THINK. RESTORE, *SUSTAINABLY*

Partnering for Smarter Sustainable Solutions

COLUMBIA TECHNOLOGIES

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Methods for Verifying LNAPL Stability

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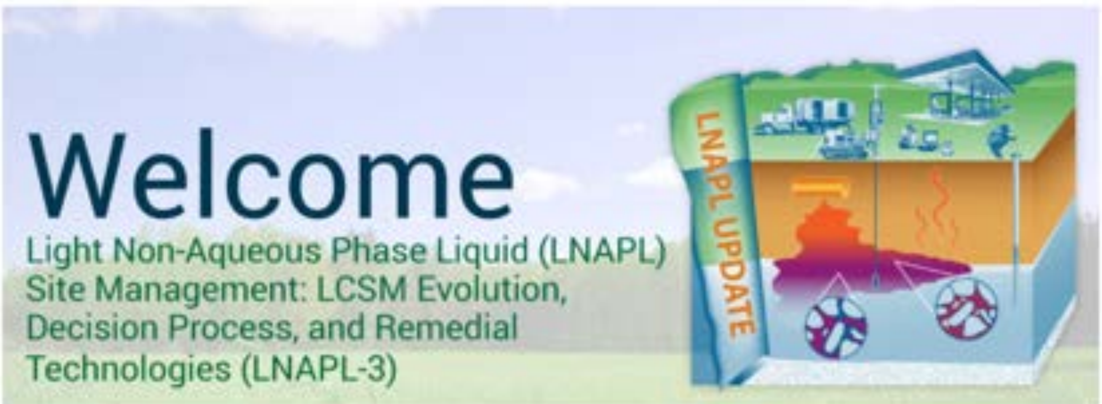
Agenda

1	**A systematic approach to building the LNAPL CSM**
2	**Methods to fully identify residual LNAPL**
3	**The important role of soil structure**
4	**Understanding LNAPL transmissivity vs time**
5	**The importance of a 3D understanding**

Guidance Documents



Are there ways to control the cost of these potentially expensive cleanups?

EPA is committed to helping state and local agencies make cleanups faster, more effective, and less expensive. EPA is working

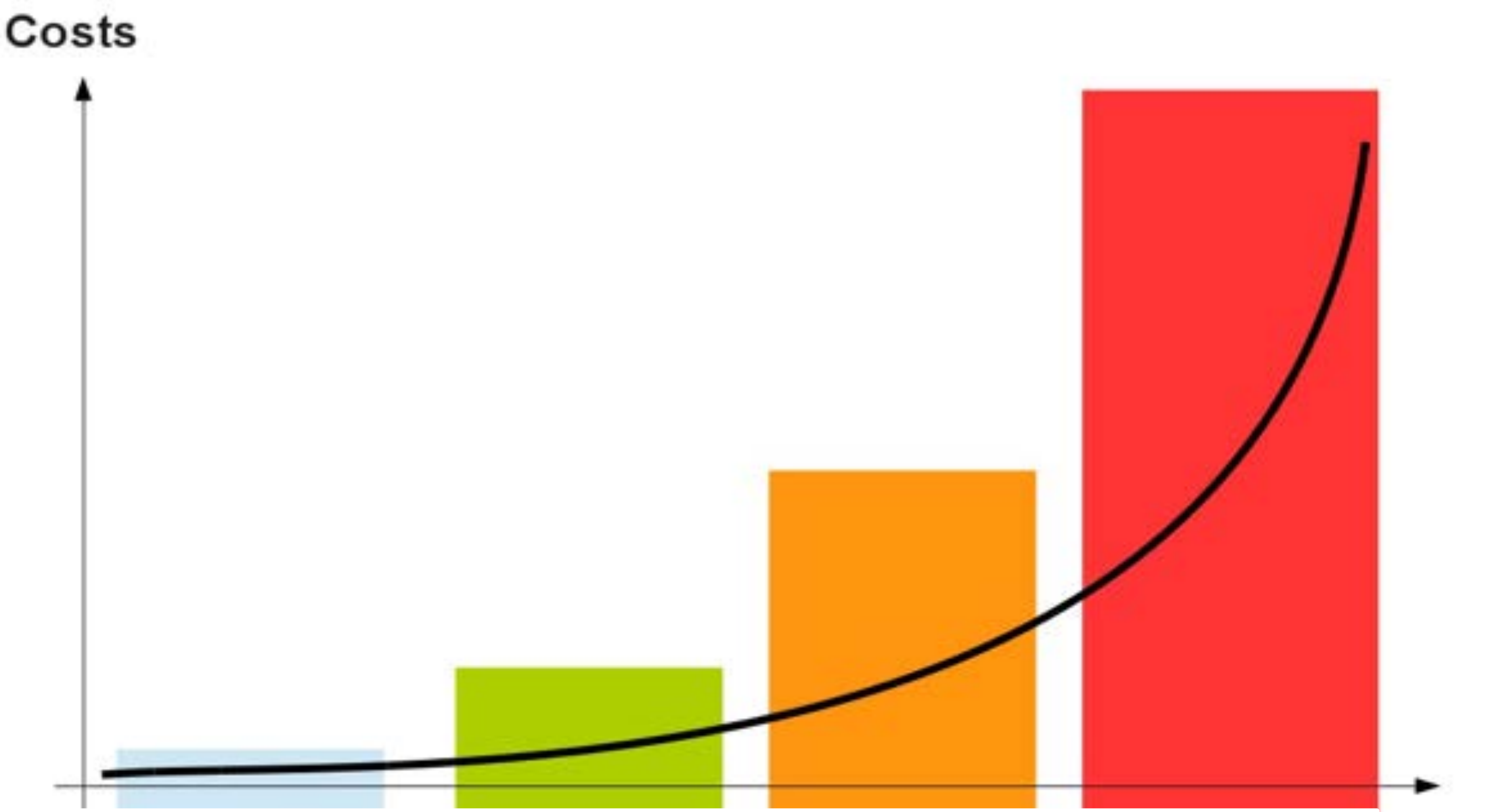
https://www.epa.gov/ust/cleaning-underground-storage-tank-ust-releases

Pay-for-Performance Cleanups

Pay-for-performance cleanups are an alternative way to contract for environmental cleanups. Pay for performance uses economic incentives and market forces to encourage cleanup contractors to keep cleanup expenditures under control and meet cleanup goals as soon as possible. In pay-for-performance cleanups, contractors are paid a set amount of money for reaching specific contamination reduction goals, which are predetermined by state cleanup experts.


Our industry spends over
US$1 BILLION each day assessing,
remediating, and making decisions on
information that is incomplete,
inaccurate, and too late.

Cost Control



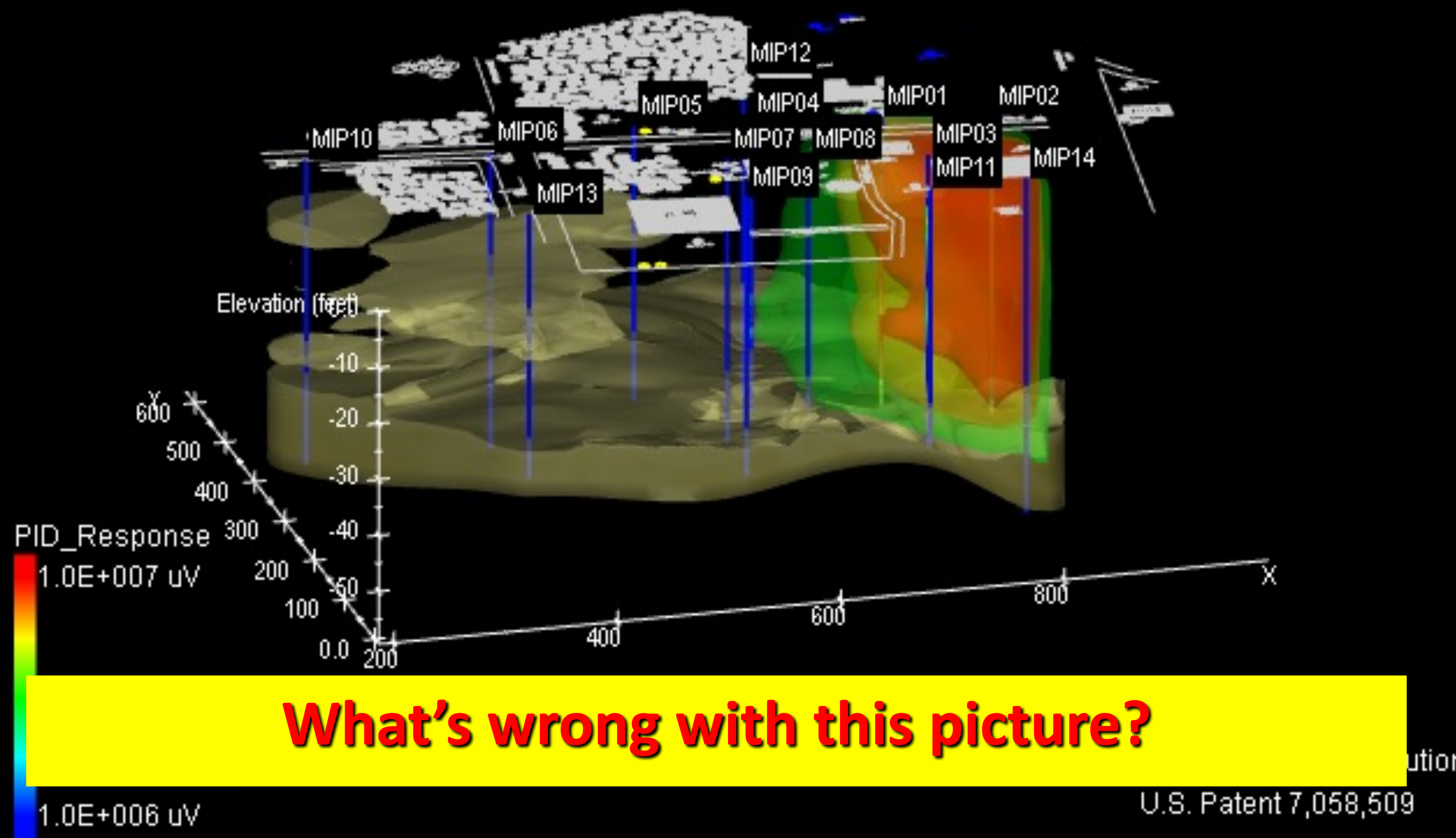
Preliminary Investigation

Secondary Investigation

Corrective Action

Long Term Monitoring

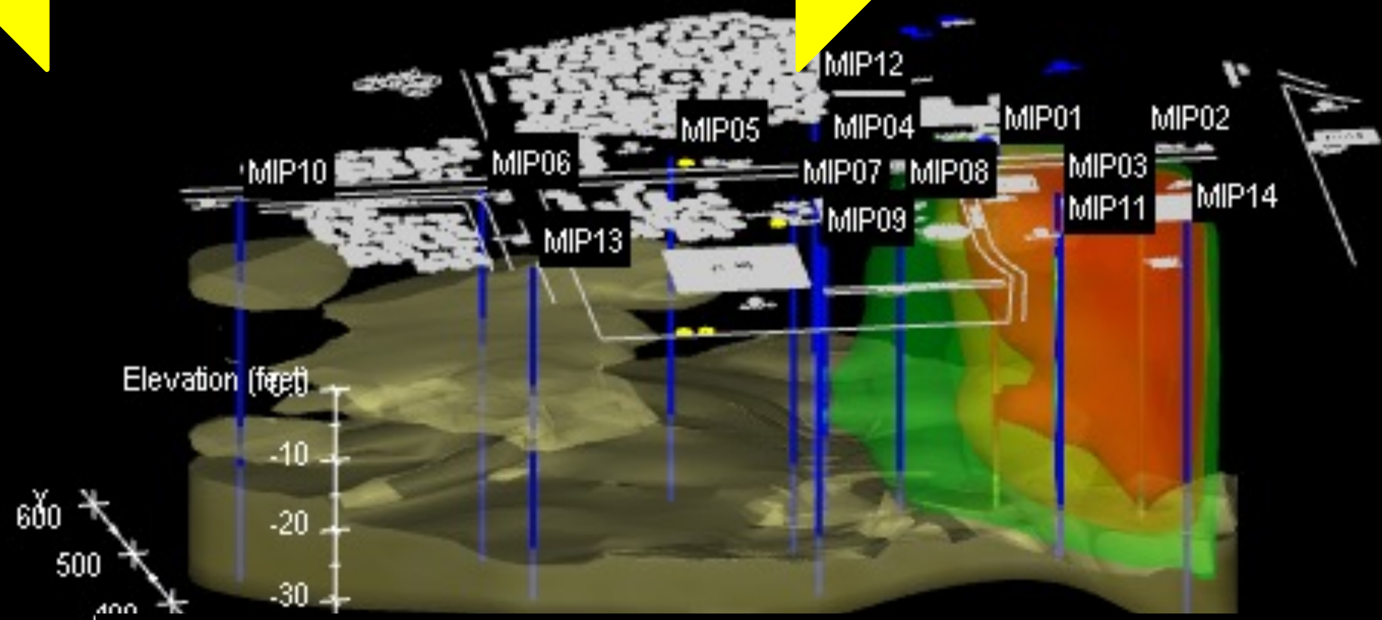
Former UST Site



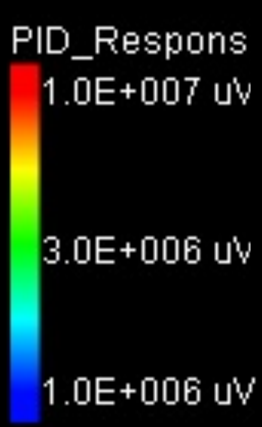
What's wrong with this picture?

Work Plan Constraints Expended 80% of the Data and Budget

Yielding 100% of the Uncertainty



How can we prevent this waste of resources?



- Systematic work planning
- Real time measurements
- Dynamic work scopes

The LNAPL CSM

What is LNAPL?

NAPL

NonAqueous Phase Liquid – a separate or "free" phase liquid; not in solution

LNAPL

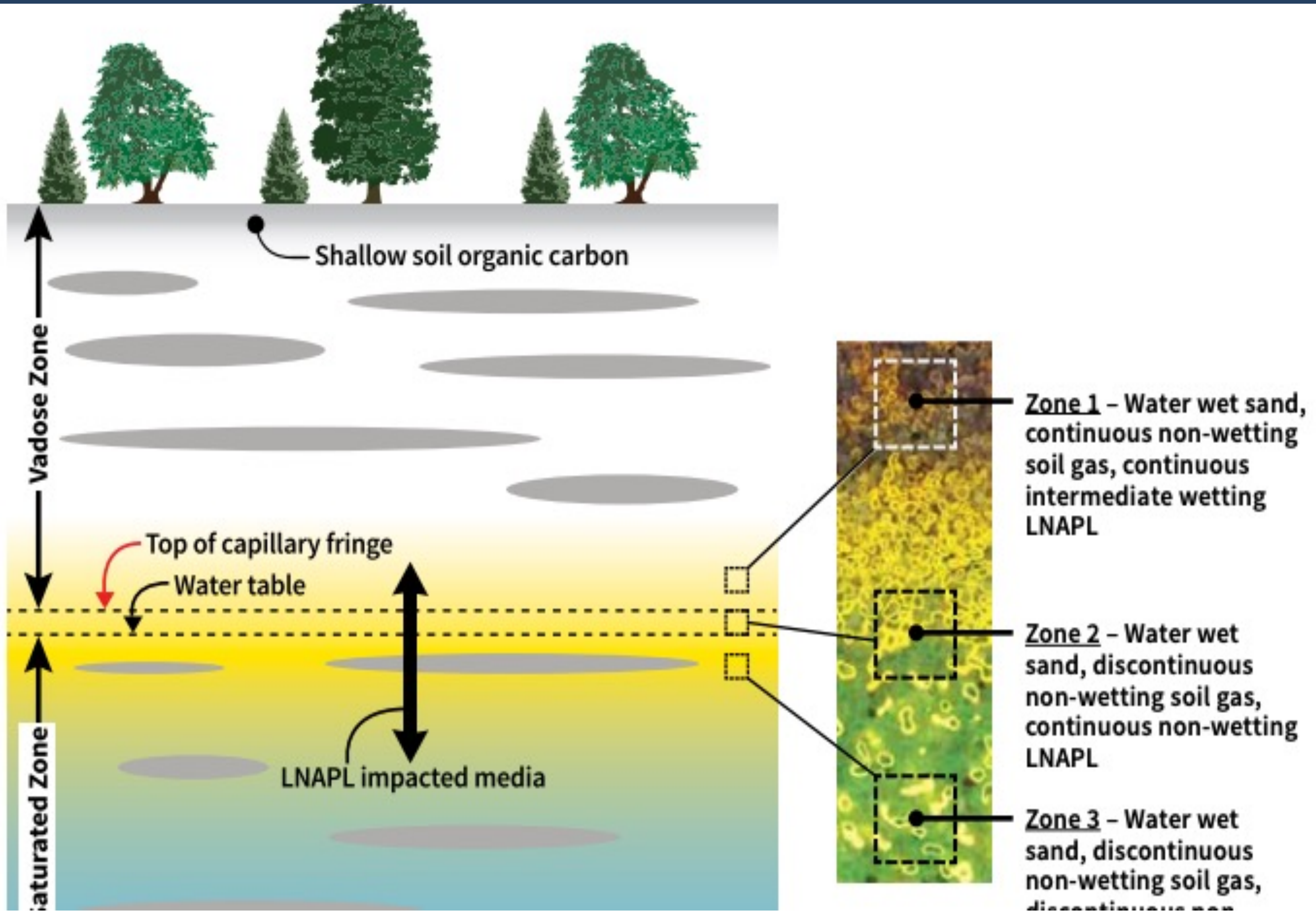
A liquid ***that is less dense than water***

Common examples of LNAPL include gasoline, diesel fuel, jet fuel, and crude oil

Can also include multi-component mixtures

Can be ***unconfined or confined by groundwater***

The Effects of Time



Complexity

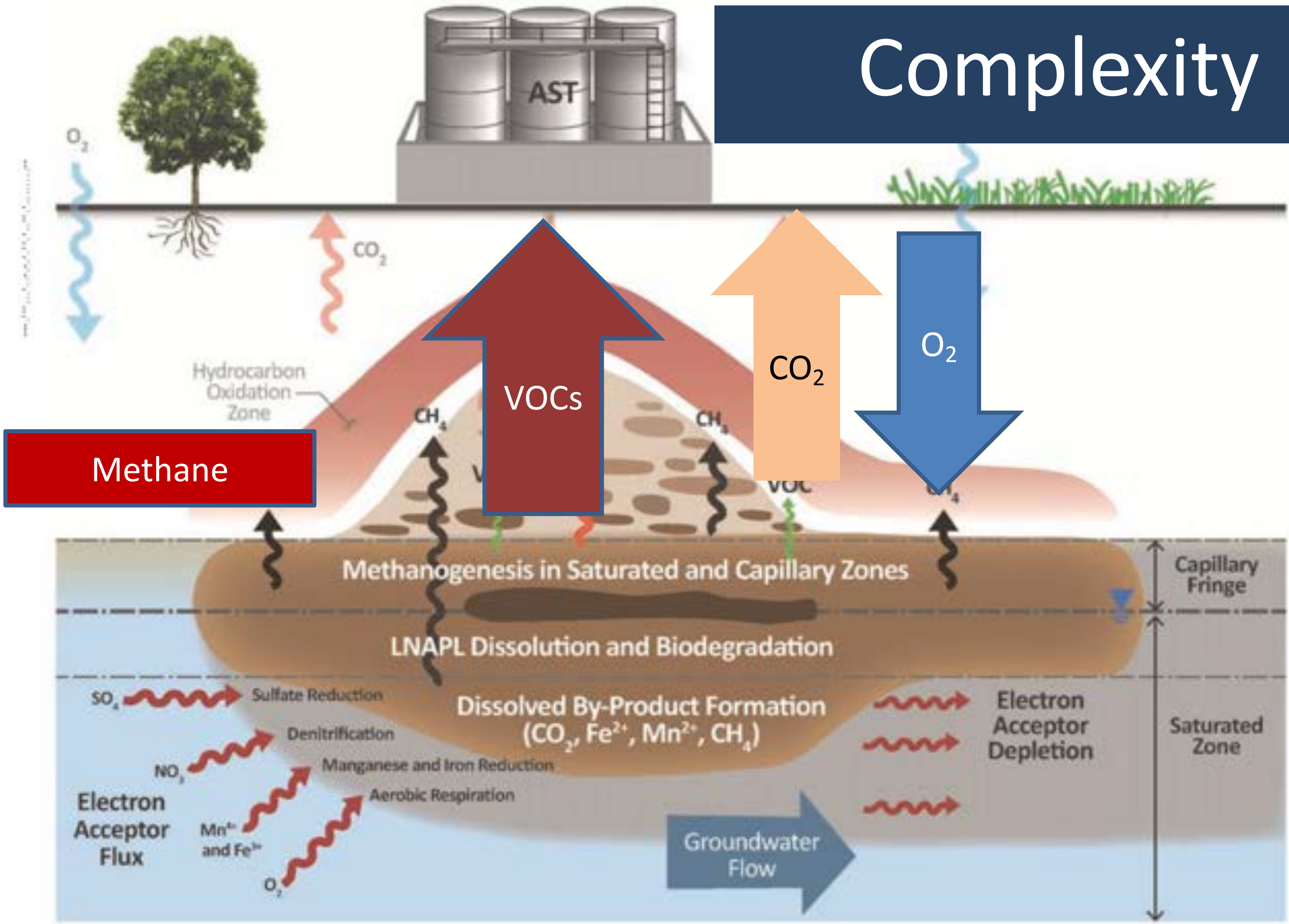
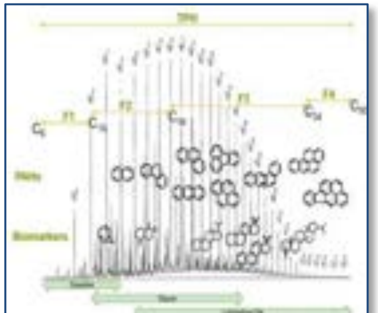
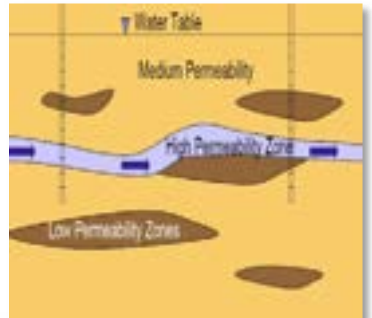


Figure 2-1—Conceptualization of Saturated Zone NSZD Processes

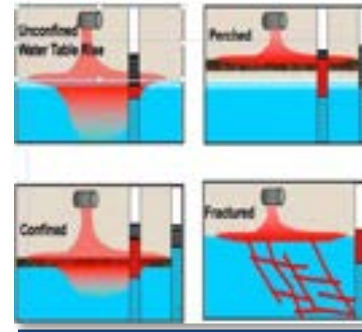
Building the LCSM?



