

FLUSHING OF CONTAMINATED HOMOGENEOUS AND HETEROGENEOUS
AQUIFERS

A Thesis

by

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ABSTRACT

Flushing is one of the most common and important remediation technologies to deal with the contaminated aquifers. However, the present solutions used to calculate contaminant flushing are sometimes too complicated to apply in engineering practice for quick screening purposes. This thesis uses the finite-element COMSOL Multiphysics as a platform to obtain a new solution to describe the flushing process on the homogeneous aquifers, which has been verified to be reliable. This thesis will investigate two kinds of heterogeneity in which: 1) the flow direction is parallel to; or 2) perpendicular to the two-zone interface. To analyze how the transport properties of the zones of these with contrasting hydraulic properties will impact on the contaminant transport during the flushing process, one or more parameter values were changed, while the other parameter values were kept constant. Then the predicted breakthrough curves (BTCs) were compared with each other. Through the analysis of a series of hypothetical scenarios, the results of this thesis are summarized as follows: 1) *For the case when the flow direction is perpendicular to the interface of two different heterogeneous zones*, the order of heterogeneous aquifers in series will not affect the flushing results, and the properties (dispersivity, porosity, and retardation factor) of heterogeneity in series can be homogenized with the arithmetic mean. Furthermore, when the averaged dispersivity increases along the flowpath from the up-gradient to the down-gradient zones, the BTC will decline slower. When the averaged porosity or retardation factor is increasing, it takes less time to flush out the same amount of contaminants, but does not affect the decline rate of the BTC; 2) *For the case when the flow direction is parallel with the*

interface of two different heterogeneous zones, a greater difference of porosities of two zones will lead to a greater mass flux between two zones; a greater difference of transverse dispersivities will lead to a greater mass flux between the two zones; and the difference of thickness of two zones will not affect the results. This research is expected to fill the gap of flushing model on homogeneous and heterogeneous aquifers.

DEDICATION

To my family

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Contributors

This work was supervised by a thesis committee consisting of Dr. Hongbin Zhan, and Dr. Peter Knappett of the Department of Geology & Geophysics, as well as Dr. Itza Mendoza-Sanchez of the Department of Environmental and Occupational Health.

All other work conducted for the thesis was completed by the student.

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NOMENCLATURE

Zone 1	The left aquifer of the heterogeneous aquifers in series.
Zone 2	The right aquifer of the heterogeneous aquifers in series.
Zone 3	The upper layer of the layered heterogeneous aquifers.
Zone 4	The lower layer of the layered heterogeneous aquifers.
q	Darcy velocity, (L/T).
v	Average pore velocity, (L/T).
t	Observation time, (T).
R	Retardation factor.
\bar{R}	Averaged retardation factor.
α_L	Longitudinal dispersivity, (L).
α_T	Transverse dispersivity, (L).
$\bar{\alpha}$	Averaged dispersivity, (L).
D_L	Longitudinal (x -direction for this study) dispersion coefficient, (L ² /T).
D_T	Longitudinal (y -direction for this study) dispersion coefficient, (L ² /T).
D^*	The molecular diffusion coefficient, (L ² /T).
θ	Porosity.
$\bar{\theta}$	Averaged porosity.
λ	Reaction rate, (1/T).
B	Thickness of the layer in the layered heterogeneous aquifers, (L).
L_1	Length of zone-1 in the heterogeneous in series, (L).
L	The total length of the contaminated aquifer, (L).

C	Concentration of adsorbate in solution, (M/L ³).
C^*	The mass of solute sorbed per dry unit weight of solid, (M/M).
C_0	Initial concentration of the contaminated aquifer, (M/L ³).
K_d	Distribution coefficient, (L ³ /M).
F	The mass flux of solute per unit area per unit time, (M/T/L ²).
ρ	The bulk density of soil, (M/L ³).
α	An adsorption constant related to the binding energy, (L ³ /M).
β	The maximum amount of solute that can be adsorbed by the solid, (M/M).
x	Longitudinal dimension along the direction of flow, (L).
y	Longitudinal dimension perpendicular with the direction of flow, (L).
Pe	Peclet number.
t_R	The number of pore volume.
w_1, w_2	Weight coefficients.
a, b	Undetermined coefficients.
K, N	Constants of Freundlich sorption isotherm.
dC/dx	The concentration gradient, (M/L ³ /L).
$erfc$	Complementary error function.
R^2	Coefficient of determination.
$RMSE$	Root-mean-square error.

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1. INTRODUCTION

1.1 Background

Groundwater is an essential natural resource and has a significant role in the economy as it represents about 30% of world's fresh water (Covich, 1993). However, various hazardous chemical substances and industrial waste in soils and aquifers cause significant damage to the environment and human health as a result of their mobilities and solubilities, including organic chemicals, inorganic ions, pathogens, and radionuclides. Most of these materials will dissolve in water to varying degrees. Some of the organic compounds, however, are only slightly soluble and will exist in both a dissolve form and as an insoluble nonaqueous phase, which can also migrate through the groundwater. Inorganic ions come from naturally occurring processes but may also come from anthropogenic sources. Similarly, some radionuclides are naturally occurring and can some come from mining, milling, and processing ore, industrial uses, and disposal of radioactive waste (Fetter *et al.*, 1999).

There are many remediation techniques available for removing contaminants from groundwater. Those techniques are based on extraction and physical separation, precipitation, immobilization and toxicity reduction. Each method has its own advantages and disadvantages that need to be carefully evaluated. The selection of the most appropriate technique depends on aquifer characteristics, pollutant concentration, types of pollutants to be removed, and the used of the contaminated medium (Diels and Vanbroekhoven, 2008).

Pump-and-treat is a common method for cleaning up groundwater contaminated with dissolved chemicals, including industrial solvents, metals, and fuel oil. Groundwater is pumped from wells to an above-ground treatment system that removes the contaminants. Once treated water meets regulatory standards, it may be discharged for disposal or further use. An example is the full-scale groundwater treatment based on sulfate-reducing bacteria (Webb *et al.*, 1998; Weijma *et al.*, 2002). The main body of this system is an UASB (Upflow Anaerobic Sludge Blanket) reactor with a three-phase separator on the top. The hydrogen sulfide is oxidized in a biological sulfide oxidation reactor. A tilted-plate settler removes the solids, metal sulfides and biomass flushed along with the effluent. A DynaSand filter further removes the suspended solids from the water. The system efficiently removes metals (for example, zinc can be treated from 230 mg/L to less than 0.3 mg/L) from the water, and it has been proved to be reliable in treatment for sulfate- and metal-contaminated water. Pump-and-treat method is relatively easy to implement and control. However, this method consumes substantial energy for pumping, requires high treatment costs, and produces large amounts of waste products and water that must be discharged. Also, pumping the aquifer at high rates can drive decreasing water tables, causing land subsidence.

Biodegradation is also an important remediation method. Some principals of this practice were published by Alexander (1985) and others. Atlas (1981) published the general aspects of biodegradation of hydrocarbons. Wilson *et al.* (1986) were one of the first to discover the anaerobic biodegradation of BTEX and to implement it into in-situ bioremediation of groundwater. The anaerobic biodegradation of hexachlorocyclohexane (HCH) was proven in the laboratory by Bachmann *et al.* (1988) and in the field by

Doelman *et al.* (1990). The biodegradation of dioxine by halo-respiration has been suggested by Bunge *et al.* (2003). However, limited biodegradation of organics is often due to non-optimal environmental conditions (Doelman and Breedveld, 1999).

Bioremediation is the process of decontaminating polluted sites through the usage of either endogenous or external microorganism (Rittmann *et al.*, 1994). In-situ bioremediation has been used for several years in the restoration of ground water contaminated by petroleum hydrocarbons. The time required to treat subsurface pollution using in-situ bioremediation can often be faster than other remediations. A gasoline spill was remediated in 18 months using in-situ bioremediation, while pump-and-treat techniques were estimated to require 100 years to reduce the concentrations of gasoline to potable water levels (Raymond *et al.*, 1986). In-situ bioremediation often costs less than other remedial options. The areal zone of treatment using bioremediation can be larger than with other remedial technologies because the treatment moves with the plume and can reach areas that would otherwise be inaccessible. There are also disadvantages to in-situ bioremediation programs. Many organic compounds in the subsurface are resistant to degradation. In-situ bioremediation usually requires an acclimated population of microorganisms which may not develop for recent spills or for recalcitrant compounds. Heavy metals and toxic concentrations of organic compounds may inhibit activity of indigenous microorganisms. Injection wells may become clogged from profuse microbial growth resulting from the addition of nutrients and oxygen (Lee *et al.*, 1988). In addition, bioremediation projects require continuous monitoring and maintenance for successful treatment.

Major research and development efforts have been directed at finding alternative remedies that can clean up groundwater and eliminate risks or reduce them to an acceptable level (F. F. Council, 1997; N. R. Council, 1994). Recent efforts have increasingly focused on the pollutant flushing method (N. R. Council, 1994; EPA, 1988), as a remediation process. This method is useful to estimate the clean-up time in simple aquifer systems that is contaminated with chemicals that interact with the solid matrix in a way that can be represented by linear sorption. The flushing method simulates a situation in which clean water is circulated through a zone of the aquifer that initially contains contaminated ground water; the approach assumes simple advective displacement of contaminated water, thus neglecting dispersive transport. It further assumes that the contaminant concentration in the influent water is always zero as the water enters the contaminated region, but that the pore water composition adjusts instantly to be at equilibrium with the remaining sorbed contaminant mass as the water passes through the contaminated region. This study will focus on advancing our understanding of flushing of homogeneous and heterogeneous aquifers, considering not only advection, but also dispersion, and mass exchanges between two neighboring heterogeneous zones. The basic idea of flushing is to use solute-free water to drive a previously contaminated groundwater from the aquifer until the concentration in the aquifer drops below a predefined low level such as the drinking water standard or a regulated water quality standard.

The main processes of the contaminant transport in aquifers are assumed to be advection, dispersion, sorption, radioactive decay, and other chemical reactions (Freeze and Cherry, 1979; McCarty *et al.*, 1981). Advection is the transport of a substance or

quantity by bulk motion. Dispersion has been demonstrated by Taylor (1953) and subsequently discussed extensively by many others (Bear, 1972; Freeze and Cherry, 1979), which is composed of both molecular and mechanical dispersion. Mechanical dispersion describes the process whereby solutes are mechanically mixed by velocity variations at the microscopic level during advection transport. Molecular dispersion, as known as diffusion, is the movement from higher concentration to lower concentration under the influence of Brownian motion. Sorption of chemicals to the surfaces of sediments and rock that comprise the aquifer drives the aqueous phase concentration lower without changing the total mass through chemical reaction or microbiological interaction (Mackay *et al.*, 1986). Radioactive decay is the process by which an unstable atomic nucleus loses energy by radiation.

The contaminant transport in porous media is commonly assumed to be governed by the advection-dispersion equation (ADE) (Bear, 1972), which is built on the basis of Fick's law to describe the transport of solutes in saturated porous media, and is still broadly used, particularly in solving practical engineering problems related to groundwater remediation. The derivation of ADE is based on the conservation of mass of solute flux into and out of a small representative elementary volume (REV) of the porous media. The flow is at a macroscopic scale, which means that it accounts for the differences in flow from pore to pore (Ogata, 1970). Start from this governing equation, Van Genuchten (1982) developed a model solution to calculate the solute concentration at a given distance along the flowpath at a specified time since flushing began assuming that the recharging water contains no solute. Over the years, this solution has been widely-used, for example, Radloff *et al.* (2017) used this model solution to estimate how

the relationship between groundwater As concentrations and groundwater age could evolve over geologic time due to flushing. However, this solution is sometimes difficult to use for quick screening purpose in engineering practices as it contains special functions such as complementary error function (erfc) and commonly involves an inverse process to figure out the number of volumes required to flushing out a certain contaminated mass from the aquifer.

Furthermore, the contaminated aquifer is often not homogeneous, but heterogeneous, consisting of various zones with different transport properties. There are several approaches that are commonly used to deal with the solute transport in a spatially stationary heterogeneous aquifers (meaning that the heterogeneous aquifer is statistically homogeneous): single-rate mobile and immobile theory (Rao *et al.*, 1980), multi-rate mobile and immobile theory (Silva *et al.*, 2009), and fractional advection dispersion equation (Benson *et al.*, 2000). However, applying these mentioned approaches for contaminant transport in a spatially nonstationary heterogeneous media is still challenging. For some special cases, the media may be composed of several homogeneous zones and the transport properties for those zones could be well defined (Leij and Van Genuchten, 1995).

There are two kinds of multi-zone media problems: the flow direction is paralleled or perpendicular to the multi-zone interfaces. When dealing with practical problems, engineers always use the averaging approach (or homogenization) to study the flow and transport simulation. The general method for homogenization is the representative elementary volume (REV) method, which calculates equivalent parameters and uses them as the effective parameters for the whole region (Amaziane *et al.*, 1991; Durlafsky, 1991).

