DYE-ENHANCED LASER INDUCED FLOURESCENCE (DyeLIF) FOR DELINIATING MULTI-COMPONENT DNAPL

Lake City Army Ammunition Plant (LCAAP)
Independence, Missouri

Presented at:

Federal Remediation Technologies Roundtable
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Washington, D.C.

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Acknowledgements

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- Work was performed with oversight by U.S. Environmental Protection Agency (USEPA) Region 7 and Missouri Department of Natural Resources
- Work was supported by Environmental Works, Inc.

The 60 Year History of Area 17B Oil & Solvent Pits

- 1960s-1979: Operated as disposal pits and received large volumes of solvent wastes
- 1979: Pits closed, backfilled to grade and revegetated
- 1980: Area 17B identified as a restoration site and periodic groundwater sampling initiated
- 1987: LCAAP placed on National Priorities List (NPL)
- 1989: Preliminary Assessment / Site Inspection (PA/SI) completed
- 1990: Phase I Remedial Investigations (RI) completed with 9 new monitoring wells
- 1995: Phase II RI completed with site characterization and analysis penetrometer (SCAPs) and 14 new monitoring wells
- 2006: Phase III RI completed with Membrane Interface Probe (MIP) and 50 new monitoring wells
- 2008: Area 17B remedy implemented with 53 new monitoring and injection wells
- 2008-Current: Remedial Action Operation [RA(O)] with Periodic Injections, Groundwater Monitoring and Annual Reporting with 74 new monitoring and injection wells
- 2010, 2015, 2020: CERCLA Five-Year Reviews and remedy performance assessments
- 2020: DyeLIF Investigation of the western and central pits

Evolution of the Area 17B Remedy

- 2006: Enhanced Reductive Dechlorination (ERD) via In Situ Reactive Zones (IRZ) pilot study
- 2007: Zero Valent Iron (ZVI) mixing
- 2008: Five IRZ lines constructed and quarterly injections with molasses
- 2008-Today: Annual to Biennial IRZ injections and quarterly / semi-annual groundwater monitoring
- 2014: ERD amendments switched to Emulsified Vegetable Oil
- 2015 Hydraulic permeability enhancement of IRZ Line 2 and Line 3
- 2020: Dye enhanced laser induced fluorescence (DyeLIF) investigation
- 2021: Expansion of the IRZ Line 5 barrier
- 2022: Construction of the In-Situ Thermal Remediation (ISTR)
- 2023: Operation of the ISTR system





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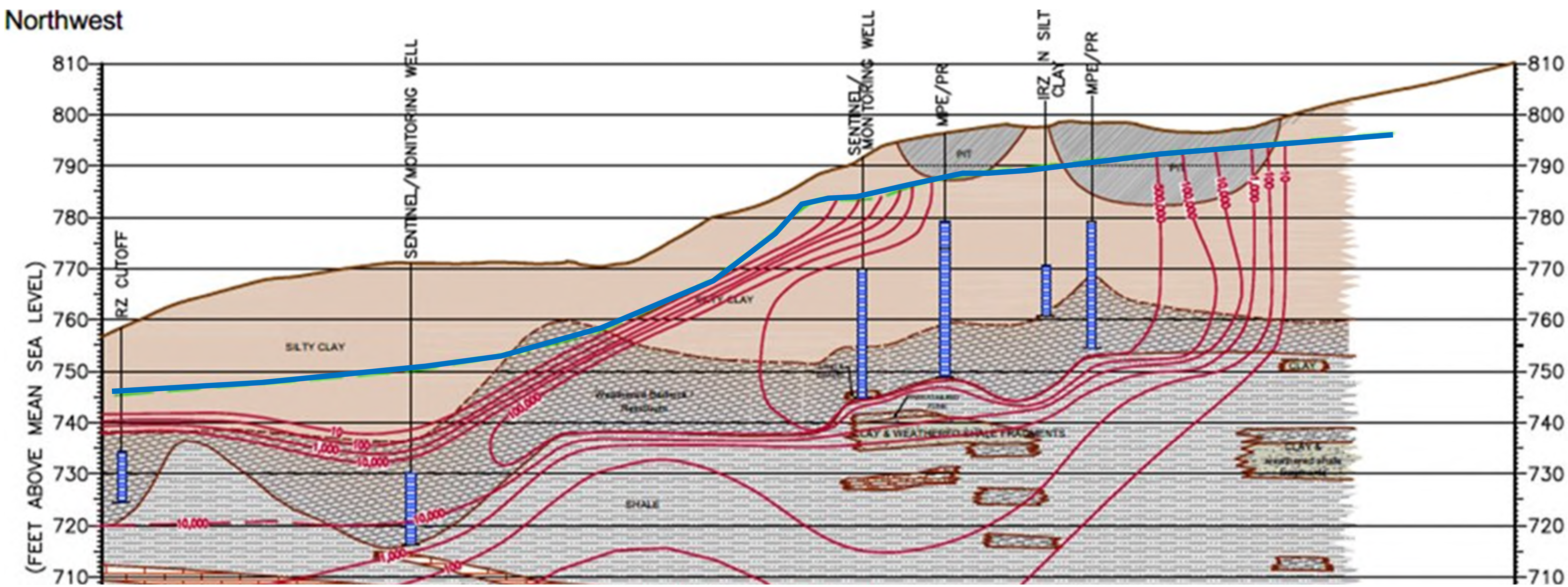
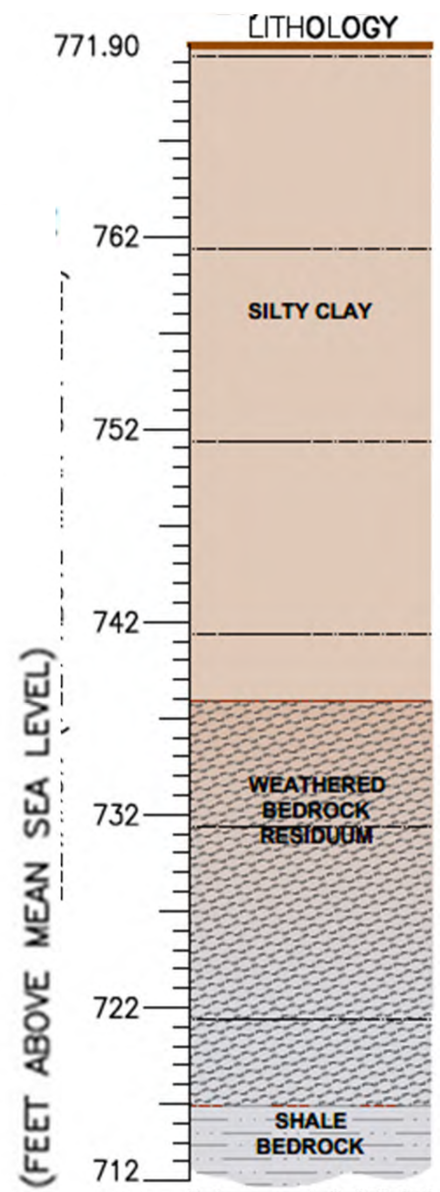
Area 17B Conceptual Site Model

- Primary contaminant is trichloroethylene (TCE) and daughter products as a non-aqueous phase liquid (NAPL)
- Fingerprint analysis indicates TCE is 17 wt.% of the total NAPL mass, but 63 wt.% of the volatile fraction
- Low conductivity silty clay and weathered bedrock residuum to 55 ft below ground surface, underlain by shale bedrock
- Depth to groundwater at pits is 7 ft bgs and flow is ~85 feet / year in weathered bedrock residuum to the northwest (>20 feet / year in silty clay)

