Rapid DNAPL Source Zone Characterization with Dye-Enhanced Laser Induced Fluorescence (DyeLIF)

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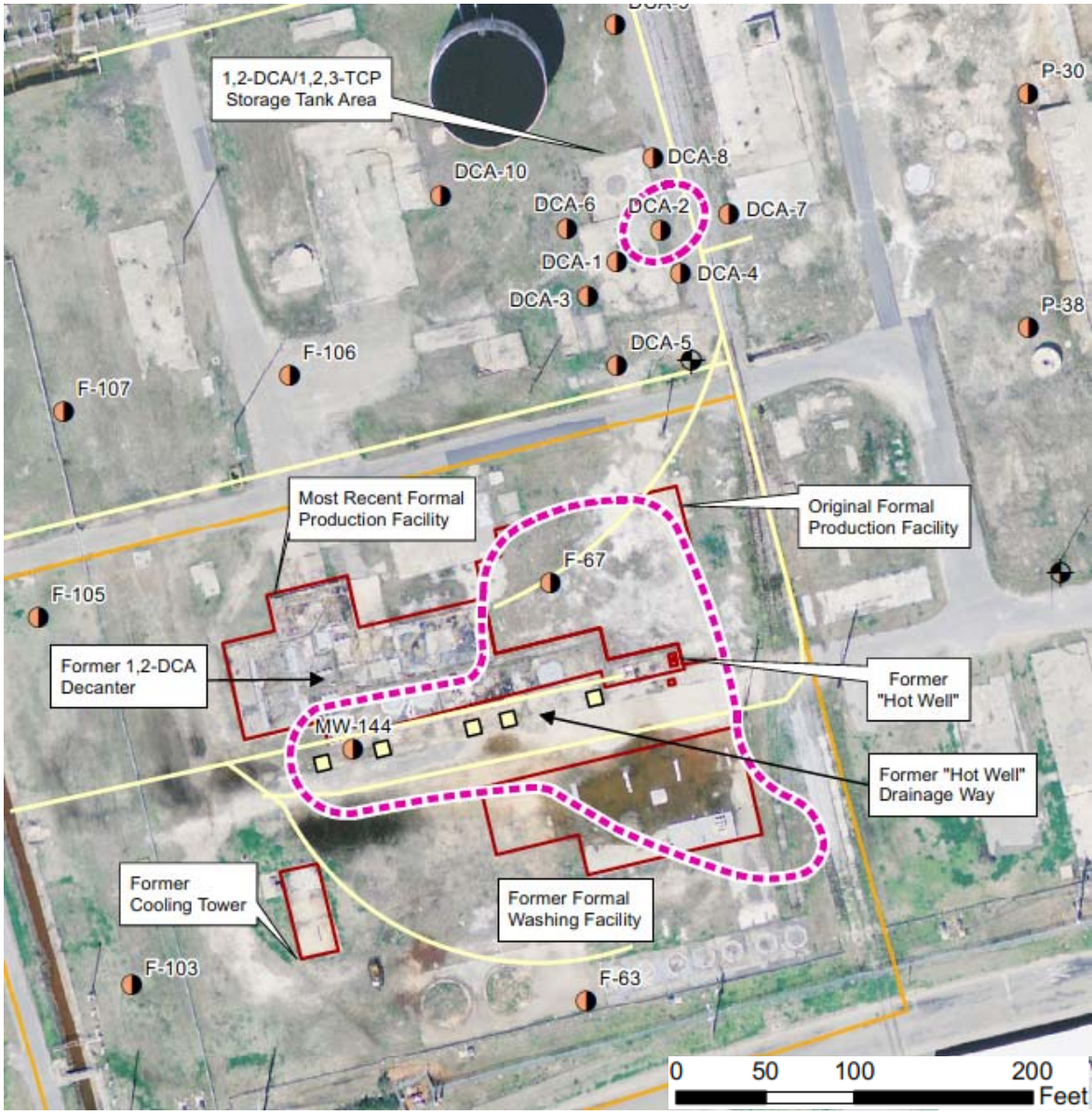
Randy St. Germain (Dakota Technologies)

April 12, 2018

Site Background

- Began operations in 1952
- Ceased operations in 2001
- DNAPL identified in “Formal Area” and “1,2-DCA/1,2,3-TCP Storage Tank Area”



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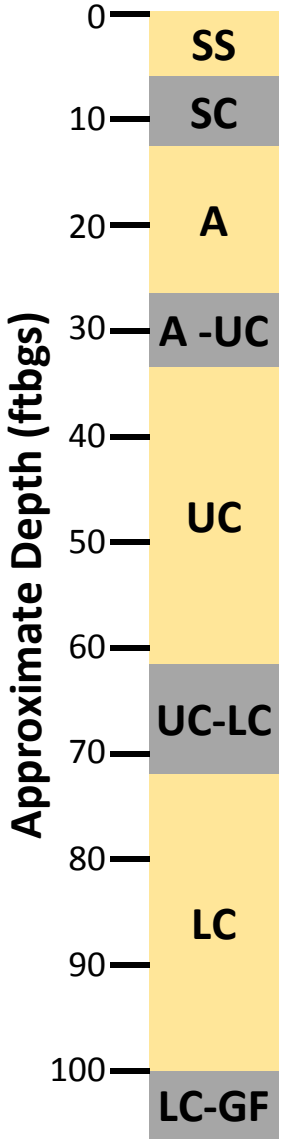
General Stratigraphy

- Uppermost transmissive unit is of alluvial origin. Sand with silt and clay interbeds.
- Aquitards are an organic rich clay
- Citronelle units are clean sand



Surficial Sand	**FILL** (variable, not always present)
Surficial Clay	Sandy **CLAY**, plant roots
Alluvial	**SAND** with silt and clay interbeds K= 1.5 x 10^{-3} cm/sec
A-UC Clay	**CLAY** some silt and sand interbeds, wood fragments
Upper Citronelle	**SAND** K= 1.2 x 10^{-2} cm/sec
UC-LC Clay	**CLAY**, wood fragments
Lower Citronelle	**SAND** K= 1.4 x 10^{-2} cm/sec
LC-GF Clay	**CLAY**, wood fragments

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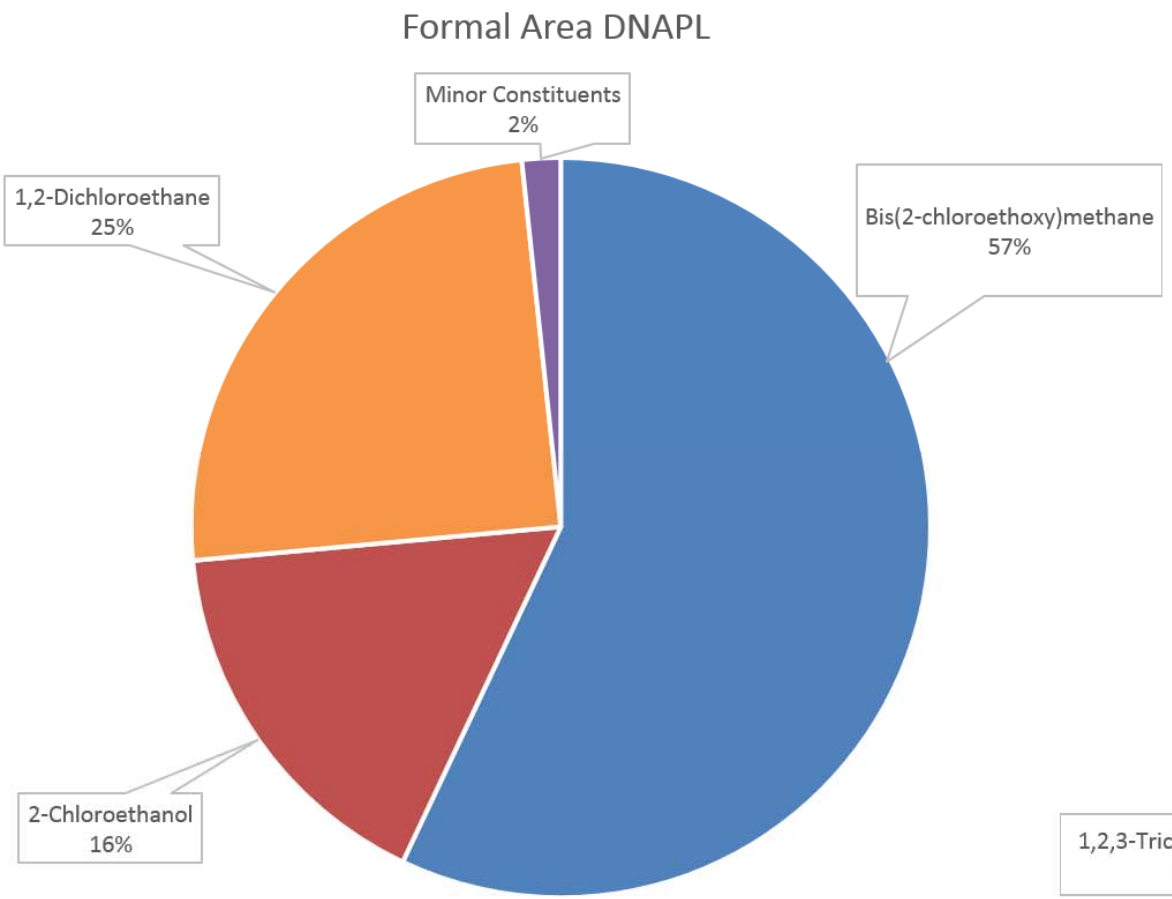
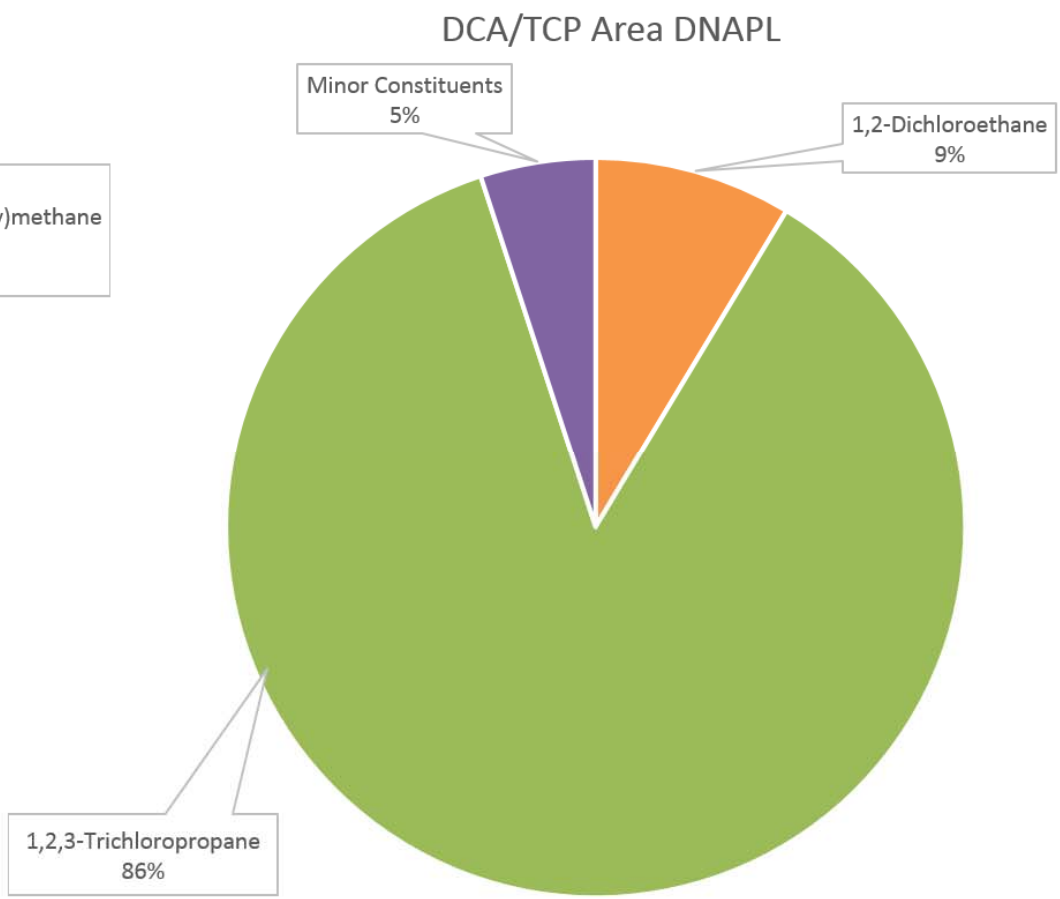
DNAPL Composition





