Measuring the Degradation Rate of Subsurface Petroleum by Naturally Occurring Biochemical Processes

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SANBORN HEAD

Building Trust. Engineering Success.

Industry Sponsors And Research for University Consortium

- Sanborn Head Industrial Partnership with Consortium
- Founded in 1988 as University Consortium for Solvents in Groundwater Research
- Led by the Colorado State University and University of Guelph, Ontario
- Sponsored by Industry

Current Universities and Principals

University of Guelph
- Beth Parker
- John Cherry

University of Waterloo
- Ramon Aravena
- Robert Gillham
- Tadeusz Górecki
- Andre Unger

UC Davis
- Douglas Mackay
- Nick De Sieyes

University of New Bruswick
- Tom Al

Colorado State University
- Tom Sale
- Julio Zimbron

Colorado State University
Civil and Environmental Engineering
CCH
Center for Contaminant Hydrology

University of British Columbia
- Ulrich Mayer

University of Florida
- Mike Annable
- Kirk Hatfield

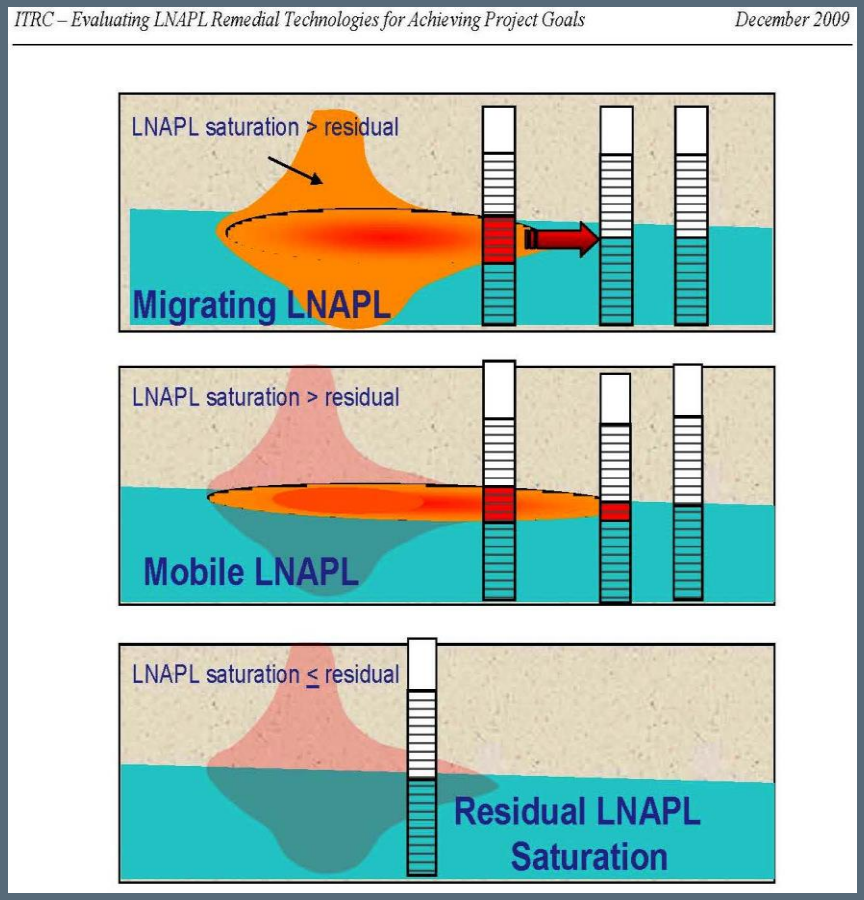
Arizona State
- Paul Johnson

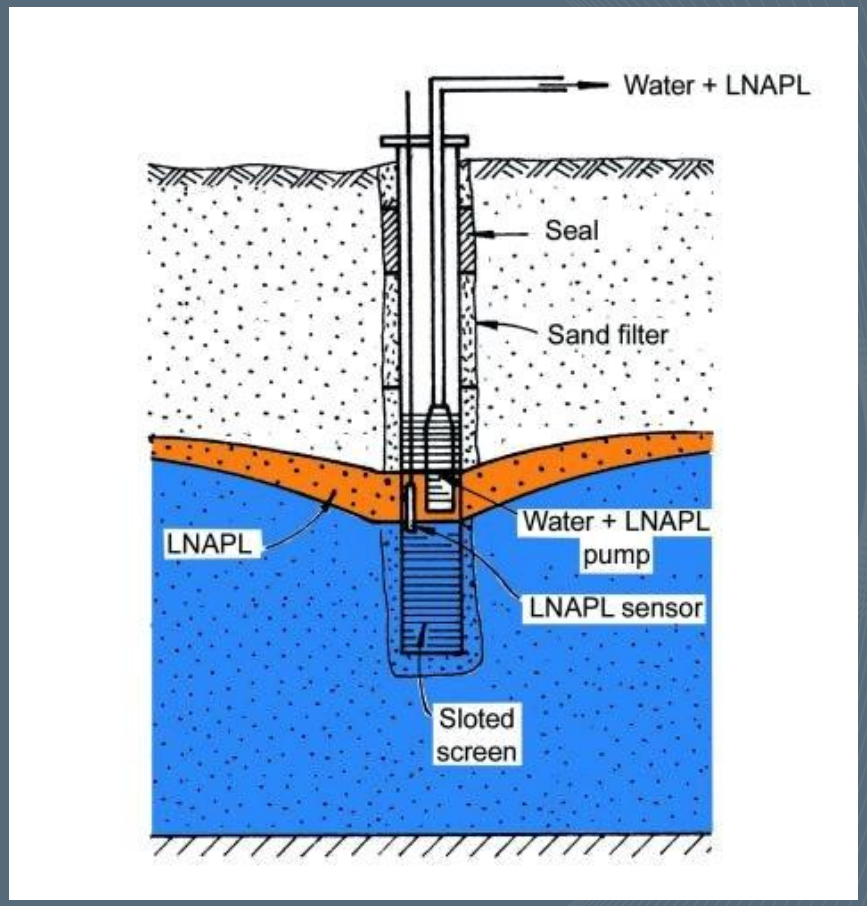
http://g360.uoguelph.ca/app/webroot/assets/PDF/Consortium_Overview_Presentation.pdf

Early Understanding of LNAPL

In 80s & 90s – LNAPL Body Thought of as a "Pancake"

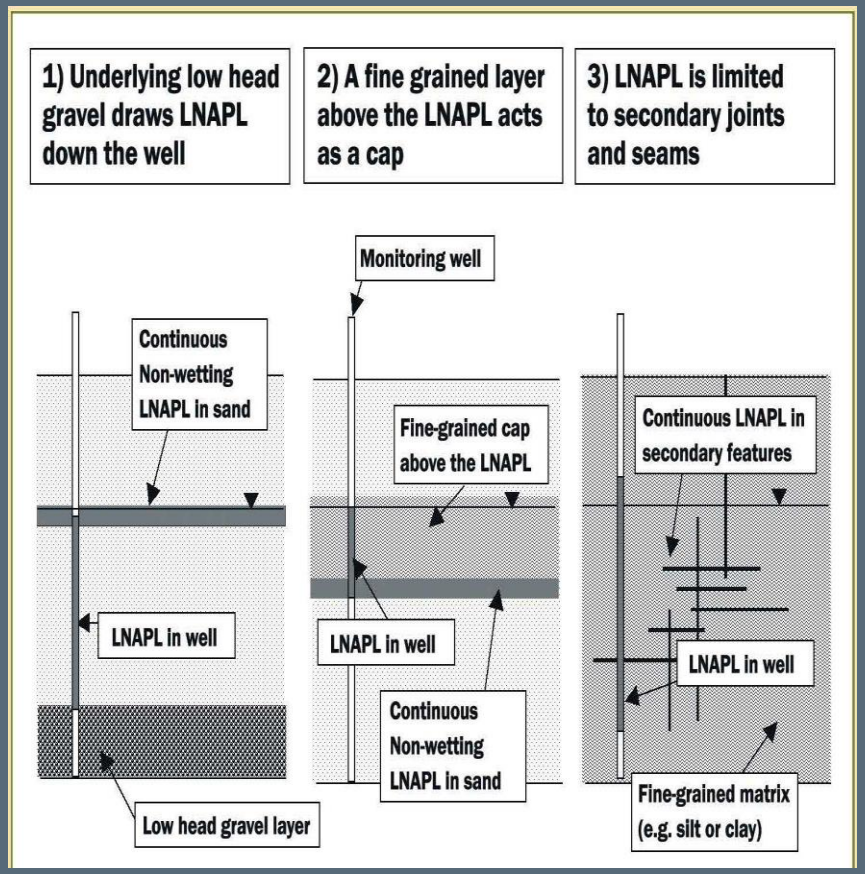
Historically, LNAPL Recovery Focused on Pumping



