

디스크소스로부터 NAPL의 확산손실에 관한 수학적 모델

Mathematical Models on Diffusive Loss of Non-Aqueous Phase Organic Solvents from a Disk Source

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ABSTRACT

Matrix diffusion from planar fractures was studied mathematically and through physical model experiments. Mathematical models were developed to simulate diffusion from 2D and 3D instantaneous disk sources and a 3 D continuous disk source. The models were based on analytical solutions previously developed by Carslaw and Jaeger (1959). The mathematical simulations indicated that the 2D scenario produces significantly different results from the 3D scenario, the time for mass disappearance is significantly larger for continuous sources than for instantaneous sources, the normalized concentration generally decreased over time for instantaneous sources while it increased over time for continuous sources, diffusion rates decrease significantly over time and space, and the normalized mass loss from the source zone never reaches 1 for continuous sources due to the semi-infinite integral. The simulations also showed that disappearance times increase exponentially with increasing source radii and matrix porosity, and decrease with increasing aqueous-phase NAPL solubilities.

Key words : Fracture, Matrix diffusion, Disk source, Mathematical model, NAPL

요 약 문

평평한 fractures에서 공극을 가진 모암으로의 NAPL 확산을 수치적인 방법으로 해석하였다. 2D와 3D에 대한 일회성 디스크 소스와 3D 연속 디스크소스에 대한 모델은 Caralaw and Jaeger(1959)의 이론을 바탕으로 개발하였다. 3D 연속 디스크소스에 대해 공극모암으로 확산되는 NAPL의 총량을 계산할 수 없기 때문에 확산이 반구형으로 이루어진다고 가정하여 등농도선의 합을 이용하여 공극모암으로 확산되는 NAPL의 총량을 계산하였다. 수치적 계산에 따르면 2D 대비 3D의 경우에 NAPL 손실 시간이 현저히 빠른 것으로 나타났으며, 디스크 소스의 중심점에서 normalized된 농도는 일회성 디스크 소스는 시간에 따라 감소하고, 연속 디스크 소스는 증가하는 것으로 나타났으며, 시간과 공간에 따라 확산율은 감소하는 것으로 나타났다. 그리고 NAPL의 mass 손실은 1에 도달하지 못하였으며, 이는 연속 디스크 소스를 semi-infinite로 가정하고 적분했기 때문이다. 확산에 의해 사라지는 시간은 소스의 크기 및 모암 공극률 크기 증가에 비례해서 지수함수적으로 증가하고, 반면 NAPL의 용해성이 증가하면 감소하는 것으로 나타났다.

주제어 : 공극모암, 확산, 디스크 소스, 수치모델, NAPL,

1. Introduction

Historically, the term “NAPL (*non-Aqueous Phase Liquid*)”

was first coined in 1981 (Pankow and Cherry, 1996). A black and denser-than-water, immiscible organic liquid was discovered in the soil and bedrock during studies

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of a hazardous waste landfill in Niagara Falls, New York (Pankow and Cherry, 1996). Although the groundwater community had become aware of the presence of NAPL in soil and groundwater environments by 1981, they did not know how much existed, or how to remediate the dissolved chlorinated solvents located in the subsurface environments until the late 1980s.

Many kinds of petroleum products and chlorinated solvents were produced after the industrial revolution of the late nineteenth century. Chlorinated solvents were first produced in Europe in the nineteenth century, and production of these chemicals began in the early twentieth century in the United States (Pankow and Cherry, 1996). Carbon tetrachloride (CTC), the first chlorinated solvent, was generally used as dry cleaning and spot-removing agent in the late nineteenth century, and at that time it was imported from Germany into the United States (Doherty, 2000). After the use of CTC as a dry-cleaning solvent, perchloroethylene (PCE) and trichloroethylene (TCE) also became widely used in Europe and the United States. The decline in the use of these substances in the following years was mainly due to increased evidence of toxicity, recognition of the risk to human health, and the advent of environmental regulations. In spite of the widespread use of chlorinated solvents, their presence in soil and groundwater went largely unrecognized until the late 1970s. Kueper et al. (2003) explained that the primary reason for this lack of recognition by the research community was the lack of availability of analytical methods and equipment for detecting low concentrations of chlorinated solvents in groundwater. Since the recognition of the existence of NAPL source zones in subsurface systems, a significant body of research has focused on DNAPL migration and its subsequent fate in subsurface environments (e.g., multiphase flow, entrapment, dissolution and matrix diffusion of DNAPLs) (e.g., Abriola and Pinder, 1985, 1995; Smith and Gillham, 1999; Silliman et al., 2001; Dickson and Thomson, 2003; Feenstra, 1984; Cherry, 1984; Miller, 1984; Eckberg and Sunada, 1984; Parker et al., 1994, 1997). These investigations have employed laboratory investigations, field experiments, and mathematical models.

