}\left(2T_C - t\right)} & T_C < t \le T_C + t_S \\ e^{\frac{2q}{a}\left(2T_C + t_S - t\right)} - e^{\frac{2q}{a}\left(2T_C - t\right)} & T_C + t_S < t \le 2T_C \\ e^{\frac{2q}{a}\left(2T_C + t_S - t\right)} - 1 & 2T_C < t \le 2T_C + t_S \end{cases}, \quad (25)$$

for Family II.

Exact Solution of Two-Way Solute Transfer

The exact solution for two-way transfer is obtained by noting that if the water being forced from the conduit into the matrix has the same concentration of solute as the conduit water (i.e., chemical reaction at the wall can be neglected), the solute concentration in the conduit will not change except for a time delay due to be transport along the conduit. This can be understood from the Lagrangian point of view (i.e., study of problems by tracking of a fixed object/particle). Once the solute concentration at the middle of the conduit length is known (i.e., where the seepage switches from $q > 0$ to $q < 0$), the solute concentration at the conduit exit can be determined by adding the time delay (i.e., T_C).

The solute concentration at the middle of the whole conduit has been described in the Supplementary file of Li (2009). The solutions can be made dimensionless using a time scale $\tau = a/2q$. Comparing the approximate solution in this paper with the exact solution, it was found that when $T_C << \tau$, the two solutions will be close. In Figures 5 and 6 we set $T_S = T_C/2$ and $T_S = 2T_C$, respectively, with $T_C = 0.1\tau$. The approximate solution agrees well with the exact solution although the approximate breakthrough curve (BTC) has a higher concentration than does the exact curve. This is because the approximate solution the solute flux from the lower conduit segment into the matrix is set to zero even though water transfer is from the conduit into the matrix. In contrast, for the exact solution the negative solute flux at the wall tends to decrease the concentration at the conduit exit, according to Equation (9). As such, a higher concentration appears in the approximate curve.

Discussion

For our problem, a dimensional analysis must lead to

$$\frac{C(\lambda/a, t/\tau)}{C_m^0} = F\left(\frac{T_C}{\tau}, \frac{t_S}{\tau}\right), \quad (26)$$

although it is unclear whether the dimensionless conduit length λ/a is a controlling parameter for the BTC at the conduit exit. According to Equation (14) (the solution in terms of an integral in the space domain), the curve is generally dependent on the conduit length. However, for the above simple advective-transport model of two-way transfer between conduit and matrix, Equations (24) and (25) state that the curve is not directly dependent on the dimensionless conduit length, but on the dimensionless T_C and T_S. This is also evident in the solution in terms of an integral in the time domain (see equation (9) in Li (2009)). Therefore, the solutions developed in this paper provide new insight into advective transport in a solution conduit that cannot be obtained from the dimensional analysis.

Although numerical solutions are a powerful method for understanding transport problems, numerical simulations often cannot accurately simulate the transport of a contaminant plume near the sharp edge of the plume. This occurs when Peclet numbers are large because dispersion is small relative to advection, which results in undesirable numerical dispersion that becomes dominant. This numerical dispersion results in a decrease in the accuracy of numerical solutions. Nonphysical numerical oscillations may also occur. With variations in conduit cross-sections and variable seepages at the conduit wall, dispersion becomes very complicated. However, analytical solutions that ignore dispersion (although not applicable to transport with large dispersion) provide a complementary approach to explore transport with small dispersion.

For the transport problem in this study, whether dispersion can be neglected depends on the definition of solute (i.e., whether a major solute plume in the conduit is of adequate length relative to the conduit length). If solute refers to calcium in the matrix, then dispersion can be neglected because such a solute is always persistent and its plume is sufficiently long. In

contrast, if solute refers to an external anthropogenic solute temporarily stored in the solution conduit, dispersion cannot be ignored because its major plume released *a posteriori* is much shorter than the conduit length. Sampling discharge water close to the BTC peak and when concentrations are steady will result in the most representative data. Neglecting conduit dispersion can over-estimate the early arrival time of a solute plume, or equivalently, the (actual) solute plume has an earlier first-arrival time than our model without conduit dispersion predicts. However, the arrival time of the peak only changes slightly between model with conduit dispersion and model without, according to Li and Loper (2011).

