Abstract. Dense, non-aqueous phase liquids (DNAPLs) are common organic contaminants in subsurface environment. Once spilled or leaked underground, they slowly dissolved into groundwater and generated a plume of contaminants. In order to manage the contaminated site and predict the behavior of dissolved DNAPL in heterogeneous subsurface requires a comprehensive numerical model. In this work, the Crank-Nicolson finite-element Galerkin (CN-FEG) numerical scheme for solving a set coupled system of partial differential equations that describes fate and transport of dissolved organic compounds in two-dimensional domain was developed and implemented. Assumptions are made so that the code can be compared and verified with available analytical solutions.

Key words. Groundwater, Advection-Dispersion, Crank-Nicolson, Finite Element Galerkin, Mass Transfer

1. Introduction

Non-aqueous phase liquids (NAPLs) are immiscible in water, representing another phase of concern in groundwater contamination problems. These liquids pose special problems for the hydrogeologists, regulators, and engineers because their fate and transport are difficult to simulate. Most NAPLs are health hazard and some are known to be carcinogens. Partial or full exposure to polluted groundwater results in a high risk for those who are located downstream of the DNAPL source zone. Although aqueous solubility of components in NAPLs is low, its concentration level is much higher than the regulated drinking water standards. Therefore, there is a need for immediate action to clean-up contaminated aquifers. In order to predict NAPL source’s longevity or to estimate the clean-up duration of the selected remediation technologies, a validated numerical model is needed. Mathematical models are commonly used as a tool to evaluate DNAPL source zone longevity, cost/benefit of a selected remediation technology, and to predict the extent of groundwater contamination before and after remediation [1]. These models are developed using both finite-difference and finite-element methods and range from simple to sophisticated formulations. Unfortunately, available numerical models that deal with both groundwater flow and NAPL contamination are very limited. This is particularly due to the mathematical complexity of the multiphase flow and the dissolution of DNAPL in the heterogenous subsurface.

Numerical modeling of groundwater flow and contaminant transport has long been studied and their development have become relatively mature. Both analytical and numerical models have been proposed. Several numerical models are available.

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for a wide range of applications related groundwater flow and contaminant transport [2, 3, 4, 5]. However, finite-element based computer code for solving this kind of problem in heterogeneous porous media is still at an early stage [6]. Relatively little effort has been made to develop a truly coupled model due to the complexity of the problem and the sophistication of the mathematical formulation as well as its numerical implementation. Traditional modeling exercise for the problem of this type assumes that the solute concentration does not affect the fluid density, viscosity, nor the soil’s hydraulic conductivity. Based on these assumptions, groundwater modelers usually solve the two processes of groundwater flow and contaminant transport separately (i.e., uncoupled), thus, simplifying the model, its numerical implementation, and the computational power requirement. With an addition of the interphase mass transfer process to groundwater flow and solute transport, the model becomes more complicated and highly non-linear. Simple analytical solution to this problem does not exist unless simplifying assumptions are made. Available numerical models such as MODFLOW-MT3DMS suite [2, 3], SUTRA [4], and the finite-element groundwater flow/contaminant transport program by Istoš [7] may not be able to handle this kind of problem, since these simulators do not capture processes occurring due to the presence of non-aqueous phase liquid. Delshad et al. [5] developed a multi-phase, multi-component compositional finite-difference model (called UTCHEM) to solve the migration and dissolution of the non-aqueous phase liquids. This model, however, has experienced some numerical difficulties and it can not simulate complex boundary conditions prevents it from widely acceptance. Saenton et al. [8] and Saenton [9] have developed an explicitly coupled finite-difference mass transfer model based on existing groundwater flow program, MODFLOW [2], and reactive contaminant transport or RT3D [10] by adding the dissolution package (DSS) to the program module. They have successfully simulated the dissolution of entrapped tetrachloroethene (PCE) in the sandbox experiment under both normal and (surfactant-) enhanced conditions. However, these simulations required a very small time-step size in order to satisfy the stability criteria due to the use of a technique called operator splitting. This can cause excessively long execution time. The major limitation of the finite-difference model is that finite-difference grids do not conform to boundaries that are not parallel to the co-ordinate axes. Stair-step approximations to angular boundaries are inconvenient to specify and can cause local variations in the ground-water flow field or contaminant plume that are not realistic.

Khebchareon and Saenton [11] have recently developed a one-dimensional Crank Nicolson finite-element Galerkin numerical model to solve a coupled system of partial differential equations which include groundwater flow, advection-dispersion, and rate-limited dissolution of entrapped NAPL equations. They have also verified the code using analytical solution of a 1-D steady-state NAPL dissolution. Subsequently, the code is validated using experimental data obtained from soil column dissolution cell [12]. Although the developed program has successfully simulated the dissolution behavior of PCE in a soil column, it clearly needs further development and modifications in order to be used in real situations.