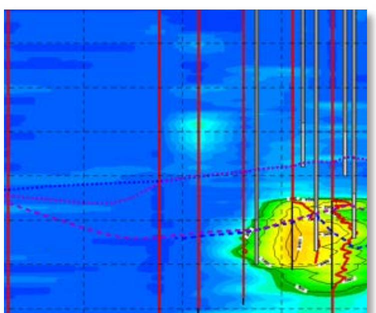
LNAPL CHEMISTRY



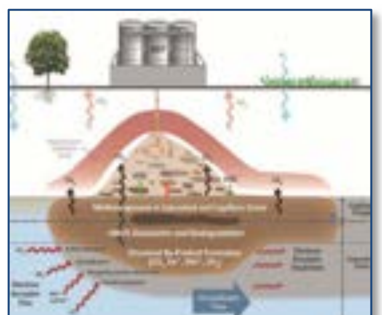
SOIL PERMEABILITY



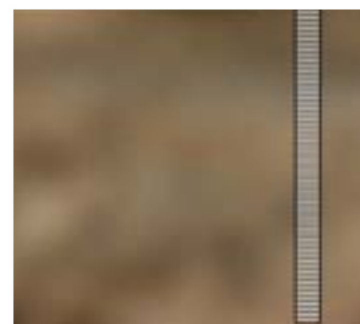
GROUND WATER



DISSOLVED PHASE

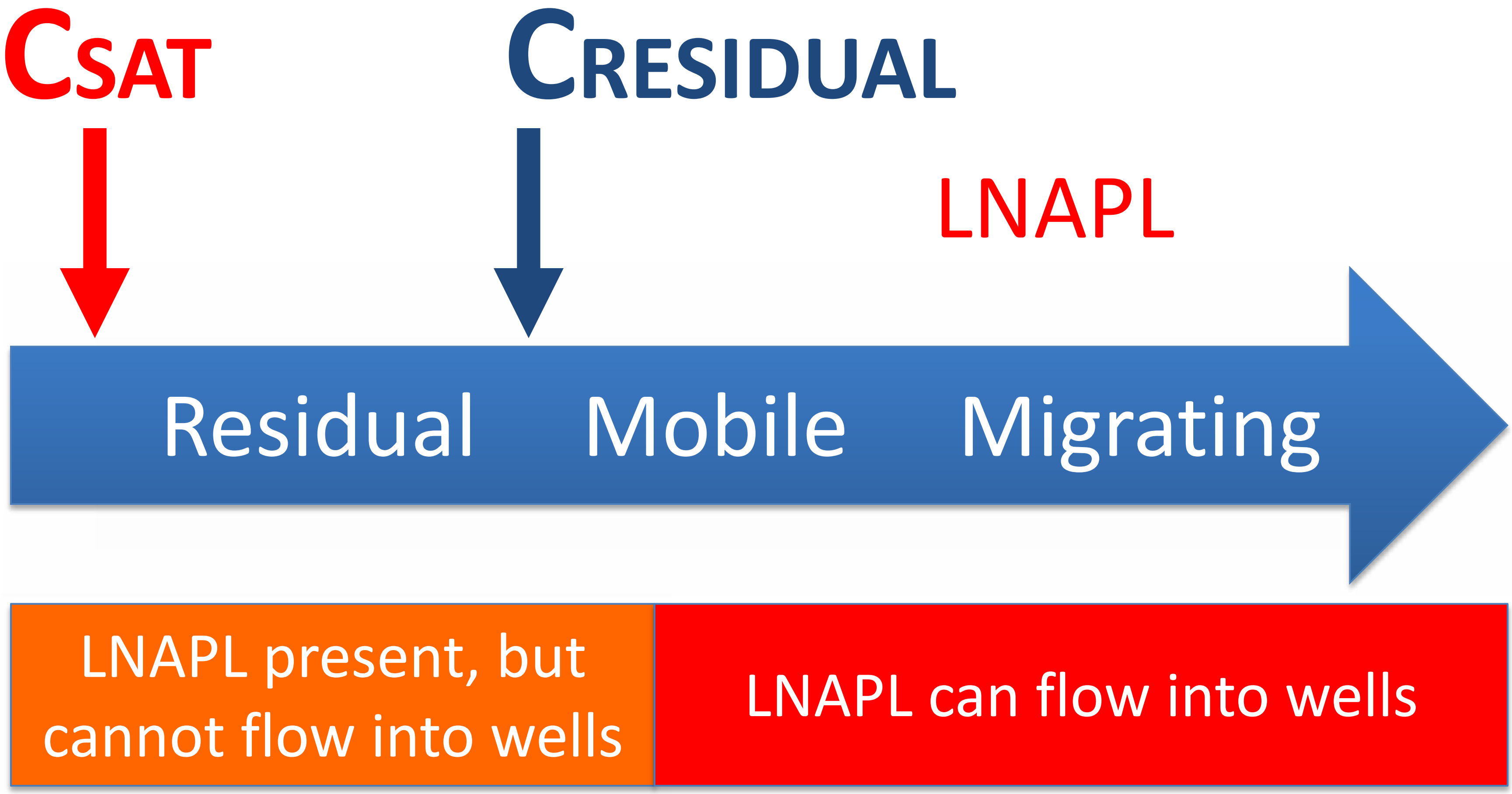


VAPOR PHASE



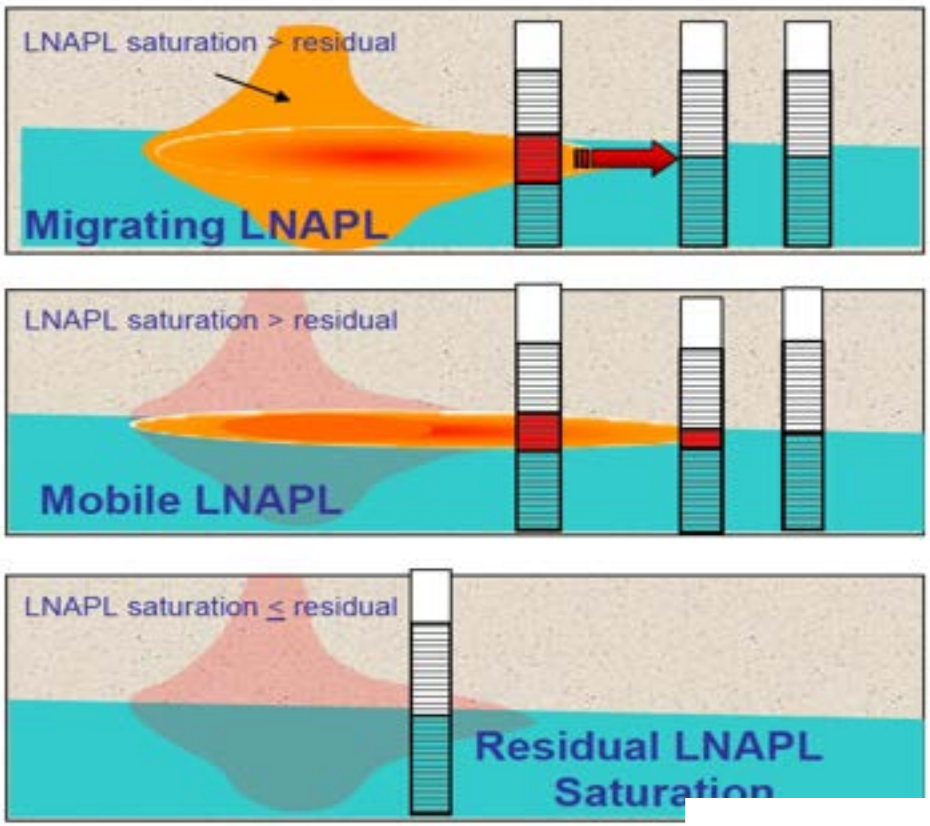
SPATIAL ALIGNMENT

Measurements of Plume Stability

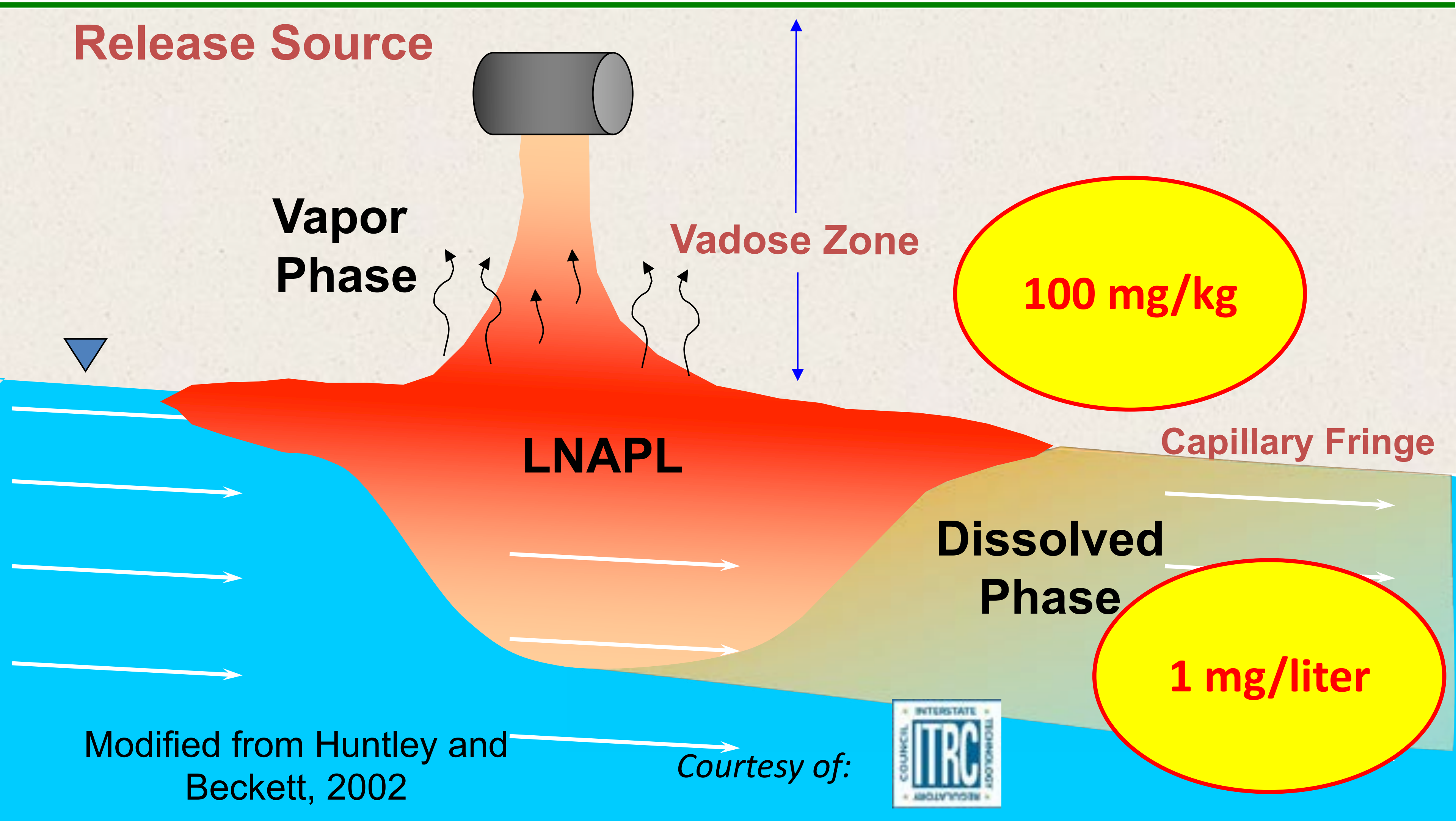


Courtesy of:

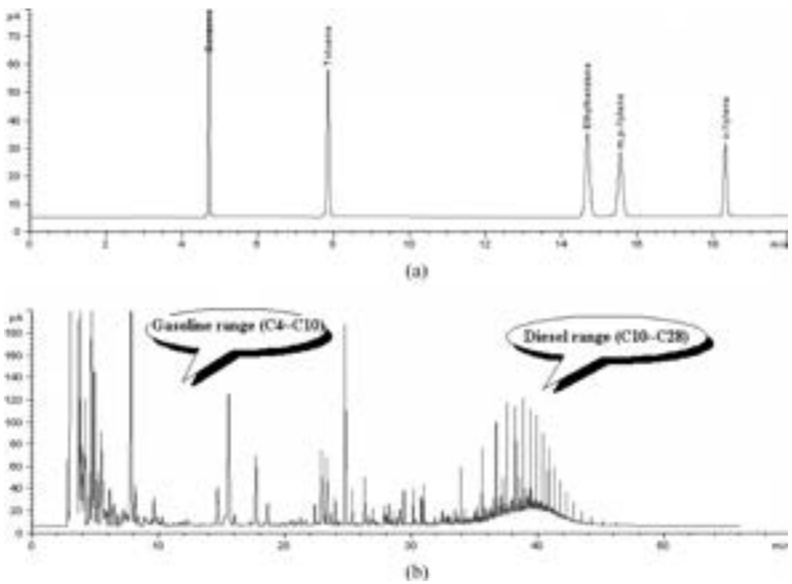
MW Thickness = Indicator Only



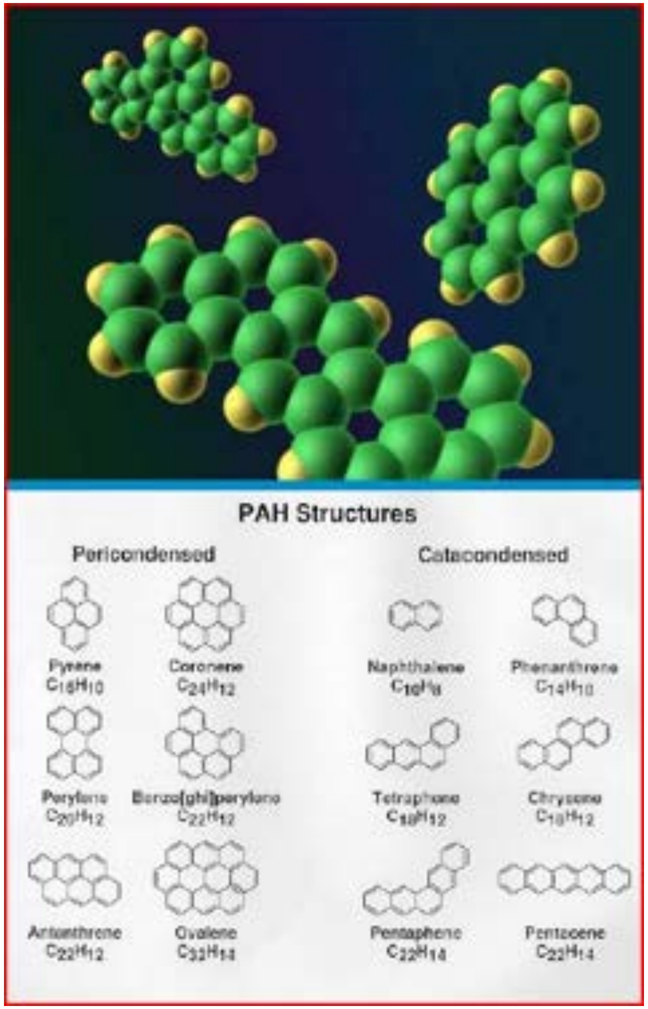
Lab Results as Indicators of LNAPL



There is a LOT in LNAPL than BTEX

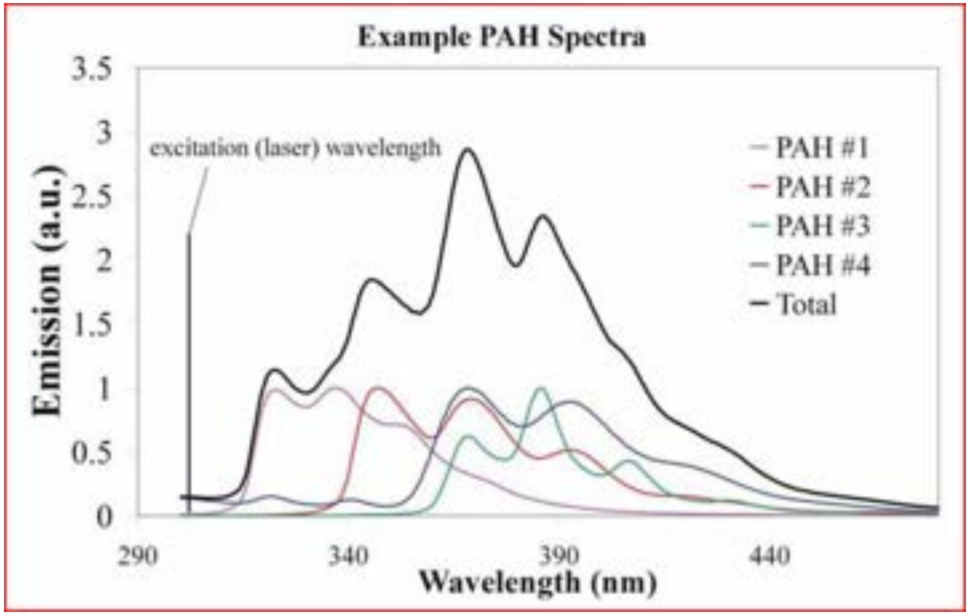


Petroleum Fluorescence



PAHs fluoresce when struck with UV light

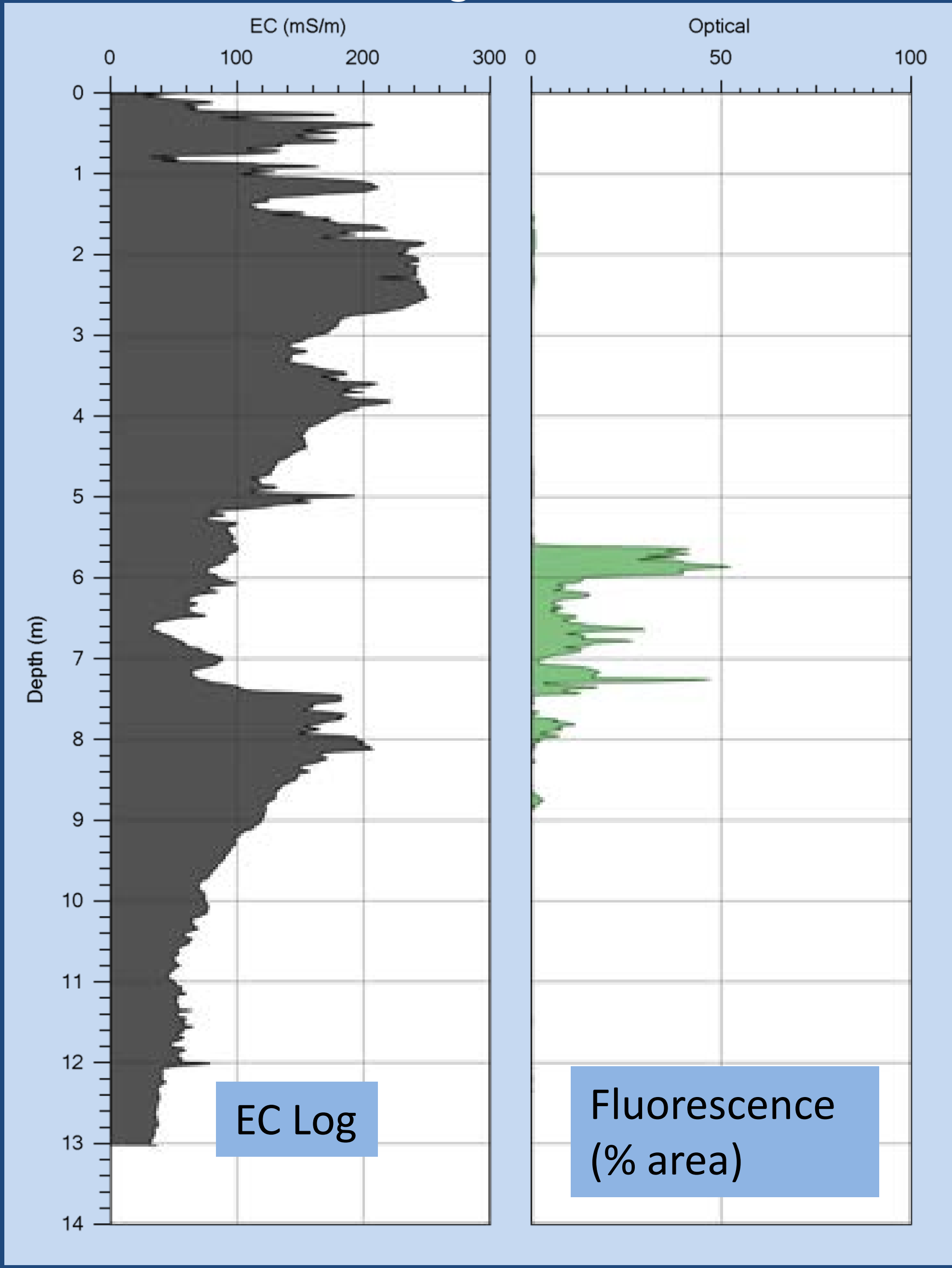
Each PAH has a unique fluorescence spectrum



The OIP Log

- Images captured every 15mm (.05 ft.).
- Images are analyzed for fluorescence in real time.
- The percent of the image area representing fuel fluorescence is recorded on the log.

