DyeLIF – Direct Push Optical Sensor for High Resolution Real-Time Mapping of Chlorinated Solvent DNAPL in the Subsurface

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GRA Annual Meeting
Concord, California

HALEY ALDRICH

DYE-LIF Project Team

- Murray Einarson and Adrian Fure (Haley & Aldrich)
- Randy St. Germain (Dakota Technologies)
- Beth Parker and Steve Chapman (University of Guelph)

ESTCP Project ER-201121

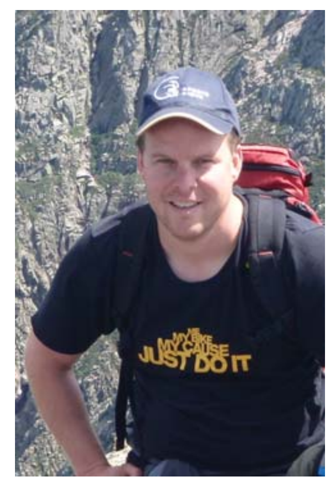
Murray

Adrian

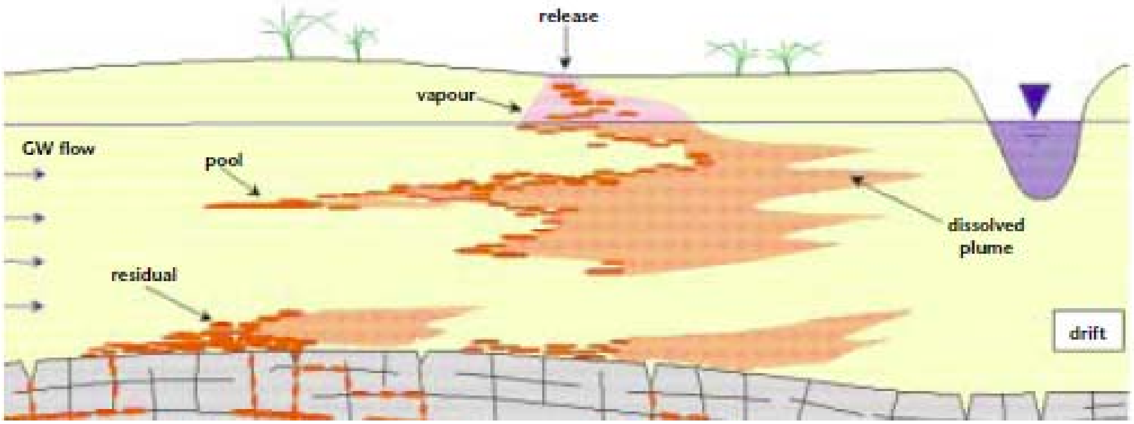
Randy

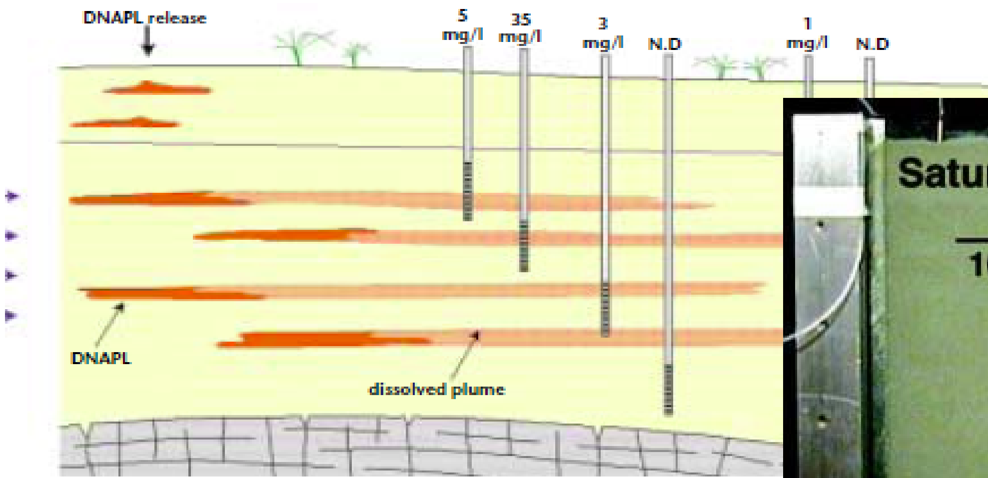
Beth

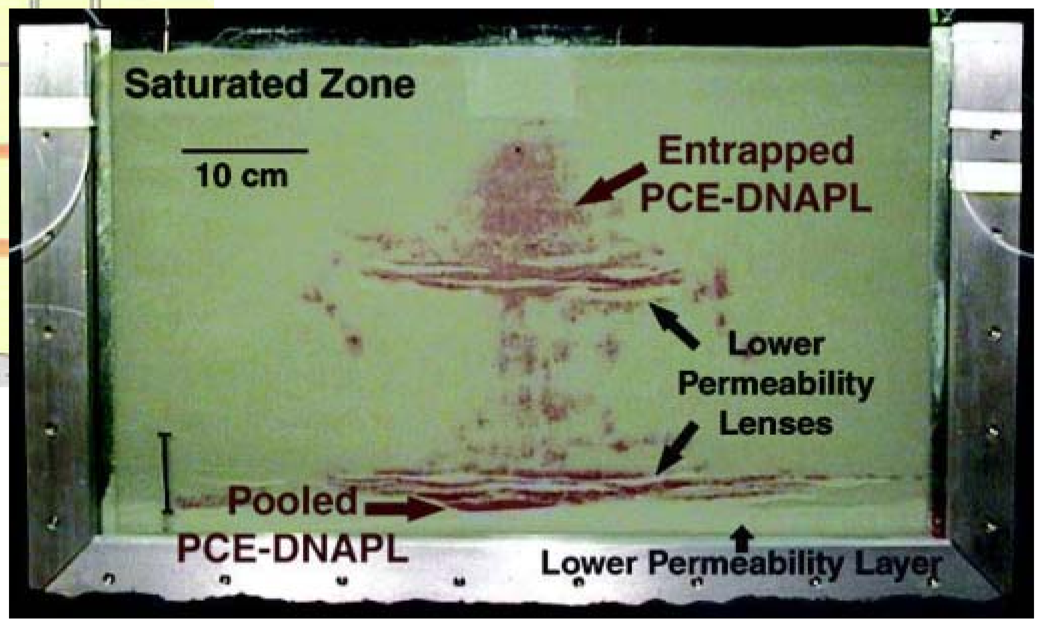
Steve



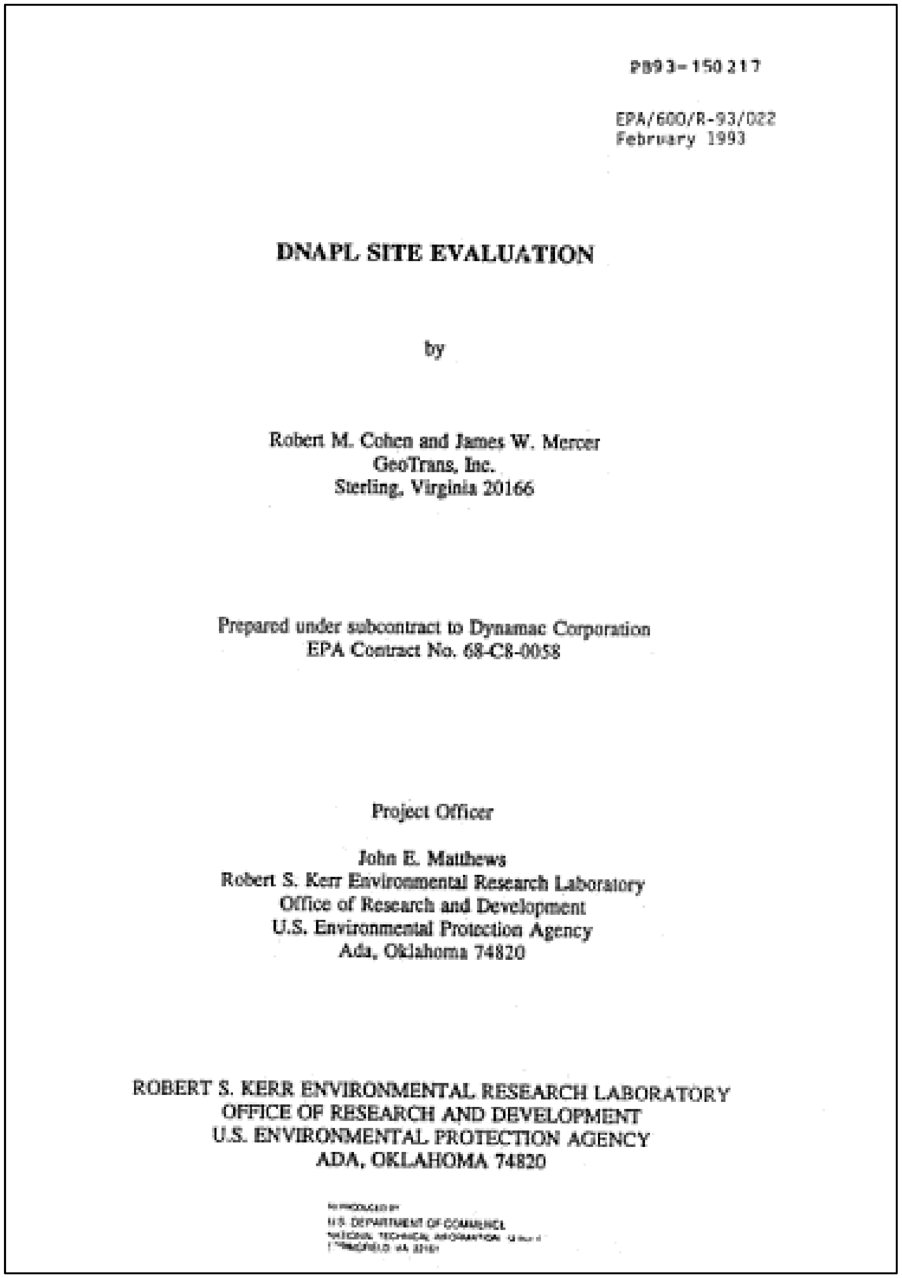
Models of DNAPL source zones







Source: Kueper et al. 2003


PB93-150217

EPA/600/R-93/022
February 1993

DNAPL SITE EVALUATION

by

Robert M. Cohen and James W. Mercer
GeoTrans, Inc.
Sterling, Virginia 20166

Prepared under subcontract to Dynamac Corporation
EPA Contract No. 68-C8-0058

Project Officer

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Few new (or old), good options for delineating DNAPL in the subsurface

- Soil concentrations
- Direct observations
- Dye-tests
- ROST/SCAPS?

7.3 Screening of soil borings

Soil samples can be taken from unconsolidated deposits both above and below the water table using a variety of techniques such as hollow stem auguring, push sampling and trial pits. During drilling operations, soil samples can be taken and subjected to visual examination. If DNAPL is present at high saturations (that is, pooled DNAPL) it will be probably be readily noticeable. If the DNAPL is present at low saturations (that is, residual saturation) or if the DNAPL has the same colour as the soil matrix, it may not be visually apparent and a dye shake test may be required. A dye shake test involves mixing a small quantity of a hydrophobic dye such as SUDAN IV with the soil sample in a sealed glass jar. In the case of SUDAN IV, the dye is red in colour and will partition only into a NAPL phase; it will not partition into water. If a NAPL is present in the soil sample, it will manifest itself as red globules interspersed within the soil matrix. Other field screening methods for soil borings include headspace analysis using a portable vapour analyser with photoionisation detection (PID) or flame ionisation detection (FID), and the use of fluorescence analysis. Fluorescence analysis involves taking the obtained soil sample and subjecting it to a fluorescent light in a dark space. Many hydrocarbons such as aromatic and polyaromatic hydrocarbons having one or more benzene rings (for example, coal tar, creosote and PCBs) will fluoresce, along with DNAPL mixtures

exposed to DNAPL. Additional screening techniques when drilling in bedrock include inspecting the drill return water for visual or olfactory evidence of hydrocarbons (for example, iridescent sheens or odours) and headspace analysis of rock core that may contain high concentrations of contaminants diffused into the matrix. Exposure to hazardous substances should, however, be controlled and sniffing cores is not appropriate unless it is clear that it is safe to do so. Prior use of calibrated PID/FID equipment may be appropriate where there is any doubt.