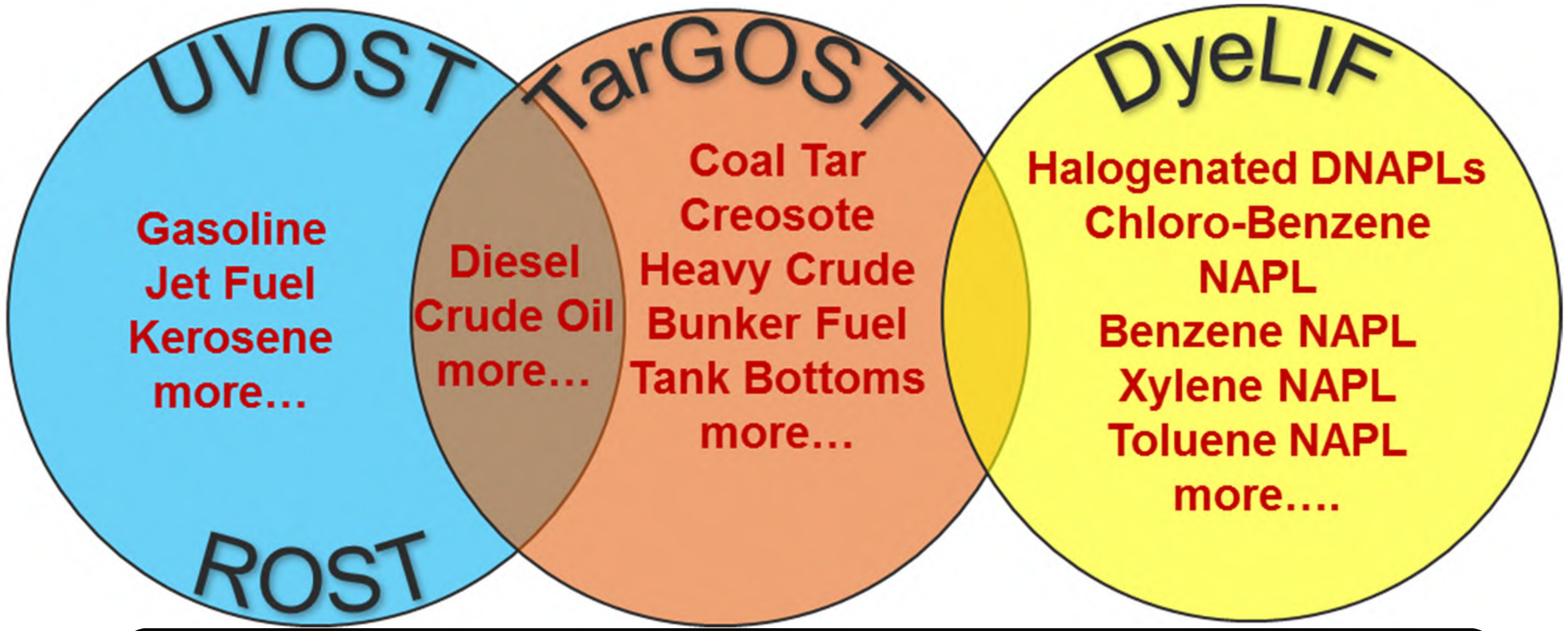


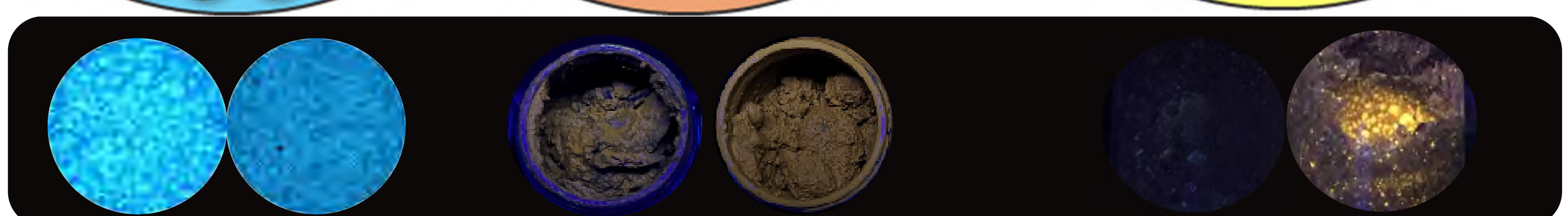
Strat Column



LIF Technology Options

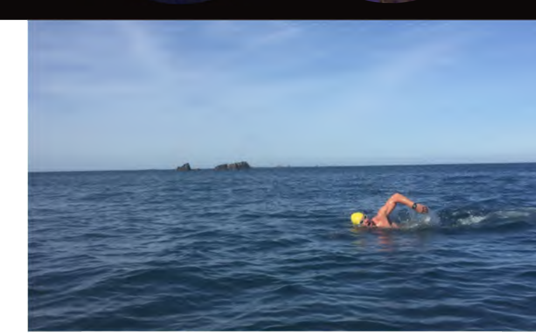
- NAPL fluorescence behavior varies considerably based on chemical composition
- Important to choose the optimal LIF tool to match the site NAPL





Ideal

Energy Transfer



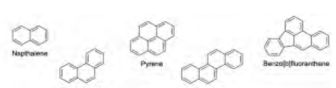
PAH-Starved

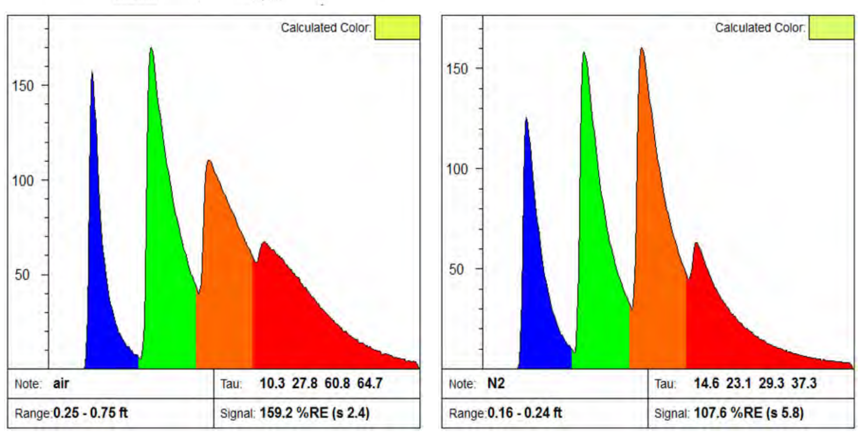
LIF Waveforms: Contain color, brightness, and lifetime

Diesel | **Gasoline** | **Coal Tar** | **Creosote** | **Dye Fluid** | **DNAPL w/Dye**

UVOST

Pulsed (~2 ns) UV laser
four colors (channels)

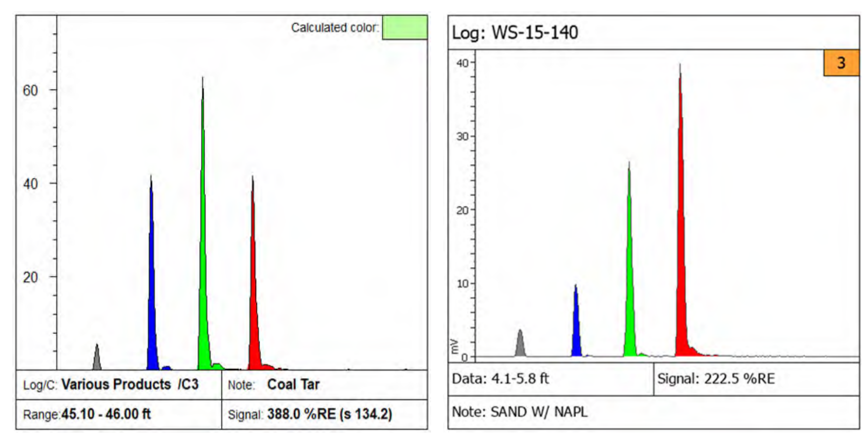




Long-lived, smaller PAHs fluoresce efficiently

TarGOST

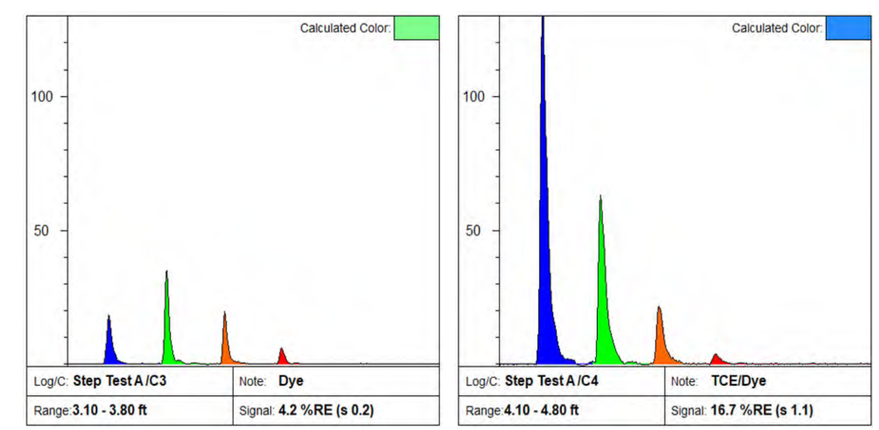
Pulsed (~1 ns) green laser
four colors (one laser scatter and three fluorescence)



Short-lived, smaller PAHs have excited state energy stolen by larger PAHs

DyeLIF

Pulsed (~1 ns) green laser
four colors (four fluorescence, optimized to detect dye)



Short-lived when no DNAPL present

Long-lived, bluer and very intense when present

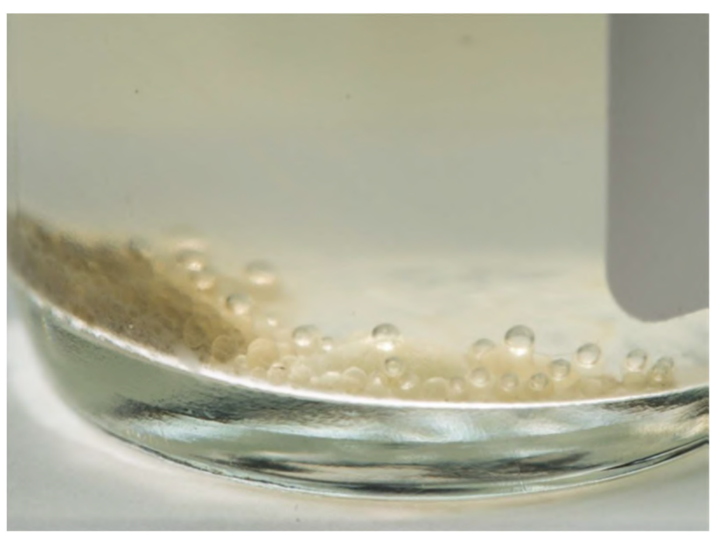
ECCC ARCADIS DAKOTA TECHNOLOGIES

Vetting Performance Prior to Mobilization

- Bench testing 17B NAPL prior to mobilization
  - Can DNAPL solvate dyes?... i.e., DyeLIF approach viable?
  - If so, what will waveforms look like?
- Area 17B NAPL yielded no observable ability to solvate Oil Red O (which changes color in oils / NAPLs)
- Area 17B NAPL DyeLIF response to fluorescence dye was weak
- This is in stark contrast to "classic" chlorinated solvent DNAPLs tested with Oil Red O

