Density-dependent Transport and Sequential Biotransformation of Trichloroethylene in a Variably Saturated Zone

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Introduction

- **Density-driven advection of gas phase**
  - Is generated by density-gradient within gas phase.
  - Occurs near contaminant source zones.

\[ \rho_g = f(P_g, C_g) \]

- Infiltration
- Atmospheric losses

- Gas phase
  - Density-driven advection
  - Dispersion
  - Partitioning

- Water phase
  - Advection
  - Dispersion
  - Biotransformation
  - Partitioning
  - Sorption

- Saturated zone
- Groundwater flow

- Unsaturated zone
- Ground surface

- Multiphase environments
- Trichloroethylene (TCE, C₂HCl₃)
  - Concentration in gas (kg/m³)
  - Gas density (kg/m³)
  - Atmospheric losses
  - Infiltration

**NAPL**

- Multiphase environments
- Vaporization
- Partitioning
- Biotransformation
- Dissolution
- Sorption

**Soil grains**

**Gas**

**Water**

**NAPL**

NAPL = Non-Aqueous Phase Liquid
Study objectives

- **Objective is:**
  - To investigate density-driven transport of multi-species with biological reactions in a variably saturated subsurface.

- **Model development activities:**
  - Develop a three-dimensional numerical model
  - Verify and validate the model using analytical solutions, experimental data, and numerical results available in literature

- **Assumptions:**
  - First-order relations
    - Biotransformation, sorption, and partitioning
  - Gas phase: $\rho = f(P,C)$ and $\mu = f(C)$
  - Water phase: Constant properties
  - NAPL: Immobile residuals
Flow equations

- From mass conservation and continuity equations

\[
\frac{\partial (\phi s_f \rho_f)}{\partial t} - \nabla \cdot \left( \rho_f \frac{k_m k_{rf}}{\mu_f} \left( \nabla (\psi_f \rho_w g) - \rho_f g \right) \right) = I_f + \rho_f^* \dot{Q}_f
\]

- Gas density

\[
\rho_g (P_g, C) = \rho_{air} + \gamma_g P_g + \sum_{i=1}^{N} C^i_g \left( 1 - \frac{\rho_{air}}{\rho^*_v} \right)
\]

- Relative permeability \( = f \) (effective saturation)
  - Water phase \( k_{rw} = s_{we}^{1/2} \left[ 1 - \left( 1 - s_{we}^{1/m} \right)^m \right]^2 \) (van Genuchten, 1980)
  - Gas phase \( k_{rg} = s_{ge}^{1/2} \left[ 1 - \left( 1 - s_{ge} \right)^{1/m} \right]^{2m} \) (Parker et al., 1987)

- Effective saturation

\[
s_{we} = \left[ 1 + \left( \alpha_{gw} \psi_{gw} \right)^n \right]^{-m} \\
s_{ge} = 1 - s_{we} - s_{ne}
\]

- Gas viscosity \( = f \) (concentration) as gas mixture (Wilke equation, Reid et al., 1987)
**Contaminant Transport Equations**

- **Multi-species in water and gas phases**
  \[
  \frac{\partial (\phi_s f C^i_f)}{\partial t} = \nabla (\phi_s f D^i_f \nabla C^i_f) - \nabla (q_f C^i_f) + I^i_f + Q_f C^{*i}_f
  \]
  - Dispersion
  - Advection
  - Mass transfer / Bioreaction
  - Pumping / Injection

- **Contaminant (ith) in water phase**
  \[
  I^i_w = \phi_s w \lambda_D^i (C_{we}^i - C_w^i) + \phi_s g \lambda_H^i (C_g^i - H^i C_{w}^i) + \phi_s w \lambda_B^{i-1} Y_{i-1/i} C_{w}^{i-1} - \phi_s w \lambda_B^i C_w^i
  \]
  \[= \rho_b K_D^i \frac{\partial C_{w}^i}{\partial t}
  \]
  - (1) Dissolution
  - (2) Partitioning: water-gas phase
  - (3) Generation by biodegradation of parent contaminant, i-1
  - (4) Biodegradation of contaminant, i
  - (5) Vaporization from NAPL

- **Contaminant (ith) in gas phase**
  \[
  I^i_g = \phi_s g \lambda_v^i (C_{ge}^i - C_g^i) - \phi_s g \lambda_H^i (C_g^i - H^i C_{w}^i)
  \]