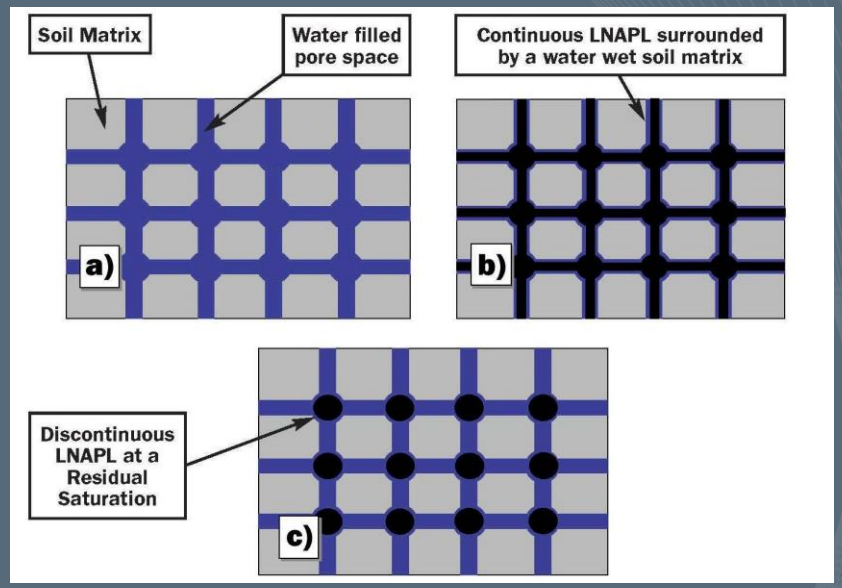


New Concepts Emerging that are Relevant to LNAPL Migration

Geology and Capillary Properties Greatly Affect LNAPL Thickness in Wells



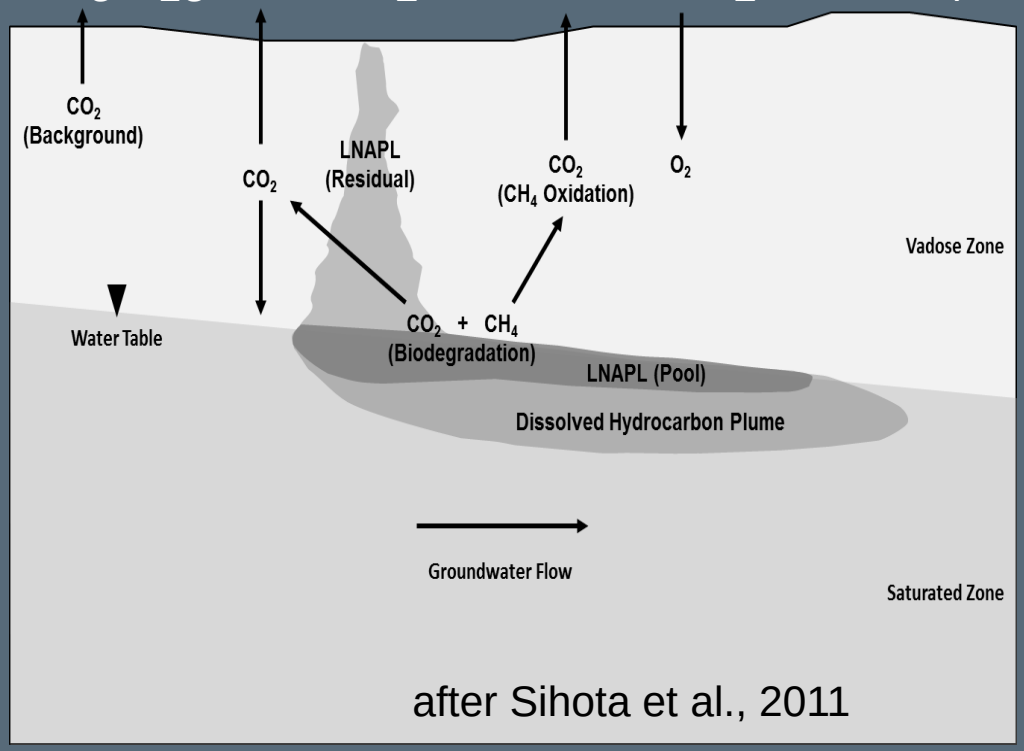
LNAPL Transmissivity is the Key Variable



