The Effect of Oxygen Transport on Biotransformation of Trichloroethylene in the Subsurface

Wonyong Jang and Mustafa M. Aral

Multimedia Environmental Simulations Laboratory (MESL)
School of Civil and Environmental Engineering
Georgia Institute of Technology, Atlanta
Oxygen and Groundwater Contamination

- Trichloroethylene (TCE) at contaminated sites can be biologically transformed by indigenous microorganisms under **aerobic** and **anaerobic** environments.
- **Oxygen** transport (influx and outflux) from the atmosphere to the subsurface can play an important role in determining oxygen levels in the contaminated zone.

NAPL = Nonaqueous phase liquid

[Image of diagram showing the interaction between atmosphere, TCE vapor, soil, groundwater, and bioreactions]

- Gas flow in the subsurface (ex. Density-driven flow)
- Pressure variation at the ground surface

NAPL = Nonaqueous phase liquid
Biological Processes of TCE

- **Bioreactions**
  - Anaerobic dechlorination
  - Aerobic cometabolism

- **Target contaminants**
  - Trichloroethylene (TCE)
  - cis-1,2-Dichloroethylene (cDCE)
  - Vinyl chloride (VC)

**Anaerobic dechlorination**

- TCE → 1,1-DCE → cis-1,2-DCE → trans-1,2-DCE → VC → Ethene

**Aerobic cometabolism**

- CO₂, CO, HCl, formate, glyoxylate, trichloroethanol, dichloroacetaldehyde

**Oxidative (cometabolic)**

- CO₂, HCl, glyoxal, chloroacetaldehyde, glycoaldehyde, CO₂, HCl, biomass
Study objectives

This study investigates:

- The effect of oxygen transport on the aerobic and anaerobic biological transformations of TCE and associated byproducts
  - $O_2$ transport in the unsaturated zone by gas flow with air influx from the atmosphere into the subsurface.
  - $O_2$ transport in the saturated zone by the groundwater flow.
- The fate of TCE, cDCE, and VC in the subsurface.
Subsurface System

- Multiple phases
  - Groundwater
  - Soil
  - Gas/vapor in the unsaturated zone
  - NAPL

- Multiple contaminant transport
  - Advection
  - Dispersion/diffusion
  - Biological processes
  - Physical/chemical reactions

Multi-species transport in multiphase flow
From mass conservation and continuity equations

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

Subscript \( f \) = fluid phases (water, gas)
\( \psi_f \) = Pressure head of fluid
\( s_f \) = Saturation
\( k_{rf} \) = Relative permeability
\( \rho_f \) = Density

Gas density

\[
\rho_g = \rho_{air} + \gamma_g P_g + \sum_{i=1}^{N} C_g^i \left( 1 - \frac{\rho_{air}^i}{\rho_v^i} \right)
\]

The density of soil vapor near NAPL TCE sources can increase due to its evaporation.
⇒ Density-driven gas flow will be generated.*

Multispecies Transport

- **Multi-species in water and gas phases**
  \[
  \frac{\partial (\phi s_f C_f^i)}{\partial t} = \nabla (\phi s_f D_f \nabla C_f^i) - \nabla (q_f C_f^i) + I_f^i
  \]
  Dispersion \hspace{1cm} Advection \hspace{1cm} Mass transfer / Bioreaction

- **Biological processes: 1st order kinetics**

  1st order kinetics for dechlorination
  \[
  I_w^i = \phi s_w \varepsilon_X \left( \lambda_B C_w^i - \phi s_w \lambda_B C_w^i \right)
  \]
  \[
  \varepsilon_X = \frac{K_1^{O_2}}{K_1^{O_2} + C_w^{O_2}}
  \]
  Coefficient for anaerobic bioreaction.

  1st order kinetics for cometabolism
  \[
  I_w^i = -\phi s_w \varepsilon_O \lambda_B C_w^i
  \]
  \[
  \varepsilon_O = \frac{C_w^{O_2}}{K_S^{O_2} + C_w^{O_2}}
  \]
  Coefficient for aerobic bio-reaction.

  Oxygen utilization by cometabolism
  \[
  I_w^{O_2} = \phi s_w \sum_{TCE,EDCE,VC} \gamma_{O_2,i} \varepsilon_O \frac{k_B^i C_w^i}{K_S^i + C_w^i}
  \]
  subscript \( i = \) by-product contaminant;
  \( i-1 = \) parent contaminant.
Numerical Method & Codes

- **Galerkin Finite Element Method**
  - Modified Picard method
  - Element of domain
  - Rectangular prism (8 nodes each element)

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

- **Numerical codes**
  - TechFlowMP: 3D multiphase flow and multispecies transport codes.
  - Program language: C/C++ and Microsoft Visual C++
  - Supporting platform: Linux/Unix with OpenMP, and Microsoft Windows
Simulation for TCE and its Byproducts

- Source contaminant: nonaqueous-phase-liquid TCE
- Model domain: the unsaturated and saturated zones

TCE source: Initial NAPL saturation = 5 %
Modeling Scenarios and Parameters

Simulation scenarios
• Case 1: No free-flux at the ground surface and no density-driven advection of gas phase.
• Case 2: Limited flux at the ground surface with the density-driven advection of gas phase.
• Case 3: Free-flux at the ground surface with the density-driven advection of gas phase.

