Expansion of the discontinuous gas phase and its effect on mass flux from a non-aqueous phase liquid (NAPL) pool

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Mass flux from a non-aqueous phase liquid pool considering spontaneous expansion of a discontinuous gas phase

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Abstract

The partitioning of non-aqueous phase liquid (NAPL) compounds to a discontinuous gas phase results in the repeated spontaneous expansion, snap-off, and vertical mobilization of the gas phase. This mechanism has the potential to significantly affect the mass transfer processes that control the dissolution of NAPL pools by increasing the vertical transport of NAPL mass and increasing the total mass transfer rate from the surface of the pool. The extent to which this mechanism affects mass transfer from a NAPL pool depends on the rate of expansion and the mass of NAPL compound in the gas phase. This study used well-controlled bench-scale experiments under no-flow conditions to quantify for the first time the expansion of a discontinuous gas phase in the presence of NAPL. Air bubbles placed in glass vials containing NAPL increased significantly in volume, from a radius of 1.0 mm to 2.0 mm over 215 days in the presence of tetrachloroethene (PCE), and from a radius of 1.2 mm to 2.3 mm over 22 days in the presence of trans-1,2-dichloroethene (tDCE). A one-dimensional mass transfer model, fit to the experimental data, showed that this expansion could result in a mass flux from the NAPL pool that was similar in magnitude to the mass flux expected for the dissolution of a NAPL pool in a two-fluid (NAPL and water) system. Conditions favouring the significant effect of a discontinuous gas phase on mass transfer were identified as groundwater velocities less than ~0.01 m/day, and a gas phase that covers greater than ~10% of the pool surface area and is located within ~0.01 m of the pool surface. Under these conditions the mass transfer via a discontinuous gas phase is expected to affect, for example, efforts to locate NAPL source zones using aqueous concentration data, and predict the lifetime and risk associated with NAPL source zones in a way that is not currently included in the common conceptual models used to assess NAPL-contaminated sites.

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Gas phase expansion
Dissolution mass flux
Tetrachloroethene
Dichloroethene
Groundwater

1. Introduction

The contamination of soil and groundwater by non-aqueous phase liquids (NAPLs) is a multi-billion dollar problem in North America (USEPA, 2003). Light non-aqueous phase liquids (LNAPLs), such as gasoline and diesel fuel, and dense non-aqueous phase liquids (DNAPLs), such as chlorinated solvents and creosote, are released to the subsurface through accidental spills and improper disposal practices. Once released, NAPL flow is controlled by gravitational, viscous, and capillary forces resulting in the formation of source zones above and below the water table that are characterized by complex combinations of residual ganglia and high-saturation pools located at capillary interfaces (Schwille, 1988). Since the aqueous solubility of many NAPLs is orders of magnitude above drinking water limits, these source zones represent a long-term threat to groundwater quality.

An understanding of the processes that control NAPL dissolution is essential for the location of NAPL source zones...
using aqueous concentration data, the design of many NAPL remediation technologies (Khachikian and Harmon, 2000), and the accurate assessment of long-term risk due to source zone dissolution. Several detailed experiments conducted in two-fluid systems (NAPL and water) have lead to a better understanding of NAPL dissolution from both residual and pooled sources below the water table (Khachikian and Harmon, 2000; Oostrom et al., 2006). Although some studies considered mass transfer to and from a gas phase, most of these studies focused on transport via a continuous gas phase in the unsaturated zone, which resulted in transport of NAPL compounds up and downwards to the saturated zone (e.g. Sleep and Sykes, 1989; Conant et al., 1996).

The study of NAPL mass transfer in NAPL/water systems and in systems containing a continuous gas phase has lead to a significant improvement in our understanding of NAPL dissolution. However, by focusing on these two systems an important scenario for NAPL mass transfer has been overlooked: the mass transfer of NAPL in systems containing a discontinuous gas phase. Instead of resulting in the advective/dispersive transport of gaseous NAPL compound, as is the case for a continuous gas phase, mass transfer to a discontinuous gas phase may result in the expansion (Cirpka and Kitanidis, 2001) and subsequent mobilization (Tsimplanogiannis and Yortsos, 2004) of the gas phase. This will affect the hydraulic properties of the system (Amos and Mayer, 2006a), the concentration of other dissolved gases (Cirpka and Kitanidis, 2001), and the vertical mass transfer rate of volatile compounds (Amos and Mayer, 2006b).

The role of discontinuous gas phases in groundwater systems is receiving increased attention in the literature, particularly with respect to multi-component gases (e.g. Cirpka and Kitanidis, 2001; Holocher et al., 2003; Amos et al., 2005; Geistlinger et al., 2005; Amos and Mayer, 2006a,b; Roy and Smith, 2007). The presence of a discontinuous gas phase is most often associated with groundwater in the vicinity of the water table where recharge or water table oscillations have lead to the entrainment of atmospheric gases (e.g. Ronen et al., 1989; Ryan et al., 2000; Williams and Oostrom, 2000). However, a discontinuous gas phase could also be created by the biogenic production of gases from microbial populations in excess of dissolved oxygen (Cirpka et al., 2000; Williams and Oostrom, 2000). These observations suggest that transient changes in source zone morphology and mass transfer processes can occur for NAPLs in the presence of discontinuous gas phases. These changes are not currently considered in common conceptual models of NAPL-contaminated sites and will complicate efforts to locate, characterize, and model the dissolution of NAPL source zones.