The present study, therefore, aims to develop a numerical code based on Crank-Nicolson scheme in time and finite element Galerkin method in spatial discretization
method that is capable of simulating groundwater flow, contaminant transport, and mass transfer processes in NAPLs contaminated aquifers.

2. Mathematical Models

The governing equations for groundwater flow, mass transfer and transport, which are of our interest in this work, are illustrated below.

A general expression of transient groundwater flow can be written as

\[ S_s \frac{\partial h}{\partial t} = \nabla \cdot (K \nabla h) + q, \]

where \( h(x, y, z, t) \) is the total hydraulic head, \( K \) is the effective hydraulic conductivity tensor of the porous media, \( q \) denotes source or sink such as well or river, and the parameter \( S_s \) refers to specific storage of an aquifer. For confined aquifer, \( S_s = S/b \) where \( b \) is the aquifer thickness and \( S \) is storativity of an aquifer. On the other hand, the storativity for an unconfined aquifer is \( S = S_y + hS_s \) where \( S_y \) is a specific yield.

The mathematical expression for advection-dispersion of a reactive solute emanating from NAPL dissolution (or interphase mass transfer) can be written as

\[ \frac{\partial C}{\partial t} = -\nabla \cdot (\bar{v}C - D \nabla C) - \frac{\partial}{\partial t} \left( \rho_n \phi_0 S_n \right), \]

where the unknowns \( C(x, y, z, t) \) and \( S_n(x, y, z, t) \) are dissolved solute concentration, and NAPL saturation, respectively. NAPL saturation, representing the quantity of non-aqueous phase liquid in aquifer, is defined as a ratio of the volume of non-aqueous phase liquids to the void volume of the porous medium. The first term on the right-hand side represents advection and dispersion of a dissolved solute with parameters \( \bar{v} \) and \( D \) denoting average linear pore velocity vector and hydrodynamic dispersion coefficient tensor, respectively. The last term on the right-hand side of (2) represents an interphase mass transfer or dissolution of a solute from a NAPL phase.

The parameter \( \bar{v} \) is an average linear pore velocity vector that can be calculated from \( \bar{v} = -K \nabla h/\phi \). The parameter \( \phi \) is an effective porosity and it is defined as \( \phi = (1 - S_n)\phi_0 \) where \( \phi_0 \) is aquifer’s porosity without NAPL entrapment. The variables \( K \) and \( K_s \) are effective and water-saturated hydraulic conductivity tensors, respectively. They are related to each other by the relationship \( K = k_{r,w} K_s \) where \( k_{r,w} \) is a relative permeability function that depends on the amount of entrapped NAPL (\( S_n \)). Several expressions of this function were proposed in literature [13, 14, 15]. The proposed numerical model in this study is not only able to incorporate any relative permeability function, it is also flexible that it accepts an experimentally derived relative permeability function, i.e., the discrete relative permeability function. Generally, the relative permeability function takes the form \( k_{r,w} = (S_e)^\gamma \), where \( S_e \) is effective water saturation or \( S_e = (1 - S_n - S_{r,w})/(1 - S_{r,w}) \), \( S_{r,w} \) is residual water saturation and the parameter \( \gamma \) is a relative permeability exponent which can range from 2 to 4 depending on the type of fluids and aquifer materials.

A process that is fundamental to this study is the dissolution of entrapped NAPL to the flowing aqueous phase. Based on methods developed in chemical engineering, a linear-driving force model for mass transfer from single-component, stably
entrapped NAPLs in soils has been proposed [16]:

\[
\frac{\partial}{\partial t} (\rho_n \phi_0 S_n) = -k_{La}(C_s - C),
\]

where the left-hand-side term represents a dissolved mass flux due to dissolution of NAPL per unit volume of porous medium, \(C\) and \(C_s\) are dissolved concentration and aqueous solubility, respectively. The value of \(k_{La}\), an overall mass transfer coefficient is calculated based on experimentally-derived correlations containing a modified form of dimensionless Sherwood (Sh) number: \(k_{La} = D_m Sh/d_{50}^2\). The parameters \(\rho_n\), \(d_{50}\), and \(D_m\) are NAPL density, average grain size of soils, and molecular diffusion coefficient, respectively.

