Title: Partitioning Tracers for the Measurement of DNAPL Saturation in Saturated Subsurface Systems

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INTRODUCTION

Dense nonaqueous phase liquids (DNAPLs) occur in the subsurface at numerous contaminated sites and can act as long-term sources of both vapor-phase and groundwater contamination. Both effective risk assessment and remediation of NAPL-contaminated sites is limited by current site characterization techniques, which include analysis of soil gas, core sampling, cone penetrometer testing, and monitoring well sampling. These costly methods provide data at discrete points but are not able to determine the areal distribution and quantity of DNAPL at the site. Spatial variability of the subsurface environment and of contaminant distribution can further complicate proper description. A new method of DNAPL zone characterization involves the use of partitioning tracers, which have been shown to distribute into DNAPLs, and are thus retarded and separated from non-partitioning tracers. The purpose of this work is to explore the use of an innovative in-situ method for the detection and quantification of DNAPLs in heterogeneous media by using an integrated approach. The approach combines intermediate-scale flow cell experiments, physical methods for DNAPL description (including dual-energy gamma radiation), and advanced modeling techniques. Difficulties in analyzing the

behavior of partitioningtracers may arise due to nonideal transport caused by factors such as subsurface heterogeneity (e.g., spatially variable hydraulic conductivity), variable distribution of NAPL, and rate-limited mass transfer. The impact of these factors on the partitioning tracer method has not yet been examined in detail and is being investigated in this work.

THEORY OF PARTITIONING TRACERS

The experimental and theoretical basis for the retention of dissolved solutes by immobile, immiscible liquid phases and the resultant impact on solute (tracer) transport has been described previously (Brusseau, 1992; Jin et al, 1995). Organic-fluid phases retain the partitioning tracer, which retards its transport with respect to that of conservative tracers. The procedure for estimating S_n, NAPL saturation, involves calculation of a retardation factor (R) for the partitioning tracer, which is done by a comparative moment analysis with the conservative tracer. The retardation factor is defined as the velocity of water (conservative tracer) divided by the velocity of the partitioning tracer. With knowledge of K_{nw} (NAPL-water partition coefficient), K_d (sorption coefficient), ρ_b (dry soil bulk density), and θ_w (volumetric water content), S_n can be calculated by use of:

$$R = 1 + (\rho_b / \theta_w) K_d + [(S_n / 1 - S_n)] K_{nw} \qquad (1)$$

The terms on the right-hand side of the equation describe retention of the tracer by the aqueous, porous media, and NAPL phases, respectively. For a tracer with no sorption to the porous media:

$$R = 1 + [(S_n/1- S_n)]K_{nw} \qquad (2)$$

PAST/CURRENT PARTITIONING TRACER WORK:

(1) Tucson International Airport Area Superfund Site
[saturated and vadose zone (gas-phase)]
Nelson and Brusseau, 1996

(2) Hill Air Force Base [saturated zone]
Brusseau et al, 1998 (in review)

(3) City of Tucson Fuel Depot [saturated and vadose zone]

(4) Maricopa Research Station [vadose zone]
Nelson et al, 1997 (presentation)
Brusseau et al, 1997

Subsurface Transport Over Multiple Phases

STOMP

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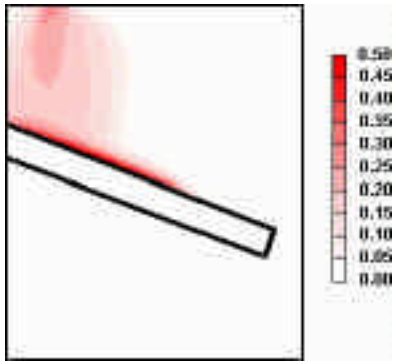
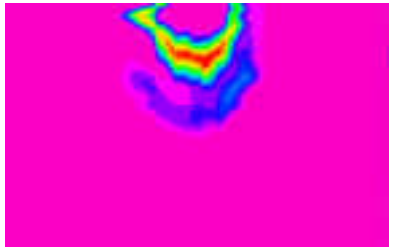
Subsurface Transport Over Multiple Phases

