EVALUATING LNAPL BODY STABILITY AT A CRUDE OIL RELEASE SITE

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September 29, 2015
Introduction

- Regulatory policies for LNAPL sites
  - Have been changing nationally
  - LNAPL recoverability = LNAPL Transmissivity is a valid endpoint metric
  - Demonstrating stability of dissolved, vapor, & liquid phase plumes more commonly required

- ITRC (2009) and ASTM (2014) Guidance address these policies

- But methods and technologies are evolving
Stability by Multiple Lines of Evidence

- LNAPL release occurred decades ago
- Significant remedial actions have reduced mobility
- Dissolved and vapor phase plumes are stable
- Wells/borings near leading show no LNAPL
- Low-K materials near water table ensure low mobility
- LNAPL transmissivity estimates from baildown test are in the 0.01 to 0.8 ft²/day (ITRC, 2009)
- Non-wetting fluid resistance at leading edge prevents further spreading
Topics to Cover

- Processes that control LNAPL spreading
- Quantitative methods for demonstrating stability
- Case study of research that tested the methods
- Implications whenever LNAPL reaches groundwater
Conceptual Model for Mass Losses

Source: Lundy, 2010
Is a Mass Balance Mechanism at Work?

- **Mass Balance** between inflow into, and outflow from a specified area
- **Resistance** at leading edge of the specified area

**Ice Sheet-Glacier Analogy**
Newer More Quantitative Approach

- A mass-balance approach sounds reasonable.

- Can we measure a mass balance between spreading and mass depletion rates?

- Can we measure resistance at leading edge, and is it temporary and spatially dependent?

- How reliable are the field/lab methods – should we consider spatial variability and uncertainty?
Estimating Mass Gain and Loss Areas

- Infer LNAPL body migration history
- Define mass inflow & outflow areas
- Select a hinge-line separating them
Estimating Inflow of LNAPL Mass

- **Darcy Expression for LNAPL Mass Inflow:**
  \[ M_o = T_o \left( \frac{d\rho_o}{dx} \right) W_o \rho_o \]
  
  - \( T_o = LNAPL\ Transmissivity \)
  - Baildown tests
  - Tracer tests
  - Lab/field parameters
  - Generic parameters
  - API guidance
  
  - \( dh_o/dx = LNAPL\ Gradient \)
    - LNAPL-air interface gradient
    - Mean water table gradient x 1/LNAPL specific gravity
  
  - \( W_o = Width\ of\ LNAPL\ body\ along\ the\ hinge-line \)

- \( \rho_o = LNAPL\ density \)
Estimating Mass Depletion in Outflow Area

- Basic Expression for Mass Flux balance

\[ \hat{M}_{oil} \leq \hat{M}_{vap} + \hat{M}_{aqu} + \hat{M}_{bio} \]

- But \( M_{vap} \) and \( M_{aqu} \) losses are negligible
  - **Vapor phase is degraded in vadose zone**
  - **Aqueous phase leaving LNAPL zone is a small relative to \( M_{bio} \) in the LNAPL zone**
Consequently...

- Rate of Biogenic Gases Reaching the Land Surface can Represent 95+ % of total LNAPL Mass Depletion
Tools to Measure CO₂ Efflux

“CO₂ Trap”
(McCoy, 2012)

“Dynamic Closed Chamber”
(Sihota et al. 2011, 2012)

Samples extracted in lab after several weeks of passive CO₂ collection at each station.

Samples collected and analyzed in the field. Multiple readings at each station are then averaged.
Case Study

USGS Research Site Near Bemidji, MN
Footprint Areas of 1979 Excavations and North Pool Leading Edge Migration to 2012
3 Decades of Well Gauging Data

a) Well 315

\[ y = 1.16 \times 10^4 \times e^{-0.027x} \]

\[ R^2 = 0.4751 \]

b) Well 411

\[ y = 1.53 \times 10^4 \times e^{-0.15 \times e^{-0.02x}} \]

\[ R^2 = 0.403 \times 0.01 \]

c) Well 421B

\[ y = 9.46L \times 10^1 \times e^{1.94 \times 0.01} \]

\[ R^2 = 0.615 \times 0.01 \]
Average Water Table Configuration and BTEX Plume
Geochemical Zonation

Source: http://mn.water.usgs.gov/projects/bemidji/gif/xsect1.gif
Hypotheses Tested

- Historical mass loss trends and rates based on LNAPL composition changes should agree with losses based on biogenic CO₂ efflux from the LNAPL zone.

- LNAPL in contact with groundwater will spread laterally to a stable configuration with ongoing internal migration balanced by mass depletion in a downgradient area.