The magnitude of the effect that an expanding discontinuous gas phase has on the mass transfer from a NAPL source zone will depend on the rate of expansion of the gas phase and the concentration of NAPL compound in that gas phase. Rapidly expanding gas phases will mobilize more frequently and, if they contain a significant mass of NAPL compound, will result in a higher average mass flux of NAPL compound vertically away from the NAPL source. No information exists in the current literature concerning the expected expansion rate of a discontinuous gas phase in the presence of NAPL, or the potential effect of that expanding gas phase on the overall mass transfer from a NAPL source. Therefore, the objectives of this study were to 1) quantify the expansion of a discontinuous gas phase in the presence of NAPL, and 2) develop a screening-level modeling tool to provide insight into the general conditions under which this mechanism may be significant. The second objective was met by deriving an analytical model for the expansion of a discontinuous phase under effective steady-state conditions, which was used to compare the magnitude of the mass transfer from a NAPL pool via a discontinuous gas phase to that expected via advection and dispersion in a strictly NAPL/water scenario.

Bench-scale experiments were used to measure the expansion of a discontinuous gas phase above a NAPL pool in a diffusion-controlled (no-flow) system for both tetrachloroethene (PCE) and trans-1,2-dichloroethene (tDCE). These NAPLs represent common groundwater contaminants (Moran et al., 2007) and are expected to result in spontaneous gas phase growth in porous media at different rates due to their significantly different vapour pressures (Roy and Smith, 2007).

2. Conceptual model

The analytical model derived in this study is based on the theory presented by Cirpka and Kitanidis (2001) for the partitioning of multiple dissolved gases to a discontinuous gas phase. This theory has been implemented in several numerical solutions (e.g. Cirpka and Kitanidis, 2001; Geistlinger et al., 2005; Amos and Mayer, 2006a). However, for the assessment of NAPL-contaminated sites it is important to determine if mass transfer via the repeated expansion, snap-off, and vertical mobilization of a discontinuous gas phase is significant prior to...
conducting detailed numerical simulations. If not, then detailed numerical simulations are not warranted. The analytical solution derived in this study will help to determine the general conditions where this mechanism may be significant, and serve as a screening-level modeling tool.

The analytical solution is derived based on the following assumptions: 1) the transport of all components to the gas phase occurs at an effectively steady rate, which leads to an effectively constant composition of the gas phase at later-time, 2) the partial pressure of compounds in the gas phase is in local equilibrium with the aqueous concentration at the gas–liquid interface, 3) the transport of NAPL compounds from the surface of the NAPL pool to the gas–liquid interface is described by the one-dimensional diffusion equation, and 4) the fragmentation of a gas cluster following snap-off produces two clusters with equal compositions. The physical context of these assumptions is discussed in the presentation of the conceptual model below.

The conceptual model for the expansion, snap-off, and vertical mobilization of a discontinuous gas phase above a NAPL pool due to the partitioning of NAPL and other dissolved gases is illustrated in Fig. 1. An approximately uniform distribution of discontinuous gas clusters is assumed to exist above the entire surface of a horizontally extensive NAPL pool (Fig. 1a), and lie within the concentration boundary layer created by the dissolution of the NAPL. The term gas cluster here refers to a discontinuous gas phase that occupies one or more pore bodies. Initially, these gas clusters do not contain any gas-phase NAPL compound and are in equilibrium with the dissolved gases in the surrounding aqueous phase. Therefore, a concentration gradient exists between the dissolved NAPL in the surrounding groundwater and the gas–liquid interface, which results in mass transport from the pool surface to the gas–liquid interface. The partitioning of NAPL compound to the gas phase increases the volume of the gas phase while lowering the partial pressure of the other gases in the gas cluster according to the theory for the partitioning of multiple components to a discontinuous gas phase (Cirpka and Kitanidis, 2001). The lower partial pressure of the other gases creates concentration gradients from the bulk aqueous phase to the gas–liquid interface, resulting in the mass transport of those dissolved gases to the interface and continued expansion of the gas phase (Fig. 1b). The composition of the gas phase achieves an effective steady-state relatively rapidly,

Fig. 1. Conceptual schematic for the partitioning of NAPL compounds and other dissolved gases to a discontinuous gas phase above a NAPL pool showing (a) the initial condition of NAPL-free gas clusters uniformly distributed above the pool surface, (b) the steady transport of volatile NAPL and other dissolved gases resulting in the expansion of the gas phase, and (c) continued vertical expansion and snap-off of the gas phase, which results in a vertically mobile upper gas cluster and a lower gas cluster of equal composition that is able to undergo repeated expansion.
where the partial pressure of each of the dissolved gases and the NAPL compound is effectively constant at a value lower than that which would be in equilibrium with the bulk aqueous phase. This effective steady-state results in the steady transport of all volatile species to the discontinuous gas phase.

At all times the pressure in the discontinuous gas phase is controlled by Dalton’s law and the capillary pressure (i.e. the difference in pressure between the non-wetting and wetting fluids) as

\[ P_g = P_w + P_c = \sum_{i} P^{\text{fi}}_i \]  

where \( P_g \) is the gas pressure, \( P_w \) is the bulk fluid pressure, \( P_c \) is the capillary pressure, and \( P^{\text{fi}}_i \) is the partial pressure of compound \( i \) in the gas phase. The capillary pressure is given by the Young–Laplace equation

\[ P_c = \sigma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) = 2\sigma \frac{r}{r} \]  

where \( \sigma \) is the gas–liquid interfacial tension, \( r_1 \) and \( r_2 \) are the principal radii of curvature of the gas–liquid interface, and \( r \) is the effective radius of curvature of the gas–liquid interface. The partial pressure of each compound in the gas phase is given by Henry’s law

\[ P^{\text{fi}}_i = K_{\text{Hi}} C_i \]  

where \( K_{\text{Hi}} \) is the Henry’s law coefficient for compound \( i \), and \( C_i \) is the aqueous phase concentration of compound \( i \). This theory for the partitioning of multiple dissolved gases to discontinuous gas phases has been applied to the transport of partitioning tracers for the quantification of entrapped gas (Cirpka and Kitanidis, 2001), the dissolution of atmospheric gases from entrapped air (Holocher et al., 2003), the dissolution of bubbles that remain following gas injection (Geistlinger et al., 2005), and the transport of methane at a petroleum hydrocarbon contaminated site (Amos and Mayer, 2006a). It shows that where the sum of the partial pressures that would be in equilibrium with the concentrations of dissolved gases in the bulk aqueous phase is less than the gas pressure, a discontinuous gas phase will dissolve. However, where this sum is greater than the gas pressure, a discontinuous gas phase will expand. This expanding condition is expected for discontinuous gas phases present at NAPL-contaminated sites, where the volatile NAPL compounds contribute an additional partial pressure above the other dissolved gases present in the surrounding groundwater.