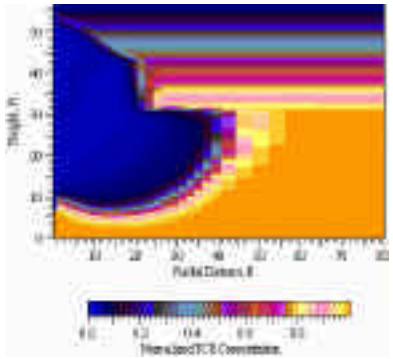
STOMP is a computer model, designed to be a general purpose tool for simulating subsurface flow and transport, that complements other analytical capabilities developed by Pacific Northwest National Laboratory's Subsurface Flow and Transport Group. The simulator was specifically designed to provide scientists and engineers from varied disciplines with multidimensional analysis capabilities for modeling subsurface flow and transport phenomena. STOMP's target capabilities were guided by proposed or applied remediation activities at sites contaminated with volatile organic compounds and/or radioactive material. Developed with the support of the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, the simulator's modeling capabilities address a variety of subsurface environments, including variably saturated, multiple-phased, nonisothermal, and variably frozen soils.
http://www.pnl.gov/etd/stomp



NAPL Distribution above a Sloped Capillary Barrier



Normalized Tritium Conc. Distribution at the Las Cruces Trench Site



TCE Conc. for In-Well Vapor Stripping Remediation

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Modeling Partitioning-Tracer Transport

Water-Oil w/ Rate-Limited Transport

Flow Solution

- Coupled Water and Oil Mass Conservation Equations
- Aqueous and NAPL Phases with a Passive Gas Phase
- NAPL Entrapment via Kaluarachchi and Parker [1992] and White and Oostrom [1998]

Solute Transport Solution (TVD Algorithms)

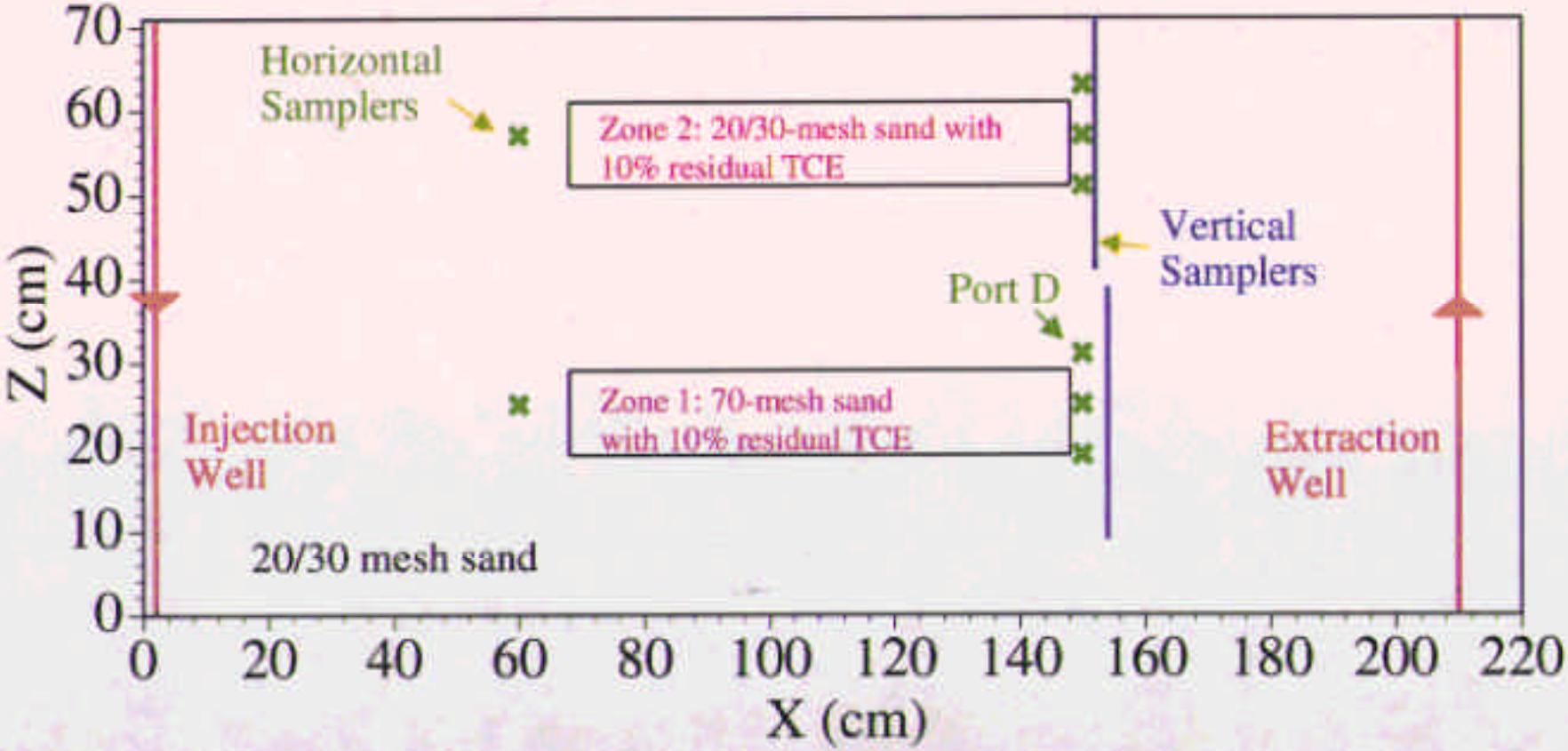
- Rate-Limited Partitioning between the Aqueous and NAPL Phases
- Rate-Limited Solid-Phase Sorption
- Equilibrium Partitioning between the Aqueous Phase and Aqueous-NAPL Interface
- Three Coupled Solute Mass Conservation Equations