The simplest multi-zone problem is the two-zone problem, i.e., the aquifer consists of two zones with different transport properties, which will be the focus of this thesis. For such a two-zone heterogeneous system, we will investigate two representative schemes including 1) the groundwater flow direction is perpendicular to the interface of two zones, and 2) the groundwater flow direction is parallel to the interface of two zones. It is my hope that the insights gained from such two-zone problems may be helpful for understanding the flushing process in much more complex multi-zone problems.

1.2 Objectives

The objectives of this thesis are to achieve the following key scientific goals:

1) The existing solution for flushing model of homogeneous aquifers is not convenient for quick screening purpose in engineering practice, therefore the goal of this work is to find a new and simple surrogate solution to describe the flushing model of homogeneous aquifers.

2) For cases where the groundwater flow direction is perpendicular to the interface of two zones, the goal of this work is to investigate the influence of the transport properties on the results and to find an averaging technique to describe the flushing of such a two-zone heterogeneous system using an averaged homogeneous system.

3) For cases where the groundwater flow direction is parallel to the interface of two zones, the goal of this work is to describe the mass flux between two layers during the flushing process.

1.3 Organization

This thesis is organized in six sections. The first section is the introduction section, which includes background, objectives, and organization part of this thesis. The second section shows the conceptual models, and the flushing model solution (Van Genuchten, 1982) on the homogeneity. In the third section, a new solution is developed to describe the flushing model in a homogeneous aquifer using COMSOL Multiphysics, and to verify the new solution by numerical solution and the solution by Van Genuchten (1982) for a specific homogeneous case.

After that, the influence of properties (dispersivity, porosity, and retardation factor) of the heterogeneous aquifers in series is discussed in Section 4.1. Here the heterogeneous aquifers in series means that groundwater flow direction is perpendicular to the interface of two zones. To do so, the concentration distribution in the heterogeneous aquifers with different transport properties is calculated, and then BTCs at the end of the aquifers are compared with each other. After that, in order to homogenize the heterogeneous aquifers, three general means (arithmetic mean, geometric mean, and harmonic mean) are compared. Section 4.2 focuses on the layered heterogeneous aquifers, which implies that the groundwater flow direction is parallel to the interface of two layers. The aim of this section is to figure out how the properties (porosity, transverse dispersivity, and the thickness) of two layers would affect the results of flushing. The mass flux between two layers during the flushing process is also investigated in some great details.

In the fifth section, a brief conclusion and the contribution of the research are discussed. And the last section shows a number of potential researches of the future work.

2. PROBLEM STATEMENT

2.1 Conceptual Models

To understand the flushing process of the homogeneous and heterogeneous aquifers, numerical models with different aquifer combinations are constructed, and the commercial finite element software package, COMSOL Multiphysics, is employed to simulate the fluid flow and contaminant transport on some selected cases.

The conceptual model of the homogeneous aquifer is illustrated in Fig. 1. The initial contaminant concentration of this column is C_0 , from $t = 0$, it is flushed by solute-free clean water. The flux flows in the positive x -axis direction, and the Darcy velocity is q . The inlet and outlet boundaries are defined at $x = 0$ and $x = L$.

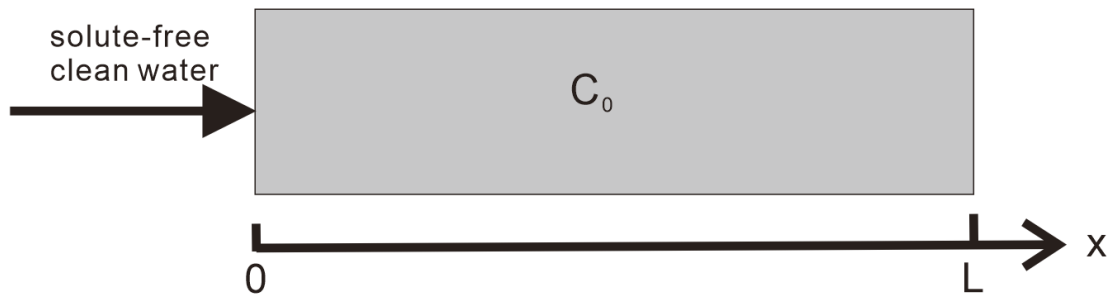


Figure 1. Schematic of a flushing model in a homogeneous zone.

The conceptual model is composed by two individual homogeneous zones, named zone 1 and zone 2, with different transport properties, as illustrated in Fig. 2. The column with an initial concentration of C_0 for a conservative solute, flushed by solute-free clean water. The flux flows in the positive x -axis direction, which is perpendicular with the

interface of zone 1 and zone 2. The inlet and outlet boundaries are defined at $x = 0$ and $x = L$. Each zone has its own porosity (θ), longitudinal dispersivity (α), and retardation factor (R). The length of zone-1 is L_1 , and the total length of two zones is L .

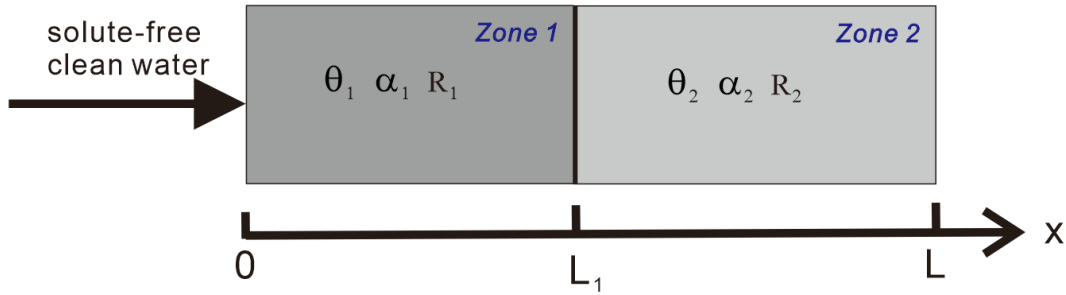


Figure 2. Schematic of a flushing model in the heterogeneous aquifers in series.

A flushing schematic diagram in a layered heterogeneous porous medium formed by two zones is represented in Fig. 3. The upper layer is zone 3, whose thickness is B_3 ; the lower layer named zone 4, whose thickness is B_4 . Assuming that the fluid flows along the x -direction only, which means the flow direction is paralleled to the two-zone interface. Both zones are homogeneous porous media by themselves, but the materials of the two zones are different, forming a layered heterogeneous porous medium. This leads to different longitudinal dispersivities (α_L), transverse dispersivities (α_T), and porosities (θ) in the two zones. The steady-state fluid from the inlet at the left boundary ($x = 0$) flows to the right along the x -axis. The initial concentrations in both zones are C_0 , and it is flushed by solute-free clean water at the same time. The solute transport in the two zones is coupled with the continued concentrations and the mass fluxes at the interface of two zones.

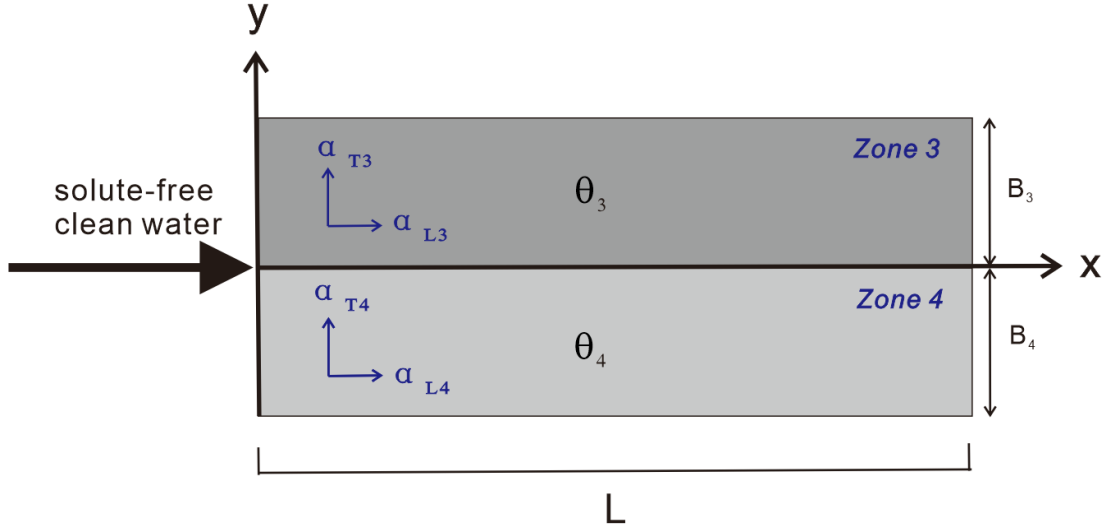


Figure 3. Schematic of a flushing model in the layered heterogeneous aquifers.

2.2 Flushing Model Solution

The flushing model solution by Van Genuchten (1982) starts from ADE (Bear, 1972), which is widely used to describe the solute transport in homogeneous, as well as heterogeneous aquifers. The simplest form of ADE for one-dimensional transport with a linear sorption (or a constant retardation factor) without decay or sink/source can be expressed as:

$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} \quad (2-1)$$

where C is the concentration of the solute in the dissolved phase $[M/L^3]$, $v = q/\theta$ is the advection velocity $[L/T]$, q is Darcy velocity $[L/T]$, θ is the aquifer porosity [dimensionless], t is time $[T]$, x is the distance along the flow path $[L]$, D is the hydrodynamic dispersion coefficient $[L^2/T]$, and R is a retardation factor [dimensionless], which is related to the distribution coefficient K_d by the following expression:

$$R = 1 + \frac{\rho K_d}{\theta} \quad (2-2)$$

where ρ is the aquifer bulk density [M/L³], and K_d is the distribution coefficient [L³/M].

If the average linear groundwater velocity is v_x , the average velocity of the solute front where the concentration is one-half of the original, v_c [L/T], is given by

$$v_c = \frac{v_x}{R} \quad (2-3)$$

The distribution coefficient, K_d , measured at equilibrium, is a useful concept that expresses the relative affinity for a sorbate in solution to sorb to a particular solid. The parameter has been used extensively in models to predict the behavior of contaminants in the environment. The batch method is often used to determine this coefficient in the laboratory and the results extrapolated to field situations. The K_d is defined as

$$K_d = \frac{(\text{mass sorbed/mass of solid})}{(\text{mass in solution/volume of solution})} \quad (2-4)$$

The magnitude of K_d is a function of the properties of the solid phase, such as mineralogical composition, particle size, and organic carbon content, and of the solution phase, like pH, ionic strength or salinity, and concentration of complexing ligands. The influence of these factors can generally be rationalized within the frameworks of solution and surface chemistry.

For the equilibrium surface reaction, there are three kinds of sorption isotherm. If there is a direct, linear relationship between the amount of a solute sorbed onto solid, C^* , and the concentration of the solute, C , the adsorption isotherm of C as a function of C^* will plot as a straight line. The resulting linear sorption isotherm is described by the equation

$$C^* = K_d C \quad (2-5)$$

where C^* is the mass of solute sorbed per dry unit weight of solid (M/M); C is the concentration of solute in solution in equilibrium with the mass of solute sorbed onto the solid (M/L³). A more general equilibrium isotherm is the Freundlich sorption isotherm. This is defined by the nonlinear relationship

$$C^* = K C^N \quad (2-6)$$

where K and N are constants. The Langmuir sorption isotherm was developed with the concept that a solid surface possesses a finite number of sorption sites. When all the sorption sites are filled, the surface will no longer sorb solute from solution. The form of the Langmuir sorption isotherm is

$$\frac{C}{C^*} = \frac{1}{\alpha\beta} + \frac{C}{\beta} \quad (2-7)$$

where α is an adsorption constant related to the binding energy (L³/M); β is the maximum amount of solute that can be absorbed by the solid (M/M).

A tube is filled with sand and then saturated with water, and water is made to flow through the tube at a steady rate. A solution containing a tracer is then introduced into the sand column in place of the water. The rate of injection is considered to be constant, with the injected mass of the solute proportional to the duration of the injection. The initial concentration of the solute in the aquifer is zero, and the concentration of the solute being injected is C_0 . The solution to this condition is (Sauty, 1980)

$$C = \frac{C_0}{2} \left[\operatorname{erfc} \frac{(Rx - vt)}{2\sqrt{DRt}} - \exp\left(\frac{vx}{D}\right) \operatorname{erfc} \frac{(vt + Rx)}{2\sqrt{DRt}} \right] \quad (2-8)$$

where erfc is the complementary error function and defined as

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-t^2} dt \quad (2-9)$$

However when it is under flushing condition, the concentration is initially equilibrated along the entire flow path at a concentration C_0 , and recharge water entering the aquifer at one end of the flow path contains no solute, the analytical solution for the ADE model is given by Van Genuchten (1982) :

$$C(x, t) = \frac{1}{2} C_0 \left[\operatorname{erfc} \frac{(vt - Rx)}{2\sqrt{DRt}} + \exp\left(\frac{vx}{D}\right) \operatorname{erfc} \frac{(Rx + vt)}{2\sqrt{DRt}} \right] \quad (2-10)$$

Sauty (1980) defined a Peclet number, the rate of transport by advection against the rate of transport by hydrodynamic dispersion, as

$$Pe = \frac{vx}{D} \quad (2-11)$$

where $D = D_m + D^*$, and D_m and D^* are the mechanical dispersion coefficient and effective molecular diffusion coefficient (which is usually computed by a product of a less than unity tortuosity factor and the free-water diffusion coefficient) in the aquifer (L^2/T), respectively. Also the number of pore volume should be introduced as a dimensionless time, which is

$$t_R = \frac{vt}{x} \quad (2-12)$$

So the Equation (2-10) can be expressed in dimensionless form as:

$$\frac{C(t_R, Pe)}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{t_R - 1}{2\sqrt{\frac{t_R}{Pe}}} \right) + \exp(Pe) \operatorname{erfc} \left(\frac{t_R + 1}{2\sqrt{\frac{t_R}{Pe}}} \right) \right] \quad (2-13)$$

which shows that the relative concentration C/C_0 depends on the number of pore volume t_R , and the Peclet number.

