

Article

Mathematical Modeling of Non-Fickian Diffusional Mass Exchange of Radioactive Contaminants in Geological Disposal Formations

Anna Suzuki ^{1,*}, Sergei Fomin ², Vladimir Chugunov ³ and Toshiyuki Hashida ⁴

¹ Institute of Fluid Science, Tohoku University, Sendai, Miyagi 980-8577, Japan

² Department of Mathematics and Statistics, California State University, Chico, CA 95929, USA; sfomin@csuchico.edu

³ Institute of Mathematics, Informatics and Natural Sciences, Moscow City University, 129226 Moscow, Russia; CHugunovVA@mgpu.ru

⁴ Fracture & Reliability Research Institute, School of Engineering, Tohoku University, Sendai, Miyagi 980-8579, Japan; hashida@rift.mech.tohoku.ac.jp

* Correspondence: anna.suzuki@tohoku.ac.jp; Tel.: +81-22-217-5284

† Current address: 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan.

Received: 30 July 2017; Accepted: 23 January 2018; Published: 29 January 2018

Abstract: Deep geological repositories for nuclear wastes consist of both engineered and natural geologic barriers to isolate the radioactive material from the human environment. Inappropriate repositories of nuclear waste would cause severe contamination to nearby aquifers. In this complex environment, mass transport of radioactive contaminants displays anomalous behaviors and often produces power-law tails in breakthrough curves due to spatial heterogeneities in fractured rocks, velocity dispersion, adsorption, and decay of contaminants, which requires more sophisticated models beyond the typical advection-dispersion equation. In this paper, accounting for the mass exchange between a fracture and a porous matrix of complex geometry, the universal equation of mass transport within a fracture is derived. This equation represents the generalization of the previously used models and accounts for anomalous mass exchange between a fracture and porous blocks through the introduction of the integral term of convolution type and fractional derivatives. This equation can be applied for the variety of processes taking place in the complex fractured porous medium, including the transport of radioactive elements. The Laplace transform method was used to obtain the solution of the fractional diffusion equation with a time-dependent source of radioactive contaminant.

Keywords: radioactive contaminant; fractional derivative; analytical solution

1. Introduction

High-level nuclear wastes are a by-product of nuclear power generation and other applications of nuclear fission or nuclear technology which must be shielded from humans and the environment for a long time. Subsurface nuclear waste repositories consist of engineered and geological barriers that isolate the radioactive materials from the human environment. If the radioactive contaminants leak to aquifers, the damage would be serious because it directly contaminates our drinking water. We need to answer how and when the contaminants leak from the power plants or the waste repositories unintentionally, and how much they affect human beings and the natural environment. Safe disposal of nuclear wastes requires an evaluation of the risks of contaminants for aquifers and prediction of the possible migration of contaminated groundwater.

Fluid flow and contaminant transport in aquifers are dominated by fractures and large pores. Numerous studies indicate that the real nature of solute transport in geological formations

exhibits anomalous behavior [1–4]. Multiscale subsurface systems often produce power-law tails in breakthrough curves [5–8], as well as in a nuclear waste repository site [9]. The breakthrough curves are not adequately described by the typical advection-dispersion with an exponential residence time (e.g., [10,11]).

Problems of solute transport in a single fracture-matrix system have been addressed, and the analytical solutions have been developed based on the advection-dispersion equation [12,13]. Alternative transport models are proposed to capture the effects of spatial heterogeneities in fractured rocks and the effects of flow channeling or velocity dispersion [14,15]. The models have extended to the mass transfer models with time- or space-dependent dispersion coefficients (e.g., [16]), the multi-rate mass transfer models [17], the continuous time random walk approach [18], the time-domain random walk approach, the fractional advection-dispersion equation approach [19], and the stochastic approach [20].

The fractional derivative can be understood as a convolution of an integer-order derivative with a memory function [21], and the time convolution can capture memory effects, allowing particles to reside for long periods. The temporal fractional derivatives can produce power law residence times of solute transport. Liu et al. [22] considered the time fractional advection-dispersion equation, and the solution was obtained by using variable transformation. Fomin et al. [23] studied mass transport in a fractured-porous aquifer (i.e., aquifer filled with porous blocks) and modeled the effects of interaction with porous blocks in the aquifer by temporal fractional derivatives. Numerical study shows that varying the variations of order of fractional derivatives enables the description of different power law decays obtained from a homogeneous porous medium to a fractured medium [24].

This study proposes a mathematical model of radioactive contaminant transport in a single fracture within a confining porous matrix. Usually, sources of radioactive contamination vary with time. For example, an exponentially decaying source boundary condition is frequently used in radioactive waste disposal or non-aqueous phase liquid sites [25]. We derive the universal equation of mass transport for dissolved molecular size contaminants within a fracture, which accounts for the complexity of the confining porous matrix and temporal decay of the contaminant concentration. In this equation, the specific features of mass transport in the surrounding matrix and mass exchange between the fracture and matrix are modeled by the special function $Q_1(t)$, which represents the integral of convolution. This paper provides the analytic derivation of the function $Q_1(t)$ in its most general form, so that the majority of the well documented models can be obtained as particular cases of the presented model. For example, in the absence of radioactive decay, the solution presented in this paper reduces to the solution obtained by Fomin et al. [23] for $\Lambda = 0$ and $Q_1 = Q_0$. When mass flux is Fickian with $\Lambda = 0$ and $\alpha = 1$, the solution was obtained by Tang et al. [12], which also follows as a particular case from the solution obtained in this paper.