Bioreaction coefficients* and oxygen consumption

<table>
<thead>
<tr>
<th></th>
<th>TCE</th>
<th>DCE</th>
<th>VC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anaerobic bioreaction</strong> (d⁻¹)</td>
<td>3.0×10⁻³</td>
<td>2.5×10⁻³</td>
<td>3.8×10⁻³</td>
</tr>
<tr>
<td><strong>Aerobic biodegradation</strong> (Cometabolism) (d⁻¹)</td>
<td>7.4×10⁻⁴</td>
<td>4.5×10⁻³</td>
<td>7.9×10⁻³</td>
</tr>
<tr>
<td>Oxygen consumption†</td>
<td>0.55</td>
<td>0.83</td>
<td>1.41</td>
</tr>
</tbody>
</table>

†stoichiometric coefficient.

\[ TCE: 2C_2H_3Cl + \frac{11}{2}O_2 \rightarrow 4CO_2 + 3H_2O + Cl^- \]
## Parameters of Soil and Chemicals

<table>
<thead>
<tr>
<th>Porous soil medium</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>$5.3 \times 10^{-11} \text{ m}^2$</td>
</tr>
<tr>
<td>Porosity, $\phi$</td>
<td>0.35</td>
</tr>
<tr>
<td>Longitudinal dispersivity, $\alpha_L$</td>
<td>1.0 m</td>
</tr>
<tr>
<td>Transverse dispersivity, $\alpha_T$</td>
<td>0.01 m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>TCE</th>
<th>cDCE</th>
<th>VC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>131.4</td>
<td>96.9</td>
<td>62.5</td>
</tr>
<tr>
<td>Vapor density, kg/m$^3$</td>
<td>5.56</td>
<td>4.10</td>
<td>2.64</td>
</tr>
<tr>
<td>Henry constant, dimensionless</td>
<td>0.227</td>
<td>0.097</td>
<td>0.756</td>
</tr>
<tr>
<td>Sorption coefficient, $K_{oc}$, L/g</td>
<td>0.1</td>
<td>0.049</td>
<td>0.003</td>
</tr>
<tr>
<td>Vapor pressure, mmHg</td>
<td>45.1</td>
<td>129.3</td>
<td>2178.6</td>
</tr>
</tbody>
</table>
TCE Transport in Water Phase

Case 1.

Case 2.

Case 3.

Gas flow

Reference Vectors (m/s)

5E-009

5E-006

□ : NAPL TCE source
The cDCE concentrations at the source area are lower in Case 3 than in Case 1.
The dilution and the atmospheric release of cDCE contribute to decreasing its concentration at and near the source area.
Oxygen Concentration Profiles

Case 3

- t=100 days
- t=200 days
- t=300 days

Case 1

- t=300 days

Anaerobic zone  Aerobic zone
Concentration of TCE in Gas Phase

Case 1
- NAPL TCE (Source)
- Dissolved TCE (Water phase)
- Vaporized TCE in the unsaturated zone.
- At t=300 days
- Atmospheric release
- Dilution
- Aerobic/anaerobic biological reaction

Case 3
- NAPL TCE (Source)
- Dissolved TCE (Water phase)
- Vaporized TCE in the unsaturated zone.
- Atmospheric release
- Dilution
- Aerobic/anaerobic biological reaction
Concentration of DCE in Gas Phase

Case 1

Vaporized cDCE in the unsaturated zone.
- Atmospheric release
- Dilution

Dissolved cDCE (Water phase) generated by TCE dechlorination
- Aerobic/anaerobic biological reaction

Case 3

t=300 days

[16]
Concentration of VC in Gas Phase

Case 1

Case 3

Vaporized VC in the unsaturated zone.

Dissolved VC (Water phase) generated by eDCE dechlorination

Vaporized VC in the unsaturated zone.

Dissolved VC (Water phase) generated by eDCE dechlorination

Vaporized VC in the unsaturated zone.

Dissolved VC (Water phase) generated by eDCE dechlorination
Fate of TCE

Biotransformation

TCE in NAPL and Water

Case 1 - Anaerobic B.
Case 3 - Anaerobic B.
Case 1 - Aerobic B.
Case 3 - Aerobic B.
Case 1 - NAPL
Case 3 - NAPL
Case 1 - Water
Case 3 - Water
Fate of cDCE

cDCE Generation

Water
Soil
Bioreaction

Cometabolism

Anaerobic dechlorination

[19]
Summary

- Air flux into the ground, initiated by the density-driven advection of gas phase, increased oxygen levels in the unsaturated zone and accelerated aerobic biodegradation of TCE and its byproducts.

- The size of the anaerobic zone increased as contaminated groundwater plume spread out. The bioreaction processes became more important with time. The anaerobically-dechlorinated contaminants were much greater than the aerobically-cometabolized contaminants.

- Oxygen levels could be an important factor to determine the concentrations of TCE and its byproducts. The coexisting anaerobic-aerobic-bioreaction approach can be used to model heterogeneous biological processes of organic compounds in the subsurface.

- The density-driven advection decreased contaminant concentrations near the ground surface around the source area. This is mostly due to advective contaminant-transport, dilution, atmospheric release, and biological processes.
Thank you