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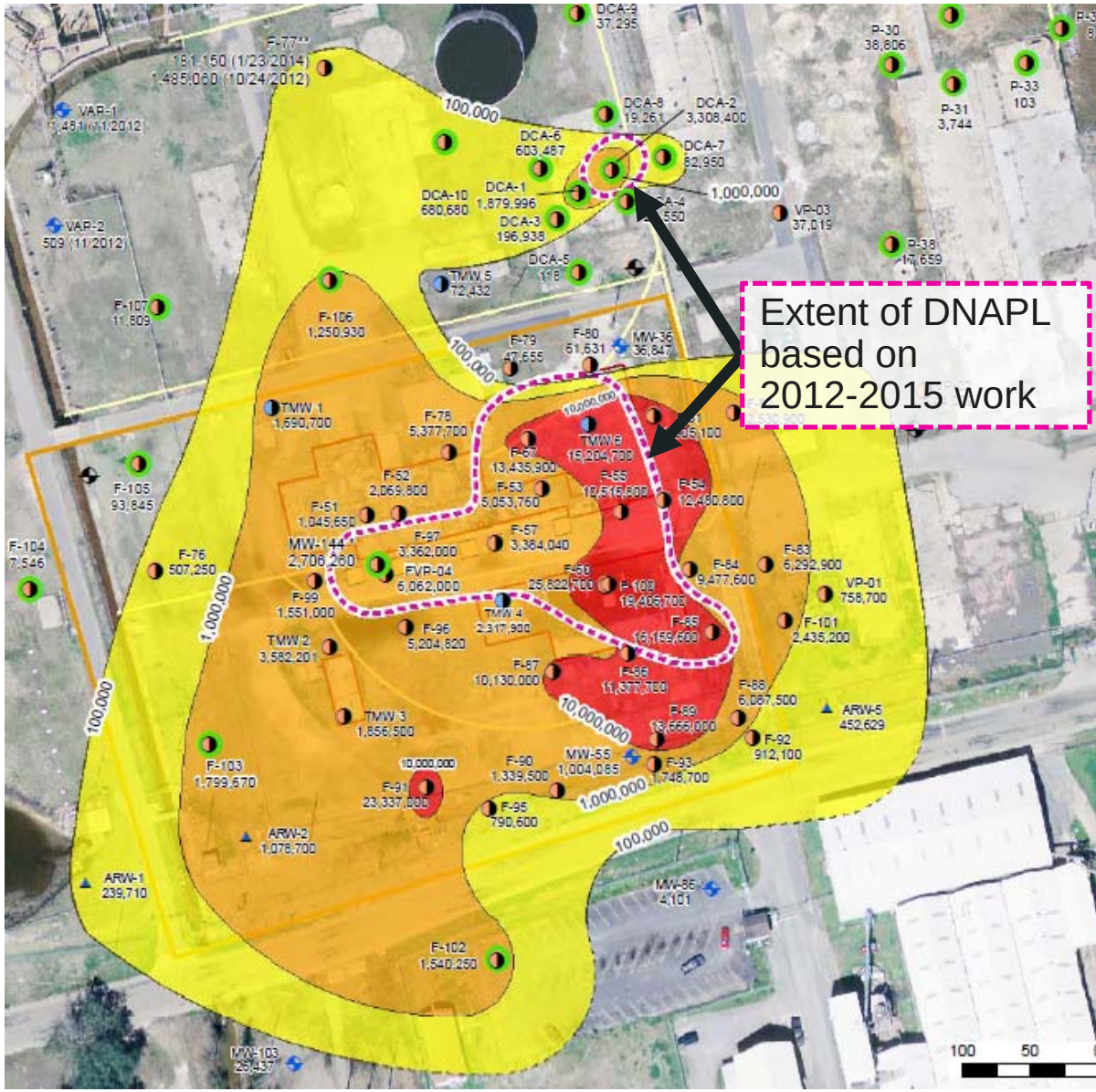
Previous Work

- 2012-2015: Phase 1/2/3/4 investigations
- 85 locations with soil and/or groundwater sampling
- 8 monitoring wells where DNAPL accumulated



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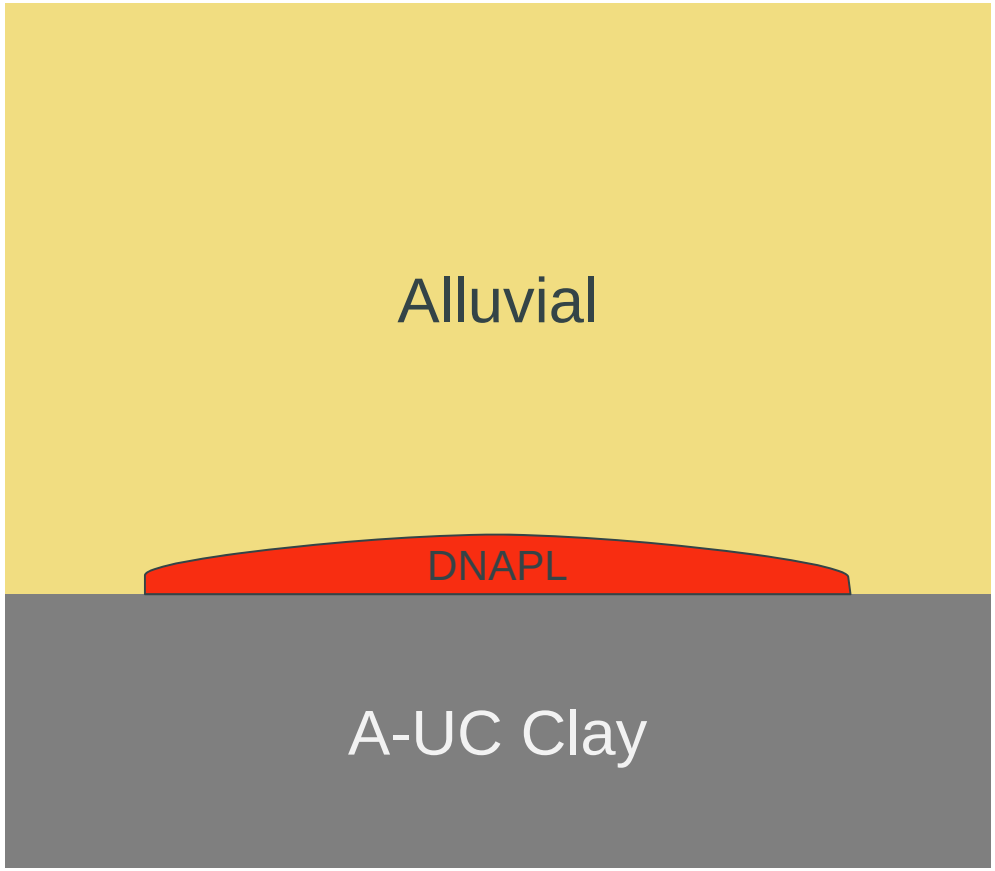
Previous DNAPL Conceptual Model

- Based on:
  - Observation in core (no dye)
  - Observation in temporary monitoring wells
- Assumed to be sitting atop a sand-clay interface (A-UC Clay)
- Assumed to be uniform thickness (5ft) for mass estimates



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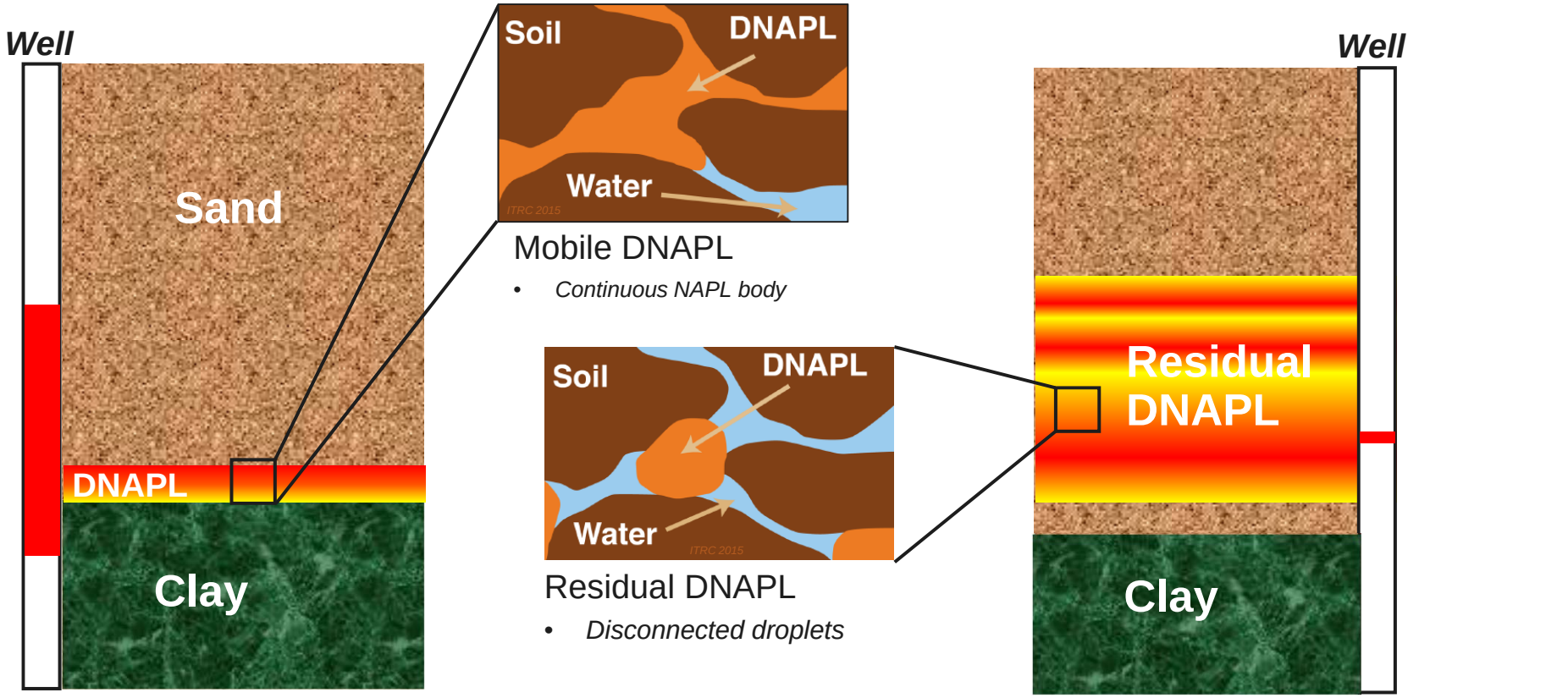
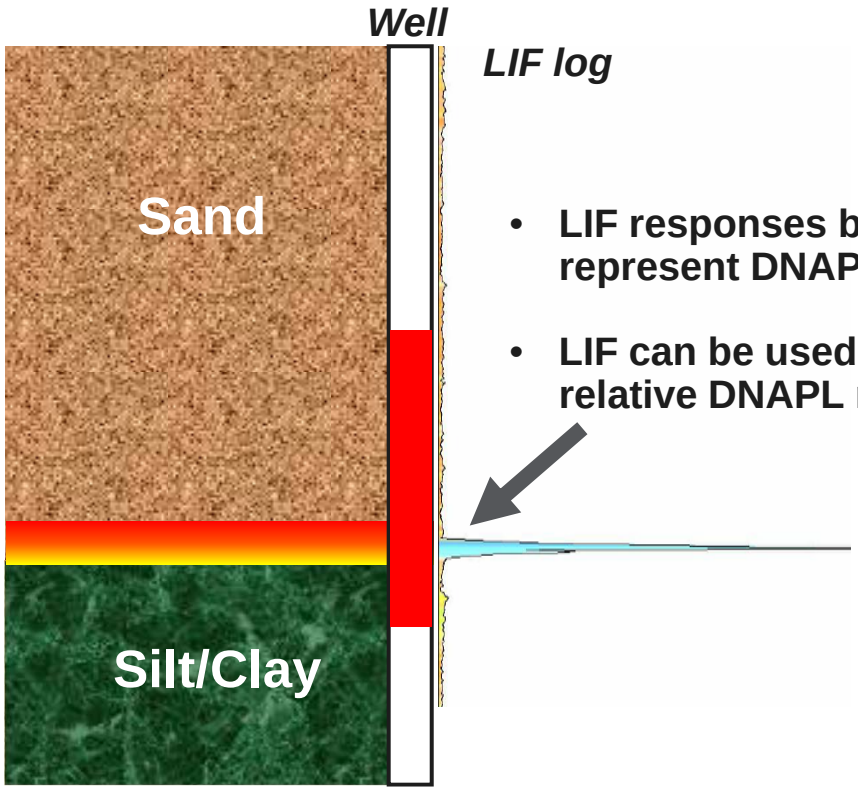
How to map DNAPL in the subsurface