2. Model

2.1. Governing Equation

We consider radioactive solute transport in a single fracture surrounded by porous rocks. The fracture does not contain any porous inclusions, which is different from the concept in the previous study [23]. A schematic sketch of a fracture and rock matrix is presented in Figure 1. A parallel plate fracture is confined by porous rocks, which have same physical properties for the upper and lower sides. Cartesian coordinates (x, y) are chosen in such a manner that fluid in the fracture flows in the x -direction and that the coordinate y is perpendicular to the x -direction. Transport processes can be symmetrical with regard to the median line of the fracture at $y = -h$ (dashed line in Figure 1). This leads to the mass flux of 0 at $y = -h$, and the solutions in the sub-domains below and above this line are identical. Thus, we can only consider the upper half of the domain ($y = -h$).

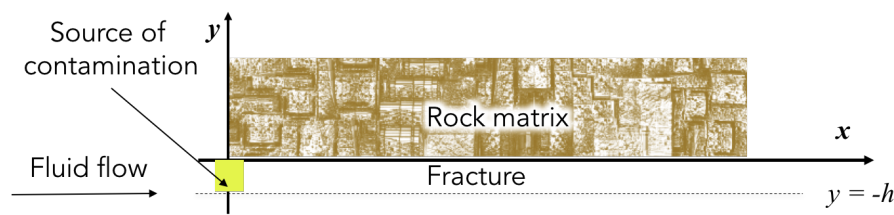


Figure 1. Schematic of a fracture surrounded with porous rocks.

Let c_1 and c_2 be the concentrations of the solute within the porous matrix and the fracture, respectively. We consider only dissolved molecular-size contaminants, not suspended particles in the aqueous phase radioactive particles. Because the thickness of the fracture is much smaller than its length, the mean concentration of the solute within the fracture can be given by $c = \frac{1}{h} \int_{-h}^0 c_2 dy$. Mass transport in this system consists of (i) advection and (ii) diffusion in the fracture, (iii) absorption on the fracture walls, (iv) diffusion into the surrounding rocks, (v) adsorption on the walls of the pores in the surrounding rocks, and (vi) radioactive decay of radioactive contaminants both in fracture and porous matrix. Each governing equation within the fracture and within the rock matrix can be written as [12]:

$$\frac{\partial c}{\partial \tau} + \frac{1}{h} \frac{\partial s}{\partial \tau} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - \lambda(c + \frac{1}{h}s) - \frac{q}{h}, \quad 0 < x < \infty, \tau > 0, \tag{1}$$

$$\frac{\partial c_1}{\partial \tau} + \frac{\rho_m}{\theta} \frac{\partial s_1}{\partial \tau} = -\frac{1}{\theta} \frac{\partial q}{\partial y} - \lambda(c_1 + \frac{\rho_m}{\theta}s_1), \quad 0 < y < \infty, \tau > 0, \tag{2}$$

where τ is time. s and s_1 are the mass of the solute adsorbed on the walls of the fracture and pores in the rock matrix, respectively. v is the average velocity of the solution in the fracture. D and D_1 are the effective diffusivities in the fracture and in the porous medium, respectively, which include dispersion and molecular diffusion in the fracture and in the porous medium. λ is a radioactive decay constant. q is the mass flux on the wall of the fracture. ρ_m is the density of the rock matrix, and θ is the matrix porosity.

It has been observed that pore spaces and micro-cracks in the rock matrix are distributed in various sizes and different orientations [26]. We assume that contaminants not only penetrate in the matrix due to molecular diffusion, but also migrate through micro-cracks due to advection. Thus, the effective diffusivity, D_1 , accounts for dispersion and molecular diffusion. If micro-cracks within the surrounding matrix have an orientation perpendicular to the conducting fracture, contaminants may migrate long distances and lead to a faster process than diffusion (super diffusion). We should predict the worst scenario to evaluate the risks of contaminants' migration. Thus, in order to account for the advective process in the surrounding rocks, this study used the generalized Fickian mass flux in the matrix by introducing a fractional derivative, in the following form [27]:

$$q = -\theta D_1 \frac{\partial^\alpha c_1}{\partial y^\alpha}, \tag{3}$$

where α is the order of fractional derivative ($0 < \alpha < 1$). The value of $1/2 < \alpha < 1$ leads to faster (superdispersive) spreading, while the value of $0 < \alpha < 1/2$ causes slower (subdiffusive) spread [25]. Equation (3) describes Fickian diffusion when the index on space fractional derivative is $1/2$ (i.e., $\alpha = 1/2$). The fractional derivative can be defined by means of Laplace transformation \mathcal{L} , from the equation $\mathcal{L}[\frac{\partial^\alpha c_1}{\partial y^\alpha}] = p^{\alpha-1}(p\mathcal{L}[c_1] - c_1(\tau, 0))$, which is equivalent to the Caputo definition [28],

$$\frac{d^\alpha c_1}{dy^\alpha} = \int_0^y \frac{(y-\xi)^{-\alpha}}{\Gamma(1-\alpha)} \frac{dc_1}{d\xi} d\xi.$$

The relationship between c and s in Equation (1) and between c_1 and s_1 in Equation (2) can be assumed [12] as

$$s = K_f c, \tag{4}$$

$$s_1 = K_m c_1, \tag{5}$$

where K_f and K_m are given constants. Substituting correlations (4) and (5) into Equations (1) and (2) yields

$$R \frac{\partial c}{\partial \tau} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - R\lambda c + \frac{\theta D_1}{h} \frac{\partial^\alpha c_1}{\partial y^\alpha} \Big|_{y=0}, \tag{6}$$

$$R_1 \frac{\partial c_1}{\partial \tau} = D_1 \frac{\partial}{\partial y} \left(\frac{\partial^\alpha c_1}{\partial y^\alpha} \right) - R_1 \lambda c_1, \tag{7}$$

where $R_1 = 1 + \frac{\rho_m K_m}{\theta}$ and $R = 1 + \frac{K_f}{h}$ are retardation coefficients.