Mechanisms of LNAPL Degradation

- <u>Mechanisms</u>
  - Volatilization
  - Diffusion
  - Transfer between vapor and aqueous phases
  - Biochemical degradation in aqueous phase

$$C_8H_{18} + H_2O \rightarrow CO_2 + CH_4$$



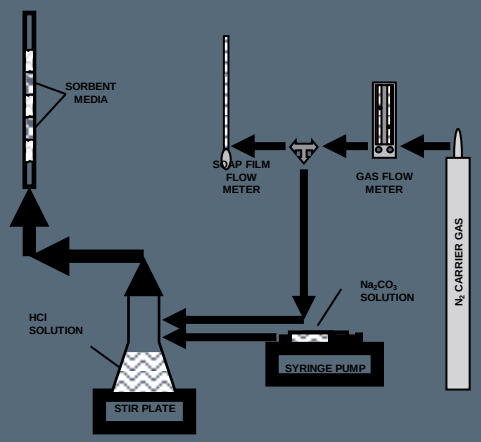
after Sihota et al., 2011

- Approximately 98% of carbon from degradation is emitted as carbon dioxide (Mollins et al 2010 – modeling study)

- CO_2 flux ($\mu mol/m^2/sec$) → LNAPL biodegradation rate (gallons/acre/year)

CSU Research - Capturing CO_2 Quantitatively

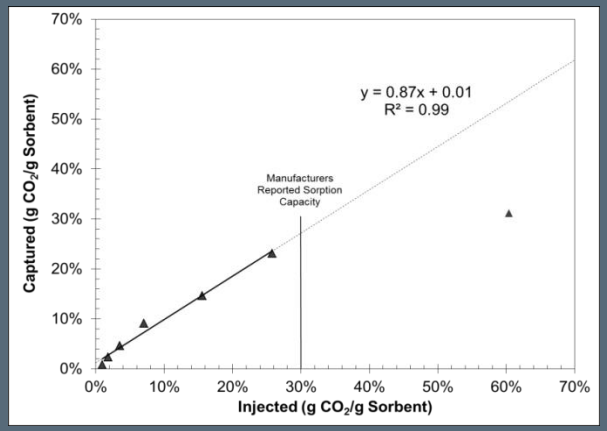
Small scale, closed system

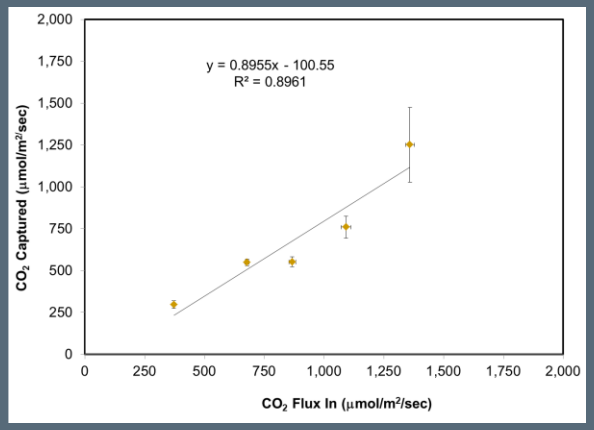


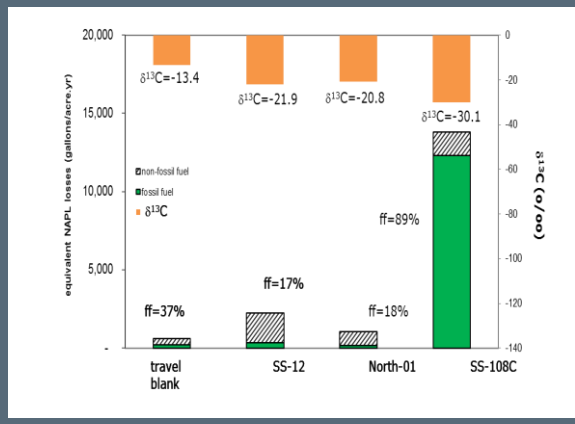
Large scale, open system

Carbon (^{14}C) isotope analysis

- Fossil fuel fraction of CO_2 production corroborates trap findings in the field