- **Wells can over-estimate and under-estimate DNAPL in the formation.**

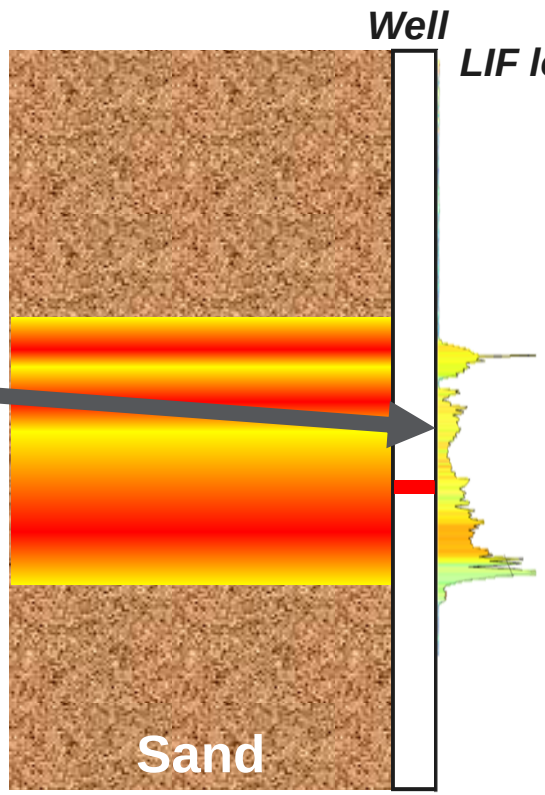


How to map DNAPL in the subsurface

- **LIF methods measure the fluorescence associated with NAPL, and records presence of both mobile and residual NAPL.**

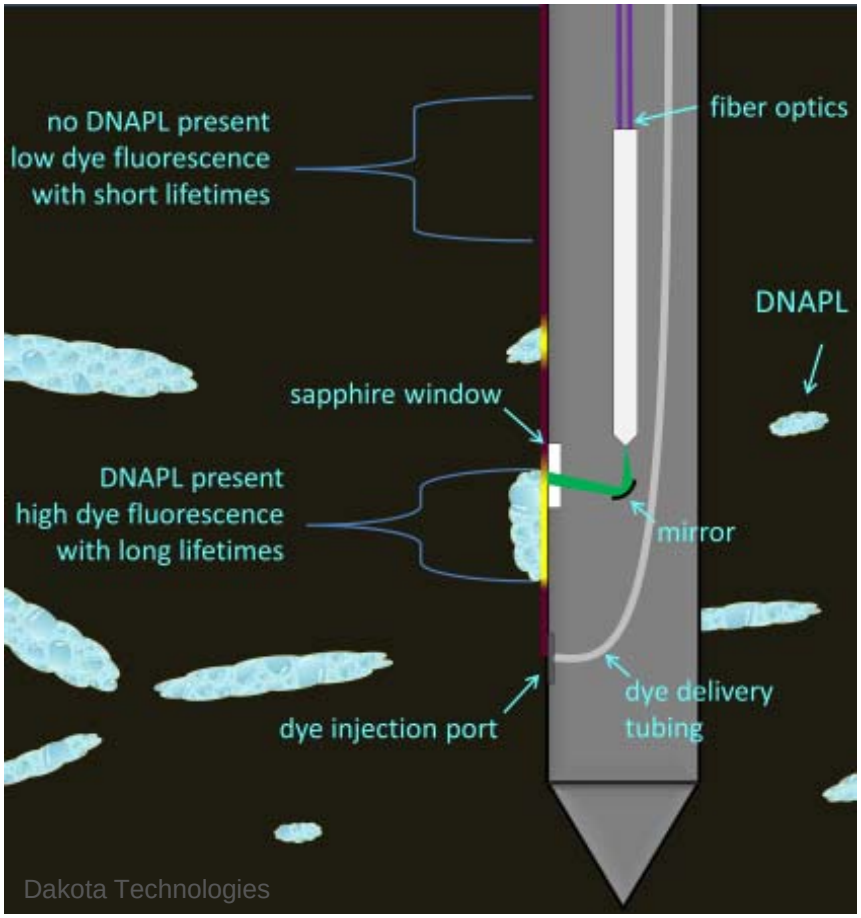


- **LIF responses better represent DNAPL in formation**
- **LIF can be used to identify relative DNAPL mobility**



What is DyeLIF?

- Modification of traditional LIF, which is a well-established, mature technology for mapping LNAPL.
- Traditional LIF does *not* work for chlorinated DNAPLs (because they do not naturally fluoresce).
- DyeLIF modifies LIF by addition of a fluorescent hydrophobic dye in to DNAPLs.
- Theory is same as a dye shake test for NAPL; DyeLIF is analogous to performing 1000s of downhole dye shake tests in a single borehole
- Capable of detecting DNAPL at <1% pore saturation



DyeLIF History

1992
U.S. Army Corps of Engineers develops sapphire window concept

1994
First optical screening tools for LNAPL available

1994-current
Hundreds of optical screening tool projects for mapping LNAPL completed

2013
ESTCP project to develop DyeLIF tool for chlorinated DNAPL (St. Germain et al. 2014; Einarson et al. 2016)

2014
First commercial application of DyeLIF (Welty et al. 2016)

2014-2018
Multiple additional DyeLIF investigations completed

2018

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Test tube with dye/sand mixture:

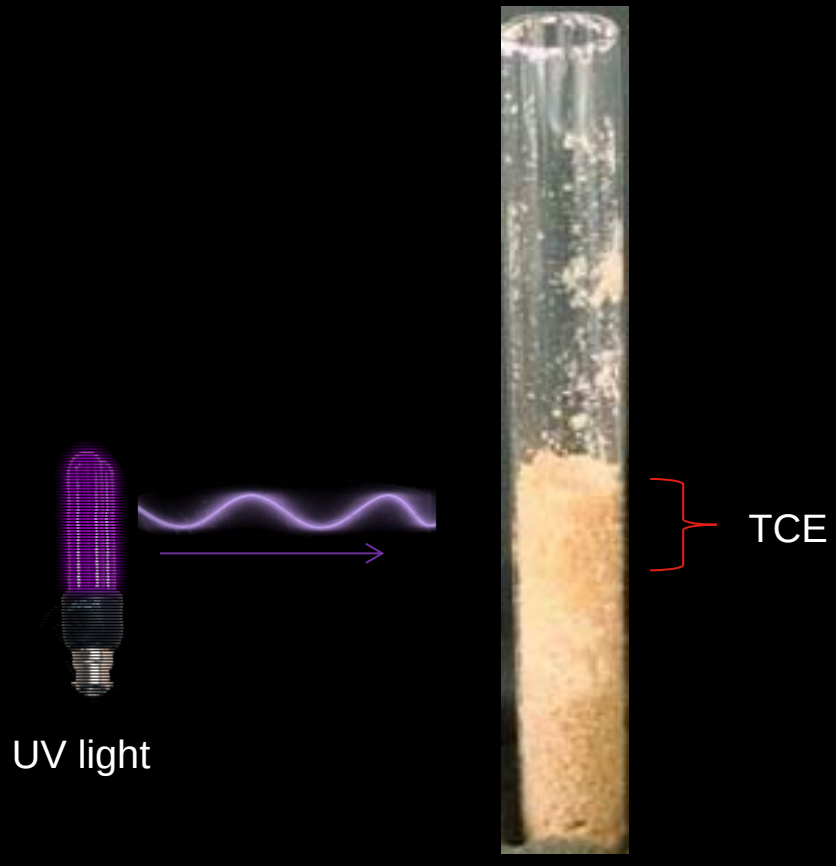
TCE poured in from top

TCE present at top of sand

Natural light

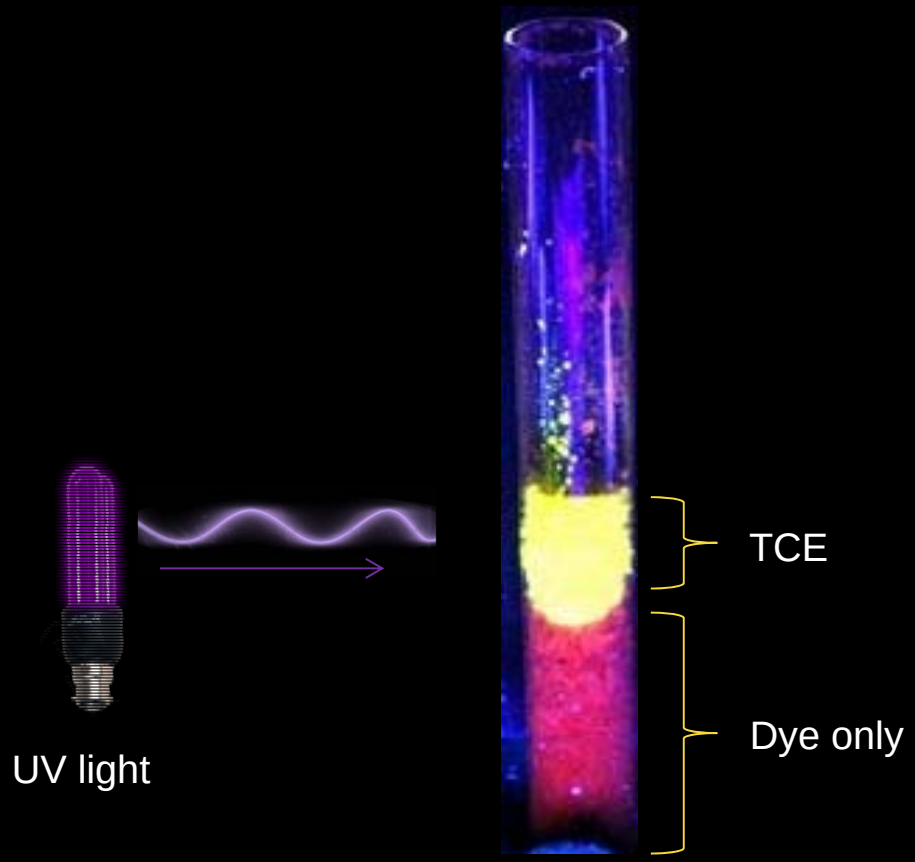
St. Germain et al., 2014

Test tube with dye/sand mixture:



St. Germain et al., 2014

Test tube with dye/sand mixture:



St. Germain et al., 2014

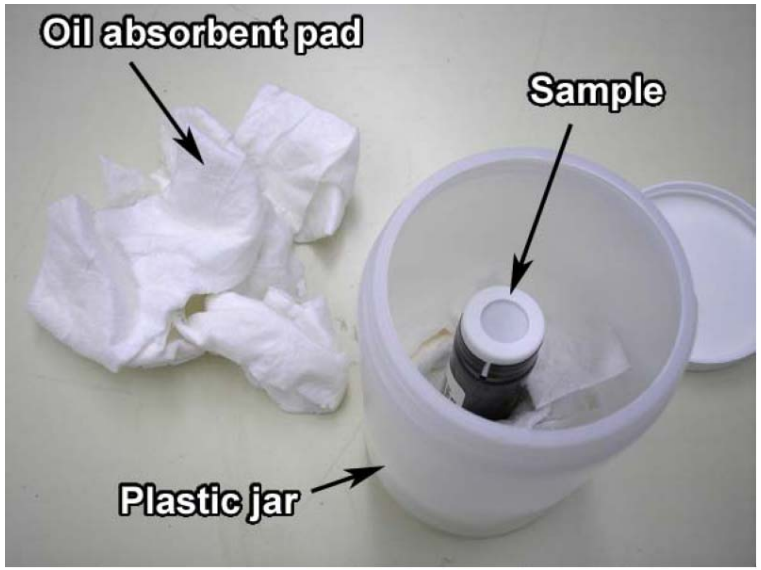
Soil/Water/DNAPL
+ Dye

Visible light

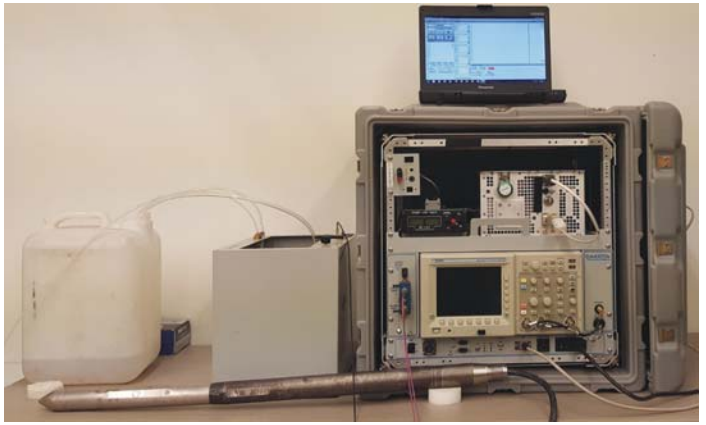
UV light

Site-Specific DNAPL Bench Testing

VOA with DNAPL, sealed with tape



Packing for shipping



Bench testing

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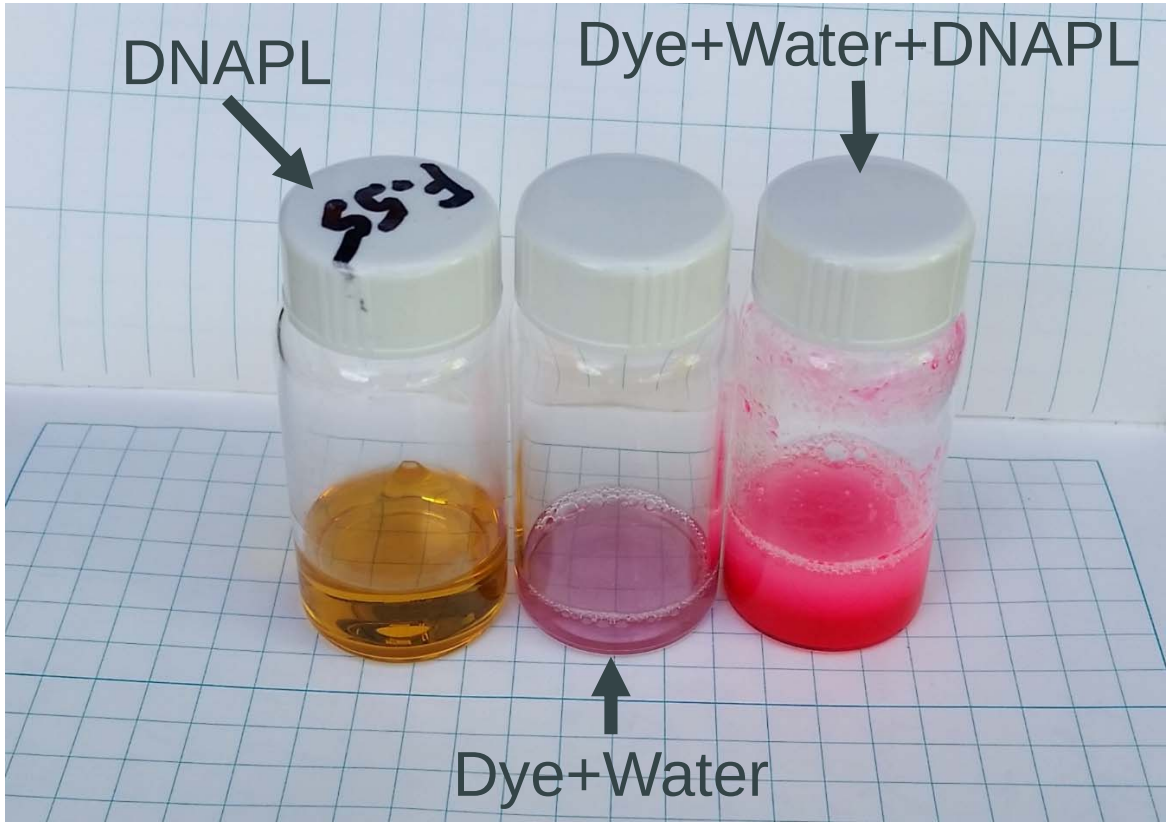
Venom™ Dye

- Dakota's new and improved hydrophobic fluorescent dye

- Fluorescence response 10 to 100 times greater than initial dye developed for the Dye-LIF technology



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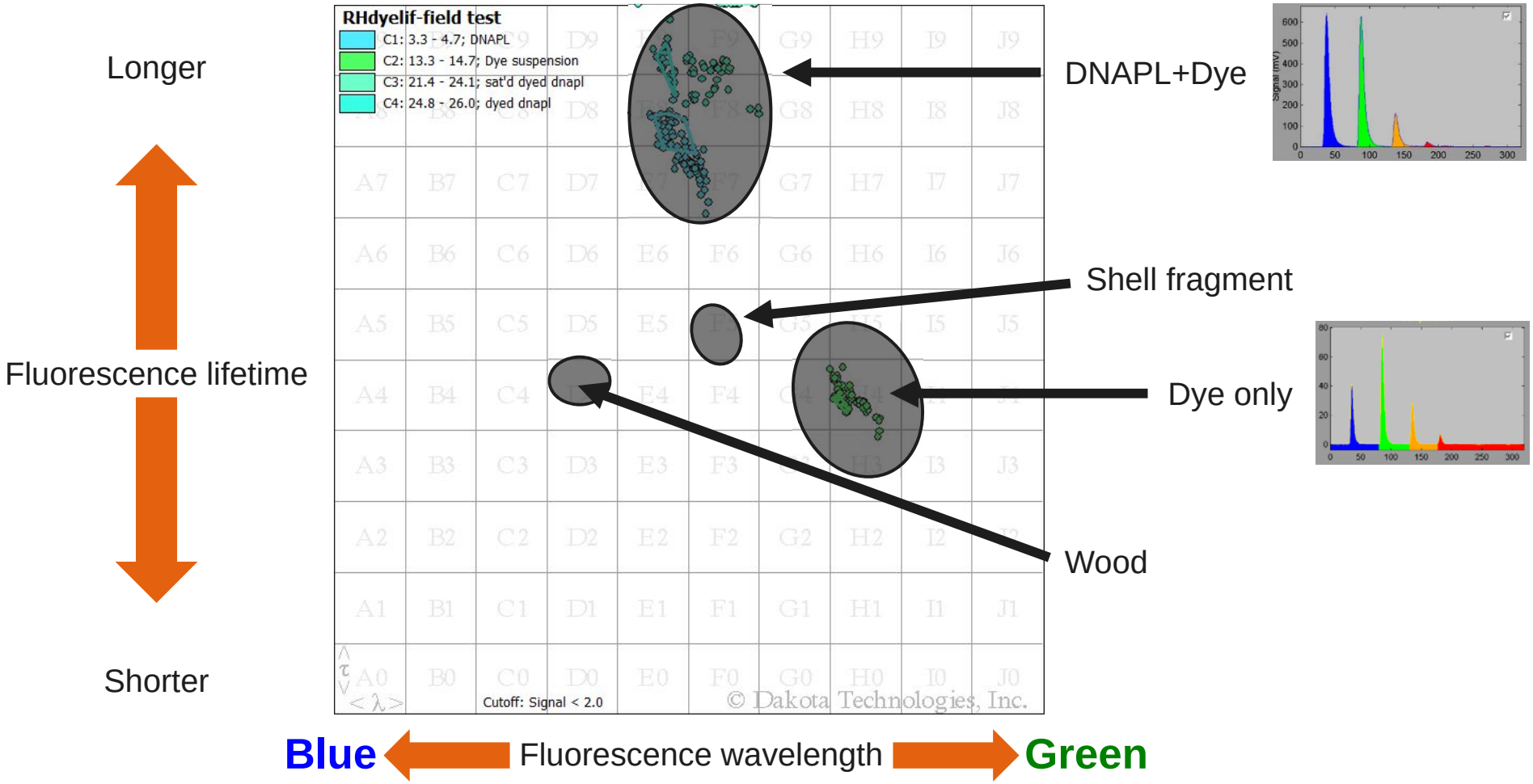
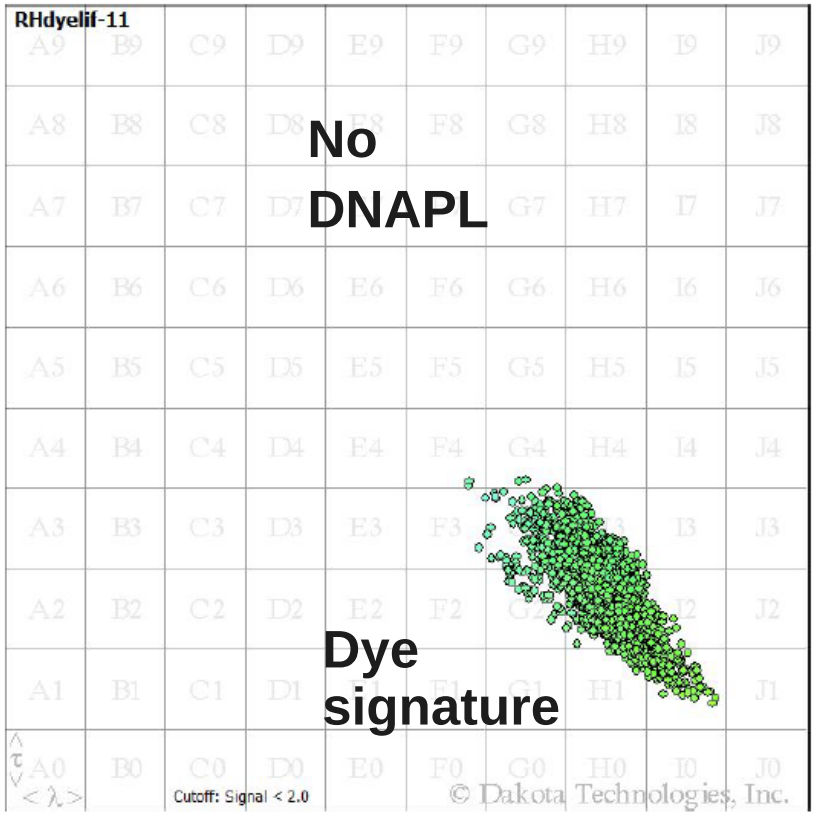
Fluorescence Signature