A simple and direct application of our analytical solution is calculation of calcium (or CO_2) concentration at the outside of a conduit which can at first be assumed to have a distribution along the conduit. The seepage from the matrix into the conduit may be assumed to be a constant. The resulting theoretical BTC of calcium (or CO_2) can be fitted against the observed BTC at the spring to obtain a good approximation of the real distribution of solute at the subsurface in the vicinity of the conduit. This can help overcome the difficulty in the instrumentation and measurement of solute concentration at the outside of conduits.

Conclusions

The most important contribution of this study is that nonuniform conduit radius and nonuniform seepage at the conduit wall were both considered for transport in a solution conduit. For any given conduit cross section and any specific fluxes of water and solutes, the solution requires a relatively small computational effort that only involves numerical integration. Generally, transport in a conduit is coupled with transport in the aquifer matrix. In this paper we make use of the wall solute flux $J(z, t)$, as an interface quantity to represent transport in the matrix and connect with transport in the conduit.

This paper is focused on theory. The solution achieved is only for steady seepage between a solution conduit and the aquifer matrix. There is no gradual spreading or long tailing in the BTCs, because in this model, solute that enters the matrix is not allowed to return back into the conduit. If the direction of seepage is extended to change with time the solutes sequestered earlier (during the time that they flush through the conduit) may be released from the matrix back into the conduit later when the seepage direction reverses. This retarded release is expected to contribute to the skewness and generate long BTC tails, similar to the processes in the CXTFIT program and as noted in Birk et al. (2006).

Our solution has significant potential for application to real karst aquifers and their conduit systems. Fluxes of water and solutes exchanged between a trunk conduit and its tributaries at their junctions can be represented by adjusting or extending the definitions of seepages of water and solutes in this paper. In reality, fluxes of water and solutes between different conduits at the junctions can be conceptualized as localized seepages of water and solutes. For application of this model, knowledge of conduit cross sections and steady water seepages between conduits and matrix is required. Meanwhile, at locations where conduit water moves into the matrix, it is not necessary that solute concentrations in the conduit subsurface be known. At other conduit locations, where matrix water releases into the

conduits, solute concentrations in the matrix water must be known or assumed to enter our model and yield spring BTCs.

For those instance in which conduit water is partially lost to the matrix, but then discharges into another part of the aquifer (rather than back into the same conduit), the solute concentration in the conduits and springs will not be affected. This is because any branching of conduit water and its solute cannot affect the solute concentration in a conduit, except for a partial loss of mass of both water and solute in the conduit.

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Appendix

If longitudinal conduit dispersion is ignored, transport of solute in the conduit is governed by the following equation.

$$a(z)^2\frac{\partial C}{\partial t} + \frac{\partial}{\partial z}\left[W(z)Ca(z)^2\right] = 2J(z,t)a(z), \quad \text{(A1)}$$

where C [M/L^3] is the solute concentration in the conduit, a [L] is the conduit radius, W [L/T] is the velocity of conduit flow averaged over the conduit cross section, and J [M/(L^{2}T)] is the specific flux of solute at the wall.

Taking Laplace Transform and using the zero initial condition yields

$$a(z)^2 p\hat{C}(z,p) + \frac{\partial}{\partial z}\left[W(z)\hat{C}(z,p)a(z)^2\right] = 2a(z)\hat{J}(z,p), \quad \text{(A2)}$$

where $\hat{C}(z,p)$ is the Laplace Transform of $C(z, t)$ and $\hat{J}(z,p)$ represents the Laplace Transform of $J(z, t)$. The above equation is essentially an ordinary differential equation because it only invokes the derivative with respect to z.