7.5 Laboratory analysis of soil samples

Soil characterisation programmes typically involve sending discrete soil samples to the laboratory for quantitative analysis of contaminant composition. The presence of NAPL in a soil sample can be evaluated using:

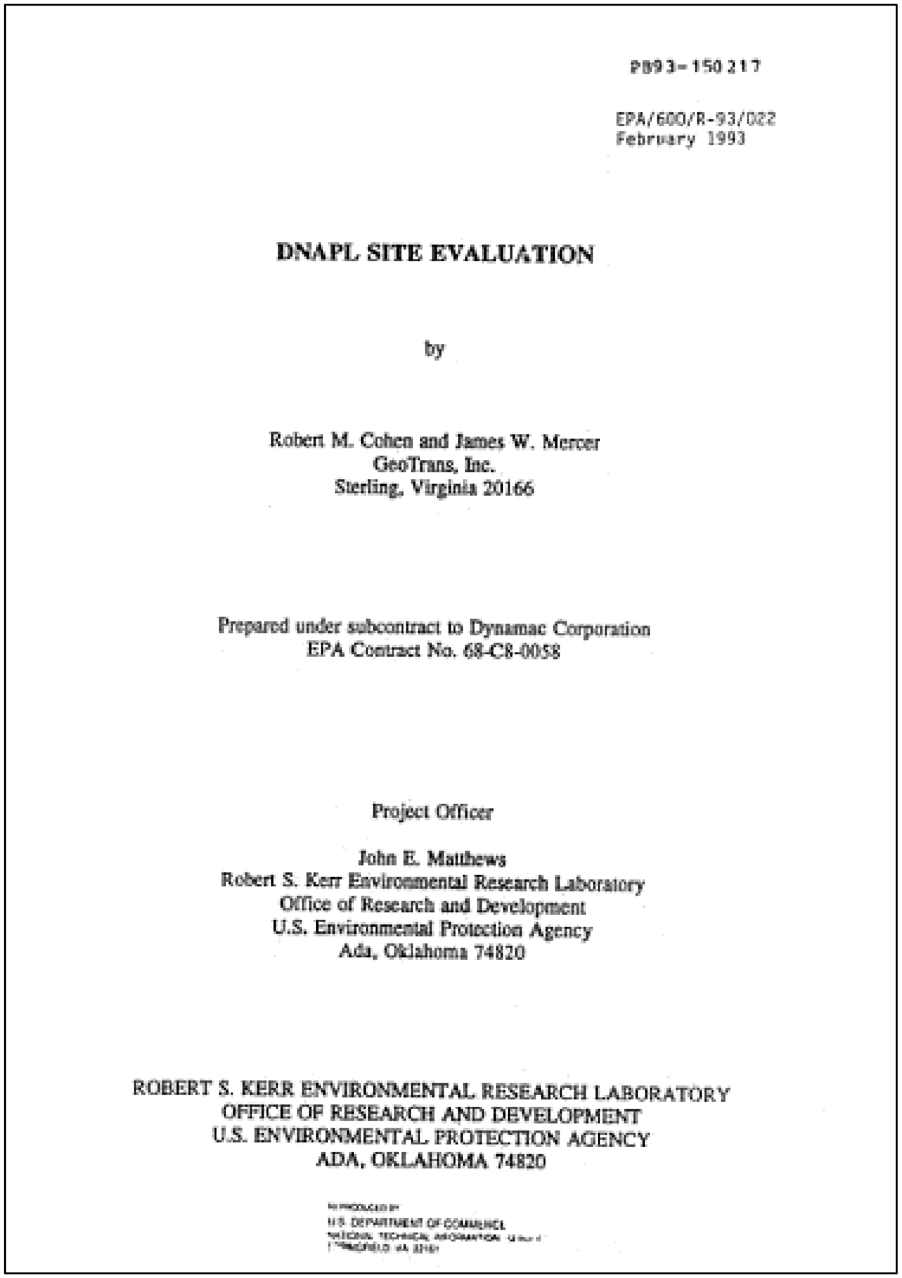
Equation 2

$$C_i^T = \frac{C_i}{P_b}(K_d P_b + \theta_w + H'\theta_a)$$

where:

C_i^T is the concentration of an organic substance at or above that which may be present in a non-aqueous phase (mg/kg);

Dye shake tests using hydrophobic dyes such as Sudan IV or Oil-Red-O



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U.S. DEPARTMENT OF COMMERCE

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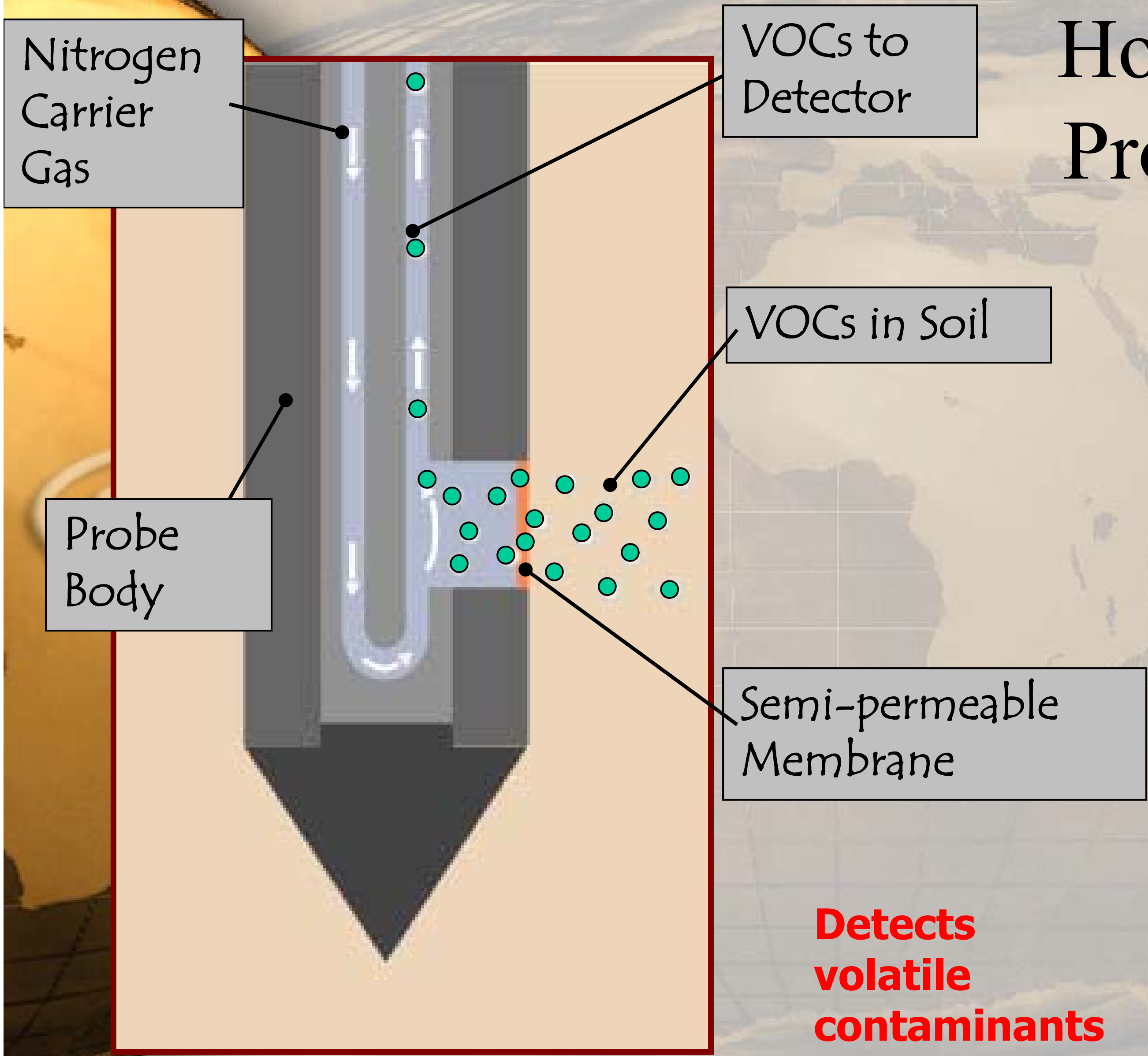
What about MIP?

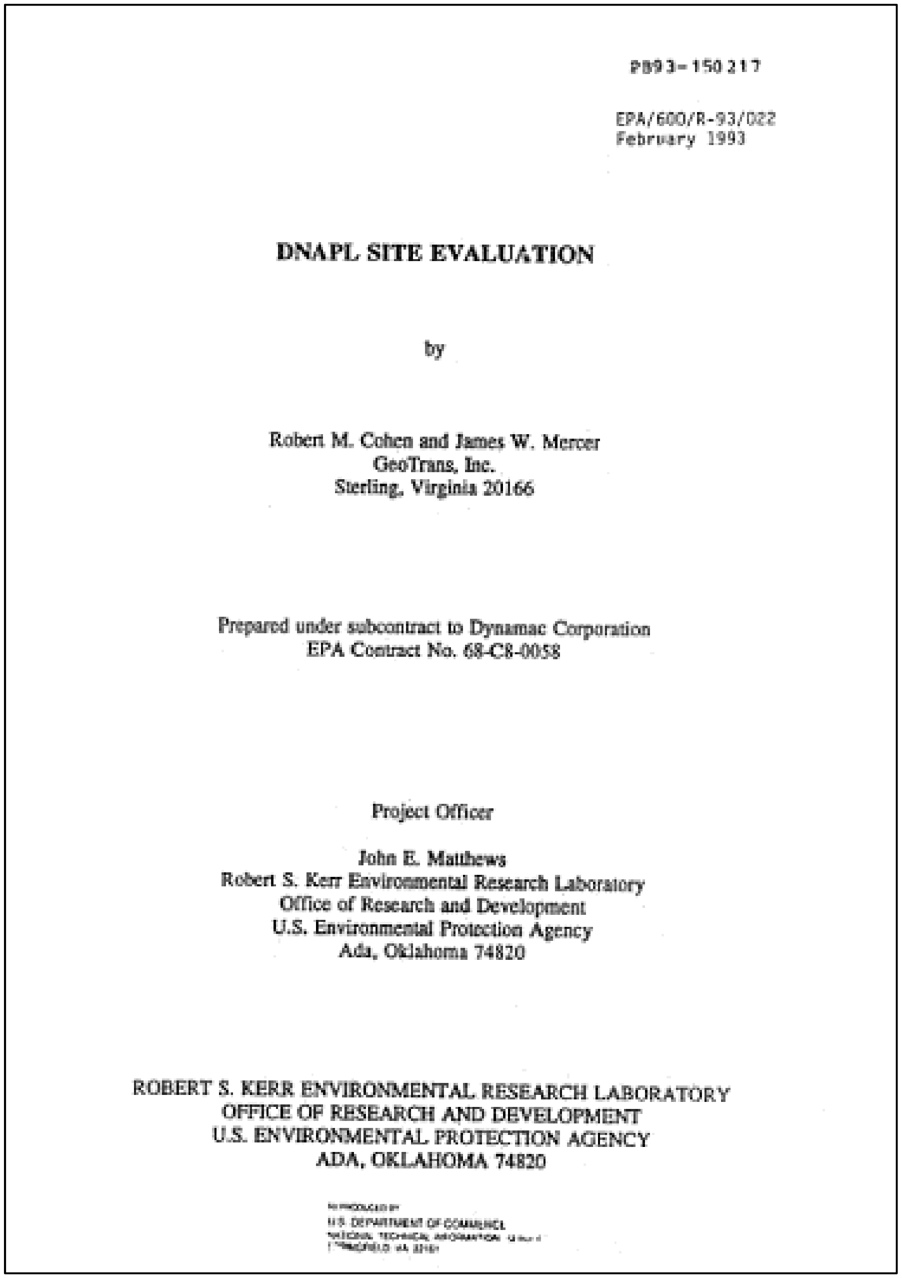


How the MIP Probe works:

Under a Concentration Gradient VOCs move across the Membrane via diffusion and then are carried to the Detector at the surface in an Inert Carrier Gas