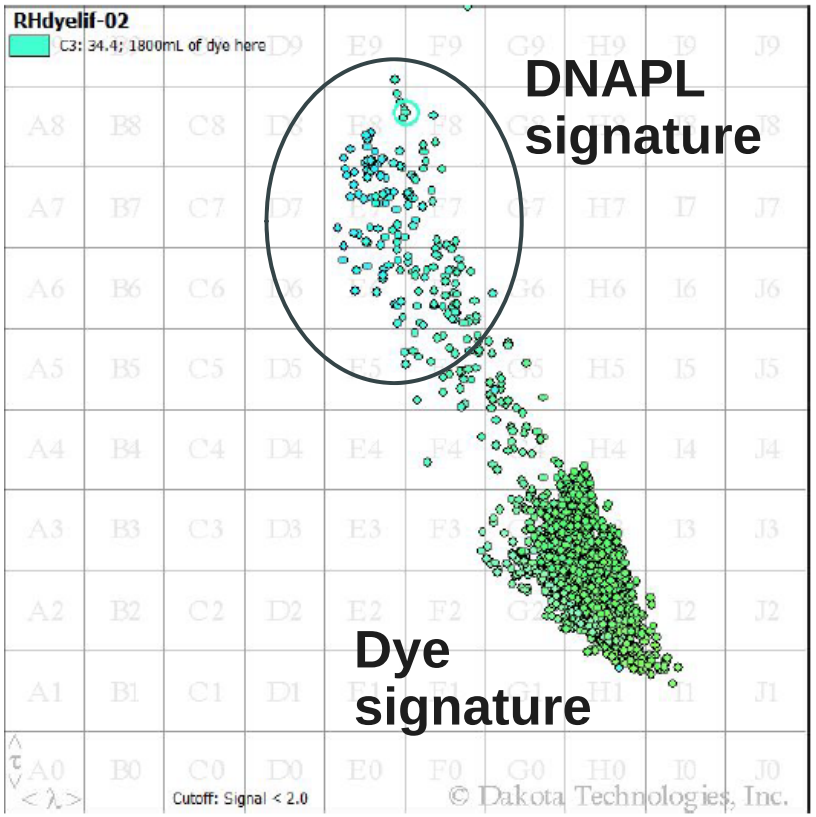


Fluorescence Signature

Negative DyeLIF location



Positive DyeLIF location



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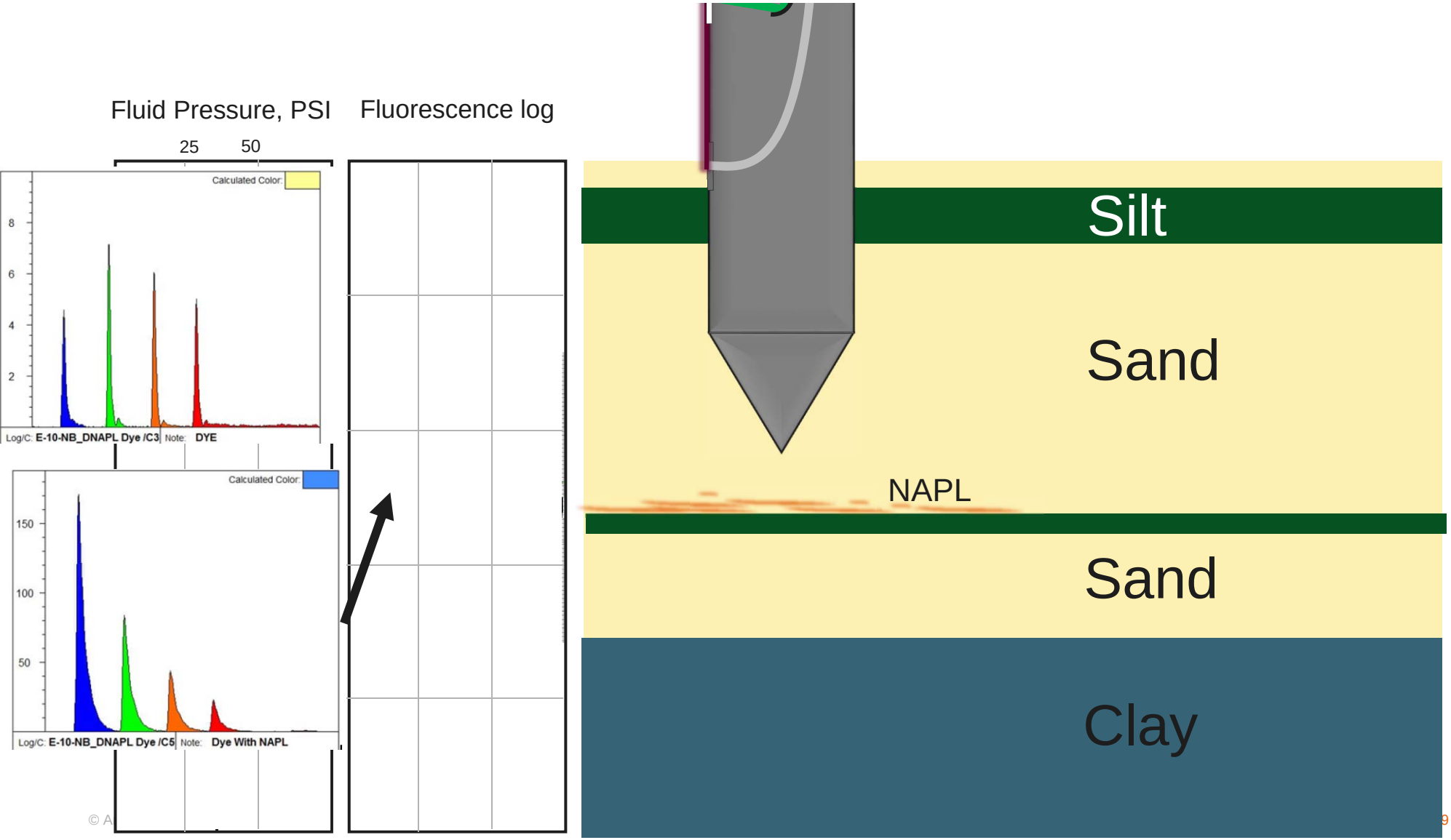
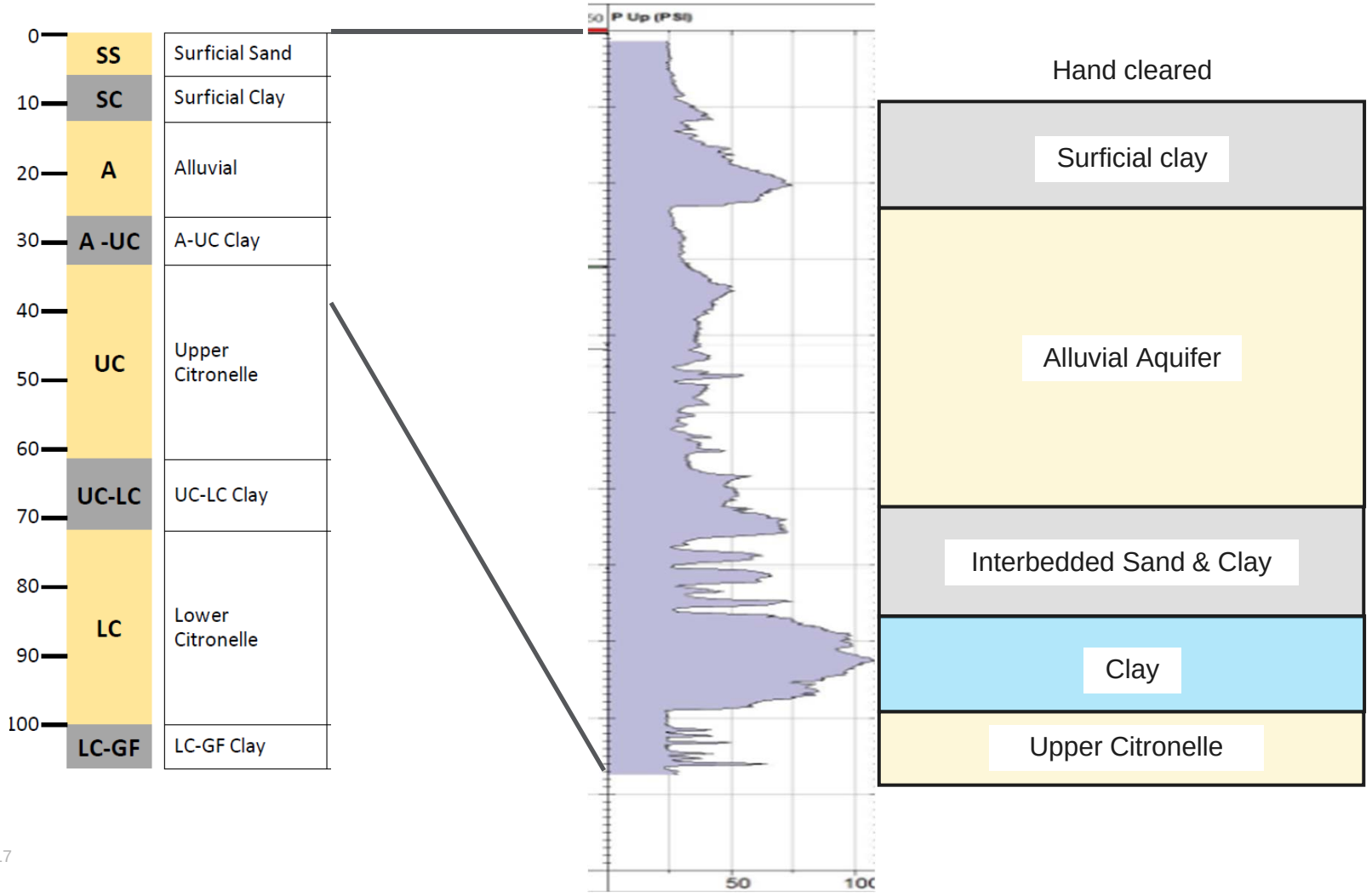
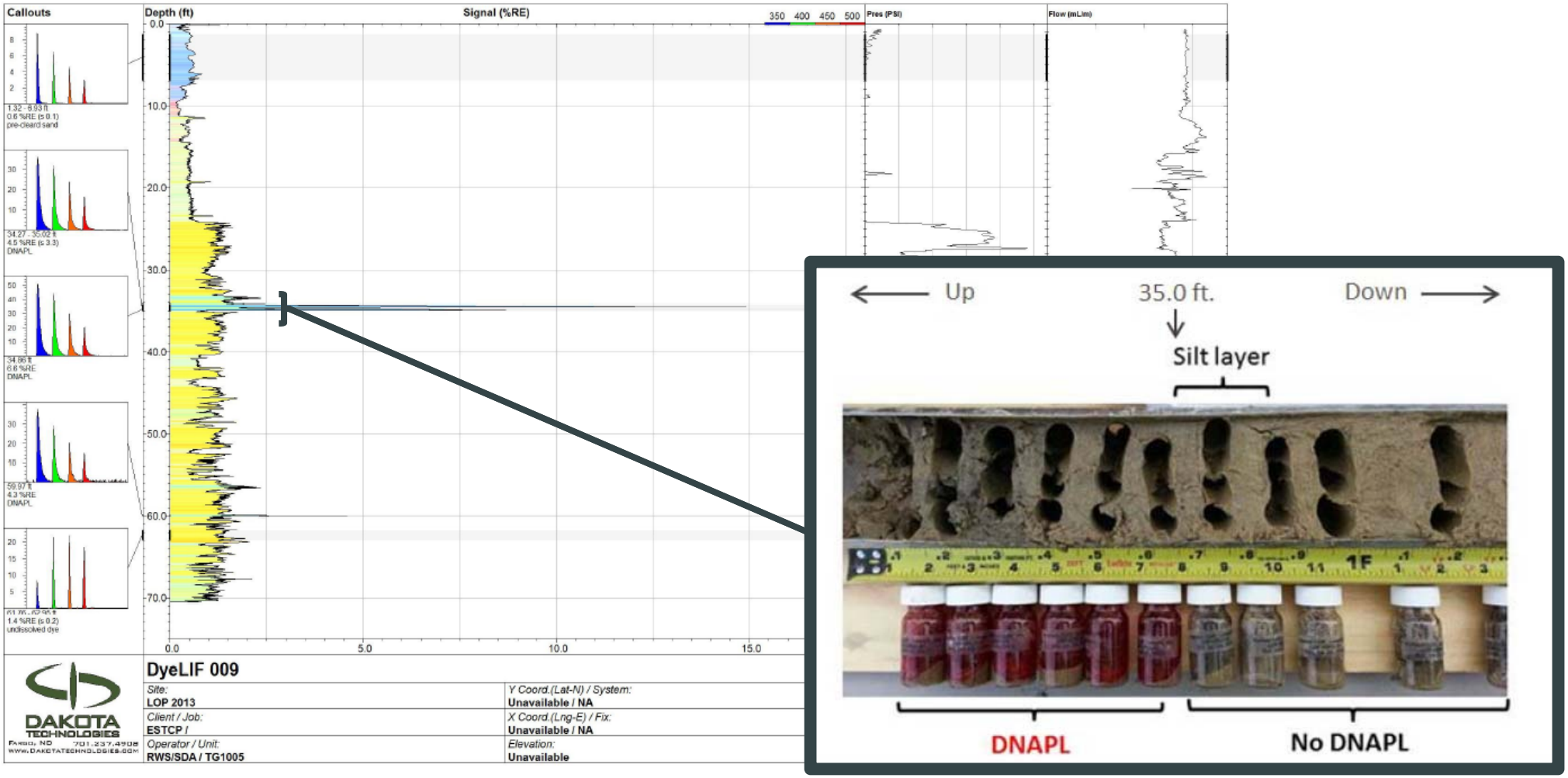
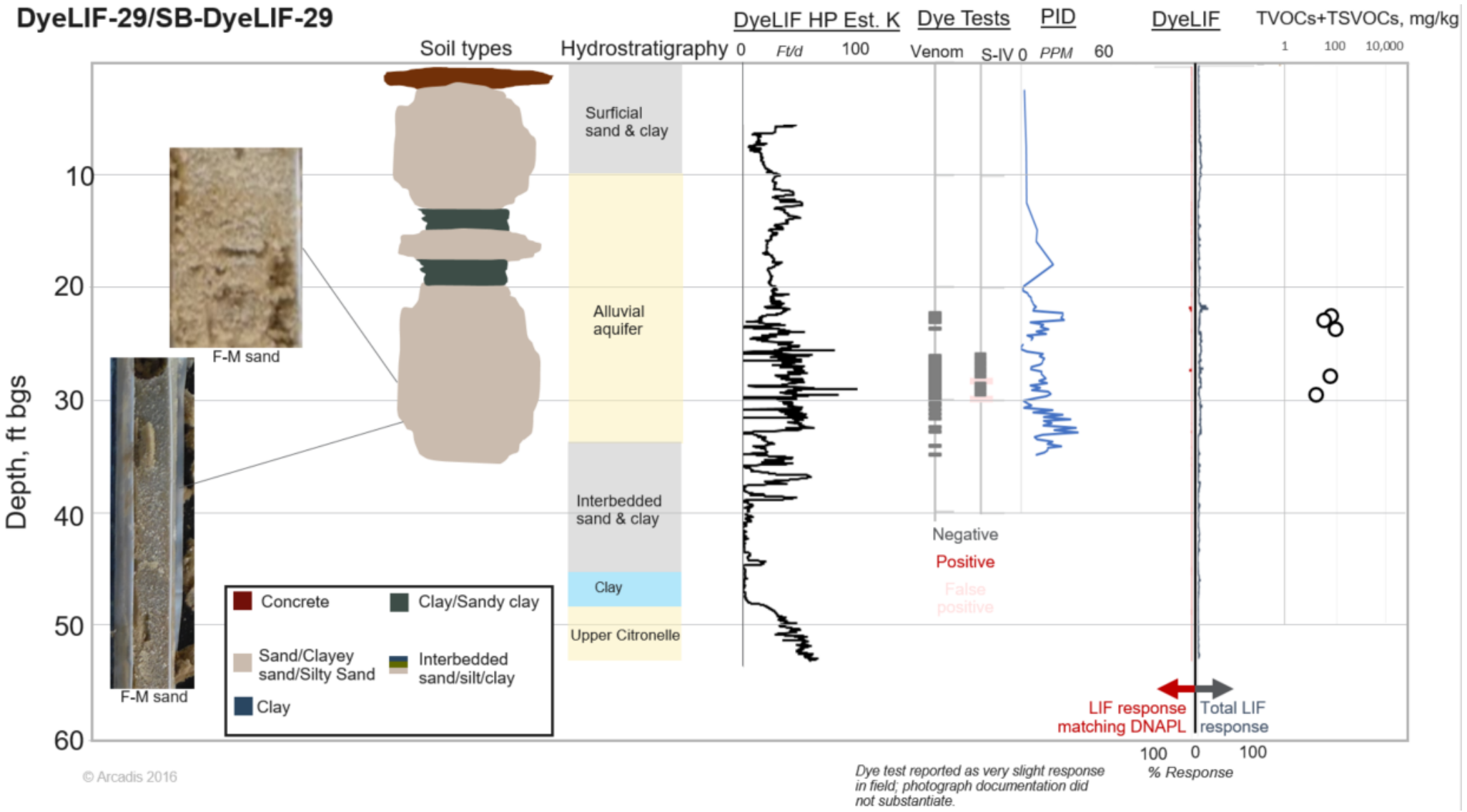