$$R_{\ell i}\frac{\partial C_\ell}{\partial t} = -\nabla\left(C_\ell \mathbf{V}_\ell\right)+\nabla\left[\left(\tau_\ell s_\ell n_D D_\ell^C + s_\ell n_D \mathbf{D}_{h_\ell}\right)\nabla C_\ell\right]+\dot{m}_\ell^C-\dot{R}^C C_\ell - I_{\ell n}^C - I_{\ell s}^C$$

$$\frac{\partial C_n}{\partial t} = -\nabla\left(C_n \mathbf{V}_n\right)+\nabla\left[\left(\tau_n s_n n_D D_n^C + s_n n_D \mathbf{D}_{h_n}\right)\nabla C_n\right]+\dot{m}_n^C-\dot{R}^C C_n + I_{\ell n}^C$$

$$\frac{\partial C_s}{\partial t} = \dot{m}_s^C-\dot{R}^C C_s + I_{\ell s}^C \qquad I_{\ell n}^C = n_D s_\ell k_{\ell n}^C\left(C_\ell-\overline{C}_{\ell n}\right) \qquad I_{\ell s}^C = n_D s_\ell k_{\ell s}^C\left(C_\ell-\overline{C}_{\ell s}\right)$$

SCHEMATIC OF FLOW CELL



EXPERIMENTAL METHODS:

Preliminary Flow Cell Experiment

- **Experimental Apparatus**

- 2.2-m long, 1.1-m high, and 0.05-m wide intermediate-scale flow cell.
- Glass front [flow visualization] and Kynar back plate [installation of sampling ports]
- 24 horizontal sampling ports (integrated across 0.05 m width) and 3 vertical sampling ports (integrated across 0.05 m width and 0.30 m height) consisting of laser drilled stainless steel tubing (Kloehn, Las Vegas). Extraction well also sampled.
- Steady-state flow field established by using equal injection and extraction rates of 50 mls/min [1 pore volume every 9 hours].

- **STOMP** Simulations used as a tool to help determine sampling schedule.

- **Porous Media**
  - 20/30 mesh and 70 mesh silica sand
  - porous media heterogeneity consisted of a 80 cm by 10 cm zone of fine grained sand (70 mesh) packed within a matrix of 20/30 mesh sand.

- **TCE Zones**
  - TCE NAPL dyed with Sudan IV to enhance visualization.
  - Distinct zones of TCE (both with $S_n = 0.1$) created by mixing TCE and sand on the bench-top prior to packing.
  - Zone 1 established within a low permeablity region (70 mesh)

- Zone 2 established within 20/30 mesh matrix material.