The zero boundary condition, i.e., $C(z=0,t)=0$, after Laplace Transform becomes

$$\hat{C}(z,p)\Big|_{z=0} = 0. \quad \text{(A3)}$$

Equation A2 can be rewritten as

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$$\frac{d\hat{C}(z,p)}{dz} + \hat{C}(z,p)\mathrm{P}(z) = \mathrm{Q}(z), \quad \text{(A4)}$$

where

$$\mathrm{P}(z) = \frac{p}{W(z)} + \frac{\partial(Wa^2)}{Wa^2\partial z}, \quad \text{(A5)}$$

$$\mathrm{Q}(z) = \frac{2\hat{J}(z,p)}{aW(z)}. \quad \text{(A6)}$$

The solution of Equation A4 subject to boundary condition A3 is (Abramowitz and Stegun 1970)

$$\hat{C}(z,p) = e^{-\int \mathrm{P}(z)dz} \int_0^z \mathrm{Q}(z) e^{\int \mathrm{P}(z)dz} dz. \quad \text{(A7)}$$

Substituting Equations A5 and A6 into Equation A7 yields

$$\hat{C}(z,p) = \frac{1}{W(z)a(z)^2} e^{-p\int_0^z \frac{dz}{W}} \int_0^z 2a(z^*)\hat{J}(z^*,p) e^{p\int_0^{z^*} \frac{dz}{W}} dz^*, \quad \text{(A8)}$$

or

$$\hat{C}(z,p) = \frac{1}{W(z)a(z)^2} \int_0^z 2a(z^*)\hat{J}(z^*,p) e^{-p\int_{z^*}^{z} \frac{dz}{W(z)}} dz^*. \quad \text{(A9)}$$

According to the property of Laplace Transform (Strauss 1992),

$$L^{-1}\left[e^{-p\tau}\hat{f}(p)\right] = \begin{cases} f(t-\tau) & t \ge \tau \\ 0 & t < \tau \end{cases}, \quad \text{(A10)}$$

where the operator L^{-1} denotes the inverse Laplace Transform.

Thus we have for the integrated function in Equation A9

$$L^{-1}\left[\hat{J}(z^*, p)e^{-pT_{z^*z}}\right] = \begin{cases} J(z^*, t - T_{z^*z}) & t \geq T_{z^*z} \\ 0 & t < T_{z^*z} \end{cases}, \quad \text{(A11)}$$

where

$$T_{z^*z} = \int_{z^*}^{z} \frac{dz}{W(z)}, \quad \text{(A12)}$$

which represents the travel time from z^* to z.

The inverse Laplace Transform of Equation A9 yields

$$C(z,t) = \frac{1}{W(z)a(z)^2}\int_0^z 2a(z^*)J(z^*, t - T_{z^*z})dz^*, \text{ for } t \geq \int_0^z \frac{dz}{W(z)}. \quad \text{(A13)}$$

If $t < \int_0^z \frac{dz}{W(z)}$, there must be a z_C^* such that

$$t = \int_{z_C^*}^{z} \frac{dz}{W(z)}. \quad \text{(A14)}$$

Here, z_C^* denotes the most upstream position in the conduit where water will reach z at time t. In this instance, the inverse Laplace Transform of Equation A9 yields

$$C(z,t) = \frac{1}{W(z)a(z)^2}\int_{z_C^*}^{z} 2a(z^*)J(z^*, t - T_{z^*z})dz^*. \quad \text{(A15)}$$

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Highlights:

1. Euler and Lagrangian approaches are used to solve transport in conduit.
2. Two-way transfer between conduit and matrix is investigated.
3. The solution is applicable to transport in conduit of persisting solute from matrix.