Fluid Pressure, PSI
Fluorescence log
25
50
Calculated Color:
8
6
4
2
Log/C: E-10-NB_DNAPL Dye /C3
Note: DYE
Calculated Color:
150
100
50
Log/C: E-10-NB_DNAPL Dye /C5
Note: Dye With NAPL
Silt
Sand
NAPL
Sand
Clay

HP Log (Relative permeability)



Example Data from ESTCP Report




DyeLIF-29/SB-DyeLIF-29
Soil types
Hydrostratigraphy
DyeLIF HP Est. K
0
Ft/d
100
Dye Tests
Venom
S-IV
0
PID
PPM
60
DyeLIF
TVOCs+TSVOCs, mg/kg
1
100
10,000
Depth, ft bgs
10
20
30
40
50
60
Surficial sand & clay
Alluvial aquifer
Interbedded sand & clay
Clay
Upper Citronelle
F-M sand
F-M sand
Concrete
Clay/Sandy clay
Sand/Clayey sand/Silty Sand
Interbedded sand/silt/clay
Clay
Negative
Positive
False positive
LIF response matching DNAPL
Total LIF response
100
0
100
% Response
Dye test reported as very slight response in field; photograph documentation did not substantiate.
© Arcadis 2016

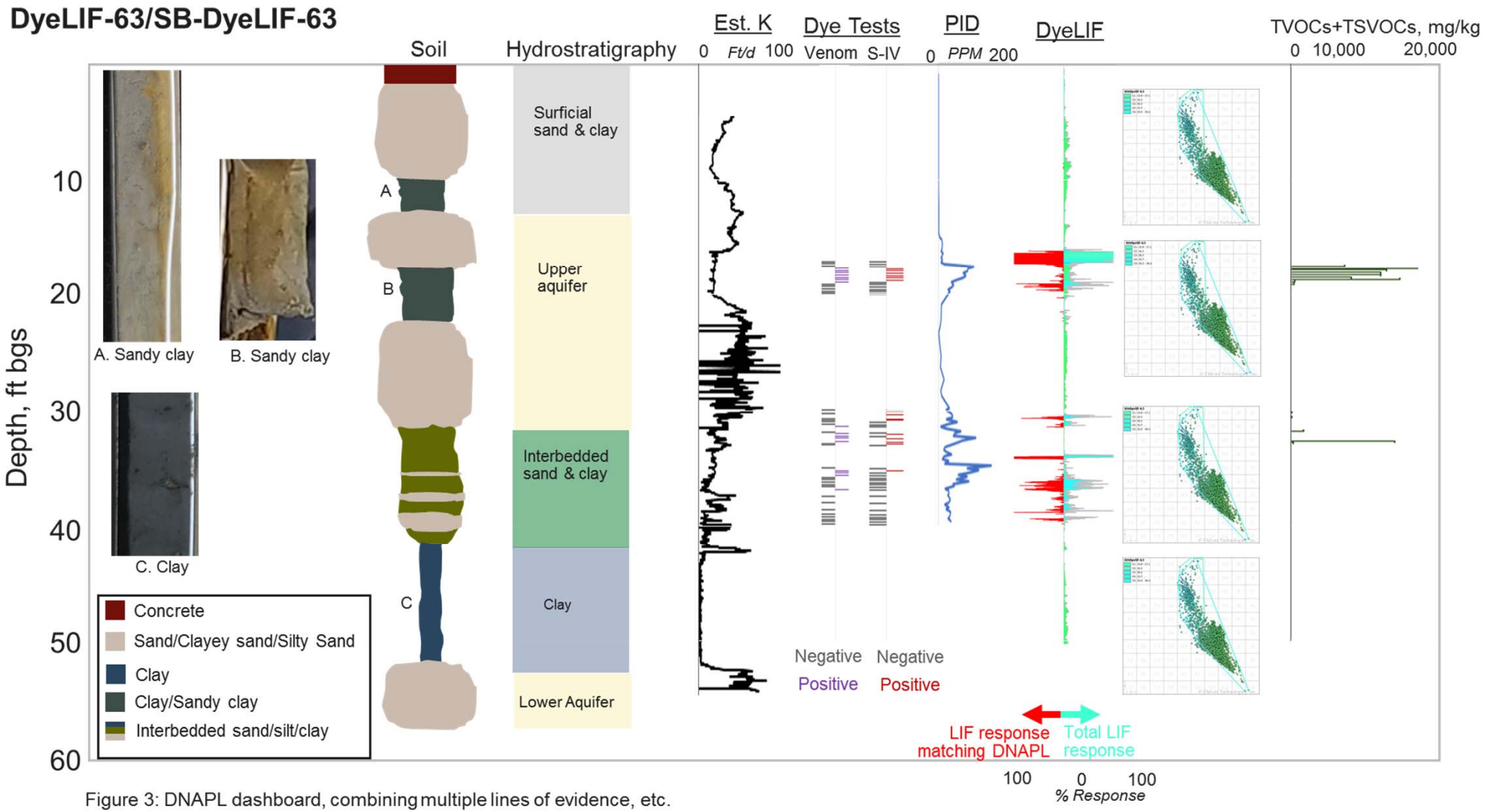
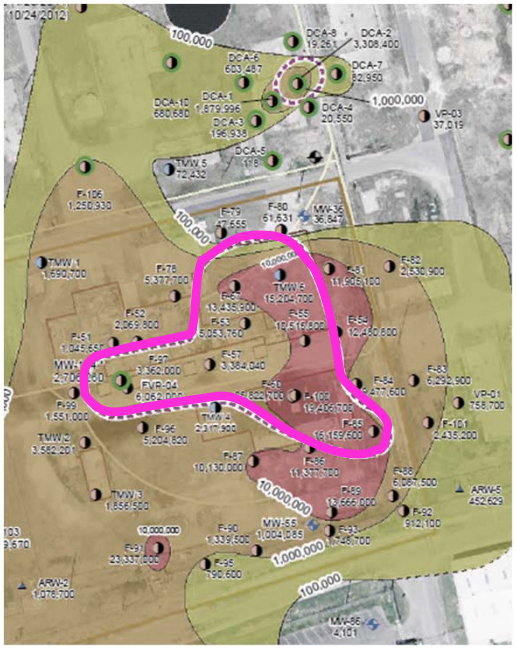
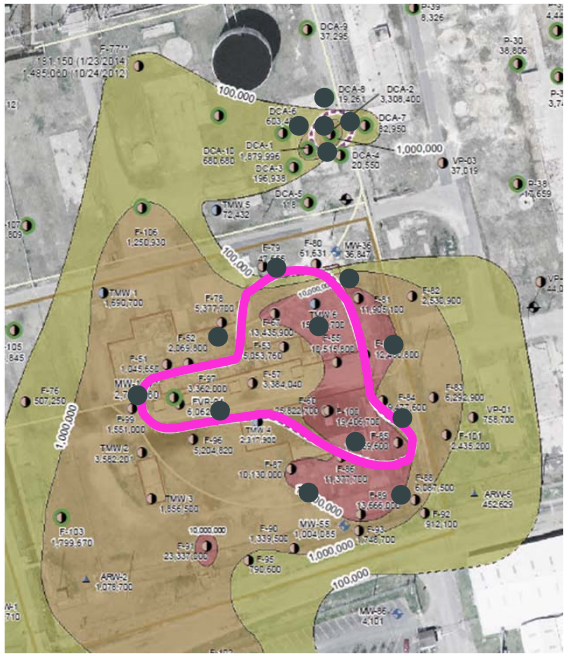


Figure 3: DNAPL dashboard, combining multiple lines of evidence, etc.

Investigation Approach



- Prior characterization



- Initial adaptive network
- Biased to east based on apparent slope in clay
- Up to 38 borings planned (33 in Alluvial, 4 in U. Citronelle)

- Final completed locations
- Additional step-out locations added around prior footprint
- 73 borings completed (69 Alluvial, 4 U.C.)

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LEGEND

- COMPLETED CONFIRMATION SOIL BORING
- COMPLETED DYE LIF BORING (NEGATIVE DNAPL RESPONSE)
- COMPLETED DEEP DYE LIF BORING (NEGATIVE DNAPL RESPONSE)
- COMPLETED DYE LIF BORING (POTENTIAL/UNDER REVIEW)
- COMPLETED DYE LIF BORING (POSITIVE DNAPL RESPONSE)
- OBSERVED DNAPL (PRE-2017)
- OBSERVED DNAPL PLUME (PRE-2017)
- WATER SUPPLY WELL
- MONITORING WELL
- TEMPORARY MONITORING WELL
- BORING
- CURRENT STORM WATER DITCH
- FORMER OPEN DITCH
- FORMER FORMAL PRODUCTION AREA
- COC GW Iso: 10,000,000+ ug/L
- COC GW Iso: 1,000,000+ ug/L
- COC GW Iso: 100,000+ ug/L

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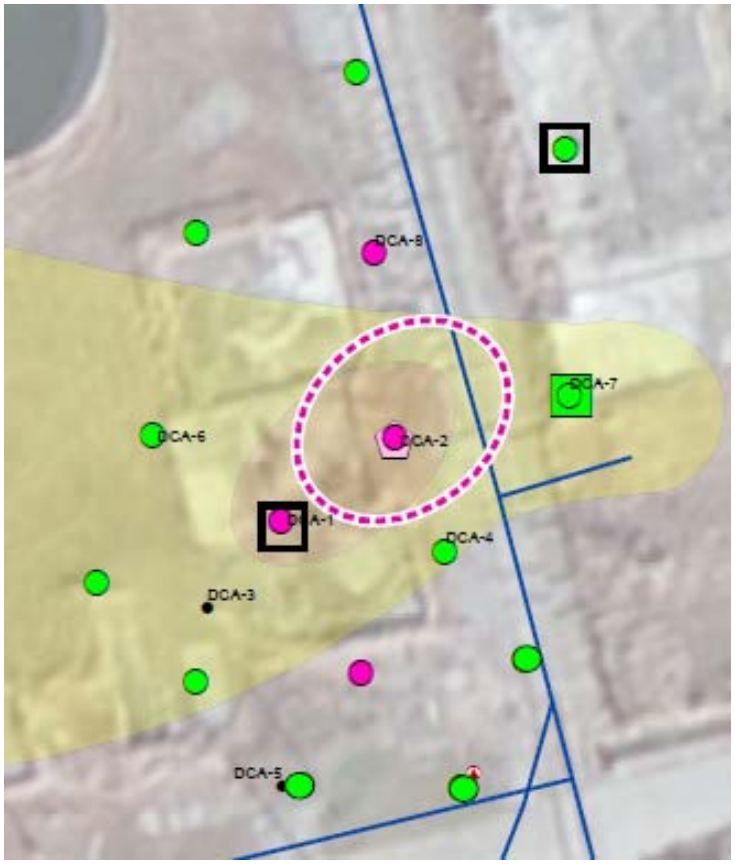
1,2-DCA/1,2,3-TCP Storage Tank Area