The process of molecular diffusion cannot be separated from mechanical dispersion in flowing ground water. The hydrodynamic dispersion coefficient, D , can be represented by the following formulas (Bear, 1972):

$$D = \alpha \cdot v + D^* \quad (2-14)$$

where α is the dynamic dispersivity (L), v is the average linear velocity (L/T). In general, the mechanical dispersion coefficient $\alpha \cdot v$ is much larger than the effective molecular diffusion coefficient D^* , so in many cases, molecular diffusion can be ignored. So that Peclet number can be simplified as:

$$Pe = \frac{vx}{D} = \frac{vx}{\alpha v + D^*} \approx \frac{vx}{\alpha v} = \frac{x}{\alpha} \quad (2-15)$$

A solute in water will move from an area of greater concentration toward an area where it is less concentrated. This process is known as molecular diffusion. Molecular diffusion will occur as long as a concentration gradient exists, even if the fluid is not moving. The mass of fluid diffusing is proportional to the concentration gradient, which can be expressed as Fick's first law; in one dimension, Fick's first law is

$$F = -D^* \times \frac{dC}{dx} \quad (2-16)$$

where F is the mass flux of solute per unit area per unit time ($M/T/L^2$); D^* is the diffusion coefficient (L^2/T); dC/dx is the concentration gradient ($M/L^3/L$). The negative sign indicates that the movement is from areas of greater concentration to those of lesser concentration.

3. FLUSHING MODEL OF A HOMOGENEITY

3.1 A New Solution for Flushing in A Homogeneous Aquifer

With COMSOL Multiphysics (COMSOL Inc., Burlington, MA, USA), a Galerkin finite-element software package, the homogeneous aquifer model is designed to be 1 meter thick, 20 meters long. The initial concentration C_0 is set to be 1 kg/m^3 , the Darcy velocity q is 0.01 m/day , the porosity θ is 0.25 , the dispersivity α is 0.2 m . More specifically, the governing equations are solved using the partial differential equation solver. The 2-D model is discretized using triangular elements, and the number of triangular elements is 1208. To ensure sufficient accuracy of the numerical solution, elements of the zone and the boundaries are refined with a minimum element size of 0.006 m and a maximum growth rate of 1.3 for the element size. This growth rate means that the element size can grow from a region with small elements to a region with larger elements using the free triangular mesh generator; that is, the element size can grow by at most 30% (approximately) from one element to another.

As plotted in Fig. 4a, the BTC shows that the relative concentration at the end of column (20 m away from the inlet) keeps in 1 until 300 days, and then declines to 0 at about 600 days, and then remains at 0 at the rest time. To analyze the result, dimensionless terms are used and only the declined part is selected (Fig. 4b), where the relative concentration is not greater than 0.99, and not less than 0.01. The x -axis of Fig. 4b is $t_R = \frac{vt}{x}$, and the y -axis is $\log_{10}(C/C_0)$. The result can be fitted with the following power-law function:

$$y = a \cdot x^b \quad (3-1)$$

where $a = -0.323$, $b = 6.506$ with a coefficient of determination $R^2=0.99699$, which means that the curve fits the simulated result very well. So for this case, the formula can be expressed as:

$$\log_{10}\left(\frac{C}{C_0}\right) = -0.323 \times t_R^{6.506} \quad (3-2)$$

which is much simpler than the original Equation (2-10). From Equation (2-13), the dimensionless solution, one can see that the concentration of the solute in the column is only related to the initial concentration C_0 , the number of pore volume t_R and the Peclet number Pe . So the coefficients a and b of Equation (3-1) are only related to the Peclet number.

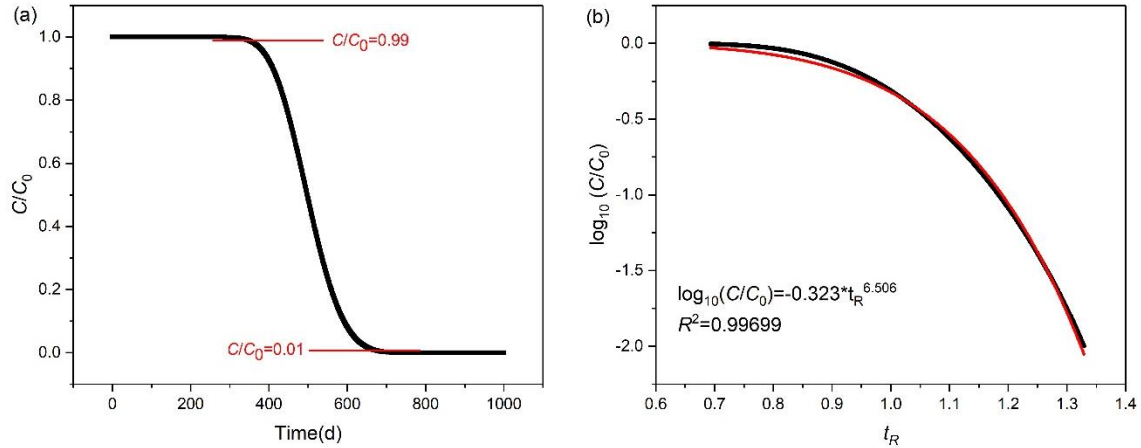


Figure 4. (a) BTC of the numerical solution in COMSOL; (b) the relationship between $\log_{10}(C/C_0)$ and t_R .

From Equation (2-13), the Peclet numbers are related to the distance x and the dispersivity α . When changing the setting of the distance or the dispersivity, different

Peclet numbers are obtained, and the coefficients a and b are varied. For every settled COMSOL situation, a Peclet number, two coefficient a and b can be fitted. Table 1 shows the relationships between the Peclet numbers and the coefficients a and b . Fig. 5(a) indicates a clear correlation between the Peclet number and the coefficient b as the following

$$b = 0.76 \times \sqrt{Pe} \quad (3-3)$$

with a high coefficient of determination $R^2 = 0.9974$, indicating that the proposed equation can be used to accurately estimate the coefficient b . With the fixed coefficient b , the coefficient a changed, so the new coefficient a are obtained, and fitted as Fig. 5(b).

The relationship between the Peclet number and the coefficient a can be expressed as

$$a = -0.25 - \frac{0.2}{\sqrt{Pe}} \quad (3-4)$$

and the high R-squared, $R^2 = 0.9216$, supports this correlation.

Table 1. Summary for parameters of coefficients a and b .

Pe	a	b	$b = 0.76 \times \sqrt{Pe}$	new a	R^2
1	-0.547	0.648	0.760	-0.464	0.938
2	-0.511	0.873	1.075	-0.401	0.972
3	-0.504	1.003	1.316	-0.361	0.964
4	-0.494	1.117	1.520	-0.330	0.954
5	-0.482	1.235	1.699	-0.313	0.949
6	-0.473	1.356	1.862	-0.305	0.947
7	-0.473	1.464	2.011	-0.303	0.939

Table 1. Continued.

8	-0.430	1.705	2.150	-0.314	0.972
9	-0.415	1.865	2.280	-0.315	0.981
10	-0.416	1.943	2.403	-0.310	0.979
20	-0.363	2.999	3.399	-0.305	0.993
30	-0.334	3.887	4.163	-0.304	0.997
40	-0.316	4.618	4.807	-0.299	0.998
50	-0.307	5.204	5.374	-0.294	0.999
60	-0.302	5.701	5.887	-0.289	0.999
70	-0.301	6.115	6.359	-0.284	0.999
80	-0.298	6.531	6.798	-0.281	0.999
90	-0.297	6.896	7.210	-0.278	0.998
100	-0.297	7.254	7.600	-0.285	0.998
200	-0.271	10.624	10.748	-0.267	0.999
300	-0.270	12.884	13.164	-0.262	0.999
400	-0.259	15.241	15.200	-0.260	0.997
500	-0.254	16.702	16.994	-0.248	0.998
600	-0.240	18.971	18.616	-0.247	0.995
700	-0.242	20.117	20.108	-0.243	0.997
800	-0.243	21.318	21.496	-0.240	0.997
900	-0.227	24.031	22.800	-0.247	0.991
1000	-0.246	24.068	24.033	-0.247	0.997

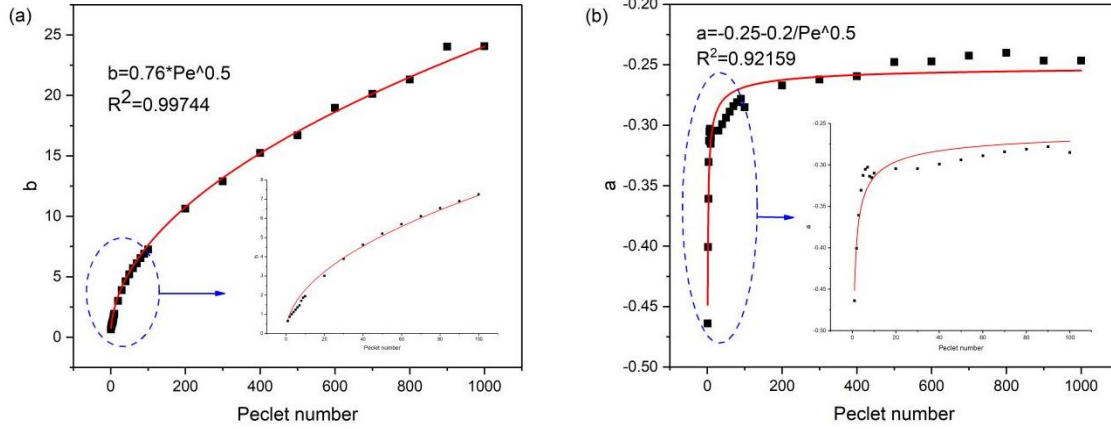


Figure 5. Variation of the coefficients a and b with the Peclet number.

So a new formula for flushing models is

$$\log_{10}\left(\frac{C}{C_0}\right) = a \times t_R^b \quad (3-5)$$

where $a = -0.25 - \frac{0.2}{\sqrt{Pe}}$, and $b = 0.76 \times \sqrt{Pe}$. This new formula is much simpler than Equation (2-10) or (2-13), so it would be more convenient for quick screening purposes in engineering practice.

3.2 Verification of the Developed Solution

The developed new solution was compared to Van Genuchten solution and the numerical solution for some special cases of one-dimensional transport in a homogeneous aquifer in this section. For the purpose of comparison, the parameters are set as follows: $q = 0.01$ m/day, $\theta = 0.25$, $\alpha = 0.2$ m, $R = 1.8$, $C_0 = 1$ kg/m³, and $L = 30$ m. The BTCs consisting of the relative concentration (C/C_0) and time at the end of column is shown in Fig. 6.