In general, concentration in the matrix c_1 is a function of both spatial coordinates, x and y : $c_1 = c_1(\tau, x, y)$. Let l and h be the characteristic scales for the length in the x -direction (along the aquifer) and y -direction, respectively. The scale l is defined by the distance of contaminant intrusion into the aquifer in the x -direction due to the advective transport, and the scale h is defined by the thickness of the aquifer. The characteristic values of the concentration gradient in x - and y -direction are C_0/l and C_0/h , respectively. Therefore, the ratio of the gradients can be estimated by the quotient of the length scales, h/l . Obviously, the scale l can be much greater than the scale h , and the ratio h/l can be very small. Hence, diffusion in the x -direction is negligibly small compared to the diffusion in y -direction. Thus, the derivative of c_1 with respect to x is ignored. This is the same assumption with Grisak and Pickens [29] and Tang et al. [12]. Dependence of c_1 on x is a consequence of the boundary conditions on the rock–fracture interface ($y = 0$), which couples c_1 with the mean concentration in the fracture, c .

In order to generalize the equations, the non-dimensional forms are derived with the proper characteristic scales. The scale for time represents the characteristic time for contaminant penetration in the rock matrix to the distance h , given by $\tau_m = \frac{h^{\alpha+1} R_1}{D_1}$. The scale for the variable x -coordinate along the fracture is the characteristic distance of contaminant migration by the characteristic time τ_m , described as $l = \frac{v \tau_m}{R} = \frac{h^{\alpha+1} v R_1}{R D_1}$. The scale for the y -coordinate is defined to be half of the aquifer, h . The initial concentration of solute at the inlet where the source of contamination is located, $c_0(0)$, can be used as the scale for solute concentration. Based on these scales, non-dimensional variables can be introduced as follows:

$$C = \frac{c}{c_0(0)}; C_1 = \frac{c_1}{c_0(0)}; Pe = \frac{vl}{D}; t = \frac{\tau}{\tau_m}; X = \frac{x}{l}; Y = \frac{y}{h}; \Lambda = \frac{\lambda R_1 h^{\alpha+1}}{D_1}. \tag{8}$$

Substituting the non-dimensional variables in Equation (8) into Equations (6) and (7) yields the following:

$$\frac{\partial C}{\partial t} - \frac{1}{Pe} \frac{\partial^2 C}{\partial X^2} + \frac{\partial C}{\partial X} + \Lambda C = \theta \frac{\partial^\alpha C_1}{\partial Y^\alpha} \Big|_{Y=0}, \quad 0 < X < \infty, t > 0, \tag{9}$$

$$\frac{\partial C_1}{\partial t} = \frac{\partial^{\alpha+1} C_1}{\partial Y^{\alpha+1}} - \Lambda C_1 \quad 0 < Y < \infty, t > 0. \tag{10}$$

The following boundary and initial conditions can be imposed:

$$t = 0, C = C_1 = 0; \tag{11}$$

$$X = 0, C = C_0(t); \tag{12}$$

$$X \rightarrow \infty, C \rightarrow 0; \tag{13}$$

$$Y \rightarrow \infty, C_1 \rightarrow 0; \tag{14}$$

$$Y = 0, C_1 = C; \tag{15}$$

where $C_0(t)$ is the non-dimensional concentration at the inlet of the fracture. Typically, the concentration distribution in the aquifer can be approximated by a parabola. Therefore, the maximum values of concentration can be reached in the middle of the aquifer, while the lowest values at the aquifer–matrix interface. In this case, assuming that the concentration C_1 on the interface $Y = 0$ is equal to the mean concentration C in the aquifer (the boundary condition (15)), which slightly overestimates the concentration on the border of the matrix. Therefore, the computed concentration C_1 in the region $(0 < Y < \infty)$ will be slightly overestimated. However, using the present model as a tool for predicting contamination in the real world situations, the slight overestimation of the possible hazardous contamination is a positive factor.

2.2. Analytical Solution

Equation (9) describes mass transport in a fracture, which contains the variables C and C_1 (i.e., concentration in the fracture and in the matrix, respectively). Let us consider the mass flux on the fracture–matrix interface on the right hand side in Equation (9), which can be written by:

$$Q = \frac{\partial^\alpha C_1}{\partial Y^\alpha} |_{Y=0}. \tag{16}$$

Based on an analogy of Duhamel’s theorem [30], the solution for the concentration in the matrix, C_1 , can be coupled with the concentration in the fracture, C , by the following equation:

$$C_1(t, X, Y) = e^{-\Lambda t} \frac{\partial}{\partial t} \int_0^t e^{\Lambda \tau} C(\tau, X) u_0(t - \tau, Y) d\tau, \tag{17}$$

where the function u_0 in Equation (17) is a solution of the following auxiliary problem:

$$\frac{\partial u_0}{\partial t} = \frac{\partial^{\alpha+1} u_0}{\partial Y^{\alpha+1}}; 0 < Y < \infty; t > 0, \tag{18}$$

$$t = 0, u_0 = 0; \tag{19}$$

$$Y = 0, u_0 = 1; \tag{20}$$

$$Y \rightarrow \infty, u_0 \rightarrow 0. \tag{21}$$

The mass flux in Equation (18) is given by:

$$Q_0(t) = -\frac{\partial^\alpha u_0}{\partial Y^\alpha} |_{Y=0}. \tag{22}$$

Mass flux differentiations, Q given by Equation (16) and Q_0 given by Equation (22), are performed with respect to the variable Y , whereas the differentiation and the integration in Equation (17) are performed with respect to the variables t and τ , respectively. We can change the order of fractional differentiation with respect to Y to the order of differentiation with respect to t and the order of integration with respect to τ . As a result, we obtain

$$Q = \frac{\partial^\alpha C_1}{\partial Y^\alpha} |_{Y=0} = e^{-\Lambda t} \frac{\partial}{\partial t} \int_0^t e^{\Lambda \tau} C(\tau, X) \frac{\partial^\alpha u_0}{\partial Y^\alpha} |_{Y=0} d\tau = -e^{-\Lambda t} \frac{\partial}{\partial t} \int_0^t e^{\Lambda \tau} C(\tau, X) Q_0(t - \tau) d\tau, \tag{23}$$

where $C(\tau, X)$ does not depend on Y . In addition, the mass flux Q given by Equation (23) can be rewritten in the form:

$$Q = -\frac{\partial}{\partial t} \int_0^t C(t - \tau, X) Q_1(\tau) d\tau, \tag{24}$$

where

$$Q_1 = e^{-\Lambda t} \frac{\partial}{\partial t} \int_0^t e^{\Lambda \tau} Q_0(t - \tau) d\tau. \tag{25}$$

The proof of the derivation of Equation (24) can be found in the Appendix.

Substituting Equations (23) and (24) into Equation (9) leads to the following boundary value problem for C (i.e., concentration in the fracture):

$$\frac{\partial C}{\partial t} - \frac{1}{Pe} \frac{\partial^2 C}{\partial X^2} + \frac{\partial C}{\partial X} + \Lambda C = -\theta \frac{\partial}{\partial t} \int_0^t C(\tau, X) Q_1(t - \tau) d\tau, \quad 0 < X < \infty, t > 0, \tag{26}$$

$$t = 0, C = 0; \tag{27}$$

$$X = 0, C = C_0(t); \tag{28}$$

$$X \rightarrow \infty, C \rightarrow 0. \tag{29}$$

Equation (26) describes the majority of the transfer processes in the fracture and the specific feature of mass exchange between the fracture and the matrix. The derivation can be done by constructing the appropriate function $Q_1(t)$ in Equation (25).

Applying the technique of the group analysis of differential equations [31], the solution of the formulated boundary-value problem (18)–(21) can be obtained in the following form [23]:

$$u_0(\eta) = 1 - \frac{\sum_{m=0}^{M-1} \frac{(-1)^m \Gamma(\frac{\alpha}{\alpha+1} + m)}{\Gamma[(\alpha+1)(m+1)]} \eta^{\alpha+m(\alpha+1)}}{\Gamma[1/(\alpha+1)] \Gamma[\alpha/(\alpha+1)]} + O(\eta^{\alpha+M((\alpha+1))}), \tag{30}$$

where $\eta = Yt^{-\frac{1}{1+\alpha}}$. $\Gamma(z)$ is Gamma function. This expression follows from (2.17)–(2.32) in [23] at $\mu = 0$.

From Equation (30), it follows that

$$\frac{\partial^\alpha u_0}{\partial Y^\alpha} \Big|_{Y=0} = -\frac{1}{\Gamma(1-\beta)} t^{-\beta}, \tag{31}$$

where $\beta = \alpha/(\alpha+1)$. Accounting for Equations (22) and (31), Equation (25) leads to the following expression:

$$Q_1 = \frac{e^{-\Lambda t} t^{-\beta}}{\Gamma(1-\beta)} + \frac{\Lambda^\beta}{\Gamma(1-\beta)} [\Gamma(1-\beta) - \gamma(1-\beta, \Lambda t)], \tag{32}$$

where $\gamma(a, z)$ is an incomplete Gamma function. Equation (32) represents the mass flux on the wall of the fracture when $C_1 = 1$ on the fracture wall.

Let us consider particular cases. If Q_0 and Q_1 were 0, mass exchange does not occur at the fracture–matrix interface. Then, the problem is reduced to the problem in [12]. If no radioactive decay occurs (i.e., $\Lambda = 0$) and diffusion is Fickian (i.e., $\alpha = 1, \beta = 1/2$), $Q_1 = \frac{1}{\sqrt{\pi t}}$. According to the definition of the fractional derivative [28], Equation (24) can be written as $Q = \frac{\partial^{1/2} C}{\partial t^{1/2}}$. If no radioactive decay occurs (i.e., $\Lambda = 0$) but diffusion is described by the generalized Fick’s law (3) (i.e., $0 < \alpha < 1$ ($0 < \beta < 1/2$)), the mass fluxes can be given as $Q_1 = t^{-\beta}/\Gamma(1-\beta)$ and $Q = \frac{\partial^\beta C}{\partial t^\beta}$. When Λ is small and time is $t = O(1)$, formula (32) approaches the following asymptotic representation:

$$Q_1 = \frac{t^{-\beta}}{\Gamma(1-\beta)} - \frac{\Lambda t^{1-\beta}}{\Gamma(1-\beta)} \left[1 - \frac{\Gamma(1-\beta)}{\Gamma(2-\beta)} \right] + O(\Lambda^2 t^{2-\beta}). \tag{33}$$

The accuracy of this asymptotic formula can be easily verified by simple numerical computations. Our computations show that the difference between the values of Q_1 computed by Equations (32) and (33) is negligibly small within the relatively long time interval from 0 to $1/\Lambda$ and $\beta \geq 0.1$ [23]. Thus, Equation (33) can be used as a good approximation for Q_1 , the exact value of which is given by