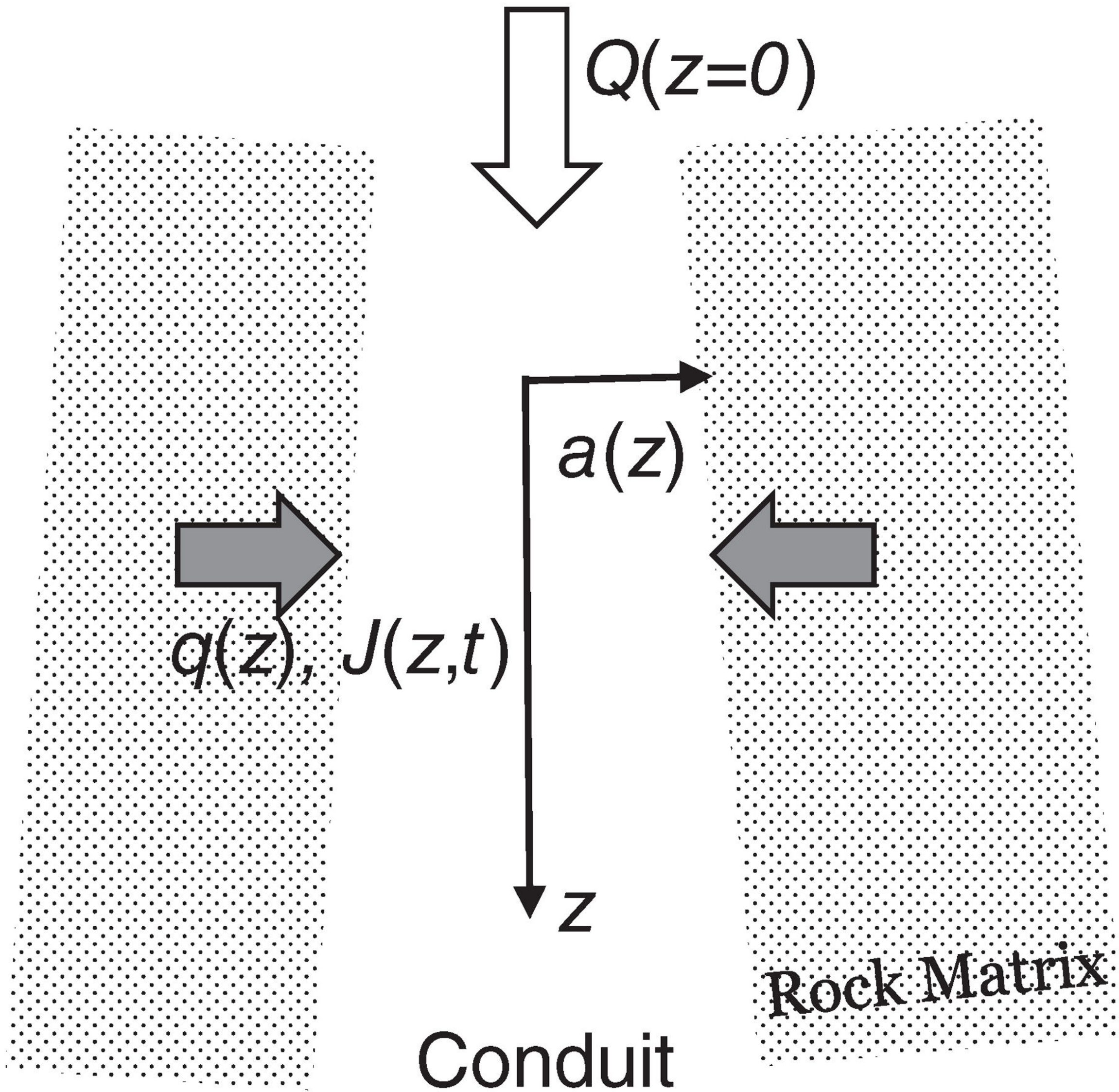

Fig. 1.

Schematic transport of solute (released from the matrix) in a conduit. The conduit radius is non-uniform, and also, non-uniform specific fluxes of water ($q(z)$) and solute ($J(z,t)$) flow from the rock matrix into the conduit.