- **<u>Dual-energy gamma radiation system</u>** used to determine distribution of DNAPL S_n.
  - Fully automated.
  - Calibration and data acquisition according to procedures described by Oostrom et al (1995, 1998).

- **<u>Tracers</u>**
  - Bromide (conservative tracer); 170 mg/l
  - Pentafluorobenzoic Acid [PFBA] (conservative tracer); 170 mg/l
  - 2,4-dimethyl-3-pentanol [DMP] (NAPL partitioning tracer, $K_{tce\text{-}water} = 68$); 170 mg/l

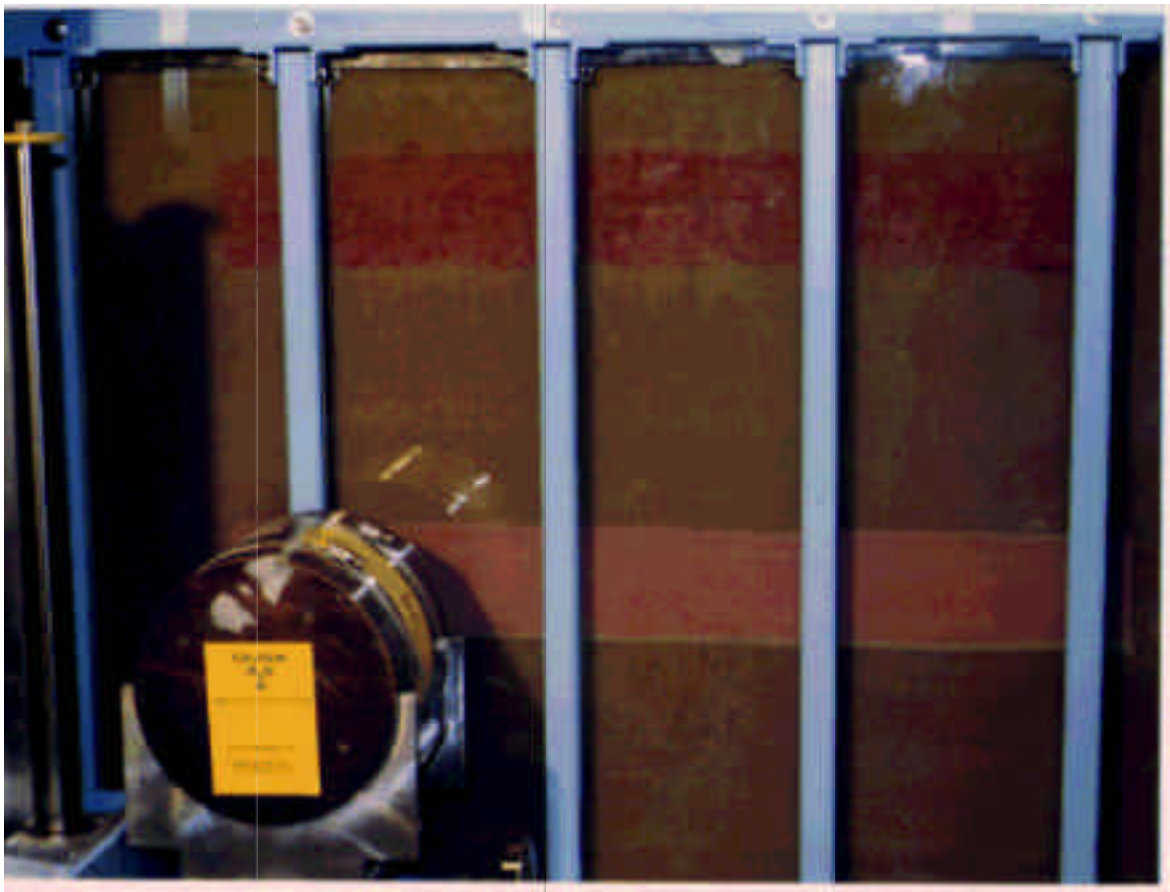
- 6-methyl-2-heptanol [MH] (NAPL partitioning tracer, $K_{tce\text{-}water}$ = 222); 170 mg/l
- Approximate 2 pore-volume tracer injection.
- Additional 16 pore volumes of tracer-free water flushed after tracer injection.