For simple flow systems, it is possible to derive relationships between Sherwood number and other dimensionless groups such as Reynolds (Re), Schmidt (Sc), or Peclet (Pe) numbers. These functional relationships are referred to as Gilland-Sherwood models. Similar system specific empirical relationships have been proposed for NAPL dissolution [16, 17, 18]. It should be noted that lumped mass transfer coefficients that are estimated using the modified Sherwood number quantifies the mass transfer that occurs at the representative elemental volume (REV) scale that is larger than the pore-scale where mass transfer occurs at the NAPL/water interfaces. In the present study, we propose the relationship as shown in (4). The development of the Gilland-Sherwood is based on a Buckingham-Pi theorem which can be found in any chemical engineering literature [19]:

\[
Sh = \alpha_0 + \alpha_1 (Re)^{\alpha_2} (Sc)^{\alpha_3} (S_n)^{\alpha_4}.
\]

The above expression accounts for the dependency of NAPL dissolution or inter-phase mass transfer on groundwater flow velocity, solute’s physicochemical property (i.e. viscosity and density), and the amount of entrapped NAPL. It is slightly different from traditional Sherwood expression developed in chemical engineering literature that the above expression has and additional term (first term) on the right-hand side. The addition of a parameter \(\alpha_0\) to the dimensionless mass transfer coefficient (or Sherwood number, Sh) enables the numerical model to simulate dissolution under static or no-flow condition where \(Re = 0\). The constants \(\alpha_0, \alpha_1, \ldots, \alpha_4\) are empirical parameters. These parameters are usually obtained by fitting a model such as the one given by (4) to data generated from dissolution experiments conducted in a controlled experiment.

3. Numerical model

This section describes the development of the Crank-Nicolson Finite Element Galerkin (or CN-FEG) scheme for solving the groundwater flow, DNAPL dissolution, and contaminant transport equations.

The program is designed to solve groundwater flow equation using effective hydraulic conductivity which is corrected for the permeability reduction due to the presence of non-aqueous phase liquid. The groundwater velocity field obtained from previous step is used in the next step where advection, dispersion, and NAPL dissolution processes are solved simultaneously. Then, NAPL saturation are updated. These processes are repeated until the targeted simulation time is reached. Below,
we briefly discuss, the formulation of CN-FEG with linear shape or basis functions, see\[7].

3.1. CN-FEG for Groundwater Flow Equation. In the finite-element Galerkin method, a domain of interest are discretized into small regions called elements. Each element consist of nodes. Our goal is to find the approximate solution to the differential equation that minimize residuals caused by this approximation.

Let $\tilde{h}^{(e)}$ be an approximate of hydraulic head within an element “e”, and it is defined by

$$
\tilde{h}^{(e)} = \sum_{i=1}^{n} \phi_i^{(e)} h_i,
$$

where $\phi_i^{(e)}$ are the basis functions for each node within an element $e$, $n$ is the number of nodes within an element “e”, and $h_i$ are the unknown values of hydraulic head for each node within an element “e”. If we substitute $(5)$ into the 2-D groundwater flow equation which is in the form

$$
\frac{\partial}{\partial x} \left( K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial h}{\partial y} \right) + q - S_s \frac{\partial h}{\partial t} = 0,
$$

we obtain residual at node $i$ contributed from element “e” or $R_i^{(e)}$ as follows:

$$
R_i^{(e)} = -\iint_{A} \phi_i^{(e)} \left[ K_x^{(e)} \frac{\partial^2 \tilde{h}^{(e)}}{\partial x^2} + K_y^{(e)} \frac{\partial^2 \tilde{h}^{(e)}}{\partial y^2} + q^{(e)} - S_s^{(e)} \frac{\partial \tilde{h}^{(e)}}{\partial t} \right] dxdy,
$$

where $A$ is the area of an element “e”, and $K_x^{(e)}$ and $K_y^{(e)}$ are assumed constant within an element. The above expression is known as a finite-element Galerkin weighted residuals method. Expand $(7)$ the first term and perform an integration by-part, we obtain residual at node $i$ contributed from element “e”, as

$$
R_i^{(e)} = \int_A K_x^{(e)} \phi_i^{(e)} \frac{\partial \tilde{h}^{(e)}}{\partial x} dxdy - \int_A \phi_i^{(e)} \frac{\partial \tilde{h}^{(e)}}{\partial x} \frac{\partial \tilde{h}^{(e)}}{\partial x} dxdy + \int_A K_y^{(e)} \phi_i^{(e)} \frac{\partial \tilde{h}^{(e)}}{\partial y} dxdy - \int_A \phi_i^{(e)} \frac{\partial \tilde{h}^{(e)}}{\partial y} \frac{\partial \tilde{h}^{(e)}}{\partial y} dxdy - \int_A \phi_i^{(e)} q^{(e)} dxdy + \int_A \phi_i^{(e)} S_s^{(e)} \frac{\partial \tilde{h}^{(e)}}{\partial t} dxdy.
$$

If a three-node triangular element is used to discretize the 2-D problem domain, where the approximate solution $\tilde{h}^{(e)}(x,y) = \phi_i^{(e)} h_i + \phi_j^{(e)} h_j + \phi_k^{(e)} h_k$ (see Fig. 1), similar expression can be written for residual at nodes $j$ and $k$ contributed from element “e” by replacing $\phi_i$ by $\phi_j$ and $\phi_k$, respectively.