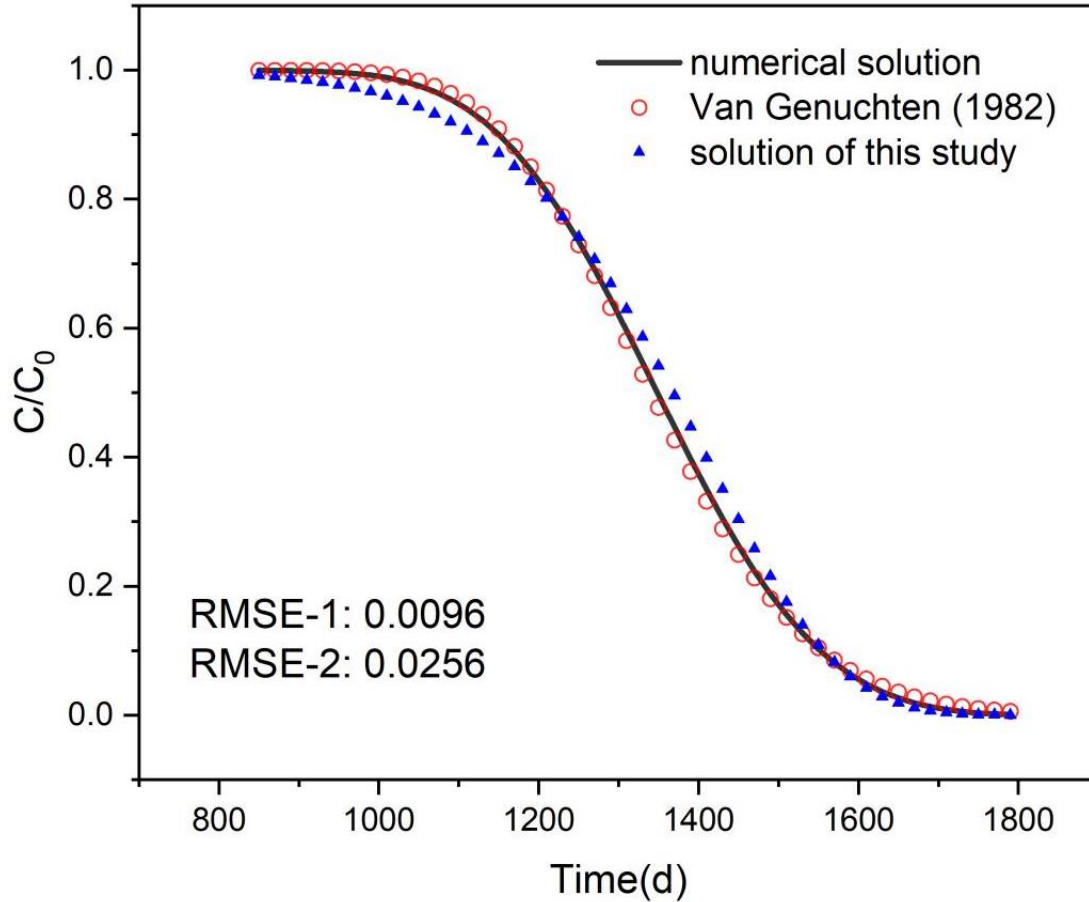


Figure 6. Comparison of the numerical solutions, Van Genuchten solution and the new solution of this study of flushing.

The results show that BTCs by the numerical solution, Van Genuchten solution, and the new solution of this study fit with each other very well. And the root-mean-square error (RMSE) between the numerical solution and the Van Genuchten solution is 0.0096, and the RMSE between the numerical solution and the solution of this study is 0.0256, which mean that the differences of these three solutions are negligibly small. From this comparison, the new solution developed in this study appears to be correct and reliable.

4. FLUSHING MODEL OF HETEROGENEOUS AQUIFERS

4.1 Heterogeneous Aquifers in Series

The conceptual model of heterogeneous aquifers in series (i.e., the groundwater flow direction is perpendicular to the interface of two zones) is illustrated in Fig. 2. This section is devoted to analyzing how the difference of transport properties and the length of zone-1 and zone-2 will impact on the contaminant transport during the flushing process. To do so, one can change one or more parameter values for zone-1 and zone-2 but keep the rest parameter values of these two zones the same. The dispersivity (α), porosity (θ), and retardation factor (R), are the main transport properties which will affect the solute transport in the porous media, on which this section will focus. For all the cases constructed with COMSOL in this section, the accuracy of the numerical solution of these cases is similar. The elements of the zone and the boundaries are refined with a minimum element size of 0.002 m and a maximum growth rate of 1.1 for the element size. This growth rate means that the element size can grow from a region with small elements to a region with larger elements using the free triangular mesh generator; that is, the element size can grow by at most 10% (approximately) from one element to another.

4.1.1 Dispersivity Influence

To investigate the dispersivity influence on the flushing model in the heterogeneous aquifers in series, the parameter values from Table 2 are used. It is notable that different dispersivities and lengths of zone-1 are used for various cases while all cases have the

same properties as following: $q = 0.01\text{m/day}$, $\theta_1 = \theta_2 = 0.25$, $R_1 = R_2 = 1$, $C_0 = 1 \text{ kg/m}^3$, $L = 100 \text{ m}$.

Table 2. Different dispersivities of conceptual Cases 1-6.

Case No.	$\alpha_1(\text{m})$	$\alpha_2(\text{m})$	$L_1(\text{m})$
1	0.1	0.5	50
2	0.1	0.5	25
3	0.1	0.5	75
4	0.5	0.1	50
5	0.5	0.1	25
6	0.5	0.1	75

In Cases 1-3, zone-1 and zone-2 has the same properties, and the total length of two zones is fixed, but the relative length of two zones is varied. When compare these three cases, we can investigate the impact of the length of zones on the flushing results.

Meantime, the same transport properties have been used for Cases 4-6, similar to what has been done in Cases 1-3. Also, in order to investigate the influence of reversing the order of the heterogeneous aquifers in series, Cases 1 and 4 (Cases 2 and 6; Cases 3 and 5) can be compared. The properties of zone-1 of Case 1 are the same with that of zone-2 of Case 4; and the properties of zone-2 of Case 1 are the same with that of zone-1 of Case 4.

Fig. 7(a) shows the BTCs for Cases 1-3, and Fig. 7(b) shows the BTCs for Cases 4-6.

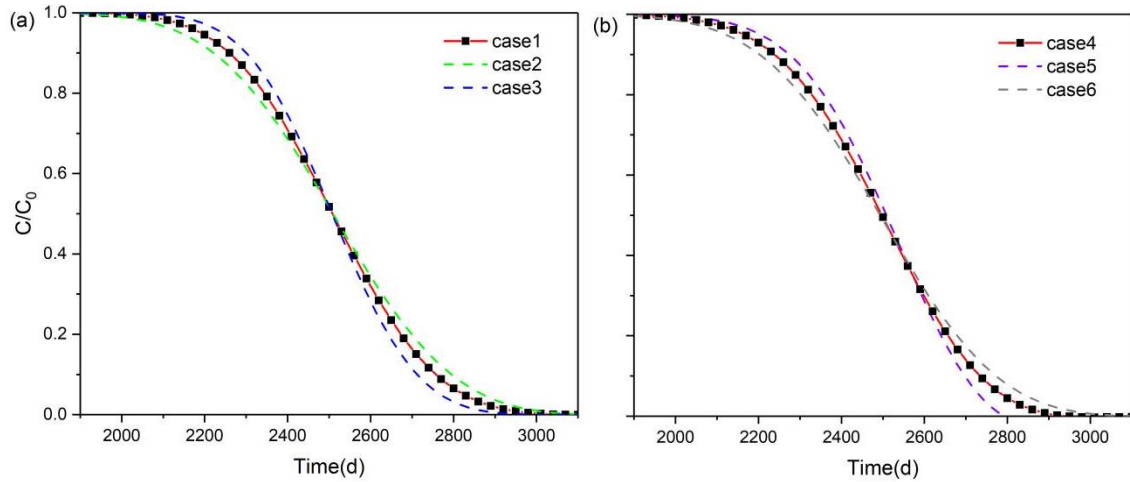


Figure 7. BTCs for Cases 1-6 when flushing in the heterogeneous aquifers in series, with different length of two zones.

From Fig.7, it is easy to find that all the cases have similar curves, suggesting that the different length of two zones does not make a considerable difference to the results. However, from Fig. 7(a), the BTC of Case 3 declines quicker than the BTCs of either Case 1 or Case 2. For Fig. 7(b), the BTC of Case 5 declines quicker than the BTCs of either Case 4 or Case 6. Both Case 3 and Case 5 have higher dispersivity of the shorter zone, which means that when two heterogeneous zones have different dispersivity values, if the ratio of the length of two zones (the high dispersivity zone versus the low dispersivity zone) is greater, the BTC will decline slower. The reason of this observation will explain later.

To investigate the influence of the order of heterogeneity, Cases 1 and 4, Cases 2 and 5, Cases 3 and 6 are compared, separately, in Fig. 8.

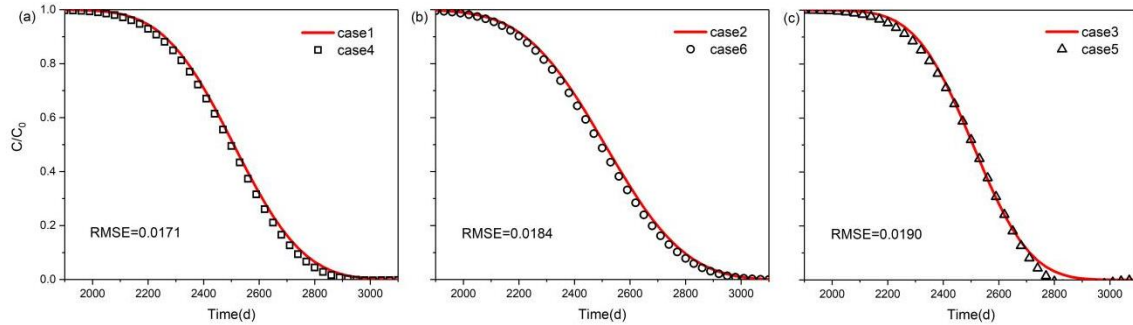


Figure 8. BTCs for Cases 1-6 when flushing in the heterogeneous aquifers in series, with change the order of different heterogeneous aquifers.

As plotted in Fig. 8, when reversing the two zones' positions, the relative concentration has little change: the BTCs fit well with each other very well, and the RMSEs are all small. So we can conclude that when changing the order of different heterogeneous aquifers, it will not affect the results considerably. Now the question is: Can we replace the heterogeneous aquifers with different dispersivity with an averaged surrogate homogeneous aquifer in terms of assessing the remediation efficacy using the flushing method? If we can do it, then what is the relationship between these heterogeneous aquifers in series with the averaged surrogate homogeneous aquifer? To this end, three general means (arithmetic mean, geometric mean, and harmonic mean) are used to average the heterogeneous aquifer in Case 2 (Table 3), and to compare these four BTCs (Fig. 9).

The arithmetic mean is the sum of a collection of numbers divided by the count of numbers in the collection (Jacobs, 1994). The collection is often a set of results of an experiment or an observational study, or frequently a set of results from a survey. For example, per capita income is the arithmetic average income of a nation's population.

While the arithmetic mean is often used to report central tendencies, it is not a robust statistic, meaning that it is greatly influenced by outliers (values that are very much larger or smaller than most of the values). The geometric mean is a mean or average, which indicates the central tendency or typical value of a set of numbers by using the product of their values. The harmonic mean is appropriate for situations when the average of rates is desired, which can be expressed as the reciprocal of the arithmetic mean of the reciprocals of the given set of observations.

In order to compare these three means, Case 2 is chosen, whose dispersivity of zone-1 is 0.1 m ($\alpha_1 = 0.1 \text{ m}$), and dispersivity of zone-2 is 0.5 m ($\alpha_2 = 0.5 \text{ m}$). The weight coefficients are the length ratios of each zone. The total length is 100 m, and the length of zone-1 is 25 m, so w_1 is the ratio of the length of zone-1 to the total length

$$(w_1 = \frac{L_1}{L} = \frac{25m}{100m} = 0.25), \text{ and } w_2 \text{ is the ratio of the length of zone-2 to the total length}$$

$$(w_2 = \frac{L-L_1}{L} = \frac{75m}{100m} = 0.75).$$

Table 3. List of average equations and goodness-of-fit of Case 2.

Function	Arithmetic Mean	Geometric Mean	Harmonic Mean
Equation	$\bar{\alpha} = \omega_1\alpha_1 + \omega_2\alpha_2$	$\bar{\alpha} = \alpha_1^{\omega_1} \times \alpha_2^{\omega_2}$	$\frac{1}{\bar{\alpha}} = \frac{\omega_1}{\alpha_1} + \frac{\omega_2}{\alpha_2}$
Averaged dispersivity	0.4000	0.3344	0.2500
RMSE	0.0078	0.0158	0.0349

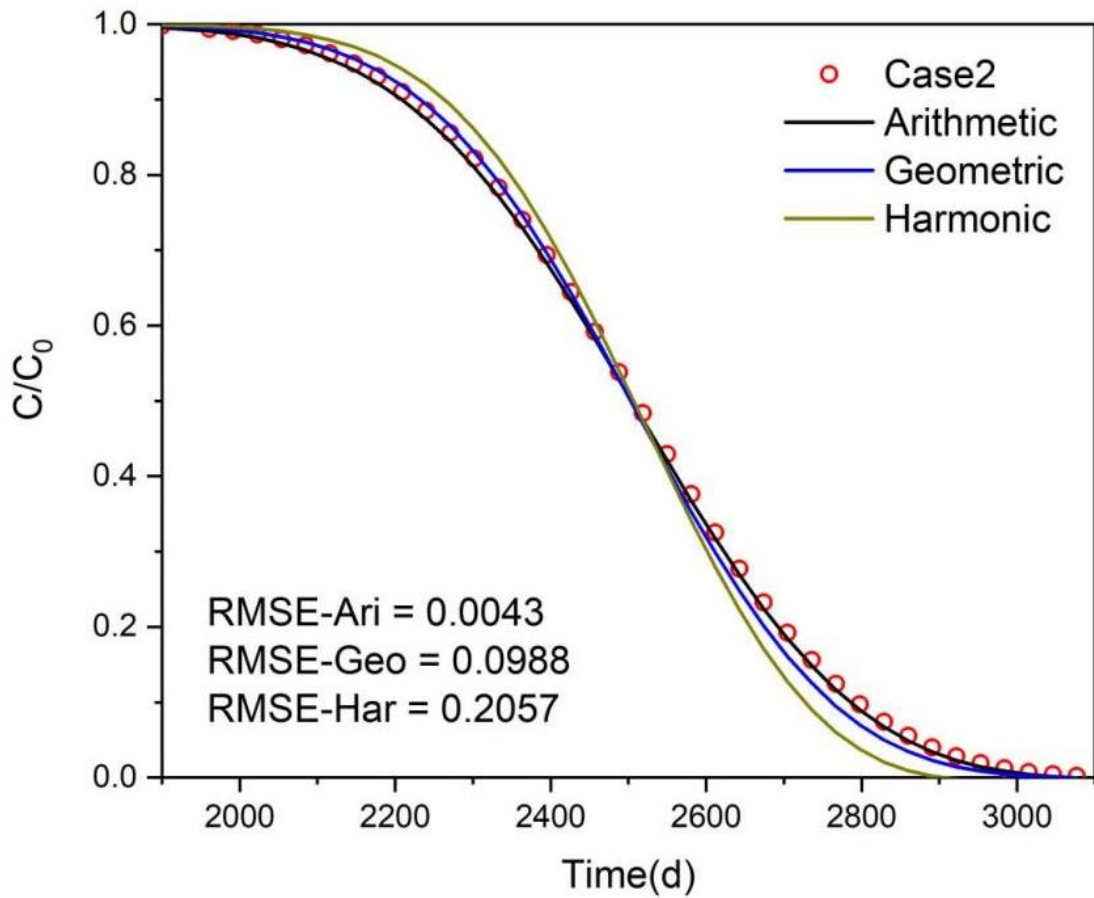


Figure 9. BTCs for Case 2 and three averaged homogeneous aquifers.