The rate of change in the pressure and volume of the gas phase due to the mass transfer of all volatile species is described by the ideal gas law under isothermal conditions

\[ \frac{dn_i}{dt} = \frac{1}{RT} \frac{d(P_g V_g)}{dt} \]  

where \( n_i \) is the total number of moles in the gas phase, \( t \) is time, \( R \) is the gas constant, \( T \) is the temperature, and \( V_g \) is the volume of the gas phase. For discontinuous gas phases in porous media the resulting changes in pressure and volume depend on the location of the gas–liquid interface within the pore geometry. If the radius of curvature of the gas phase increases with increasing volume (i.e. gas expansion within a partially gas-filled pore body) then the change will be dominated by the change in volume at approximately constant pressure, assuming that \( P_w \gg P_c \). This corresponds to the pore-filling step described by Li and Yortsos (1995). If the radius of curvature of the gas phase decreases with increasing volume (i.e. gas phase pinned at pore throats) then the change will be dominated by an increase in pressure at approximately constant volume. This corresponds to the pressurization step described by Li and Yortsos (1995). A gas cluster will initially expand as a pore-filling step until it encounters a pore throat, at which time it will pressurize. If the partial pressure of the NAPL compound in equilibrium with the bulk aqueous phase is less than the displacement pressure of all the adjacent pore throats then expansion of the gas phase in that pore will stop. If the partial pressure of the NAPL compound is sufficiently large, then the displacement pressure will be exceeded and the gas phase will expand to fill or partially-fill an adjacent pore body.

Continued expansion of the gas cluster to multiple pore bodies will result in vertically-dominated growth in relatively coarse media (Dominguez et al., 2000) and/or the snap-off and vertical mobilization of gas clusters (Roy and Smith, 2007) as buoyancy forces exceed capillary forces (Tsimplanogianiss and Yortsos, 2004) (Fig. 1c). A fragmented gas cluster will retain the same effective steady-state composition, with the upper cluster moving away from the pool surface and the lower cluster being able to undergo repeated expansion events. Under this conceptual model, the initial condition of a NAPL-free gas cluster is only true for expansion prior to the first snap-off event. For all repeated expansion events the gas cluster maintains the same effective steady-state composition.

The mechanism of repeated expansion, snap-off, and vertical mobilization will result in the partitioning of NAPL compound from the mobilized gas cluster to the groundwater well above a NAPL pool where aqueous concentrations of NAPL compound in the bulk aqueous phase are lower than those at the gas–liquid interface. Consequently, the mass transfer of NAPL compound to a discontinuous gas phase will result in greater vertical transport of NAPL mass compared to the transport by aqueous phase dispersion processes alone. This can result in greater vertical spreading of the aqueous plume above the pool and an increased rate of mass transfer from the surface of the pool (Roy and Smith, 2007).

3. Laboratory experiments

The expansion of a discontinuous gas phase above a NAPL pool was measured using a small-scale experiment under no-flow conditions. The experimental set-up consisted of an inverted 1.5-ml vial inside a 20-ml vial, which was open to the atmosphere, as shown in Fig. 2. The experiment was conducted without porous media to allow clear visualization of the gas phase and quantification of the gas-phase volume by image analysis. This set-up most closely matches the pore-filling step described above, where the radius of curvature of the gas phase increases with increasing volume.

A 5±1 µl air bubble was injected into each 1.5-ml vial, which was filled with distilled water. A NAPL pool was created.
4. Model development

4.1. Gas-phase expansion

The rate of change in the total number of moles in the gas phase can be calculated as

\[
\frac{dn_i}{dt} = \sum_j \frac{dn_j}{dt}
\]

where \( n_i \) is the number of moles of compound \( i \) in the gas phase. This approach is consistent with existing multi-component models for variable-volume discontinuous gas phases (e.g. Cirpka and Kitanidis, 2001; Holocher et al., 2003; Geistlinger et al., 2005; Amos and Mayer, 2006a), which model the transport of each component. Alternatively, the rate of change in the total number of moles in the gas phase can be expressed as

\[
\frac{dn_i}{dt} = \frac{d}{dt} \left( \frac{n_i}{y_i} \right) = \frac{1}{y_i} \frac{dn_i}{dt} + n_i \frac{d}{dt} \left( \frac{1}{y_i} \right)
\]

where \( y_i \) is the mole fraction of compound \( i \) in the gas phase. Modeling the initial, rapid approach to steady-state using Eq. (6) is more complex than using numerical solutions that employ Eq. (5) due to the challenge of calculating the second term on the right-hand side. However, after the initial early-time growth of the gas phase, effective steady-state conditions are expected to dominate the behaviour of expanding gas phases above a NAPL pool at NAPL-contaminated sites. Under these conditions the transport of all volatile components to the gas phase is expected to be effectively steady, and the mole fraction of each component in the gas phase can be treated as effectively constant. Therefore, the right-hand side of Eq. (6) reduces to a single term involving the change in moles of a single compound and the mole fraction of that compound in the gas phase. Using this approach, the transport of any one component can be used to describe the total volume change in the multi-component system. For the one-dimensional, dispersive, vertical transport of volatile components to the gas phase, this is given by