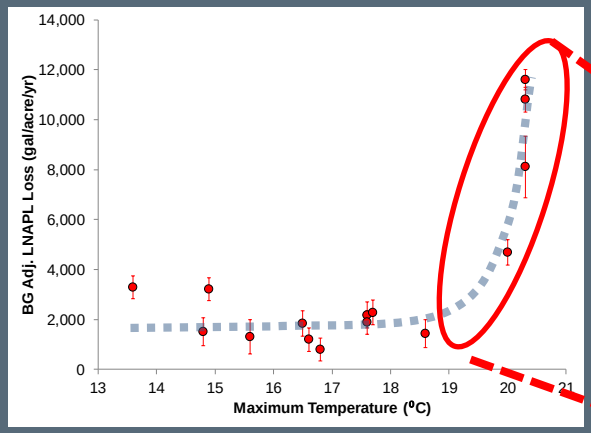


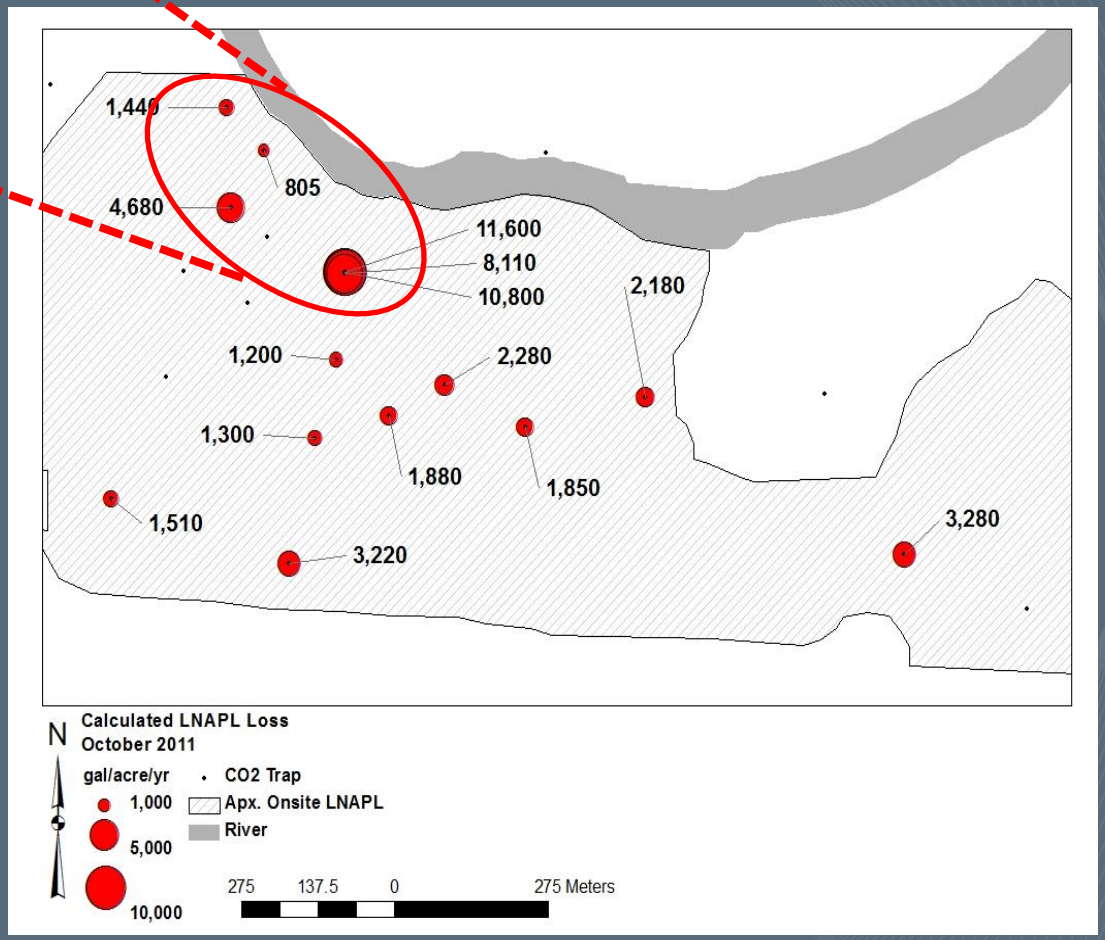




McCoy, K. 2012 CSU. M.Sc. Thesis

Temperature Dependence of LNAPL Loss