Detects volatile contaminants in any phase

Source: Geoprobe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- Direct observations
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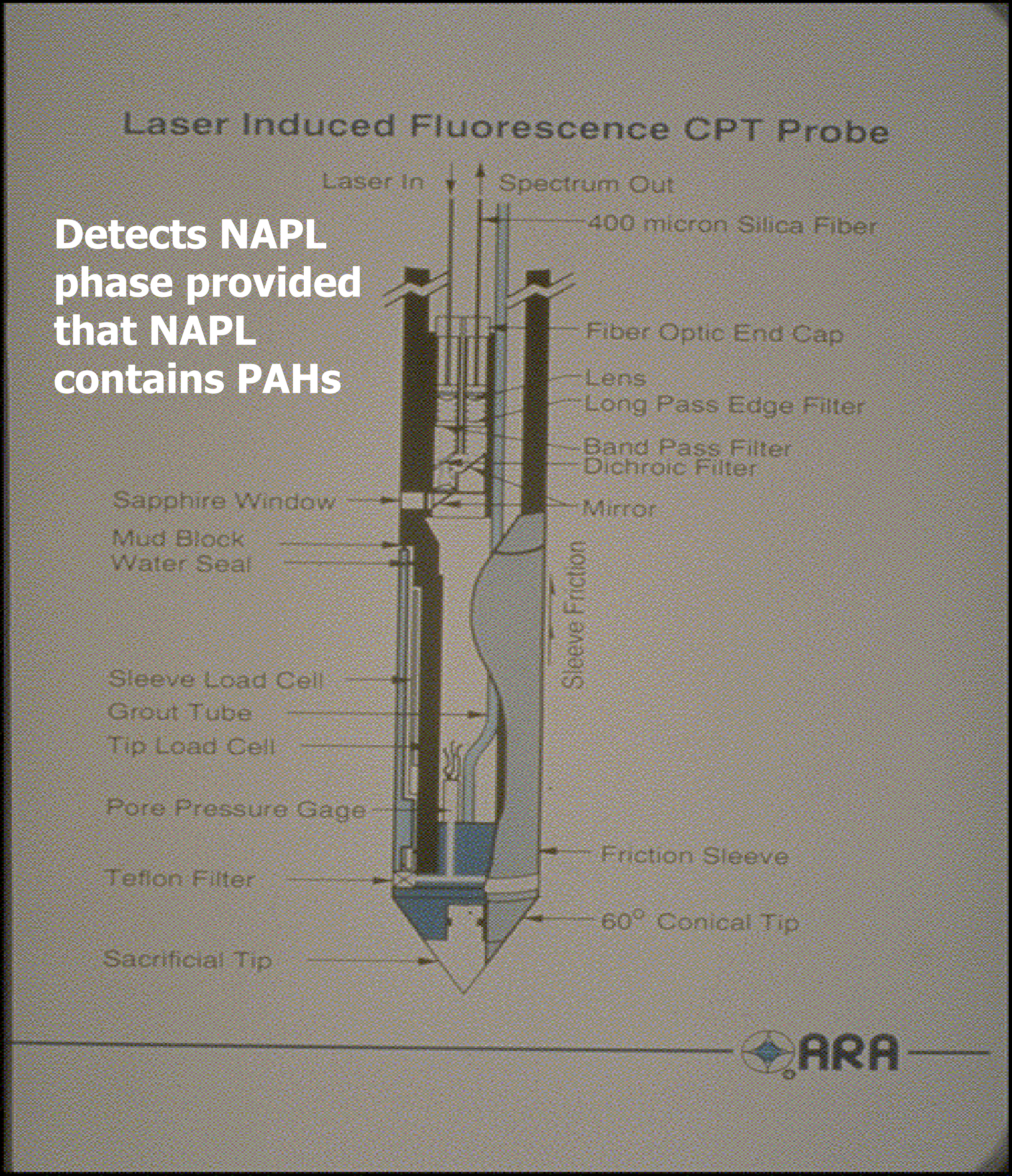
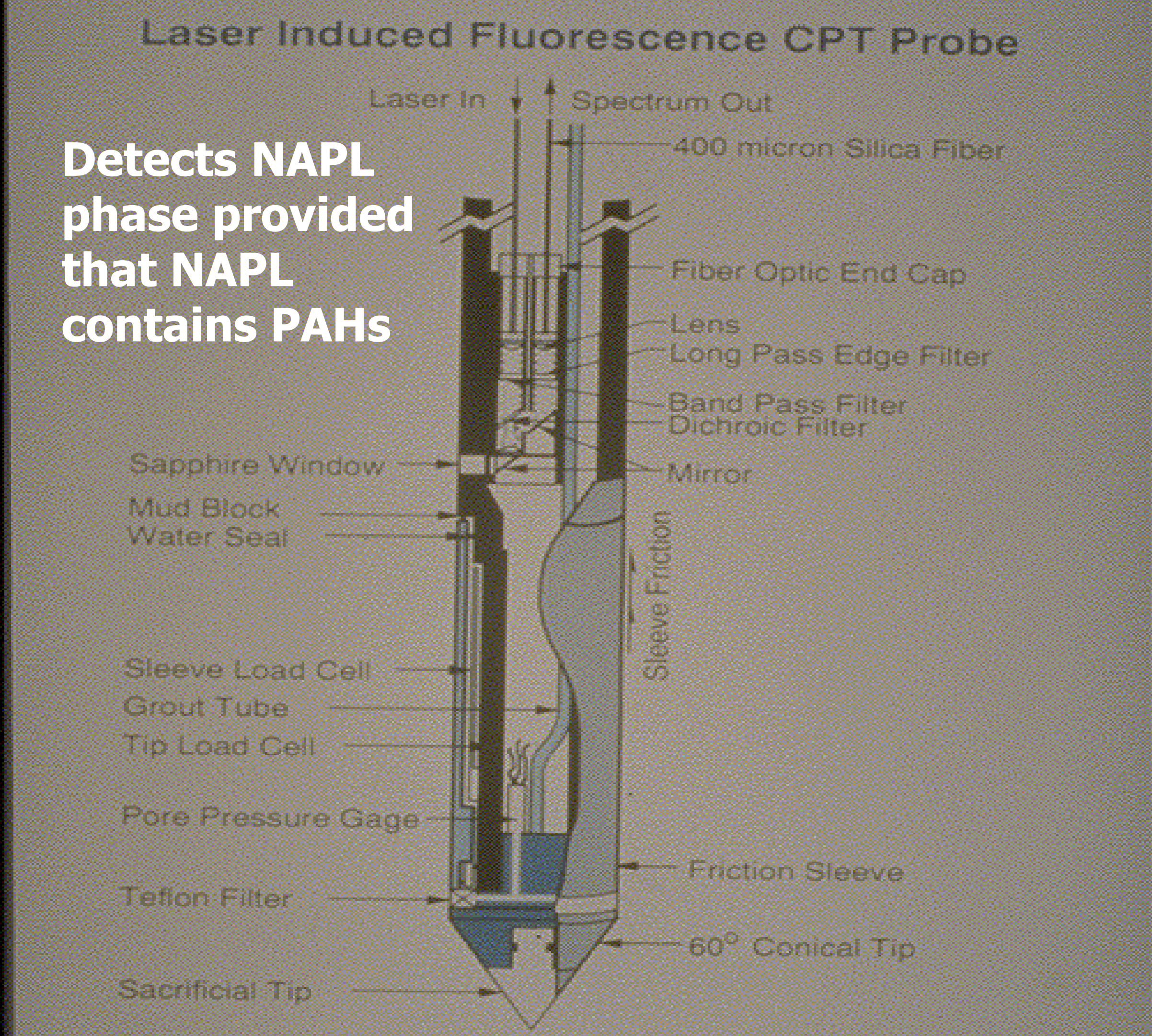
- **ROST/SCAPS?**


MACK
APPLIED RESEARCH ASSOCIATES, INC.
7 9'92

Detects NAPL phase provided that NAPL contains PAHs



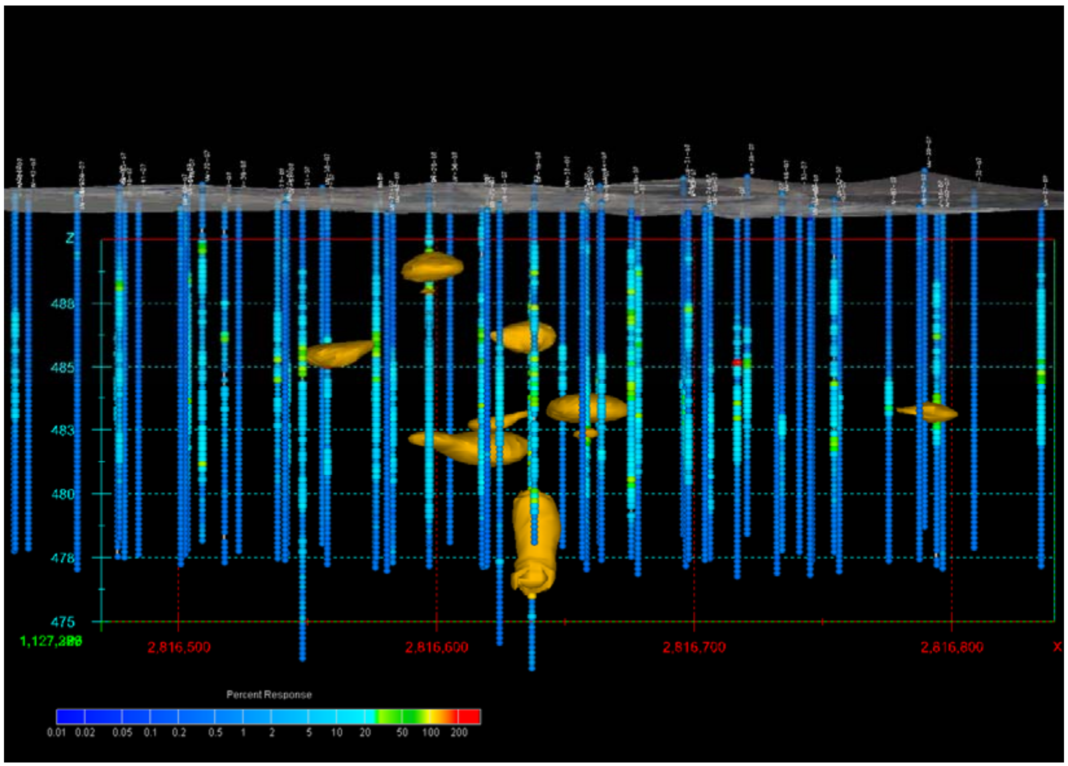


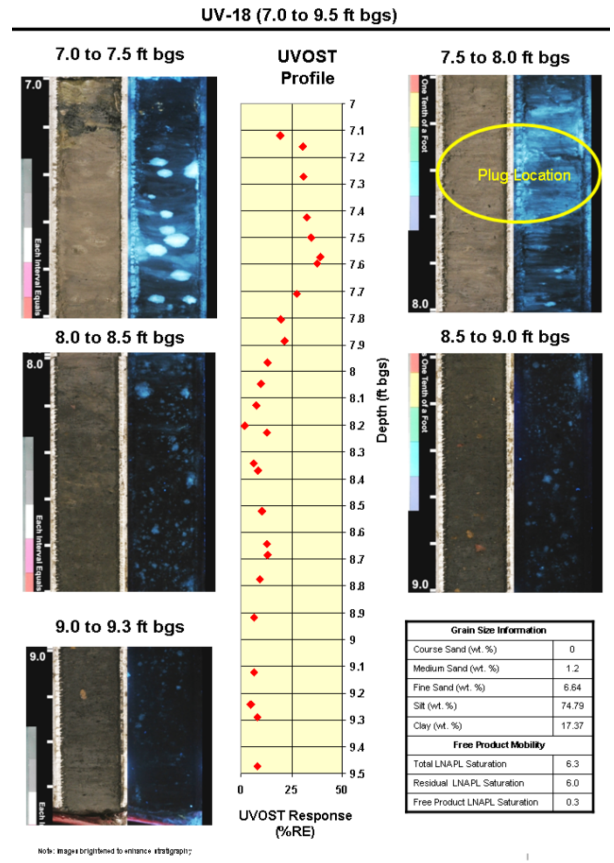
Detects NAPL phase provided that NAPL contains PAHs

