Volatilization of Non-Aqueous Phase Liquid in Porous Media: Vapor Phase Mass Transfer Characteristics

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Abstract

Interphase mass transfer is an important process that dominates overall transport processes in multi-fluid system in porous media. This process plays a key role during the volatilization of non-aqueous phase liquids (NAPLs) in porous media that usually takes place during the remediation process of volatile organic compounds (VOCs) using soil vapor extraction (SVE) technique. Previously, interphase mass transfer coefficient was usually lumped together with interfacial area between air and liquid because of inaccessibility to quantify the interfacial area due to the heterogeneous nature of the pore structure of the media and the morphology of the fluid distribution. An effort was made to estimate the air-liquid interfacial area in three glass beads media using surfactant adsorption concept and was found decreasing with increasing liquid saturation. A series of one-dimensional NAPL volatilization experiments were carried out in a horizontal column for the same three-glass beads media using Toluene as the contaminant. Experiments were conducted for NAPL saturation range of 13.8~71% and a pore gas velocity of 0.1~2 cm/s and lumped mass transfer coefficients were evaluated. Actual vapor phase mass transfer coefficients were calculated using corresponding air-liquid interfacial area for a specific NAPL saturation and was characterized in dimensionless form for all the porous media used in the study. Results showed that the vapor phase mass transfer coefficient increases with increasing pore gas velocity and grain size but decreases with increasing NAPL saturation.

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Key Words: non-aqueous phase liquid (NAPL), interphase mass transfer, porous media, interfacial area, volatilization.

1. Introduction

Seepage of organic liquids into the vadose zone through leakage, spillage or disposal of chemical waste sites or manufacturing sites poses a serious threat to groundwater. These chemicals are usually released as non-aqueous phase liquids (NAPLs) and have low miscibility in water. During NAPL migration through the unsaturated zone, a substantial portion of the NAPL is entrapped in the pore spaces due to the capillary action of the porous media. Upon reaching to the saturated zone, a NAPL with density less than water (LNAPL) will form a floating pool on the ground water and a NAPL with density higher than water (DNAPL) will continue to migrate through the saturated zone until it reaches to an impermeable layer, where a pool of contaminant may be formed (Domenico and Schwartz, 1990). In case of LNAPL, contaminant will be distributed above the floating pool according to the pore size distribution of the medium and the chemical properties of the solute. NAPL will be entrapped in the smallest pores with highest capillary rise referred to residual saturation and largest pore with lowest capillary rise referred to capillary fringe. There will be a variable zone of saturation between these two limits referred to transition or funicular zone (Fetter, 1993). However, NAPLs entrapped in this unsaturated zone may persist as a long-term contamination of subsurface soil and groundwater.

Many of these chemicals are found to be volatile organic compounds (VOCs) and the
transport and the fate of these VOCs in the sub-
surface is a problem of great importance. It is
increasing to propose innovative strategies for
subsurface remediation of VOCs (Szatkowski et
al., 1995). Among them, soil vapor extraction
(SVE), also known as soil venting, vapor stripp-
ing, or in situ volatilization, is an accepted and
cost-effective technique for the removal of VOCs
from the contaminated soils (Rathfelder, 1991;
Gierke et al., 1992; Armstrong et al., 1994; Conant
et al., 1996; Fischer et al., 1996). During SVE,
advective vapor phase flow is induced within the
subsurface to enhance the volatilization of NAPL
entrapped in unsaturated zone. This technique
has led to an increased study of operative proce-
ses in these systems including NAPL-vapor phase
mass transfer. In multi-fluid system, mass
transfer mainly governs the overall transport
process that occurs in the interface between the
two fluid phases. In order to clean up the sub-
surface soil and groundwater by SVE system, it
is necessary to understand clearly the
NAPL-vapor phase mass transfer process.

To date, the role of NAPL-vapor phase mass
transfer in residual saturation zone was described
by Wilkins et al. (1995). But characteristics for
NAPL-vapor phase mass transfer for variably
NAPL saturated zone or the heavy contaminated
zone has not been yet systematically quantified.
Moreover, researchers expressed this interphase
mass transfer as a lumped parameter with
specific interfacial area. Because of the
complexities exerted by the heterogeneous na-
ture of the porous media structure, it was very
difficult to determine the actual contact area be-
tween NAPL and vapor phase. Karkare and Fort
(1996) were the first researchers who could es-
timate this parameter through an experimental
technique. In their study, the effect of surfac-
tant (1-tetradecanol) on water movement was in-
vestedigated and reported that a reproducible criti-
cal quantity of surfactant is necessary to move
water. The air-water interfacial area was then
calculated from the number of molecules of sur-
factant required to just initiate the water move-
ment and the area occupied by each molecule at
the air-water interface. Later, Kim et al. (1997)
developed a miscible displacement technique using
interfacial tracer to estimate the air-water inter-
facial area. However, recently a method has been
developed in our laboratory to quantify the
air-liquid interfacial area based on surfactant ad-
sorption concept. In this method, air-water inter-
facial area was calculated from the amount of
surfactant adsorbed onto the air-water interface
divided by the number of surfactant monomers
per unit area. This method will be briefly
described in this paper for the convenience of
the reader. In this study, a series of NAPL
volatilization experiments were carried out in dif-
ferent porous media for heavy contaminated zone
and lumped vapor phase mass transfer coeffi-
cient was estimated under steady state condition
for different flowing phase velocities. Then the
actual NAPL-vapor phase mass transfer was
evaluated using corresponding air-liquid inter-
facial area and was characterized in terms of
dimensionless parameter.