Residual at all three nodes $i$, $j$ and $k$ contributed from element “e” can be divided into three parts: residual from conductance $R_K^{(e)}$, residual from capacitance (or storage) $R_S^{(e)}$, and residual from flux $R_F^{(e)}$.
Residual from conductance arises from the first and third terms of (8), can be rewritten in a matrix form as:

\[
R^K_{(e)} = \begin{bmatrix} R^K_{(i)} \\ R^K_{(j)} \\ R^K_{(k)} \end{bmatrix} = \begin{bmatrix} K^{(e)} \end{bmatrix} \begin{bmatrix} h_i \\ h_j \\ h_k \end{bmatrix},
\]

where a conductance matrix \([K^{(e)}]\) is

\[
K^{(e)} = \int_A \begin{bmatrix} \frac{\partial \phi^{(e)}}{\partial x} & \frac{\partial \phi^{(e)}}{\partial y} \\ \frac{\partial \phi^{(e)}}{\partial x} & \frac{\partial \phi^{(e)}}{\partial y} \end{bmatrix} \begin{bmatrix} K_{x}^{(e)} & 0 \\ 0 & K_{y}^{(e)} \end{bmatrix} \begin{bmatrix} \frac{\partial \phi^{(e)}}{\partial x} & \frac{\partial \phi^{(e)}}{\partial y} \\ \frac{\partial \phi^{(e)}}{\partial x} & \frac{\partial \phi^{(e)}}{\partial y} \end{bmatrix} dxdy.
\]

For a three-node triangular element, the conductance matrix can be evaluated to obtain analytical form as:

\[
K^{(e)} = \frac{K_x^{(e)}}{4A} \begin{bmatrix} b_i^2 & b_ib_j & b_ib_k \\ b_jb_i & b_j^2 & b_jb_k \\ b_kb_i & b_kb_j & b_k^2 \end{bmatrix} + \frac{K_y^{(e)}}{4A} \begin{bmatrix} c_i^2 & c_i c_j & c_i c_k \\ c_j c_i & c_j^2 & c_j c_k \\ c_k c_i & c_k c_j & c_k^2 \end{bmatrix}.
\]

The residual from capacitance or storage arises from the last term of (8) can be written in a matrix form as:

\[
R^S_{(e)} = \begin{bmatrix} R^S_{(i)} \\ R^S_{(j)} \\ R^S_{(k)} \end{bmatrix} = \begin{bmatrix} S^{(e)} \end{bmatrix} \begin{bmatrix} \frac{\partial h_i}{\partial x} \\ \frac{\partial h_j}{\partial x} \\ \frac{\partial h_k}{\partial x} \end{bmatrix}.
\]
where \( [S^{(e)}] \) is a conductance or storage matrix which can be written as:

\[
(12) \quad [S^{(e)}] = S^{(e)}_s \int_A \left[ \frac{\phi_{i}^{(e)}}{\phi_{i}^{(e)}} \right] \left[ \frac{\phi_{j}^{(e)}}{\phi_{j}^{(e)}} \right] \frac{\partial h}{\partial x} dA = \frac{S^{(e)}_s A}{12} \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix}.
\]

The second and fourth terms on the right-hand side of (8) is groundwater flux. For the interior nodes with no net flux, this term becomes zero because groundwater flux entering the node \( i \) of an element “e” will cancel out the flux flowing out of the node \( i \) to adjacent nodes when global matrix is assembled. For nodes at the boundary, this term is used to represent the Neumann boundary conditions, for example:

\[
- \left[ \phi_i^{(e)} K_x^{(e)} \frac{\partial h_i^{(e)}}{\partial x} \right]_\Gamma - \left[ \phi_i^{(e)} K_y^{(e)} \frac{\partial h_i^{(e)}}{\partial y} \right]_\Gamma = F_i^{(e)}
\]