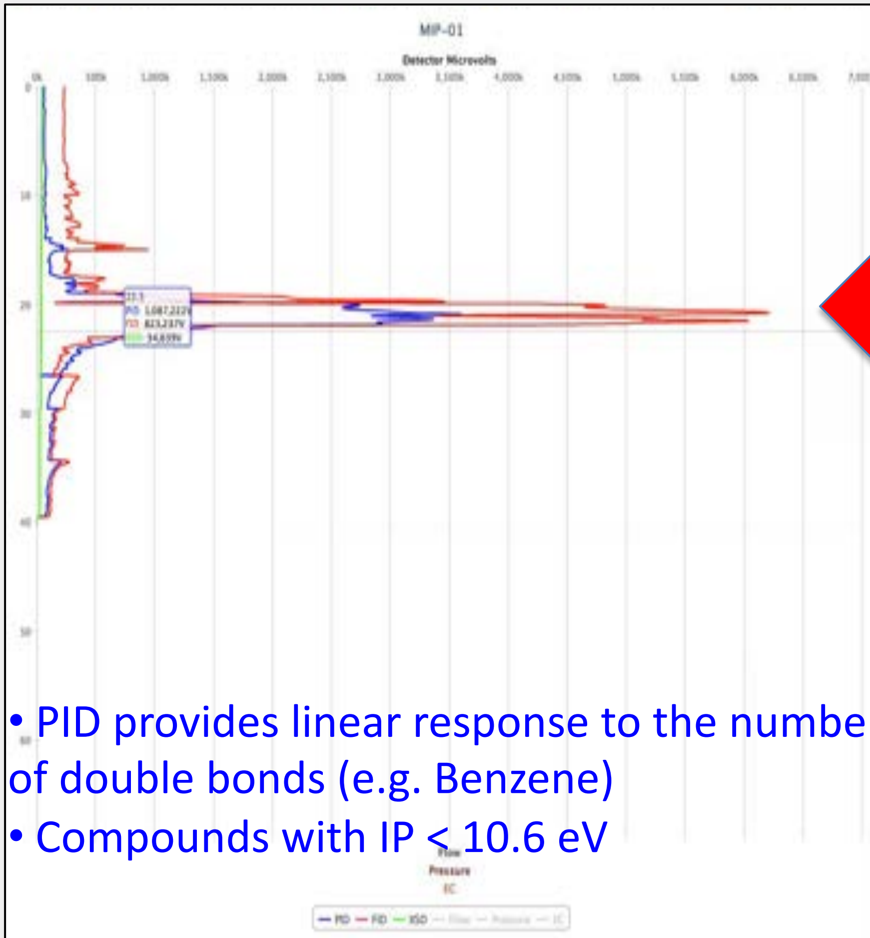
Log 8-1



3.0m
0% detected

5.7m
50.2% detected

Membrane Interface Probe



- PID provides linear response to the number of double bonds (e.g. Benzene)
- Compounds with IP < 10.6 eV

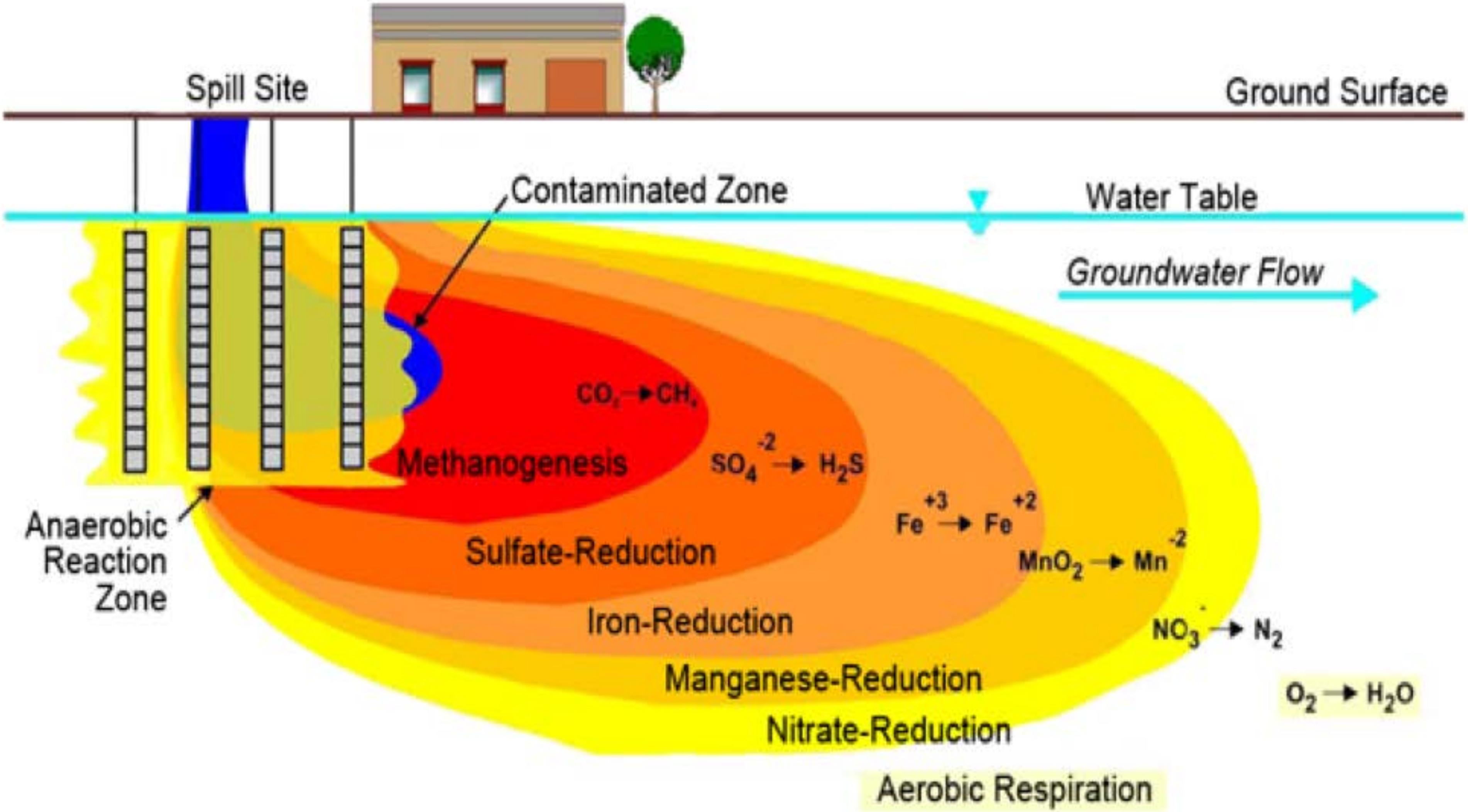
FID confirms PID

FID

PID

XSD

LNAPL - Soil Evaluation

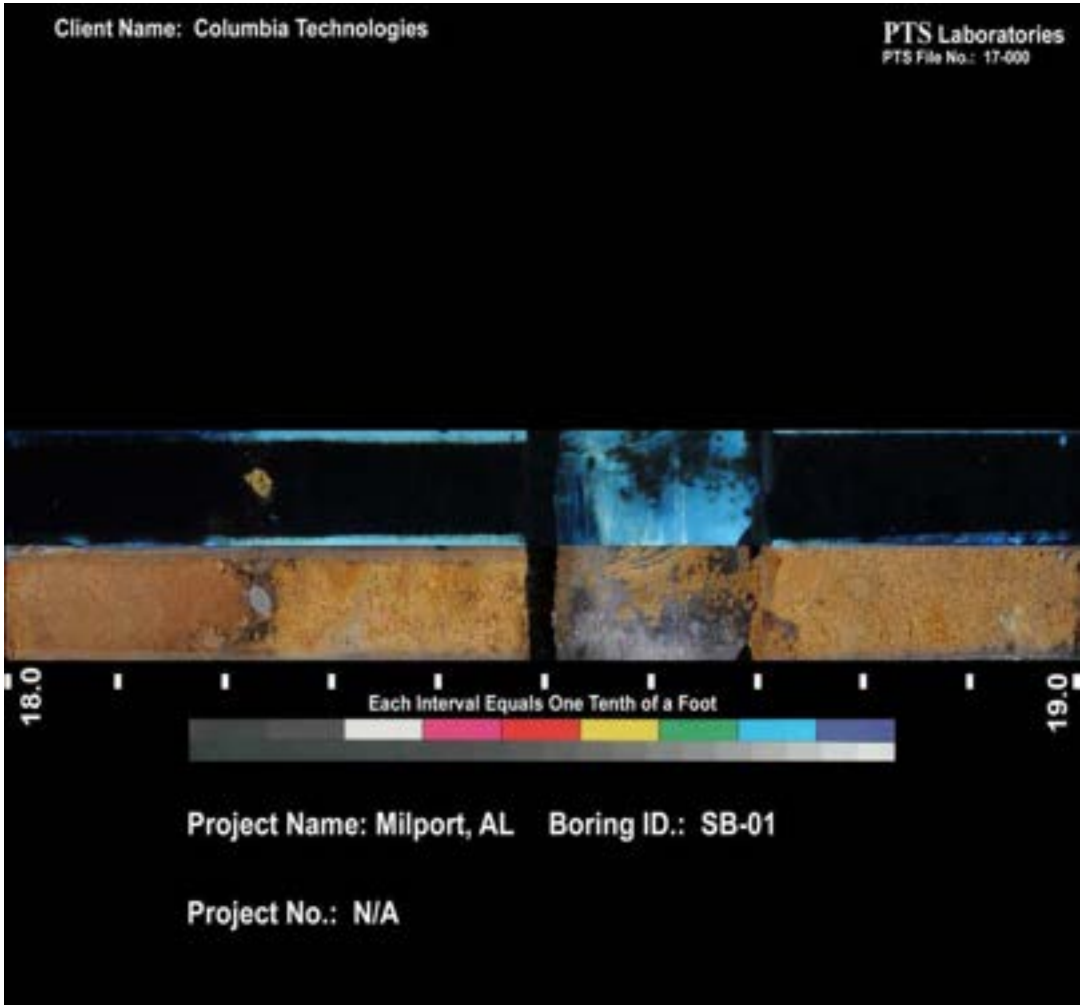


Source: API Bulletin 18 Managing Risk at LNAPL Sites 2nd edition, May 2018


trap 4
Nested
Vapor Wells
Vapor Evaluation

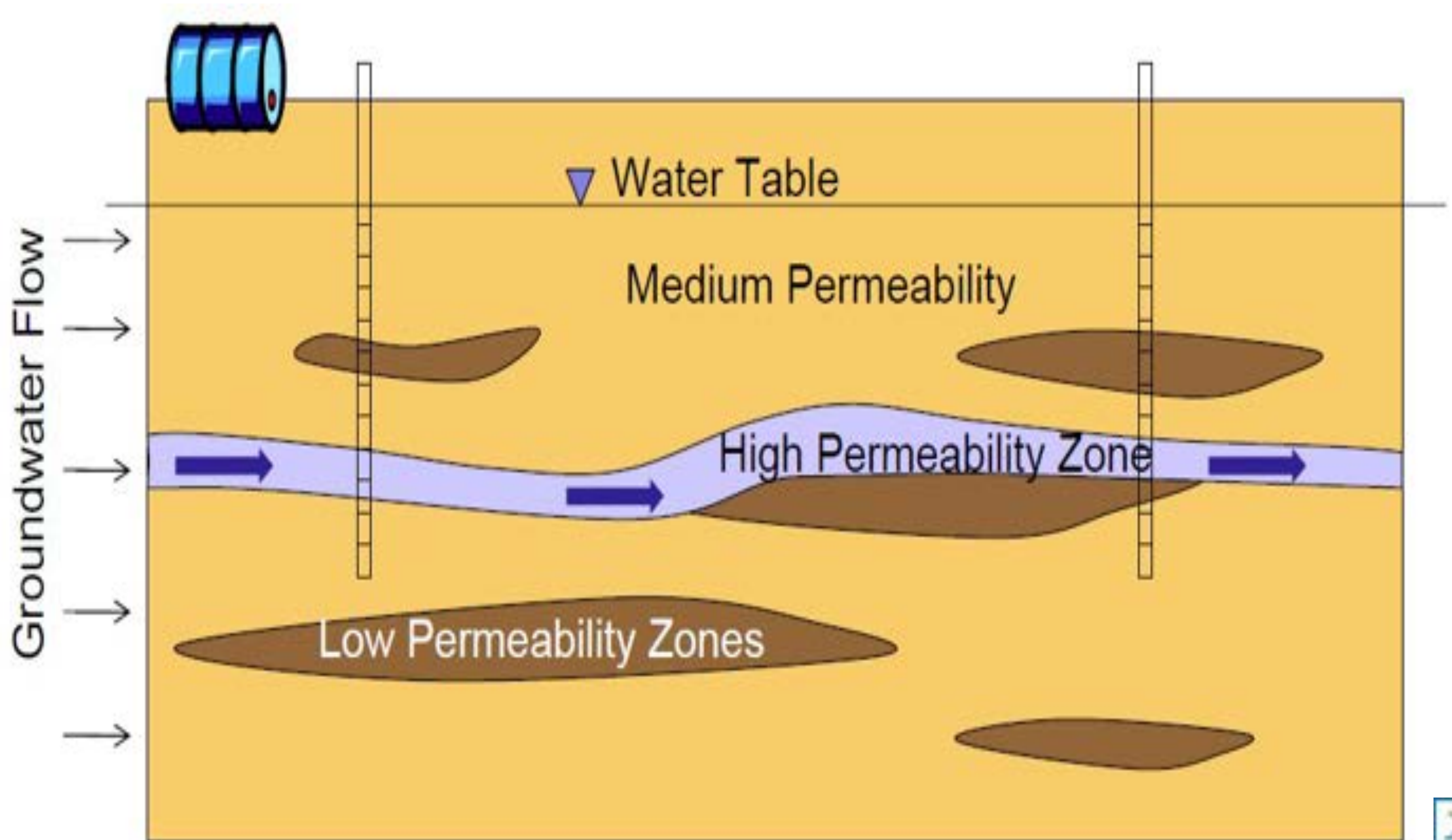
Matrix Effects

Petroleum Response to UV in Lab



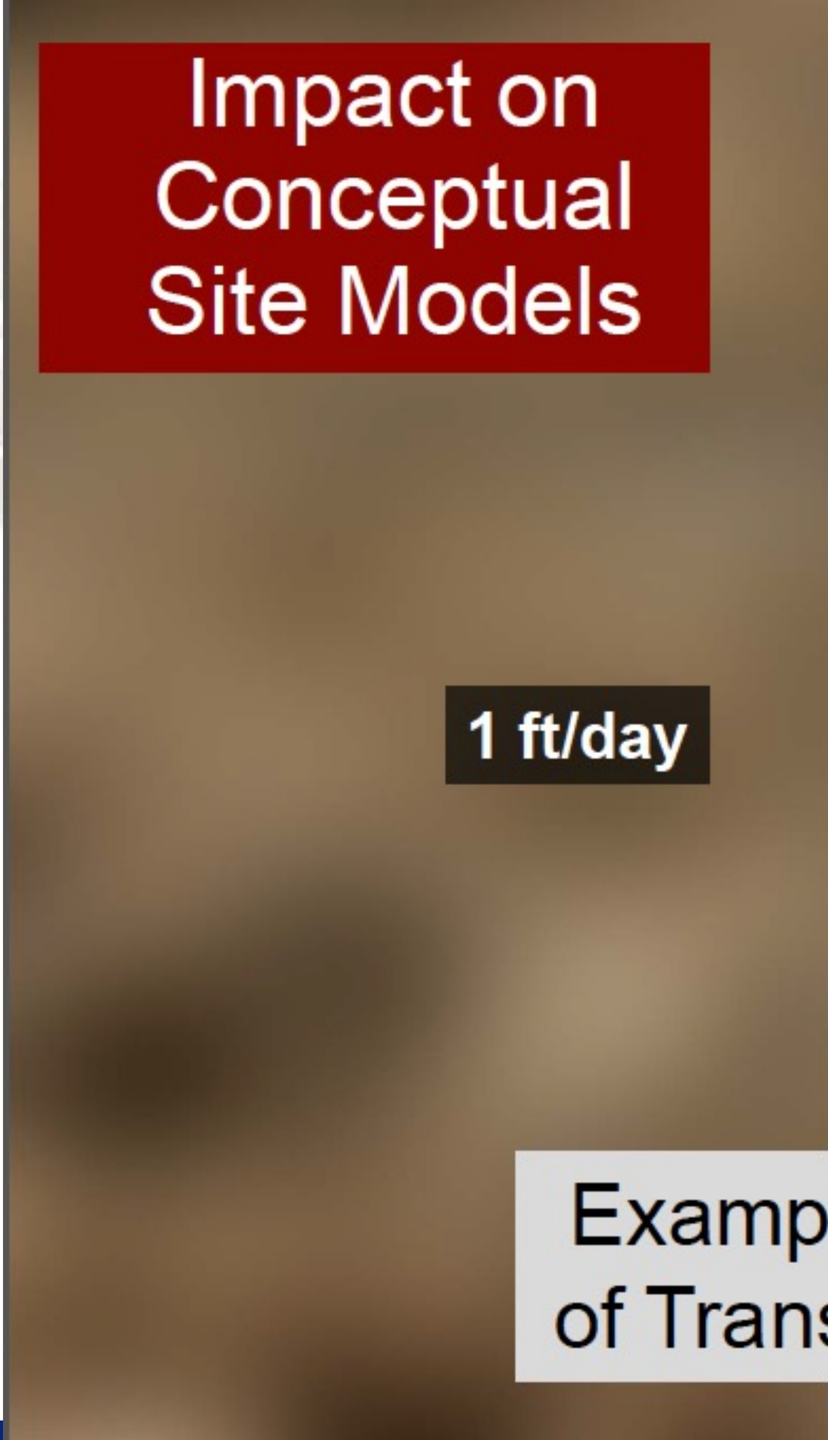
Ask what wavelength of excitation & detection?