Area 17B NAPL ~17 wt.% TCE

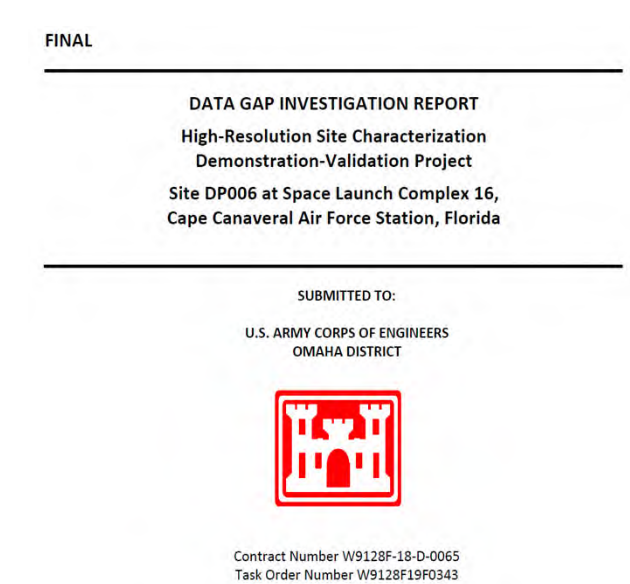
Oil Red O Solvation Test



TCE DNAPL Recovered from Cape Canaveral LC16

Same DNAPL with Oil Red O Dye

Validation Soil Sampling



FINAL

DATA GAP INVESTIGATION REPORT

High-Resolution Site Characterization Demonstration-Validation Project

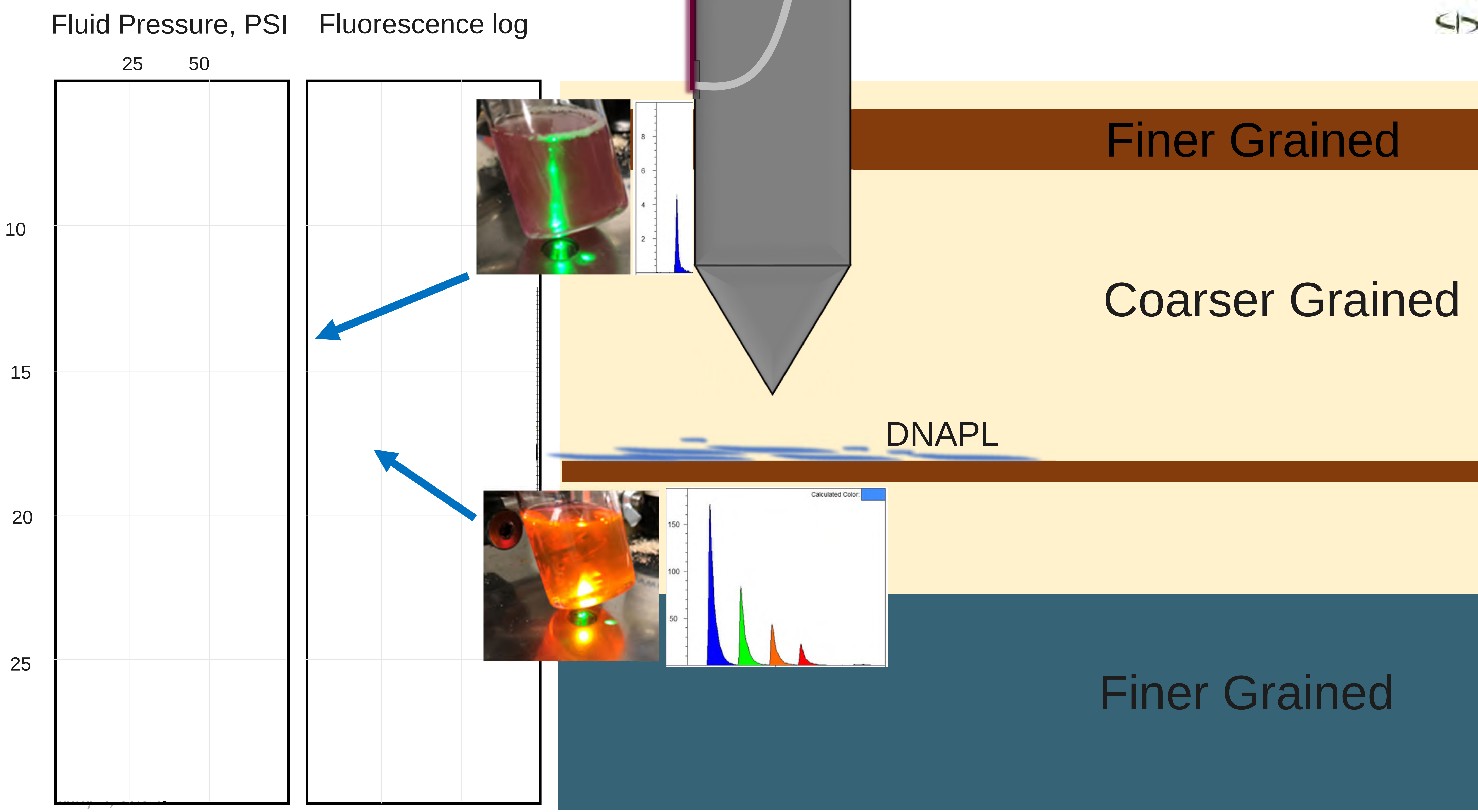
Site DP006 at Space Launch Complex 16, Cape Canaveral Air Force Station, Florida

SUBMITTED TO:

U.S. ARMY CORPS OF ENGINEERS
OMAHA DISTRICT

Contract Number W9128F-18-D-0065
Task Order Number W9128F19F0343

DyeLIF Technology



Testing Venom™ Response to Area 17B NAPL

- Area 17B NAPLs saturated onto soil looking for fluorescence of Venom dye due to NAPL solvation

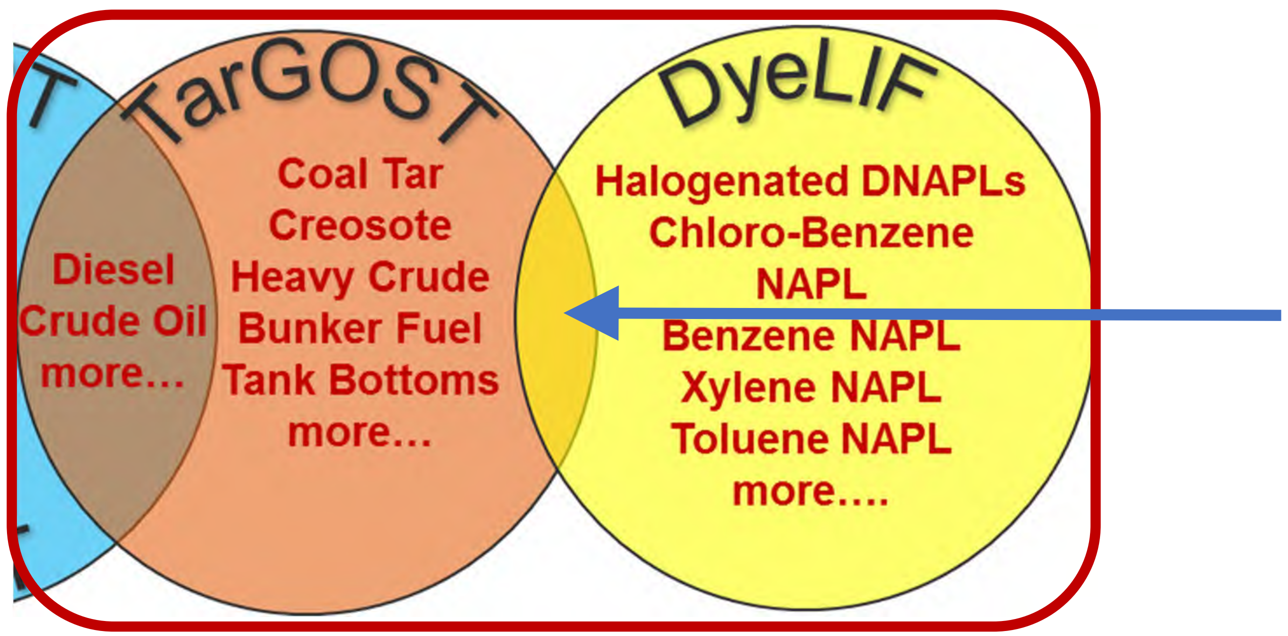
TCE W DYE | PCE W DYE | BENZENE W DYE | 033 | 033 W DYE | 013 | 013 W DYE | DYE WITH WATER

Poor enhancement... should be orders of magnitude brighter, not double

Chlorinated DNAPLs from Previous Projects

Tool Selected: TarGOST / DyeLIF Hybrid

- The target TCE NAPL was co-solvated in a low fluorescence host tar matrix
- TarGOST is designed to sense low fluorescent tars, creosotes, and bunker fuel NAPL
- A TarGOST / DyeLIF hybrid was deployed consisting of TarGOST detection along with Venom dye fluid injection. This combination was used at Chambers Works and other challenging / unusual NAPL sites.



- Injected of Venom dye served as an insurance policy in case fluorescent NAPL was encountered due to vertical fractionation of the NAPL during migration or natural attenuation with the co-located petroleum hydrocarbons