In terms of the remediation technology, several researches have indicated that it is extremely difficult to remediate DNAPL sites, particularly in highly heterogeneous environments such as fracture systems. (e.g., Parker et al., 1994; Keuper et al., 2003). In the absence of remedial strategies, the dissolution and subsequent diffusion mechanisms will remove trapped DNAPL from fractured environments. The first studies concerning DNAPL disappearance in fractures were performed by Parker et al. (1994, 1997). They developed analytical solutions, in one and three dimensions respectively, to solve for NAPL disappearance time in fractured environments. An analytical solution for 1-D diffusion of an aqueous phase mass from a planar fracture surface into the pore water of the matrix was used to calculate DNAPL disappearance times for single component NAPL (Parker et al., 1994).

The goal of this study was to further the understanding of diffusive loss of NAPLs in fractured media through computer simulations of the dissolution and subsequent diffusion mechanisms. To achieve this goal, several specific research objectives were defined: establish mathematical models for diffusion from instantaneous and continuous disk sources in 2D and 3D; compare the analytical solutions for the instantaneous and continuous disk source cases in both 2D and 3D; and conduct physical model experiments, which are discussed in the next paper, to quantify matrix diffusion in fractures.

2. Mathematical Model Development

The basic assumptions of this work are that the porous medium is homogeneous, isotropic, and saturated with distilled water, and that diffusion conditions are such that Fick's 2nd law is valid. The mathematical theory of diffusion in isotropic substances is based on the hypothesis that the rate of transfer through a unit area is proportional to the chemical potential measured normal to the section, and is expressed by Fick's first law. as follows:

$$F_{Di} = -\phi_m D_e \left(\frac{\partial C_w}{\partial x_i} \right) \quad (1)$$

where F_{Di} [M/L²/T] is the mass flux of the solute,
 ϕ_m [-] is the matrix porosity,
 D_e [L²/T] is the effective diffusion coefficient,
 C_w [M/L³] is the solute concentration, and
 x [L] is the distance over which diffusion is occurring.

ϕ_m is defined as the ratio of the volume of the voids (V_v) [L³] to the total volume of the matrix (V). D_e is a function of the free-solution diffusion coefficient (D_d), and the tortuosity factor τ ($0 < \tau < 1$), which accounts for the effect of the tortuous pathway due to the presence of the porous matrix ($D_e = D_d \times \tau$) (Bear, 1972). Fick's second law of cylindrical coordinates applies to systems where the concentration is changing with time as follows:

$$\frac{\partial C_w}{\partial t} = 1 \left\{ \frac{\partial}{\partial r} \left(r \frac{D_e}{R} \frac{\partial C_w}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\frac{1}{R} \frac{D_e}{R} \frac{\partial C_w}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(r \frac{D_e}{R} \frac{\partial C_w}{\partial z} \right) \right\} \quad (2)$$

where R [-] represents the retardation factor. If diffusion occurs on the surface of a circular cylinder whose axis coincides with the z axis, and the initial and boundary conditions are independent of the coordinates θ and z , the concentration will be a function of r and t only, and equation (2) reduces to

$$\frac{\partial C_w}{\partial t} = \frac{D_e}{R} \left[\frac{\partial^2 C_w}{\partial r^2} + \frac{1}{r} \left(\frac{\partial C_w}{\partial r} \right) \right] \quad (3)$$

Equation (3) describes a 2-dimensional disk source. When the initial and boundary conditions are independent of θ alone, the flow of solute takes place in planes through both the vertical and horizontal axes, and the diffusion equation becomes:

$$\frac{\partial C_w}{\partial t} = \frac{D_e}{R} \left[\frac{\partial^2 C_w}{\partial r^2} + \frac{1}{r} \left(\frac{\partial C_w}{\partial r} \right) + \frac{\partial C_w}{\partial z^2} \right] \quad (4)$$

Equation (4) describes 3-dimensional instantaneous and continuous disk sources.

2.1. Analytical solution development: Instantaneous disk source in 2D

Equation (3) represents a 2D instantaneous disk source in porous media with a constant diffusion coefficient. In this case, solute migration occurs in a

plane perpendicular to the z -axis, and the migration lines are radial. The initial and boundary condition are given by

$$C(r, t) = Sw, \quad r \leq a, \quad t = 0 \quad (5a)$$

$$C(r, t) = 0, \quad r > a, \quad t = 0 \quad (5b)$$

$$C(\infty, t) = 0, \quad t \geq 0 \quad (5c)$$

where a [L] represents the radius of the disk source, and Sw [M/L³] represents the aqueous phase solubility. Crank (1956) developed the following analytical solution to equation (3) with boundary conditions given by 5:

$$C(r, t) = \frac{C_o R}{2D_e t} e^{-r^2 R/4D_e t} \int_0^a e^{-r'^2 R/4D_e t} I_0 \left(\frac{R r r'}{2D_e t} \right) r' dr' \quad (6)$$