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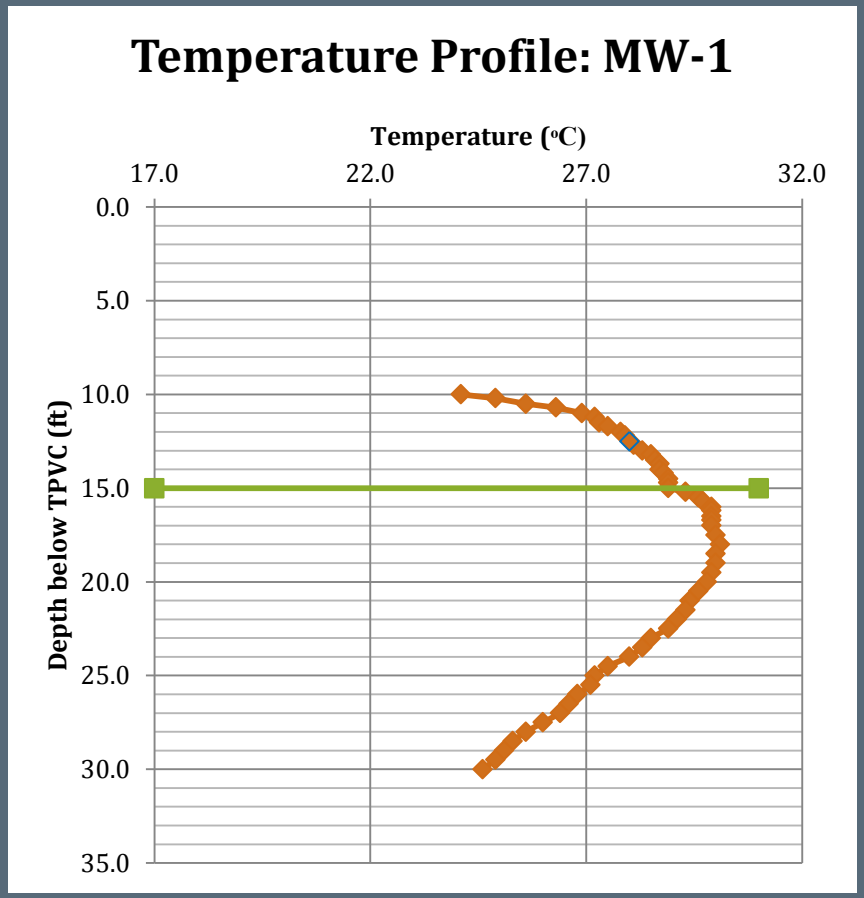
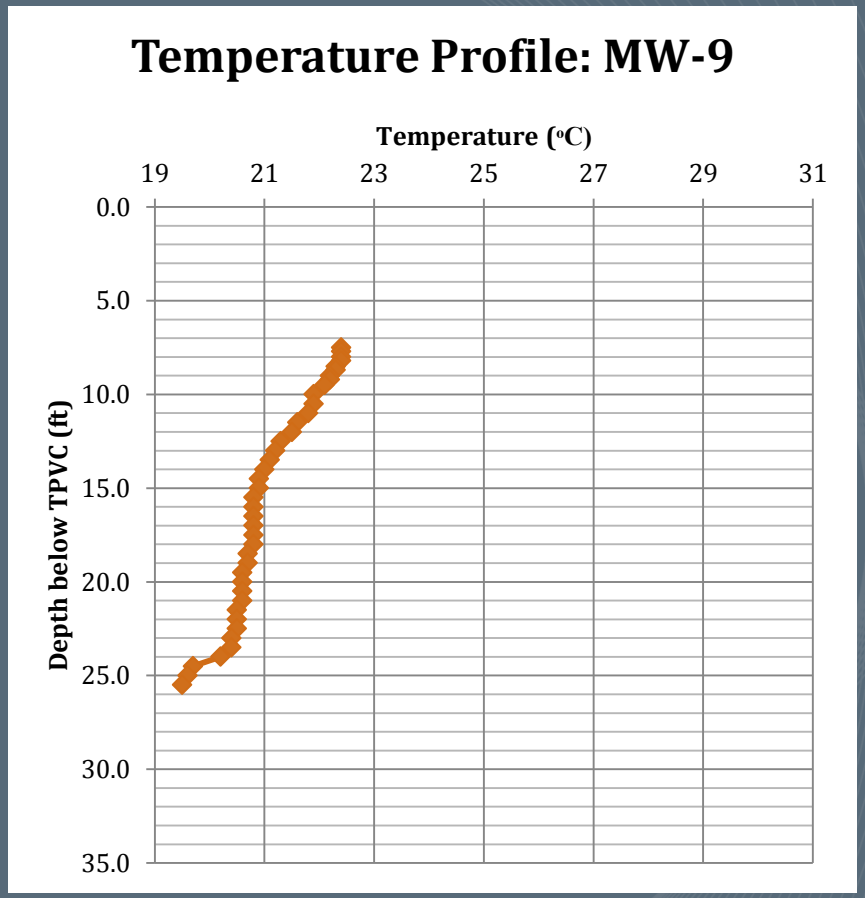
Field Screening For Biochemical Indicators (Temp., CH_4, CO_2, O_2)