2. Background

2.1 Fluid Distribution and Pore Structure
Characterization

It is necessary to understand the pore scale
fluid distribution inside the porous media in
order to quantify the interphase mass transfer
process. A porous medium may be represented
schematically as a network of narrow chambers
(called throats) that intersect at larger void
spaces (called pores), as illustrated in Fig. 1.
Moreover, the pore space is assumed to contain
connected roughness, grooves, or crevices that act
as conduits for the wetting fluids (i.e., water in
water-NAPL or water-air system), even if the cen-
ter of the pore or throat is filled with nonwet-
ting fluid (i.e., NAPL in water-NAPL or air in

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NAPL-air system) (Fenwick and Blunt, 1998). Fluid is usually entrapped inside the porous media due to the interaction among capillary, viscous and gravity or buoyancy forces (Bear, 1972). Capillary action occurs as a result of the cohesive forces within each fluid phase and the adhesive forces between the fluid phase and the solid. When the capillary forces exceed the viscous and gravity forces, the fluid is being entrapped inside the porous medium. Capillary force is directly related to the interfacial tension between the fluid phases and inversely related to the pore radius of the medium. As a result, the pore scale distribution of the fluids depends on the properties of the fluid phases and the distribution of pores. Fluid phase distributions are usually quantified as fluid saturation $S = V_f / V_v$, where $V_f$ is the volume of fluid and $V_v$ is the volume of void within the porous medium.

For the measurement of pore structure for pairs of wetting and nonwetting fluids, generally hydrologists and soil scientists use the capillary pressure-saturation ($P_c-S$) relationships that reflect the pore structure characteristics of the medium (Lenhard and Parker, 1987; Ferrand et al., 1989; Hofstee et al., 1997). When a nonwetting fluid, such as NAPL or gas invades water, or gas displaces NAPL, the process is called drainage. The nonwetting fluid may only fill a pore or throat that is adjacent to an already filled region of the pore space. Here, nonwetting fluid invades the pore or throat with the lowest threshold pressure known as bubbling pressure. Imbibition occurs when a wetting fluid invades a nonwetting fluid, like water or NAPL into a gas, or water into NAPL. Drainage and imbibition processes are typically shown in Fig. 2 in a pore radius of $r$ and a contact angle $\alpha$ between the phases.

Drainage and imbibition processes can also be distinguished from the hysteresis effect found in the capillary pressure-saturation relationship, which is depicted in Fig. 3. This curve can be characterized by the wetting phase saturation $S_w$, nonwetting saturation $S_{nw}$, the bubbling press-
sure $P_b$, which is the pressure at which pores begin to drain, and the slope of the curve ($\partial P_c/\partial S$). Curve characteristics can be conceptually related to physical pore structure properties. Very flat curve ($\partial P_c/\partial S=0$) indicates a uniform pore size distribution produced by uniform soils and steeply sloped curve indicates well-graded soil where particle size ranging from coarse to fine. (Brooks and Corey, 1966). It can be explained that the pore structure of a medium controls the manner in which fluid is being entrapped.

Thus the pore structure ensured the NAPL distribution inside the porous medium which can be expected to influence the specific surface area between the phases. Interfacial area between the fluid phases plays a significant role in transferring mass from one phase to another in multi-fluid flow system.

2.2 Interphase mass transfer processes

The net flux of a chemical species across an interface between two phases results directly from differences between the temporal and equilibrium concentrations (more appropriately chemical potentials) of that species in the respective phases (Sherwood et al., 1975). Several conceptual models that describe the interphase mass transfer processes in multiphase systems are well explained in the chemical engineering literature (Adamson and Gast, 1997; Bird et al., 1960; Sherwood et al., 1975). These models are based upon many transport processes that may occur in the vicinity of phase interfaces, such as diffusion, advection and turbulent phenomena (Miller et al., 1990). The interphase mass transfer process may be described for a NAPL of VOC where organic liquid is transported from the bulk NAPL phase to the bulk vapor phase through a NAPL-vapor interface. This concept is shown in Fig. 4 describing the stagnant film model (Sherwood et al., 1975; Miller et al., 1990). The interphase boundary layer thickness is very small (in the nanometer scale) (Carroll, 1981). For simplification, it is reasonable to assume the concentration change linearly in this region. Therefore, a linear-driving-force model is adequate to describe the interphase mass transfer process during NAPL volatilization or dissolution in porous media (Wilkins et al., 1995; Miller et al., 1990; Powers et al., 1992).

Applying Fick's law of diffusion in the system shown in Fig. 4, net mass flux, $J$ from NAPL to gas phase may be expressed as:

$$J = -D \frac{dC}{dx} = D_s \left( \frac{C^*-C_s}{\delta} \right)$$

$$= \frac{D_s}{\delta} (C^*-C_s) = h_s(C^*-C_s)$$  \hspace{1cm} (1)

where $D_s$ is the gas diffusivity of NAPL (cm$^2$/sec), $\delta$ is the thickness of the boundary (cm), $C^*$ is the concentration of NAPL at the interface (mg/l), $C_s$ is concentration of bulk

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Fig. 3 A typical capillary pressure-saturation curve shows hysteresis: I, primary drainage curve; II, main imbibition curve; III, main drainage curve.
vapor phase (mg/l) and \( k_\text{g} = D_\text{g}/\delta \) is the overall vapor phase mass transfer coefficient (cm/sec). Under ordinary circumstances, it is not physically possible to measure the solute concentration at interface, and it is therefore convenient to define the mass transfer coefficient on the basis of the equilibrium concentration of gas phase with NAPL or saturated vapor concentration of NAPL. For a pure NAPL, the saturated vapor concentration is usually calculated from ideal gas law. For a multi-component NAPL, equilibrium concentration can be estimated with ideal gas law together with Raoult’s law (Domenico and Schwartz, 1990; Rathfelder et al., 1991).