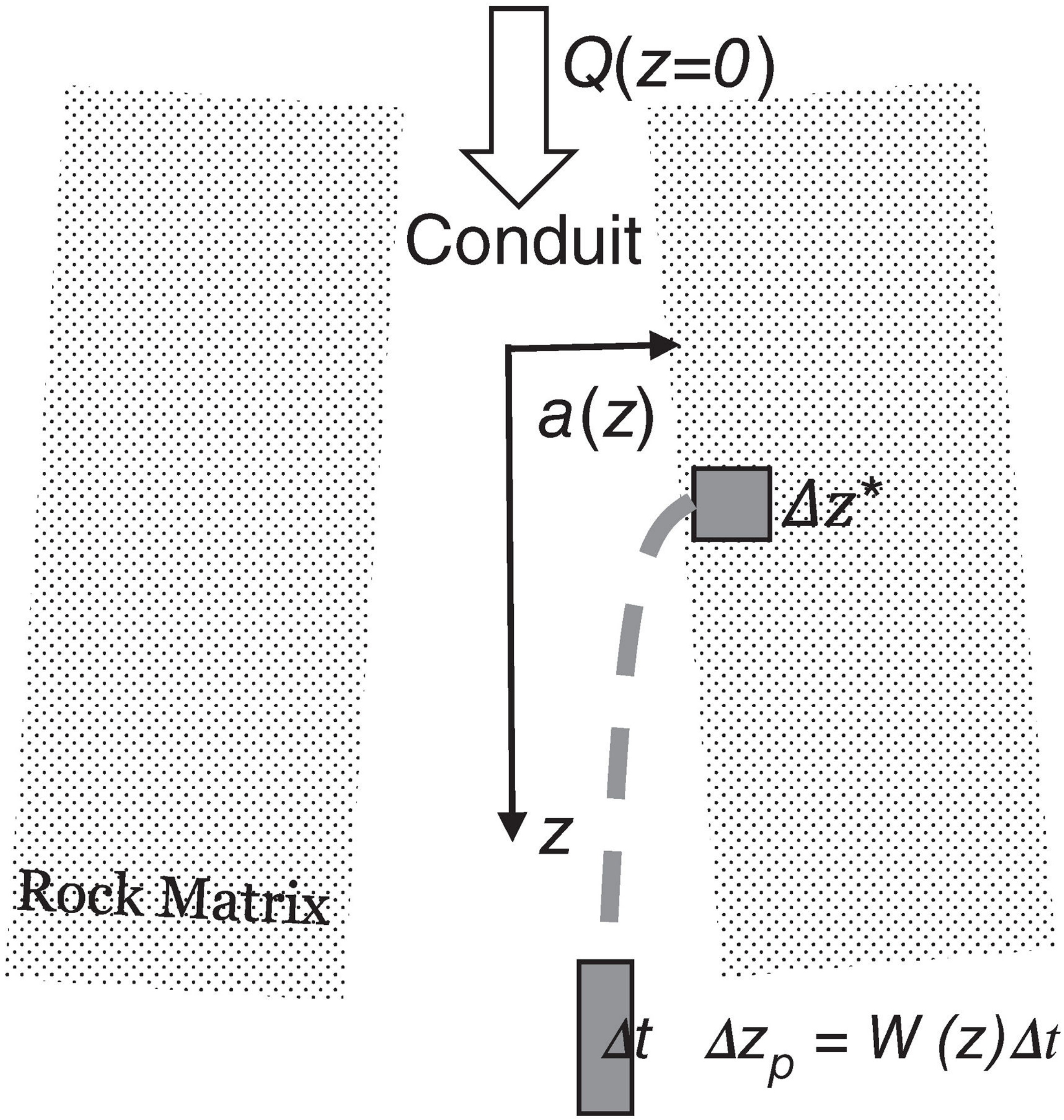

Fig. 2.
Physical analysis of advective transport using the Lagrangian approach. A solute pulse is released from the matrix at location z^*, with a length Δz^* and a release duration Δt. This pulse will evolve into a parcel with a length Δz_p, contributing to the average concentration of solute at downstream location z.

