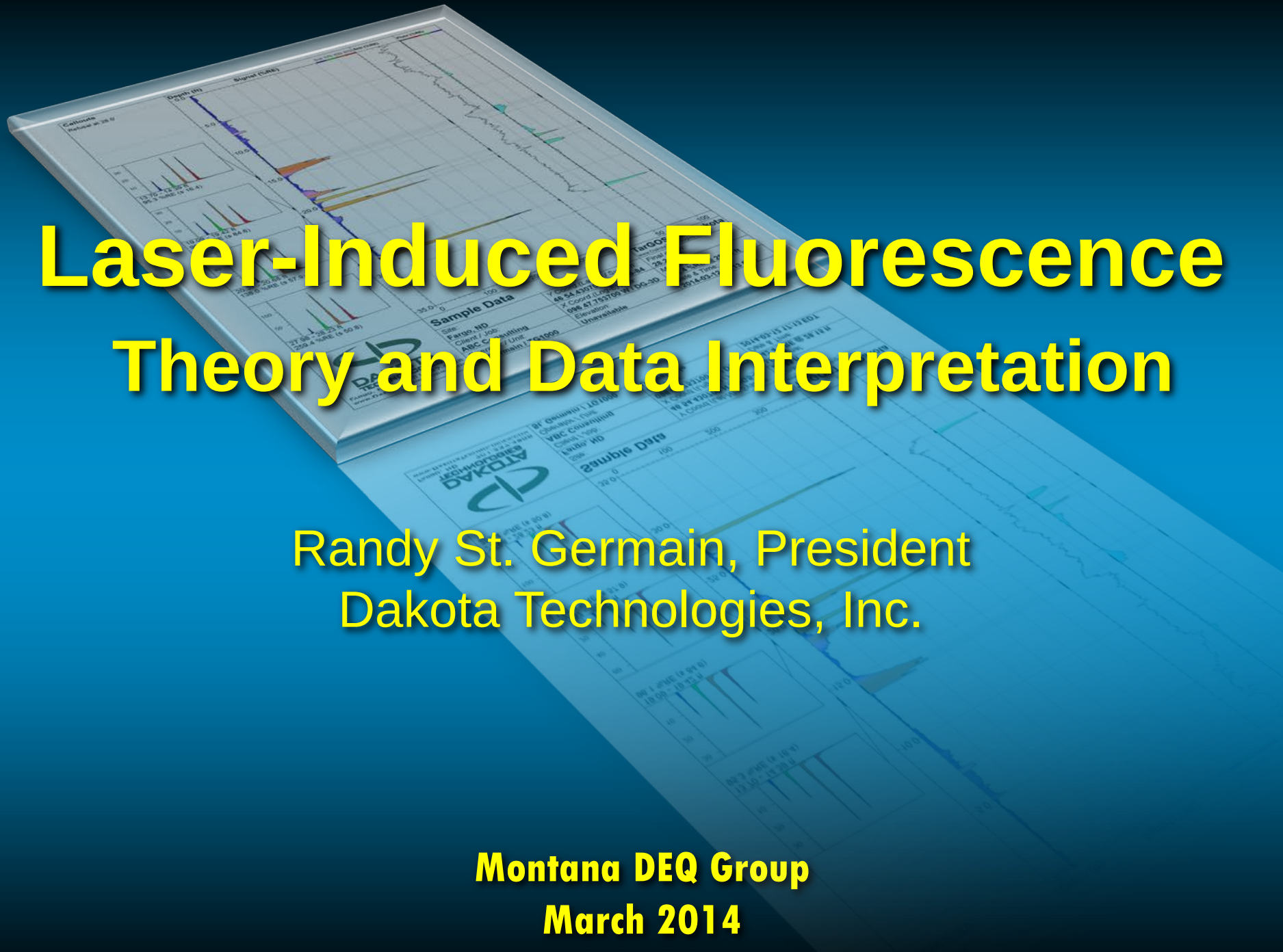


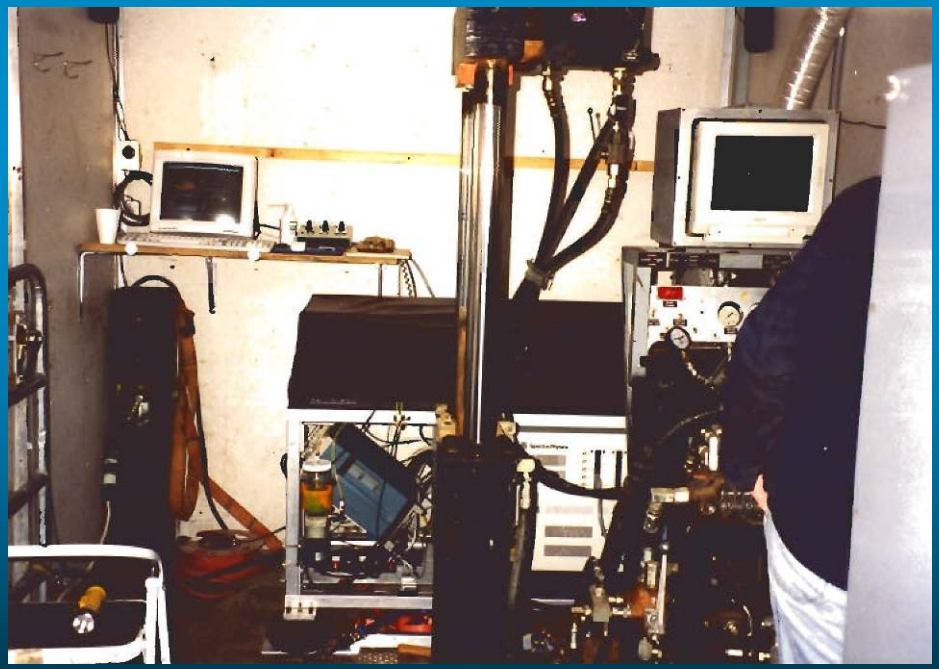
Laser-Induced Fluorescence
Theory and Data Interpretation

Randy St. Germain, President
Dakota Technologies, Inc.

Montana DEQ Group
March 2014

laser-induced fluorescence (LIF)

the people at Dakota Technologies have been making LIF measurements of PAHs for over 25 years and doing direct push LIF for fuels/oils for over 20 years



ROST Prototype circa 1991

UVOST 2007

LIF History

U.S. Army Corps of Engineers Patents Sapphire Window Concept

1992

Dakota, Hogentogler, Unisys Develop Rapid Optical Screening Tool (ROST)

1993

1994

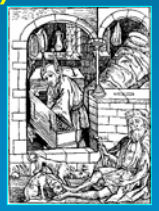
Dakota Technologies Incorporates

Dakota Develops Percussion-Capable Probe (SPOC)

1996

Lockheed Martin sells ROST Fleet to Fugro Geosciences

1997



1998

Dakota Technologies First Provides Regional "ROST" Service

"Dark Ages"