If now the above NAPL and vapor phases are assumed to be present inside the porous medium, it can be seen that the extent of interphase mass transfer depends on interfacial area or the contact area between the entrapped NAPL and gas phase (Weber et al., 1991). The rate of mass exchange per unit volume of porous medium in such system may be written as:

\[
J_{a_0} = a_0 k_j (C^* - C_g) = k_0 (C^* - C_g)
\]  

(2)

where \( a_0 \) is the specific interfacial area (the interfacial area or the contact area between the NAPL and vapor phase divided by the total volume of the porous medium). But it is extremely difficult to measure this interfacial area between NAPL and gas phase due to the configuration of NAPLs entrapped in the porous medium and the heterogeneous nature of the medium. In order to overcome this difficulty in calculation, usually a lumped mass transfer coefficient \( (k_0 = a_0 k_j) \) which is the product of specific interfacial area and overall mass transfer coefficient was used by the previous researchers (Wilkins et al., 1995; Miller et al., 1990; Powers et al., 1992). Recently, an effort was made to estimate this interfacial area using surfactant adsorption consideration that is briefly described in the next subsection (§ 2.3). Using this interfacial area, one may express the interphase mass transfer process in terms of actual mass transfer coefficient rather than the lumped one.

When the fundamental theoretical models are found to be inadequate to describe a particular phenomenon, dimensional analysis is often used to formulate a set of dimensionless variables, which facilitate a description of such processes. Interphase mass transfer process is also such process and is often described through the use of dimensionless variable analysis. Interphase mass transfer for NAPL-vapor phase system may be described as the dimensionless Sherwood number, \( S_a \), which can be defined as the ratio of mass transfer resistance to the molecular diffusion resistance (Sherwood et al., 1975) and can be expressed as:

\[
S_a = \frac{k_0 l_c}{D_a}\]

(3)

where \( l_c \) is a characteristic length over which mass transfer occurs. Sherwood number may be
characterized with another dimensionless parameter expressed for flowing phase velocity known as Peclet number $P_e$, which is the ratio of advective mixing to molecular diffusion, expressed as:

$$P_e = \frac{v_g l}{D_a}$$  \hspace{1cm} (4)

where $v_g$ is the flowing phase velocity (i.e. pore gas velocity). In the analysis of mass transfer process at the phase boundary in porous media, the characteristic length is usually defined as the mean grain diameter (Miller et al., 1990).

2.3 Surfactant adsorption concept to estimate air-liquid interfacial area

The surfactant (surface active agent) molecules have a strong tendency to accumulate at the interfacial regions such as, solid-liquid, liquid-liquid or air-liquid interfaces in an oriented fashion (Rosen, 1989). In an unsaturated soil water system with surfactant concentration $C_s$ ($C_s < CMC$, Critical Micellar Concentration), it is usually found that some surfactant monomers are remained in liquid phase while some others are adsorbed in solid-liquid and air-liquid interfaces. This phenomenon is schematically shown in Fig. 5. Total surfactant mass per unit volume, $M_t$ (mol/cm$^3$) in such system can be expressed as:

$$M_t = M_s + M_l + M_a$$  \hspace{1cm} (5)

where $M_s$ and $M_l$ are the surfactant mass adsorbed per unit volume at solid-liquid and air-liquid interface respectively (mol/cm$^3$) and $M_a$ is the surfactant mass per unit volume (mol/cm$^3$) in the bulk liquid phase.

In order to find out the air-liquid interfacial area in unsaturated porous medium, it is usually assumed that surfactant molecules culminate a monolayer coverage at the air-liquid interface and each molecule occupies a known molecular area (Saripalli et al., 1997). This provides the opportunity to estimate the surfactant mass adsorbed at the air-water interface in an unsaturated soil water system. The air-water interfacial area in such system may be expressed as:

$$a_0 = \frac{M_t}{\Gamma}$$  \hspace{1cm} (6)

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**Fig. 5** Schematic representation of surfactant monomers distribution in unsaturated soil-water system.
where $\Gamma$ is the surface (excess) concentration of the surfactant or the number of molecules adsorbed per unit area (mol/cm$^2$).

3. Materials and Methods

3.1 NAPL Volatilization

3.1.1 Materials

A single component contaminant, Toluene (purity $>$ 99%; supplied by Yoneyama yakuhin kogyo co. ltd., Japan) was selected as NAPL for the volatilization experiments because of its common presence in subsurface environments with a relatively high vapor pressure. It has a density less than water and hence it is called LNAPL (light non-aqueous phase liquid). Its physicochemical properties are listed in Table 1.

Three glass beads of different sizes were chosen as porous media for the purpose of the experiments because of their high air permeability. High air permeability is a required parameter to conduct SVE system efficiently. The properties of the glass beads are shown in Table 2. A peristaltic pump was used to induce advective airflow in the system. All the tubings were made of Teflon.