The integral in equation (6) must be evaluated numerically except on the axis $r = 0$, where equation (6) becomes:

$$\begin{aligned} C(0, t) &= \frac{C_o R}{2D_e t} e^{-r^2 R/4D_e t} \left[(2D_e t/R) \times (1 - e^{-a^2 R/4D_e t}) \right] \\ &= C_o \left(1 - e^{-a^2 R/4D_e t} \right) \end{aligned} \quad (7)$$

The total mass diffused into the porous media at any time t is numerically calculated using the relationships between the initial mass (M_0) in the instantaneous disk source and the remaining mass ($Q(t)$) in the disk source region ($r \leq a$) at any time $t > 0$. Therefore the total mass diffused is calculated using the concentration profile in the source zone ($r \leq a$) at any selected time t .

$$M_D(t) = M_0 - Q(t) = \{ 1 - (Q(t)/M_0) \times M_0 \} (r \leq a) \quad (8)$$

2.2. Analytical solution development: Instantaneous disk source in 3D

Carslaw and Jaeger (1959) developed an analytical solution for diffusion from an instantaneous disk source in 3D with the following initial and boundary conditions:

$$C(r, z, t) = Sw, \quad r \leq a, \quad t = 0, \quad z = 0 \quad (9a)$$

$$C(r, z, t) = 0, \quad r > a, \quad t = 0, \quad z = 0 \quad (9b)$$

$$C(r, z, t) = 0, \quad z > 0, \quad t = 0 \quad (9c)$$

$$C(\infty, \infty, t) = 0, \quad t \geq 0 \quad (9d)$$

Analytical solutions for a 3D Instantaneous disk source are as follows;

$$C(r, z, t) = \frac{q(R^3)^{1/2}}{4(\pi D_e^3 t^3)^{1/2}} \int_0^a e^{-R(r^2+z^2+r'^2)/4D_e t} I_0\left(\frac{Rr r'}{2D_e t}\right) r' dr' \quad (10)$$

Therefore, at $r=0$ equation (10) becomes

$$C(0, z, t) = \frac{q(R)^{1/2}}{2(\pi D_e t)^{1/2}} \left(1 - e^{-a^2 R/4D_e t}\right) e^{-z^2 R/4D_e t} \quad (11)$$

The solution to the system of equations (10) can be obtained for case-specific initial and boundary conditions. Therefore, the concentration at the disk-source is initially constant and equal to the aqueous solubility, S_w ($C=S_w$ at $r \leq a, z=0, t=0$), and the initial aqueous concentration in the matrix pore water is zero ($C(r, z, t)=0$ at $r>a$) (Carslaw and Jaeger, 1959). The total mass diffused into the porous media at any selected time ($M_D(t)$) is calculated as follows:

$$M_D(t) = \left\{ 1 - \left(\pi a^2 C_0 - \left(\sum_{r=a}^0 \pi r^2 \Delta C / \pi a^2 C_0 \right) \right) \right\} \pi a^2 C_0 \quad (r \leq a) \quad (12)$$

2.3. Analytical solution development: Continuous disk source in 3D

The assumptions used in the development of the solution are the same as those used for the instantaneous disk source in 3D. The following initial and boundary conditions were used to describe the continuous disk source for the development of the solution:

$$-K \frac{\partial C(r, 0, t)}{\partial z} \begin{cases} q \text{ for } 0 < r < a \\ 0 \text{ for } r > a \end{cases} \quad (13a)$$

$$C(r, z, t) = 0, \quad r \rightarrow \infty \text{ and } z \rightarrow \infty \quad (13b)$$

$$C(r, z, t) = 0 \quad z > 0, \quad r > a \quad (13c)$$

Where K is the hydraulic conductivity, and has the same value in all directions due to the assumption of assumed media. The exact solution is given by Carslaw and Jaeger (1959):

$$\frac{C(r, z, t)}{q a / K} = \frac{1}{2} \int_0^\infty J_0(\lambda r) J_1(\lambda a) \times \left\{ e^{-\lambda z} \operatorname{erfc} \left[\frac{z}{2(D_e t)^{1/2}} - \lambda((D_e t)^{1/2}) \right] \right\} d\lambda$$

$$e^{-\lambda z} \operatorname{erfc} \left[\frac{z}{2(D_e t)^{1/2}} - \lambda((D_e t)^{1/2}) \right] \frac{d\lambda}{\lambda} \quad (14)$$