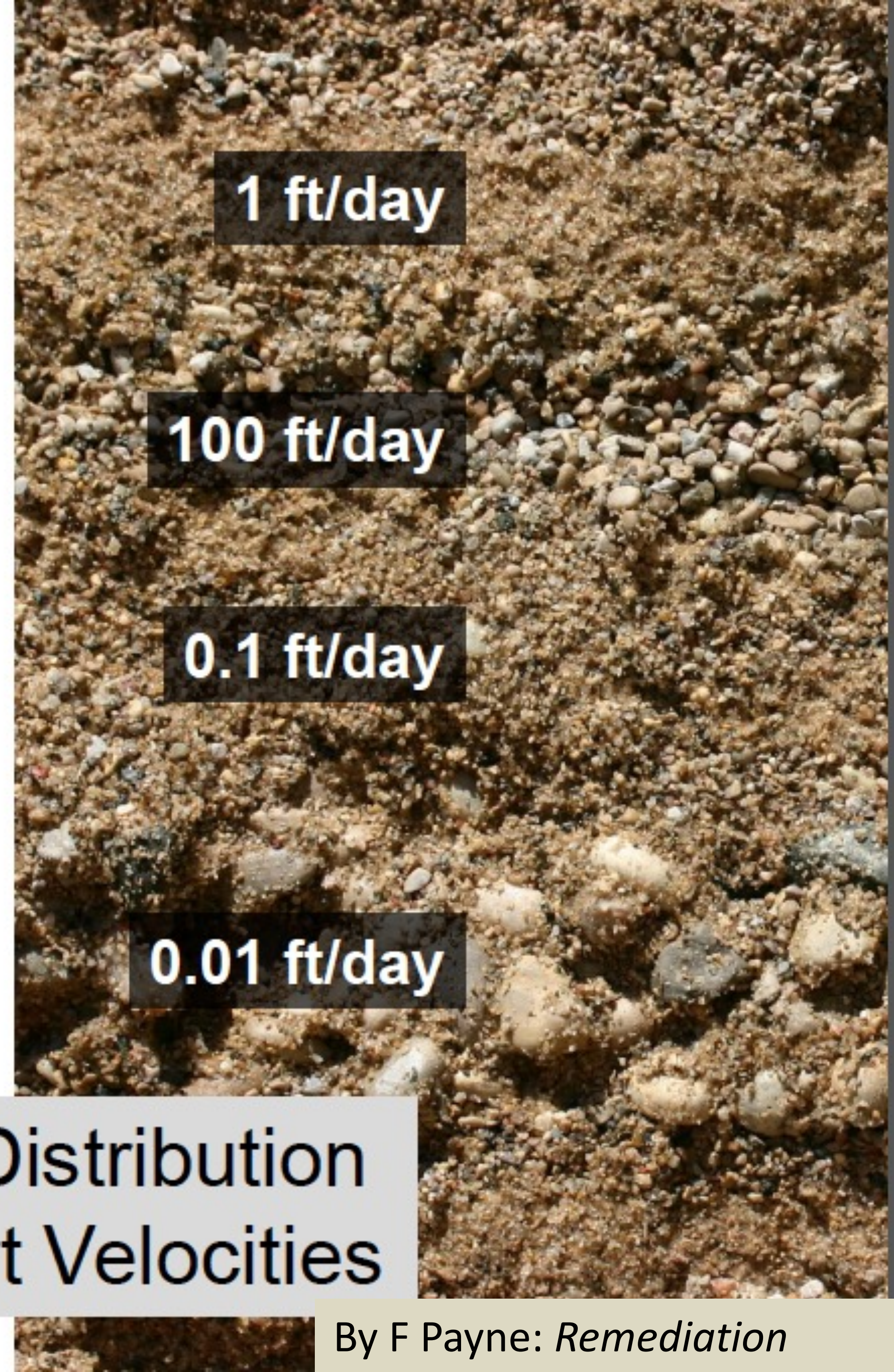
Dealing with Heterogeneity



Courtesy of: ITRC

Impact on Conceptual Site Models

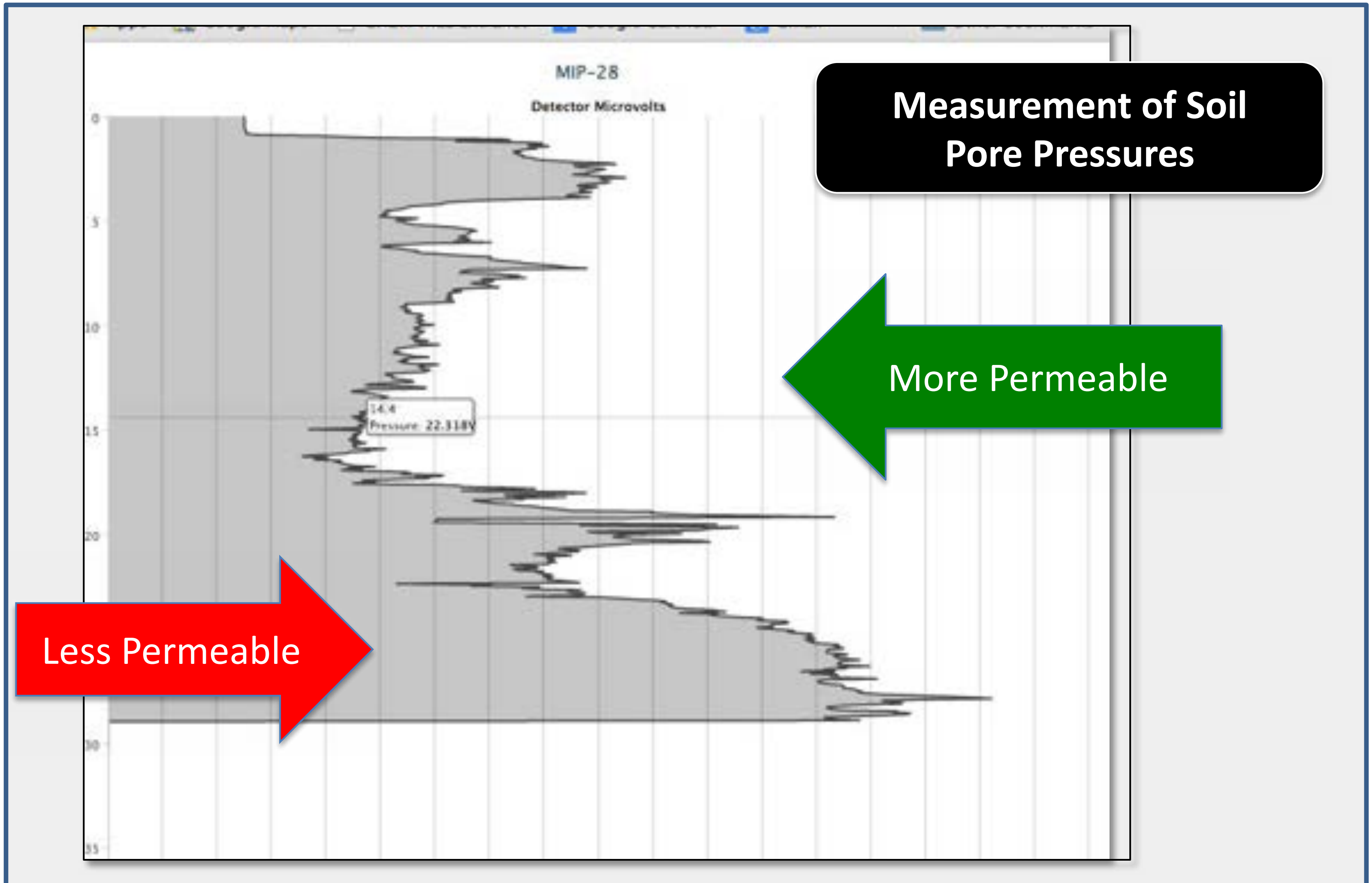




Example: Distribution of Transport Velocities

By F Payne: *Remediation*

Hydraulic Profiling Tool (HPT)



Optical Imaging Profiler (OIP)

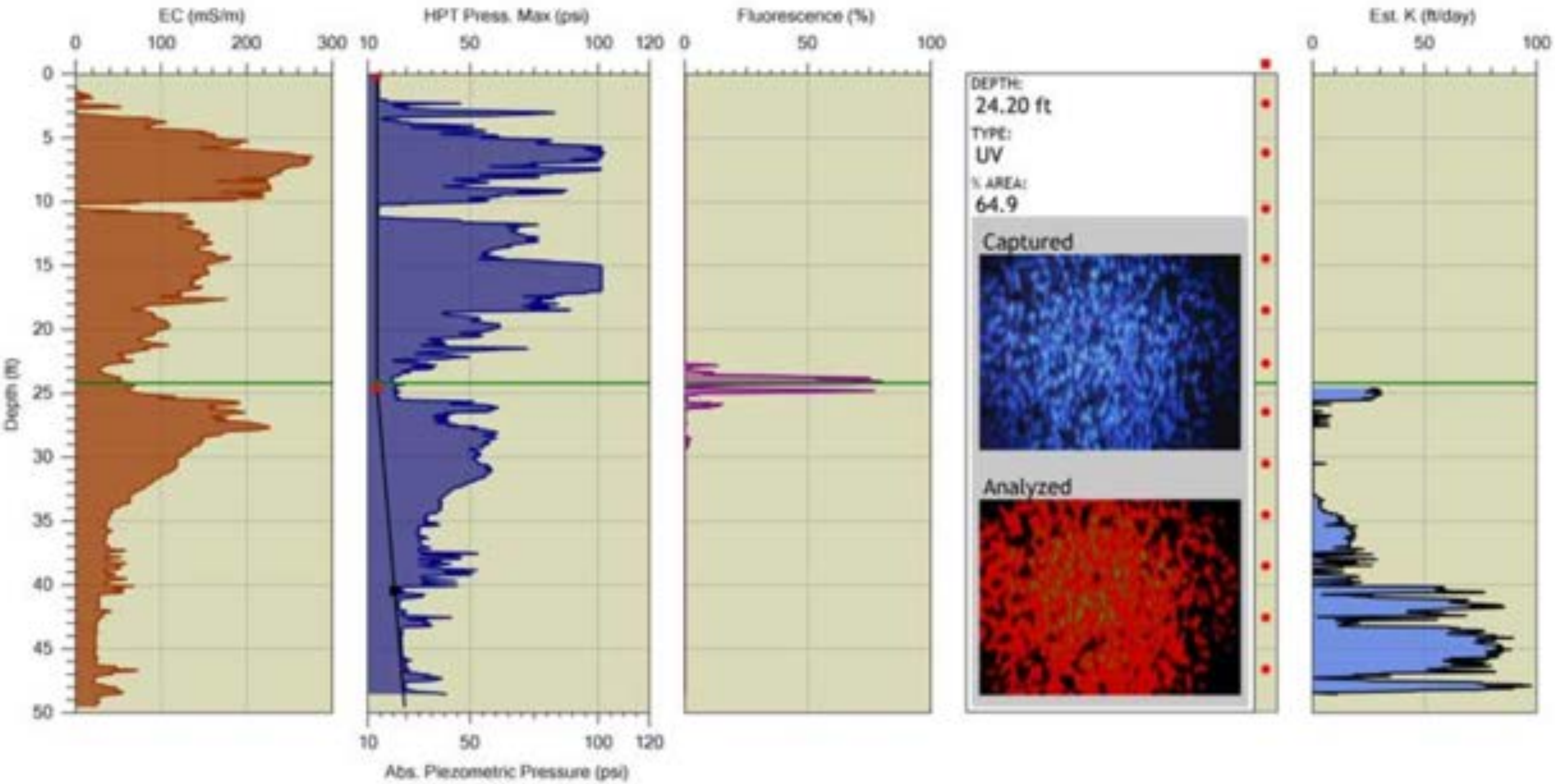
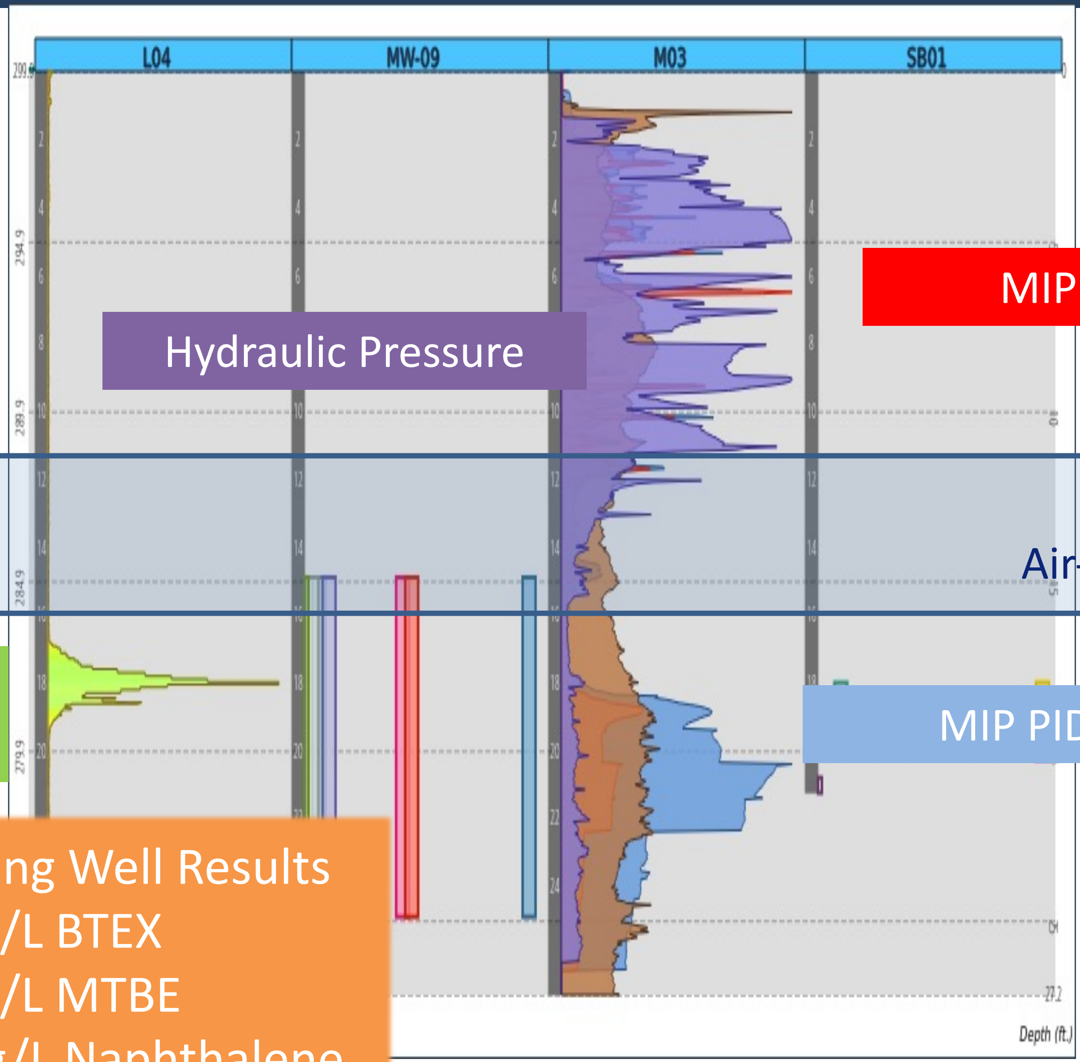


Figure 6: Graphs left to right: Soil EC, HPT pressure (formation permeability) along with absolute piezometric pressure (secondary axis), UV percent area Fluorescence, saved UV image from 24.20ft, and estimate hydraulic conductivity (estimated K).

Source: Geoprobe Systems Inc.

LNAPL + Matrix Relationship



MIP FID

Hydraulic Pressure

Range of
Air-Water Interface

UV-IF Response
(not BTEX)

MIP PID

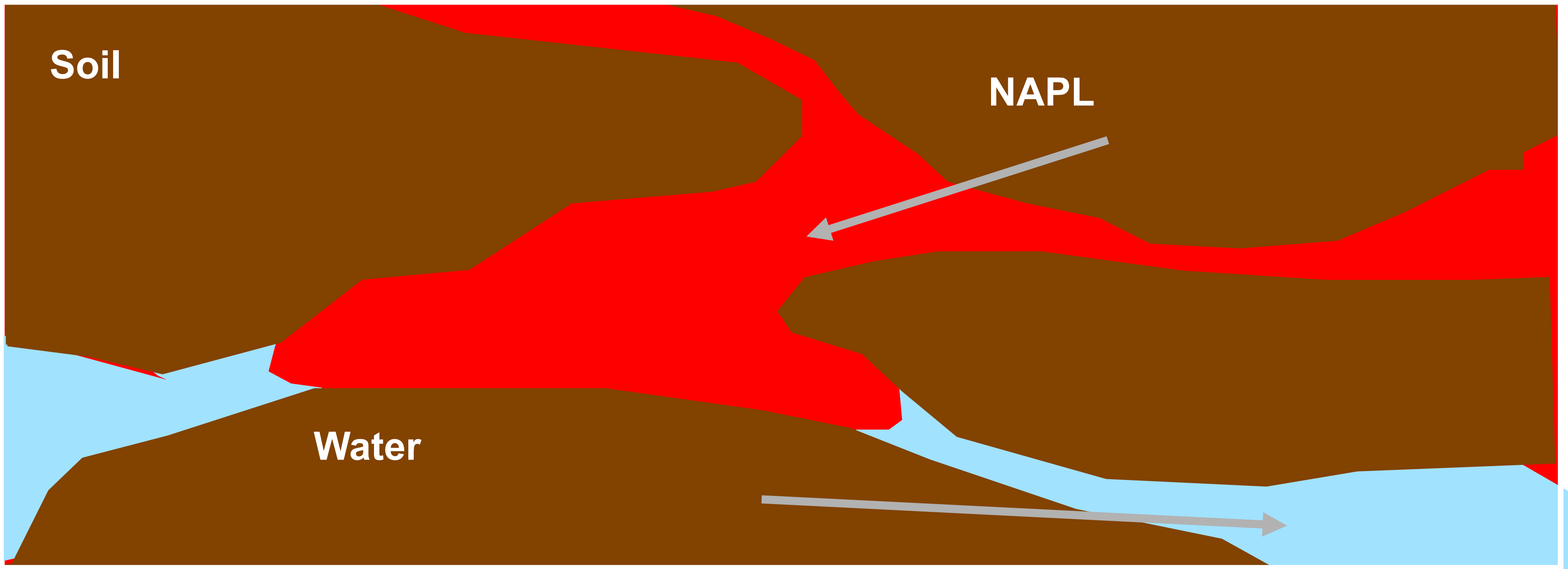
Monitoring Well Results
9.34 mg/L BTEX
0.33 mg/L MTBE
ND mg/L Naphthalene

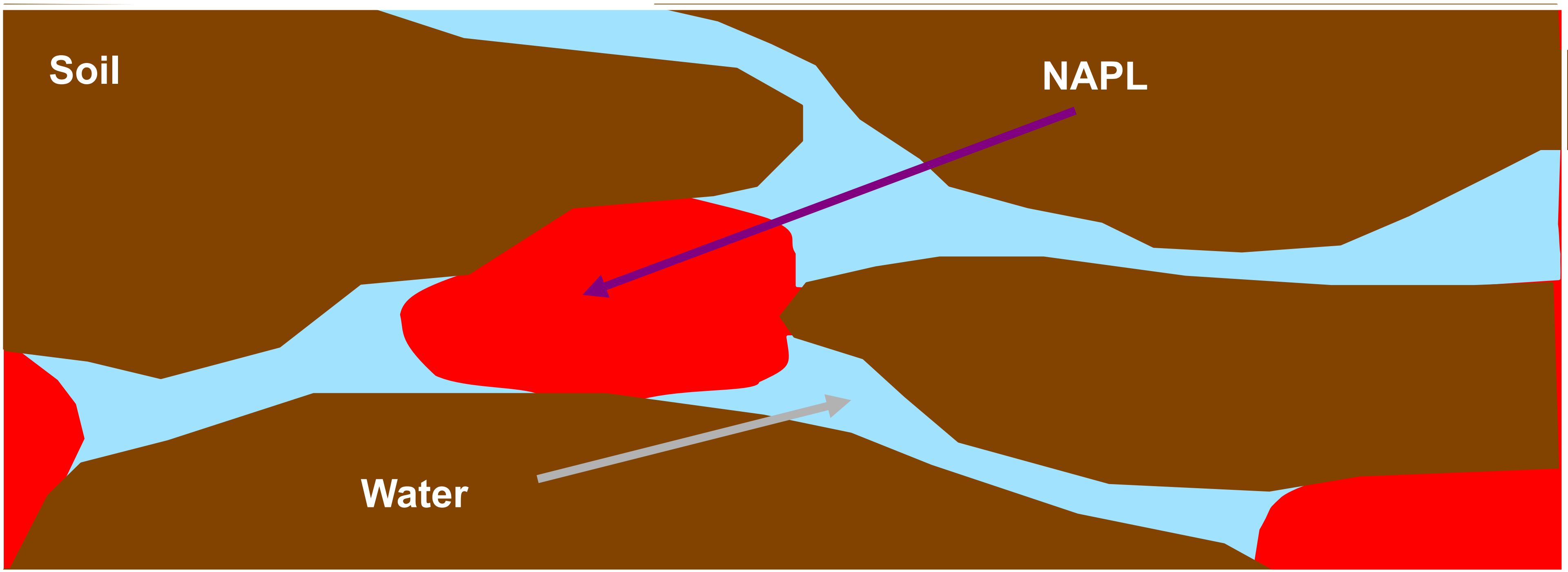
LNAPL Transmissivity

Lines of Evidence to Assess Mobility

- LNAPL type
- LNAPL release date
- LNAPL release volume
- Soil type
- Plume stability