Equation (32). Using formula (33), the mass flux Q defined by Equation (24) can be presented through the fractional derivatives:

$$Q = \frac{\partial^\beta C}{\partial t^\beta} - \Lambda \left[1 - \frac{\Gamma(1-\beta)}{\Gamma(2-\beta)} \right] (1-\beta) \frac{\partial^\beta}{\partial t^\beta} \int_0^t C(\tau, X) d\tau + O(\Lambda^2). \tag{34}$$

Let us turn to solution of the boundary value problem (26)–(29). In the case where $\Lambda = 0, \beta = 1/2$, and converting to originals, we obtain

$$C(T, X') = H(T - X') \operatorname{erfc} \left[\frac{X'}{2\sqrt{T - X'}} \right]. \tag{35}$$

Or, in the case where $\Lambda \neq 0, \beta = 1/2$, then

$$C(T, X') = \frac{e^{-\Lambda X'} H(T - X')}{2} \left(e^{-X' \sqrt{\Lambda}} \operatorname{erfc} \left[\frac{X'}{2\sqrt{T - X'}} - \sqrt{\Lambda(T - X')} \right] + e^{X' \sqrt{\Lambda}} \operatorname{erfc} \left[\frac{X'}{2\sqrt{T - X'}} + \sqrt{\Lambda(T - X')} \right] \right). \tag{36}$$

Equations (35) and (36) are well-known solutions in [12,14]. Solution (36) does not follow from (35), while solution (35) follows from (36) at $\Lambda = 0$.

The function Q_1 at the right hand side in Equation (26) is given by Equation (33). If the time range is from 0 to $1/\Lambda$ for Equation (26), it is convenient to rescale Equation (26) with new time variable $T = \Lambda t$. In this case, the new spatial variable should be defined as $X' = X(\Lambda + \theta \Lambda^\beta)$. With these new non-dimensional variables, Equation (26) can be presented in the following form:

$$w_1 \frac{\partial C}{\partial T} + \frac{\partial C}{\partial X'} - \epsilon \frac{\partial^2 C}{\partial X'^2} + C = -w_2 \frac{\partial}{\partial T} \int_0^T C(T - \tau, X') \Psi_\beta(\tau) d\tau, \tag{37}$$

where $w_1 = \frac{\Lambda}{\Lambda + \theta \Lambda^\beta}, w_2 = \frac{\theta \Lambda^\beta}{\Lambda + \theta \Lambda^\beta}, \epsilon = \frac{\Lambda + \theta \Lambda^\beta}{Pe}$, and $\Psi_\beta = Q_1 \Lambda^{-\beta} - 1$. Note that the expression for Ψ_β can be presented as $\Psi_\beta = [T^{-\beta} e^{-T} - \gamma(1 - \beta, T)] / \Gamma(1 - \beta)$, according to Equation (33). The third term at the left hand side in Equation (37) including ϵ describes diffusion in the fracture. Because $\Lambda \ll 1$ and $Pe = O(1)$, parameter ϵ in Equation (37) is small ($\epsilon \ll 1$). Hence, in major cases within time of the order of $1/\Lambda$, the effects of the diffusive transport in the fracture is negligible. Equation (37) can be rewritten as follows:

$$w_1 \frac{\partial C}{\partial T} + \frac{\partial C}{\partial X'} + C = -w_2 \frac{\partial}{\partial T} \int_0^T C(T - \tau, X') \Psi_\beta(\tau) d\tau. \tag{38}$$

Applying Laplace transformation \mathcal{L} with respect to time to the Equation (38), we obtain

$$\frac{d\bar{C}}{dX'} + (sw_1 + 1 + sw_2 \bar{\Psi}_\beta) \bar{C} = 0, \quad 0 < X' < \infty, \tag{39}$$

$$X' = 0, \quad \bar{C} = \bar{C}_0, \tag{40}$$

where $\bar{C} = \mathcal{L}[C], \bar{\Psi}_\beta = \mathcal{L}[\Psi_\beta]$. Substituting $\bar{\Psi}_\beta = [(s + 1)^\beta - 1] / s$ into Equation (39) and integrating it accounting for the boundary condition (40) yields

$$\bar{C} = \bar{C}_0 e^{-[(s+1)w_1 + (s+1)^\beta w_2] X'}. \tag{41}$$

3. Results

First, we consider the case where the concentration at the inlet is constant (i.e., $C_0 = 1$ and $\bar{C}_0 = 1/s$). For this case, let us describe the concentration as C_c . The inverse Laplace transformation leads to the following expression:

$$C_c(T, X') = L^{-1} \left[\frac{1}{s} \exp(-w_1 X') \exp(-sw_1 X') \exp(-w_2 X' (s + 1)^\beta) \right] = e^{-w_1 X'} H(T - w_1 X') G(T - w_1 X', X'), \tag{42}$$

where $H(z)$ is a Heaviside step function and

$$G(T, X') = L^{-1} \left[\frac{\exp(-w_2 X' (s+1)^\beta)}{s} \right] = e^{-w_2 X'} - \frac{1}{\pi} \int_0^\infty e^{-T(\xi+1)} \exp[-\zeta^\beta w_2 X' \cos(\pi\beta)] \sin[\zeta^\beta w_2 X' \sin(\pi\beta)] \frac{d\xi}{\xi+1}. \tag{43}$$

when concentration in the inlet is an arbitrary function of T (i.e., $C_0 = C_0(T)$), then concentration in the fracture can be obtained by utilizing Duhamel’s theorem [30]:

$$C(T, X') = \frac{\partial}{\partial T} \int_0^T C_0(T - \tau) C_c(\tau, X') d\tau, \tag{44}$$