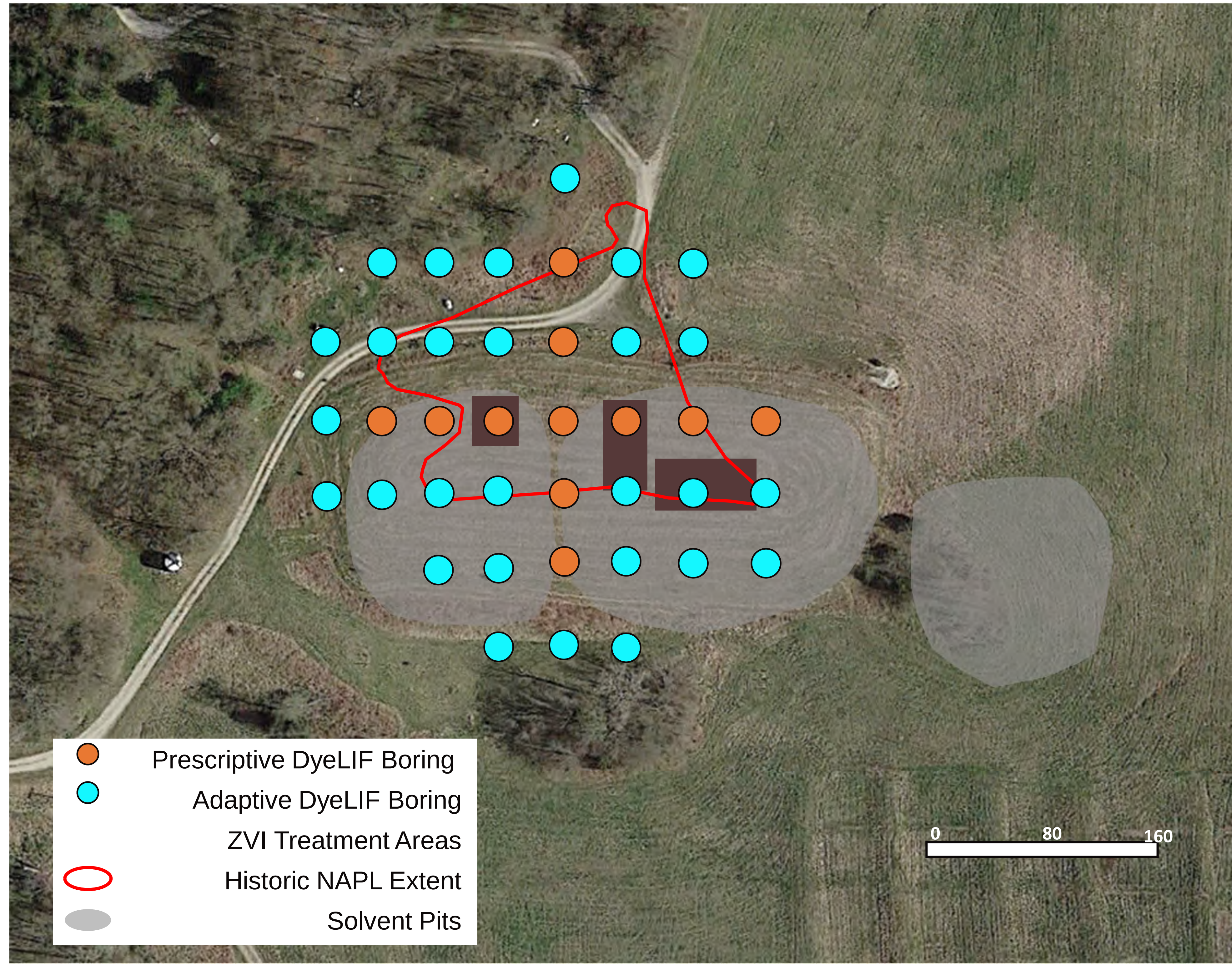
Dynamic Work Plan

Objectives

- Assess presence / absence of NAPL
- Estimate contaminant mass
- Compare future thermal mass removal to source mass estimate
- Assess ZVI treatment effectiveness

Scope Elements

- DyeLIF borings (Prescriptive & Adaptive)
- WCSS borings with sub-core sampling
    - Laboratory analyses – VOCs, SVOCs, & TPH
    - DyeLIF bench testing
    - Field dye tests



Workflow

Week 1
Prescribed DyeLIF

Weeks 2 & 3
Adaptive DyeLIF & Sonic WCSS

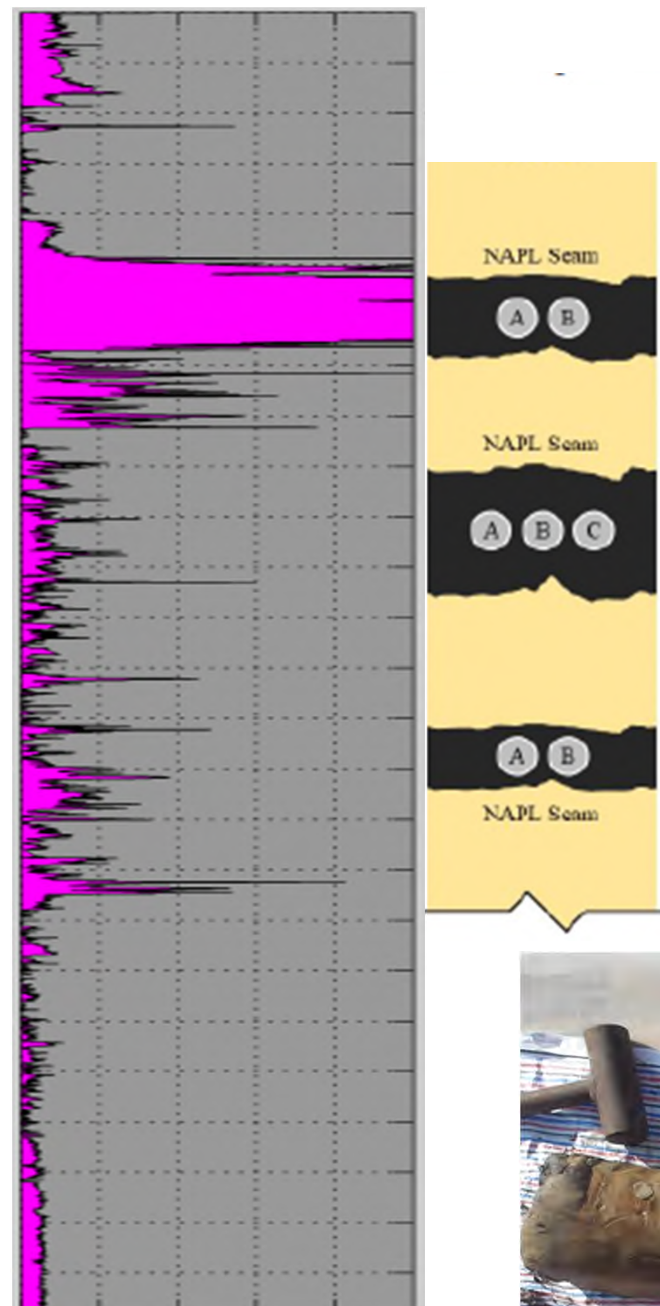
Week 4
Sonic WCSS

- DyeLIF borings from 11/2 to 11/20/2020 (~3 weeks) using a direct push Geoprobe 7822DT
  - 69 borings to refusal up to 55 ft bgs
- Whole core soil sampling (WCSS) borings from 11/6 to 12/4/2020 (~3 weeks) using a sonic Boart Longyear LS250
  - 18 borings advanced 1 ft into competent shale bedrock
- Key point – DPT DyeLIF and Sonic rig overlapped to collect soil cores at key locations to understand DyeLIF response

Benchtop DyeLIF Calibration

Different types of samples analyzed with and without dye

- Soil samples from WCSS borings
  - 170 soil vials with and without NAPL
  - 230 samples for VOCs, SVOCs, and TPH analysis
  - NAPL saturated wood
  - Subsurface waste materials including plastic, wood, and latex gloves
- NAPL and groundwater samples from Area 17B monitoring wells
- Area 17B bioremediation amendments of Emulsified Vegetable Oil
- TCE NAPL standards