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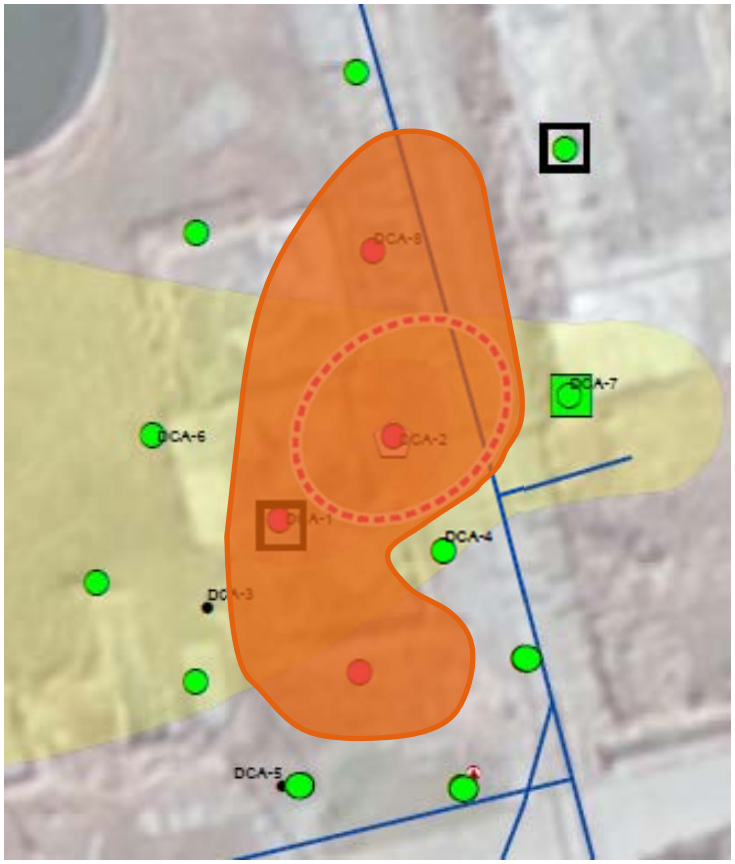
1,2-DCA/1,2,3-TCP Storage Tank Area



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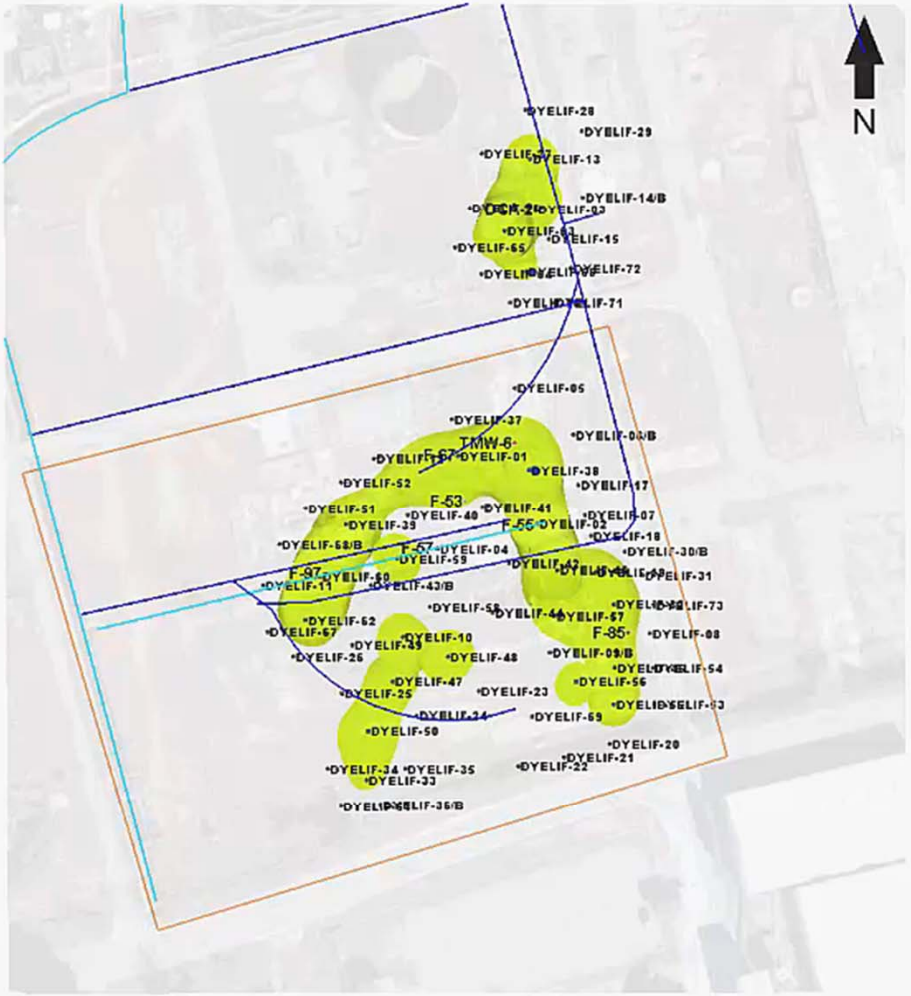


DNAPL Observations
- Significant Recovery
- Trace Recovery
- Observed

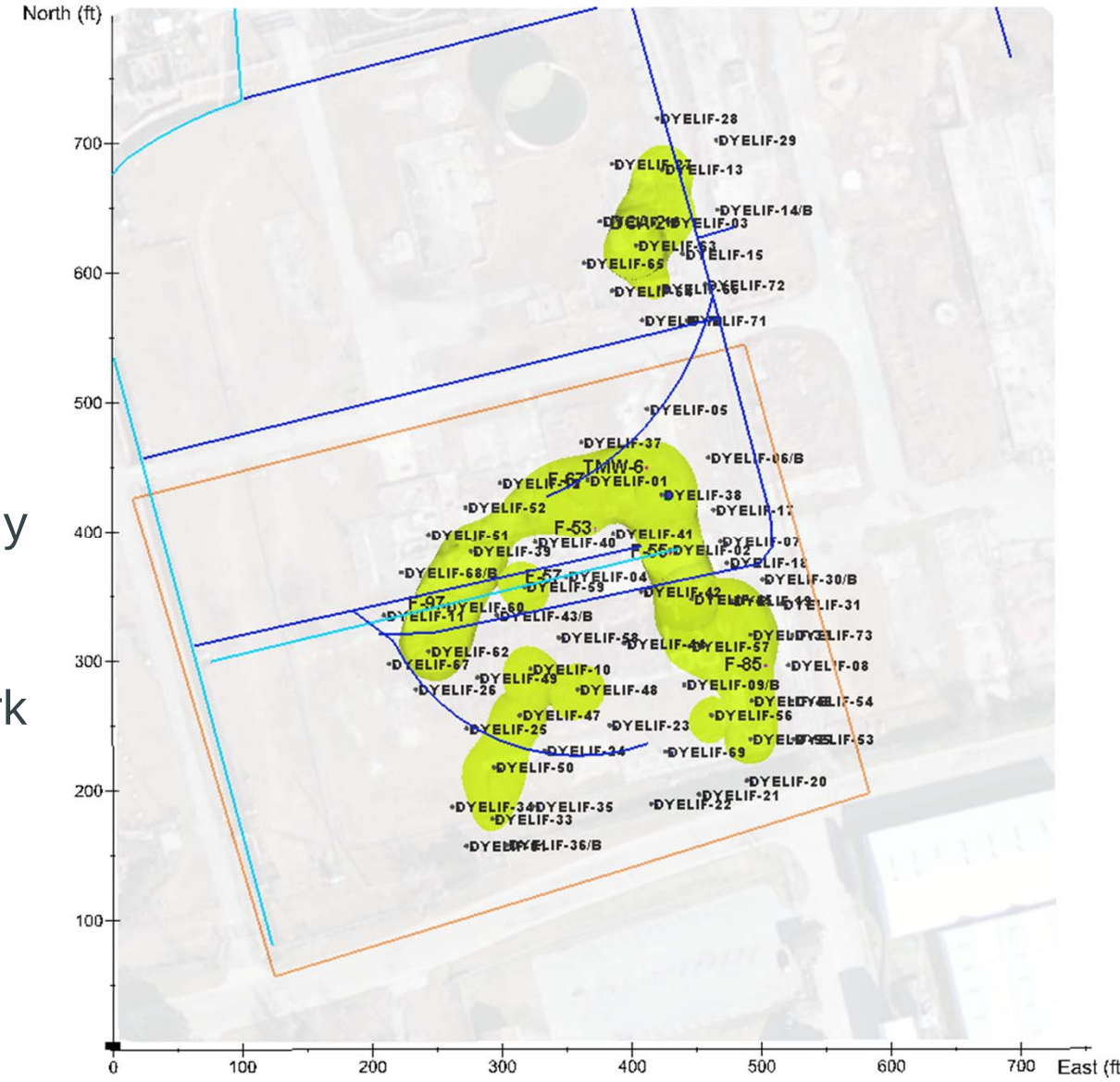
DYE-LIF %RE NAPL - Color Range Shown as Tubes:
0-5%RE (Blue)
5-100%RE (Blue to Red Gradient)

Approximate NAPL plume shown in yellow

3D-Model (Plan View)

DNAPL distribution informed by:

- Dye-LIF
- Confirmation borings with closely spaced dye shake tests
- Observations from previous work



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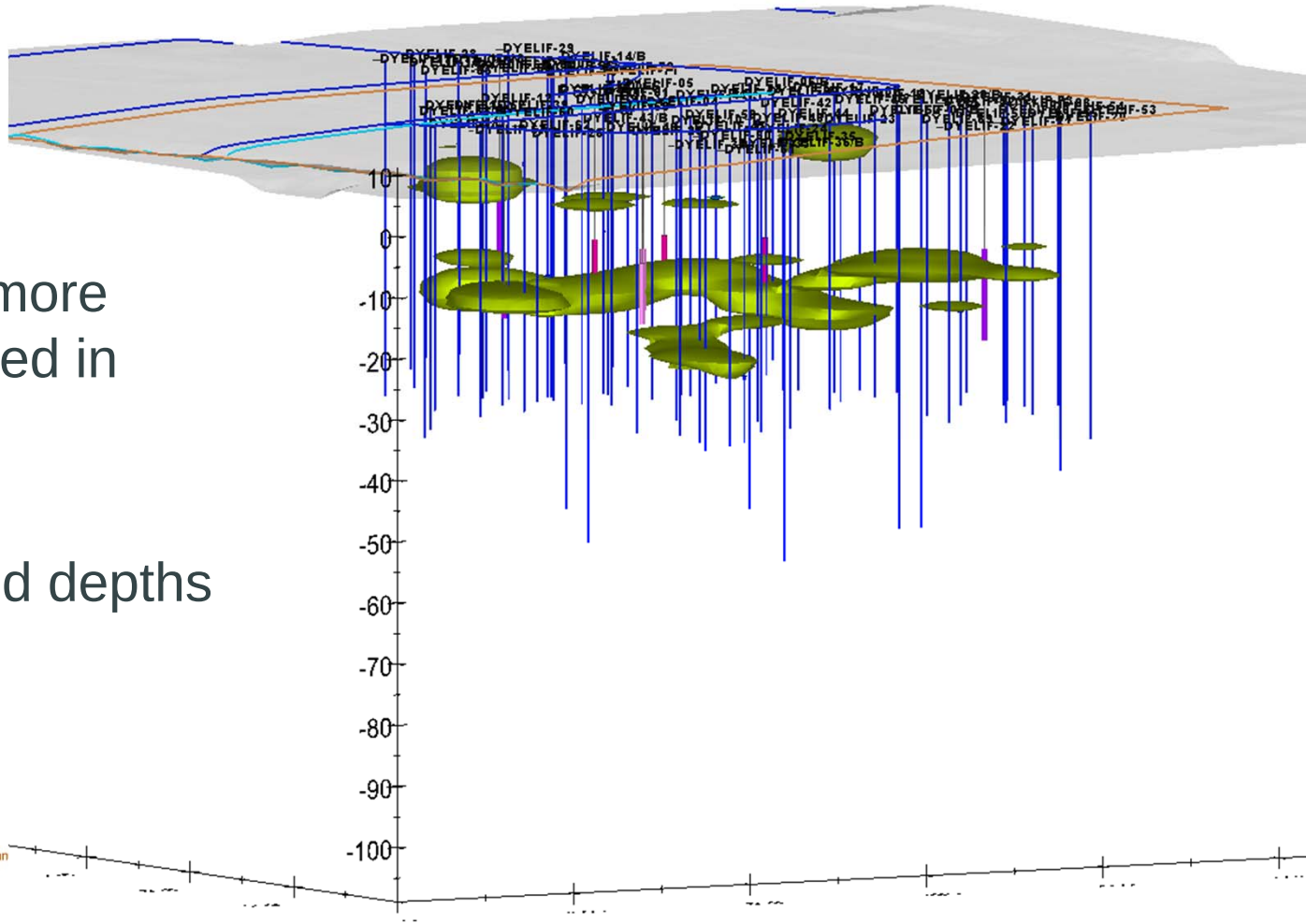
3D-Model (Vertical Distribution)