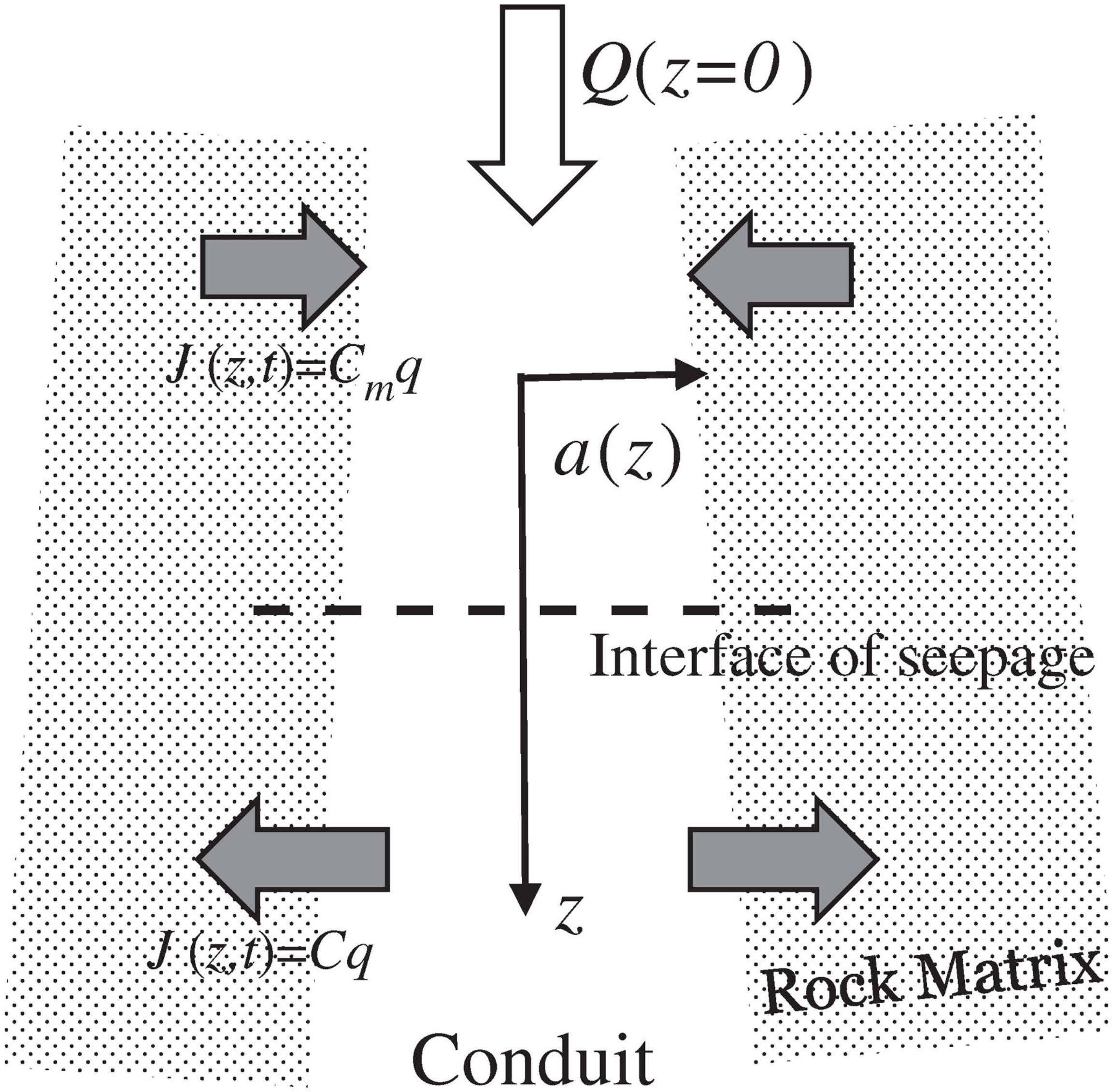

Fig. 3.
Two-way transfer of solute between a conduit and the matrix. Upstream of the interface of seepage, solute is driven from the matrix into the conduit, while downstream of the interface, solute is emplaced from the conduit into the matrix.

