Influence of Wetting and Mass Transfer Properties of Organic Chemical Mixtures in Vadose Zone Materials on Groundwater Contamination by Nonaqueous Phase Liquids

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1. Motivation

- Approximately 750,000 kg of CCl_4 was discharged to the vadose zone with large volumes of wastewater (13,400,000L) at the Hanford site.
- Assuming equilibrium partitioning, an estimated 64% remains as NAPL in the vadose zone.
- The presence of NAPL has not been observed in soil cores.
- Efforts to remove CCl_4 using soil vapor extraction have resulted in removal of only 11% of the estimated original mass.
- Either the conceptual model used to calculate CCl_4 mass is incorrect, or NAPL volatilization during SVE is far below what one would expect.
- It is difficult to determine if CCl_4 in the vadose zone contributes to groundwater contamination at the Hanford site, or if continued SVE efforts will mitigate this contribution.

2. Objectives

- **Overall Objective:** Develop a new conceptual model for CCl_4 at the Hanford site based on new information about process coupling in chemical mixtures
  - Critical information on NAPL mixtures must be determined before an accurate conceptual model at the Hanford site is possible.
  - Organic acids, organic bases, and detergent-like chemicals change surface wettability; such chemicals were present in the wastewater and NAPL mixtures discharged at the Hanford site
- **Specific Objectives**
  - Determine the effect of organic chemical mixtures on surface wettability
  - Determine the effect of organic chemical mixtures on CCl_4 volatilization rates from NAPL
  - Determine the migration, entrapment, and volatilization of organic chemical mixtures.

3. Background (results from our prior support)

- Vapor density gradients induce gas flow from the atmosphere to the vadose zone and downward liquid flow enhances gas flow
- Induced gas flow enhances NAPL evaporation and mass losses to the atmosphere.
- After 38 years, only 54.3 % of total CCl_4 mass discharged was retained in the vadose zone; 42.7% flowed out of the model domain in the vapor phase through the ground surface, and only 2.9% moved across the water table.
- Changes in NAPL wettability and composition of mixtures will alter NAPL migration rates and change these results

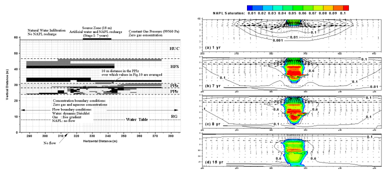

Figure 1. (left) Numerical domain, boundary conditions, and distribution of heterogeneous permeability in stratigraphic units. (right) Snapshots of total NAPL saturation (color bar), gas concentration (g/L, contour lines), and gas velocity (vectors).

- SVE removes mass from high permeability zones relatively quickly.
- Residual and trapped NAPL in low permeability zones is removed more slowly.
- The amount of residual and trapped NAPL will increase if conditions change from water to NAPL wetting.

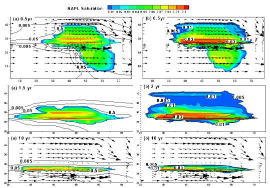

Figure 2. (a) Snapshots of NAPL saturation (color bar) and gas concentrations (g/L, contour lines) at different times. (b) The spatial distributions of total NAPL saturation (color bar) and trapped NAPL saturation (contour lines) at different times.

4. Approach

•Task 1: Prepare and age NAPL mixtures

- MIX1 (NAPL) - carbon tetrachloride, lard oil, tributyl phosphate, dibutyl phosphate, dibutyl butyl phosphonate
- Wastewater1 - nitric acid, fluoride, nitrate, phosphate

- MIX2: MIX1
- Wastewater2: Wastewatewr1 + tributyl phosphoric acid +bis-(2-ethylhexl) phosphate

- MIX3: MIX2 + dodecylamine
- Wastewater3: Wastewater2

•Task 2: Measure interfacial tension, contact angle, and capillary pressure-saturation curves

- Interfacial tension with fresh and reaction-aged NAPL.
- Contact angles on quartz and calcite crystals.
- Measure two-phase capillary pressure-saturation curves

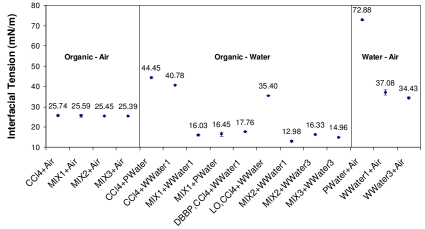

Figure 4. Interfacial tension data for pure CCl4, pure water, and mixtures

- Organic-water interfacial tension is affected by the additional of DBBP to MIX1
- The water-air interfacial tension is affected by the addition of nitric acid and nitrate salts to the solution

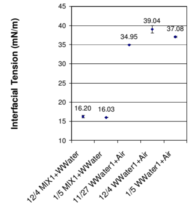

Figure 5. (left) Interfacial tension data for fresh and aged NAPL mixtures

- Chemical aging over more than a month does not appreciably change the interfacial tension results for MIX1 or Wwater1.

- Pre-equilibrating quartz slides in MIX1 markedly reduces the organic-water-quartz contact angle

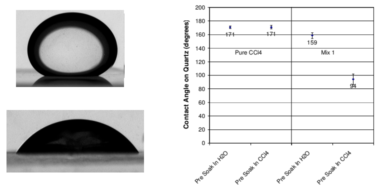

Figure 6. (left) Contact angle drops and (right) measurements for pure CCl4 and mixtures.

•Task 3: Measure interface mass transfer rate

- Image entrapped NAPL and measure volatilization rates of re ed
NAPL from micromodels in the presence of residual wastewat

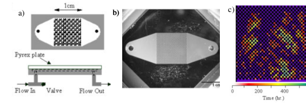

Figure 7. a) Schematic of micromodel. b) Stereomicro etched micromodel pore network. c&d) Composite o NAPL trapped in a homogeneous and heterogeneous

•Task 4: Intermediate-Scale Column and Flow Experiment

- Test P-S and K-S relationships with column experiments
- Evaluate effects of heterogeneity in flow cell experiments

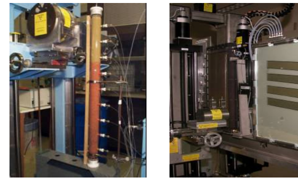

Figure 8. (left) Photograph of the meter-long colum photograph of intermediate-scale flow-cell with layere

•Task 5: Modeling

- Modify a three-dimensional multiphase flow simulator (S lel phase partitioning and mass transfer of NAPLs mixtures.
- Adapt and further refine the k-S-P model proposed by Bra orkers and Lenhard and Oostrom
- Use intermediate-scale experimental system to test the ST r.
- Apply the modified STOMP model to different spill scena ıford Site.
- Use the modified model to evaluate how different remedia can mitigate the impact of CCl_4 in the vadose zone upon groun contamination.