The fifth term in (8) represents specified flow boundary of the domain. Therefore, \( \int_A \phi_i^{(e)} q^{(e)} dA \) can be incorporated into the flux term, namely, \( F_i^{(e)} \) which is used to represent the flux for node \( i \) of an element “e”. \( F_i^{(e)} \) is positive if groundwater flux is entering the domain. If, however, groundwater flux originates from line or surface sources (e.g. drains, rivers, or recharge and evapotranspiration), this third term must be evaluated prior to the assembly of the global matrix. For three-node triangular element, the residual contributed from the flux term can be written as:

\[
(13) \quad R_F^{(e)} = \int_A \left\{ \frac{\phi_i^{(e)}}{\phi_j^{(e)}} \right\} q^{(e)} dA = \begin{bmatrix} F_i^{(e)} \\ F_j^{(e)} \\ F_k^{(e)} \end{bmatrix},
\]

Once every term is evaluated, the total residuals at all three nodes \( i, j \) and \( k \) contributed from element “e” or \( R^{(e)} = R_K^{(e)} + R_S^{(e)} + R_F^{(e)} \) can be written as:

\[
(14) \quad R^{(e)} = \begin{bmatrix} R_i^{(e)} \\ R_j^{(e)} \\ R_k^{(e)} \end{bmatrix} = [K^{(e)}] \begin{bmatrix} h_i \\ h_j \\ h_k \end{bmatrix} + \frac{S^{(e)}_s A}{12} \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix} \begin{bmatrix} \frac{\partial h_i}{\partial t} \\ \frac{\partial h_j}{\partial t} \\ \frac{\partial h_k}{\partial t} \end{bmatrix} - \begin{bmatrix} F_i^{(e)} \\ F_j^{(e)} \\ F_k^{(e)} \end{bmatrix}.
\]

In short, the above expression (14) can be written as

\[
(15) \quad \{ R^{(e)} \} = [K^{(e)}] \{ h \} + [S^{(e)}] \left\{ \frac{\partial h}{\partial t} \right\} - \{ F^{(e)} \},
\]

where \([K^{(e)}], [S^{(e)}], \) and \( \{ F^{(e)} \} \) are conductance matrix, source/sink vector, and capacitance or storage matrix of an element “e”, respectively. Equations, like (15), for all elements will be assembled to obtain a global system of differential equations that can be solved for hydraulic heads. The resultant system of equation (global) is

\[
\{ R \} = [S] \left\{ \frac{\partial h}{\partial t} \right\} + [K] \{ h \} - \{ F \}.
\]

If a time derivative of the hydraulic head is discretized using finite difference approach, let \( \{ h \} = (1 - \omega)\{ h \}_t + \omega \{ h \}_{t+\Delta t} \) and \( \{ F \} = (1 - \omega)\{ F \}_t + \omega \{ F \}_{t+\Delta t} \), and
set residual $\{R\} = 0$, we obtain a system of equations to solve for hydraulic heads
at any time $t$ as:

$$
\{[S] + \omega \Delta t[K]\} \{h\}_{t+\Delta t} = \{[S] - (1 - \omega)\Delta t[K]\} \{h\}_t + \Delta t(\omega\{F\}_{t+\Delta t} + (1 - \omega)\{F\}_t).
$$

The above expression is called a finite-element Galerkin scheme for solving groundwater flow equation. A parameter $\omega$ is used to change the scheme from fully-implicit ($\omega = 1.0$) to fully-explicit schemes ($\omega = 0$). If $\omega = 0.5$, a scheme is called Crank-Nicolson finite-element Galerkin or CN-FEG scheme.

### 3.2. CN-FEG for Mass Transfer and Transport Equations.

The equation for two-dimensional advection-dispersion-dissolution or contaminant transport in a non-uniform flow field is written as

$$
D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - \frac{\partial (v_x C)}{\partial x} - \frac{\partial (v_y C)}{\partial y} - \frac{\partial C}{\partial t} - k_{La}(C - C_s) = 0,
$$

along with the approximate solution for contaminant concentration defined as

$$
\bar{C}^{(e)} = \sum_{i=1}^{n} \phi_i^{(e)} C_i = \phi_i^{(e)} C_i + \phi_j^{(e)} C_j + \phi_k^{(e)} C_k
$$

can be used to develop similar scheme that was derived for groundwater flow equation in the previous section. Using the weighted residual method, the residual of an element “$e$” that is contributed from node $i$, can be written as,

$$
R_i^{(e)} = -\int_A \phi_i^{(e)}(x,y) \left[ D_x \frac{\partial^2 \bar{C}^{(e)}}{\partial x^2} + D_y \frac{\partial^2 \bar{C}^{(e)}}{\partial y^2} - \frac{\partial (v_x^{(e)} \bar{C}^{(e)})}{\partial x} - \frac{\partial (v_y^{(e)} \bar{C}^{(e)})}{\partial y} - \frac{\partial \bar{C}^{(e)}}{\partial t} - k_{La}^{(e)} \bar{C}^{(e)} + k_{La}^{(e)} C_s \right] dxdy,
$$