\[
\frac{dn_i}{dt} = 1 \frac{dn_i}{dt} = D_{z,AD} \frac{C_i - C_{i,g}}{L_g} + n_i \frac{d}{dt} \left( \frac{1}{y_i} \right)
\]

where \( L_g \) is the mass transfer path length, \( C(z=L_g) = C_{i,L} \) is the aqueous concentration at the far boundary, \( C(z=0) = C_{i,g} \) is the aqueous concentration at the gas–liquid interface, \( z \) is the vertical distance away from the gas–liquid interface, \( D_{z,AD} \) is the vertical dispersion coefficient (assumed equal to the molecular diffusion coefficient in these experiments), and \( A_D \) is the area available for mass transfer. For the purpose of this study, \( i \) was taken to be PCE or tDCE in the NAPL experiments, and dissolved air in the control experiments.

Eq. (7) is advantageous since it can be used to derive an analytical solution for the expansion of a discontinuous gas phase above a NAPL pool. This will serve as a screening-level modeling tool for assessing the general conditions under which this mechanism may be significant at NAPL-contaminated sites, where the information required for more detailed numerical models (Cirpka and Kitanidis, 2001; Holocher et al., 2003; Geistlinger et al., 2005; Amos and Mayer, 2006a) may
not be available and the effort required for detailed simulation may not be warranted.

The linear concentration gradient used in this expression is different from those used to derive expressions for the expansion of a discontinuous gas phase in free solution (e.g. Epstein and Plesset, 1950) or in the application of solution gas-drive (Li and Yortsos, 1995; Firoozabadi and Kashchiev, 1996; Tsimpanogiannis and Yortsos, 2002), which assume a radially symmetric concentration field and, therefore, employ a one-dimensional radial diffusion model. Such models would be more applicable to the expansion of a discontinuous gas phase in a NAPL residual source zone or a dissolved NAPL compound plume.

Combining Eqs. (1)–(4) and (7), assuming that the discontinuous gas phase is spherical (r=r_g), and that the bulk fluid pressure and interfacial tension are constant, gives the differential equation for the gas-phase radius as

\[
yt P\frac{d^2 r_g}{dt^2} + \frac{4}{3} \rho \sigma r_g^3 \frac{d r_g}{dt} = \frac{D_{Ld} A_0 RT}{4 \pi L_d K_{Hh}}
\]

where \(P_L\) is the partial pressure in equilibrium with \(C_L\), and \(r_g\) is the radius of the gas phase. Integrating between \(r_g(t=0)=r_0\) and \(r_g(t)=r_g\) gives the analytical expression for the gas-phase radius as

\[
\frac{\beta_1 \rho_2^2}{3} \left( r_g^3 - r_0^3 \right) + \frac{\beta_2 \rho_2^3}{2} \left( r_g^2 - r_0^2 \right) - \beta_3 \beta_4 \left( r_g - r_0 \right) = \frac{\beta_1 D_{Ld} A_0 RT}{4 \pi L_d K_{Hh}} t
\]

where

\[
\beta_1 = y_t P_w
\]

\[
\beta_2 = P_L - y_t P_w
\]

\[
\beta_3 = \frac{2}{3} y_t \sigma (2P_L + y_t P_w)
\]

\[
\beta_4 = -2y_t \sigma
\]

4.2. Estimated mass flux from a NAPL pool

An expression for the mass flux of NAPL compound from the pool surface to the discontinuous gas phase is derived by taking \(i\) to be the NAPL compound of interest, dividing Eq. (7) by the area of the NAPL pool, substituting Eq. (3), and assuming that \(C_i=C_S\) at the surface of the NAPL pool to give

\[
M_{\text{gas}} = \frac{D_{Ld} A_0 C_S}{L_d \rho_{\text{NAPL}}} \left( 1 - \frac{P_{g\text{eq}}}{P_{g\text{eq}}^{*}} \right)
\]

where \(M_{\text{gas}}\) is the mass flux from the NAPL pool to the discontinuous gas phase, \(A_0\) is the surface area of the NAPL pool, \(C_S\) is the aqueous solubility of the NAPL compound, \(P_{g\text{eq}}\) is the partial pressure of NAPL in the gas phase, and \(P_{g\text{eq}}^{*}\) is the vapour pressure of the NAPL in equilibrium with \(C_S\). \(M_{\text{gas}}\) describes the steady-state, area-averaged vertical mass transfer of NAPL compound from the surface of the pool to the first gas–liquid interface encountered above the pool surface. Once transported to the gaseous phase, this NAPL mass will partition to the gas phase and be transported away from the NAPL pool by a vertically mobile gas phase, where it can partition to the groundwater well above the pool surface. \(P_g^{*}\) is assumed here to be constant, which results in the steady transport of NAPL mass to the gas phase. This is not true during the initial expansion of the gas phase prior to the first snap-off event when the gas phase is initially NAPL-free, but it is a reasonable approximation for the expansion that occurs between all other snap-off events, which result from the fragmentation of a gas cluster. Although the transport of mass to the gas phase is steady the mass transport away from the area immediately above the NAPL pool will be periodic as the gas phase undergoes repeated periods of expansion followed by snap-off and mobilization (Roy and Smith, 2007). The average mass transfer at steady-state, however, will be controlled by the transport of NAPL compound to the gas–liquid interface given by Eq. (10). This study makes no attempt to model the transport of NAPL mass away from the area immediately above the surface of the NAPL pool, which will depend strongly on the buoyancy- and capillary-driven movement of the mobilized gas phase.