Analytical Methods

Bromide: Ion Chromatography [EMSL]

PFBA: High Pressure Liquid Chromatography [EMSL]

DMP, MH, and TCE: Gas Chromatography (GC) /Mass Spectrometry [EMSL] and GC with Flame Ionization Detector [University of Arizona]



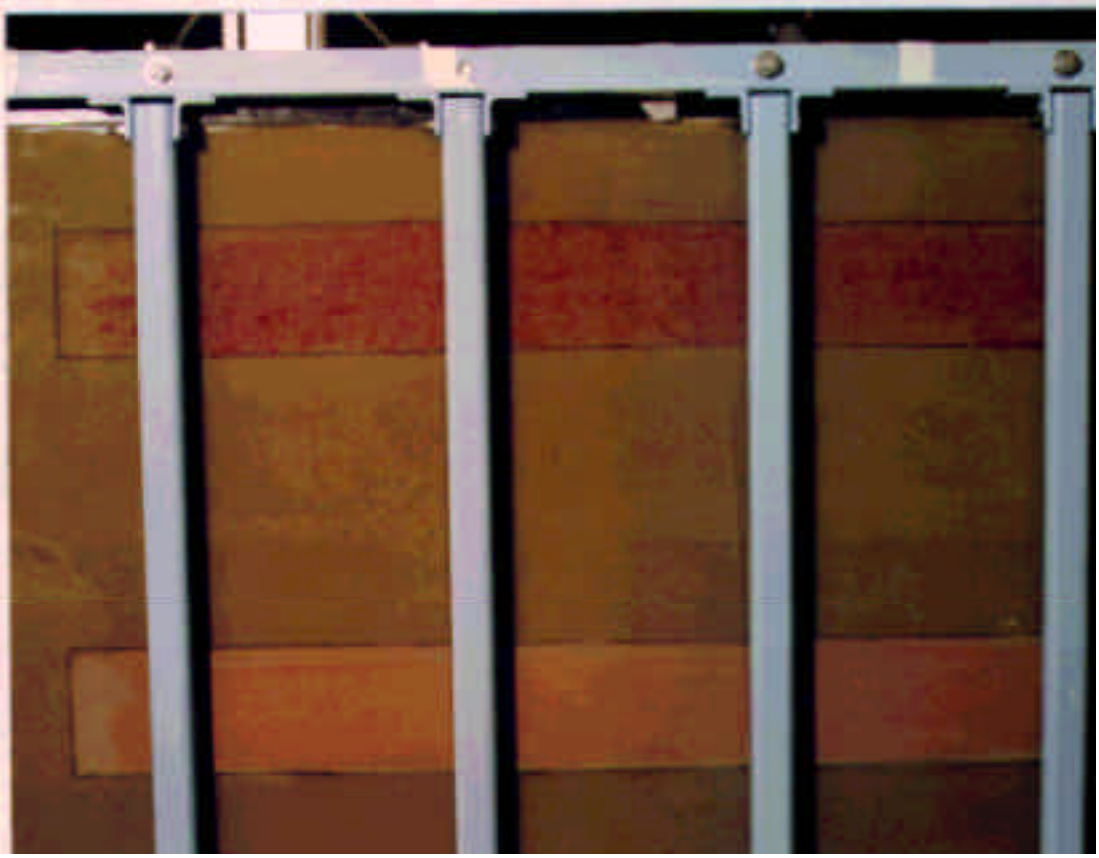
← Dual-Energy Gamma System Taking Measurements