and $R_j^{(e)}$, $R_k^{(e)}$ are defined similarly. Perform the integration similar to the previous section, and we obtain expressions for residual of a three-node triangular element “$e$” contributed from all three nodes $i$, $j$, and $k$ as follows:

$$
\begin{align*}
\{R_i^{(e)}\} &= [D^{(e)}] \begin{bmatrix} C_i \\ C_j \\ C_k \end{bmatrix} + \left[ F_i^{(e)} \right] \begin{bmatrix} \frac{\partial C_i}{\partial h} \\ \frac{\partial C_j}{\partial h} \\ \frac{\partial C_k}{\partial h} \end{bmatrix} - \left\{ M^{(e)} \right\}, \\
\{R_j^{(e)}\} &= [D^{(e)}] \begin{bmatrix} C_i \\ C_j \\ C_k \end{bmatrix} + \left[ F_j^{(e)} \right] \begin{bmatrix} \frac{\partial C_i}{\partial h} \\ \frac{\partial C_j}{\partial h} \\ \frac{\partial C_k}{\partial h} \end{bmatrix} - \left\{ M^{(e)} \right\}, \\
\{R_k^{(e)}\} &= [D^{(e)}] \begin{bmatrix} C_i \\ C_j \\ C_k \end{bmatrix} + \left[ F_k^{(e)} \right] \begin{bmatrix} \frac{\partial C_i}{\partial h} \\ \frac{\partial C_j}{\partial h} \\ \frac{\partial C_k}{\partial h} \end{bmatrix} - \left\{ M^{(e)} \right\},
\end{align*}
$$

where

$$
[D^{(e)}] = \frac{D_x}{4A} \begin{bmatrix} b_i^2 & b_i b_j & b_i b_k \\ b_i b_j & b_j^2 & b_j b_k \\ b_i b_k & b_j b_k & b_k^2 \end{bmatrix} + \frac{D_y}{4A} \begin{bmatrix} b_i^2 & c_i c_j & c_i c_k \\ c_i c_j & c_j^2 & c_j c_k \\ c_i c_k & c_j c_k & c_k^2 \end{bmatrix},
$$

$$
[\bar{v}^{(e)}] = \frac{\bar{v}_x^{(e)}}{6} \begin{bmatrix} b_i & b_i & b_i \\ b_i & b_j & b_j \\ b_i & b_k & b_k \end{bmatrix} + \frac{\bar{v}_y^{(e)}}{6} \begin{bmatrix} c_i & c_i & c_i \\ c_i & c_j & c_j \\ c_i & c_k & c_k \end{bmatrix} + \frac{k_{La} A}{12} \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix},
$$

$$
[A^{(e)}] = \frac{A}{12} \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix}, \quad \text{and} \quad \left\{ M^{(e)} \right\} = \frac{k_{La} C_s A}{3} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix},
$$
The above equation (18) can be written in a shorter notation for elemental matrix as

\[
\begin{bmatrix}
R^{(e)}
\end{bmatrix} = \begin{bmatrix}
D^{(e)}
\end{bmatrix} \{C\} - \{F^{(e)}\} + \left[ \frac{\partial C}{\partial t} \right] - \{M^{(e)}\}.
\]

After assembling the global matrix and setting residual equal to zero, we derive system of ordinary differential equation for the contaminant concentration as

\[
\begin{bmatrix}
A
\end{bmatrix} \left\{ \frac{\partial C}{\partial t} \right\} + \begin{bmatrix}
D
\end{bmatrix} \{C\} = \{F\} + \{M\}.
\]

Using a finite-difference approximation for the time derivative, and with \( C = (1 - \omega)\{C\} + \omega\{C\}_t + \Delta t \) and \( F = (1 - \omega)\{F\} + \omega\{F\}_t + \Delta t \), we will have a finite-element scheme for solving advection-dispersion-dissolution equation as follows,

\[
\begin{bmatrix}
A\
\end{bmatrix} \left\{ \frac{\partial C}{\partial t} \right\} + \begin{bmatrix}
D
\end{bmatrix} \{C\}_t + \Delta t = \left[ \begin{bmatrix}
A\
\end{bmatrix} - (1 - \omega)\Delta t \begin{bmatrix}
D
\end{bmatrix} \right] \{C\}_t + \Delta t \{F\} + \Delta t \{M\}.
\]

If \( \omega = 0.5 \), a scheme is called Crank-Nicolson Finite-Element Galerkin or CN-FEG scheme. Equations (16) and (21) are used to solve for groundwater flow and contaminant transport. Unlike traditional simulation for the problem of this kind, where time step size or \( \Delta t \) for groundwater flow is larger than contaminant transport simulations, this simulation use the same time step size for both groundwater flow and contaminant transport simulations. This is because the depletion of NAPL (due to dissolution) results in the change in relative permeability. Hence, groundwater flow field will change accordingly.