Doesn't work with chlorinated solvent DNAPL

New generation LIF

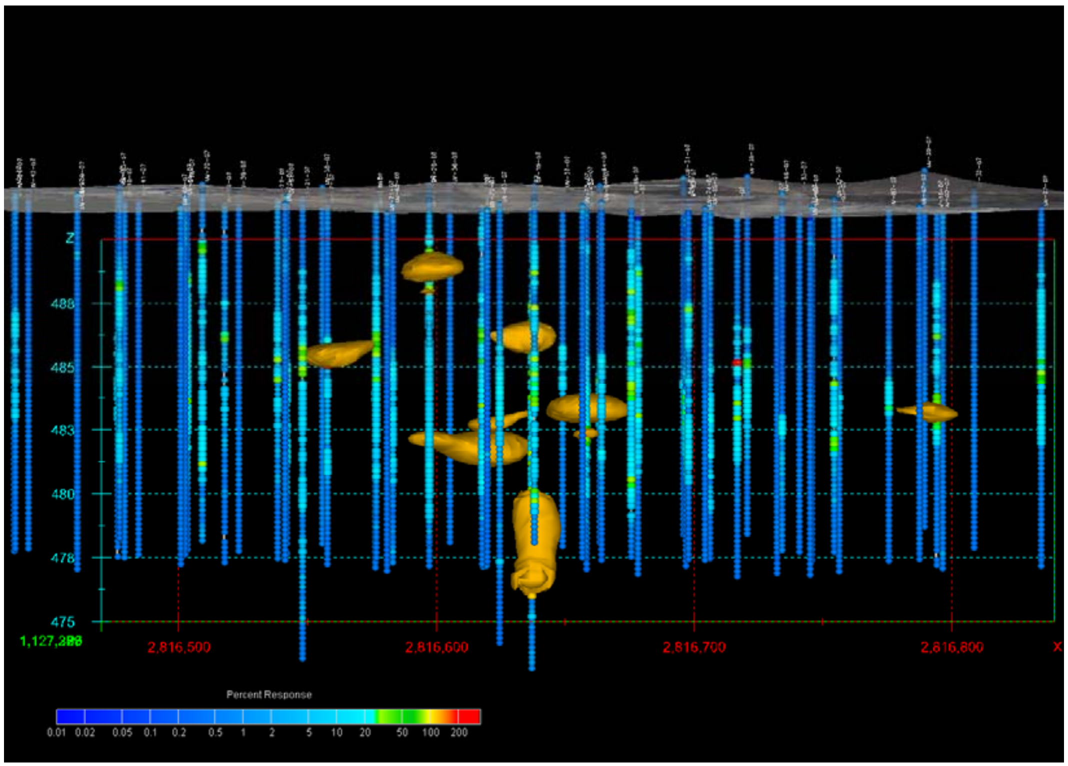
Signatures of NAPL distribution in fine grained soils – **highly complex NAPL distribution**

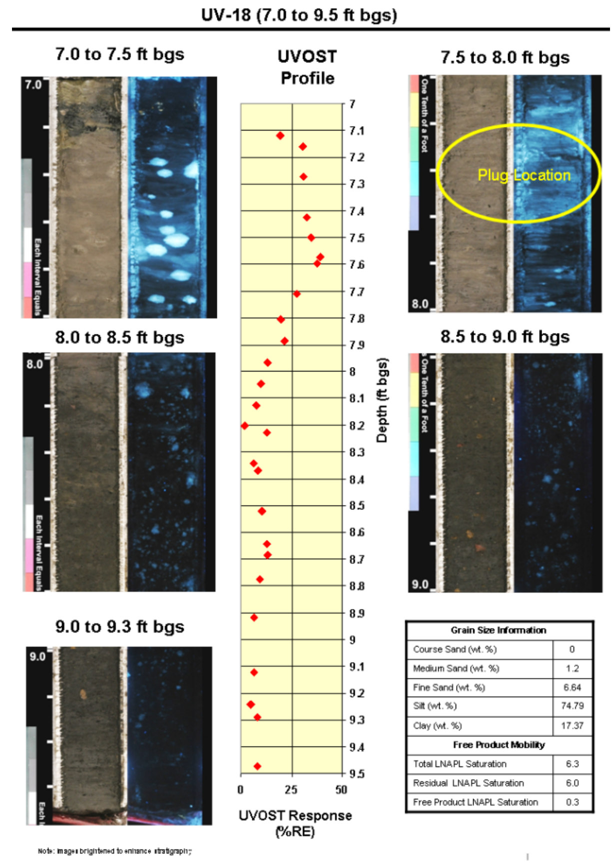




New generation LIF

Signatures of NAPL distribution in fine grained soils – **<u>highly complex NAPL distribution</u>**



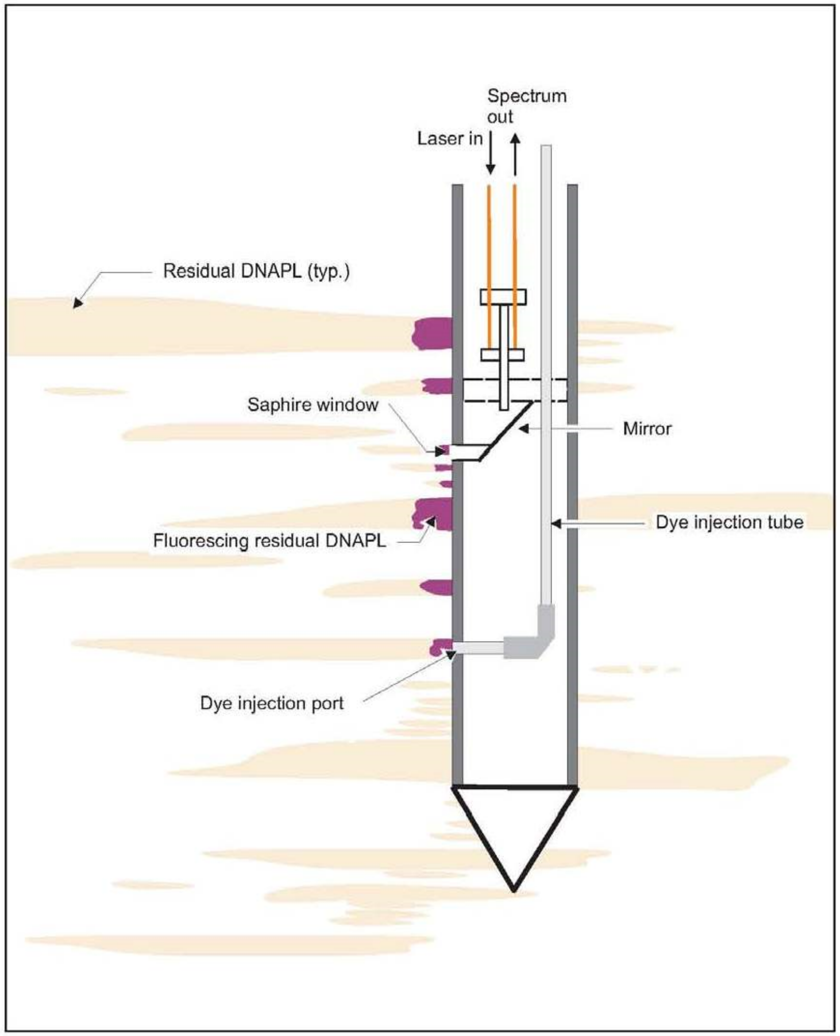


Grain Size Information	
Course Sand (wt. %)	0
Medium Sand (wt. %)	1.2
Fine Sand (wt. %)	6.64
Silt (wt. %)	74.79
Clay (wt. %)	17.37
Free Product Mobility	
Total LNAPL Saturation	6.3
Residual LNAPL Saturation	6.0
Free Product LNAPL Saturation	0.3

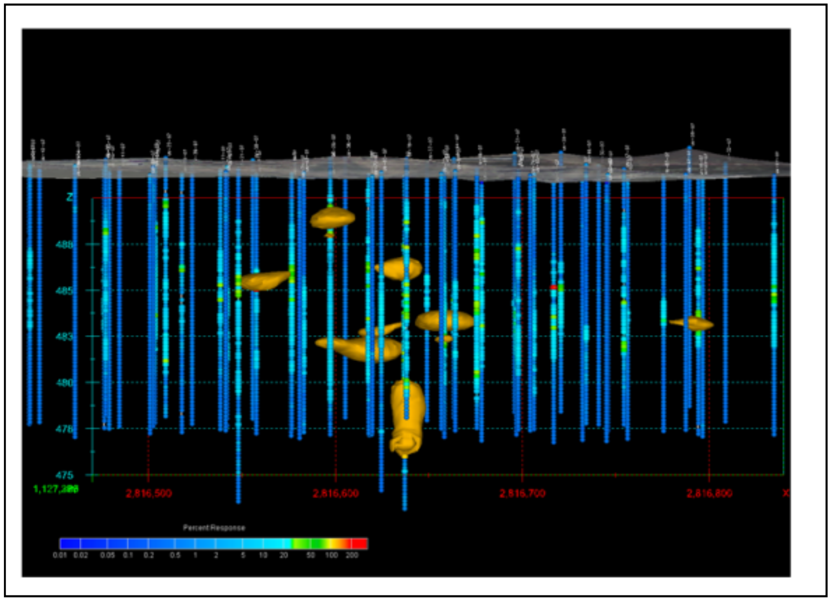
Still not able to detect chlorinated solvent DNAPL

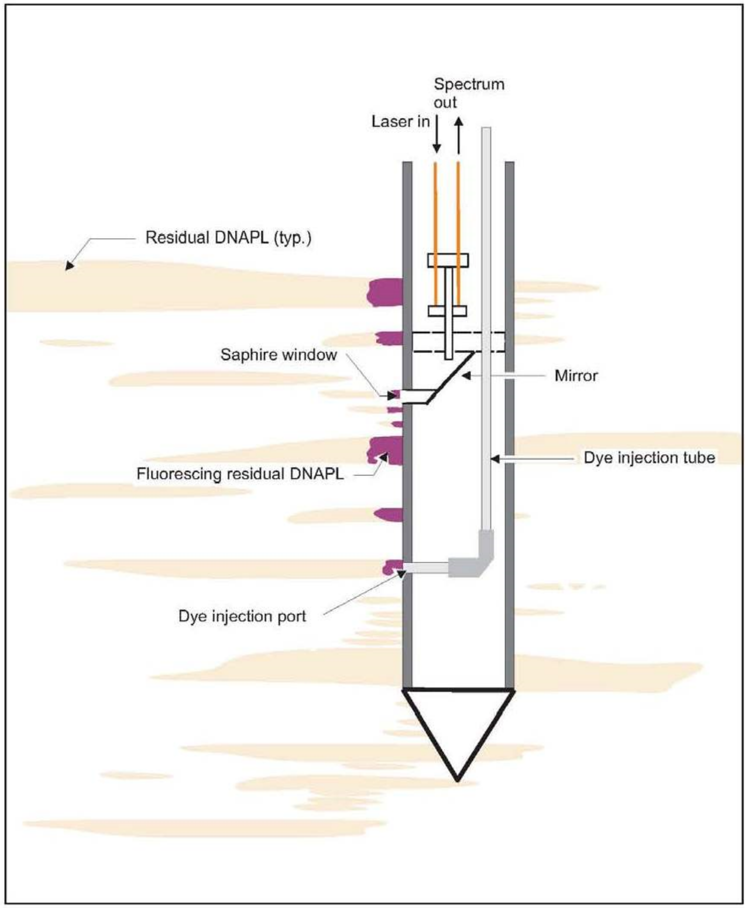
Technology/Methodology Description

- Modification of existing LIF technology
- Adds a small port below excitation source/optics for injecting a fluorescing hydrophobic dye
- Once solvated in NAPL, the dye fluoresces, allowing for detection with conventional LIF tooling



Project ER201121
A new direct-push LIF tool for mapping DNAPL in the subsurface



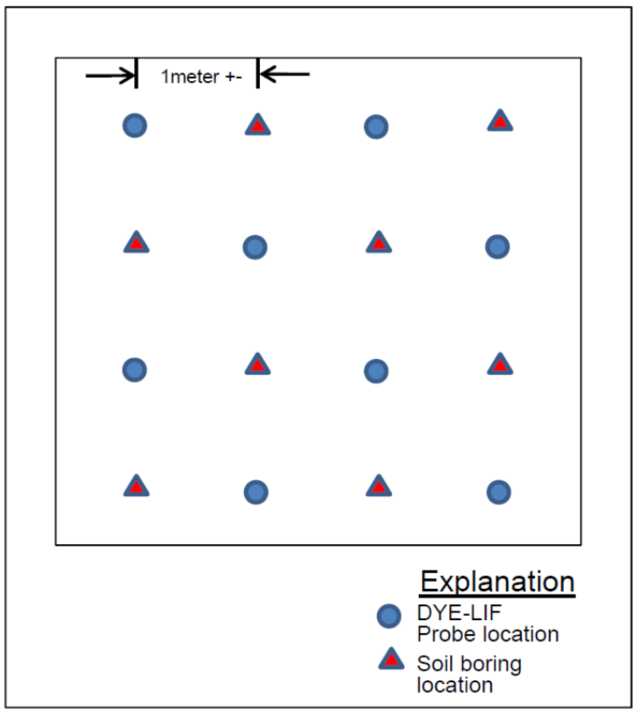


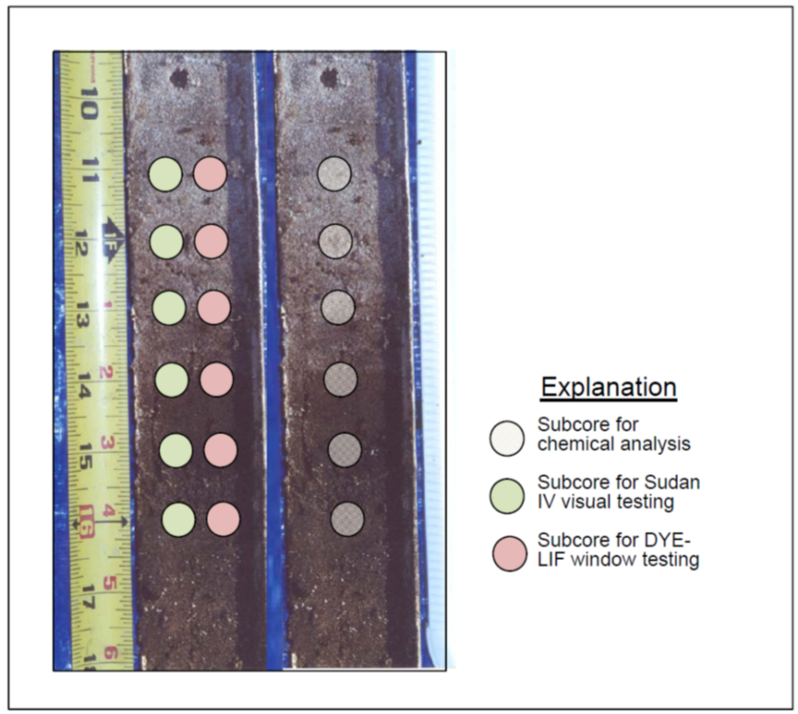
Project scope

1. Laboratory testing of various dyes w/ DNAPL samples
   - DNAPL Chemistry
   - Optical response
2. Stacked disk testing
3. Field testing

Test Design
Future Field Demonstrations

- Week of DYE-LIF probing.
- Follow-up week of detailed side by side soil coring for comparison purposes. Subcores collected for chemical analysis, visual testing with Oil-Red-O dye, table-top LIF window testing.