Sampling Array →

TCE Residual Zones at Different Times During Experiment

T = 0 hr

T = 24 hr



T = 72 hr

T = 144 hr

Fluorescein Dye Experiment

T = 1 hr

T = 3 hr

T = 5 hr

T = 8 hr

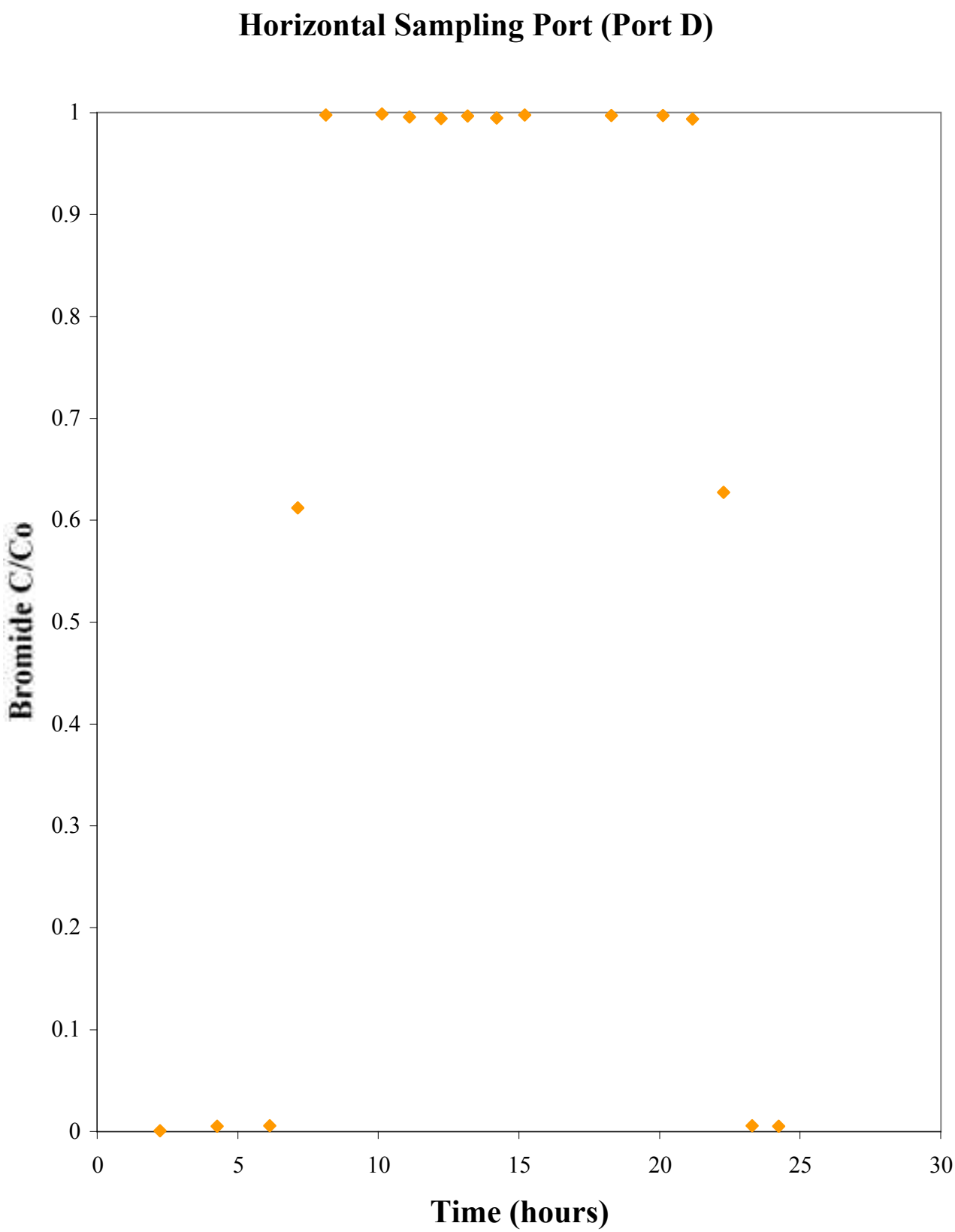
PRELIMINARY RESULTS

- Bromide breakthrough curve at Port D (a horizontal port) is smooth and symmetrical indicating ideal transport.