- LNAPL body stability is supported by non-wetting fluid capillary resistance at the leading edge, but a) only after a mass balance is reached, and b) will vary spatially.
Re-delineated the LNAPL Body in 2011

- Laser-Induced Fluorescence (LIF) Survey
- Revised Maps/Sections
LIF-Inferred Historical LNAPL Flow Pattern
Delineation of Inflow and Outflow Areas
Baildown Tests in the LNAPL Inflow Area

- **Sampling Starts a Test**
- **LNAPL Transmissivity**
Model of Historical LNAPL Transmissivity

- Ten parameters control LNAPL transmissivity
  - 5 fluid properties measured in lab (archived & recent samples)
  - 4 hydraulic parameters estimated from baildown test results
  - Historical records of LNAPL thickness at baildown wells

- Historical Saturation Profiles and Transmissivity calculated
Lab Analysis of Archived and Recent Oil Samples

- **Physical Properties**
  - (a) Oil Density
  - (b) Oil Viscosity

- **Chemical Compositions**
  - (a) Bemidji Pipeline - 1984
  - (b) Well 411 - 1989
  - (c) Well 411 - 2010
LNAPL Mass Remaining Based on Changes in Moles Normalized to Pristane

- RE: to 1984 Reference Oil
- Mass Remaining Since 1979

**11(a) Mass Fraction Remaining**

\[ y = e^{0.13008x} \]
\[ R^2 = 0.7115 \]

**11(b) Total Mass Remaining**

\[ y = 109210e^{0.031x} \]
\[ R^2 = 1 \]
Mass Depletion Based on Compositional Changes vs. CO$_2$ Efflux Estimates

![Graph showing depletion rate over time]

- $y = 11.13e^{-0.03x}$
- $y = 9.22e^{0.08x}$
- $y = 7.30e^{-0.03x}$
North Pool Efflux of CO$_2$ in 2010

Average Mass Flux as C$_{10}$H$_{22}$ = 2.6 µmol/m$^2$/sec = 3.3 gm/m$^2$/day

Source: Sihota et al. 2011
Mass Losses at Selected Wells

Approximate 2012 LNAPL Footprint Area

Full Extent of Oil Body Undefined

Pipeline Release Point

Source: Sihota, 2013, personal communication

Carbon Dioxide Efflux Distribution and Oil Body Footprint

Legend

CO₂ Flux EBK

Filled Contours

Micromoles/m²/sec

0.626176671 – 2.99498335
2.99498335 – 4.32356992
4.32356992 – 5.03854786
5.03854786 – 5.4231273
5.4231273 – 5.63037368
5.63037368 – 6.01613855
6.01613855 – 6.73011648
6.73011648 – 8.05870306
8.05870306 – 10.5275097
10.5275097 – 15.115067
Gains and Losses in Discharge Area

a) Calculated Gains and Losses

- Base Gain Rate
- Base Gain + 1 C.I.
- Base Gain - 1 C.I.
- Base Loss Rate
- Base Loss + 1 C.I.
- Base Loss - 1 C.I.

Mass Gain or Loss, kg/day

Elapsed Time, years
Gain and Loss Trend Projection Needed

![Projected Gains and Losses](image)

- Stability Window of Opportunity
Fits with Plot of Leading Edge Advancement
Findings at the Bemidji Site – North Pool

- Rates and 1st order decay trends of oil composition-based mass losses agreed with those based on biogenic CO₂ efflux.

- USGS 1991 LNAPL volume estimate of 88,000 L represents ~ 68% of initial volume that reached the water table; hence, ~ 110,000 L in the USGS footprint area in 1979. But a larger footprint area mapped with LIF data in 2011 indicates release was > 110,000 L.

- Historical advancements of the LNAPL leading edge were consistent with historical rates of mass inflow exceeding mass depletion over an enlarging downgradient area.

- Stability by mass balance will occur within 16 yr (± 7 yr confidence interval) and fits with observed slowing of leading edge movement.
Potential Applications at other LNAPL Sites

- Estimated time to reach stability at North Pool, 42 to 56 years, is comparable to LNAPL release and body ages at many facilities.

- Mass depletion based on composition changes require a knowledge of starting compositions to use as a reference; applications limited.

- Composition-based mass loss should agree with CO₂ efflux measurements; are widely applicable.

- CO₂ efflux measurements over a downgradient area in combination with LNAPL transmissivity, density, and gradient estimates allows mass-balance testing; widely applicable.

- Combining those results with qualitative evidence of a stable LNAPL footprint can support a closure argument; widely applicable.
Questions and Answers

- Now or Later
- Thanks for Attending