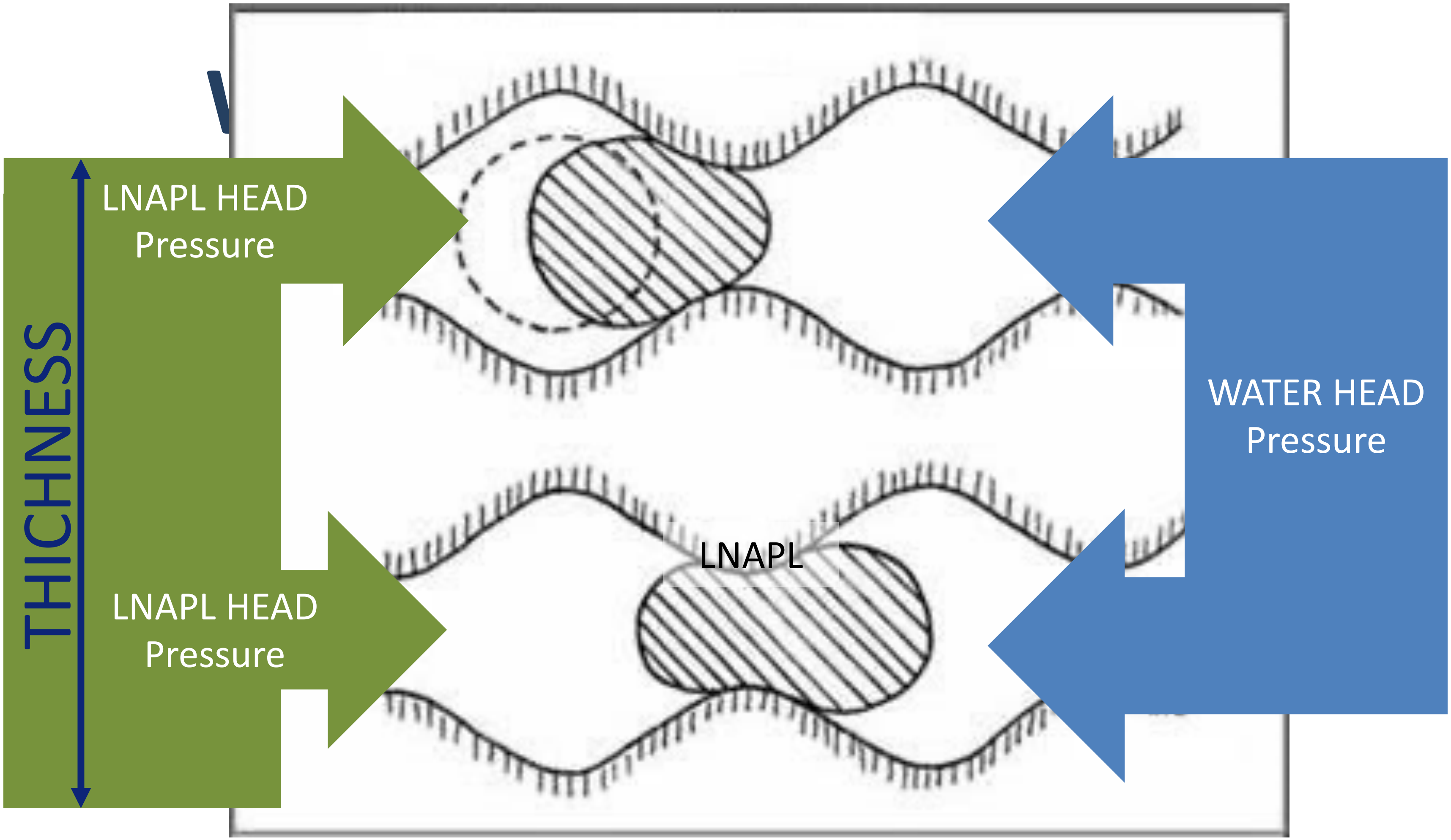
Courtesy of: ITRC


Soil
NAPL
Water


Soil
NAPL
Water

LNAPL Mobility vs Equilibrium

For water wet media



LNAPL vs Groundwater

API Bulletin No. 9

American Petroleum Institute

gri

SOIL & GROUNDWATER RESEARCH BULLETIN

A summary of research results from the American Petroleum Institute & GRI.

June 2000 No. 9

NON-AQUEOUS PHASE LIQUID (NAPL) MOBILITY LIMITS IN SOIL

EDWARD J. BROST • GEORGE E. DEVAULL • EQUILON ENTERPRISES LLC • WESTHOLLOW TECHNOLOGY CENTER • HOUSTON, TEXAS

C_{res} for Petroleum Product by Matrix

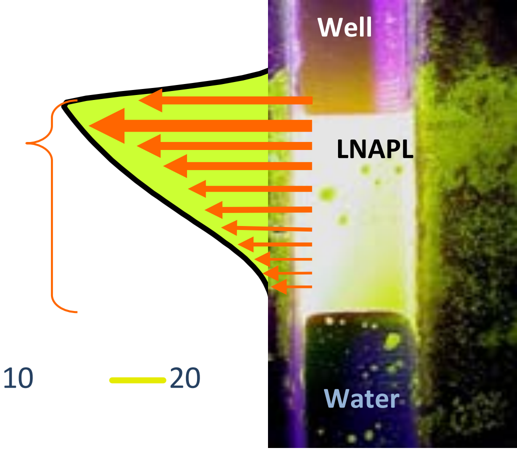
Table 1. Residual NAPL Concentration in Soil Compared to Soil Saturation Limit.

Name	Ref	S_r residual NAPL in the void fraction (cm^3/cm^3)	$C_{res,soil}$ residual NAPL concentration in soil (mg/kg)	$C_{sat,soil}$ soil saturation limit (mg/kg)	ρ_o liquid chemical density (g/cm^3)	MW molecular weight (g/g-mol)	S aqueous solubility (mg/L)	P_{vap} vapor pressure (mm Hg)
trichloroethylene (TCE)	a	0.2	70,000	1,045	1.46	131	1,100	75
benzene	b	0.24	53,000	444	0.88	78	1,750	95
o-xylene	c	0.01	2,000	143	0.88	106	178	6.6
gasoline	d,e	0.02 to 0.6	3,400 to 80,000	106	0.78	99	164	102
diesel	d,f	0.04 to 0.2	7,700 to 34,000	18	0.94	207	3.9	0.79
fuel oil	d,f	0.08 to 0.2	17,000 to 50,000	18	0.94	207	3.9	0.79
mineral oil	g	0.1 to 0.5	20,000 to 150,000	3	0.81	244	0.36	0.035

Notes: Unsaturated zone fine to medium sand. Nominal values $\theta_w = 0.12\ cm^3/cm^3$, $f_{oc} = 0.005$ g/g in $C_{sat,soil}$ calculation.
a = Lin et al. (1982); b = Lenham and Parker (1987); c = Boley and Overcamp (1998); d = Fussell et al. (1981); e = Hoag and Marley (1986); f = API (1980); g = Pfannkuch (1984).

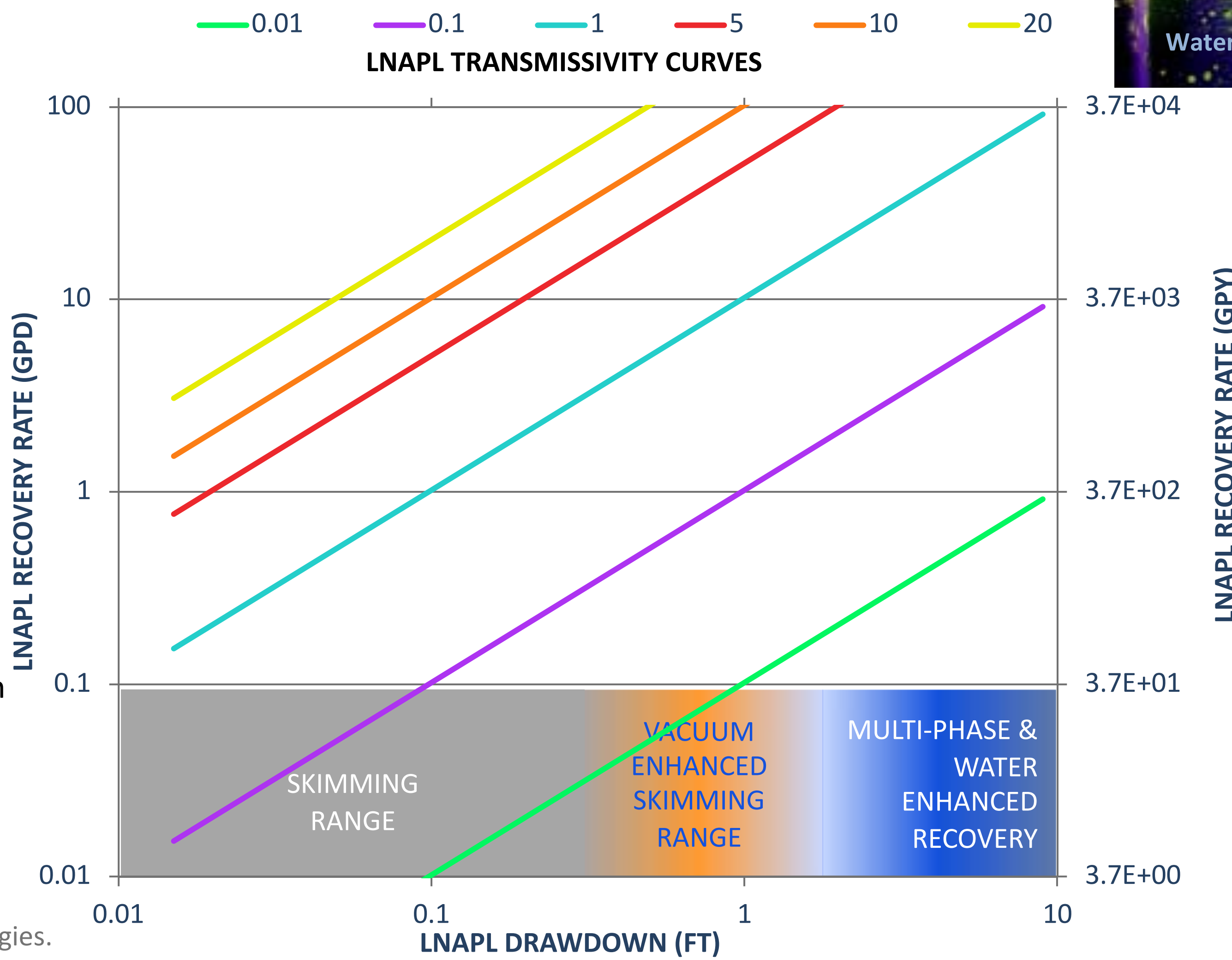
LNAPL Transmissivity Rate Reference

$$T_o = \sum K_o \Delta b_o$$



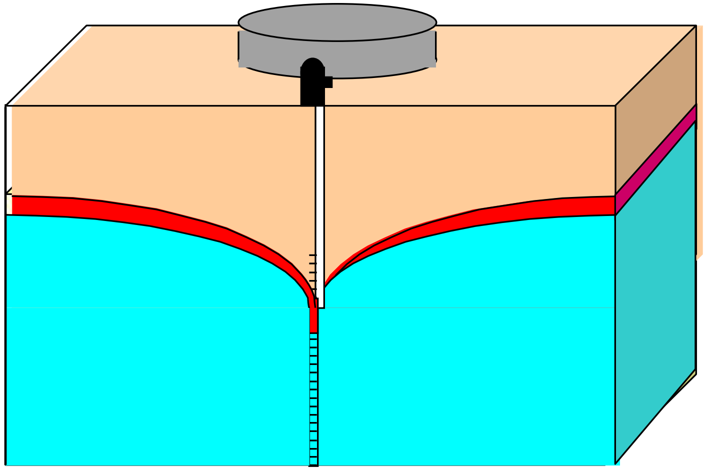
- **LNAPL Transmissivity accounts for**
  - **Thickness of mobile LNAPL**
  - **Fraction of pores occupied by LNAPL**
  - **Permeability of the soil**
  - **LNAPL density**
  - **LNAPL viscosity**

- Skimming LNAPL at 0.1 ft^2/day results in less than 200 GPY recovered
- Skimming LNAPL at 5 ft^2/day results in 7300 GPY



Methods of Estimating Potential Recovery

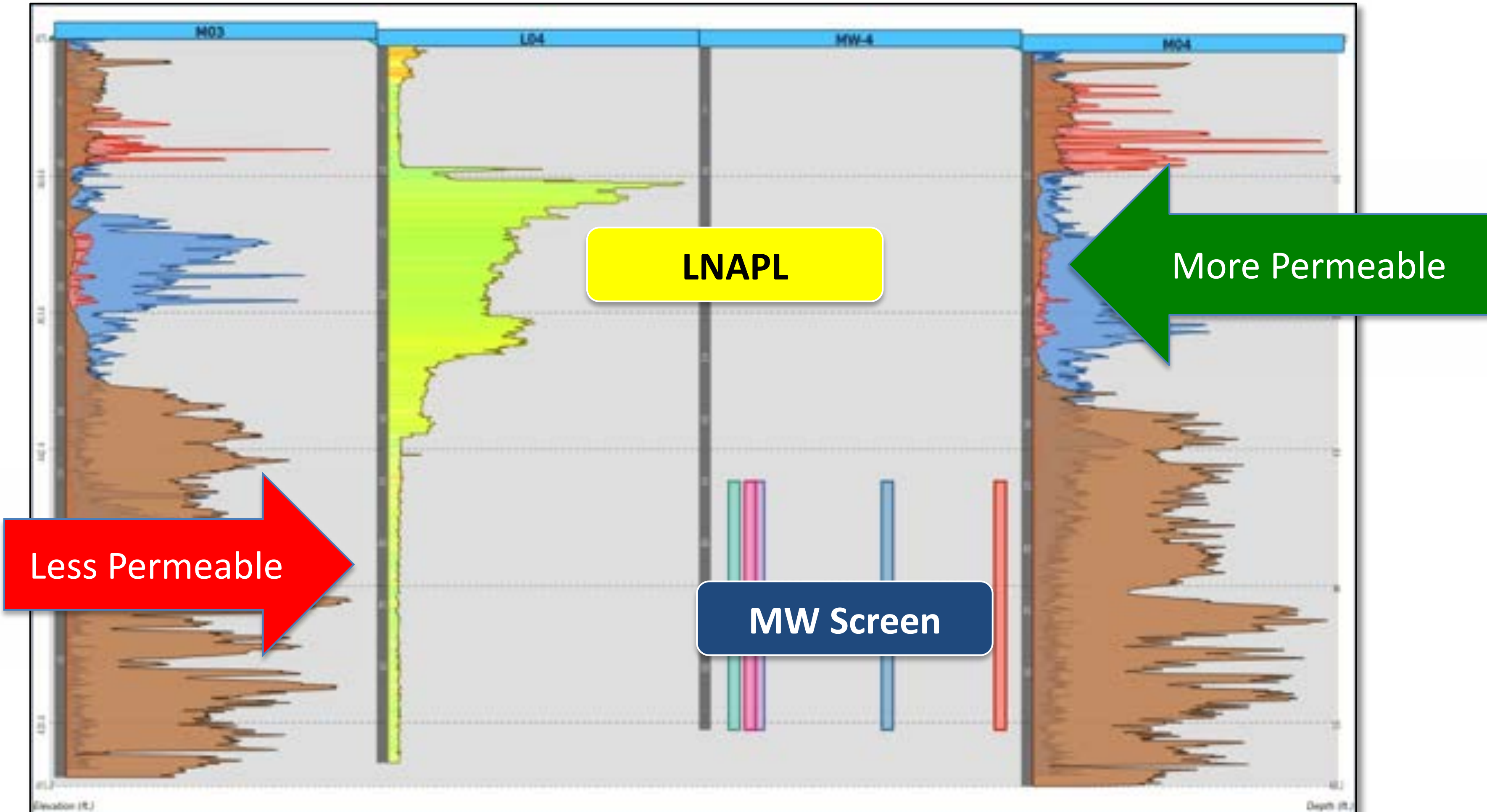
- Weight of evidence
- Field methods
  - Baildown tests
  - Pilot test technologies
- Desktop methods
  - Extrapolate existing system performance
  - Predictive models



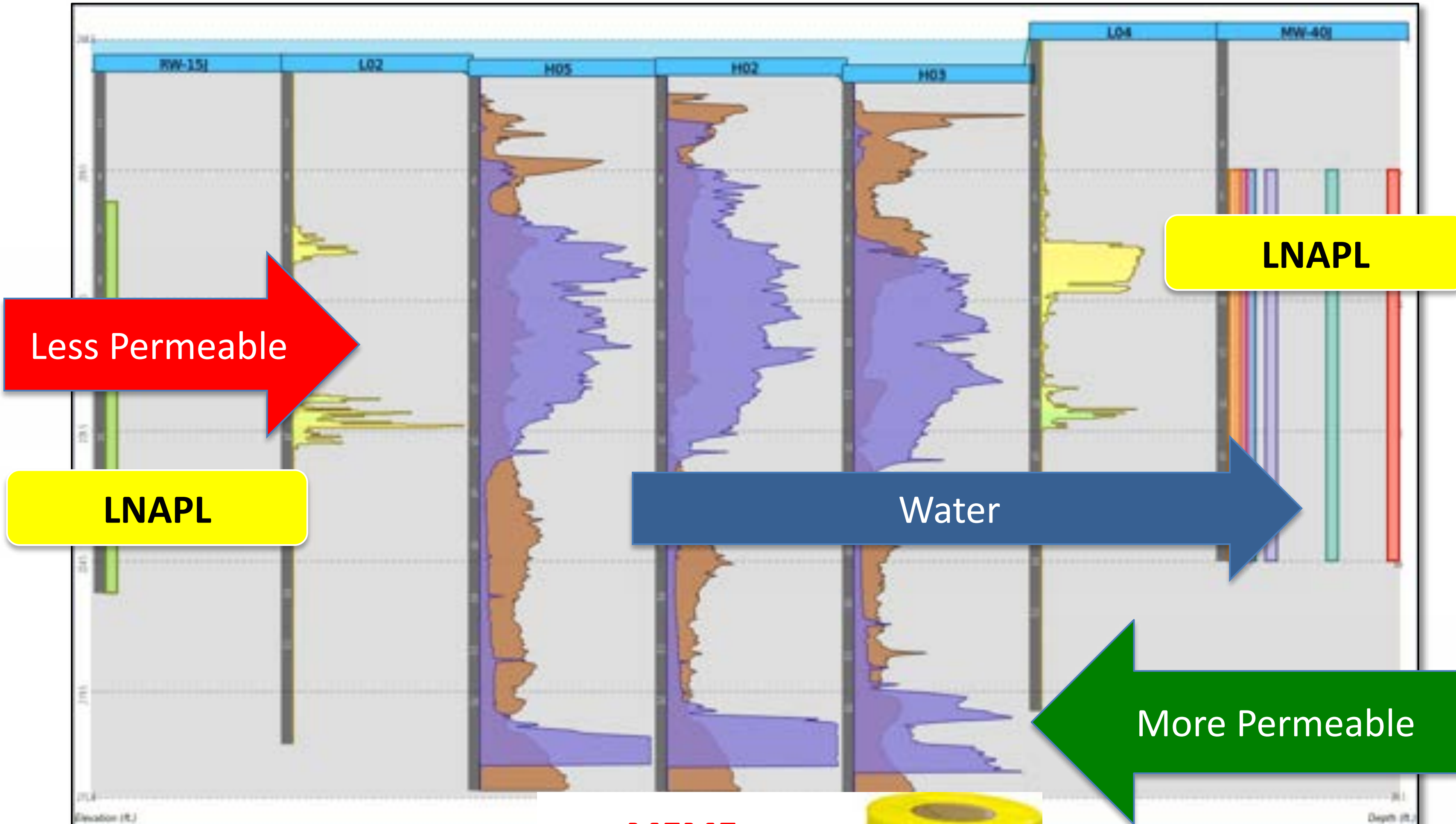
Courtesy of:

Spatial Alignment

LNAPL Above MW



MW Breach of Permeability Zones



Case Example – Tiger Oil

1980 Release

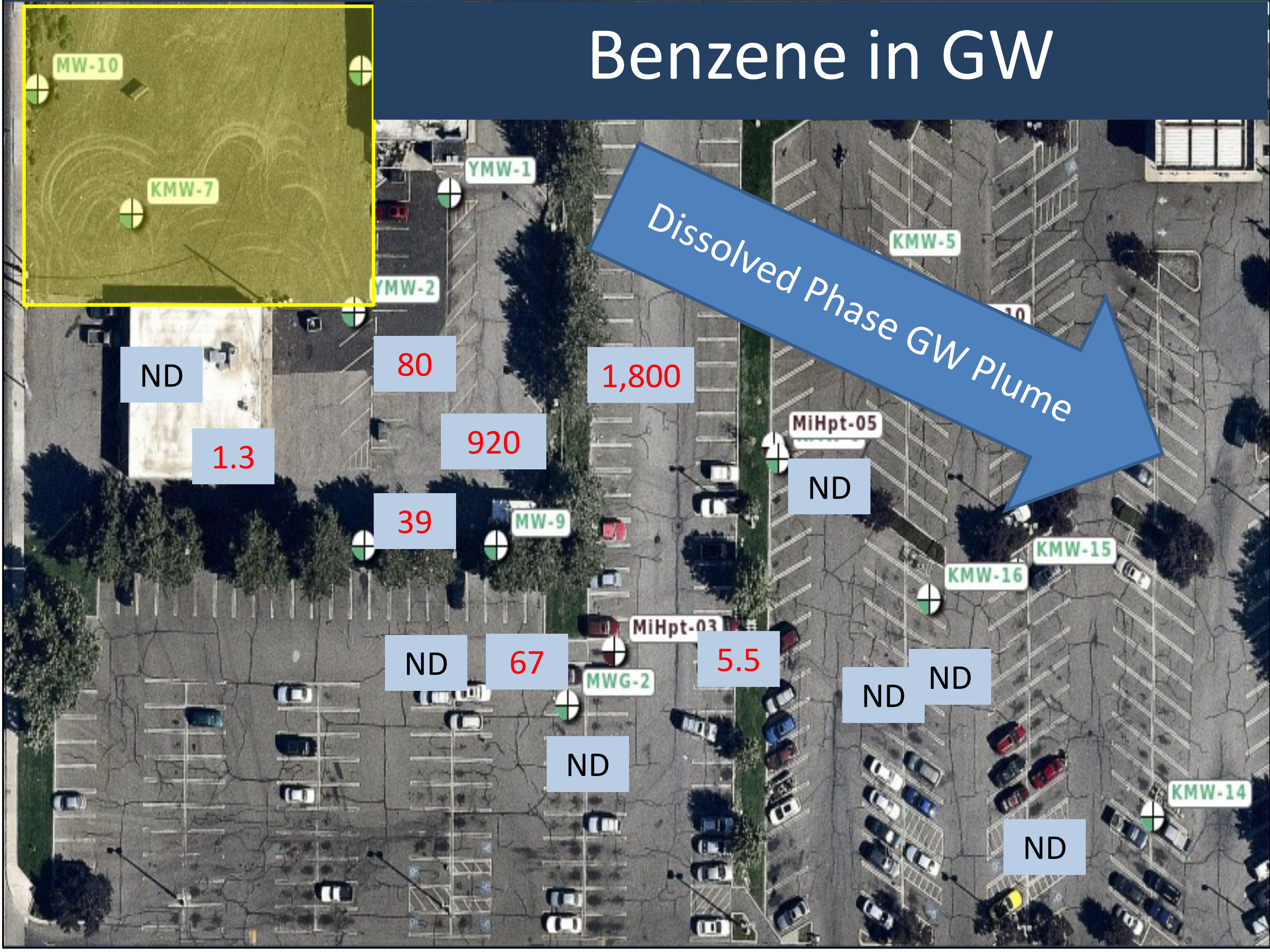
- Tank Removal
- Preliminary Investigation
- Secondary Investigation
- Excavation & backfill
- SVE & GW Extraction
- ISOC treatment
- Long term monitoring

Free Product Still Present

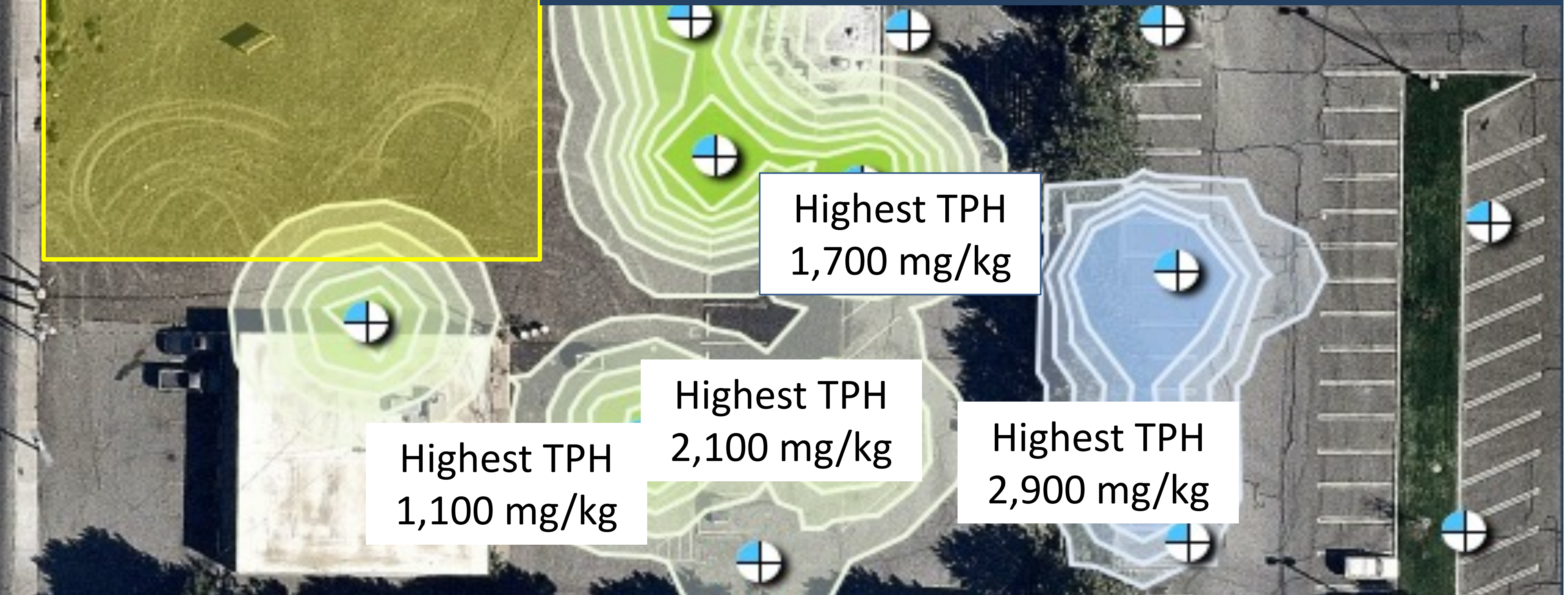
30 Years Later

Outcome of Traditional Approach

Benzene in GW

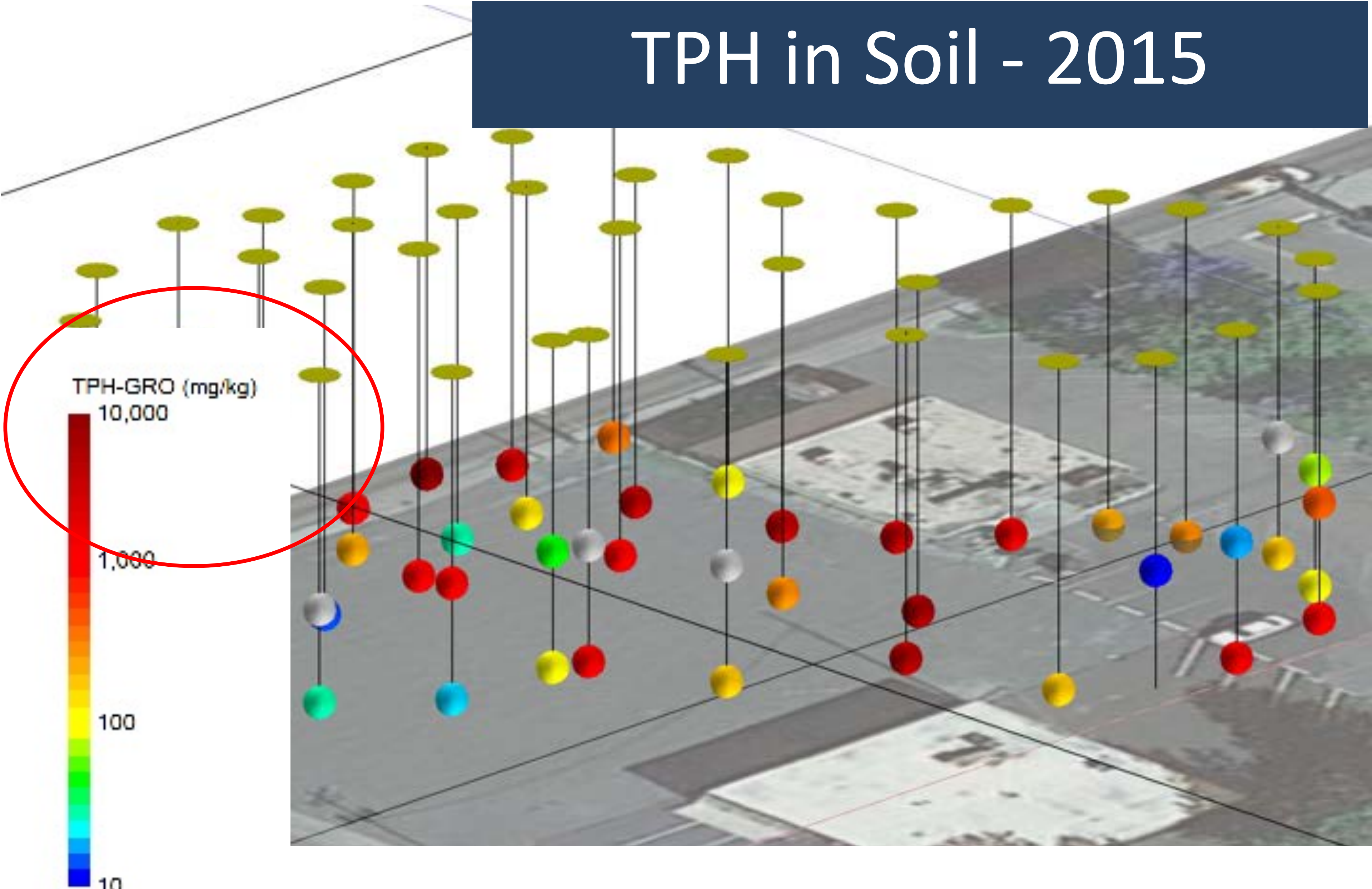


TPH in Soil



Residual Saturation Screening Values (API Bulletin No. 9, 2000)				
LNAPL Type	Soil Type	C_{Sat} mg/kg	C_{Res} mg/kg	S_r cm^3/cm^3
Gasoline	M-C Sand	143	3,387	0.02
Gasoline	M-F Sand	215	5,833	0.03
Gasoline	Silt – F Sand	387	10,000	0.05
Middle Distillates	M-C Sand	5	7,742	0.04
Middle Distillates	M-F Sand	9	13,333	0.06
Middle Distillates	Silt – F Sand	18	22,857	0.1