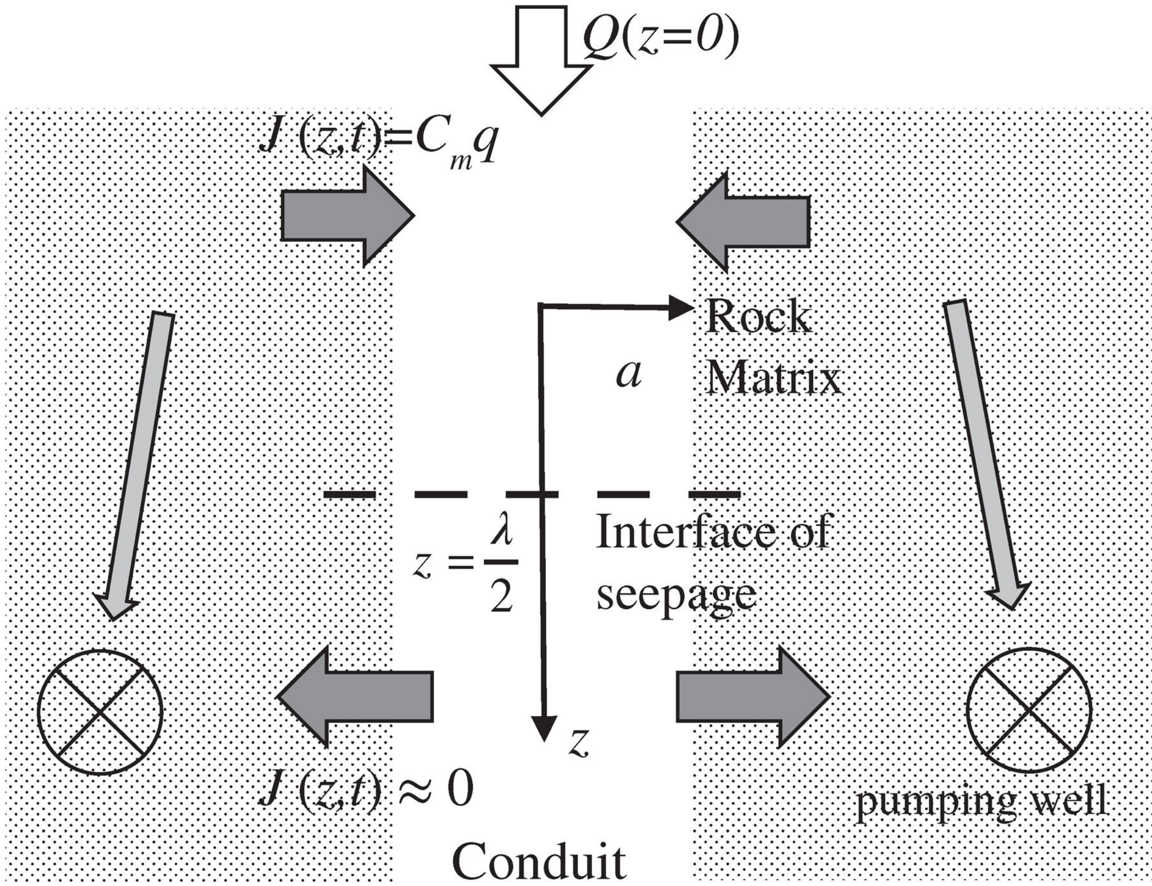

Fig. 4.

A theoretical advective-transport model for two-way transfer between a conduit and the matrix. In the model, the solute flux from the conduit into the matrix is intentionally ignored, to facilitate solution of the two-way problem. The pumping wells do not only induce matrix seepage directly, but also induce some matrix water to flow indirectly via the conduit to the wells.