From Fig. 9, the BTC of the arithmetic mean is the best fit with the BTC of Case 2, and the RMSE is the smallest for the arithmetic mean method, which is 0.0043. This means that the arithmetic mean can be used to average the heterogeneous aquifers with different dispersivity values.

From Equation (2-13), one can see that when dispersivity is increasing, the Peclet number will decrease, which will lower the parameters a and b , as can be seen from Equations (3-3) and (3-4). Meantime, t_R is not relative to the dispersivity, so $\log_{10}(C/C_0)$

will drop. In another word, when dispersivity is greater, $\log_{10}(C/C_0)$ will be smaller. Furthermore, if the total length of two zones is fixed, then when the ratio of the length of the zone with a higher dispersivity over the length of the zone with a fixed dispersivity is greater, the averaged dispersivity will be greater as well. Consequently, the BTC declines slower, as clearly illustrated in Fig. 7.

4.1.2 Porosity Influence

To investigate the influence of porosity on the flushing model in the heterogeneous aquifers in series, the parameter values from Table 4 are used. One can see that different porosity and length of zone-1 are used for those cases. All cases have the same properties as following: $q = 0.01\text{m/day}$, $\alpha_1 = \alpha_2 = 0.1$, $R_1 = R_2 = 1$, $C_0 = 1 \text{ kg/m}^3$, $L = 100 \text{ m}$.

Table 4. Different porosities of conceptual Cases 7-12.

Case No.	θ_1	θ_2	$L_1(\text{m})$
7	0.2	0.5	50
8	0.2	0.5	25
9	0.2	0.5	75
10	0.5	0.2	50
11	0.5	0.2	25
12	0.5	0.2	75

In Cases 7-9, zone-1 and zone-2 have the same properties, and the total length of two zones is fixed, but the relative length of two zones is varied. When comparing these three cases, we can investigate the impact of the length of zones on the flushing results. Meantime, the same transport properties have been used for Cases 10-12, similar to what has been done in Cases 7-9. Also, in order to investigate the influence of reversing the order of the heterogeneous aquifers in series, Cases 7 and 10 (Cases 8 and 12; Cases 9 and 11) can be compared. The properties of zone-1 of Case 7 are the same with that of zone-2 of Case 10; and the properties of zone-2 of Case 7 are the same with that of zone-1 of Case 10. Fig. 10 shows the BTCs for Cases 7-12.

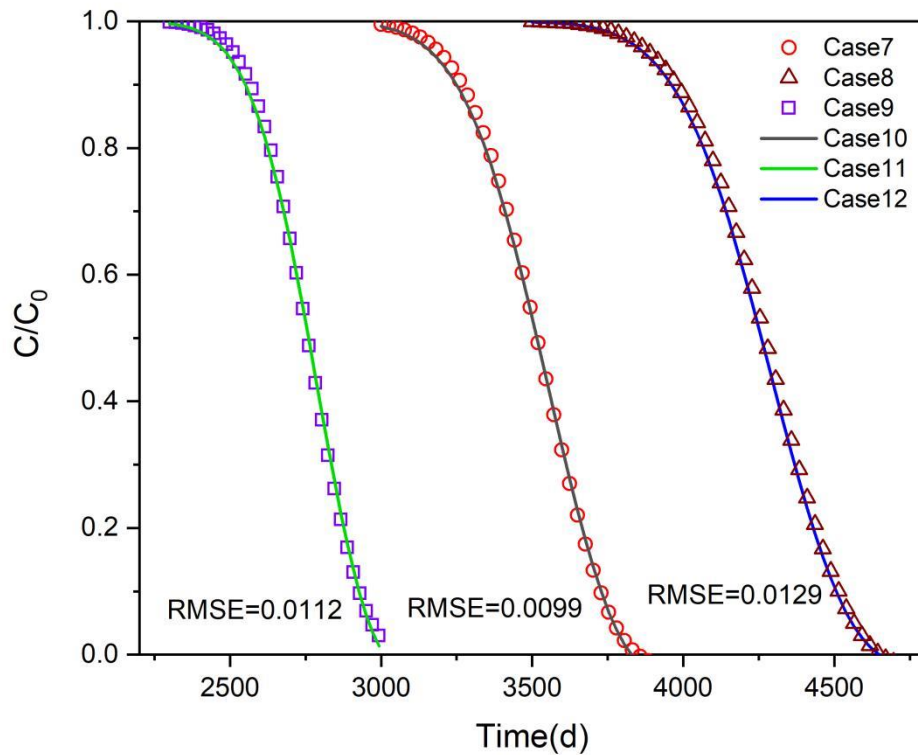


Figure 10. BTCs for Cases 7-12 when flushing in the heterogeneous aquifers in series.

From Fig.10, when comparing Cases 7-9 (or Cases 10-12), the BTC of Case 9 (or Case 11) is the first to decline and the first to approach 0, then Case 7 (or Case 10) is the second to decline and to approach 0, and the last one is Case 8 (or Case 12). Both Case 9 and Case 11 have a higher porosity of the shorter zone, which means that when two heterogeneous zones have different porosity, and they are in series, if the ratio of the length of two zones (the high porosity zone versus the low porosity zone) is lesser, the BTC will start to decline earlier. According to the equation $v = q/\theta$, we can find that when the porosity is increasing, the linear velocity will decrease, provided that the Darcy velocity remains the same, thus it will take a longer time to flush away the same amount of contaminants.

Also we can investigate that, from Fig. 10, the BTCs of Cases 7 and 10, Cases 8 and 12, Cases 9 and 11 fit well with each other very well, and the RMSE values are very small, which means that the order of different heterogeneous aquifers will not affect the results considerably. To find the relationship between these heterogeneous aquifers in series, three general means (Table 5) are used to find the best averaged homogeneous aquifer, and the BTCs are shown in Fig. 11.

In order to compare these three means, Case 8 is chosen, whose porosity of zone-1 is 0.2 ($\theta_1 = 0.2$), and the porosity of zone-2 is 0.5 ($\theta_2 = 0.5$). The weight coefficients are the length ratios of each zone. The total length is 100 m, and the length of zone-1 is 25 m, so w_1 is the ratio of the length of zone-1 to the total length ($w_1 = \frac{L_1}{L} = \frac{25m}{100m} = 0.25$), and w_2 is the ratio of the length of zone-2 to the total length ($w_2 = \frac{L-L_1}{L} = \frac{75m}{100m} = 0.75$).

Table 5. List of average equations and goodness-of-fit of Case 8.

Function	Arithmetic Mean	Geometric Mean	Harmonic Mean
Equation	$\bar{\theta} = \omega_1\theta_1 + \omega_2\theta_2$	$\bar{\theta} = \theta_1^{\omega_1} \times \theta_2^{\omega_2}$	$\frac{1}{\bar{\theta}} = \frac{\omega_1}{\theta_1} + \frac{\omega_2}{\theta_2}$
Average porosity	0.4250	0.3976	0.3636
RMSE	0.0091	0.2054	0.4069

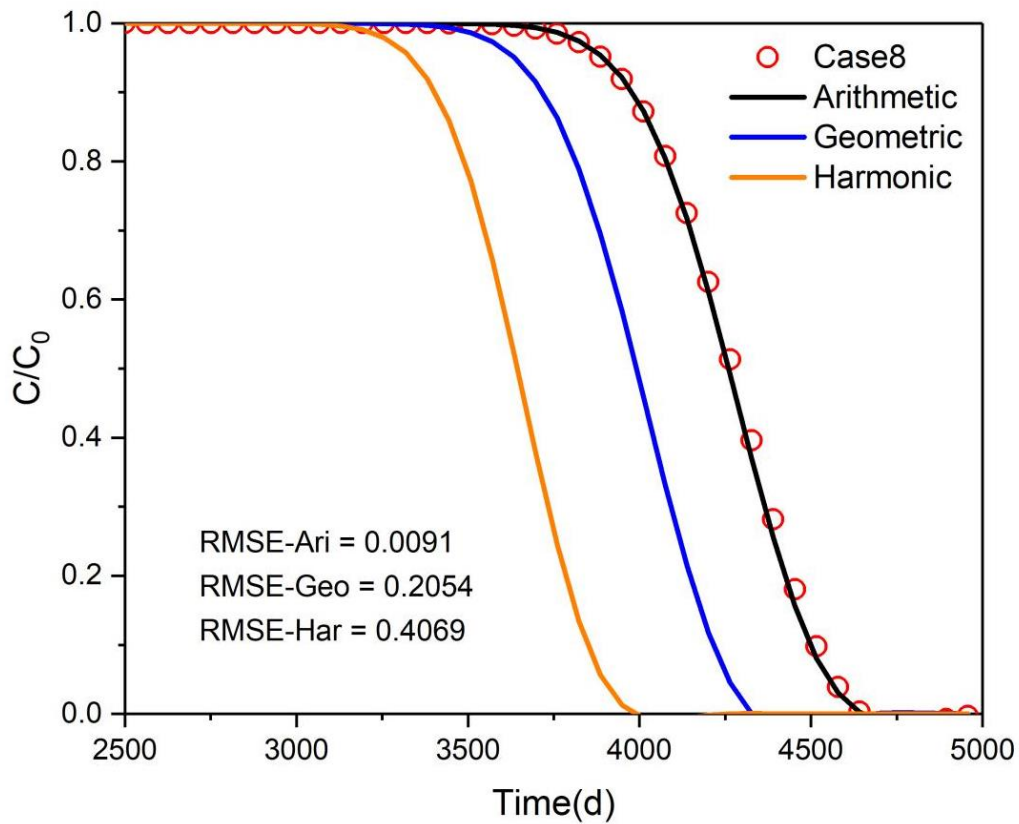


Figure 11. BTCs for Case 8 and three averaged homogeneous aquifers.

From Fig. 11, the BTC of arithmetic mean is the best fit with the BTC of Case 8, and the RMSE for this case is the smallest (RMSE-Ari = 0.0091), which means that the

arithmetic mean can be used to average the heterogeneous aquifers in series with different porosity.

4.1.3 Retardation Factor Influence

To investigate the influence of retardation factor on the flushing model in the heterogeneous aquifers in series, the transport parameters are listed in Table 6, which shows the different retardation factors and lengths of zone-1 of every case. All cases have the same properties as following: $q = 0.01\text{m/day}$, $\alpha_1 = \alpha_2 = 0.1$, $\theta_1 = \theta_2 = 0.25$, $C_0 = 1\text{ kg/m}^3$, $L = 100\text{ m}$. Due to the Equation (2-2), the retardation factor is related to density, porosity, and sorption behavior. In the following cases, only the distribution coefficient is changed to obtain different retardation factors, the density and porosity are kept the same.

Table 6. Different retardation factors of conceptual Cases 13-18.

Case No.	R ₁	R ₂	L ₁ (m)
13	1.2	2	50
14	1.2	2	25
15	1.2	2	75
16	2	1.2	50
17	2	1.2	25
18	2	1.2	75

In Cases 13-15, zone-1 and zone-2 have the same properties, and the total length of two zones is fixed, but the relative length of two zones is varied. When comparing these three cases, we can investigate the impact of the length of zones on the flushing results. Meantime, the same transport properties have been used for Cases 16-18, similar to what has been done in Cases 13-15. Also, to investigate the influence of reversing the order of the heterogeneous aquifers in series, Cases 13 and 16 (Cases 14 and 18; Cases 15 and 17) can be compared. The properties of zone-1 of Case 13 are the same with that of zone-2 of Case 16; and the properties of zone-2 of Case 13 are the same with that of zone-1 of Case 16. Fig. 12 shows the BTCs for Cases 13-18.