where C_c is the concentration when the concentration at the inlet is constant, defined by Equation (42). If the radioactivity decays exponentially at the inlet, the boundary concentration and its Laplace form are given as $C_0 = e^{-T}$ and $\bar{C}_0 = 1/(s + 1)$. The solution C can be obtained by the inverse Laplace transform directly from Equation (41) as:

$$C(T, X') = L^{-1} \left[\frac{1}{s+1} \exp[-w_1 X' (s + 1)] \exp[-w_2 X' (s + 1)^\beta] \right] = e^{-T} H(T - w_1 X') G'(T - w_1 X', w_2 X'), \tag{45}$$

where

$$G'(T, X') = L^{-1} \left[\frac{1}{s} e^{-X' s^\beta} \right] = 1 - \frac{1}{\pi} \int_0^\infty \frac{e^{-\xi T}}{\xi} \exp[-X' \xi^\beta \cos(\pi\beta)] \sin[X' \xi^\beta \sin(\pi\beta)] d\xi. \tag{46}$$

The effects of the order of fractional derivatives on radioactive contaminant transportation are shown in Figures 2 and 3. Analytical solutions for the constant concentration at the inlet given by Equation (42) are plotted for different β in Figure 2a,b. The initial concentration is $C(T = 0, X') = 0$, and the boundary source concentration at $x = 0$ is $C_0 = 1$. As shown in Figure 2a, concentrations at far points from the inlet were larger for $\beta = 0.5$ than that for $\beta = 0.1$. For the case of larger β , contaminants are most likely to migrate through the fracture. In contrast, small β describes transport with longer delays, which derive from diffusion into the surrounding rocks or adsorption and desorption to the fracture walls. Thus, smaller β describes a longer memory effect.

The mass flux on the fracture–matrix interface in Equation (3) is taken account for the generalized Fick’s law with fractional spatial derivative, and does not describe the effect of temporal memory. However, since we deal with the mass flux on the fracture–matrix interface where the concentration of the transported contaminant significantly depends on time, it is physically obvious that the mass flux at the given moment of time depends not only on concentration at this moment of time, but also on how this concentration varied in the previous moment of time. This feature can be called the effect of temporal memory and mathematically described by the convolution integral in Equation (24). Equation (31) also explains that the generalized Fick’s law with fractional spatial derivative accounts for the memory effect. Incidentally, Equation (24) allows the mixed problems of calculating concentration on the fracture–matrix interface to be split into separate problems of calculating concentration in the matrix and calculating concentration in the fracture, respectively. The latter significantly simplifies the analysis of mass transport in the matrix–fracture system.

As shown in Figure 3a, concentration for constant boundary source approached certain values of concentration, which did not reach the injected concentration ($C_0 = 1$). We can see that larger β shows larger concentration at the late time, showing the phenomenon of longer memory as discussed above.

Analytical solutions for the time-dependent boundary sources given by Equation (45) are plotted for different β in Figures 2b and 3b. With the same conditions as above, the initial concentration is $C(T = 0, X') = 0$. The boundary source was set to time-dependent $C_0 = \exp(-T)$. Concentration at $x = 0$ was 1 for constant boundary source (Figure 2a), while concentration for time-dependent

boundary source started from 0.37 when $t = 1$ (Figure 2b). In the case of the time-dependent boundary source, concentrations decayed at the late time.

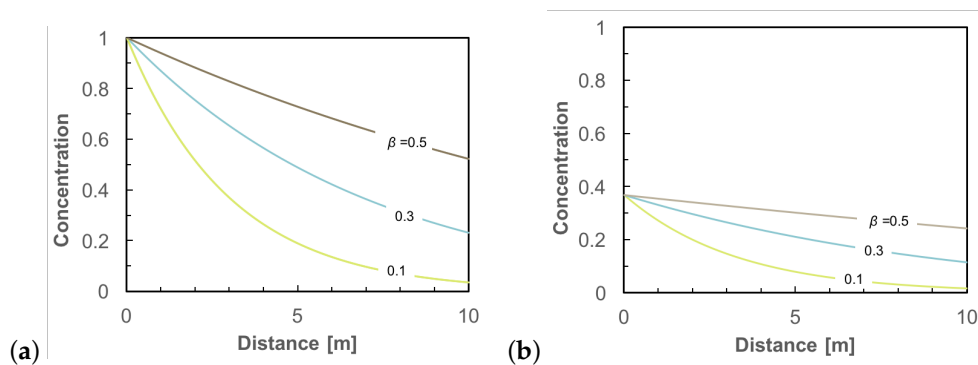


Figure 2. Effects of beta on spatial distribution at $t = 1$ with $\Lambda = 0.5$ and $\theta = 0.01$. (a) Constant boundary source concentration and (b) time-dependent boundary source concentration.

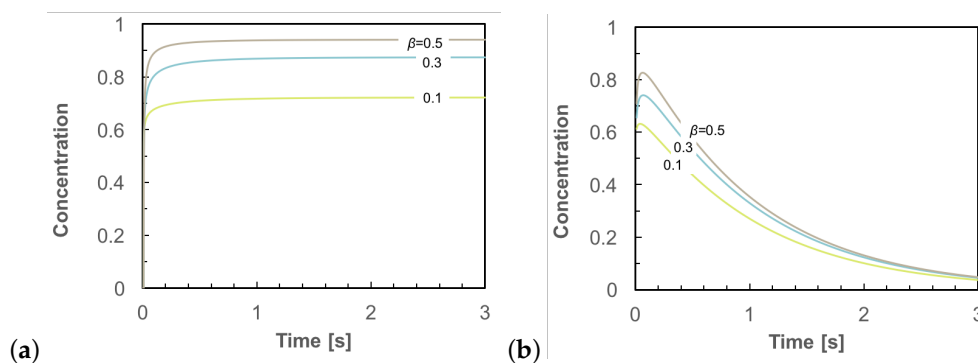


Figure 3. Effects of beta on time history at $x = 1$ with $\Lambda = 0.5$ and $\theta = 0.01$. (a) Constant boundary source concentration and (b) time-dependent boundary source concentration.