2003

Dakota Technologies Introduces TarGOST Service

2006

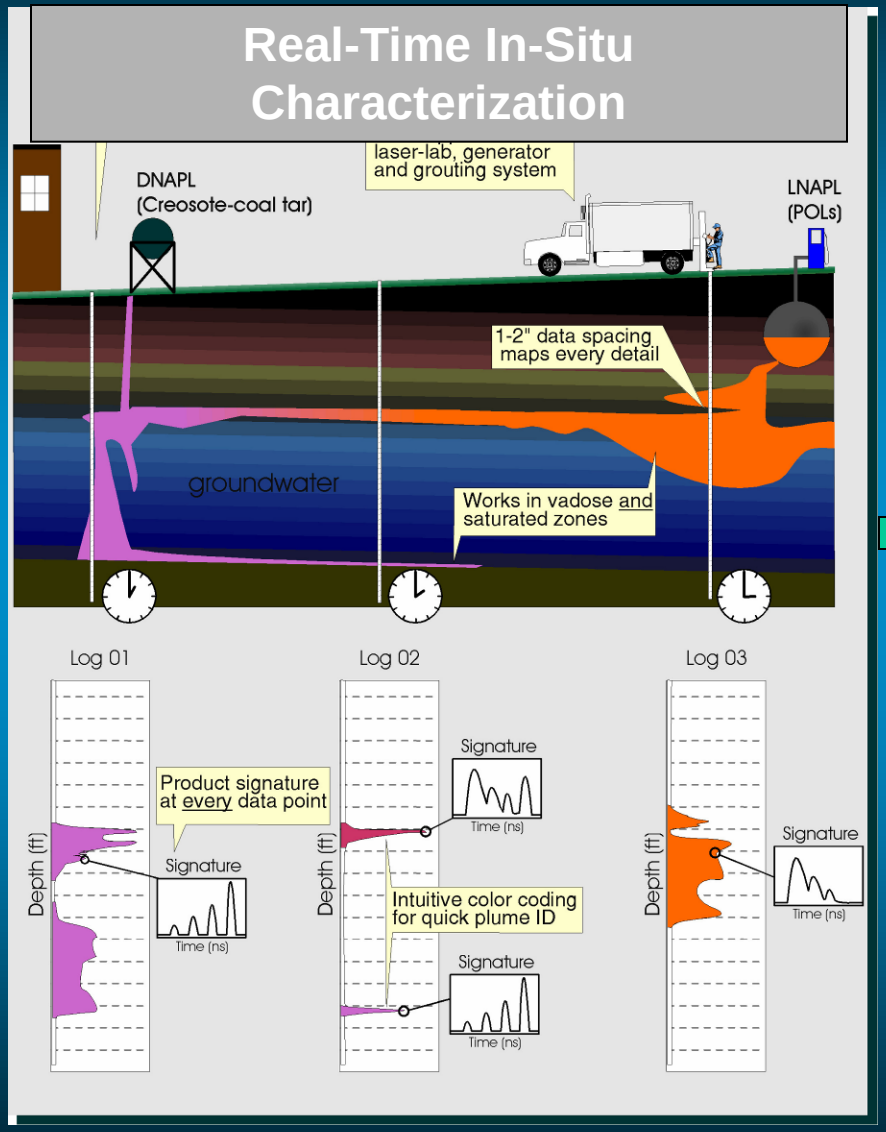
Dakota Technologies Introduces UVOST

2007

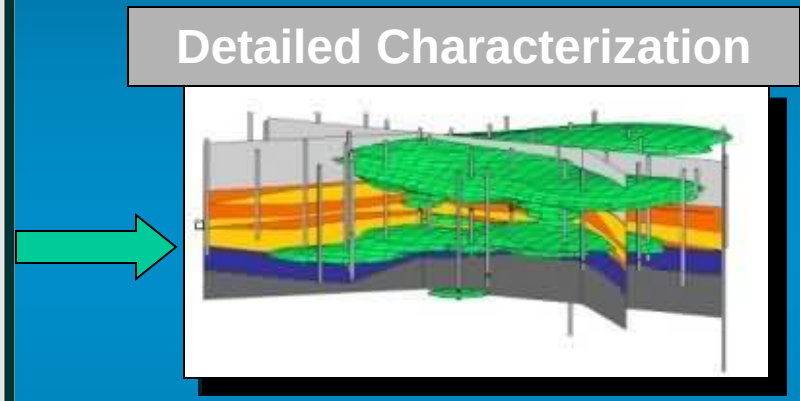
Dakota Secures U.S. ACE Sapphire Window Sub-License