3.1.2 Volatilization Experiments

A series of one-dimensional volatilization experiments were carried out in a horizontal Teflon column of 20 cm long and 1.6 cm diameter as shown in Fig. 6. Two brass tubes of same diameter were attached at two ends keeping an outlet and inlet for gas phase flow. Column was packed with dry glass beads in small increments and was tapped each time. This procedure ensured the uniform packing of the glass beads in the column. In order to induce advective airflow at the influent end of the column, a peristaltic pump was calibrated ($r^2=0.99$) for each porous medium. Based on the targeted saturation, a predetermined volume of NAPL was added to the medium by a syringe and was well shaken by hand to obtain uniform distribution of NAPL inside the porous medium. The column diameter was chosen very small (1.6cm $<$ capillary fringe height of the glass bead medium used) and was kept horizontally on a weigh meter. Horizontal column with small diameter helped to maintain the uniform NAPL distribution vertically during the experiments. Overall uniform

Table 1 Properties of Toluene at 25°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C$_6$H$_5$-CH$_3$</td>
<td>**</td>
</tr>
<tr>
<td>Molecular weight, $M$ (g/mol)</td>
<td>92.14</td>
<td>**</td>
</tr>
<tr>
<td>Density, $\rho_c$ (g/cm$^3$)</td>
<td>0.867</td>
<td>**</td>
</tr>
<tr>
<td>Surface tension, $\sigma$ (dyn/cm)</td>
<td>32.8</td>
<td>(Wilkins et al., 1995)</td>
</tr>
<tr>
<td>Vapor pressure, $P_v$ (mm Hg)</td>
<td>28.3</td>
<td>(Wilkins et al., 1995)</td>
</tr>
<tr>
<td>Saturated vapor concentration, $C'$ (mg/l)</td>
<td>140.3</td>
<td>Calculated using ideal gas law</td>
</tr>
<tr>
<td>Gas diffusion coefficient in air, $D_a$ (cm$^2$/sec)</td>
<td>0.075</td>
<td>Calculated using Fuller, Schtler and Gidding method (Sherwood et al., 1975)</td>
</tr>
</tbody>
</table>

** Value given by the supplier (Yoneyama yakuhin kogyo co. ltd., Japan) of Toluene.
NAPL distribution was confirmed by preliminary tests. Separate column was saturated with targeted Toluene saturation and was well shaken by hand. The column was then cut into pieces and the Toluene content measured gravimetrically was found almost uniform (±2%) all through the column. Several columns were tested in this process and the uniform distribution of NAPL inside the column was confirmed. The same procedure of shaking was used to saturate the column before NAPL volatilization experiments.

The influent end was connected with the air pump and effluent end was connected to exhaust hood by Teflon tube via a sampling port prepared by septum. A gas tight syringe was used to collect the gas phase effluent sample. Gas sample of 2ml was immediately injected to a gas chromatograph (GC-14B, Shimadzu Corporation, Kyoto, Japan) equipped with a packed column (SBS-120, 12% Shincarbon A 80-100; manufactured by Shinwa-kako co. ltd., Japan) and a flame ionization detector (FID) for analysis. Chromatogram results were standardized with vapor phase concentration of NAPL at the NAPL-vapor interface taken as the saturated vapor concentration.

NAPL saturation used was varied from 13.8% ~71%. For each NAPL saturation experiment, pore gas velocity was varied between 0.1~2

<table>
<thead>
<tr>
<th>Porous medium</th>
<th>Range of diameter (μm)</th>
<th>Average diameter (mm)</th>
<th>Bulk density (g/cm³)</th>
<th>Porosity φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass bead</td>
<td>212-300</td>
<td>0.25</td>
<td>1.55</td>
<td>0.387</td>
</tr>
<tr>
<td>Glass bead</td>
<td>425-600</td>
<td>0.50</td>
<td>1.53</td>
<td>0.373</td>
</tr>
<tr>
<td>Glass bead</td>
<td>600-850</td>
<td>0.75</td>
<td>1.51</td>
<td>0.368</td>
</tr>
</tbody>
</table>

![Fig. 6 Experimental setup for NAPL volatilization in porous medium.](image-url)
cm/sec as pore gas velocity is found to be less than 2 cm/sec in a typical SVE system (Baehr et al., 1989). Each experiment with one NAPL saturation and different pore gas velocities were run for 42 to 62 minutes. All experiments were carried out under steady state conditions at a constant room temperature of 25 ± 1°C. The amount of NAPL volatilized during each experiment was determined both gravimetrically (from weigh meter reading) and through the integration of chromatogram results as a function of flow rate and time. It was confirmed from the analysis that only 1.5 to 7% of NAPL was removed during steady state volatilization. Here steady state condition refers to the early achievement of a uniform effluent concentration during the volatilization process prior to significant contaminant removal and alteration of the entrapped NAPL distribution. So it was reasonable to assume that NAPL saturation remain constant for one experiment and small removal of NAPL in steady state volatilization did not substantially alter the specific interfacial area between NAPL and vapor phase over the course of the experiments.

3.2 Experiments for air-liquid interfacial area

A column composed of several stainless steel rings (3 cm length and 9.6 cm diameter) was used to carry out the saturated/unsaturated experiments in three glass beads media (properties shown in Table 2). The experimental setup is schematically shown in Fig. 7. An anionic surfactant sodium dodecylbenzene sulfonate (SDBS) and sodium chloride (NaCl) was used as the surface reactive and nonreactive tracers respectively. To estimate the surfactant mass adsorption onto solid surfaces (\(M_s\)), miscible displacement experiments were performed using NaCl and SDBS tracers under water saturated conditions (i.e., no air-water interface). NaCl concentration was measured by electrodes installed at the column outlet (Matsubayashi et al., 1995) and SDBS concentration was measured by UV spectrophotometer (IUV-1200, Iuchi Science Co. Ltd., Japan) set at 235 nm wavelength (Kim et al., 1997). Thus, the breakthrough curves (BTCs) were obtained for NaCl and SDBS and were used to estimate \(M_s\).