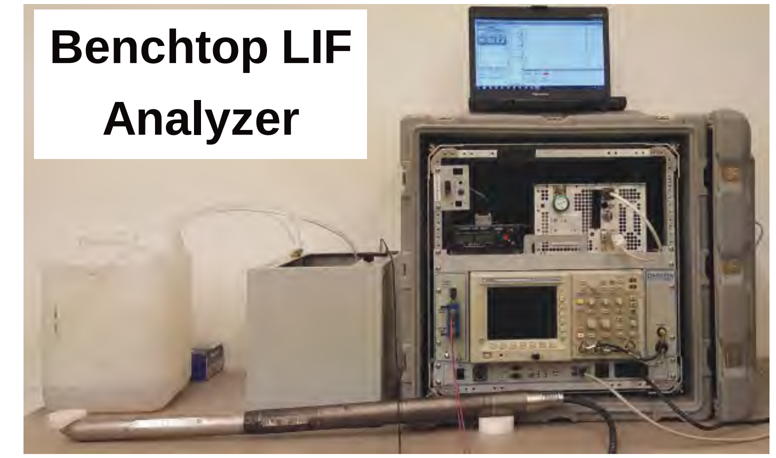


Soil Sub-Samples

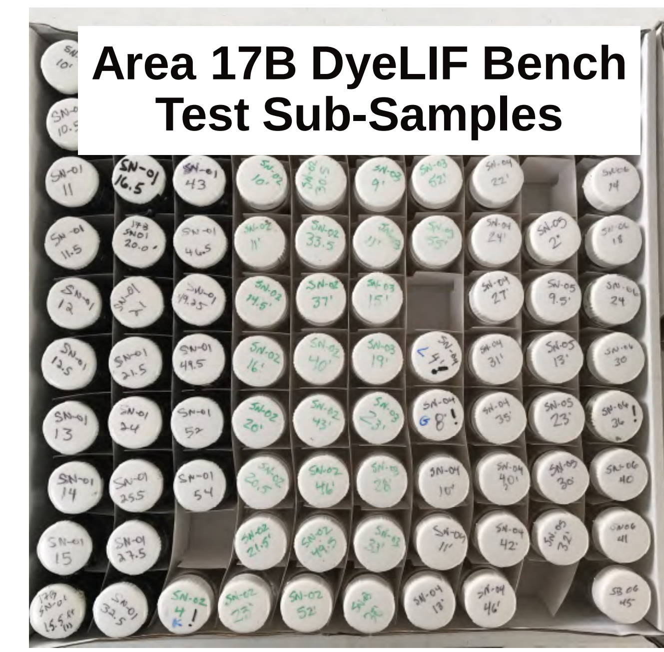
A: VOC lab sample

B: DyeLIF bench test sample

C: TPH and SVOCs lab sample



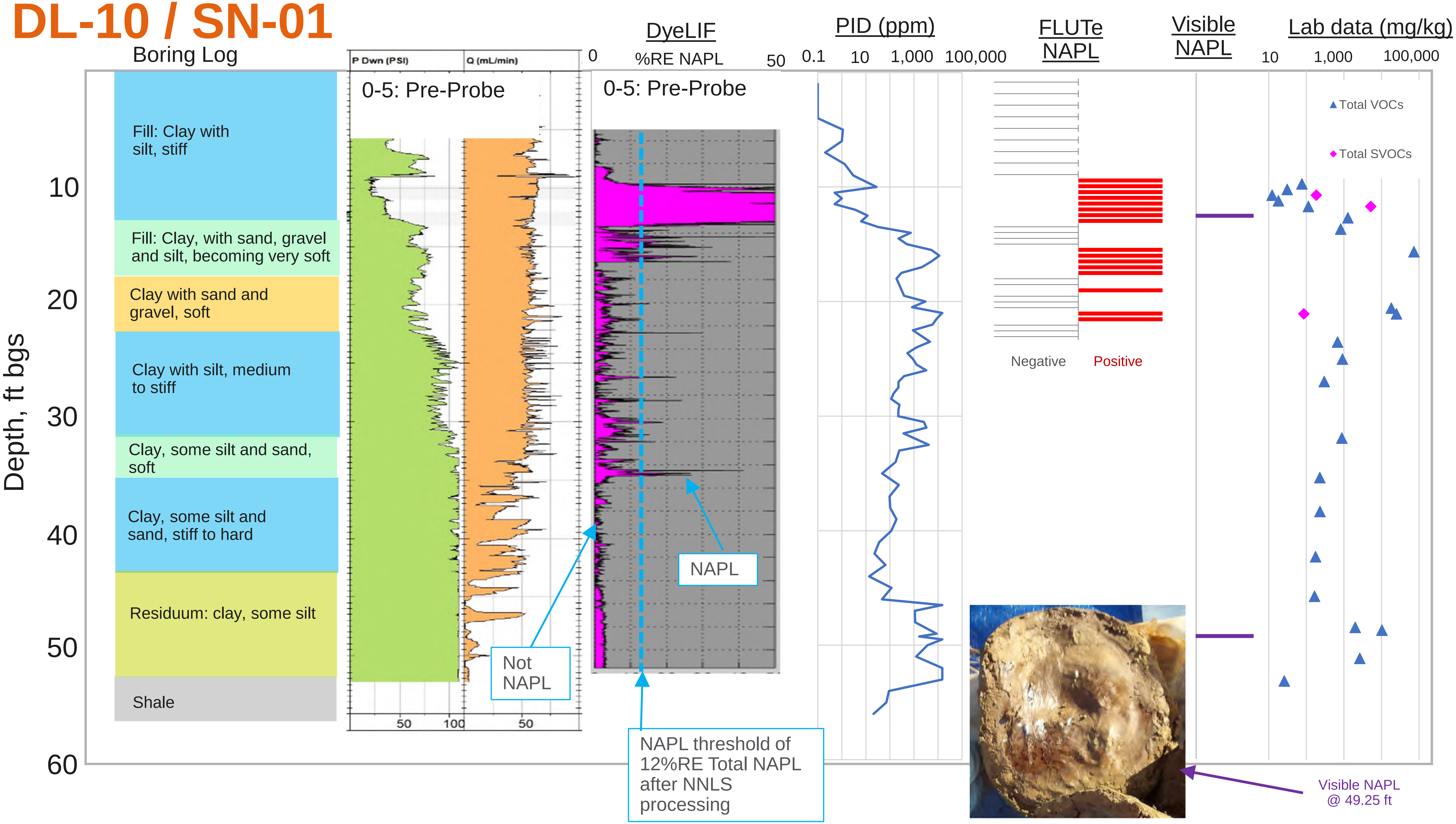
Benchtop LIF Analyzer



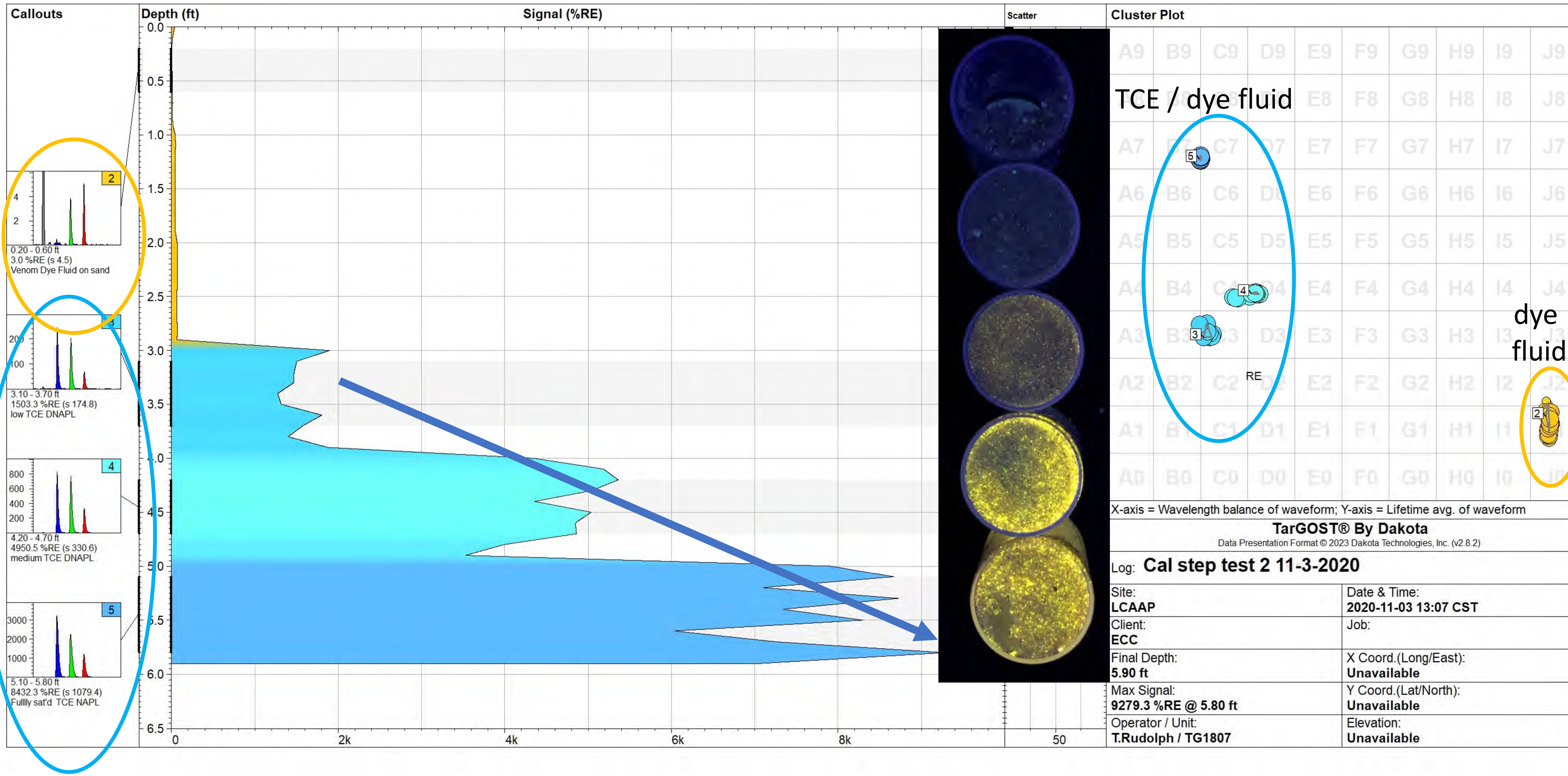
Area 17B DyeLIF Bench Test Sub-Samples

Area 17B Sonic Boring 17B-SN01 (10-15 ft bgs)