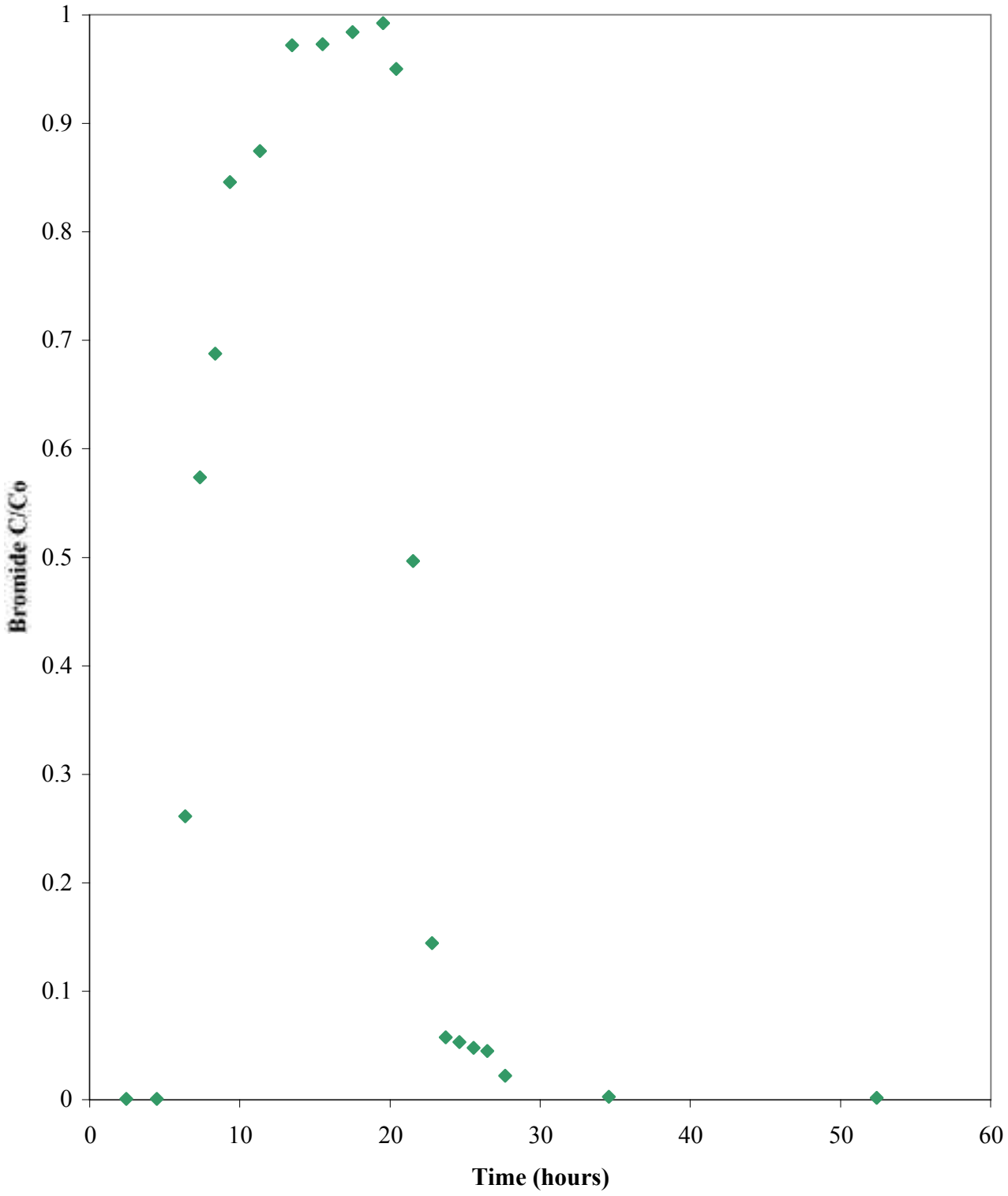
- Bromide breakthrough curve at Port K (vertically integrated port for Zone 2) demonstrates tailing associated with spatially variable hydraulic conductivity. This tailing is a common characteristic of vertically integrated samples (wells).