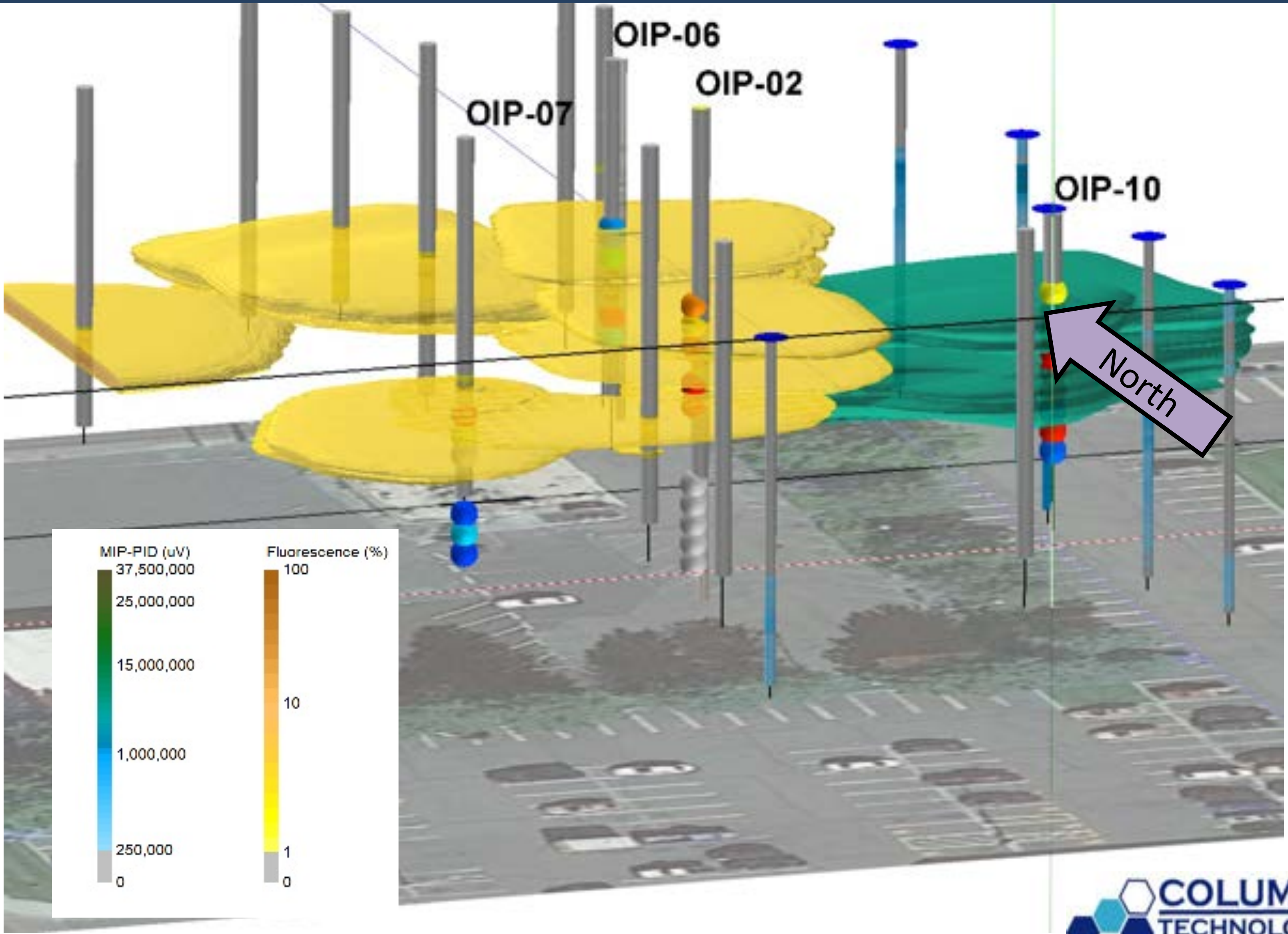
TPH in Soil - 2015



2015 Soil Sample Results

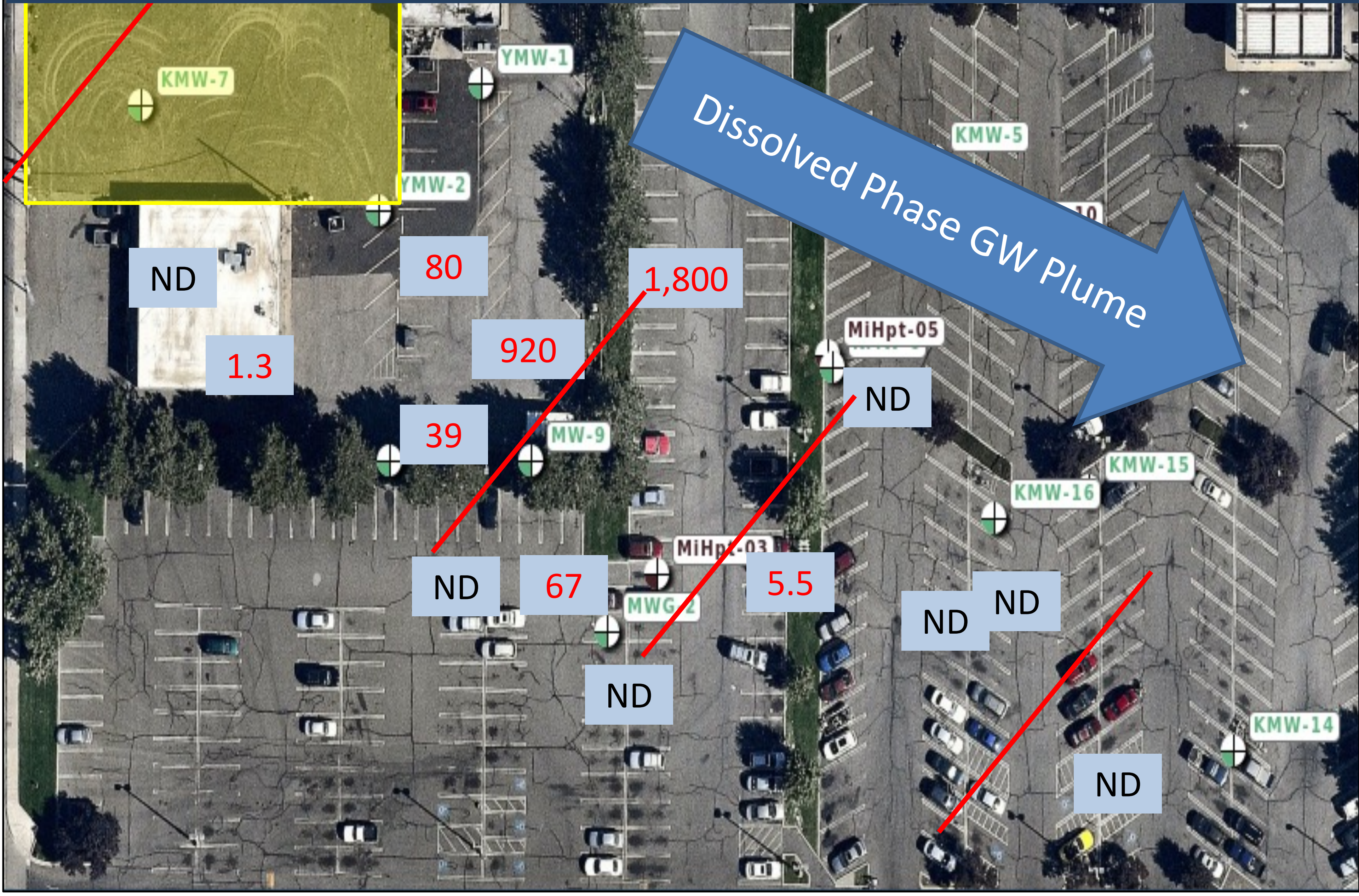
Optical Imaging Profiler

OIP + MIP-PID

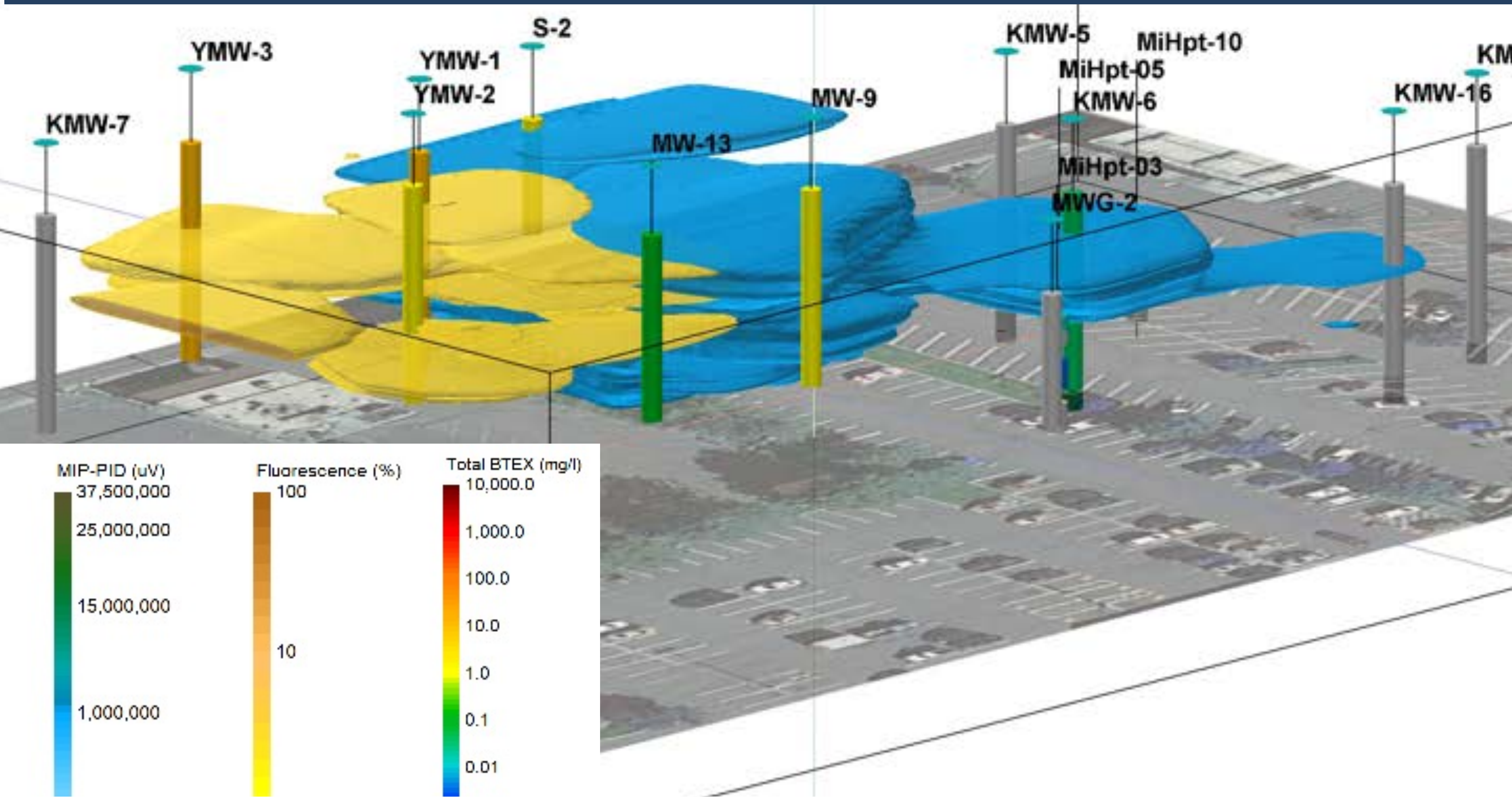


OIP-06
OIP-02
OIP-07
OIP-10
North
MIP-PID (uV)
37,500,000
25,000,000
15,000,000
1,000,000
250,000
0
Fluorescence (%)
100
10
1
0

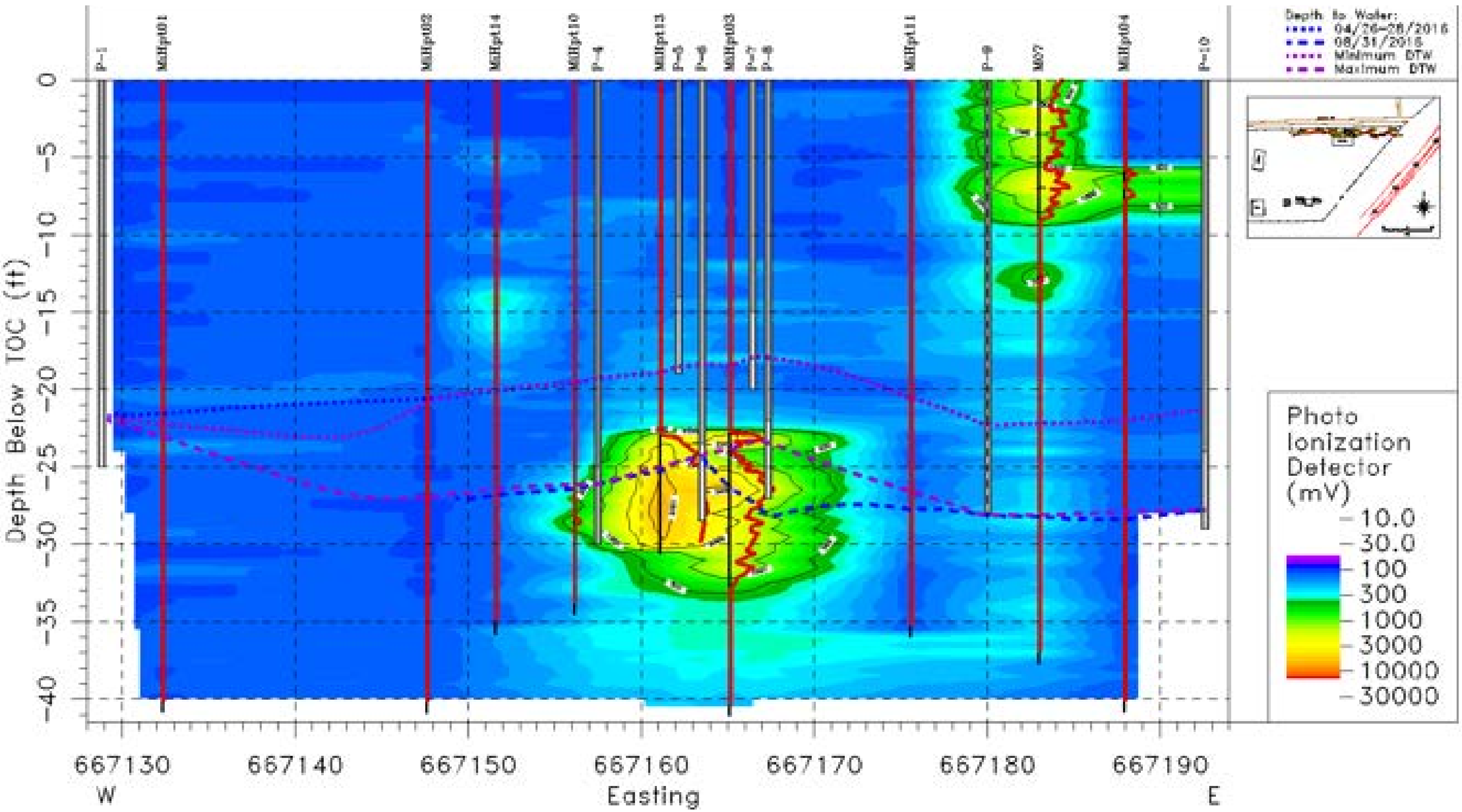
Benzene in GW



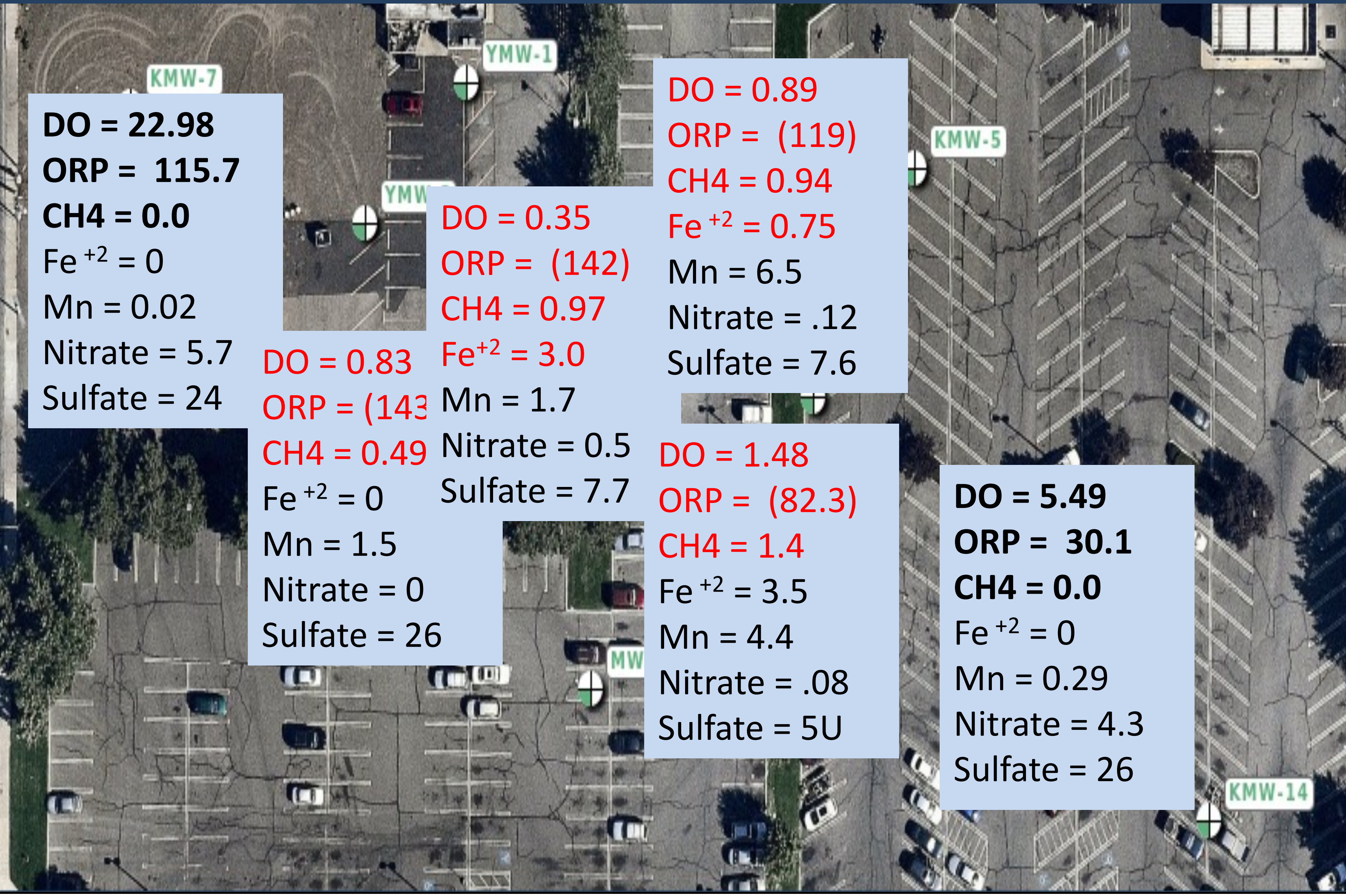
OIP + MIP-PID vs GW Results

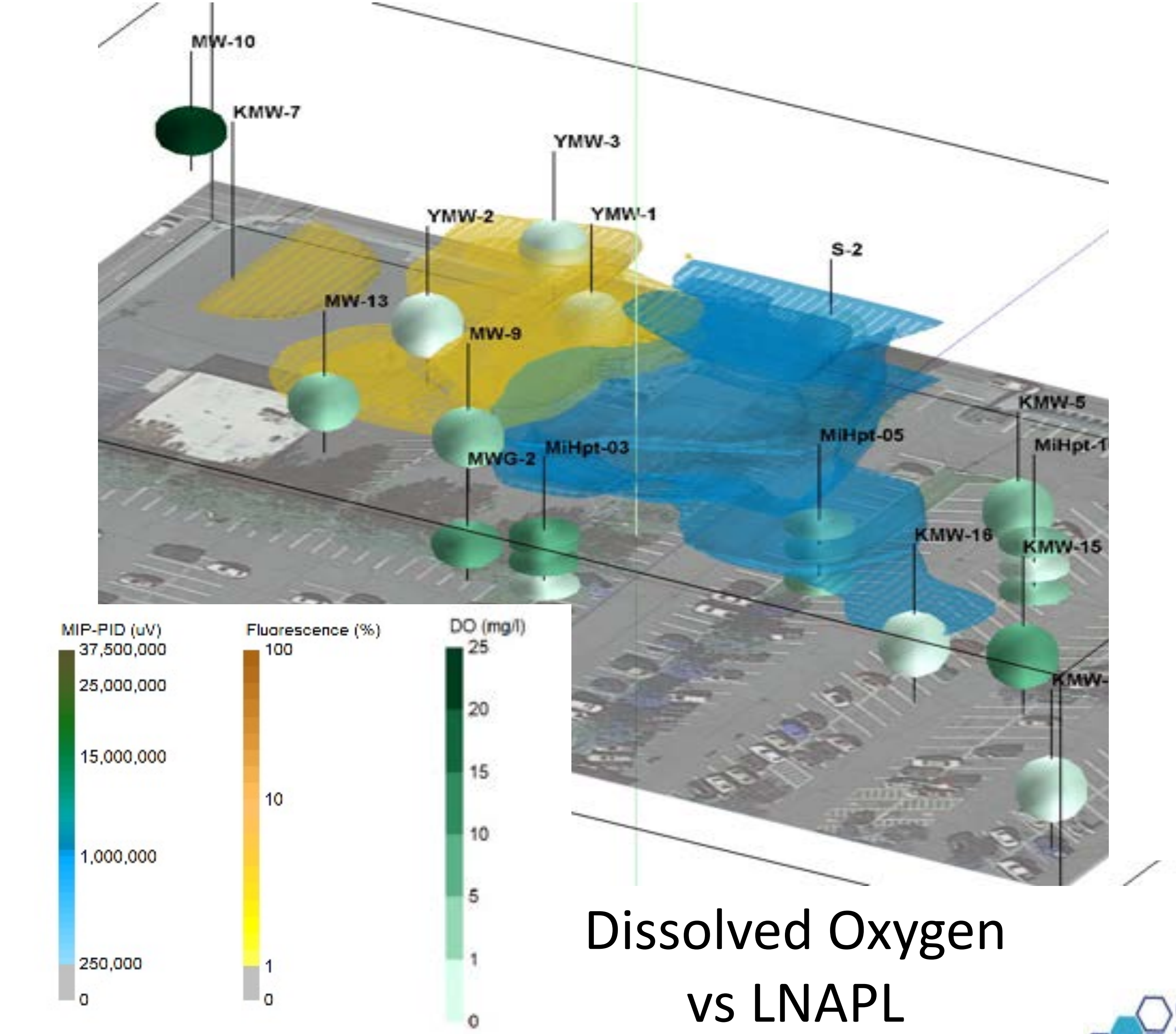


Mass Transport



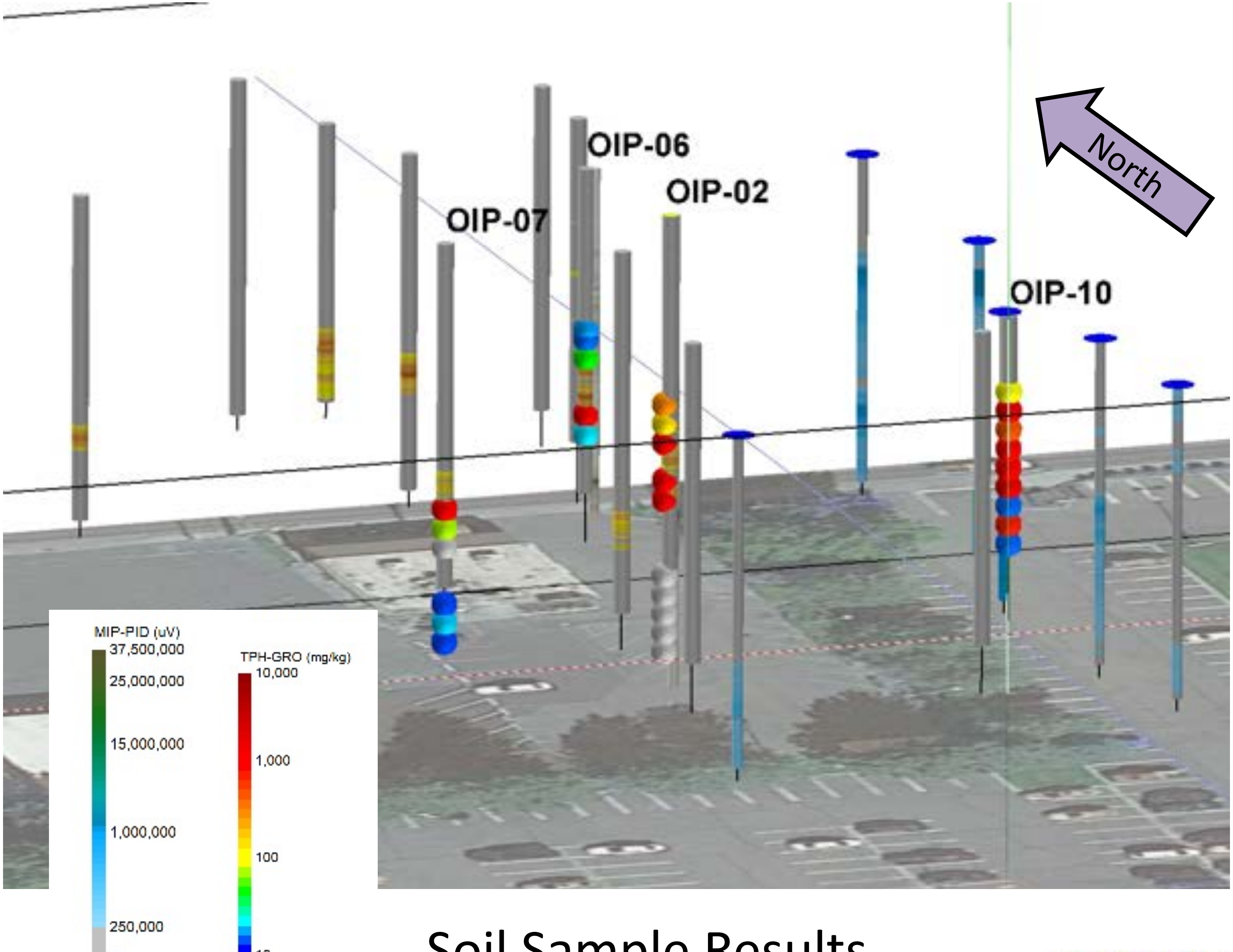
Geochemical Profiles





Dissolved Oxygen vs LNAPL

Soil Evaluation



Soil Sample Results

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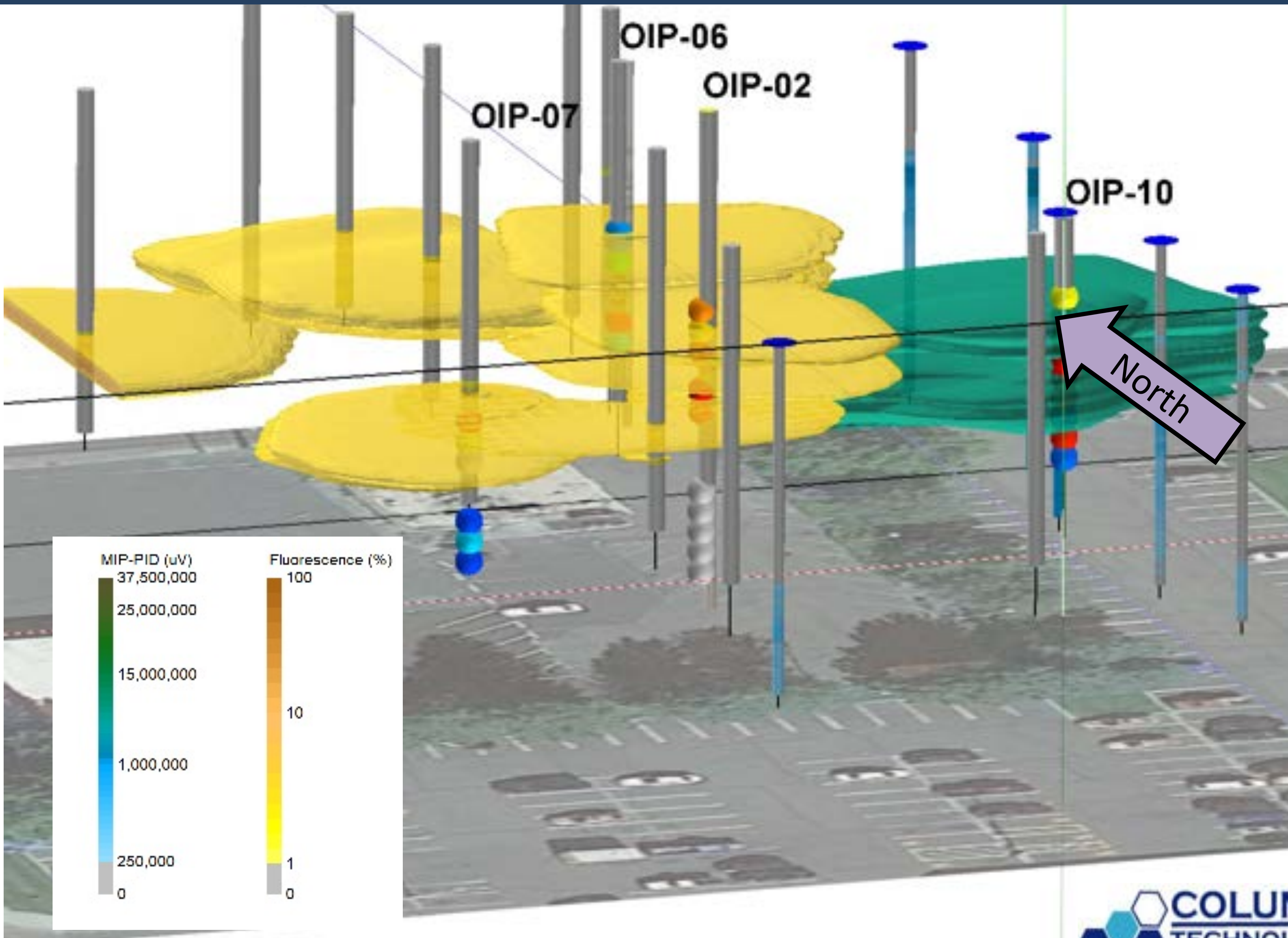
OIP + MIP-PID vs Soil Results