Equation (14) is valid for all r , and for z greater than zero. At $z=0$, equation (14) reduces to:

$$\frac{C(r, z, t)}{q a / K} = \int_0^\infty \operatorname{erfc} [\lambda(D_e t)^{1/2}] \frac{J_0(\lambda r) J_1(\lambda a)}{\lambda} d\lambda \quad (15)$$

Equation (15) is too difficult to evaluate numerically. For convenience, it can be rewritten in dimensionless form with the following variables:

$$r^+ = \frac{r}{a} \quad z^+ = \frac{z}{a}, \quad \lambda^+ = \lambda a, \quad t^+ = \frac{D_e t}{a^2}, \quad C^+(r^+, z^+, t^+) = \frac{C(r, z, t)}{q a / K}$$

James (1981) stated that equation (15) is not valid for all times and locations within the system, and developed a series solution to equation (14), with initial and boundary conditions given by equation (13) for all z at $r=0$:

$$C(0, z, t) = 2t^{1/2} \left[\operatorname{ierfc} \left(\frac{z}{2t^{1/2}} \right) - \operatorname{ierfc} \left(\frac{z^2+1}{2t^{1/2}} \right) \right] \quad (16)$$

as well as a series solution for all r at $z=0$:

$$C(r, 0, t) = C(r, 0, \infty) - \frac{1}{2\sqrt{\pi t}} \times \left\{ 1 - \frac{1+2r^2}{24t} + \frac{1}{480t^2} (1+6r^2+3r^4) - \frac{1}{1075t^3} (1+12r^2+18r^4+4r^6) + \dots \right\} \quad (17)$$

In general, the total mass diffused into the porous media at any selected time t can be calculated by the integration of the concentration for r and z directions as given by equation (18). In this study, the total mass diffused into the porous media was calculated by the summation of the iso-concentration lines, which were assumed to be a semi-spherical shape, and subsequent multiplication of the concentrations (equation 19).

$$M_D(t) = \phi_m \int_{-\infty}^\infty \int_{-\infty}^\infty C(r, z, t) dr dz \quad (18)$$

$$= \phi_m \sum_0^t \left[\left\{ \frac{1}{2} \pi r_1^2 b_1 \times C_1 \right\} + \left\{ \left(\frac{1}{2} \pi r_2^2 b_2 - \frac{1}{2} \pi r_1^2 b_1 \right) \times C_2 \right\} + \dots + \left\{ \left(\frac{1}{2} \pi r_n^2 b_n - \frac{1}{2} \pi r_{n-1}^2 b_{n-1} \right) \times C_n \right\} \right] \quad (19)$$

Table 1. Values assigned to variables for computational purposes

Variable	Symbol	Units	Value	Representative Compound
Effective diffusion coefficient	D_e	cm ² /sec	0.96×10^{-5} *	n-Butanol
Water solubility	S_w	g/L	63.2**	n-Butanol
Radius of sample	r	cm	Infinity	N/A
Radius of disk source	a	cm	1.0	N/A
Time	T	days	30	N/A
Initial concentration	C_o	mg/L	63,200	N/A
Retardation factor	R	–	1.0	Silica flour
Matrix porosity	ϕ_m	–	1.0	N/A

* McCall et al., (1959) ** P.H. Howard and W.M. Meylan (1997)

3. Results and Discussion

For computational purposes, typical values were assigned to the variables listed in Table 1. These values were held constant between all three scenarios for comparison purposes.

3.1. Comparison of the computational results from a 2D and 3D instantaneous disk source

Equation (10) indicates that the concentration at a given point and time is directly proportional to the radius of disk source (a), the mass flux (q), and the retardation factor (R), and indirectly proportion to the effective diffusion coefficient (De). For consistency and comparison purposes, the computations in this section will use the values assigned to De , S_w , r , C_o , ϕ_m and a in Table 1.

Fig. 1 represents normalized concentration profiles as a function of dimensionless distance for both 2D and 3D instantaneous disk sources with boundary conditions given by equation (5) and (9) respectively, at $z=0$ and various dimensionless times. The relative concentration at $r=0$ and $(D_e t/a^2)^{1/2} = 1$ for the 3D instantaneous case approached 0.02, which is more than an order of magnitude lower than for the 2D instantaneous disk source (0.22). This reinforces the fact that vertical diffusion is significant.