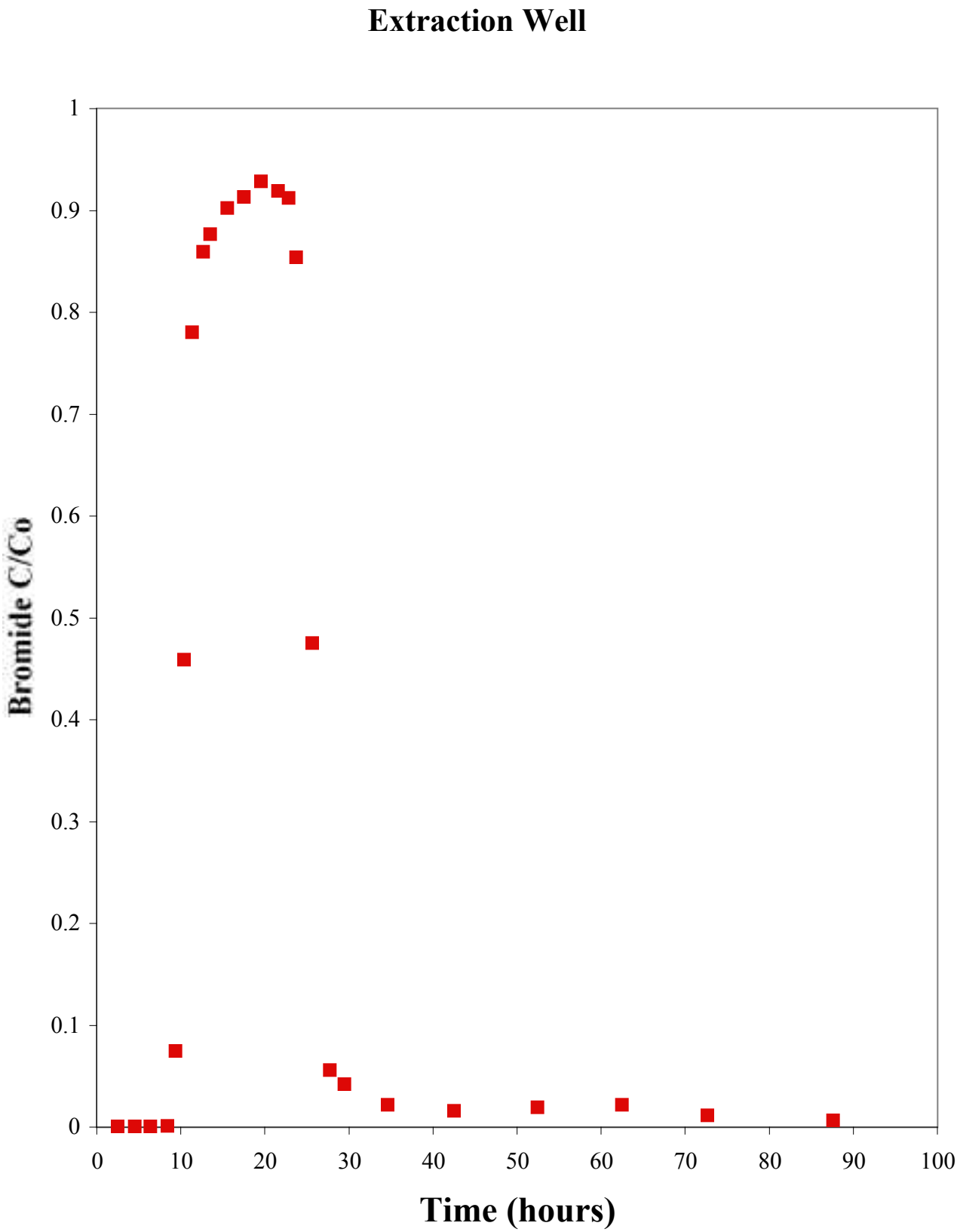
- Bromide breakthrough curve at extraction well demonstrates tailing associated with spatially variable hydraulic conductivity. This tailing is a common characteristic of extraction well data.

- In general, the bromide breakthrough curves indicate a well-controlled flow field and pulse-like tracer injection.


Horizontal Sampling Port (Port D)
Bromide C/Co
Time (hours)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30

Vertically Integrated Port for Zone 2




Extraction Well
Bromide C/Co
Time (hours)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
10
20
30
40
50
60
70
80
90
100

FUTURE WORK

- Analysis of the preliminary experiment will be completed.

- STOMP will be used to simulate the results from the preliminary flow-cell experiment.

- Several additional tracer experiments will be conducted including:

  (1) experiments with different flow-rates.

  (2) experiment with a pool of NAPL established in the flow-cell.

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T = 1 hr

T = 3 hr

T = 5 hr

T = 8 hr