The column was made unsaturated from the saturated condition step by step by reducing the flow rate with recycling the SDBS solution (i.e., way I closed; Fig. 7). This helped to form a constant air-water interfacial area inside the porous medium and became homogeneous surfactant concentration inside the system. It may be considered that a stable pressure-saturation relation would establish inside the porous media in each step of flow rate. The constant concentration in each step was checked by measuring the aqueous phase concentration with UV spectrophotometer time to time and found that 10 to 12 hours were sufficient to obtain steady concentration in the aqueous solution for each flow rate. Thus the last flow rate was very small and finally the flow was stopped to obtain equilibrium in the system.

After establishing equilibrium in the system, the column was dismantled. Soil samples from each ring were collected in order to extract the total mass of surfactant (\(M_s\)) present in the unsaturated soil-water system. The aqueous sample from the outlet tank was collected at the end of the experiment to analyze the aqueous phase concentration. Total volumetric water content for each ring was evaluated gravimetrically.

4. Analysis and Discussion

4.1 Evaluation of air-liquid interfacial area

To estimate the surfactant mass adsorption onto solid surfaces (\(M_s\)), one-dimensional transport equation for conservative chemicals was used for aqueous transport of surfactant solution in saturated porous medium (i.e., no air-liquid interface) (Bear and Verruijt, 1987) as:
where \( v_w \) is pore water velocity (cm/s), \( D_w \) is the hydrodynamic dispersion coefficient (cm²/s), \( C_s \) is the surfactant concentration in the bulk liquid phase (mol/cm³), \( \phi_t \) is the total porosity, \( \rho_s \) is the bulk density of the medium (g/cm³), \( k_d \) (\( k_d = 0 \) for non-adsorptive and \( k_d > 0 \) for adsorptive solute) is the linear distribution coefficient for surfactant adsorption onto solid phase (cm³/g). Rearranging equation (7):

\[
R_i \frac{\partial C_s}{\partial t} = D_w \frac{\partial^2 C_s}{\partial z^2} - v_w \frac{\partial C_s}{\partial z} \tag{7}
\]

\[
R_i = 1 + \frac{\rho_s k_d}{\phi_t} \tag{9}
\]

\( R_i \) was calculated by comparing the breakthrough curves (BTCs) obtained from the miscible displacement experiments for both reactive and non-reactive tracers respectively. \( R_i \) was found to be unity for the glass bead medium, which indicates no sorption (i.e., \( k_d = 0 \)) onto the solid surfaces. Thus, \( M_s \) was taken as zero for the glass beads medium used in this study.

The collected soil samples were used to estimate the total surfactant mass \((M_t)\) in unsaturated soil-water system for each ring. The mass was extracted and analyzed by two-phase Hyamine 1622 titration method (Brewer, 1972; Bettahar et al., 1999). The surfactant concentration in the bulk aqueous phase was also determined by the same titration technique and was
converted to the surfactant mass in liquid phase ($M_i$) in each ring using moisture content for that ring. Thus the air-water interfacial area was evaluated from equations (5) and (6) for different water content, $\theta_w$ (cm$^3$/cm$^3$) as:

$$\alpha_0 = \frac{M_i - \theta_w C_s}{\Gamma}$$  \hspace{1cm} (10)

Direct measurement of surface (excess) concentration of the surfactant, $\Gamma$ at the air-water interface is usually not feasible. It is determined by Gibbs adsorption equation using the relationship between surface tension, $\sigma$ and the bulk surfactant concentration, $C_s$ (Davies and Rideal, 1961; Rosen, 1989) as:

$$\partial \sigma = -RT \Gamma \partial (\ln C_s)$$  \hspace{1cm} (11)

where $\sigma$ is the surface tension (dyn/cm), $T$ is absolute temperature (°K), and $R$ is the ideal gas constant. The adsorption equation was developed by measuring surface tension of surfactant solution for different concentration at constant temperature and was used to estimate the surface (excess) concentration of surfactant ($\Gamma$). The $\Gamma$ value was calculated as $2.87 \times 10^{-10}$ (mol/cm$^3$) and was used to estimate the air-liquid interfacial area in equation (10).

Estimated air-water interfacial area for different glass beads media are presented in Fig. 8 with water saturation. Results follow the general concept of decreasing $\alpha_0$ with increasing saturation, $S_w$ (Reeves and Celia, 1996; Bradford and Leij, 1997; Cary, 1994; Kawanishi et al., 1998; Karkare and Fort, 1996; Kim et al., 1997).

The Fig. 8 also shows that $\alpha_0$ is decreasing with increasing grain size, which in fact, supports the frequency distribution of the pores in the medium. The diameter of the pores for the smaller grain size porous medium are usually smaller but have a very high frequency which in turn, provides larger specific area of the pores as well as the interfacial area. The validity of the results were made confirmed by comparing the interfacial area at $S_w=0$ with that of solid surface area. The specific solid surface area was calculated for each porous media assuming that all particles are perfectly spheres and identical in size (Dullien, 1979) and the interfacial area at zero saturation was taken from Fig. 8 by extrapolating the experimental data. These values are shown in Table 3. These two results were compared and found that the experimental results were closer to the theoretical value, which provides the reasonable estimation of interfacial

![Fig. 8 Relationship between air-water interfacial area and water saturation.](image)
4.2 Characterization of NAPL-vapor phase mass transfer

Measurements from each volatilization experiment consisted of effluent concentrations, NAPL saturation and pore gas velocity. In order to characterize NAPL-vapor phase mass transfer first, normalized vapor phase effluent concentration \( \frac{C_e}{C^*} \) was plotted with pore gas velocity and NAPL saturation. These results are presented in Fig. 9 and Fig. 10 respectively for 0.25mm glass beads medium. Results show that \( \frac{C_e}{C^*} \) is deviated from unity, which indicates the departure from local equilibrium assumption (LEA). Deviation of \( \frac{C_e}{C^*} \) from unity represents the existence of rate-limited mass transfer process (Wilkins et al., 1995). These deviations were also observed by Kearl et al. (1991) in their soil vapor extraction study. However, they used NAPL saturation in their investigation as the residual one. Here it is extended for higher NAPL saturation range and normalized concentration was found much more deviated from unity, which provides an opportunity to assume nonequilibrium NAPL volatilization in unsaturated porous media for the experimental conditions used here.