4. Conclusions

We derived the analytical solution of the boundary value problem (26)–(29) for radioactive contaminant transport through a fracture. By deriving the formula (24), This formula allows the mixed problems of calculating concentration on the fracture–matrix interface to be split into separate problems of calculating concentration in the matrix and calculating concentration in the fracture, respectively. The latter significantly simplifies the analysis of mass transport in the matrix–fracture system. When the solute concentration at the inlet is constant, the concentration in the fracture can be obtained by Equation (42). When the source boundary concentration at the inlet decays exponentially, the concentration in the fracture can be obtained by Equation (45). We plotted the analytical solutions for different values of β , which indicate that the value of β allows the evaluation of the residence time of contaminants in the aquifer. This analysis, based on the analytical solutions of fractional diffusion equation, can provide simple and quick results to evaluate solute transport in fractured rocks. Most of the cases where radioactive contaminants cause troubles would be in unexpected situations. At that time, the simple and quick analysis proposed by this research will help instant management strategies.

Acknowledgments: This work was supported by the Japan Society for the Promotion of Science, under Grant-in-Aid for Young Scientists(A)(717H049760), whose support is gratefully acknowledged.

Author Contributions: Sergei Fomin, Vladimir Chugunov, and Anna Suzuki contributed to the development of the mathematical model and derivation of the analytical solutions. Anna Suzuki and Toshiyuki Hashida solved numerically the analytical solutions, and Anna Suzuki wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

By substituting $t - \tau = \xi$ in the integral in Equation (23), the mass flux Q can be written in the form:

$$\begin{aligned} Q &= -e^{-\Lambda t} \frac{\partial}{\partial t} \int_0^t e^{\Lambda(t-\xi)} C(t-\xi, X) Q_0(\xi) d\xi \\ &= -\Lambda \int_0^t e^{-\Lambda\xi} C(t-\xi, X) Q_0(\xi) d\xi - \frac{\partial}{\partial t} \int_0^t e^{-\Lambda\xi} C(t-\xi, X) Q_0(\xi) d\xi \end{aligned} \quad (\text{A1})$$

This is equivalent to the mass flux Q on the left hand side in Equation (24). Now we consider the differentiation and the integration on the right hand side in Equation (24). Let's introduce the following function:

$$Q_1 = e^{-\Lambda t} \frac{\partial}{\partial t} \int_0^t e^{\Lambda\tau} Q_0(t-\tau) d\tau \quad (\text{A2})$$

In the same way as Q in Equation (A1), the function Q_1 is transformed as:

$$Q_1 = \Lambda \int_0^t e^{-\Lambda\xi} Q_0(\xi) d\xi + e^{-\Lambda t} Q_0(t) \quad (\text{A3})$$

By substituting function (A3), Equation (24) can be written in the form:

$$\begin{aligned} Q &= -\frac{\partial}{\partial t} \int_0^t C(t-\tau, X) Q_1(\tau) d\tau \\ &= -\frac{\partial}{\partial t} \int_0^t C(t-\tau, X) (\Lambda \int_0^t e^{-\Lambda\xi} Q_0(\xi) d\xi + e^{-\Lambda t} Q_0(t)) d\tau \\ &= -\frac{\partial}{\partial t} [\int_0^t C(t-\tau, X) e^{-\Lambda t} Q_0(t) d\tau] - \Lambda \frac{\partial}{\partial t} [\int_0^t C(\eta, X) (\int_0^{t-\eta} e^{-\Lambda\xi} Q_0(\xi) d\xi) d\tau] \\ &= -\frac{\partial}{\partial t} [\int_0^t C(t-\tau, X) e^{-\Lambda t} Q_0(t) d\tau] - \Lambda \int_0^t C(\eta, X) e^{-\Lambda(t-\eta)} Q_0(t-\eta) d\eta \\ &= -\Lambda \int_0^t e^{-\Lambda\xi} C(t-\xi, X) Q_0(\xi) d\xi - \frac{\partial}{\partial t} \int_0^t e^{-\Lambda\xi} C(t-\xi, X) Q_0(\xi) d\xi \end{aligned} \quad (\text{A4})$$

The latter expression in the right hand side in Equation (A4) is equivalent to the expression in Equation (A1). Thus, Equation (24) can be derived.