The magnitude of the mass flux described by Eq. (10) was compared to the theoretical mass flux from a NAPL pool expected to result from steady horizontal advection and vertical dispersion in a strictly NAPL/water scenario. This theoretical mass flux is given by (Johnson and Pankow, 1992)

\[
M_{\text{NAPL/water}} = \frac{2 \theta C_S}{\pi L_f} \sqrt{\frac{D_V}{\pi L_f}}
\]

where \(M_{\text{NAPL/water}}\) is the mass flux from the NAPL pool expected in a NAPL/water scenario, \(\theta\) is the porosity of the porous medium, \(L_f\) is the length of the pool in the direction of groundwater flow, and \(v\) is the pore-water velocity.

Eqs. (10) and (11) each assume that the vertical transport of NAPL mass occurs via transverse vertical dispersion. In Eq. (11) the vertical concentration gradient is controlled by advection and dispersion processes that create a concentration boundary layer, which changes in height along the pool surface in the direction of flow (e.g. Johnson and Pankow, 1992; Chrysikopoulos et al., 2003). In Eq. (10) the vertical concentration gradient is controlled by the buoyant transport of mobilized gas clusters and the competitive partitioning of multiple volatile species (Cirpka and Kitanidis, 2001) to the discontinuous gas phase, in addition to advection and dispersion processes. The buoyant transport of gas-phase mass limits the mass that is available for aqueous advective transport further along the pool and the partitioning of multiple species can result in lower aqueous concentrations than would be expected at similar distances in a strictly NAPL/water scenario due to local equilibrium with gas-phase partial pressures. The cumulative effect of these processes on the vertical concentration gradient is not currently known. Therefore, to allow an assessment of the magnitude of the mass transfer due to an expanding discontinuous gas phase, the concentration gradient (bracketed term on the right-hand side of Eq. (10)) is defined using a representative value of \(P_g^{*}\).

The two magnitudes of the mass transfers described by Eqs. (10) and (11) were compared using the dimensionless expression

\[
\frac{M_{\text{gas}}}{M_{\text{NAPL/water}}} = \sqrt{\frac{\pi}{2 \theta}} A^* \left( 1 - \frac{P_{g\text{eq}}^{*}}{P_{g\text{eq}}^{*}} \right) \frac{1}{L^* \rho_{\text{NAPL}}}
\]
where $A^*=A_D/A_P$ is the fraction of NAPL pool area available for mass transfer to the discontinuous gas phase, $L^*=L_D/L_P$ is the ratio of the dispersive mass transfer path length to the advective mass transfer path length, and $Pe_z=\nu L_D/D_z$ is the transverse vertical Peclet number.

5. Results and discussion

5.1. Interfacial tension measurements

Great care was taken to measure the gas–liquid interfacial tension for aqueous and gas phases saturated with PCE or tDCE, and the results are shown in Table 1. These equilibrium gas–liquid interfacial tension values can have a significant effect on the behaviour of unsaturated systems (e.g. Hofstee et al., 1998; Oostrom et al., 2003), but to the authors’ best knowledge directly measured values do not appear previously in the literature for many compounds, including PCE and tDCE. The gas–liquid interfacial tension values of 70.0±0.2 mN/m and 64.9±0.2 mN/m for PCE and tDCE, respectively, are higher than what might be expected based on literature values of other similar NAPLs such as carbon tetrachloride (Oostrom et al., 2003) or by approximations based on the application of Antonow’s rule (Adamson, 1990). However, Hofstee et al. (1998) report the drainage of 391 mL of water from a fine sand following the emplacement of PCE, which they attribute to a decrease in the air–water interfacial tension due to PCE contamination. Taking the height of the tension-saturated zone in their fine sand to be 40 cm based on their data, and the decrease in height to be 11 cm based on the volume of water drained and the physical properties of the cell (tank dimensions 1.7 m×1.0 m×0.05 m; fine sand porosity of 0.406), the change in air–water interfacial tension can be approximated as decreasing from 72 mN/m to 70 mN/m. This is in excellent agreement with our directly measured result.

5.2. Expansion of the discontinuous gas phase

Expansion of the discontinuous gas phase above a PCE and a tDCE pool is shown in Fig. 3. Only one vial each of the NAPL and control experiments are shown for clarity, and show results typical of replicate experiments. Visual inspection of the images clearly shows the expansion of the gas phase in the vials containing PCE and tDCE, with expansion in the presence of tDCE occurring at a much faster rate. This expansion is consistent with the theory presented above for the partitioning of multiple volatile compounds to a discontinuous gas phase. If only a single compound was being transported to the interface and partitioning to the gas phase, that compound would rapidly reach thermodynamic equilibrium and expansion of the gas phase would stop. These results also show that the mechanism of gas-phase expansion due to the mass transfer of NAPL compounds does not require NAPL-gas contact. Therefore, the mechanism is relevant in the vicinity of pools, residuals, and dissolved plumes, as suggested by Roy and Smith (2007).

The gas-phase radius is plotted versus time in Fig. 4 as the average of replicate experiments. The average gas-phase radius increased from 1.0 mm to 2.0 mm in the PCE experiments over 215 days, and increased from 1.2 mm to 2.3 mm in the tDCE experiments over 22 days. The average gas-phase radius decreased from 1.1 mm to 0.8 mm in the control experiments over 215 days. The decrease in the gas-phase radius in the control experiments is expected since the laboratory air in the initial bubble is subjected to a higher pressure (i.e. the sum of hydrostatic and capillary pressures) and is thereby out of equilibrium with the surrounding water, which is in equilibrium with the atmosphere via the opening in the vial top. Therefore, a concentration gradient exists resulting in mass transfer to the bulk aqueous phase and the dissolution of the gas phase.