4. Model verification

This section describes and illustrates the verification of the developed finite-element codes by comparing with existing analytical solutions. The scheme was implemented using FORTRAN programming language. The implementation is built upon modifying groundwater flow and contaminant transport codes developed by Istok [7]. Modifications are made to all subroutines in order to accommodate the changes in governing equations that include NAPL dissolution. In addition, three new subroutines were added to the program structure to account for the presence of non-aqueous phase liquids in the problem.

The first test problem involves the simulation of groundwater flow and transport of conservative tracer in a large-scale two-dimensional domain. The second test problem involves the simulation of steady-state mass transfer (i.e. NAPL dissolution) from stably entrapped PCE in the same two-dimensional domain as described in the first test problem.


In this test problem, a conservative tracer transport simulation was conducted in a two-dimensional domain. The domain size is 3000-m wide and 4500-m long in \( y \) and \( x \) directions, respectively (see Fig. 3). A line source of conservative tracer (1000-m long) is applied to an initially clean system instantaneously on the left boundary and kept constant through time. Groundwater flows uniformly from left to right with an average linear pore velocity \( \bar{v} \) of 1.0 m day\(^{-1}\). Longitudinal \( (\alpha_L) \) and transverse \( (\alpha_T) \) dispersivities are 200
and 60 m, respectively. Mathematically, this problem can be written in terms of both governing equation and boundary conditions as shown in (22):

\[
\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - v \frac{\partial C}{\partial x},
\]

\(C = 1, \quad x = 0 \text{ and } 1000 < y < 2000,\)

\(C = 0, \quad x = 0 \text{ and } y < 1000 \text{ or } y > 2000,\)

\(C, \frac{\partial C}{\partial y} = 0, \quad y = 0,\)

\(C, \frac{\partial C}{\partial y} = 0, \quad y = 3000,\)

\(C, \frac{\partial C}{\partial x} = 0, \quad x \to \infty.\)
The analytical solution to the problem posed in (22) is given by [20] as (23).

\[
C(x, y, t) = \sum_{n=0}^{\infty} L_n P_n \cos(\eta y) \cdot \left\{ \exp \left[ \frac{x(V - \beta)}{2D_x} \right] \text{erfc} \left[ \frac{(x - \beta t)}{2\sqrt{D_x t}} \right] \right. \\
+ \exp \left[ \frac{x(V + \beta)}{2D_x} \right] \text{erfc} \left[ \frac{(x + \beta t)}{2\sqrt{D_x t}} \right] \right\},
\]

where \( L_n = \left\{ \begin{array}{ll} 1/2, & n = 0 \\ 1, & n > 0 \end{array} \right. \)

\( P_n = \left\{ \begin{array}{ll} 1/3, & n = 0 \\ \frac{\sin(\frac{2n\pi}{3}) - \sin(\frac{n\pi}{3})}{n\pi}, & n > 0 \end{array} \right. \)

\( \eta = n\pi/3000, \quad n = 0, 1, 2, 3, \ldots \)

\( \beta = \sqrt{v^2 + 4D_x(\eta^2D_y)}. \)

A computer program Mathematica® is used to evaluate the numerical values of tracer concentrations from (23). Concentration of tracer was calculated for the entire domain at times 1,500 and 3,000 days. These analytically evaluated solutions are then compared with concentrations obtained from finite element model developed in Section 3. The problem domain was discretized into 2,700 triangular elements and 1,426 nodes as shown in Fig. 3. Groundwater flow was simulated using constant heads in both left and right boundaries resulting in a steady-state flow field. The time step size used in transient transport simulation is \( \Delta t = 10 \) and 30 days.

The simulation results for both times (1,500 and 3,000 days) are illustrated in Fig. 4 along with maximum numerical error obtained for each case. These contour plots of numerical solutions (black solid-line) are compared with analytical solutions (red dash-line) described in (23). As illustrated, the results from both numerical and analytical solutions are comparable having errors in the order of 2.5%.