- **NAPL saturation**
  \[
  \frac{\partial}{\partial t} (\rho_n \phi_s n) = -\phi_s w \lambda_D (C_{we} - C_w) - \phi_s g \lambda_v (C_{ge} - C_g)
  \]
  - (1) Dissolution
  - (5) Vaporization

- First-order relation coefficients: \(\lambda_D, \lambda_H, \lambda_B, \lambda_V\)
- Yield coefficient = DCE mw / TCE mw

**Sequential bioreaction of TCE**

- 1st-order biorxn
  - Contaminant,i-1
  - TCE
  - cis-1,2-DCE
  - VC

- 1st-order biorxn
  - Contaminant,i
  - Cl
  - H
  - λ\(^i\)

- 1st-order biorxn
  - Contaminant,i+1
  - Cl
  - H
  - λ\(^i\)

Numerical method

- **Galerkin Finite Element Method (FEM)**
  - Modified Picard method
  - Element of domain
    - Rectangular prism
    - 8 nodes each element
  - Three-dimensional mesh generator

- **Material balance calculation**
  - Accuracy and error checking

- **Numerical codes (TechFlowMP)**
  - Program language
    - C, C++, and Visual C++
  - Support platform
    - Linux
    - Unix (High Performance Computing)
    - Microsoft Window

TechFlowMP
Graphical user interface and 3D mesh generator
Model verification

1. Density-driven transport in the unsaturated zone
   • Numerical results published by Mendoza and Frind (1990)
   • Density-driven gas flow and contaminant transport

2. Biotransformation of contaminant in the saturated zone
   • Analytical solutions in a three-dimensional domain
   • Transport of three contaminants
Model verification: 1. Density-driven transport

- **Gas flow and transport in the unsaturated zone (2D)**

  - No advective flow of gas phase in the unsaturated zone at t=0 (no pressure gradient at gas phase)
  - No reaction except equilibrium between water and gas phases
  - Constant concentration at source zone

  ![Diagram showing gas flow and transport in the unsaturated zone](image)

### Soil medium

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability, $k$</td>
<td>$1.0 \times 10^{-10}$ m²</td>
</tr>
<tr>
<td>Porosity, $\phi$</td>
<td>40 %</td>
</tr>
<tr>
<td>Water saturation, $s_w$</td>
<td>20 %</td>
</tr>
<tr>
<td>Residual water saturation, $s_m$</td>
<td>20 %</td>
</tr>
<tr>
<td>Pore-size index, $\lambda$</td>
<td>1.65 g/cm³</td>
</tr>
<tr>
<td>Longitudinal dispersivity, $\alpha_L$</td>
<td>0.15 m</td>
</tr>
<tr>
<td>Transverse dispersivity, $\alpha_T$</td>
<td>0.0075 m</td>
</tr>
<tr>
<td>Temperature, $T$</td>
<td>20 °C</td>
</tr>
</tbody>
</table>

### Generic VOC

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, $M_C$</td>
<td>100.625 g/mol</td>
</tr>
<tr>
<td>Molecular diffusion coefficient, $D^*$</td>
<td>$9.0 \times 10^{-6}$ m²/s</td>
</tr>
<tr>
<td>Vapor viscosity, $\mu_C$</td>
<td>1.0 $\times 10^{-5}$ Pa s</td>
</tr>
<tr>
<td>Henry’s constant, $H$</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Model verification: 1. Density-driven transport (continued)

- Contaminant transport in gas phase in the unsaturated zone at \( t=4 \) days

**Molecular diffusion (No advection)**
Gas density = constant

**Density-driven transport (Advection + dispersion)**
Gas density = \( f \) (concentration)

**Darcy velocity of gas**

Density-driven transport

Advection (gas flow) due to density gradient in gas phase
Model verification: 2. Biotransformation

- **Transport of reactive contaminants in ground water flow (3D)**

  - Sequential biotransformation (First-order relations)
  - Three contaminants
    - For example, TCE, DCE, and VC
  - Initial condition
    - At source: \( C_1 = 1 \), Constant
    - \( C_2 \) and \( C_3 = 0 \). in domain
  - Simulation domain
    - Size = 40 m \( \times \) 24 m \( \times \) 24 m
    - \( dx, dy, dz = 0.25 \text{ m} \sim 1.0 \text{ m} \)

\[
TCE \xrightarrow{k_1} DCE \xrightarrow{k_2} VC \xrightarrow{k_3} \text{ethene}
\]

\[
C_1 \quad C_2 \quad C_3 \quad : \text{Concentration}
\]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_w ), m/d</td>
<td>0.2</td>
</tr>
<tr>
<td>( k_1, k_2, k_3 ), d(^{-1})</td>
<td>0.05, 0.02, 0.01</td>
</tr>
<tr>
<td>( D_x, D_y, D_z ), m(^2)/d</td>
<td>0.3, 0.3, 0.1</td>
</tr>
</tbody>
</table>