LNAPL Zone



Background Conditions



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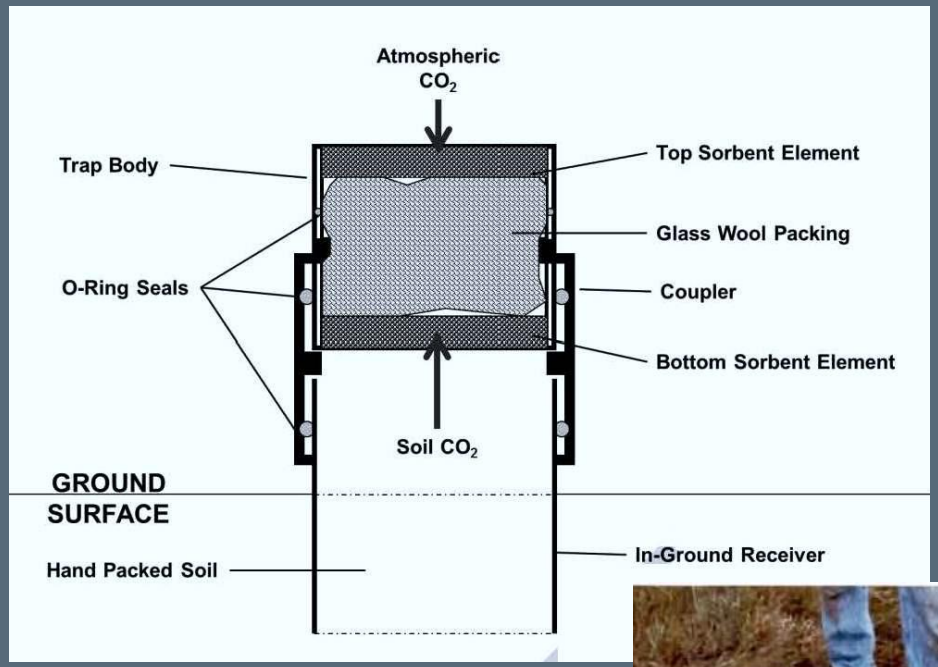
CO_2 Trap Design

- CO2 trap secured to shallow, in-ground receiver pipe, which is open to the atmosphere

- Two sorbant elements in trap
  - Top element traps atmospheric CO_2
  - Bottom element traps soil CO_2