4.2. Steady-State Dissolution of Entrapped NAPL. This test problem is designed to represent a steady-state PCE dissolution in 2-D domain. This 2-D domain of the size 3000 \( \times \) 4500 m\(^2\) contains an emplaced source of tetrachloroethene (or PCE) with an initial saturation of \( S_n = 0.20 \). The source zone has the size of 400 \( \times \) 600 m\(^2\) as shown in Fig. 5. Groundwater velocity is uniform (and strictly east-west) and has an average linear pore velocity of 1.0 m day\(^{-1}\). Longitudinal (\( \alpha_L \)) and transverse (\( \alpha_T \)) dispersivities are 100 and 10 m, respectively. Aqueous solubility of PCE (\( C_s \)) is 200 mg L\(^{-1}\) and mass transfer coefficient is kept constant at \( k_{La} = 10^{-3} \) day\(^{-1}\).

The (semi-) analytical solution to the above problem was given by Sale and McWhorter [21] called MASST. In order to obtain MASST solution, the source zone was subdivided into \( N = 24 \) subzones (see Fig. 6). The steady-state concentration of PCE in the geometric center \( C_a(x_i, y_i) \) of each of the subzones can be obtained from

\[
C_a(x_j, y_j) = \sum_{i=1}^{N} k_{La}(C_k - C_a(x_i, y_i)) \cdot F(x_j - x_i, y_j - y_i) \quad i, j = 1, 2, \ldots, N
\]
Figure 3. Test problem domain for conservative tracer simulation.

Figure 4. Contour plots of conservative tracers simulation result at times 1,500 and 3,000 days comparing with analytical solution.
or

\[ C_a = C_s ([F] + k_{La}^{-1} [I])^{-1} [F] U, \]

where \( C_a \) is an \( N \) component vector of concentrations at the geometric centers of the subzones, \([F]\) is an \( N \) by \( N \) matrix of transport constraint functions, \([I]\) is an \( N \) by \( N \) identity matrix, and \( U \) is an \( N \) component vector of unit values. The transport constraint matrix can be evaluated from

\[
F(i, j) = \frac{1}{\sqrt{\pi}} \int_0^\infty f_x(x_j - x_i, t) f_y(y_j - y_i, t) dt \quad i, j = 1, 2, ..., N;
\]

where

\[
f_x(x - x_i, t) = \frac{1}{2} \left[ \text{erf} \left( \frac{x - x_i + a - \bar{v} t}{\sqrt{4D_L t}} \right) - \text{erf} \left( \frac{x - x_i - a - \bar{v} t}{\sqrt{4D_L t}} \right) \right],
\]

\[
f_y(y - y_i, t) = \frac{1}{2} \left[ \text{erf} \left( \frac{y - y_i + b}{\sqrt{4D_T t}} \right) - \text{erf} \left( \frac{y - y_i - b}{\sqrt{4D_T t}} \right) \right].
\]

The parameters \( a \) and \( b \) refer to the half-length and half-width of the subzone respectively. The quantities \( \bar{v}, D_L \), and \( D_T \) are average linear velocity of groundwater, longitudinal and transverse dispersion coefficients, respectively. Once the steady-state PCE concentration at the geometric centers of all subzones are calculated, the concentration of dissolved PCE at any location (particularly, centers of all blocks shown in Fig. 6) can be obtained from

\[
C(x, y, z) = \sum_{i=1}^{N} k_{La}(C_s - C_a(x_i, y_i, z_i)) \cdot F(x - x_i, y - y_i, z - z_i).
\]

The numerical solution to this steady-state PCE dissolution problem is obtained from a modified FEM code developed in Section 3. The modifications made to FEM
include (i) PCE mass can never be depleted so that steady-state condition can be attained and (ii) groundwater flow is steady-state. For finite-element simulation, the problem domain was discretized into 2,700 equal-area triangular elements which results in 1,426 nodes. Fig. 7 shows the discretization for this problem with an emplaced source of PCE in the shaded area. PCE dissolution and transport simulation are executed (using variable $\Delta t$ ranging from 1, 10, 100, and 1,000 days) until the steady-state concentration profile is reached everywhere.

Simulation results of steady-state rate-limited mass transfer and transport of dissolved PCE from both MASST and CN-FEG program are shown in Fig. 8. These pictures show contour lines and color shades of equal dissolved PCE concentration.
(mg/L). As expected, the dissolved PCE plume extends from left to right according to groundwater flow, and it also diffuses around the source zone due to hydrodynamic dispersion. The results from both the CN-FEG and MASST method appear to be comparable with maximum absolute error of 6.10 mg/L or 3.05%.

5. Conclusions

The 2-D Crank-Nicolson finite-element Galerkin numerical scheme is successfully developed, implemented, and tested. The code is verified with existing (semi-) analytical solutions. The code is demonstrated that the finite-element model can capture conservative tracer behavior and steady-state rate-limited mass transfer and transport of dissolved PCE behavior relatively well.
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References


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