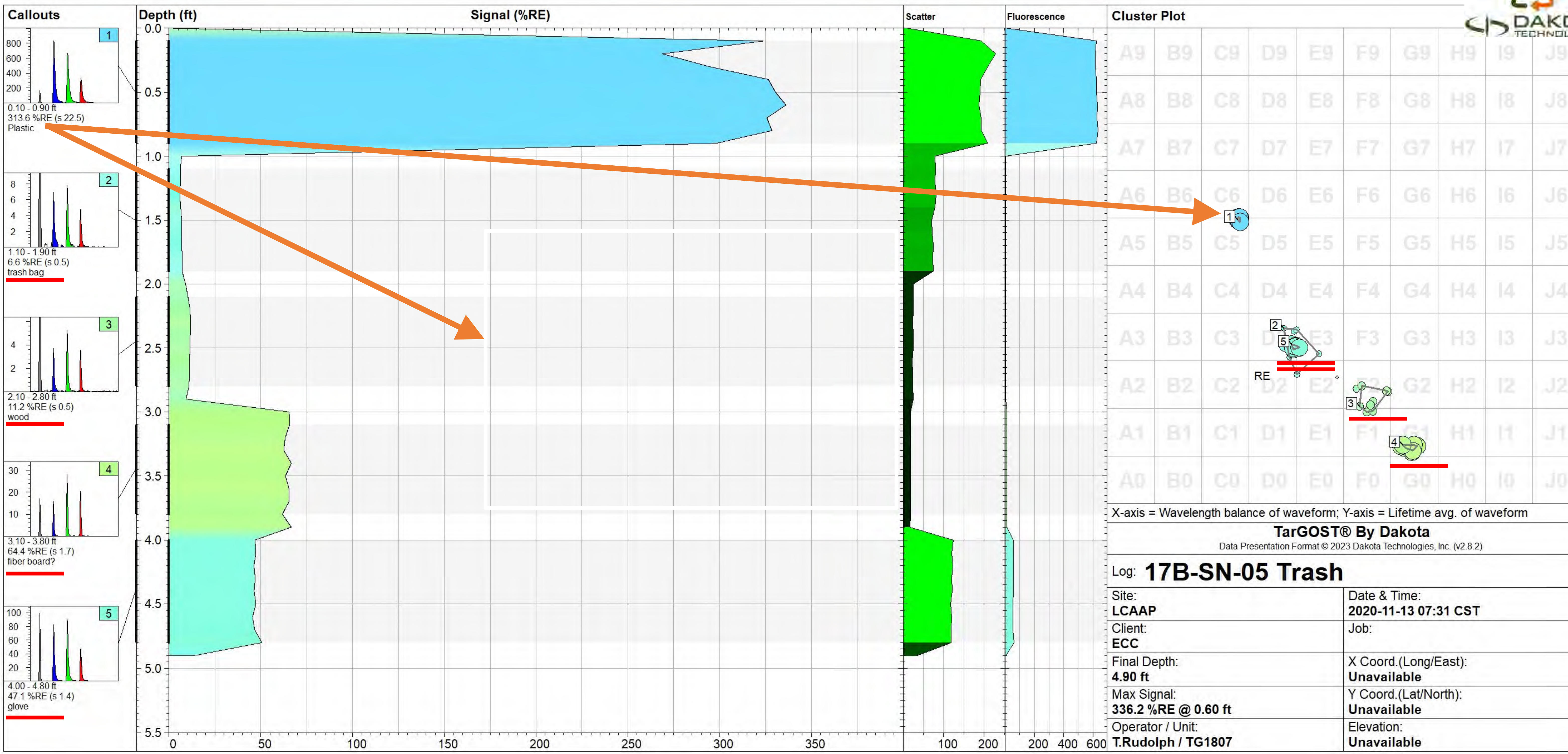
DL-10 / SN-01


Boring Log
Fill: Clay with silt, stiff
Fill: Clay, with sand, gravel and silt, becoming very soft
Clay with sand and gravel, soft
Clay with silt, medium to stiff
Clay, some silt and sand, soft
Clay, some silt and sand, stiff to hard
Residuum: clay, some silt
Shale
Depth, ft bgs
10
20
30
40
50
60
P Dwn (PSI)
Q (mL/min)
0-5: Pre-Probe
50
100
50
DyeLIF
%RE NAPL
0
50
0-5: Pre-Probe
NAPL
Not NAPL
NAPL threshold of 12%RE Total NAPL after NNLS processing
PID (ppm)
0.1
10
1,000
100,000
FLUTe NAPL
Negative
Positive
Visible NAPL
Lab data (mg/kg)
10
1,000
100,000
Total VOCs
Total SVOCs
Visible NAPL @ 49.25 ft

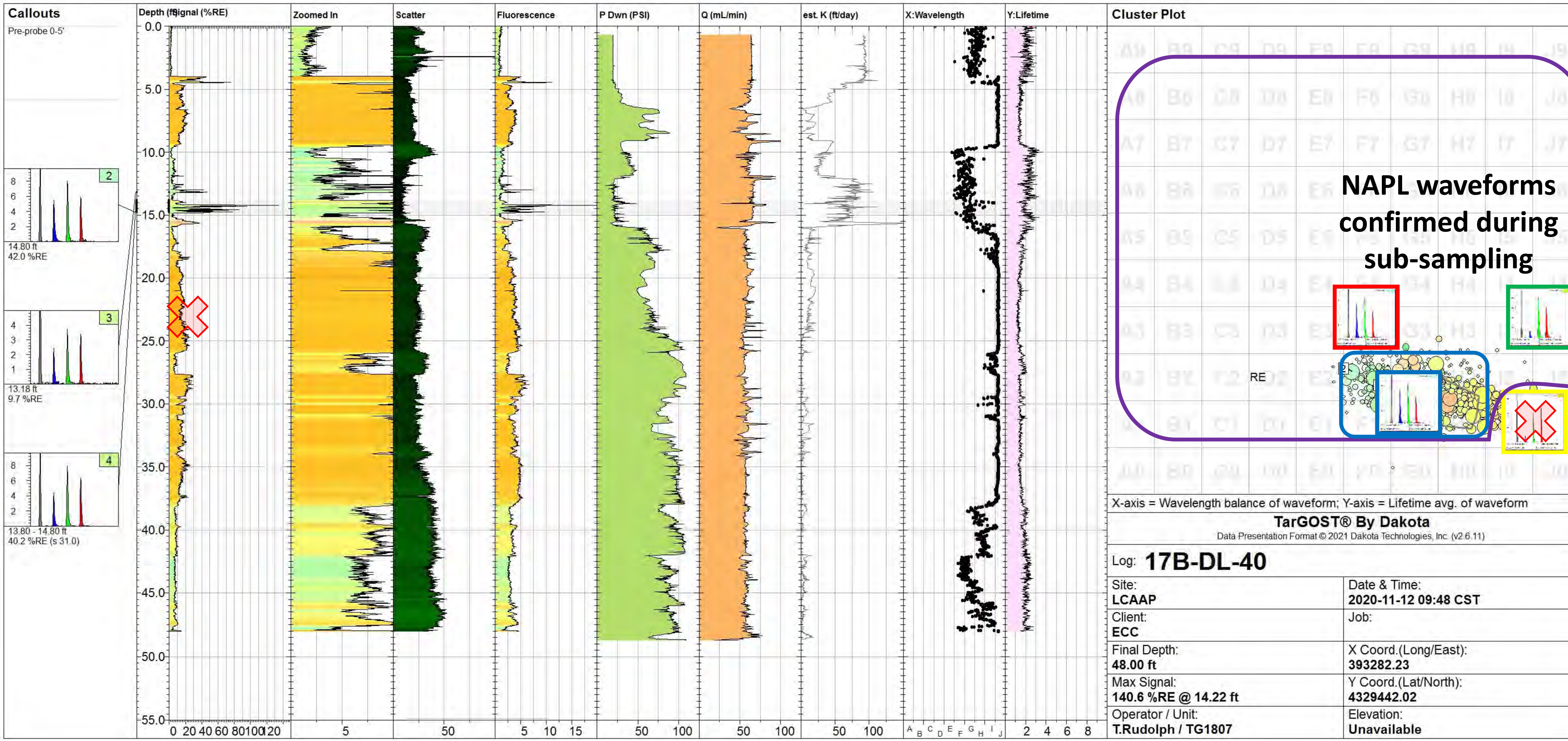
Benchtop Test Validating the TarGOST / DyeLIF Hybrid's Response to TCE