5.3. Modeling gas-phase expansion

Eq. (9a–e) was used to model the data in Fig. 4 using the parameter values listed in Table 1. Image analyses were used to estimate $A_D$ and $L_P$ from the cross-sectional area of the inner vial and distance from the pool surface to the bubble. The atmospheric pressure was taken to be $10^5$ Pa based on

<table>
<thead>
<tr>
<th>Parameter</th>
<th>All experiments</th>
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<td>Area for diffusion (mm$^2$)</td>
<td>80</td>
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<tr>
<td>Diffusive path length (mm)</td>
<td>30</td>
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<tr>
<td>Depth of water above gas phase (mm)</td>
<td>6</td>
</tr>
<tr>
<td>Atmospheric pressure (Pa)</td>
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<tr>
<td>Temperature (K)</td>
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<td>Gas constant (L·atm/mol·K)</td>
<td>0.08206</td>
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</table>

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PCE</th>
<th>tDCE</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous diffusion coefficient (m$^2$/s)</td>
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<td>$1\times10^{-9}$</td>
<td>$2\times10^{-9}$</td>
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<tr>
<td>Henry’s Law coefficient (atm·m$^3$/mol)</td>
<td>0.0174</td>
<td>0.00916</td>
<td>1.2826</td>
</tr>
<tr>
<td>Vapour pressure (Pa)</td>
<td>$2.5\times10^4$</td>
<td>$4.2\times10^4$</td>
<td>$1.0\times10^5$</td>
</tr>
<tr>
<td>Interfacial tension (mN/m)</td>
<td>70.0±0.2</td>
<td>64.9±0.2</td>
<td>72</td>
</tr>
<tr>
<td>Average initial gas-phase radius (mm)</td>
<td>1.0</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Mole fraction in gas phase</td>
<td>$2.5\times10^{-2}$</td>
<td>$4.1\times10^{-1}$</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ PCE and tDCE values calculated using the Wilke–Chang equation (Perry et al., 1997).

$^b$ Air value from Epstein and Plesset (1950).

$^c$ PCE and tDCE values from Pankow and Cherry (1996).

$^d$ Air value from Perry et al. (1997).
barometric pressure data available from Environment Canada, and the ambient temperature was taken to be 25 °C. Measurements of the water depth above the gas phase were used to estimate $P_w$, and $P_{i,L}$ was assumed to be equal to the NAPL vapour pressure. The control experiments were modeled using a composite dissolved air as the only volatile compound, and the PCE and tDCE experiments were modeled assuming the aqueous phase contained both dissolved air and the NAPL compound. The mole fraction of the controlling compound was taken as $y_i=1$ for the control experiments, and was used as the only fitting parameter for the PCE and tDCE experiments. The interfacial tension for the PCE-saturated and tDCE-saturated systems were measured as described in Section 3, and all other parameters were based on literature values (Table 1).

Eq. (9a–e) fit the data from the control experiments well without the use of any fitting parameters, and fit the data from the PCE and tDCE experiments well by using $y_i$ as a fitting parameter. The good fit of the model to the control experiments indicates that a one-dimensional linear diffusion model is appropriate for the geometry of this system. Efforts to model these data using a radially symmetric mass transfer model (data not shown) resulted in the under prediction of the gas phase volume with time. The good fit of the model to the PCE and tDCE experiments supports the assumption of the steady transport of all other dissolved gases to the gas phase.
experiments is attributed to the initial diffusion of the NAPL compound and the interfacial tension of the gas–liquid interface is expected to be closer to the surface tension of water (72 mN/m) than the value of 64.9 mN/m measured for the tDCE-saturated system. This leads to a higher gas-phase pressure and slower growth, as indicated by the flatter portion of the data at early time. The transient change in interfacial tension required to reproduce this behaviour is not included in Eq. (8), which assumes constant interfacial tension. Modeling of the initial approach to an effective steady-state would require the modeling of each volatile component. This could be accomplished using existing multi-component models (Cirpka and Kitanidis, 2001; Holocher et al., 2003; Geistlinger et al., 2005; Amos and Mayer, 2006a). However, modeling this early-time behaviour is not the focus of this study since the later-time behaviour that controls the processes at NAPL-contaminated sites is expected to occur under effectively steady-state conditions. The early-time, flat portion of the data is well modeled for the PCE experiments since the gas–liquid interfacial tension of 70.0 mN/m measured for the PCE-saturated system is not substantially different from the surface tension of water.

The ability of different NAPL compounds to depress the gas–liquid interfacial tension below the value for the surface tension of water can affect the process of repeated expansion, snap-off, and vertical mobilization of discontinuous gas phases. Roy and Smith (2007) reported that two mechanisms could be responsible for the expansion of a discontinuous gas phase: the partitioning of NAPL compounds and other dissolved gases to the gas phase, and changes in the interfacial properties including interfacial tension. Although the first mechanism was dominant in their experiments, Roy and Smith (2007) suggested that an increase in interfacial tension as the NAPL compound dissolved back into the groundwater well above the pool could restrict the vertical mobility of the gas phase. This is more applicable to NAPL compounds such as tDCE that cause a more substantial reduction in the gas–liquid interfacial tension. The partitioning of these compounds to a discontinuous gas phase would result in more rapid expansion and snap-off as the interfacial tension decreased with increasing NAPL compound concentrations in the liquid and gas phases. However, this would also facilitate trapping of the mobilized gas phase closer to the surface of the NAPL pool as NAPL compound partitions to the aqueous phase and the interfacial tension rises.