References

- Coats, K.; Smith, B.D. Dead-end pore volume and dispersion in porous media. *Soc. Petrol. Eng. J.* **1964**, *4*, 73–84.
- Long, J.C.S.; Remer, J.S.; Wilson, C.R.; Witherspoon, P.A. Porous media equivalents for network of discontinuous fractures. *Water Resour. Res.* **1982**, *18*, 645–658.
- Sahimi, M. Flow phenomena in rocks: From continuum models to fractals, percolation, cellular automata, and simulated annealing. *Rev. Mod. Phys.* **1993**, *65*, 1395–1534.
- Edery, Y.; Guadagnini, A.; Scher, H.; Berkowitz, B. Origins of anomalous transport in heterogeneous media: Structural and dynamic controls. *Water Resour. Res.* **2014**, *50*, 1490–1505.
- Hatano, Y.; Hatano, N. Dispersive transport of ions in column experiments: An explanation of long-tailed profiles. *Water Resour. Res.* **1998**, *34*, 1027–1033.
- Haggerty, R.; Wondzell, S.M.; Johnson, M.A. Power-law residence time distribution in the hyporheic zone of a 2nd-order mountain stream. *Geophys. Res. Lett.* **2002**, *29*, 1640.
- Radilla, G.; Sausse, J.; Sanjuan, B.; Fourar, M. Interpreting tracer tests in the enhanced geothermal system (EGS) of Soultz-sous-Forêts using the equivalent stratified medium approach. *Geothermics* **2012**, *44*, 43–51.
- Cardenas, M.B.; Slottke, D.T.; Ketcham, R.A.; Sharp, J.M., Jr. Navier-Stokes flow and transport simulations using real fractures shows heavy tailing due to eddies. *Geophys. Res. Lett.* **2007**, *34*, L14404.
- Hodgkinson, D.; Benabderrahmane, H.; Elert, M.; Hautojärvi, A.; Selroos, J.O.; Tanaka, Y.; Uchida, M. An overview of Task 6 of the Aspö Task Force: Modelling groundwater and solute transport: Improved understanding of radionuclide transport in fractured rock. *Hydrogeol. J.* **2009**, *17*, 1035–1049.
- Becker, M.W.; Shapiro, A.M. Interpreting tracer breakthrough tailing from different forced-gradient tracer experiment configurations in fractured bedrock. *Water Resour. Res.* **2003**, *39*, doi:10.1029/2001WR001190.

11. Tsang, Y.W. Study of alternative tracer tests in characterizing transport in fractured rocks. *Geophys. Res. Lett.* **1995**, *22*, 1421–1424.
12. Tang, D.H.; Frind, E.O.; Sudicky, E.A. Contaminant transport in fractured porous media: Analytical solution for a single fracture. *Water Resour. Res.* **1981**, *17*, 555–564.
13. Sudicky, E.; Frind, E. Contaminant transport in fractured porous media: Analytical solutions for a system of parallel fractures. *Water Resour. Res.* **1982**, *18*, 1634–1642.
14. Neretnieks, I. A note on fracture flow dispersion mechanisms in the ground. *Water Resour. Res.* **1983**, *19*, 364–370.
15. Becker, M.W.; Shapiro, A.M. Tracer transport in fractured crystalline rock: Evidence of nondiffusive breakthrough tailing. *Water Resour. Res.* **2000**, *36*, 1677–1686.
16. Yates, S.R. An analytical solution for one-dimensional transport in heterogeneous porous media. *Water Resour. Res.* **1990**, *26*, 2331–2338.
17. Haggerty, R.; Gorelick, S.M. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resour. Res.* **1995**, *31*, 2383–2400.
18. Berkowitz, B.; Cortis, A.; Dentz, M.; Scher, H. Modeling non-fickian transport in geological formations as a continuous time random walk. *Rev. Geophys.* **2006**, *44*, RG2003.
19. Benson, D.A.; Wheatcraft, S.S.W.; Meerschaert, M.M. Application of a fractional advection-dispersion equation. *Water Resour. Res.* **2000**, *36*, 1403–1412.
20. Morales-Casique, E.; Neuman, S.P.; Guadagnini, A. Non-local and localized analyses of non-reactive solute transport in bounded randomly heterogeneous porous media: Theoretical framework. *Adv. Water Resour.* **2006**, *29*, 1238–1255.
21. Schumer, R.; Meerschaert, M.M.; Baeumer, B. Fractional advection-dispersion equations for modeling transport at the Earth surface. *J. Geophys. Res. Earth Surf.* **2009**, *114*, doi:10.1029/2008JF001246.
22. Liu, F.; Anh, V.V.; Turner, I.; Zhuang, P. Time fractional advection-dispersion equation. *J. Appl. Math. Comput.* **2003**, *13*, 233–245.
23. Fomin, S.; Chugunov, V.; Hashida, T. The effect of non-Fickian diffusion into surrounding rocks on contaminant transport in a fractured porous aquifer. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **2005**, *461*, 2923–2939.
24. Suzuki, A.; Fomin, S.A.; Chugunov, V.A.; Niibori, Y.; Hashida, T. Fractional diffusion modeling of heat transfer in porous and fractured media. *Int. J. Heat Mass Transf.* **2016**, *103*, 611–618.
25. Zumofen, G.; Klafter, J. Scale-invariant motion in intermittent chaotic systems. *Phys. Rev. E* **1993**, *47*, 851–863.
26. Penttinen, L.; Siitari-kauppi, M.; Ikonen, J. *Forsmark Site Investigation Determination of Porosity and Micro Fracturing Using the C-PMMA Technique in Samples Taken from Forsmark Area*; Technical Report; Svensk Kärnbränslehantering AB: Stockholm, Sweden, 2006.
27. Fomin, S.A.; Chugunov, V.A.; Hashida, T. Non-Fickian mass transport in fractured porous media. *Adv. Water Resour.* **2011**, *34*, 205–214.
28. Samko, S.G.; Kilbas, A.A.; Marichev, O.I. *Fractional Integrals and Derivatives: Theory and Applications*; Gordon and Breach Science Publishers: Philadelphia, PA, USA, 1993. doi:10.1515/fca-2016-0032.
29. Grisak, G.; Pickens, J. An analytical solution for solute transport through fractured media with matrix diffusion. *J. Hydrol.* **1981**, *52*, 47–57.
30. Carslaw, H.S.; Jaeger, J.C. *Conduction of Heat in Solids*; Clarendon Press: Oxford, UK, 1959.
31. Ibragimov, N.H. *CRC Handbook of Lie Group Analysis of Differential Equations: Volume 2: Applications in Engineering and Physical Sciences*; CRC Press: Boca Raton, FL, USA, 1994.