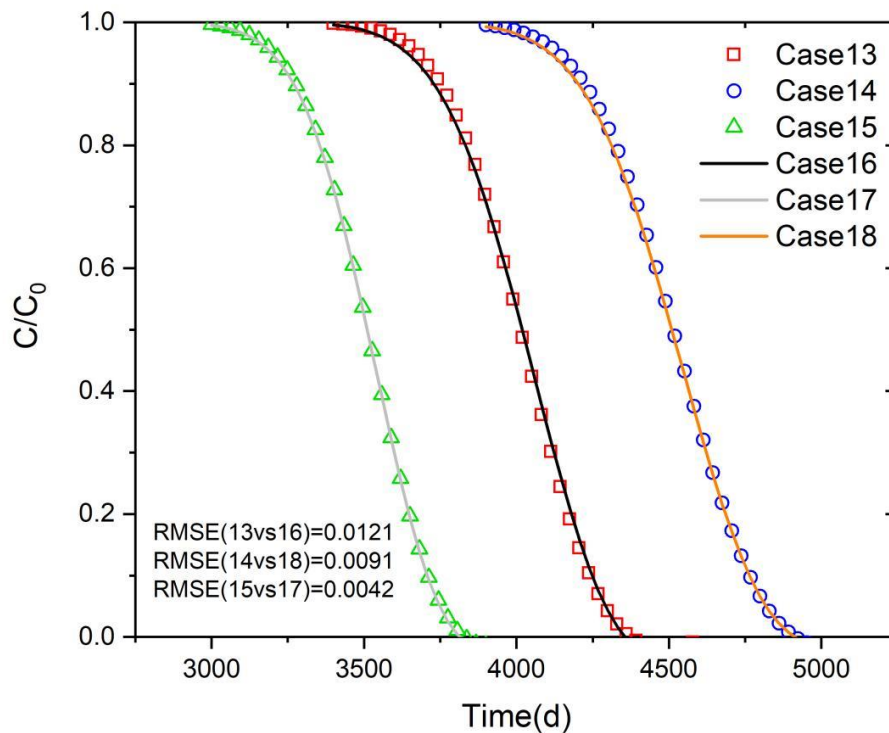


Figure 12. BTCs of Cases 13-18 in the heterogeneous aquifers in series.

From Fig.12, when comparing Cases 13-15 (or Cases 16-18), Case 15 (or Case 17) is the first to decline and the first to approach 0, then Case 13 (or Case 16) is the second to decline and to approach 0, and the last one is Case 14 (or Case 18). Both Case 15 and Case 17 have a higher retardation factor of the shorter zone, which means when two heterogeneous aquifers have different retardation factors, and they are in series, if the ratio of the length of two zones (the high retardation factor zone versus the low retardation factor zone) is lesser, the BTC will start to decline earlier. Due to the relationship $v_c = v_x/R$, when the retardation factor is increasing, the average velocity of the solute will decrease, provided that the average linear groundwater velocity remains the same, thus it will take a longer time to flush away the same amount of contaminants.

Also we can see from Fig. 12 that the BTCs of Cases 13 and 16, Cases 14 and 18, Cases 15 and 17 fit well with each other, and the RMSE values are very small, which means that the order of different heterogeneous aquifers will not affect the results considerably. To find the relationship between these heterogeneous aquifers in series, three general means (Table 7) are used to find the best averaged homogeneous aquifer.

In order to compare these three means, Case 14 is chosen, whose retardation factor of zone-1 is 1.2 ($R = 1.2$), and the retardation factor of zone-2 is 2 ($R = 2$). The weight coefficients are the length ratios of each zone. The total length is 100 m, and the length of zone-1 is 25 m, so w_1 is the ratio of the length of zone-1 to the total length

($w_1 = \frac{L_1}{L} = \frac{25m}{100m} = 0.25$), and w_2 is the ratio of the length of zone-2 to the total length

($w_2 = \frac{L-L_1}{L} = \frac{75m}{100m} = 0.75$).

Table 7. List of average equations and goodness-of-fit of Case 14.

Function	Arithmetic mean	Geometric mean	Harmonic Mean
Equation	$\bar{R} = \omega_1 R_1 + \omega_2 R_2$	$\bar{R} = R_1^{\omega_1} \times R_2^{\omega_2}$	$\frac{1}{\bar{R}} = \frac{\omega_1}{R_1} + \frac{\omega_2}{R_2}$
Average retardation factor	1.8000	1.7602	1.7143
RMSE	0.0043	0.0988	0.2057

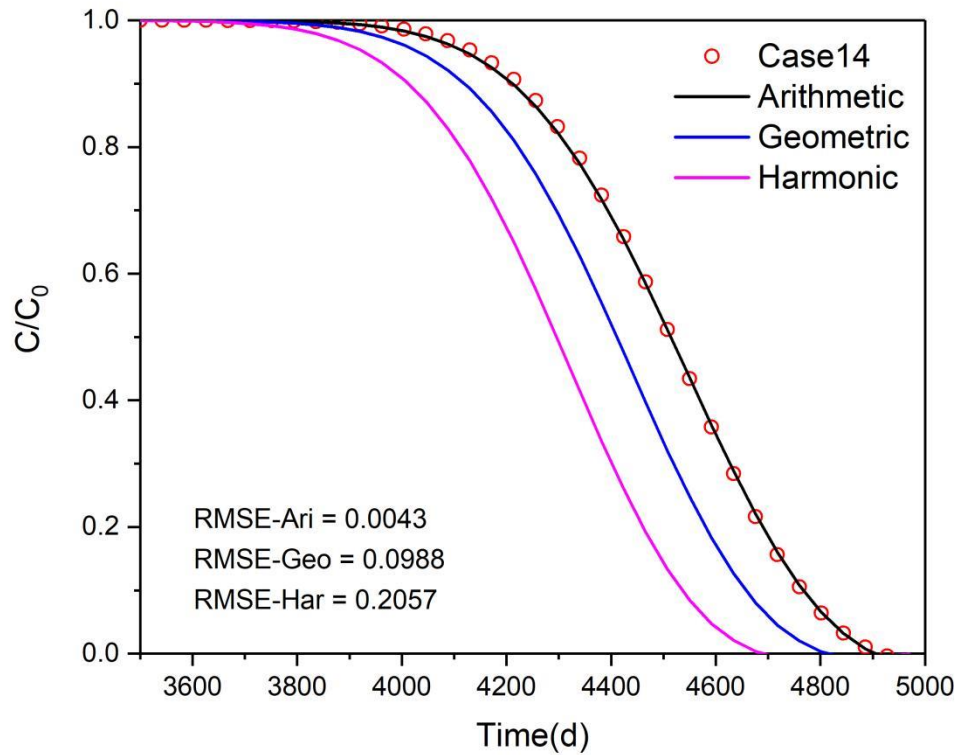


Figure 13. BTCs for Case 14 and three averaged homogeneous aquifers.

From Fig. 13, the BTC of the arithmetic mean provides the best fit with the BTC of Case 14, and the RMSE for this case is the smallest, which is 0.0043, suggesting that the arithmetic mean can be used to average the heterogeneous aquifers in series with different retardation factors.

4.2 Layered Heterogeneous Aquifers

The conceptual model of layered heterogeneous aquifers (or groundwater flow direction is parallel to the interface of two heterogeneous zones) has been illustrated in Fig. 3. This section is devoted to analyzing how the difference of transport properties of zone-3 and zone-4 will impact the contaminant transport during the flush process. Due to the differences of transport parameters, the front of flushing in one layer (or zone) may be ahead of the front of flushing in the other layer, generating a significant vertical concentration gradient across the interface of two zones, thus leading to mass exchange between the two zones due to the vertical dispersive transport. Such a mass exchange phenomenon has never been investigated before in a quantitative manner during the flushing of a two-layer system. To inspect the mass exchange between two zones, one can change one or more parameter values for zone-3 and zone-4 but keep the rest parameter values of these two zones the same. The porosity (θ), the transverse dispersivity (α_T), and the thickness (B) of two layers are the main transport properties which will affect the solute transport in the porous media, on which this section will focus.

To further illustrate the solute transport of the layered system, Fig. 14 displays the profile contours of concentration, drawn by COMSOL Multiphysics, in the two zones for

Case 19 ($\alpha_{L3} = 0.1 \text{ m}$, $\alpha_{T3} = 0.01 \text{ m}$, $\alpha_{L4} = 0.2 \text{ m}$, $\alpha_{T4} = 0.02 \text{ m}$, $\theta_3 = 0.1$, $\theta_4 = 0.2$, $q = 0.01 \text{ m/day}$, $B_1 = B_2 = 1 \text{ m}$, $C_0 = 1 \text{ kg/m}^3$, $L = 80 \text{ m}$) at three different times (1000d, 1200d, and 1400d). This model is discretized using triangular elements. To ensure sufficient accuracy of the numerical solution, elements near the interface of the two zones and the left boundary were refined with a minimum element size of 0.0001m, a maximum element size of 0.1m, and a maximum growth rate of 1.1 for the element size. This growth rate means that the element size can grow from a region with small elements to a region with larger elements using the free triangular mesh generator; that is, the element size can grow by at most 10% (approximately) from one element to another. Complete mesh consists of 44220 domain elements and 2590 boundary elements.

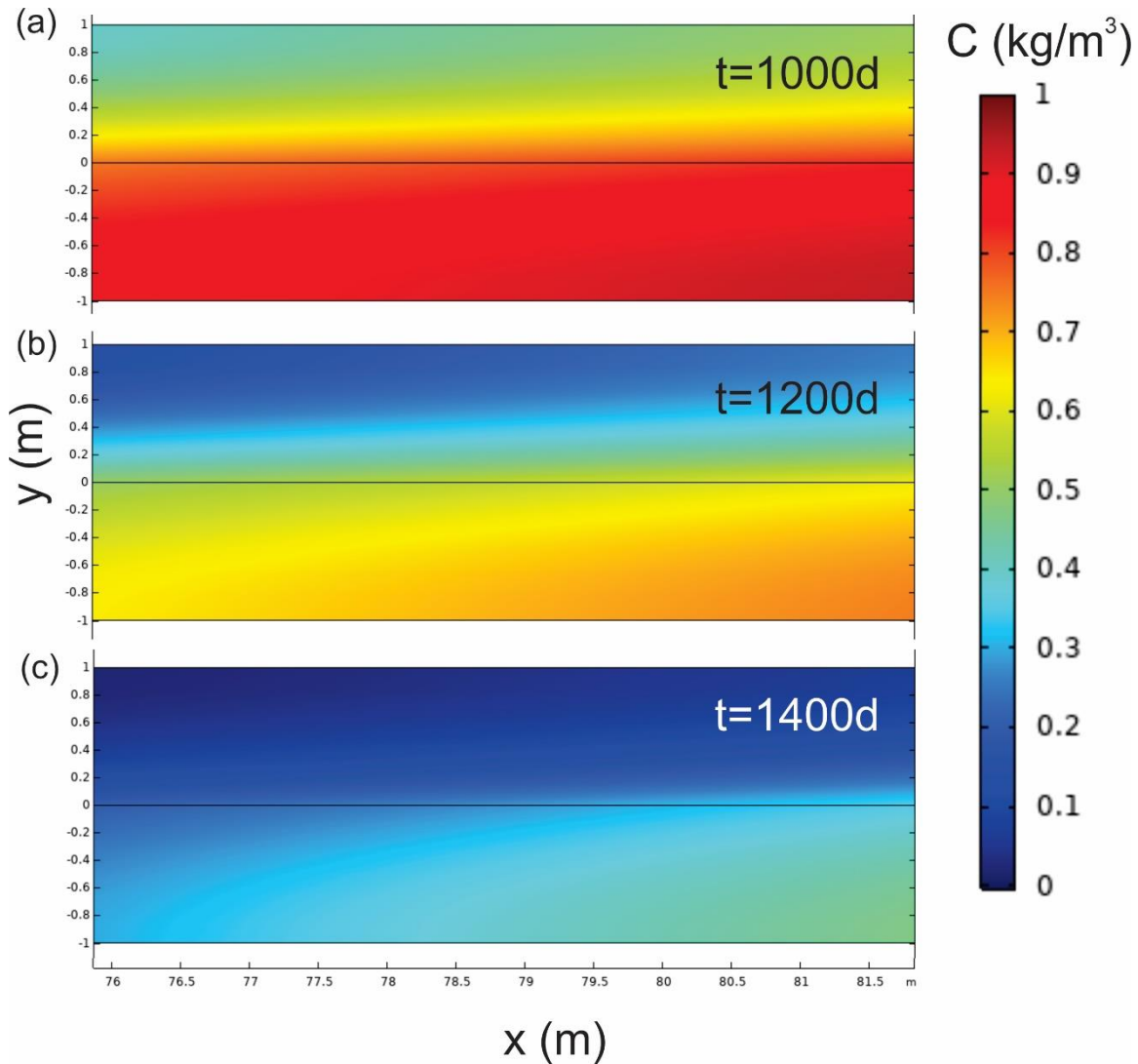


Figure 14. The contours of Case 19 for three times (1000d, 1200d, and 1400d).