Assuming that linear driving force model (Equation 1) can adequately represent interphase mass transfer in unsaturated porous media, this expression can be incorporated in one-dimensional mass balance equation for the transport of organic component in the vapor phase. This one-dimensional advective-dispersive-reactive (ADR) equation was used to analyze the column effluent data:

\[
\frac{\partial C_e}{\partial t} = \frac{\partial^2 C_e}{\partial x^2} - \phi_e \frac{\partial C_e}{\partial x} + k_0 (C^* - C_e)
\]

where \( D_e \) is the hydrodynamic dispersion or effective gaseous molecular diffusion coefficient, \( v_e \) is the interstitial or pore velocity of the gas phase, \( k_0 \) is the lumped mass transfer coefficient and \( \phi_e \) is the gas filled porosity. For low gas velocities, usually found in SVE, gas dispersion in soil is primarily due to gas diffusion through porous media. Vapor phase diffusion coefficient is found approximately \( 10^4 \) times larger than the solution diffusion coefficient (Farmar et al., 1980). Hence, it appears that diffusion predominates over mechanical dispersion for gas phase transport at low velocity. Gas phase diffusion can occur not only by molecular diffusion but also by Knudsen diffusion or Klinkenberg effect (Brusseau, 1991; Bear, 1972). Equations based on Fick’s law are then not ade-

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**Table 3** Extrapolated solid surface area and calculated solid surface area for different glass beads media.

<table>
<thead>
<tr>
<th>Glass bead medium</th>
<th>Air-water interfacial area(^a), (a_0) (cm(^2)/cm(^3)) at (S_w = 0)</th>
<th>Specific solid surface area(^b) (cm(^2)/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25mm</td>
<td>120</td>
<td>148</td>
</tr>
<tr>
<td>0.50mm</td>
<td>75</td>
<td>76</td>
</tr>
<tr>
<td>0.75mm</td>
<td>52</td>
<td>51</td>
</tr>
</tbody>
</table>

\(^a\)extrapolated from Fig. 8; \(^b\)calculated as described by Dullien (1979).
quate to represent diffusion in the systems where Knudsen diffusion are significant. However, the contribution due to Knudsen diffusion will be negligible except for very fine sand (Brusseau, 1991). Models using Fick's law to describe gas phase diffusion have been used successfully to simulate gas phase advective transport of solute in soil columns (Brusseau, 1991; Gierke et al., 1990).

The diffusion rate through a porous medium is less than that through free air because of the reduced cross sectional area available for movement and the increased path length brought about by the tortuosity of the pore channels. Many correlations exist for determining tortuosity of air filled pores in porous media. Among them, Millington's model (Millington, 1959) was applied successfully by a number of investigators (Jury et al., 1990; Brusseau, 1991; Batterman et al., 1995). Farmar et al. (1980) experimentally confirmed that Millington's model is adequate for total porosity greater than 0.3. Sallam et al. (1984) observed that Millington's model slightly underestimates the tortuosity value for low air

Fig. 9  Characterization of normalized vapor phase concentration with pore gas velocity for 0.25mm glass beads.

Fig. 10  Trend of normalized vapor phase concentration with NAPL saturation.
filled porosity. Because Millington included the effective area for diffusive flow of a gas in a porous solid and was determined only by the number of pore class drained which was in a lumped sense. Gierke et al. (1990) recognized this limitation in Millington's model and adapted the exponent of gas filled porosity as 7/3 instead of 10/3 in his study, which can be expressed as:

\[ D_g = \frac{\phi_{g}^{7/3}D_a}{\phi_{g}^{10/3}} \]  

(13)

where \( D_g \) and \( D_a \) are the gas diffusion in porous media and free air diffusion respectively. Shan and Stephens (1995) compared his analytical model with that of a numerical code for vadose zone transport called VLEACH developed for EPA (Environment Protection Agency, USA) and found that Millington's model with \( \phi_{g}^{7/3} \) rather than \( \phi_{g}^{10/3} \) agree more closely. This indicates that original form of Millington's model would underestimate the gas diffusion in the vadose zone and eventually overestimates the contamination impact to groundwater. Similar application of equation (13) to numerical codes can also be found in Falta et al. (1992). In our study, modified form of Millington's model (equation 13) was used for tortuosity correction. Under the steady-state conditions \( (\partial C_g/\partial t = 0) \) and boundary conditions \( |C_g(0)| = 0 \) and \( \partial C_g/\partial x \ (x = \infty) = 0 \), the solution of equation (12) is given by Van Genuchten and Alves (1982) as:

\[ \frac{C_g(x)}{C_{\infty}} = 1 - \exp\left(\frac{x}{2D_g}\right) \left(1 + \sqrt{1 + \frac{4D_g}{3\phi_{g}}} \right) \]  

(14)

The equation (14) can be considered as the solution of equation (12) for the experimental boundary condition \( |\partial C_g/\partial x \ (x = L)| = 0 \) because the difference is negligible. Thus equation (14) was used to estimate lumped mass transfer coefficient, \( k_0 \) from the effluent vapor phase concentration.