TCE: Trichloroethylene
cDCE: cis-Dichloroethylene
VC: Vinyl chloride
- Results are compared with analytical solutions

Analytical solutions (Wexler, 1992)
This study at x-y planes (z = 0)
This study at x-z planes (y = 0)
Density-driven transport with Biotransformation

- The simulation of this study considered:
  - Both unsaturated and saturated zones in the domain
  - Biotransformation for long-term simulation
  - Quantitative analysis
    - The contributions of important factors to ground water pollution
Modeling domain

- Simulation of TCE transport in the variably saturated zone
  - Model domain (unsaturated + saturated zone)

TCE source
Initial NAPL saturation = 5%
Initial TCE mass as NAPL = 64.9 kg
## Parameters and properties

<table>
<thead>
<tr>
<th>Parameters</th>
<th>TCE (C₂HCl₂)</th>
<th>cDCE (C₂H₂Cl₂)</th>
<th>VC (C₂H₃Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>131.39</td>
<td>96.94</td>
<td>62.50</td>
</tr>
<tr>
<td>Vapor density, kg/m³</td>
<td>5.56</td>
<td>4.10</td>
<td>2.64</td>
</tr>
<tr>
<td>Vapor dynamic viscosity, Pa s × 10⁶</td>
<td>9.38</td>
<td>9.29</td>
<td>9.27</td>
</tr>
<tr>
<td>Henry constant, dimensionless</td>
<td>0.227</td>
<td>0.097</td>
<td>0.756</td>
</tr>
<tr>
<td>Molecular diffusion in air, m²/s × 10⁶</td>
<td>7.87</td>
<td>8.84</td>
<td>10.42</td>
</tr>
<tr>
<td>Molecular diffusion in water, m²/s × 10¹⁰</td>
<td>8.206</td>
<td>8.711</td>
<td>10.65</td>
</tr>
<tr>
<td>Sorption coefficient, Koc, L/g</td>
<td>0.1</td>
<td>0.049</td>
<td>0.003</td>
</tr>
<tr>
<td>Vapor pressure, mmHg</td>
<td>41.27</td>
<td>129.2</td>
<td>2136.30</td>
</tr>
<tr>
<td>max. C_p, kg/m³</td>
<td>0.302</td>
<td>0.697</td>
<td>7.434</td>
</tr>
<tr>
<td>max. C_w, kg/m³</td>
<td>1.33</td>
<td>7.19</td>
<td>9.83</td>
</tr>
</tbody>
</table>

### Porous medium

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability, k</td>
<td>1.0 × 10⁻¹⁰ m²</td>
</tr>
<tr>
<td>Porosity, φ</td>
<td>0.35</td>
</tr>
<tr>
<td>Residual water saturation, sᵣ</td>
<td>0</td>
</tr>
<tr>
<td>Bulk density, ρ_b</td>
<td>1.6 g/cm³</td>
</tr>
<tr>
<td>Temperature, T</td>
<td>15 °C</td>
</tr>
<tr>
<td>Longitudinal dispersivity, αₜ</td>
<td>1.0 m</td>
</tr>
<tr>
<td>Transverse dispersivity, αₜ</td>
<td>0.01 m</td>
</tr>
<tr>
<td>Soil organic content, fₒ</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

#### Parameters for the unsaturated zone

- n: 2.0
- αₑₑ: 5.0 m⁻¹

TCE: Trichloroethylene  
cDCE: cis-Dichloroethylene  
VC: Vinyl chloride
Simulation scenarios

- Scenario 1. Diffusion vs. Density-driven transport

- Scenario 2. Sequential biological transformations
  : TCE → cDCE → VC
Scenario 1. Diffusion vs. Density-driven transport

- Concentration of TCE in gas phase
  - t=100 days
    - Diffusion (no advection)
    - Density-driven Transport (Adv.+Disp.)
  - t=200 days
    - Diffusion
    - Density-driven transport

Red = Contaminant in gas phase

Vectors (m/s)