The conditions of these experiments favour slow expansion of the gas phase controlled by a long mass transfer path length and transport of all gases by molecular diffusion alone. In a typical groundwater application the value of \( \lambda_g \) could be less than the 30 mm used here. For example, Roy and Smith (2007) observed the preferential expansion of a discontinuous gas phase along the surface of a NAPL pool due to the differences in the displacement pressure for gas–NAPL and gas-water systems, resulting in direct contact between the gas and NAPL phases. The value of \( D_{i,x} \) could also be greater than the value of molecular diffusion used here due to mechanical dispersion processes. The effect of mechanical dispersion on vertical mass transport is expected to be greater in systems containing discontinuous gas phases due to increased tortuosity. Due to the greater values of \( D_{i,x} \) and
lower values of \( L_0 \) than those employed in these experiments, it is expected that the expansion rate of a discontinuous gas phase above a NAPL pool in a typical groundwater application would be greater than those observed in these vial-based experiments. That is, the vial-based data represents relatively conservative behaviour.

5.4. Comparison of estimated mass fluxes

Fig. 5 compares the magnitude of the mass transfer from a NAPL pool via an expanding gas phase to that expected via advection and dispersion in a strictly NAPL/water scenario using Eq. (12) versus \( L^*P_{ez} \) for \( A^* \) values of 0.01, 0.1, and 0.5. Fig. 5 was constructed using \( \theta = 0.35 \) as a representative value for sand and gravel aquifers, and \( P_{g}^*/P_{pp}^* = 0.998 \) based on the results of the static vial experiments. Increased values of \( A^* \) represent conditions with an increased cross-sectional area of the discontinuous gas phase (in a plane parallel to the NAPL pool surface) relative to the area of the NAPL pool. Low \( L^*P_{ez} \) values represent conditions where the distance from the pool surface to the gas phase is small relative to the length of the pool in the direction of groundwater flow, advective mass transport is slow, and transverse vertical dispersive mass transport is relatively fast. For example, given a transverse vertical dispersion coefficient of \( 1 \times 10^{-9} \text{ m}^2/\text{s} \), a discontinuous gas phase located 1 mm above a 10 m long pool subjected to a groundwater velocity of 0.001 m/day corresponds to \( L^*P_{ez} = 1 \times 10^{-6} \), and a discontinuous gas phase located 10 mm above a 10 m long pool subjected to a groundwater velocity of 0.01 m/day corresponds to \( L^*P_{ez} = 1 \times 10^{-3} \). Fig. 5 shows that for large values of \( A^* \) and low values of \( L^*P_{ez} \) the mass flux of NAPL compound to the discontinuous gas phase is large relative to the dissolution mass flux from a NAPL pool expected for a NAPL/water system. \( M_{gas} \) is estimated to be 10% of \( M_{NAPL/water} \) for \( L^*P_{ez} \) values of \( 2.6 \times 10^{-5} \) and \( 6.4 \times 10^{-4} \) and \( A^* \) values of 0.1 and 0.5, respectively, and equal to \( M_{NAPL/water} \) for \( L^*P_{ez} = 6.4 \times 10^{-6} \) and \( A^* = 0.5 \).

Mass transfer from a NAPL pool to a discontinuous gas phase that is similar in magnitude to the mass transfer expected in a strictly NAPL/water scenario can fundamentally change the mass transfer from the NAPL pool in two ways. First, NAPL mass that is removed from the surface of the pool and transported to the gas phase will be transported upwards by buoyant forces at a rate that greatly exceeds the rate of dispersion in the aqueous phase (Amos and Mayer, 2006b), which controls the vertical transport of NAPL compound mass in a NAPL/water system. This will result in greater vertical spreading of aqueous NAPL compound mass as NAPL compounds dissolve in the groundwater well above the NAPL pool (Roy and Smith, 2007). This will dramatically impact efforts to characterize source zone geometry based on aqueous concentration data since current conceptual models do not include any mechanism for this type of vertical mass transfer of NAPL compound. At NAPL-contaminated sites where this mechanism is active it is likely that NAPL compounds detected in groundwater well above a pool surface would be mistakenly attributed to another NAPL source up-gradient and above the NAPL pool.

Second, for the dissolution of a NAPL pool that occurs under local equilibrium conditions the total mass transfer is limited by the rate at which NAPL compound mass is transported away from the surface of the pool (Seagren et al., 1999). Under the NAPL/water conditions that are typically considered, mass is transported by advection and dispersion processes, with advection dominating at the down-gradient edge of long pools where the concentration gradients above the pool surface are small. The presence of a discontinuous gas phase that undergoes repeated expansion, snap-off, and vertical mobilization provides an additional mechanism for the removal of NAPL compound mass from the surface of the pool, and may significantly change the shape of the aqueous concentration boundary layer. This would increase the mass transfer rate from the pool surface and impact both the calculations of risk associated with that NAPL source as well as mass removal times.

Fig. 5 assumes that the mass transfer rate of NAPL compound to the discontinuous gas phase is controlled by the mass transfer through the aqueous phase between the surface of the NAPL pool and the gas–liquid interface. This is a reasonable assumption for conditions similar to the static experiments, where the transport of other dissolved gases to the gas–liquid interface and the mass transfer at the NAPL–water interface are not limiting. Where the advective transport of other dissolved gases to the gas–liquid interface is negligible, and the diffusive path length of other dissolved gases is significantly longer than that for the NAPL compound (e.g. a discontinuous gas phase present close to a NAPL pool located well beneath the water table under low-flow conditions) then it is expected that the steady-state value of \( P_{g}^*/P_{pp}^* \) would be greater than the value of 0.998 used to construct Fig. 5 and the values of \( M_{gas}/M_{NAPL/water} \) would be less than that shown in Fig. 5. Under these conditions it is expected that an optimum groundwater velocity would exist, below which the expansion of the gas phase would be limited by the transport of the other dissolved gases.