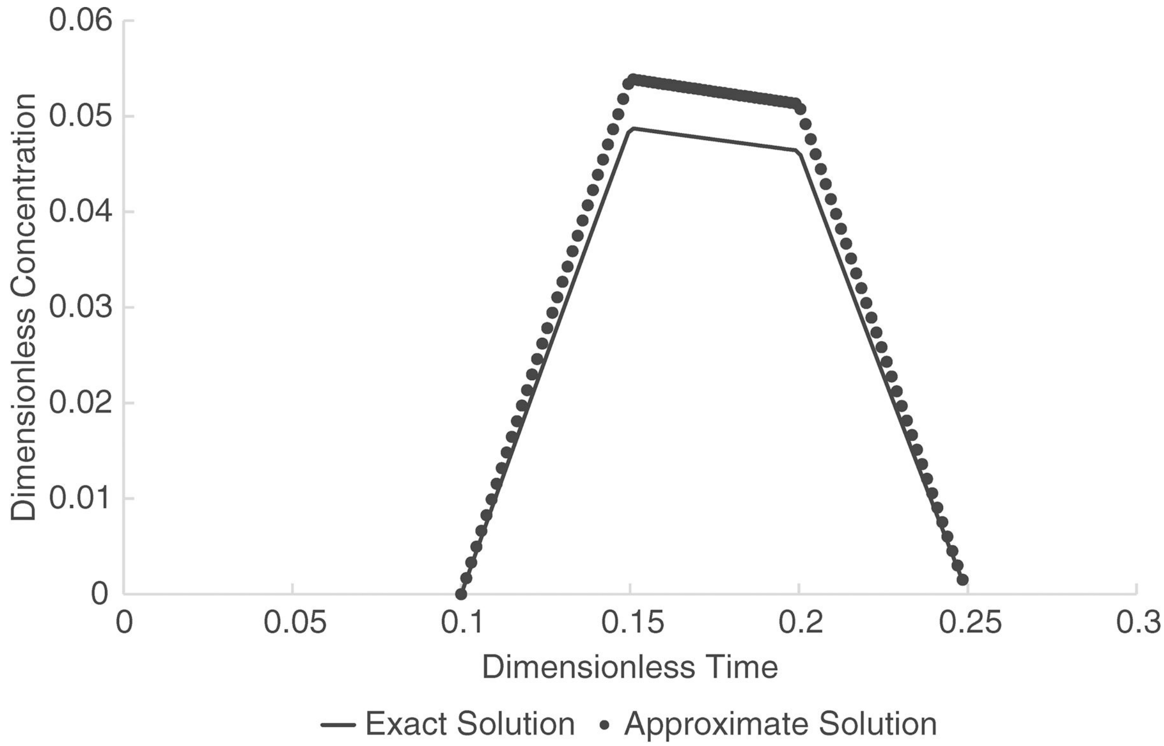

Fig. 5.

Breakthrough curve at the conduit exit, with $T_C = 0.1\tau$ and $T_S = T_C/2$, from the simple model against the exact curve. Tc is the travel time in the upper or lower segment, T_S is the duration of solute released from the upper matrix into the conduit, and $\tau = a/2q$ is a time scale defined by the conduit radius a and the specific seepage q.

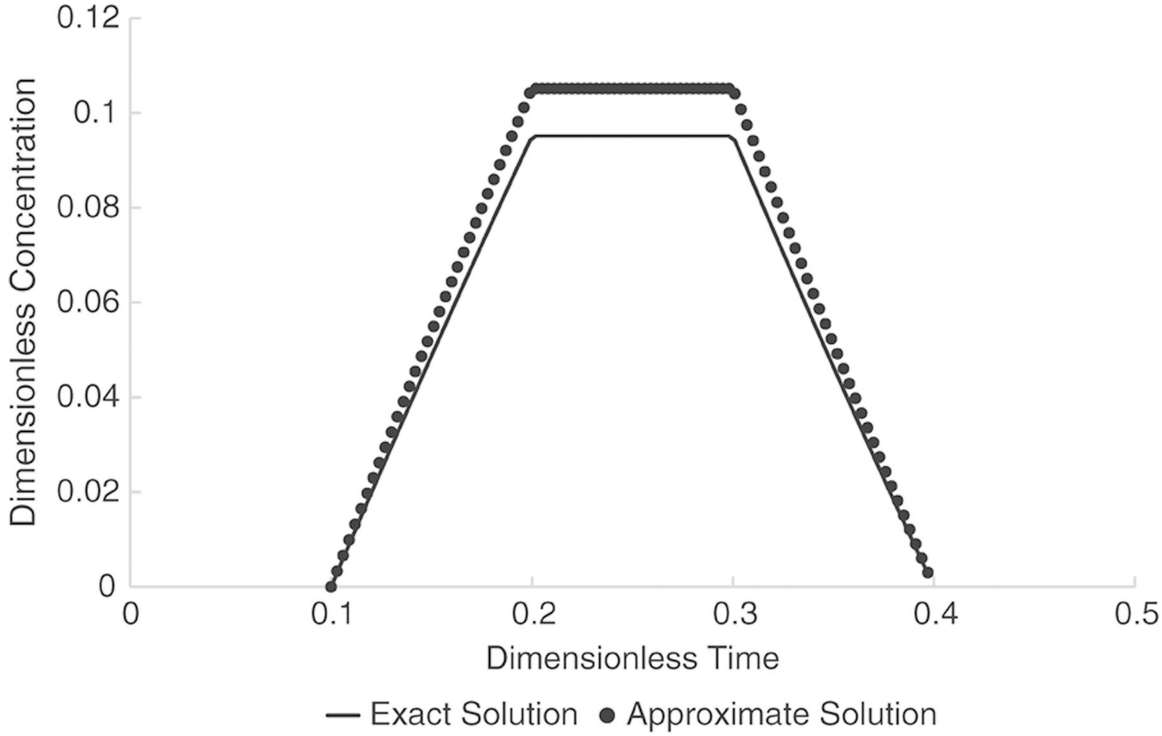

Fig. 6.
Breakthrough curve at the conduit exit, with $T_C = 0.1\tau$ and $T_S = 2T_C$, from the simple model against the exact curve. See the caption of Figure 5 for symbols.