The total mass diffused into the porous matrix for the two cases presented in Fig. 1 is shown in Fig. 2 as a function of time. The relative mass diffused approached 1 far earlier for the 3D instantaneous disk source than for the 2D instantaneous disk source,

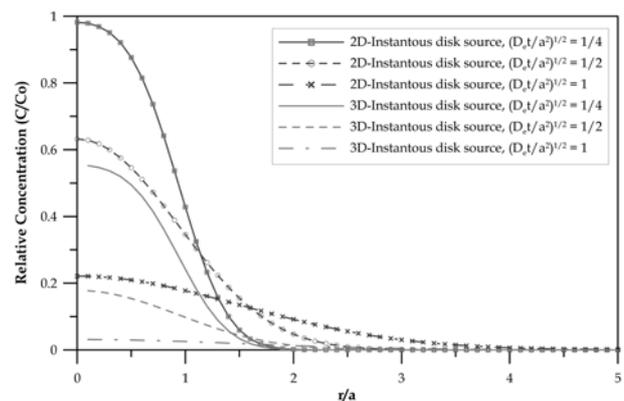


Fig. 1. Concentration distributions for instantaneous disk sources in 2D and 3D, with variable values listed in Table 1.

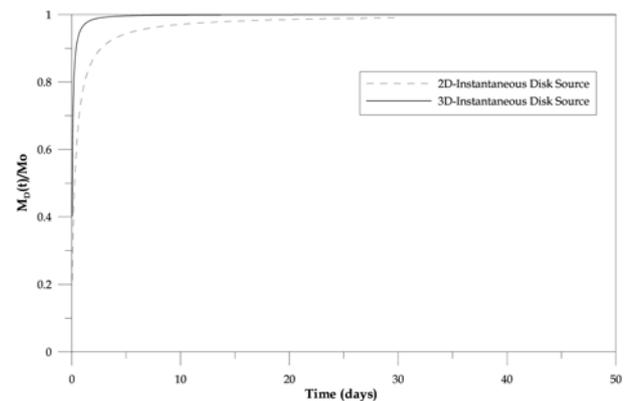


Fig. 2. The relative mass diffusing into the porous matrix for the 2D and 3D instantaneous disk sources.

indicating that the solute diffused away from the source zone much more quickly in the 3D case than in the 2D case. Again, this is due to the fact that vertical dispersion is significant, as it represents a significant increase in the area for which the chemical potential is large at early times.

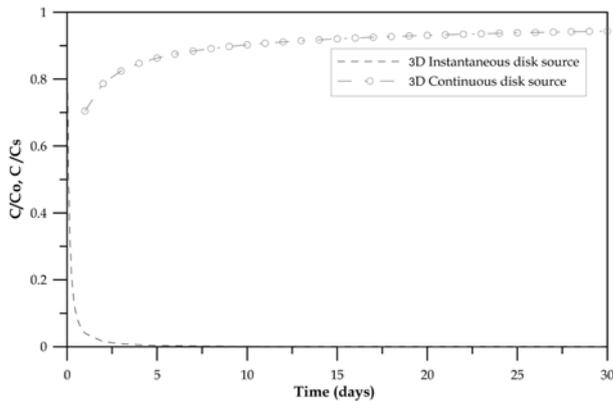


Fig. 3. Comparison of the relative concentration as a function of time for the 3D instantaneous and 3D continuous disk source solutions at $r = 0$ and $z = 0$.

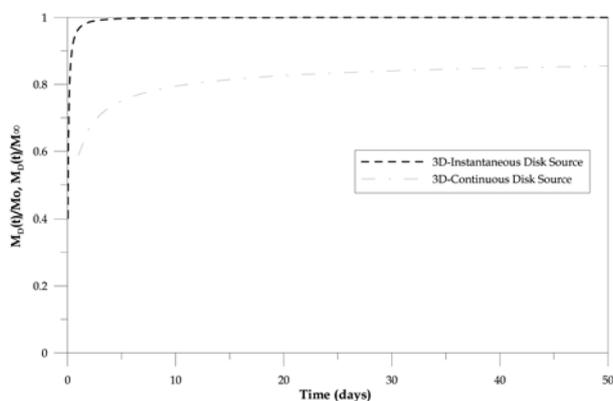


Fig. 4. Comparison of cumulative normalized mass diffused from 3D instantaneous and continuous disk sources as a function of time.

3.2. Comparison of the 3D instantaneous and Continuous Disk Source Solutions

For comparison purposes, the values of the parameters listed in Table 1 remained constant between all computations.

Fig. 3 compares the 3D instantaneous and continuous solutions in terms of relative concentration as a function of time at $r = 0$ and $z = 0$. The normalized concentration decreases over time for the instantaneous source and increases over time for the continuous source. The normalized concentration asymptotically approaches one in the continuous case, but never reaches it. Additionally, the rate of diffusion decreases more sharply in the continuous case. This is due to the fact that the chemical potential decreases more quickly in this case because of the constant concentration in the source zone.