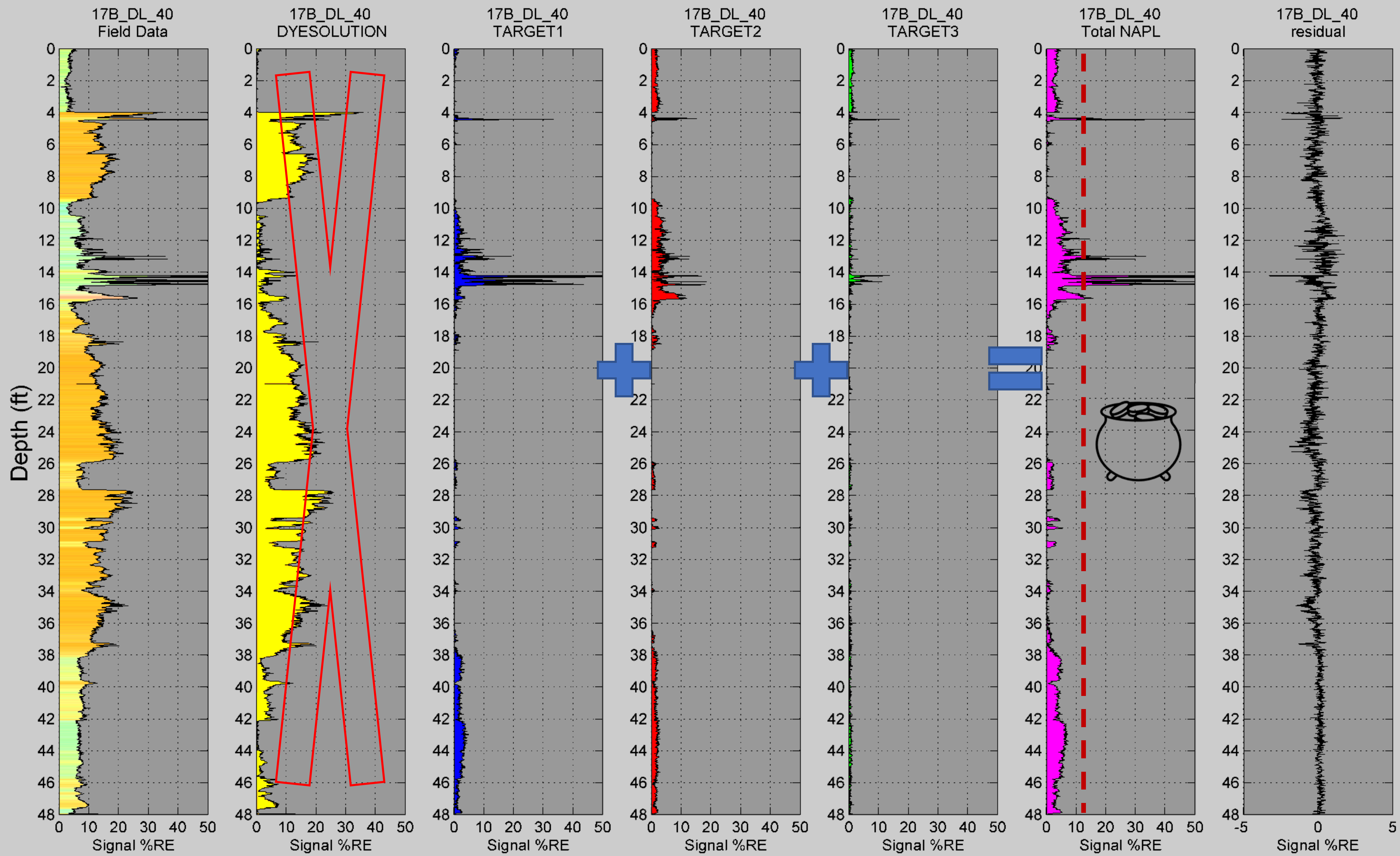
Benchtop of False Positives Encountered



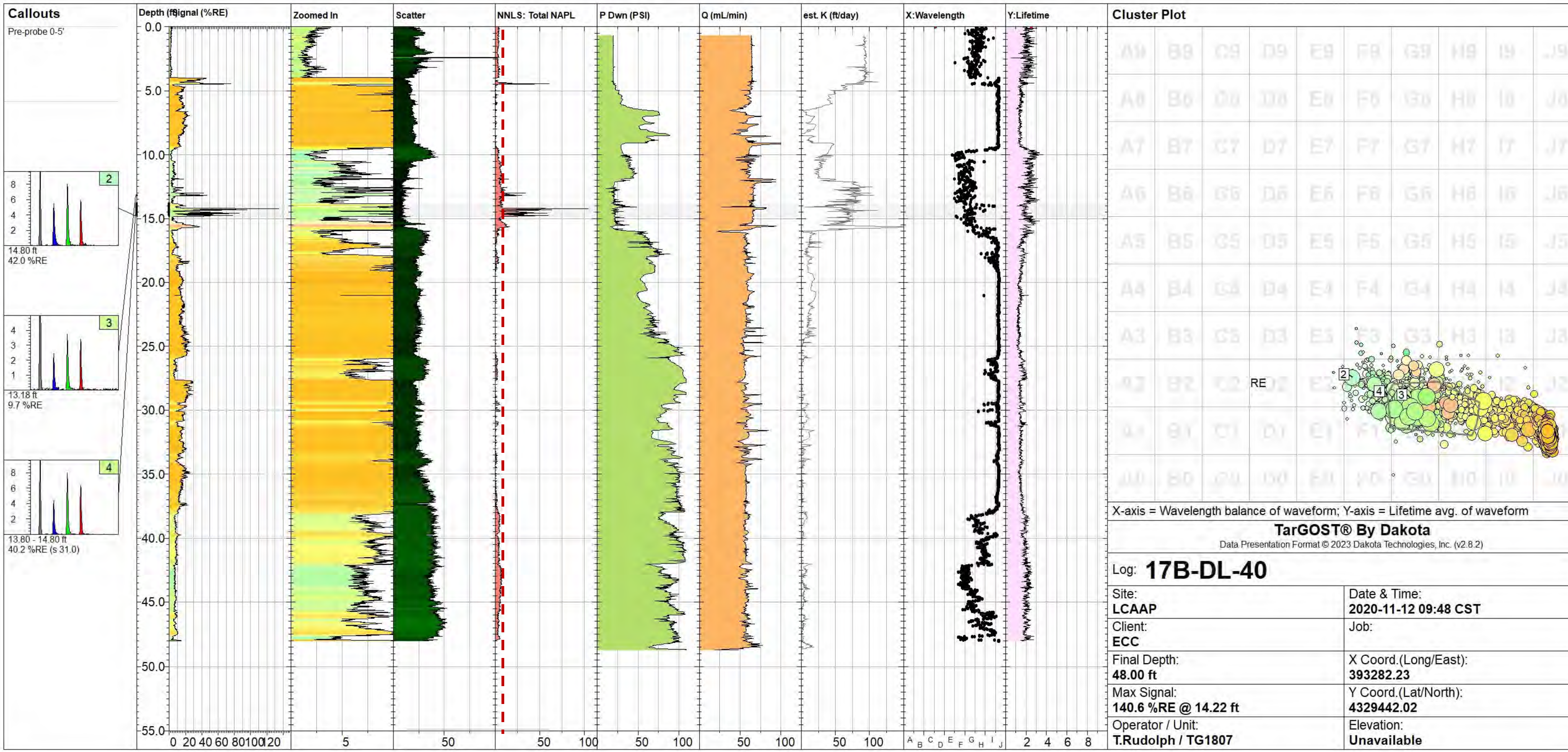
Managing the High Data Density
~1,000 – 3,000 Waveforms in Each LIF Log



Non-Negative Least Squares Processing of LIF Log



NNLS Result Added Back Into the LIF Field Log



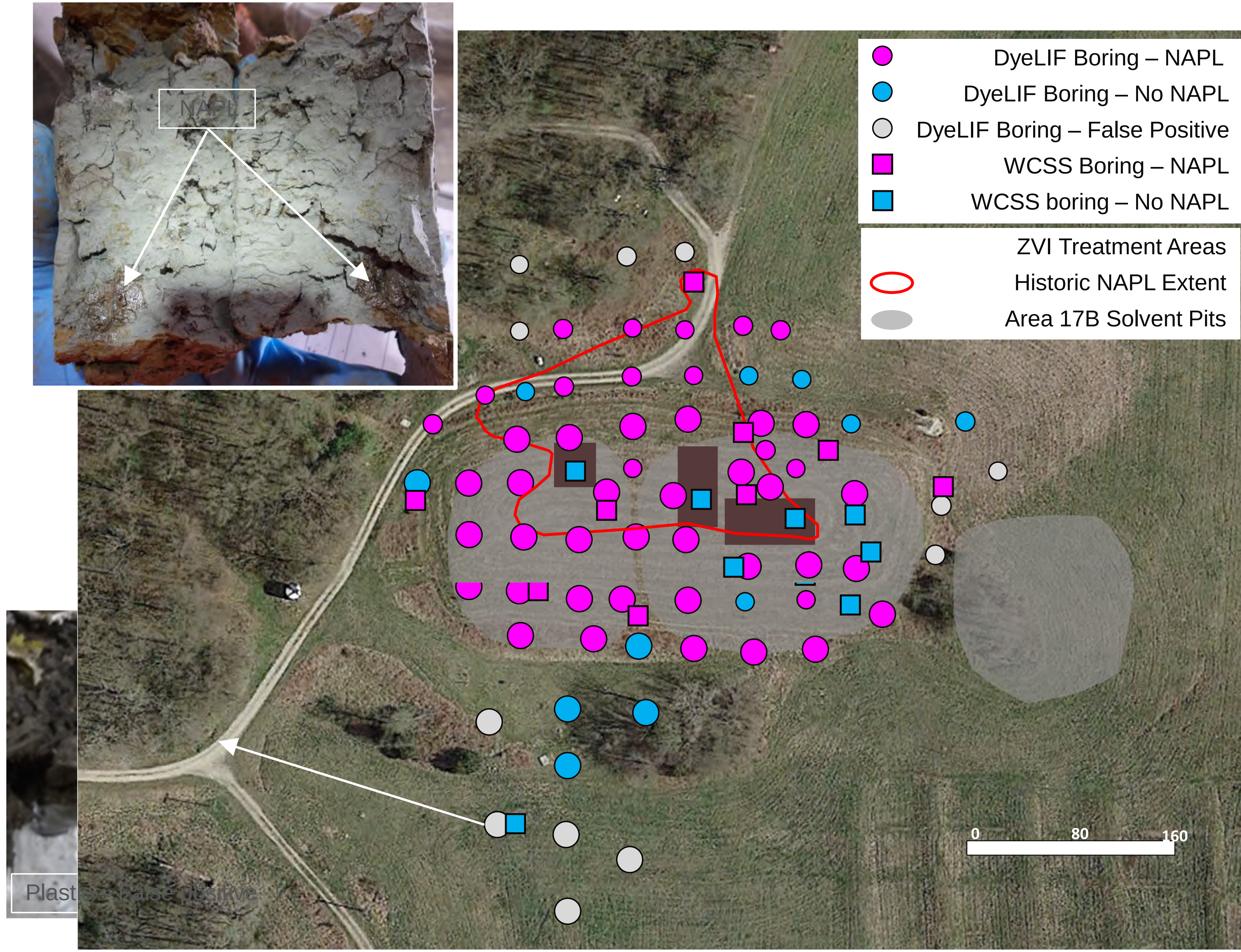
Investigation Summary

69 DyeLIF borings advanced to refusal ~ 25-55 ft bgs

- 46 NAPL
- 11 No NAPL
- 12 False positive

18 confirmation borings to validate the DyeLIF response

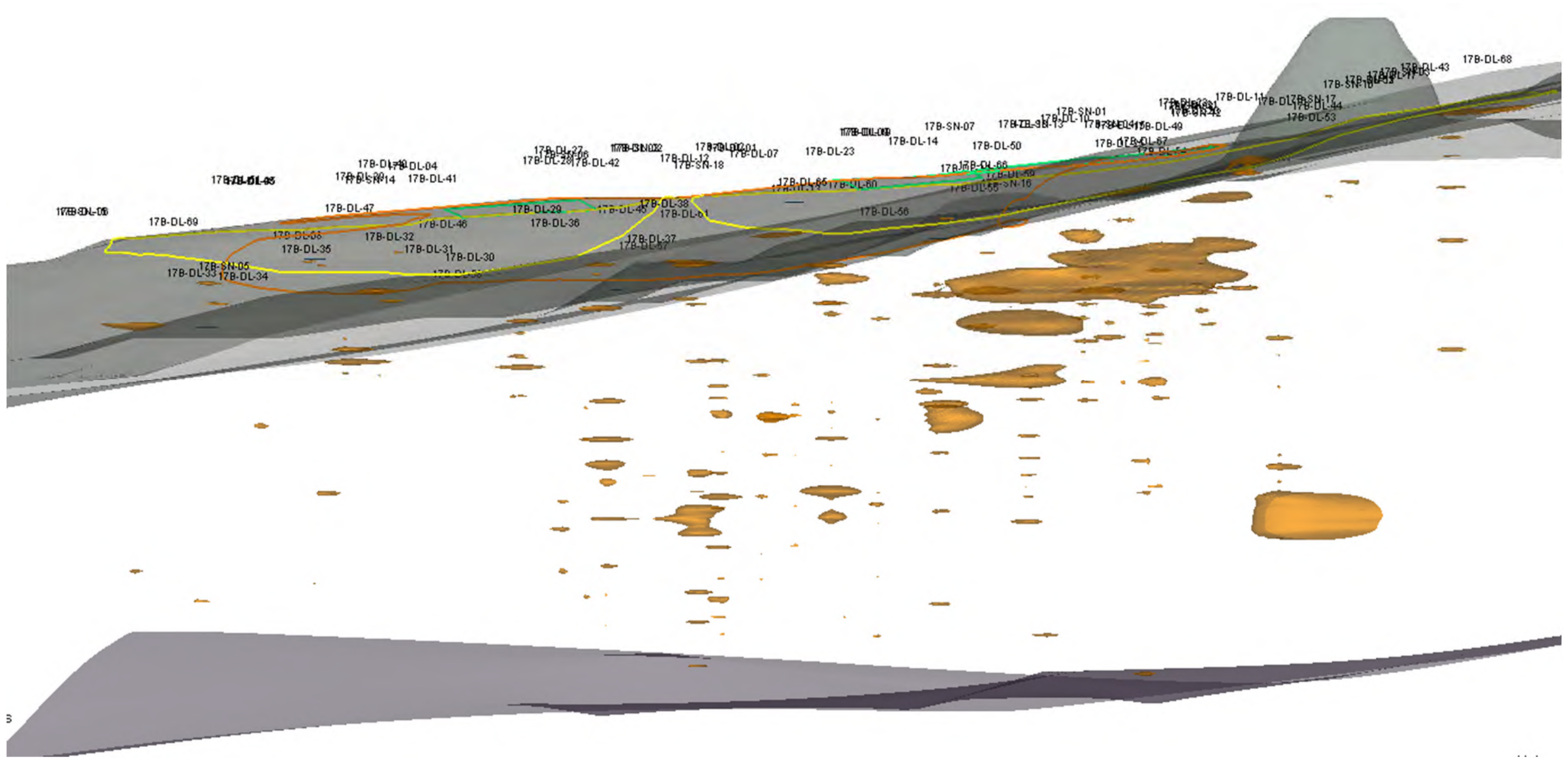
  - **170** sub-core samples (Benchtop DyeLIF & UV Screening)
  - **230** VOCs + **55** SVOCs + **55** TPH laboratory soil analyses
  - PID readings
  - Core screening with FLUTe NAPL