- Sorbant elements are analyzed for total carbon

- Approximately $1K per trap analysis

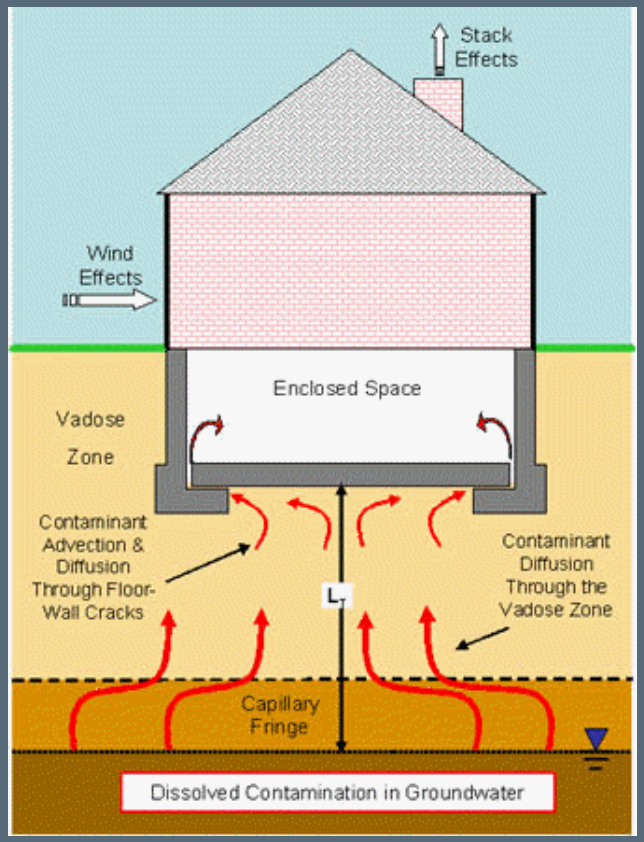


Perforated PVC shroud

LNAPL Loss Calculations

- Total CO_2 flux (mmol/m^2/sec) based on:
  - total mass of trapped carbon on bottom element,
  - diameter of receiver pipe,
  - properties of LNAPL, and
  - duration of deployment
- $\text{Flux}_{\text{tot}} = \text{Flux}_{\text{background}} + \text{Flux}_{\text{NA LNAPL}}$
  - $\text{Flux}_{\text{background}}$ based on total trapped carbon at background locations or carbon isotope analyses
- $\text{Flux}_{\text{NA LNAPL}}$ calculated in units (gal/acre/yr)

Effects of Concrete Caps on LNAPL Loss Calculations



- CO_2 Trap initially developed to be deployed in an outdoor setting
- CO_2 Trap installed in concrete capped areas can create the "chimney effect"
- LNAPL loss calculations need to be adjusted using a crack to surface area ratio to rationalize the artificially elevated flux measurements

Corroborating Lines of Evidence

- Calculated rates of LNAPL biodegradation can be supported through additional lines of evidence including:
  - Visual presence of LNAPL in the subsurface;
  - Detailed soil coring;
  - Thermal profile and gas profiles;
  - C^{13} enriched carbon isotope ratio; and
  - Groundwater monitoring /natural attenuation program findings

Benefits of CO_2 Trap Data

- LNAPL loss and cleanup rates associated with biochemical degradation can be measured
- Inexpensive metric as a baseline
  - Evaluate effectiveness of active LNAPL remediation
  - Assess LNAPL longevity
  - LNAPL remediation cost analysis
- Supports traditional MNA data
- Possibility of low temperature enhancement

CO_2 Trap Limitations

Site conditions that may be limiting include:

- *Shallow groundwater* – potentially limits the mineralization of methane (CH_4), which is not sorbed to the CO_2 trap element
- *Impermeable groundcover* – increase input uncertainty
- *Seasonal monitoring may be appropriate* – slight increased in sub-grade temperature can significantly increase LNAPL loss rate
- *Background Analysis* – assessing site-specific background C02 generation may be difficult

Questions?

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3. Mahler, N., Sale, T., and Lyverse, M., December 2012, A Mass Balance Approach to Resolving LNAPL Stability, *Ground Water, Vol. 50, Issue 6, pgs 861-871.*

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5. Zimbron, J., Sale, T., and Lyverse, M., June 2013, Measurement of Hydrocarbon Natural Attenuation Rates in Soils using Passive CO_2 Flux Traps, Battelle's 2013 Bioremediation Symposium, Jacksonville, Florida.

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