The estimated lumped mass transfer coefficient, \( k_0 \) and corresponding air-liquid interfacial area, \( \omega_0 \) (Fig. 8) were used to evaluate the actual vapor phase mass transfer coefficient, \( k_f \). Previously, interphase mass transfer process was described by \( k_0 \) by the researchers, which was completely different from one that is described in chemical engineering. Here actual vapor side mass transfer was introduced using interfacial area for two fluids system in porous media for the first time. Actual vapor phase mass transfer coefficient, \( k_f \) was used to calculate vapor phase Sherwood number, \( S_h \) using equation (3). The characteristic length needed to estimate \( S_h \) should be considered as the length over which the mass transfer process occurs. In this sense, pore diameter was more reasonable to consider as the characteristics length. But as it is difficult to get the actual size of the pore, mean grain diameter was taken as \( L \) as suggested by Miller et al. (1990). However, results obtained by this technique showed that the interphase mass transfer process depends on the properties of the fluid, dynamic characteristics of the flowing fluid and the geometry of the system of interest. These findings are similar to the results usually found in chemical engineering as given by Welty et al. (1969).

Vapor side Sherwood number, \( S_h \) is plotted with Peclet number, \( P_e \), a dimensionless parameter representing advective gas flow, and shown in Fig. 11. It is seen from here that the interphase mass transfer increases with the flow dynamics of the vapor phase. It had been seen from the Fick's law that interphase mass transfer coefficient, \( k_f \) is inversely proportional to the thickness of the interface, \( \delta \). Though \( \delta \) is not a measurable parameter, it can be realized that \( \delta \) decreases with increasing pore gas velocity. This realization reflects the results shown in Fig. 11, which revealed the increasing tendency of \( S_h \) with \( P_e \).

The interphase mass transfer decreases in a
small increment with NAPL saturation, $S_n$ and is shown in Fig. 12. When the interphase mass transfer coefficient was represented as a lumped one in previous studies, it had been seen that the interphase mass transfer decreased steeply with NAPL saturation (Miller et al., 1990). It was due to the effect of interfacial area between the fluid phases, which usually decreases with increasing NAPL saturation. But here, the effect of interfacial area has been removed and the decreasing tendency was found with a smaller gradient. Here the available void spaces for gas phase became smaller with increasing NAPL saturation and the mobile gas phase (as the nonwetting) may not have the opportunity to have a uniform access to all the pore spaces, which reflects the decreasing tendency of $S_n$ with increasing $S_n$.

From both the Figures 11 and 12, it had been seen that the interphase mass transfer rate increases with increasing grain size of the media, which is in agreement with a previous study of Wilkins et al. (1995) where they used residual saturation for three fluid (NAPL-water-gas) phase system. This can be explained with the nonwetting fluid flow characteristics and the fluid distribution inside the porous medium. Distribution of fluids in the porous matrix depends on the fluid properties and the pore size of the medium. The smaller grain size medium has smaller sizes of pore with larger frequencies, which in turn, may create many dead pores with NAPL-vacuum interface. As a result, gas, as the nonwetting flowing fluid, may not access to all those dead pores in the system. It can be said here that the probability of having dead pores is higher in smaller grain size medium and thus restricts the interphase mass transfer in small grain size medium.

In this study, $k_0$ was calculated in a NAPL-air system and $k_f$ was separated using the $(a_0) \sim (saturaion)$ relationship in water-air system. It was assumed here that the $(a_0) \sim (saturaion)$ relationship is the same between Toluene-air and water-air system. This assumption is valid only when the contact angles of Toluene-glass bead-air and water-glass bead-air systems are the same. This situation could be established when glass bead is strongly Toluene-wet as well as water-wet. In the experiments of air-water interfacial area, the glass bead was made unsaturated from saturated conditions, so the glass bead was strongly water-wet. But in
NAPL volatilization experiments, glass bead was made partially saturated with Toluene from dry conditions. In the later case, all glass beads may not be strongly Toluene-wet. As a result, possible difference in \((a_0) \sim (\text{saturation})\) relationship might cause some errors in estimation of mass transfer coefficient. Furthermore, uniform glass beads were chosen as the porous matrix and the NAPL distribution was also considered as homogeneous whereas distribution of NAPLs and the pore structure of the medium in the field site are usually heterogeneous. NAPL distribution for the heavy contaminant region of the vadose zone is more difficult to maintain homogeneous but it was achieved in this study by choosing a short horizontal column with a small diameter (less than the capillary fringe of the media used). However the methodology, for estimating mass transfer coefficient presented herein, is quite promising and can be used for further study where the porous media are heterogeneous.

5. Conclusions

Interphase mass transfer process plays a significant role in fluid transport in multi-phase system especially, during dissolution or volatilization of NAPL in porous media. It is necessary to understand this process clearly in order to design an efficient remediation technique for a NAPL contaminated site because this process dominates over other processes like advection and dispersion. Previously, mass transfer studies in porous media were restricted in residual saturation only. This research is extended over a large variety of NAPL saturation for the heavy contaminated region of vadose zone. Moreover, the interphase mass transfer rate was usually characterized as a lumped parameter together with interfacial area \((a_0)\) between two fluid phases because of the inaccessibility to estimate \(a_0\) due to the heterogeneous nature of the pore structure and fluid distribution inside the medium. In this study, an effort was made to estimate this interfacial area and separate the interphase mass transfer coefficient solely for the first time. Air-liquid interfacial area was estimated for three-glass beads media using surfactant adsorption concept and was found decreasing with increasing NAPL saturation.

A series of NAPL volatilization experiments were carried out in a horizontal column for different NAPL saturation and pore gas velocities using the same porous media. Under the steady...
state experimental conditions, the lumped NAPL-vapor phase mass transfer coefficient was calculated and was converted to actual vapor phase mass transfer coefficient using the corresponding interfacial area for a specific NAPL saturation. The actual NAPL-vapor phase mass transfer was expressed in terms of dimensionless parameter and found that it depends on the properties of the fluid, dynamic characteristics of the flowing fluid and the geometry of the system of interest. To conclude the results more specifically, the mass transfer coefficient was found to be increasing with increasing pore gas velocity and grain size and decreasing with increasing NAPL saturation.