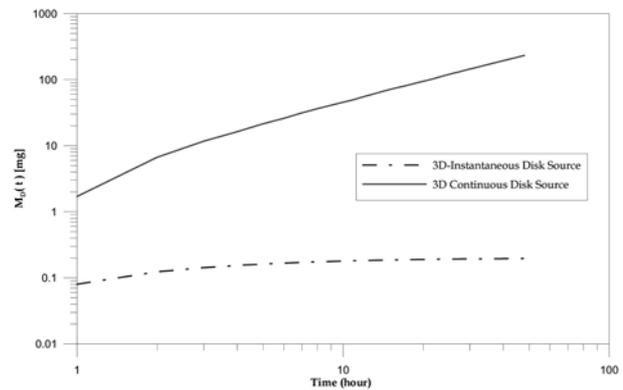


Fig. 5. Comparison of mass diffused as a function of time for 3D instantaneous and continuous disk sources.

Fig. 4 compares the normalized cumulative mass diffused away from 3D instantaneous and continuous disk sources as a function of time. The normalized mass diffused approached 1 at approximately 50 days for the instantaneous case, however, it is only approximately 0.8 at this same time, and will never reach 1, for the continuous case.

A comparison of the actual mass diffused into the porous matrix in the 3D instantaneous and continuous cases is shown in Fig. 5. The main difference between the instantaneous and continuous disk sources is the shape of the curves with respect to time. The instantaneous disk source curve is exponential whereas the continuous disk source curve varies linearly with time.

3.3. Parameter sensitivity analysis

The purpose of parameter sensitivity analysis is to evaluate the disappearance time, which is important to make remediation strategies in accordance to the radius of the disk source, chemical properties, and geologic media. As indicated by equation (12) for a 3D instantaneous disk source and equation (19) for a 3D continuous disk source, the mass loss from a source zone to the matrix is directly proportional to the matrix porosity (ϕ_m), the aqueous solubility (S_w), the radius of disk source (a), and the time (t) allowed for the diffusion mechanism to take place; it is inversely proportional to the retardation factor (R). In general, the determination of the sensitivity of the mass loss to each of these parameters is difficult. This is due to the

Table 2. Chemical properties for selected organic compounds used for diffusive mass loss calculations

Chemical	Molecular formula	S_w^1 mg/l	K_{oc} Cm ³ /g	ρ^1 g/cm ³	Do^2 Cm ² /sec
TCE	C ₂ HCl ₃	1,420 ³	92 ⁴	1.46	10.1E-06
DCM	CH ₂ Cl ₂	20,000	11 ⁴	1.33	12.4E-06
PCE	C ₂ Cl ₄	240 ³	380 ⁴	1.63	9.4E-06
1,2,4-TCB	C ₂ H ₃ Cl ₃	30 ⁵	3,200 ⁴	1.46 ⁵	5.3E-06

Source : ¹Schwille (1988), ²Bonoli and Witherspoon (1968) for 20°C, ³Broholm et al., (1992) for 23~24°C, ⁴Schwarzenbach et al., (1993) ⁵Mercer and Cohen (1990).

Table 3. Characteristics of various geologic media

Parameter	Clay ¹	Shale / Sandstone ²	Granite ³
Porosity : ϕ	0.35	0.10	0.006
Bulk density : ρ_b (g/cm ³)	1.6	2.4	2.63
Fraction organic carbon : f_{oc}	0.01	0.002	0
Apparent tortuosity : τ	0.33	0.10	0.06
Combined parameters : TCE & geologic media			
Effective diffusion coefficient : De (cm ² /s)	3.3E-06	1.0E-06	6.0E-07
Retardation factor : R	5.2	3.2	1

¹ Johnson et al. (1989) ² Feenstra et al., (1984); Barone et al., (1990) ³ Skagius and Neretnieks (1986)

fact that the physical properties of both the solute and matrix are not independent of one another. For the purpose of this sensitivity analysis, ranges in parameter values were chosen to be the same as those used by Parker et al., (1994). Trichloroethene (TCE), tetrachloroethene (PCE), 1,2,4-trichlorobenzene (TCB) and dichloromethane (DCM) were chosen as the NAPL; its physical properties are given in Table 2. The ranges of physical parameters chosen for the porous media are given in Table 3. This sensitivity analysis focuses on the effect of the radius of disk source and the matrix porosity.

3.3.1 Sensitivity of disappearance time to the radius of the disk source and chemical properties

Much research has been performed using simplified fractured porous media, which is assumed to be smooth walled. (Parker, 1994, 1997, Grisak et al., 1980, 1981). This assumption makes it easier to evaluate the diffusive mass loss from source zones. Both the fracture aperture and the diameter of the disk source play similar and important roles in NAPL disappearance time.