Fig. 14 shows that the solute transport in the zone-4 significant lags behind that of the zone-3 as time progresses. The concentrations in zone-4 are higher than those in the zone-3 at any given time. Although the solute is flushed out quicker in zone-3, the solute in zone-4 across the interface of two zones and enters zone-3 through the vertical dispersion. When the concentration of the left boundary became 0, which signaling the start of flushing, the concentrations in the left region of zone-3 would be below the

concentrations in zone-4 owing to the faster transport of solute in zone-3. Thus, the solute in the left region of zone-4 would move to zone-3, driven by the vertical dispersive transport. As a result, the contours in Fig. 14 have inclined concentration boundaries. Therefore, to investigate the solute transport of layered heterogeneous aquifers, the mass exchange between these two layers is essential to consider because it regulates the entire development process of both layers. This section will study the effect of porosity (θ), the transverse dispersivity (α_T), and the thickness (B) of two layers on the mass exchange rate between the two layering zones, as well as the solute transport in each layer.

To further investigate the mass flux between two layers, the change of concentrations of points near the boundary of two layers ($\pm 0.01\text{m}$) over time is recorded, according to the relationship $F = -D^* \times \frac{dC}{dy}$, D^* is the diffusion coefficient (L^2/T), the mass flux can be calculated. Fig. 15. shows the mass flux of Case 19 varies with distance at different time, from which we can find that, as time goes on, the maximum of mass flux between two layers is decreasing; the distance at which the maximum of mass flux is generated gets farther; and the distance at which the mass flux changes become longer. The greater mass flux means the greater mass exchange.

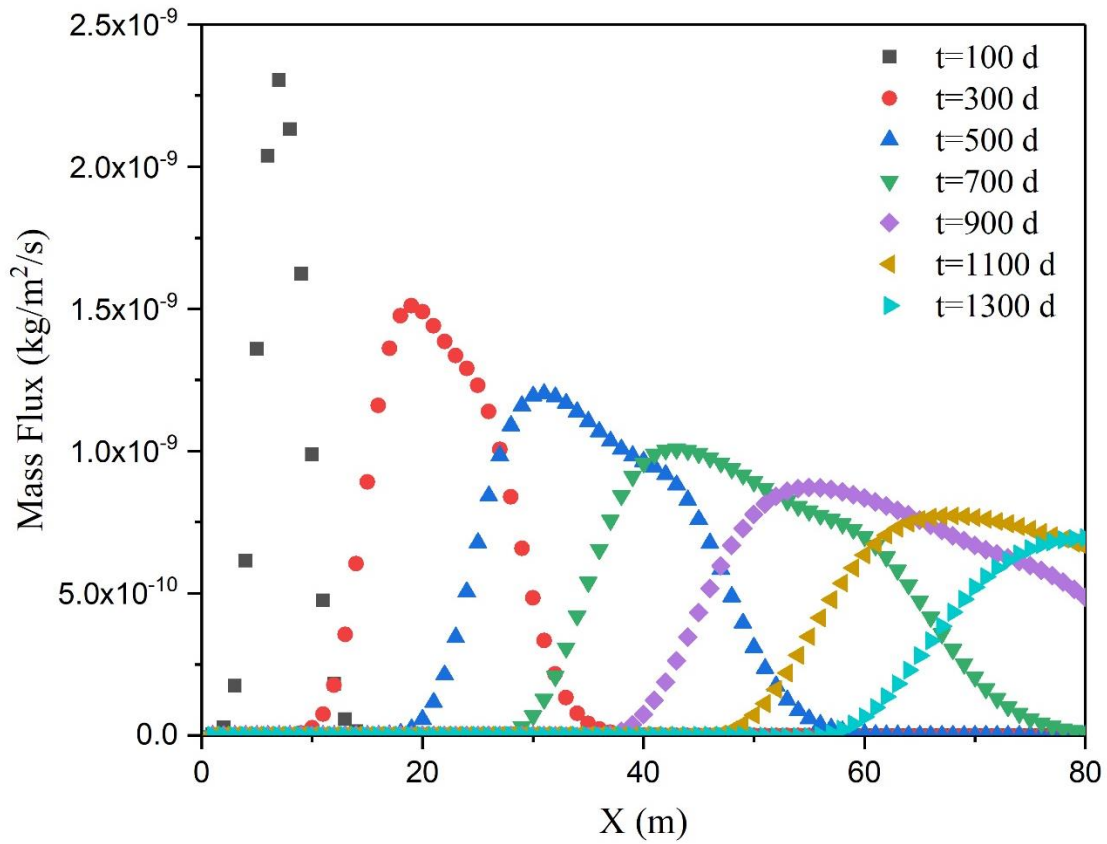


Figure 15. The vertical mass flux of Case 19 across the interface of zone-3 and zone-4 varies with distance at different times.

4.2.1 Porosity Influence

To investigate the porosity influence on the flushing model in the layered heterogeneous aquifers, the transport parameter values are listed in Table 8, which shows the different porosities of zone-3 and zone-4. All cases have the same properties as following: $\alpha_{L3} = 0.1 \text{ m}$, $\alpha_{T3} = 0.01 \text{ m}$, $\alpha_{L4} = 0.2 \text{ m}$, $\alpha_{T4} = 0.02 \text{ m}$, $q = 0.01 \text{ m/day}$, $B_1 = B_2 = 1 \text{ m}$, $C_0 = 1 \text{ kg/m}^3$, $L = 80 \text{ m}$.

Table 8. Different porosities of conceptual Cases 19-21.

Case No.	θ_3	θ_4
19	0.1	0.2
20	0.1	0.3
21	0.1	0.4

In Cases 19-21, the porosities of zone-3 are the same, but the porosities of zone-4 are different, and the difference of the porosities of two layers is increasing. Fig. 16 shows the mass flux for Cases 19-21 varies with distance at different times.

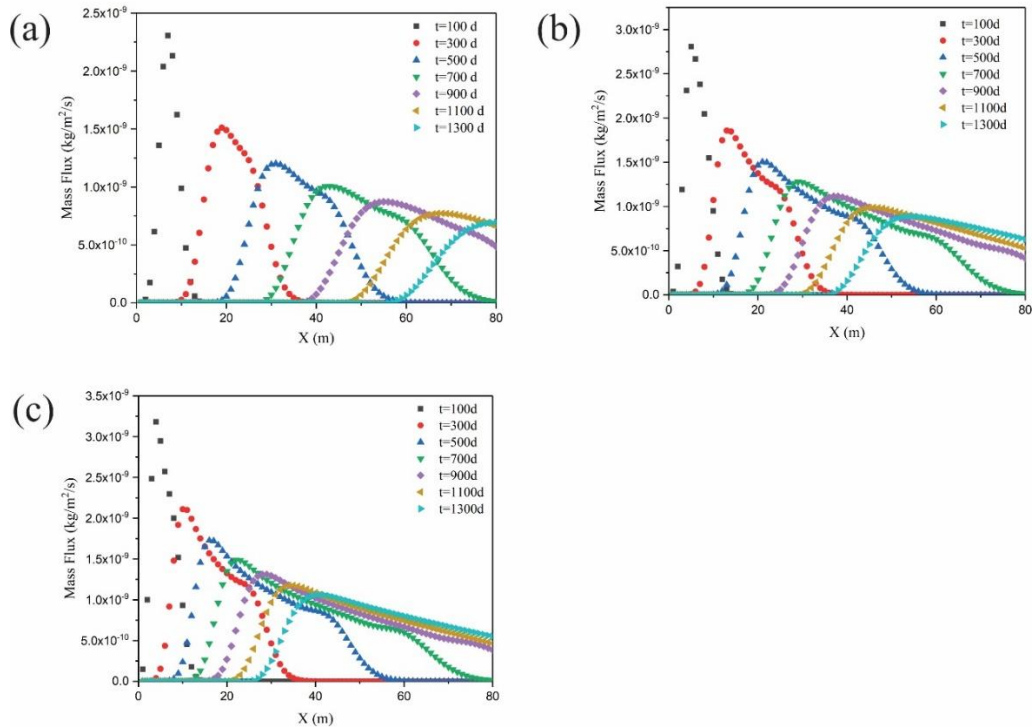


Figure 16. The vertical mass flux of Cases 19-21 across the interface of zone-3 and zone-4 varies with distance at different times. (a) Case 19; (b) Case 20; and (c) Case 21.

According to the results of Fig. 16, we can record the maximum mass flux, the distance at which the maximum of mass flux is generated (Table 9), and the distance at which the mass flux changes of each time (Table 10).

Table 9. The maximum vertical mass flux of Cases 19-21 across the interface of zone-3 and zone-4.

Time (d)	Maximum Mass Flux ($\times 10^{-9} \text{ kg/m}^2/\text{s}$)			Distance of Maximum Mass Flux (m)		
	Case 19	Case 20	Case 21	Case 19	Case 20	Case 21
	100	2.30	2.80	3.18	7	5
300	1.51	1.86	2.11	19	13	10
500	1.20	1.50	1.73	31	21	16
700	1.01	1.28	1.49	43	29	22
900	0.87	1.11	1.31	55	37	28
1100	0.77	0.99	1.17	68	46	35
1300	0.70	0.89	1.06	80	54	41

From Table 9, we can find that when enlarging the difference of the porosities of two layers, the maximum mass flux would increase, the distance of maximum mass flux is shorter. A greater difference of porosities of two layers leads to a greater difference of the linear velocities of two layers, which means that for every investigated point on the boundary, the difference of concentration of two layers is greater, so that the mass exchange at every point will be greater, so the maximum mass flux is increasing when the

difference of the porosities of two layers is increasing. Due to the relationship of $v = q/\theta$, a greater porosity means a slower groundwater flow velocity (provided that the Darcy velocity remains the same), thus causing a shorter distance for the same given time.

Table 10. The distance of the changed vertical mass flux of Cases 19-21 across the interface of zone-3 and zone-4.

Time (d)	Distance of the Changed Mass Flux (m)		
	Case 19	Case 20	Case 21
100	13	14	14
300	27	32	34
500	40	49	52
700	53	64	69

Table 10 illustrated that as the difference of the porosities of two layers increases, the distance of the changed mass flux is increasing.

4.2.2 Transverse Dispersivity Influence

To investigate the transverse dispersivity influence on the flushing model in the layered heterogeneous aquifers, the data from Table 11 are used, which shows the different transverse dispersivities of zone-3 and zone-4. All cases have the same properties as following: $\alpha_{L3} = 0.1 \text{ m}$, $\alpha_{L4} = 0.2 \text{ m}$, $\theta_3 = 0.1$, $\theta_4 = 0.2$, $q = 0.01 \text{ m/day}$, $B_1 = B_2 = 1 \text{ m}$, $C_0 = 1 \text{ kg/m}^3$, $L = 80 \text{ m}$.

Table 11. Different transverse dispersivities of conceptual Cases 22-24.

Case No.	α_{T3} (m)	α_{T4} (m)
22	0.01	0.02
23	0.01	0.03
24	0.01	0.04

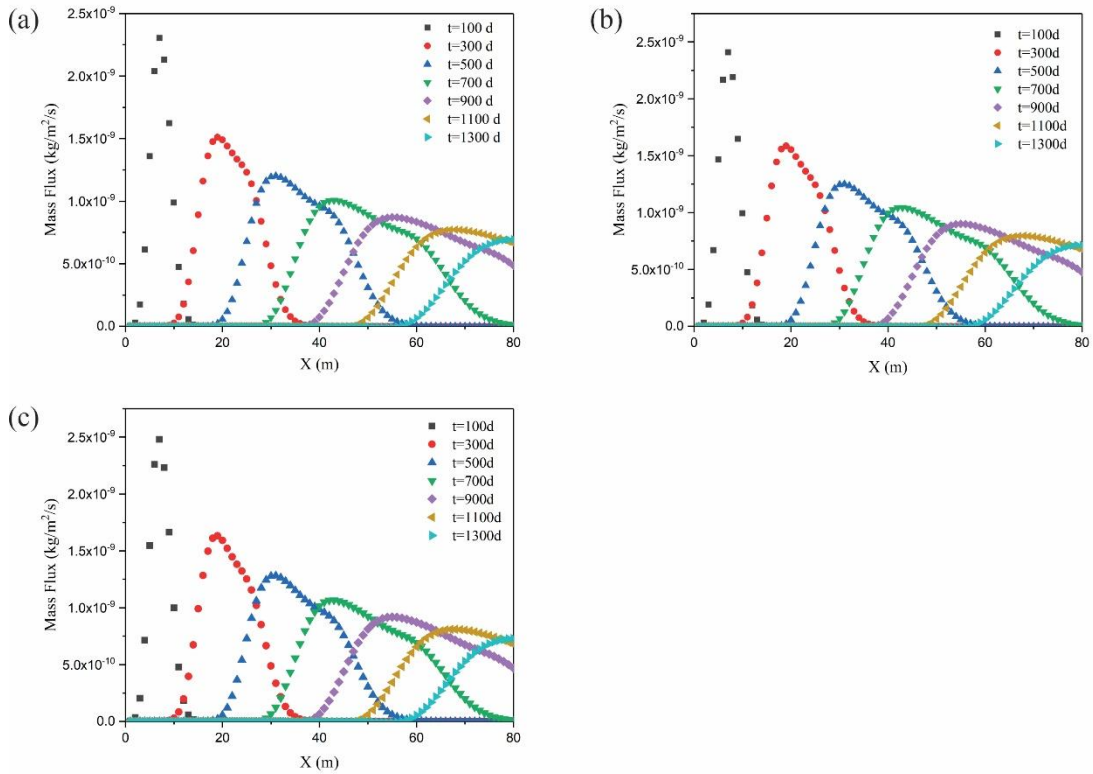


Figure 17. The vertical mass flux of Cases 22-24 across the interface of zone-3 and zone-4 varies with distance at different times. (a) Case 22; (b) Case 23; and (c) Case 24.