**Notations**

Symbols used in the study

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Dimension</th>
</tr>
</thead>
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<tr>
<td>Pe</td>
<td>capillary pressure</td>
<td>[ML$^{-1}$T$^{-2}$]</td>
</tr>
<tr>
<td>σ</td>
<td>surface tension</td>
<td>[MT$^{-2}$]</td>
</tr>
<tr>
<td>r</td>
<td>pore radius</td>
<td>[L]</td>
</tr>
<tr>
<td>d</td>
<td>grain diameter</td>
<td>[L]</td>
</tr>
<tr>
<td>d$_{50}$</td>
<td>mean grain diameter</td>
<td>[L]</td>
</tr>
<tr>
<td>V$_f$</td>
<td>volume of fluid in the porous medium</td>
<td>[L$^3$]</td>
</tr>
<tr>
<td>V$_v$</td>
<td>volume of void within the porous medium</td>
<td>[L$^3$]</td>
</tr>
<tr>
<td>P$_b$</td>
<td>bubbling pressure</td>
<td>[ML$^{-1}$T$^{-2}$]</td>
</tr>
<tr>
<td>J</td>
<td>net mass flux from NAPL to gas phase</td>
<td>[ML$^{-2}$T$^{-1}$]</td>
</tr>
<tr>
<td>D$_g$</td>
<td>free air diffusivity of NAPL</td>
<td>[L$^2$T$^{-1}$]</td>
</tr>
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<td>δ</td>
<td>thickness of the boundary between the phases</td>
<td>[L]</td>
</tr>
<tr>
<td>C$_*$</td>
<td>concentration of NAPL at the interface</td>
<td>[ML$^{-3}$]</td>
</tr>
<tr>
<td>C$_a$</td>
<td>concentration of bulk vapor phase</td>
<td>[ML$^{-3}$]</td>
</tr>
<tr>
<td>k$_f$</td>
<td>overall vapor phase mass transfer coefficient</td>
<td>[LT$^{-1}$]</td>
</tr>
<tr>
<td>k$_0$</td>
<td>lumped mass transfer coefficient</td>
<td>[T$^{-1}$]</td>
</tr>
<tr>
<td>l</td>
<td>characteristic length</td>
<td>[L]</td>
</tr>
<tr>
<td>v$_g$</td>
<td>flowing phase velocity (i.e. pore gas velocity)</td>
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</tr>
<tr>
<td>M$_s$</td>
<td>total surfactant mass per unit volume</td>
<td>[ML$^{-3}$]</td>
</tr>
<tr>
<td>M$_i$</td>
<td>surfactant mass adsorbed at solid-liquid interface</td>
<td>[ML$^{-3}$]</td>
</tr>
<tr>
<td>M$_a$</td>
<td>surfactant mass adsorbed at air-liquid interface</td>
<td>[ML$^{-3}$]</td>
</tr>
<tr>
<td>Γ</td>
<td>surface (excess) concentration of the surfactant</td>
<td>[ML$^{-2}$]</td>
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<tr>
<td>a$_0$</td>
<td>air-water interfacial area per unit volume of porous medium</td>
<td>[L$^2$]</td>
</tr>
<tr>
<td>a$_s$</td>
<td>specific solid surface area</td>
<td>[L$^2$]</td>
</tr>
<tr>
<td>v$_w$</td>
<td>pore water velocity</td>
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<td>D$_w$</td>
<td>hydrodynamic dispersion coefficient for water phase</td>
<td>[L$^2$T$^{-1}$]</td>
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<td>surfactant concentration in the bulk liquid phase</td>
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<td>ρ$_b$</td>
<td>bulk density of the medium</td>
<td>[ML$^{-3}$]</td>
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<td>ρ$_a$</td>
<td>NAPL density</td>
<td>[ML$^{-3}$]</td>
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<tr>
<td>k$_d$</td>
<td>linear distribution coefficient for surfactant adsorption on solid phase</td>
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<tr>
<td>D$_g$</td>
<td>hydrodynamic dispersion coefficient for gas phase</td>
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<td>φ$_g$</td>
<td>gas filled porosity</td>
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<td>φ$_i$</td>
<td>total porosity</td>
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<tr>
<td>S</td>
<td>fluid porosity</td>
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</tr>
<tr>
<td>S$_{sw}$</td>
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<td>S$_w$</td>
<td>water saturation</td>
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</tr>
<tr>
<td>S$_n$</td>
<td>NAPL saturation</td>
<td>[-]</td>
</tr>
<tr>
<td>S$_{sw}$</td>
<td>residual wetting fluid saturation</td>
<td>[-]</td>
</tr>
<tr>
<td>S$_{we}$</td>
<td>residual nonwetting fluid saturation</td>
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</tr>
<tr>
<td>S$_h$</td>
<td>vapor phase Sherwood number</td>
<td>[-]</td>
</tr>
<tr>
<td>P$_e$</td>
<td>Peclet number</td>
<td>[-]</td>
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</table>
\( \theta \) contact angle between the phases

\( M \) molecular weight (g/mol)

\( P_v \) vapor pressure (mm Hg)

\( T \) absolute temperature (°K)

\( R \) ideal gas constant (8314 J kmol\(^{-1}\)K\(^{-1}\))

\( \S \) section number

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References


Shan, C. and D.B. Stephens (1995): An analytical solu-


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