- DNAPL Distribution more complex than assumed in vertical dimension
- Varying thickness and depths



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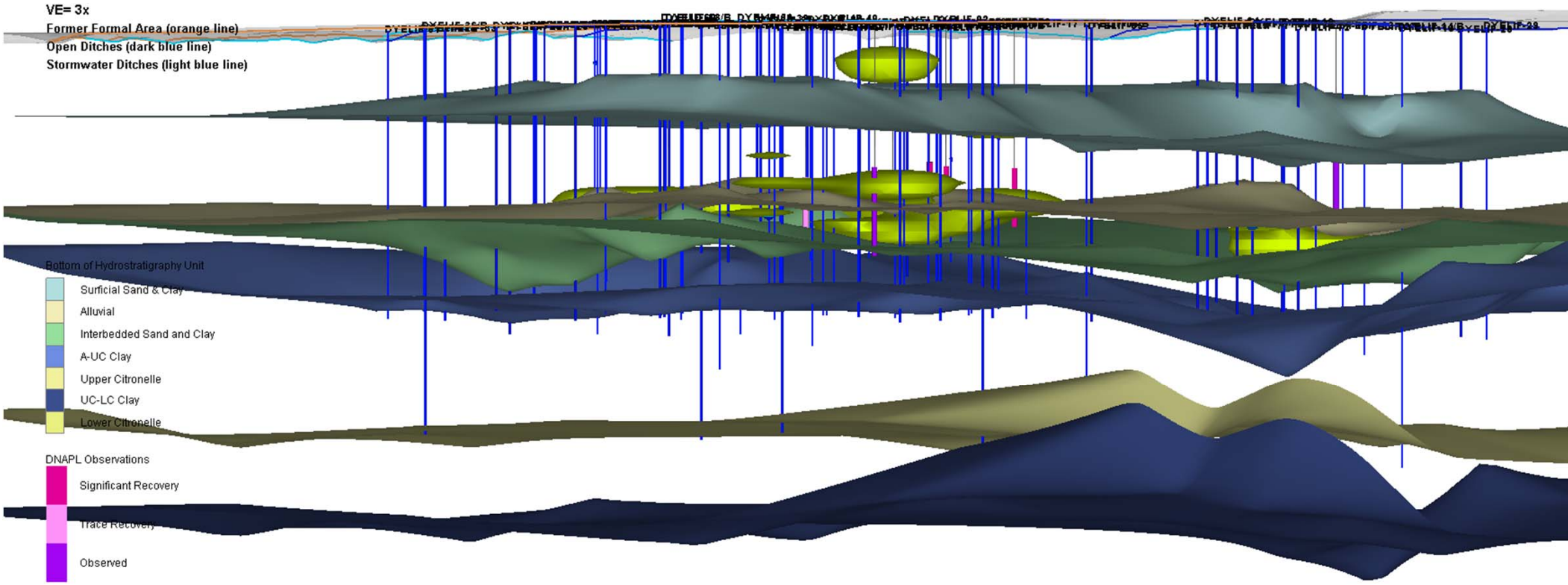
3D-Model (Geology for context)

Bottom surfaces of stratigraphic units displayed here



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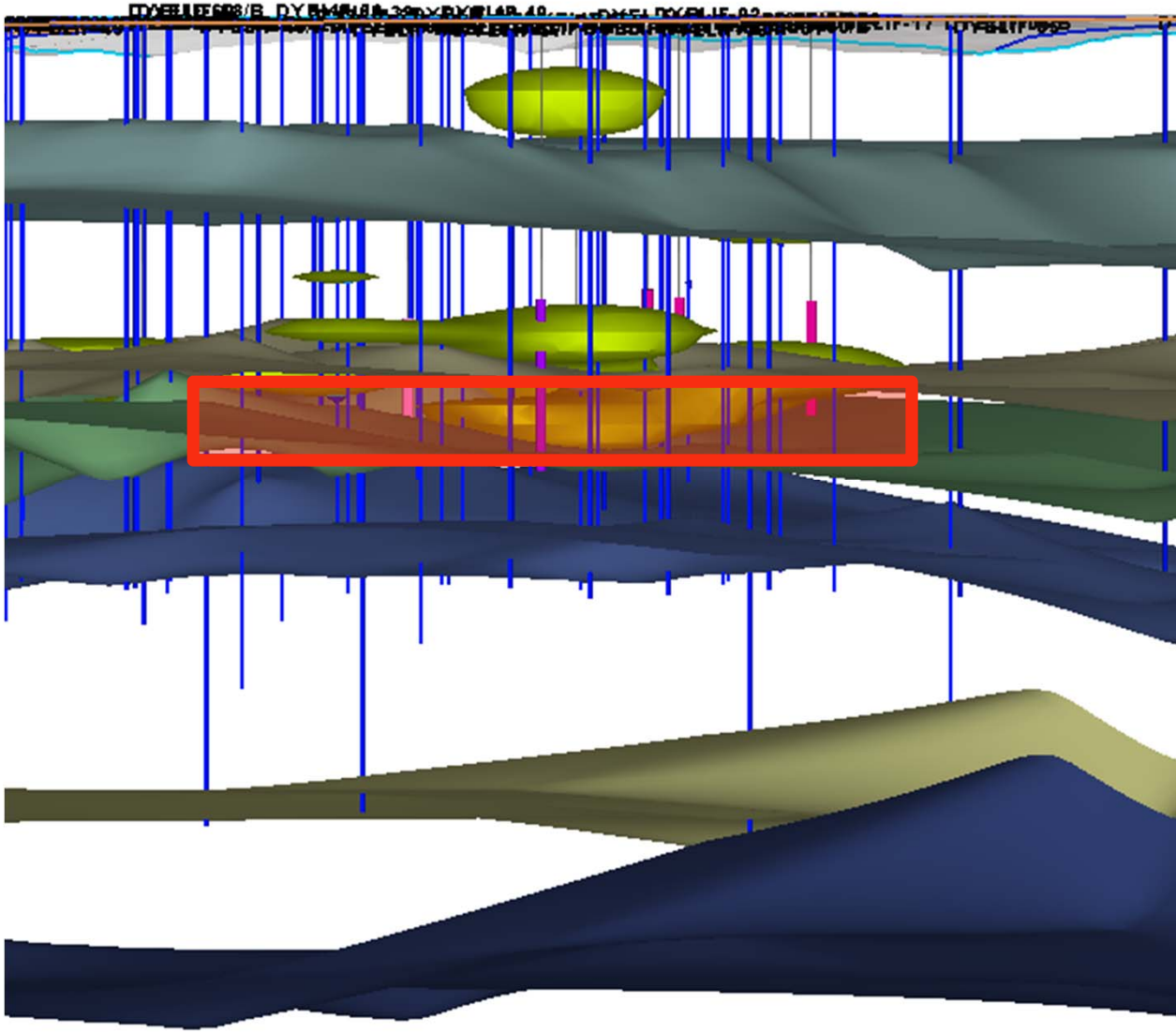
3D-Model

- Geology informed by CPT, HPT and visual core logs
- DNAPL above the bottom of the Alluvial
- Much of the DNAPL is held in the interbedded sand/clay at the base of the Alluvial
- DNAPL does not appear to penetrate through A-UC clay



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What Does This Mean?

- Monitoring wells and visual observations of core do not provide sufficient understanding of the vertical component of DNAPL distribution
- DNAPL is shown to occur within the Surficial Clay and Alluvial units
- Much of the DNAPL is bound up in sand/clay interbeds vs. pooled atop a clay interface
- The DNAPL is less mobile than was assumed
- Remedies proposed based on previous conceptual model of DNAPL distribution may not be effective.

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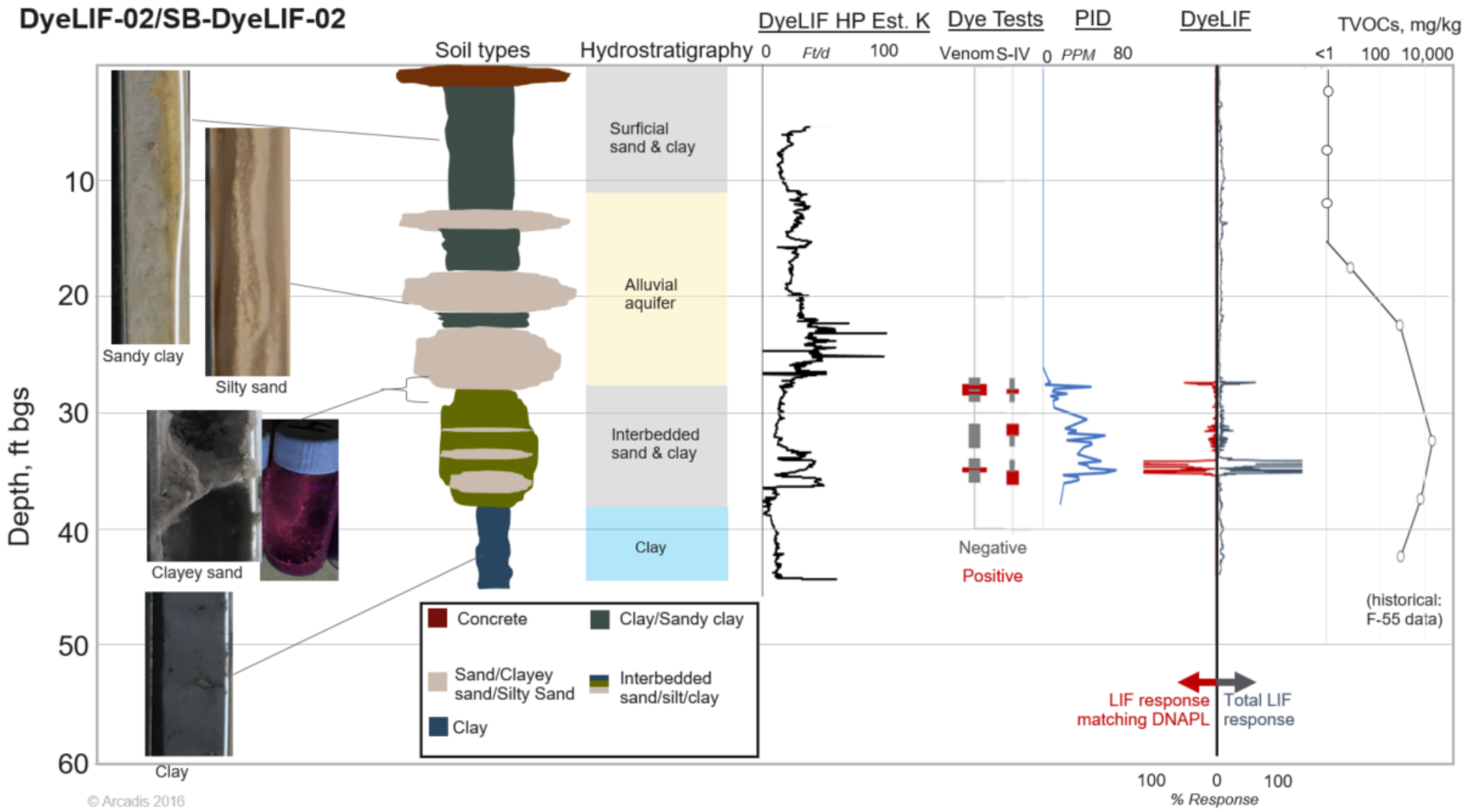
DyeLIF-02/SB-DyeLIF-02
Soil types
Hydrostratigraphy
DyeLIF HP Est. K
0
Ft/d
100
Dye Tests
Venom S-IV
PID
0
PPM
80
DyeLIF
TVOCs, mg/kg
<1
100
10,000
Surficial sand & clay
Alluvial aquifer
Interbedded sand & clay
Clay
Sandy clay
Silty sand
Clayey sand
Clay
Depth, ft bgs
10
20
30
40
50
60
Concrete
Clay/Sandy clay
Sand/Clayey sand/Silty Sand
Interbedded sand/silt/clay
Clay
Negative
Positive
(historical: F-55 data)
LIF response matching DNAPL
Total LIF response
100
0
100
% Response
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