Table 4 and Fig. 6 show the disappearance time for three geologic media for a 3D instantaneous disk source. To simplify the analysis, the value of R was set to 1 in these simulations. The end point, or disappearance time, was assume to be when $I - Q(t)/$

Table 4. Effect of the radius of an instantaneous disk source on TCE disappearance time for types of geologic media

Radius of disk source (cm)	Disappearance Time (Days)		
	Clay	Shale	Granite
1	87	122	27
10	403	575	143
100	1873	2687	680
1000	8694	12440	3174

Mo equaled 0.9999. Alternatively, it can be interpreted as the point when 0.01% of the initial mass remains in the source zone. Table 4 and Fig. 6 clearly show that disappearance time increases significantly with the size of the source zone. NAPL loss from a 3D instantaneous disk source is in the order of the shale/sandstone > clay > granite. These results clearly show that the radius of disk source also plays an important role in NAPL disappearance times, which increase exponentially as the radius increases. Therefore, the larger the disk source, the longer the time required for NAPL disappearance to occur.

Fig. 7 shows disappearance times for four chemicals in clay materials with no sorption from a continuous disk source. In general, the disappearance time increases with the radius of disk source, and the order of disappearance time is DCM < TCE < PCE < TCB for the same size of the disk source. Fig. 7 also shows that disappearance times are significantly larger for

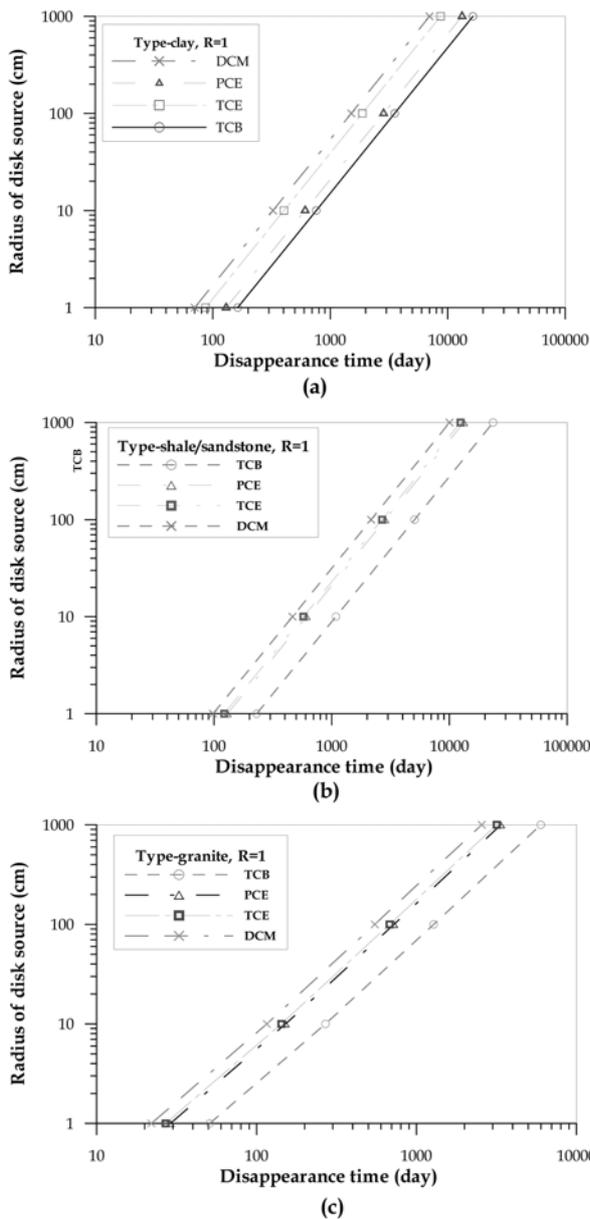


Fig. 6. NAPL disappearance times expressed in terms of the radius of disk source for a 3D instantaneous disk source with (a) a clay matrix ($R = 1$), (b) a shale/sandstone matrix ($R = 1$), and (c) a granite matrix ($R = 1$).

continuous disk sources than for instantaneous disk sources, all other conditions held equal.

3.3.2 Sensitivity of disappearance times to matrix porosity (ϕ_m)

Porosity is defined as the ratio of the volume of voids to the total volume of the media present. The diffusive loss from the disk source is directly

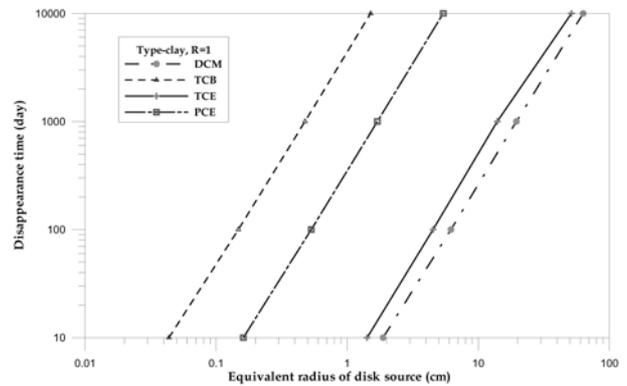


Fig. 7. NAPL disappearance times for a 3D continuous disk source for four chemicals expressed in terms of equivalent radius of disk source.