Project scope

1. Laboratory testing of various dyes w/ DNAPL samples
   - DNAPL Chemistry
   - Optical response
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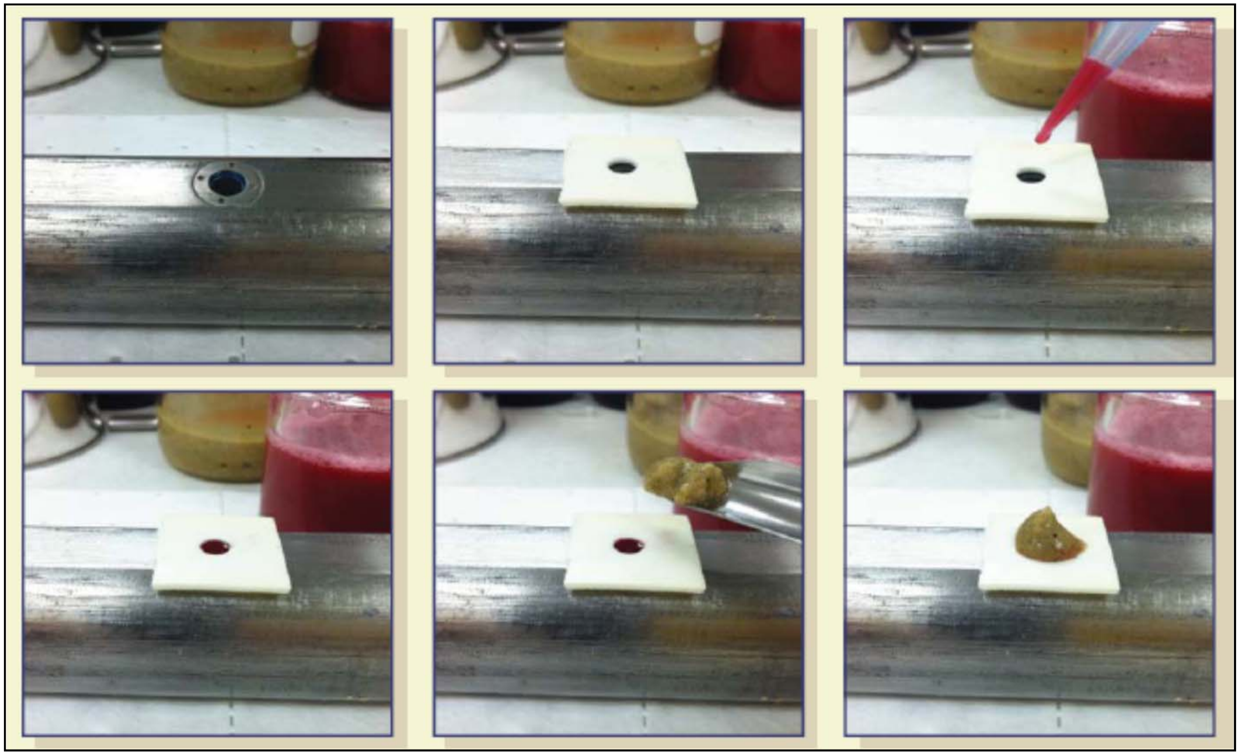
Test Design

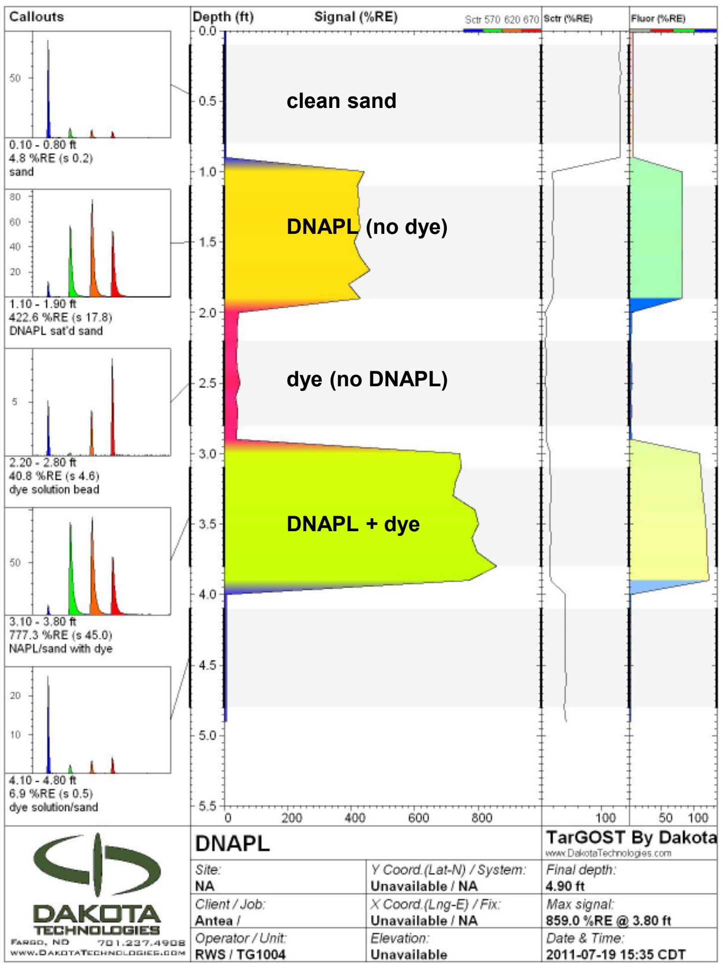
Static Probe Tests

- Create small well around probe window (mimics dye “jacket” formed during field deployment)
- Place samples of clean sand, clean sand + dye, just DNAPL (no dye), and DNAPL + dye.



Test Design

Static Probe Tests



- Developed quantitative metric for enhancement with DYE-LIF
- Referred to as Enhancement Factor or EF

$$EF = \frac{R_D - R_{dye} - R_T}{R_T}$$

- Where:
  - R_D = Response when DNAPL/sand sample placed on dye jacket (analogous to DYE-LIF moving through DNAPL zone)
  - R_{dye} = Response when clean sand placed on dye jacket (analogous to DYE-LIF moving through clean sands)
  - R_T = Response when DNAPL/sand sample placed directly on TarGOST window (analogous to TarGOST moving through DNAPL zone)
- Example:
  - DNAPL + dye = 200%
  - DNAPL (no dye) = 100%RE
  - Just dye ~ 0% RE,
  - EF = (200-100)/100 = 1 or 100% increase

Performance Assessment

Static Probe Experiments

Site Name	Sample Location	DNAPL Composition	UVOST Responses (%RE)	TarGOST Responses (%RE)							
						Dye 41-50			Dye 427		
			Sand + DNAPL	Sand	Sand + DNAPL	Sand + Dye 41-50	Sand + DNAPL + Dye 41-50	Enhancement Factor (EF)	Sand + Dye 427	Sand + DNAPL + Dye 427	Enhancement Factor (EF)
Reagent grade TCE		TCE		2.6	3.1	11.7	418.5	131.2	133.3	245.9	36.3
Reagent grade PCE		PCE									
Hill AFB		TCE			586.5						
Ontario TCA		TCA	93.2		214.8	10.0	38.4	0.0	100.0	139.2	0.0
Anderson Cleaners, NY		PCE		10.5	254.0	11.7	254.2	0.0	60.2	314.9	0.0
Parris Island	ML2-7	PCE + EVO		5.0	194.6	10.1	157.5	0.0	93.9	211.6	0.0
Parris Island	PMW-4	PCE		NA	670.6	6.9	250.7	0.0	104.9	557.3	0.0
Ypsilanti MI		?	170.3	NA	4070.6	NA	NA	NA	NA	NA	NA
Chambers Works		Chlorobenzene		2.5	56.6	7.6	27.0	0.0	113.0	106.4	0.0
Antea Columbus		?		4.8	422.6	6.9	777.0	1.8	NA	NA	NA
Hydrite, WI		TCA/PCE/TCE[1]		5	93	12.8	231	2.3	NA	NA	NA
Former LOP		TCE/TCA		4.9	152	13.5	1572	10.3	NA	NA	NA

Notes

- shading indicates detectable with just TarGOST
- shading indicates no enhancement with dyes
- shading indicates enhancement with dyes
- indicates background value of dye not tested and value is assumed based on other experiments with just the dye and the sand

1. DNAPL composition includes TCA, PCE, TCE, along with BTEX constituents. TCA is primary component

Stacked Disk Experiments

One-inch-thick disk of clean sand with PCE (50% saturation)

Disk placed in 5-gallon bucket & encased in clean sand

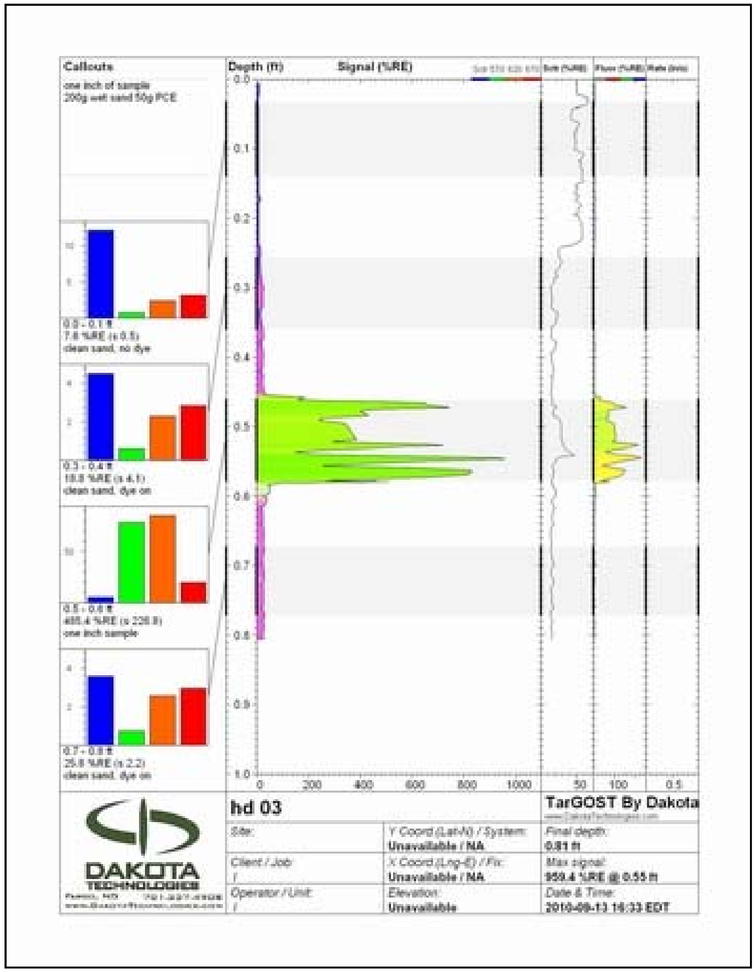
Disk placed in 5-gallon bucket & encased in clean sand

DYE-LIF probe with dye injector below sapphire window

Advancing the DYE-LIF probe through the sand bucket while injecting a hydrophobic dye