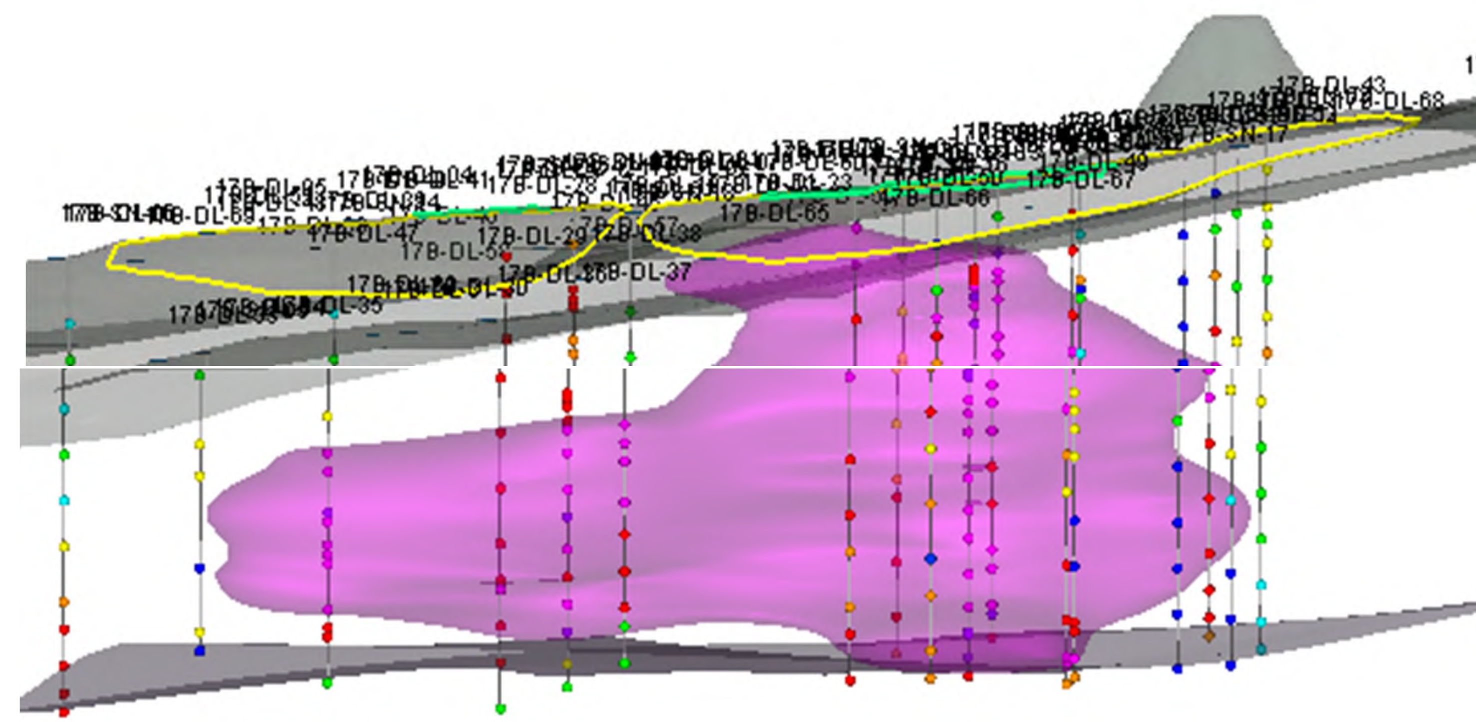
NAPL Estimates

Estimate	TarGOST / DyeLIF	Total VOCs Soil Laboratory Results
NAPL Volume	1,400 gallons	2,900 gallons
NAPL Mass	13,500 lbs	28,000 lbs

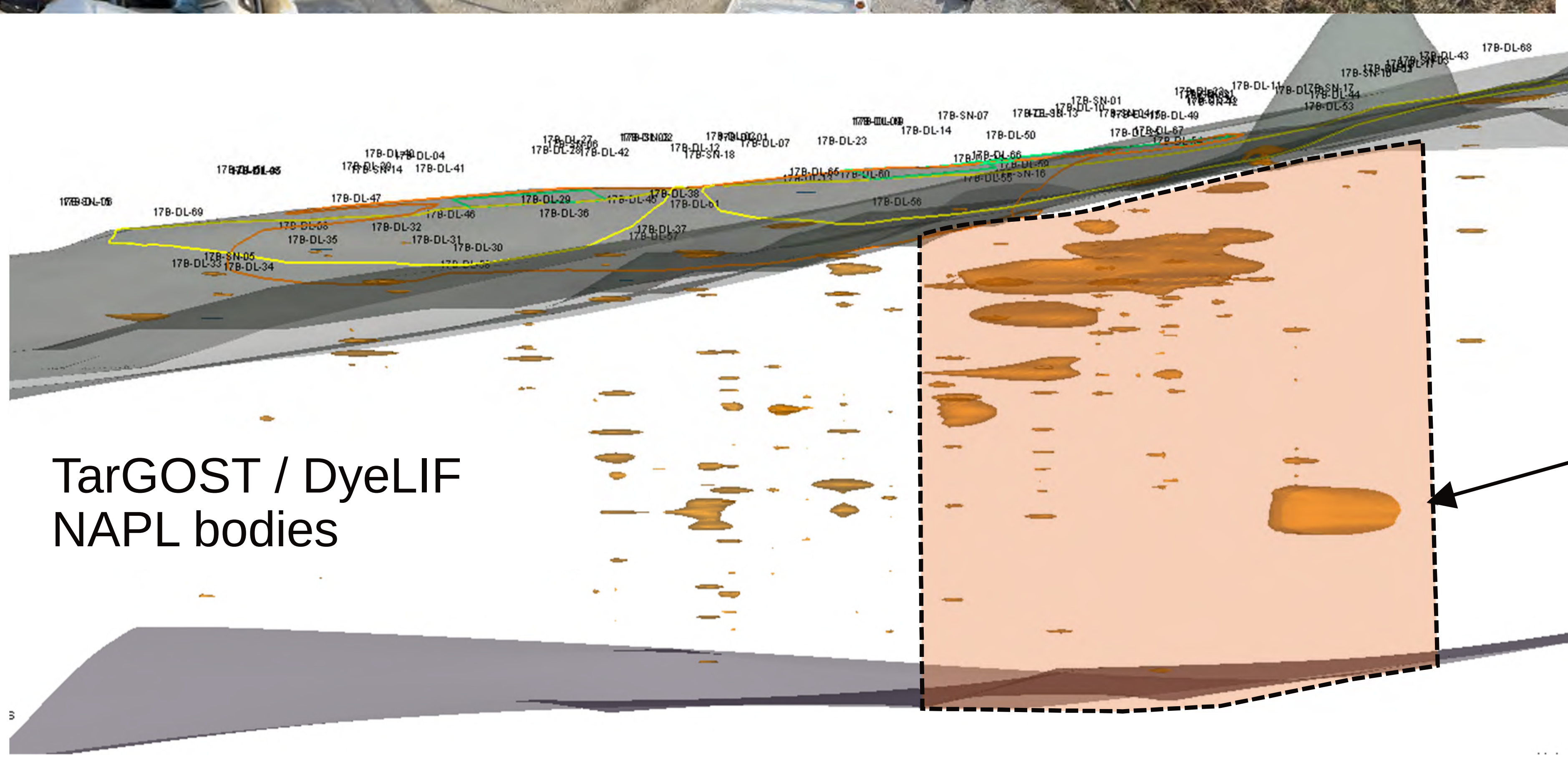
DyeLIF NAPL bodies



Total VOCs in Soil



Area 17B Thermal System



- Design based on TaGOST / DyeLIF results and only included portion of the pits
- Construction 01/03/2022 to 12/06/2022
- Started operation 2/1/2023
- Anticipated 155 days of operation
- Operation is 46% complete as of 5/5/2023
- ~5,455 lbs of VOCs extracted to date

Conclusions / Lessons Learned

- Importance of planning & stakeholder communication
- Challenging site for any investigation method due to complex NAPL distribution and composition
  - Discontinuous seams
  - Proportions of CVOCs and petroleum hydrocarbons vary both vertically and laterally
- Critical to verify fluorescence types with select companion soil borings / multiple lines of evidence
  - Dye was not solvated by weakly fluorescent NAPL / dye not solvated
  - NNLS processing identified target NAPL
- Project objectives achieved – NAPL extents and mass estimates were refined using TarGOST / DyeLIF and soil laboratory data