Table 5. Effect of the matrix porosity on TCE disappearance time for the four different chemicals

Matrix porosity (ϕ_m)	Disappearance Time (Days)			
	TCE	DCM	PCE	PCB
0.001	5	4	5	9
0.01	38	31	41	71
0.1	192	155	204	362
0.3	404	325	430	761
0.5	569	458	606	1073

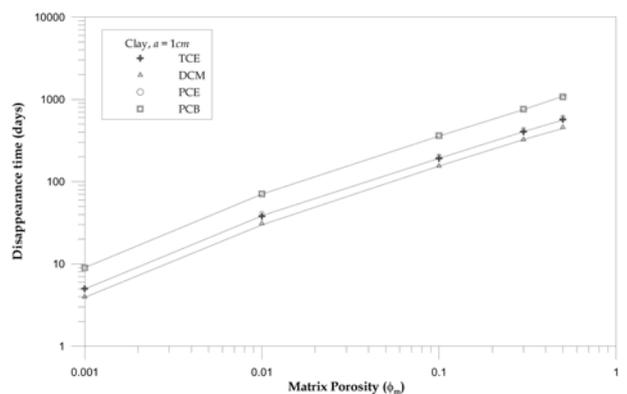


Fig. 8. Effect of matrix porosity on the rate of DNAPL disappearance for a 3D instantaneous disk source with no sorption ($R = 1$).

proportional to the matrix porosity. Additionally, the matrix porosity has an indirect effect on the retardation factor (Parker et al., 1994).

To evaluate the disappearance time the four chemicals, the value of $(I - Q(t)/M_0)$ were calculated using (12) for a 3D instantaneous disk source. The computational results are summarized in Table 5 and Fig. 8 for 3D instantaneous disk source. For the same

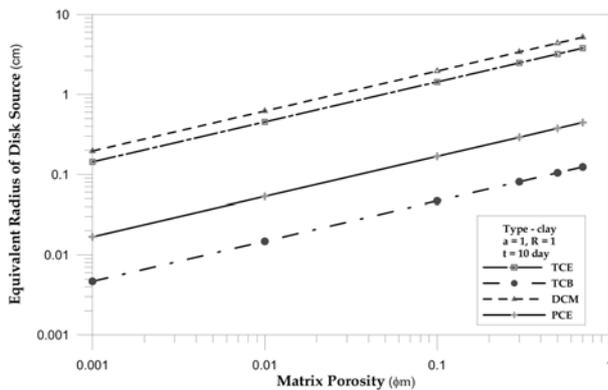


Fig. 9. Effect of matrix porosity on NAPL disappearance time expressed as equivalent radius of a continuous disk source for a clay matrix with no sorption ($R = 1$) at $t = 10$ days.

value of porosity, for instance, the disappearance time for TCE is 38 days, 31 days for DCM, 41 days for PCE, and 71 days for PCB for a instantaneous disk source. Fig. 9 shows the effects of matrix porosity on NAPL disappearance times from a 3D continuous disk source expressed as equivalent radius of disk source for four chemical compounds. It is clear that the order of NAPL disappearance is $DCM < TCE < PCE < TCB$ for the same matrix porosity.

4. Conclusions

This study focused on the understanding of diffusive loss of NAPLs in fractured media through mathematical models. The results of the simulations of the 2D and 3D instantaneous disk sources, and the 3D continuous disk source indicate the following:

- 1) the 2D approach yields significantly different results from the 3D approach; therefore a 3D modeling approach must be employed to obtain realistic results on natural conditions because matrix diffusion takes place in planes through both the vertical and horizontal axes;
- 2) the rate of n-butanol loss is significantly larger for instantaneous sources than for continuous sources;
- 3) the normalized concentration decreased over time for the instantaneous disk source, while it increased continuously and asymptotically approached 1 for the continuous disk source;

4) in both the continuous and instantaneous cases, the diffusion rate decreased over time and space due to the decreasing chemical potential;

5) the normalized mass loss from the source zone approached 1 relatively quickly for the instantaneous disk source, however can never reach 1 for the continuous source due to the semi-infinite domain;

6) the sensitivity analysis indicated that disappearance time increased exponentially with increasing disk source radii and matrix porosity, and decreased with increasing aqueous-phase NAPL solubility;

7) The disappearance time of 3D instantaneous disk source on TCE for the 1cm of the disk source are 1,873 days, 2,687 days, 680 days for clay, shale, granite, respectively; and

8) For the same value of porosity ($\phi_m = 0.1$), the disappearance time for TCE is 192 days, 155 days for DCM, 204 days for PCE, and 362 days for 3D instantaneous disk source of 1cm. This means that the time for the disappearance in natural conditions is much longer than expected.

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