Eq. (12) predicts an unbounded increase in \( M_{gas}/M_{NAPL/water} \) with decreasing values of \( L^* \). It is expected, however, that as \( L_D \) approaches zero, and \( L^* \) approaches zero, the mass transfer will be limited by the mass transfer at the NAPL–water interface. Roy and Smith (2007) reported mass discharge values that correspond to \( M_{gas}/M_{NAPL/water} = 0.5 \) for the expansion, snap-off

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**Fig. 5.** Comparison of estimated mass fluxes as a function of \( L^*P_{ez} \) and \( A^* \), assuming \( \theta = 0.35 \) and \( P_{g}^*/P_{pp}^* = 0.998 \).
and vertical mobilization of a discontinuous gas phase in direct contact with a TCE pool. Assuming $A = 0.35$, $F_i \left( \frac{\mu_p}{\rho_p} \right) = 0.998$, and $A^* = 1$, Eq. (12) predicts $M_{\text{gas}}/M_{\text{NAPL/water}} = 0.5$ for $L^* \mu_p = 1 \times 10^{-4}, A^* = 1$ was used since Roy and Smith (2007) observed the preferential expansion of the gas phase along the surface of the NAPL pool, resulting in complete coverage of the pool surface. Given the groundwater velocity of 0.23 m/day and transverse vertical dispersion coefficient of $1.2 \times 10^{-4}$ m$^2$/day used by Roy and Smith (2007), $L^* \mu_p = 1 \times 10^{-4}$ corresponds to $L_D = 0.07$ mm. This provides a reasonable lower limit on the value of $L_D$ (dispersive mass transfer path length) based on the limited data available, below which the mass transfer to the discontinuous gas phase will be limited by processes other than the transport through the aqueous phase between the surface of the NAPL pool and the gas–liquid interface.

Fig. 5 does not include the effects of capillarity (i.e. fine versus coarse porous media). Given the same mass flux to the gas–liquid interface in coarse and fine materials, greater expansion will be required in the finer material for vertical mobilization of the discontinuous gas phase to occur (Tsianopanogiannis and Yortos, 2004). However, this will simply result in the snap-off and mobilization of gas clusters at a lower frequency but containing a greater mass of NAPL compound. Therefore, the time-averaged mass flux away from the NAPL pool will be similar to that which occurs in the coarse material. However, for media that are significantly finer such that the capillary pressure required for entry into the pore throats is substantially higher than that in a gas-filled pore body then the gradient between the NAPL pool surface and the gas–liquid interface could be significantly reduced. This represents conditions under which most of the mass transfer occurs during the pressurization step described in Section 2. Under these conditions mass transfer and the corresponding expansion of the gas phase would be reduced, and potentially stopped if the vapour pressure of the NAPL is less than the displacement pressure of the adjacent pore throats.

6. Conclusions

The results of this study show that a discontinuous gas phase expands in the presence of a NAPL pool, and that this expansion is consistent with the theory for the partitioning of multiple volatile compounds to a discontinuous gas phase. When the gas phase is not in direct contact with the NAPL pool, the expansion is controlled by the rate of mass transfer of NAPL compound through the aqueous phase to the gas–liquid interface, in addition to the mass transfer of other dissolved gases. Significant expansion was observed to occur over a period of weeks to months, with more rapid expansion observed for tDCE over PCE. Modeling results show that for the conditions investigated in this study the discontinuous gas phase is nearly saturated with NAPL compound during expansion. The modeling results also show that the mass flux expected from a NAPL pool to a discontinuous gas phase will be similar in magnitude to the dissolution mass flux expected from a NAPL pool in a NAPL/water system under conditions characterized by groundwater velocities less than ~0.01 m/day, and a gas phase that covers greater than ~10% of the pool surface area and is located within ~0.01 m of the pool surface.

Where mass transfer to the discontinuous gas phase is significant, the dissolution behaviour of the NAPL pool will be different from that expected under typically considered NAPL/water conditions. The vertical spreading of dissolved NAPL mass will be significantly increased due to the transport via a mobile gas phase. In addition, the total mass transfer rate from NAPL pool will be increased under local equilibrium controlled dissolution conditions due to the additional mechanism of repeated gas phase expansion, snap-off, and mobilization, which results in the increased transport of mass away from the pool surface. These fundamental changes are expected to directly affect, for example, efforts to locate NAPL source zones using aqueous concentration data, predict the risk associated with specific NAPL sources, and predict the total lifetime of NAPL source zones. The inclusion of these considerations into our conceptual models of NAPL source zones improves our fundamental understanding, provides opportunities to better interpret system behaviours, and promises to lead to new remediation technologies and improvements in existing technologies.

The results obtained using the analytical model derived in this study showed that the presence of a discontinuous gas phase will affect the mass transfer from NAPL pools under certain conditions. The analytical model and the comparison of estimated mass fluxes shown in Fig. 5 will serve as a screening tool for assessing whether this mechanism may be significant at a particular NAPL-contaminated site. However, significant benefit will be realized through continued investigation of this mechanism and the use of more detailed mathematical models. Physically-based models for the expansion, snap-off, and mobilization of discontinuous gas clusters should be combined with kinetic models for multi-component mass transfer to discontinuous gas phases to describe transient changes in the aqueous concentration distributions and gas-phase saturations in both homogeneous and heterogeneous porous media under a variety of source zone and background gas scenarios. In addition, reaction expressions for the generation of biogenic or remediation-based gases should be incorporated to accommodate a greater variety of natural and remediation situations. Such models will be potentially powerful tools for the investigation of NAPL-contaminated sites and other applications where the mass transfer to mobile discontinuous gas phases plays a key role.

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