0.1 1 10 100 200 mg/L

Distance (m)
Scenario 1. Diffusion vs. Density-driven transport (continued)

- Concentration of TCE in water phase
  - $t=100$ days
    - Diffusion
    - Density-driven transport
  - $t=200$ days
    - Diffusion
    - Density-driven transport

Blue = Contaminant in water phase
Scenario 1. Diffusion vs. Density-driven transport (continued)

TCE distribution

Diffusion

Legend (Diffusion)
- Gas
- Water (unsat.+sat.)
- Water in unsaturated zone
- Water in saturated zone

Density-driven transport

Legend (Density-driven transport)
- Gas
- Water (unsat.+sat.)
- Water in unsaturated zone
- Water in saturated zone

Release of TCE to the atmosphere

Mass reduction in NAPL source

Mass balance:
\[
\sum_{t=0}^{\text{Initial mass}(t=0)} TCE_{\text{NAPL}} - \sum_{t=0}^{\text{Atmosphere}} TCE_{\text{Atmosphere}} - \sum_{t=0}^{\text{Water}} TCE_{\text{Water}} = \sum_{t=0}^{\text{Gas}} TCE_{\text{Gas}} - \sum_{t=0}^{\text{Soil}} TCE_{\text{Soil}} - \sum_{t=0}^{\text{residual NAPL}} TCE_{\text{residual NAPL}} \approx 0
\]
Scenario 2. Biotransformation

- Assumed TCE is dehalogenated via sequential reactions
  - It occurred under the anaerobic condition
  - First-order reactions

- Effect of biological transformation of TCE
  - To investigate byproducts
    - DCE and VC
  - First-order bioreaction coefficients (Three cases)

<table>
<thead>
<tr>
<th>Rate(day⁻¹)</th>
<th>TCE</th>
<th>DCE</th>
<th>VC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I*</td>
<td>3.0x10⁻³</td>
<td>2.5x10⁻³</td>
<td>3.8x10⁻³</td>
</tr>
<tr>
<td>Case II</td>
<td>1.5x10⁻³</td>
<td>1.3x10⁻³</td>
<td>1.9x10⁻³</td>
</tr>
<tr>
<td>Case III**</td>
<td>1.1x10⁻⁴</td>
<td>1.6x10⁻³</td>
<td>1.0x10⁻³</td>
</tr>
</tbody>
</table>

*Suna et al. [2001]
**Clement et al. [2000]
Scenario 2. Biotransformation (continued)

- TCE concentration in water phase at 280 days

No biorxn

Case I.

- TCE in gas phase at 280 days

No biorxn

Case I.
Scenario 2. Biotransformation (continued)

- DCE concentration in water

Case I.

Case II.

Case III.

Source zone $x=50-55$ m, $z=13-15$ m

Reference Vectors (m/s)

Gas flow
Scenario 2. Biotransformation (continued)

- DCE concentration in gas phase

**Case I.**

**Case II.**

**Case III.**
Scenario 2. Biotransformation (continued)

- VC concentration in water phase at t=280 days

**Case I.**

**Case II.**

**Case III.**

- VC in gas phase

**Case I.**
Scenario 2. Biotransformation (continued)

Mobilized TCE at 300 days

<table>
<thead>
<tr>
<th>Bioreaction</th>
<th>Mobilized TCE (Dissolved + Vaporized TCE)</th>
<th>Mass$^1$, Kg</th>
<th>Ratio, %$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I</td>
<td></td>
<td>21.43</td>
<td>33.55</td>
</tr>
<tr>
<td>Case II</td>
<td></td>
<td>21.30</td>
<td>33.35</td>
</tr>
<tr>
<td>Case III</td>
<td></td>
<td>21.18</td>
<td>33.16</td>
</tr>
</tbody>
</table>

1) Mobilized TCE (kg) = Dissolved + Vaporized TCE from NAPL source
2) % = Mass of mobilized TCE (kg) / Initial TCE mass (kg)
Scenario 4. Biotransformation (continued)

- Distribution of DCE and VC

![Graphs showing the distribution of DCE and VC over time in different cases.](image-url)
Summary

- **Density-driven transport in the unsaturated zone increases**
  - The spreading of contaminants
  - Contaminant transport to groundwater
  - Contaminant removal to atmosphere

- **Biotransformation**
  - Can generates new toxic contaminants
  - Is important near/in the saturated zone
  - Have an important influence on the distribution of new contaminants
  - Should be considered for long-period simulations.
References