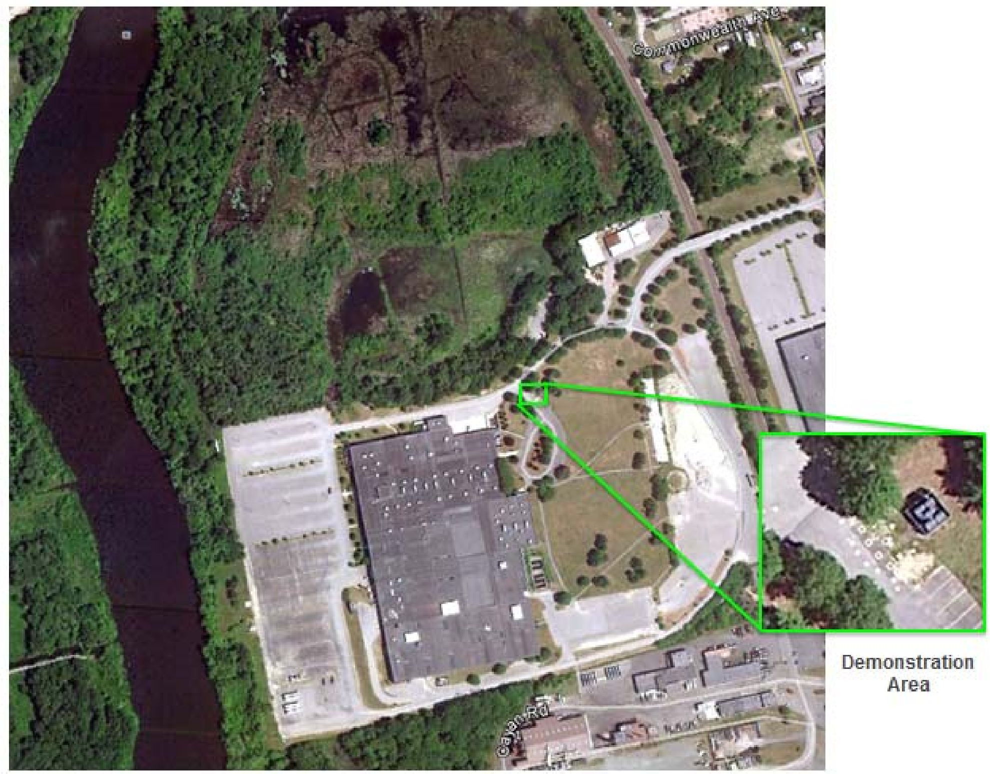
Laser visible through sapphire window

One-inch-thick thick layer of PCE-impacted sand (50% saturation) perfectly detected. Note no drag-down of PCE into deeper clean sand



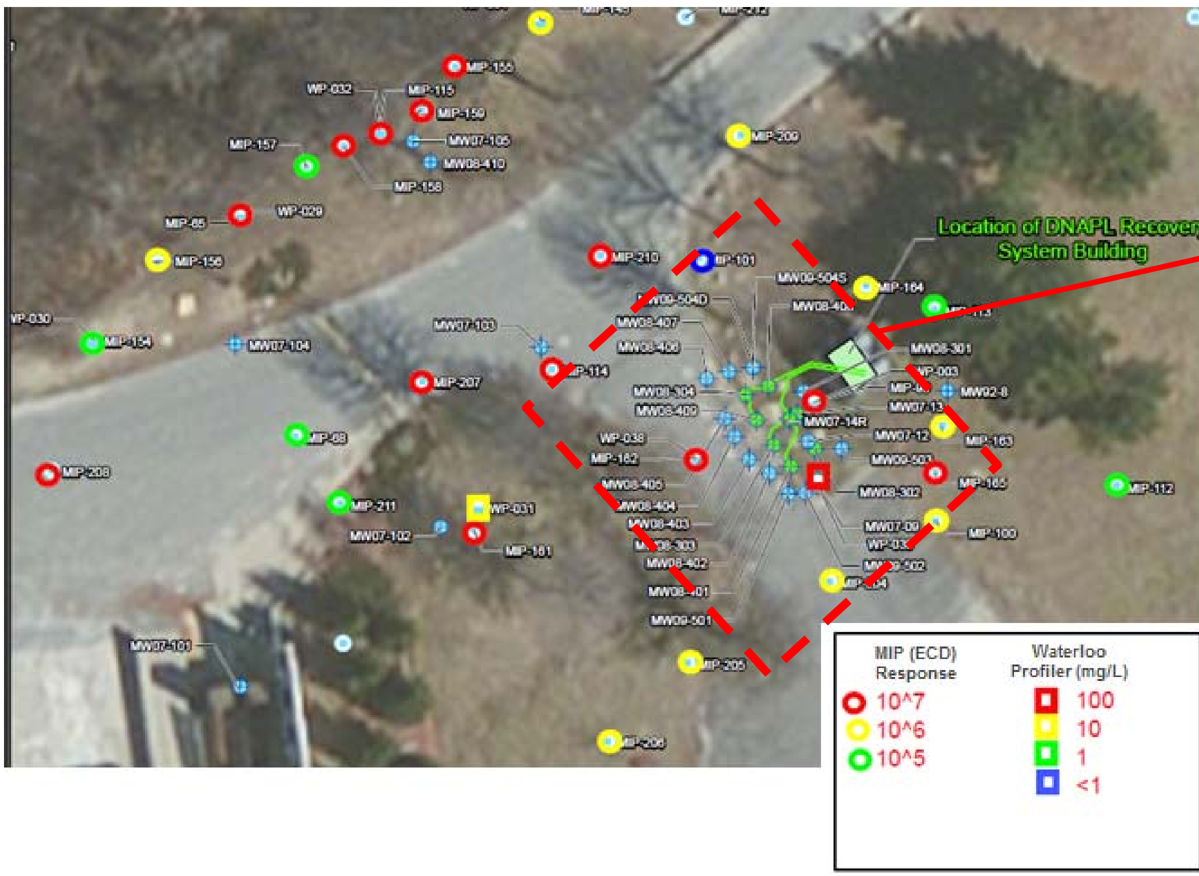
Field Testing -- Site Description

- Formerly used defense site in Lowell, MA.
- Ideal site because of the following:
  - ♦ DNAPL present in site wells (can collect and perform lab testing)
  - ♦ Lots of existing high resolution site characterization data (HRSC) data – MIP, Waterloo Profiler
  - ♦ Had a “near-source” transect of MIP and Waterloo Profiler data, which we consider integral component of DNAPL source characterization
  - ♦ Amenable to direct push
  - ♦ Reasonable depth to DNAPL <70 ft



Test Design

Week 1 – Grid of DYE-LIF Borings



Existing HRSC data (MIP, Waterloo Profiler) + DNAPL gauging data used to define area of investigation

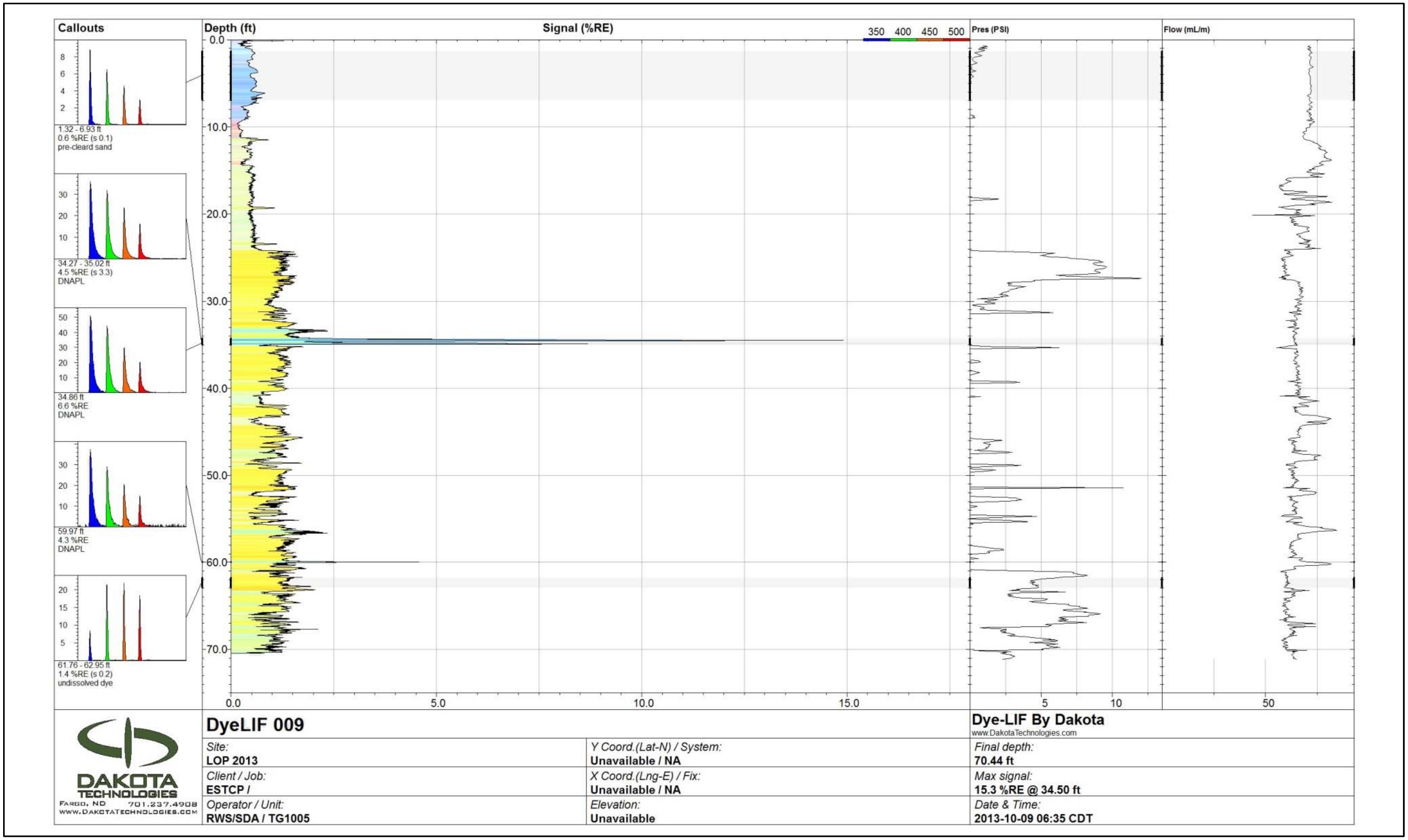
Test Design

Week 1 (October 7 to 11) – Grid of DYE-LIF Borings

ESTCP DEMONSTRATION PROJECT
DYE-LIF LOGGING – WEEK ONE

- 59% trichloroethylene, 34% 1,1,1-trichloroethane DNAPL spill
- conducted 25 DyeLIF locations to an average depth of 70 ft (21.3m)
- averaged 395 ft/day (<10 hour days) `1.8 hours per 70 foot hole!
- rate of penetration average 0.4 inch/second (1 cm/sec)
- 0.01 g/second dye solution delivery rate (equates to ~2-3 g per log)
- pushed majority of locations with a Geoprobe® 5400 – remainder with 7720
- one parabolic mirror adjustment during the week, no downtown from repairs and no damaged tooling
- DNAPL body was ‘bounded’ - with exception of small building in the way

EXAMPLE DYELIF LOG



ESTCP DEMONSTRATION PROJECT
SAMPLING/SCREENING – WEEK TWO

- extremely challenging sampling conditions – even with an experienced team of high-resolution sampling experts with decades of sampling experience
- after trying numerous techniques arrived at Geoprobe MC7™ sampler with sealed piston adaptation to improve recovery
- after three days of technique refinement (and anguish), average recovery climbed to 65%
- lateral heterogeneity made encountering Dye-LIF-identified DNAPL a “hit/miss” affair
- persistence eventually yielded a sufficient number of cores and 260 depth-discrete sub-sample horizons were obtained
- PID, Oil-Red-O visual, and DYE-LIF were run on high-resolution sub-samples
- 50% of the sub-sampled horizons (133) sent to lab for VOC analyses