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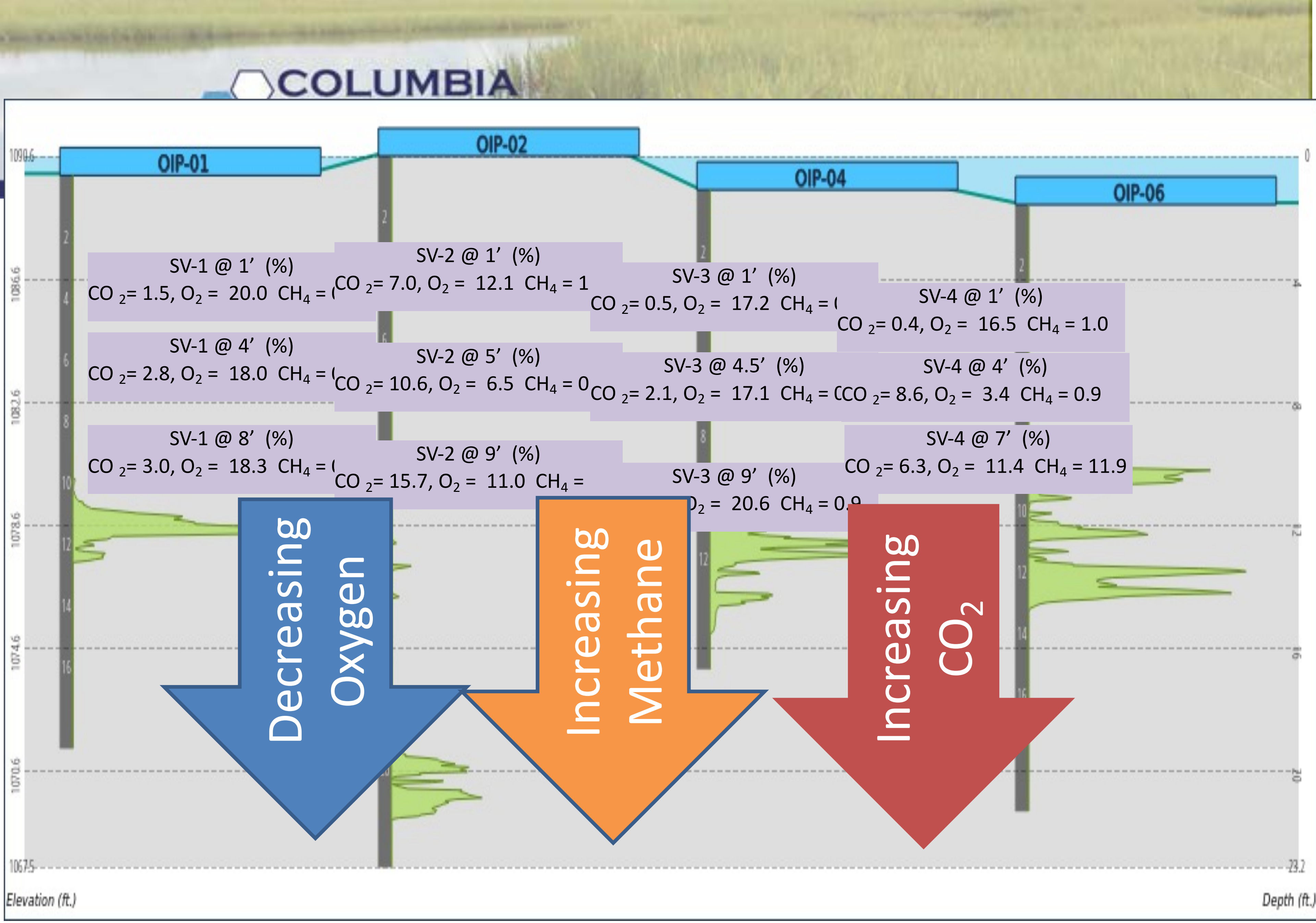
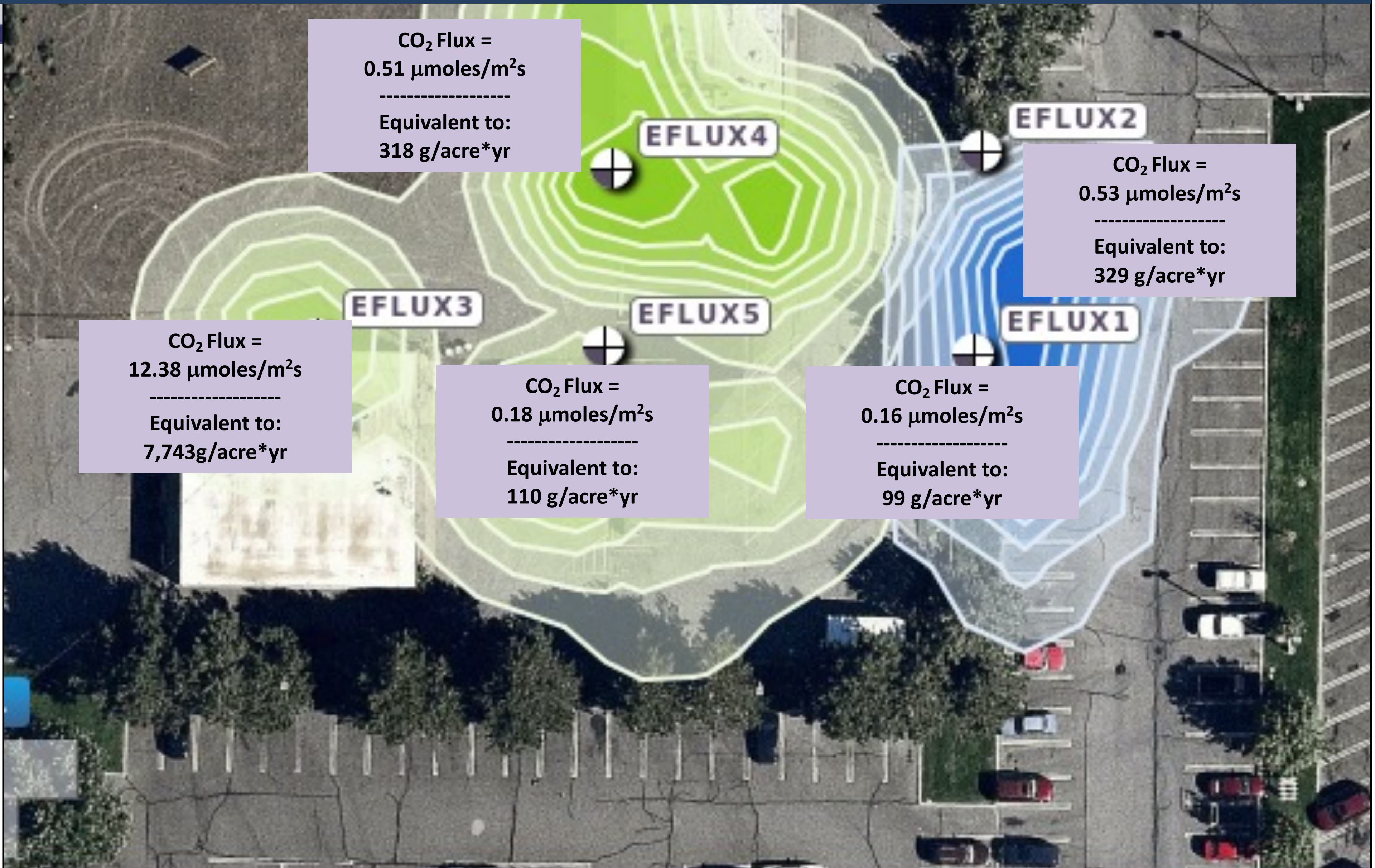
Vapor Phase Evaluation

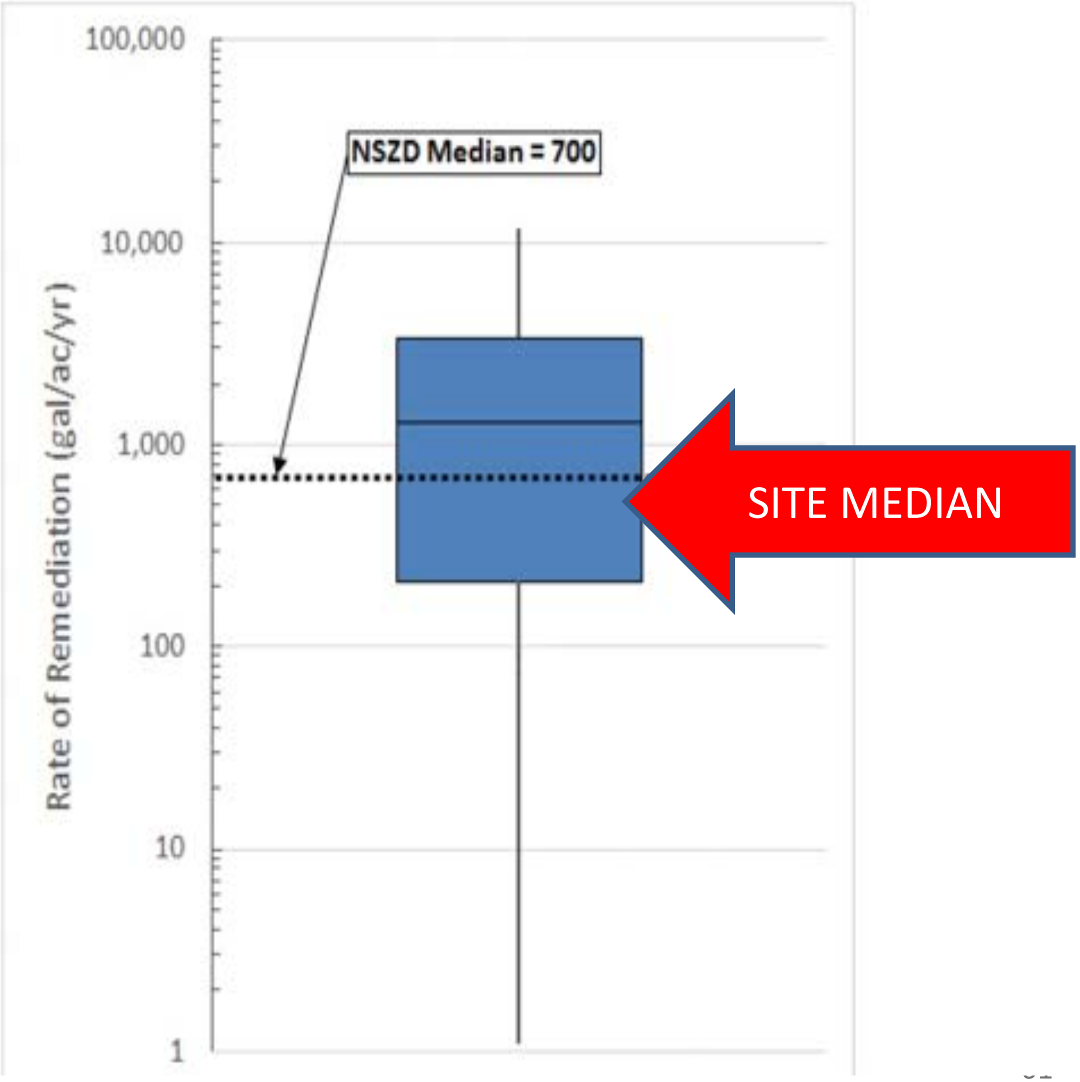

COLUMBIA
OIP-01
OIP-02
OIP-04
OIP-06
SV-1 @ 1' (%)
CO 2= 1.5, O2 = 20.0 CH4 = (
SV-2 @ 1' (%)
CO 2= 7.0, O2 = 12.1 CH4 = 1
SV-3 @ 1' (%)
CO 2= 0.5, O2 = 17.2 CH4 = (
SV-4 @ 1' (%)
CO 2= 0.4, O2 = 16.5 CH4 = 1.0
SV-1 @ 4' (%)
CO 2= 2.8, O2 = 18.0 CH4 = (
SV-2 @ 5' (%)
CO 2= 10.6, O2 = 6.5 CH4 = 0
SV-3 @ 4.5' (%)
CO 2= 2.1, O2 = 17.1 CH4 = (
SV-4 @ 4' (%)
CO 2= 8.6, O2 = 3.4 CH4 = 0.9
SV-1 @ 8' (%)
CO 2= 3.0, O2 = 18.3 CH4 = (
SV-2 @ 9' (%)
CO 2= 15.7, O2 = 11.0 CH4 =
SV-3 @ 9' (%)
O2 = 20.6 CH4 = 0.9
SV-4 @ 7' (%)
CO 2= 6.3, O2 = 11.4 CH4 = 11.9
Decreasing Oxygen
Increasing Methane
Increasing CO2
1090.6
1086.6
1082.6
1078.6
1074.6
1070.6
1067.5
Elevation (ft.)
Depth (ft.)

Measuring NSZD

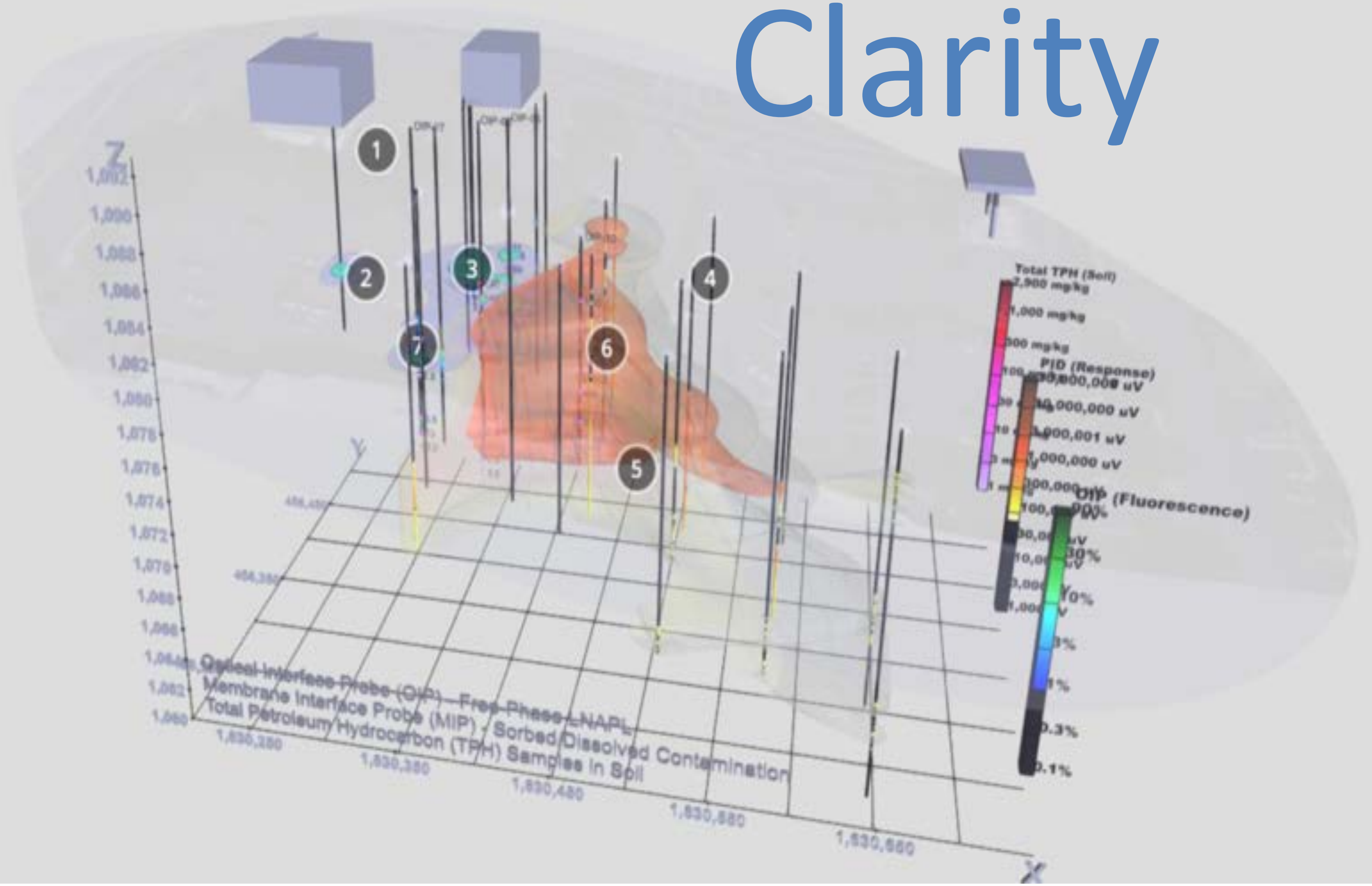


Cleaning Power of NSZD

Cleanup Costs



Clarity


Optical Interface Probe (OIP) – Free-Phase LNAPL
Membrane Interface Probe (MIP) - Sorbed/Dissolved Contamination
Total Petroleum Hydrocarbon (TPH) Samples in Soil
Total TPH (Soil)
2,900 mg/kg
1,000 mg/kg
PID (Response)
OIP (Fluorescence)
1
2
3
4
5
6
7
Z
Y
X

Key Takeaway Points

- **Scale appropriate** information is critical to minimizing the uncertainty in the Site Conceptual Model
- Understanding the **soil matrix** is critical
- **Remediation parameters** are not the same as risk parameters (i.e. BTEX in water does not represent TPH mass in soil)
- **Multiple lines of evidence** are required – much more than monitoring well data

THINK.
RESTORE,
Sustainably

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Next Steps

ITRC 17 LNAPL Remedial Technologies

- Excavation
- Physical containment
- In-situ soil mixing
- Natural source zone depletion (NSZD)
- Air sparging/soil vapor extraction (AS/SVE)
- LNAPL skimming
- Bioslurping/EFR
- Dual pump liquid extraction
- Multi-phase extraction, dual pump
- Multi-phase extraction, single pump
- Water/hot water flooding
- In situ chemical oxidation
- Surfactant- enhanced subsurface remediation
- Cosolvent flushing
- Steam/hot-air injection
- Radio frequency heating
- Three and six-phase electrical resistance heating

Courtesy of:

Treatment "Trains"

1. LNAPL mass recovery
2. LNAPL phase change remediation
3. LNAPL mass control
4. LNAPL phase change remediation and mass recovery

Dual pump liquid extraction

Air sparging/soil vapor extraction (AS/SVE)

Natural source zone depletion (NSZD)

Courtesy of:

What additional information do we need?

- **Risk-Based Drivers**
  - Reduce risk-level or hazard
  - Exposure pathway/LNAPL specific

- **Non-Risk Factors (examples)**
  - Reduce LNAPL volatilization or dissolution
  - Reduce source longevity
  - Reduce LNAPL mass or well thickness
  - Reduce LNAPL transmissivity
  - Abate LNAPL mobility
  - Corporate policy – liability/risk tolerance

- **Regulatory driver:** "recover to maximum extent practicable" – State's interpretation?

Set Goals for each applicable Objective

A good LCSM supports identification of appropriate Objectives and setting relevant Goals

Courtesy of: ITRC