In Cases 22-24, the transverse dispersivities of zone-3 are the same, but the transverse dispersivities of zone-4 are different, and the difference of the transverse

dispersivities is increasing. Fig. 17 shows the mass flux for Cases 22-24 varies with distance at different times.

According to the results of Fig. 17, we can record the maximum mass flux, the distance at which the maximum of mass flux is generated (Table 12), and the distance at which the mass flux changes of each time (Table 13).

Table 12. The maximum vertical mass flux of Cases 22-24 across the interface of zone-3 and zone-4.

Time (d)	Maximum Mass Flux			Distance of Maximum Mass Flux		
	$(\times 10^{-9} \text{ kg/m}^2/\text{s})$			(m)		
	Case 22	Case 23	Case 24	Case 22	Case 23	Case 24
100	2.30	2.41	2.48	7	7	7
300	1.51	1.59	1.63	19	19	19
500	1.20	1.25	1.28	31	31	31
700	1.01	1.04	1.07	43	43	43
900	0.87	0.90	0.92	55	55	55
1100	0.77	0.80	0.81	68	68	68
1300	0.70	0.72	0.73	80	80	80

From Table 12, we can find that when enlarging the difference of the transverse dispersivities of two layers, the maximum mass flux would increase, and the distance of maximum mass flux remains. A greater transverse dispersivity leads to a quicker mass exchange rate. Therefore, when the solute concentration of zone-3 is less than that of

zone-4, the solute in zone-4 would move back to zone-3, and in Case 23, the “move rate” is greater than that of Case 22. So the maximum mass flux of Case 23 is greater than that of Case 21, and the maximum mass flux of Case 24 is greater than that of Case 22 at any given time. And the transverse dispersivity has no impact on the linear velocity, so there is no change on the distance at which the maximum mass flux is generated.

Table 13. The distance of the changes vertical mass flux of Cases 22-24 across the interface of zone-3 and zone-4.

Time (d)	Distance of the Changed Mass Flux (m)		
	Case 22	Case 23	Case 24
100	13	13	13
300	27	28	28
500	40	41	41
700	53	53	52

Table 13 illustrated that as the difference of the transverse dispersivities of two layers increase, there is no difference on the distance of the changed mass flux.

4.2.3 Thickness Influence

To investigate the thickness influence on the flushing model in the layered heterogeneous aquifers, the data from Table 14 are used, which shows the different thickness of zone-3 and zone-4. All cases have the same properties as following: $\alpha_{L3} = 0.1 m$, $\alpha_{T3} = 0.01 m$, $\alpha_{L4} = 0.2 m$, $\alpha_{T4} = 0.02 m$, $\theta_3 = 0.1$, $\theta_4 = 0.2$, $q =$

0.01 m/day, $C_0 = 1 \text{ kg/m}^3$, $L = 80 \text{ m}$. These models are discretized using triangular elements. To ensure sufficient accuracy of the numerical solution, elements near the interface of the two zones and the left boundary were refined with a minimum element size of 0.0001m, a maximum element size of 0.1m, and a maximum growth rate of 1.1 for the element size. For Case 25, the complete mesh consists of 44220 domain elements and 2590 boundary elements; For Case 26, the complete mesh consists of 127590 domain elements and 2670 boundary elements; For Case 27, the complete mesh consists of 233022 domain elements and 2770 boundary elements.

Table 14. Different transverse dispersivities of conceptual Cases 27-30.

Case No.	B_3 (m)	B_4 (m)
25	1	1
26	5	1
27	10	1

In Cases 25-27, the thicknesses of zone-4 are the same, but the thicknesses of zone-3 are different, and the difference of the thicknesses of two layers is increasing. Fig. 18 shows the mass flux for Cases 25-27 varies with distance at different times.

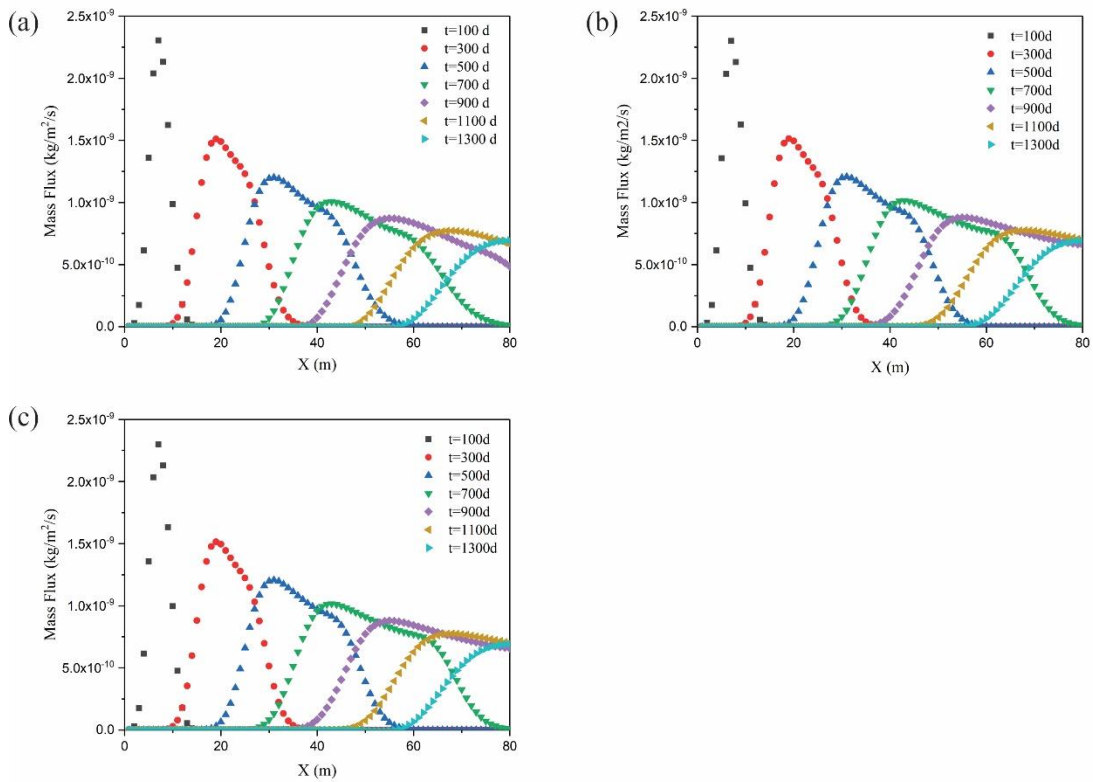


Figure 18. The vertical mass flux of Cases 25-27 across the interface of zone-3 and zone-4 varies with distance at different time. (a) Case 25; (b) Case 26; and (c) Case 27.

According to the results of Fig. 18, we can record the maximum mass flux, the distance at which the maximum of mass flux is generated (Table 15), and the distance at which the mass flux changes of each time (Table 16).

Table 15. The maximum vertical mass flux of Cases 25-27 across the interface of zone-3 and zone-4.

Time (d)	Maximum Mass Flux ($\times 10^{-9} \text{ kg/m}^2/\text{s}$)			Distance of Maximum Mass Flux (m)		
	Case 25	Case 26	Case 27	Case 25	Case 26	Case 27
	100	2.30	2.30	2.30	7	7
300	1.51	1.51	1.51	19	19	19
500	1.20	1.21	1.21	31	31	31
700	1.01	1.02	1.02	43	43	43
900	0.87	0.88	0.88	55	55	55
1100	0.77	0.78	0.78	68	68	68
1300	0.70	0.69	0.69	80	80	80

Table 16. The distance of the changed vertical mass flux of Cases 25-27 across the interface of zone-3 and zone-4.

Time (d)	Distance of the Changed Mass Flux (m)		
	Case 25	Case 26	Case 27
100	13	13	13
300	27	27	27
500	40	41	44
700	53	53	53

From Table 15 and Table 16, we can find that there is negligible impact on the results when change the thickness of the layered heterogeneous aquifers. This is understandable as the vertical mass flux between zone-3 and zone-4 is mostly controlled by the vertical concentration gradient near the interface of these zones, thus is much less impacted by the thickness of either zone-3 or zone-4. However, if zone-3 or zone-4 is extremely thin, then the thickness of zone-3 or zone-4 may impose some impact on such a vertical flux.

5. CONCLUSION AND DISCUSSION

This thesis investigates the solute transport in homogeneous and heterogeneous aquifers under the conditions of flushing a mobile dissolved chemical plume. Several models addressing various cases are constructed in COMSOL Multiphysics to help the study.

The first conclusion of this thesis is an easier solution to describe the flushing model of a homogeneous aquifer, which required less parameters than the flushing solution by Van Genuchten does, and removes the need for *erfc* function, makes it much easier to calculate with other equations. The breakthrough curves of hypothetical contaminants using three difference methods (the new solution of this study, the solution by Van Genuchten, and the numerical solution) were compared to verify the reliability of the new solution. This new solution provides a quick screening tool in engineering practice for designing the real-world contaminant remediation plans. For example, it can be used to estimate how long it would take to flush the contaminant from the aquifer assuming the aquifer's physical and physico-chemical properties which influence contaminant transport were known.

Next, this thesis focuses on the flushing model of the heterogeneous aquifers in series, especially the influence of dispersivity (α), porosity (θ), and retardation factor (R). Firstly, we find that when only changing one parameter of these three parameters, and reversing the two zones' position, the relative concentration has little change, which means that the order of heterogeneous aquifers does not appear to affect the results noticeably. Secondly, when these three parameters are changing, a surrogate

homogeneous aquifer can be used to approximate a heterogeneous aquifer and the parameters of the surrogate homogeneous aquifer are estimated using arithmetic means of their counterparts of the heterogeneous aquifer. Thirdly, the results show that when the averaged dispersivity is increasing, the BTC will decline slower; when the averaged porosity is increasing, it takes longer time to flush away the same amount of contaminants but does not affect the decline rate of the BTC; when the averaged retardation factor is increasing, it takes longer time to flush away the same amount of contaminants, but does not affect the decline rate of the BTC.

The third conclusion is about the influence of porosity (θ), transverse dispersivity (α_T), and thickness (B) of two layers on flushing in the layered heterogeneous aquifers. Firstly, we find that when enlarge the difference of porosities of two zones, the mass flux between two layers will increase. Secondly, a greater difference of transverse dispersivity leads to a greater mass flux between two layers. Lastly, the difference of thickness of two layers does not affect the mass exchange between two layers.

Some of the conclusions in this thesis can be used for in the real-world engineering problems, and related future studies will be summarized in the final section.

6. FUTURE WORK

In this thesis, there are still some issues need to be resolved in the future.

This thesis discussed two ideal heterogeneous systems, which are formed by two homogeneous aquifers. However, for the real-world heterogeneous aquifers can be much more complex than what has been investigated here. For instance, there may be more than two heterogeneous zones, or a fracture-matrix system may exist, or heterogeneous nature of the aquifer cannot be characteristics at all using the zoning process. More investigation should be discussed for these more complicated issues in the future. Furthermore, this study is limited to one-dimensional and two-dimensional problems only and its extension to three-dimensional problems should be carried out in the future.

This study has figured out an easier solution to deal with the flushing model on the homogeneous aquifer, and we have compared it with the solution by Van Genuchten and the numerical solution. To further confirm its reliability, we should compare it with the laboratory or field experiments in the future.

The homogenization of parameter is dependent on the curve fitting of BTCs, which use the initial estimated valued to find the unknown parameter with the sum of the absolute values of the deviation between the approximate curve and observed curve minimized. The accuracy of fitting result is relative to the initial estimated value in some extent. There is still room for improvement for this method.

Furthermore, the laboratory and field experiments need to be established to verify the validity and accuracy of this method when using in the real-world problems.

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