Test Design

Week 2 (October 14 to 18)– High Resolution Soil Sampling

Core is split, taping knife is used to scrape off top layer of soil

ESTCP

Photograph of core is taken

Core is covered with foil to minimize volatile losses

ESTCP

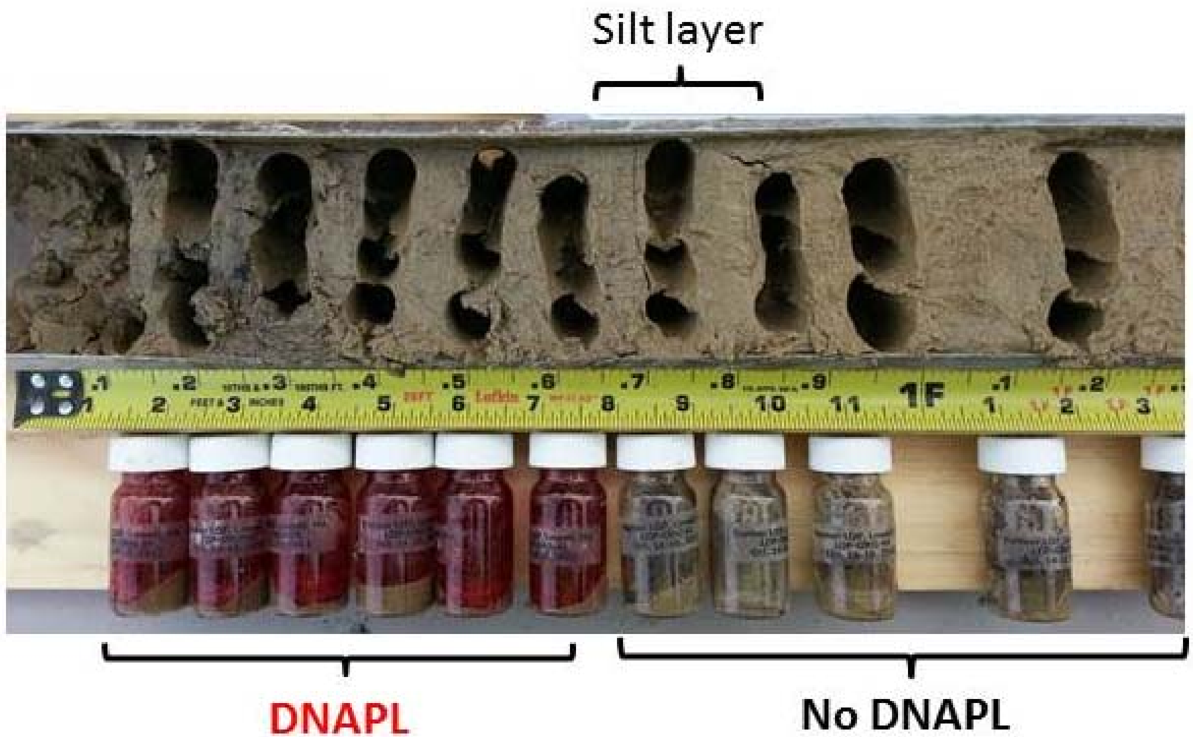
Marker is used to demarcate sampling intervals on the foil. Subsamples collected for VOC analysis, Oil-Red-O screening, and table-top DYE-LIF screening

A second person is used to expedite sampling procedure.

PID screening also conducted at each sampling interval.

After sampling is completed at first depth interval, foil is peeled back at the next location for sampling.

After sampling has been completed, the core is logged by field geologist and additional samples are collected for physical properties analysis (e.g. grain size analysis)

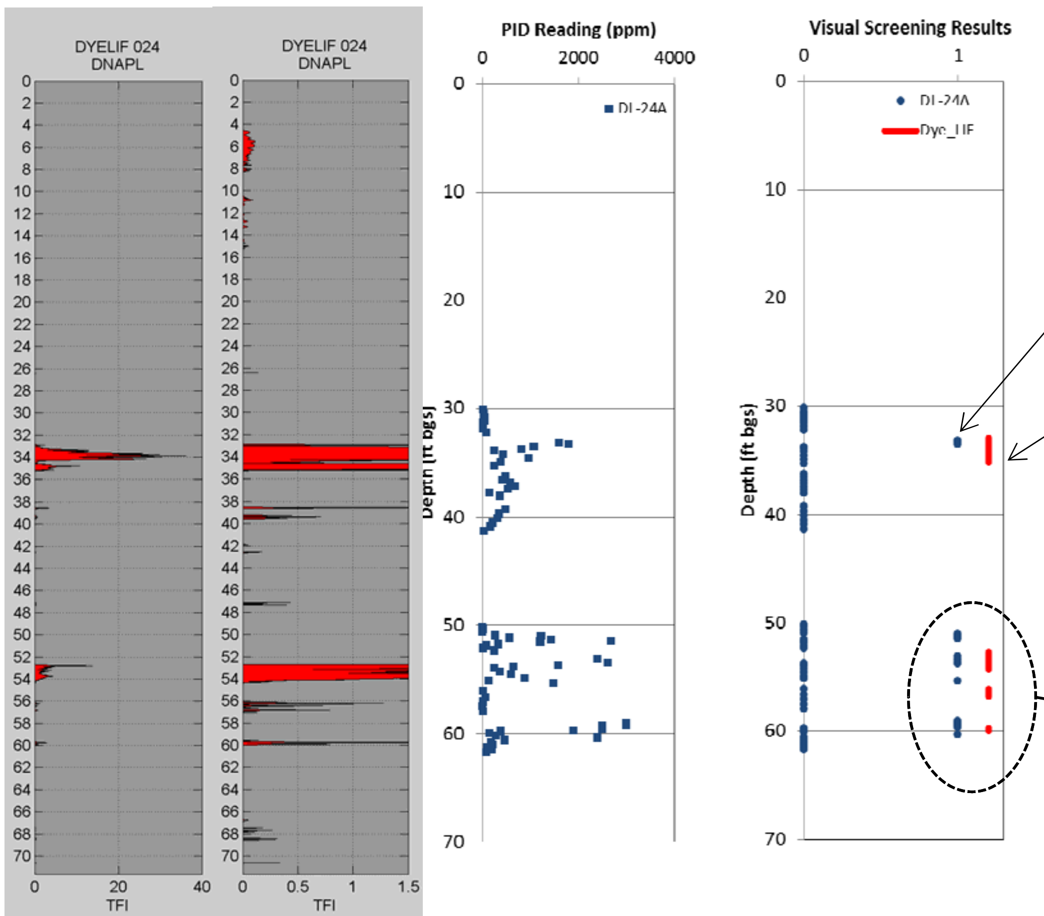


Vials showing positive DNAPL results with Oil-Red-O above a fine grained silt layer

Above ground testing with DYE-LIF. A small amount of dye solution is added to the sample vial and the vial is placed on the probe laser/window for reading.

Samples prepped for above ground analysis with DYE-LIF.

CORRELATION BETWEEN DYE-LIF & SAMPLING



positive ID with DYE shake test

positive ID with table-top DYE-LIF (adjacent log, sub-core data not fully processed yet

Table-top DYE-LIF is able to see thin lamina of DNAPL with new data processing; consistent with dye shake test

CORRELATION BETWEEN DYE-LIF & SAMPLING

- Good agreement between cores and adjacent DyeLIF logs (heterogeneity effects taken into consideration)

- Up-hole "re-analysis" of sub-samples with DyeLIF achieved excellent correlation with ORO visual shake test:
  - 100% match for samples of > 2.5% pore saturation DNAPL
  - 98% match for samples of > 0.7% pore saturation DNAPL

- Field detection limit of between 1.0% and 0.1% pore saturation, but will vary from site to site

ESTCP

HALEY & ALDRICH

CPT DELIVERY 3 DAYS IN MARCH, 2014

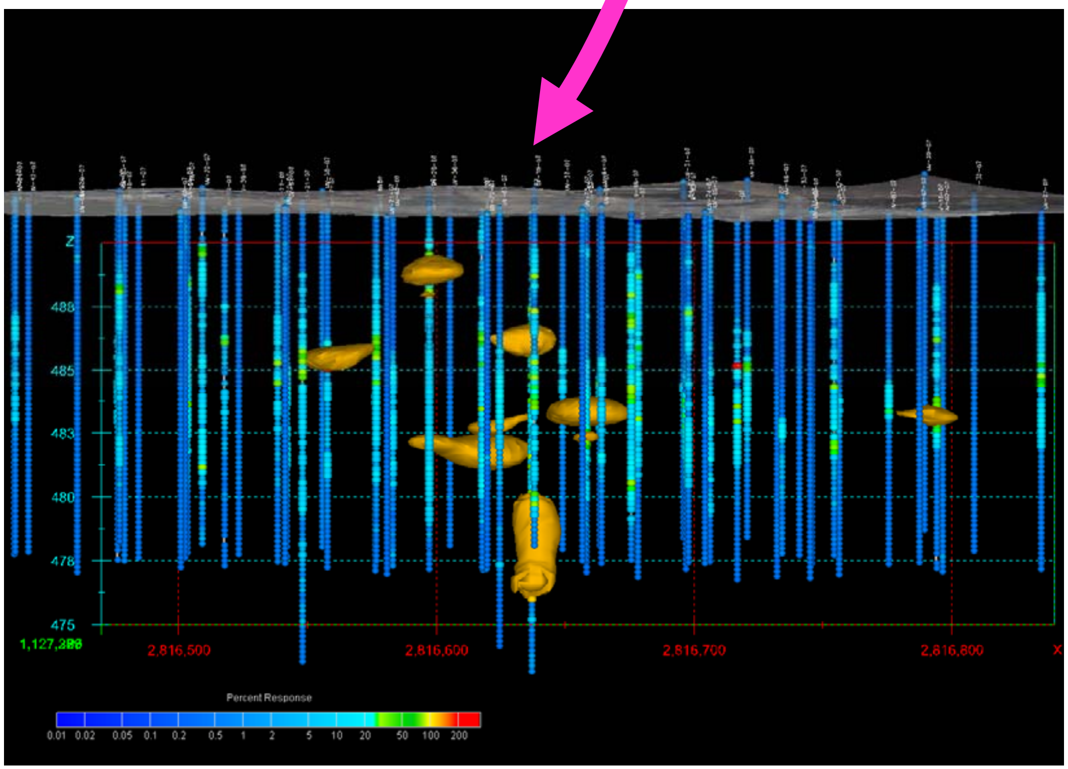
- Pushed 11 logs to >68 ft, total of 805 ft in 3 days which included integration and takedown of DyeLIF system
- maximum penetration was 78 ft (bedrock)
- unfortunately not allowed to push in “the DNAPL’s heart” (wanted to compare to 2013 DyeLIF percussion logs)
- pushed at 1.5 cm/sec (ASTM bottom limit) – we feel 1.0 cm/sec would be optimal
  (higher resolution to detect smaller ganglia)

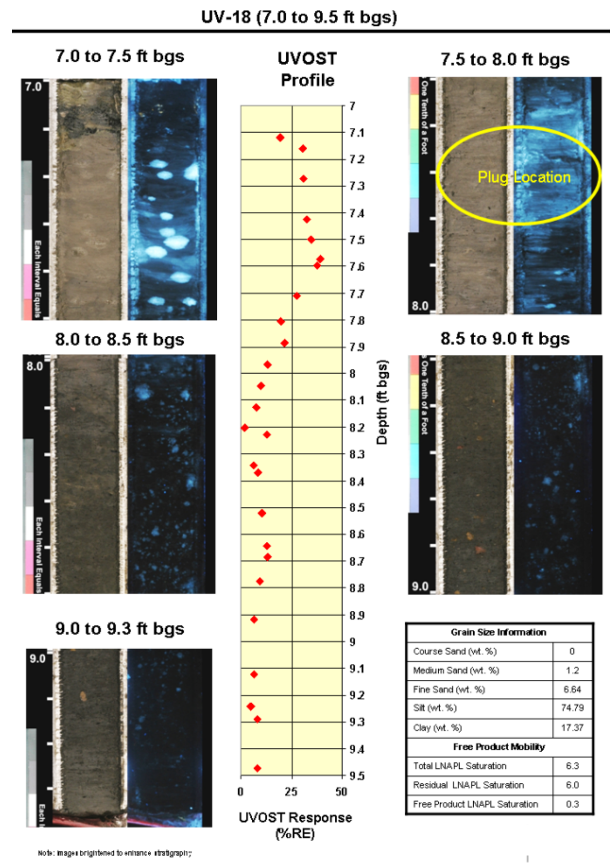
CONCLUSIONS

- the DYE-LIF probe technology is compatible with both percussion and CPT direct push platforms
- the DYE-LIF responded preferentially to DNAPL (zero dissolved phase response as expected)
- preliminary LoD of ~1.0%-0.1% DNAPL pore saturation
- DYE-LIF produced the equivalent of an Oil-Red-O shake test at 0.5 cm spacing - with average daily production of 395 ft
- in other words, under these site conditions the DYE-LIF generated the equivalent of 12,039 ORO shake tests per day - with 100% “recovery”
- tracking the indicator dye solution’s flow and pressure reveals details of hydraulic conductivity with depth

Reminder: Our goal:

Be able to do this   at chlorinated solvent DNAPL sites





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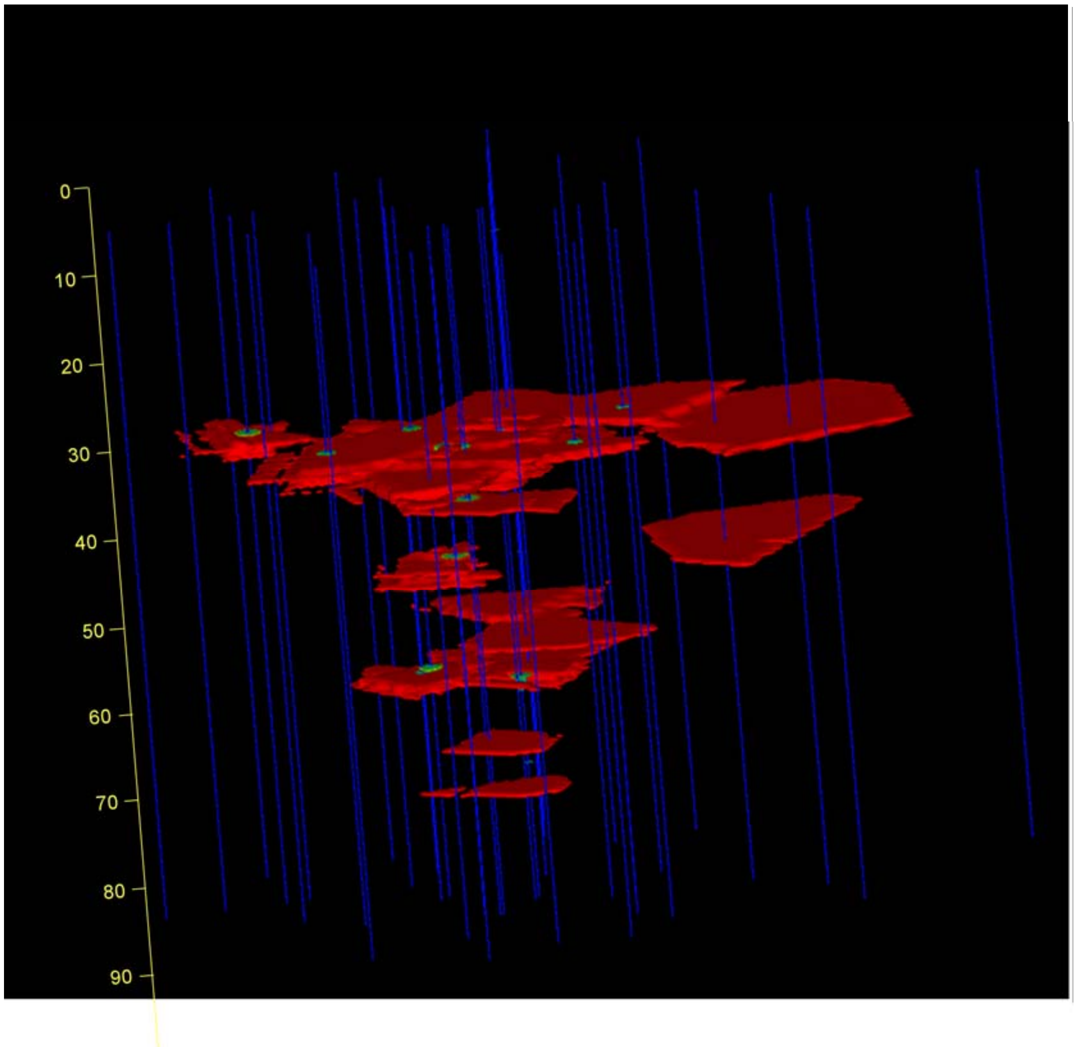
Free Product Mobility	
Total LNAPL Saturation	6.3
Residual LNAPL Saturation	6.0
Free Product LNAPL Saturation	0.3

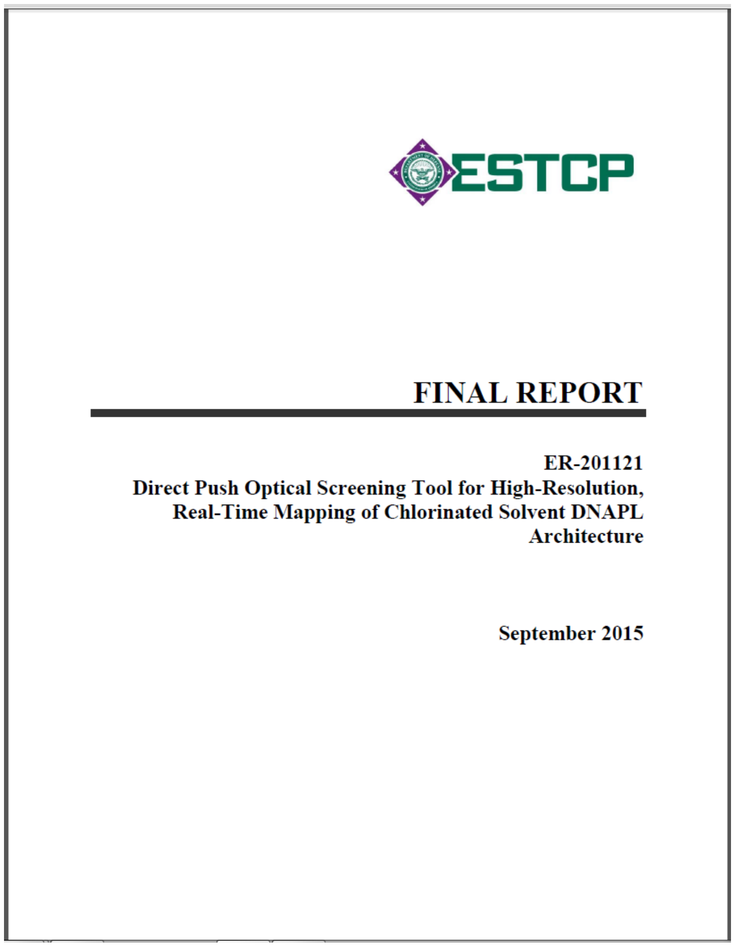
We now ARE able to detect chlorinated solvent DNAPL

Performance Assessment

Three-Dimensional Rendering of DNAPL Source Zone, Lowell MA Site



Technology Status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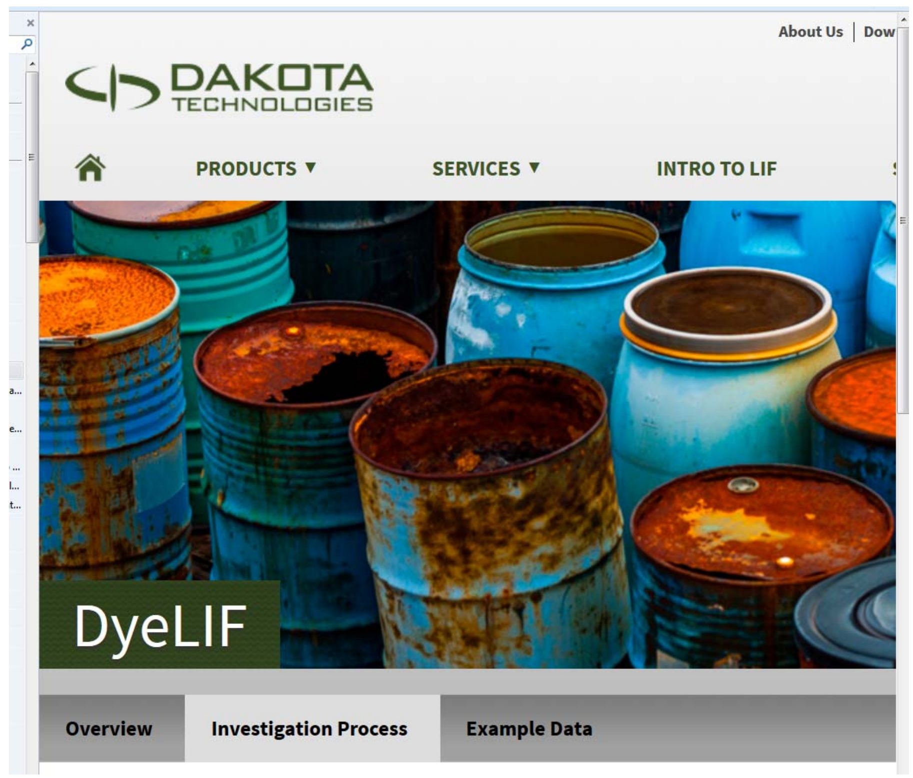
FINAL REPORT

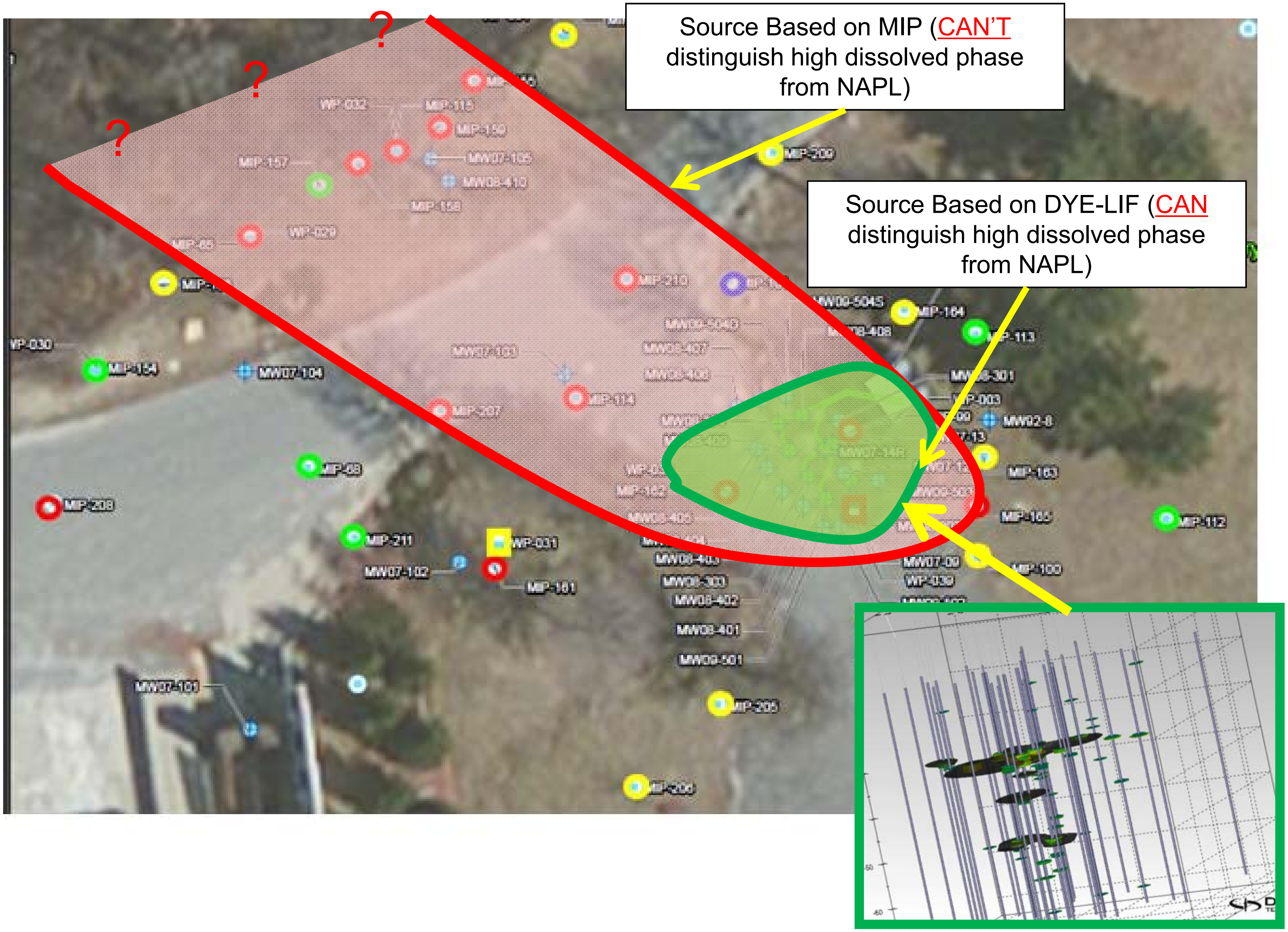
ER-201121
Direct Push Optical Screening Tool for High-Resolution, Real-Time Mapping of Chlorinated Solvent DNAPL Architecture

September 2015

Final report under review

DyeLIF is now commercially available:
http://www.dakotatechnologies.com/services/dyelif




Source Based on MIP (CAN'T distinguish high dissolved phase from NAPL)
Source Based on DYE-LIF (CAN distinguish high dissolved phase from NAPL)