DAKOTA TECHNOLOGIES

LIF Method

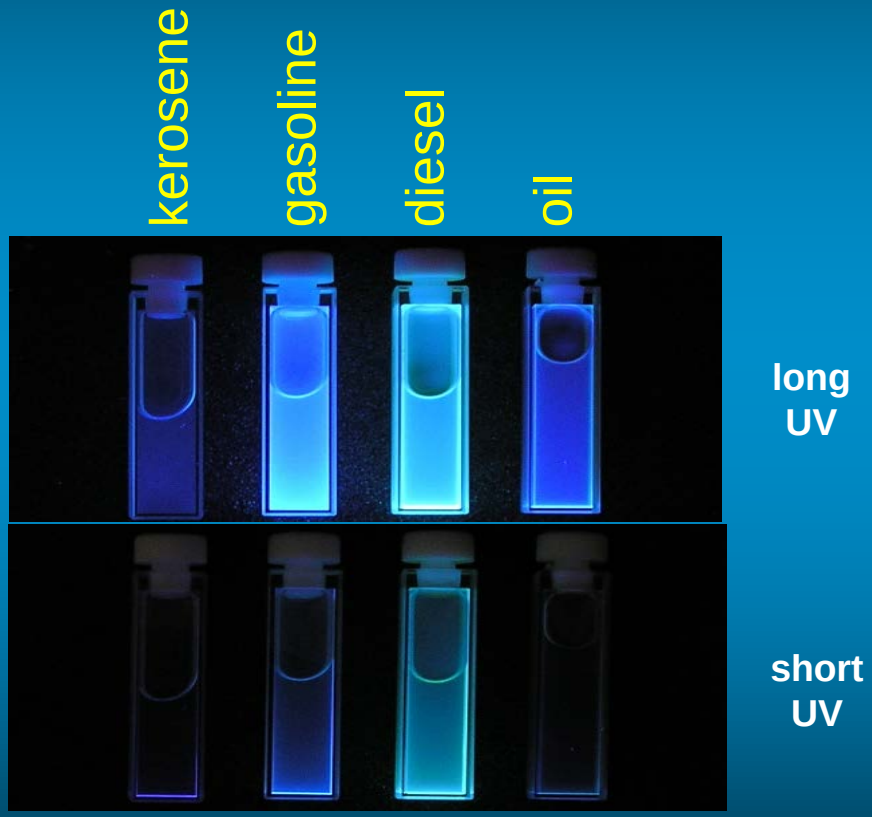


Desired Result



fortunately all non-aqueous phase liquids (NAPLs)
that contain polycyclic aromatic hydrocarbons (PAHs),
even small amounts (<1%), will fluoresce

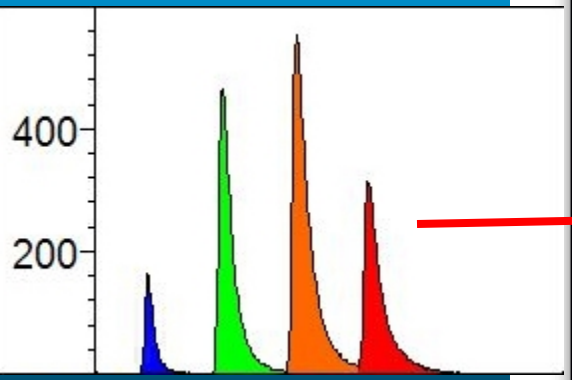
in this way we can usually detect them by their fluorescent “glow”

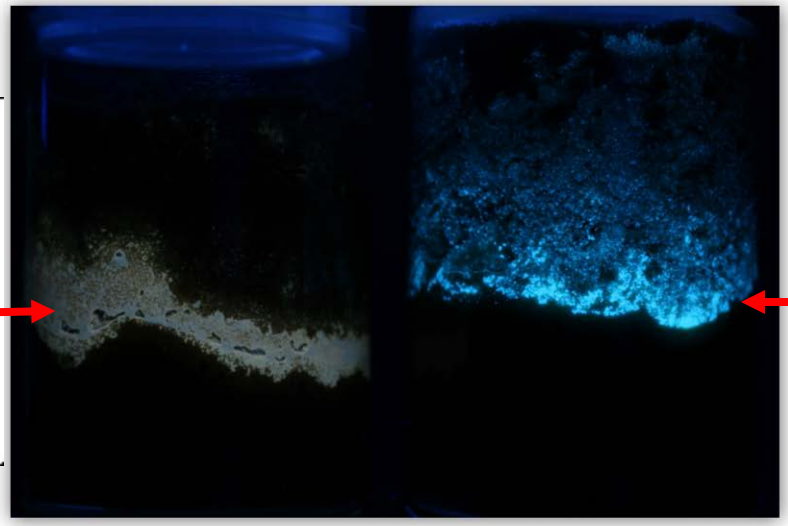


fluorescence

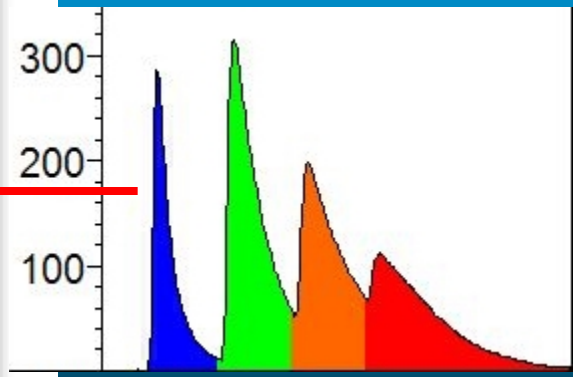
crude oil **diesel**

what UVOST “sees”





what UVOST “sees”



basics of Optical Screening Tools…

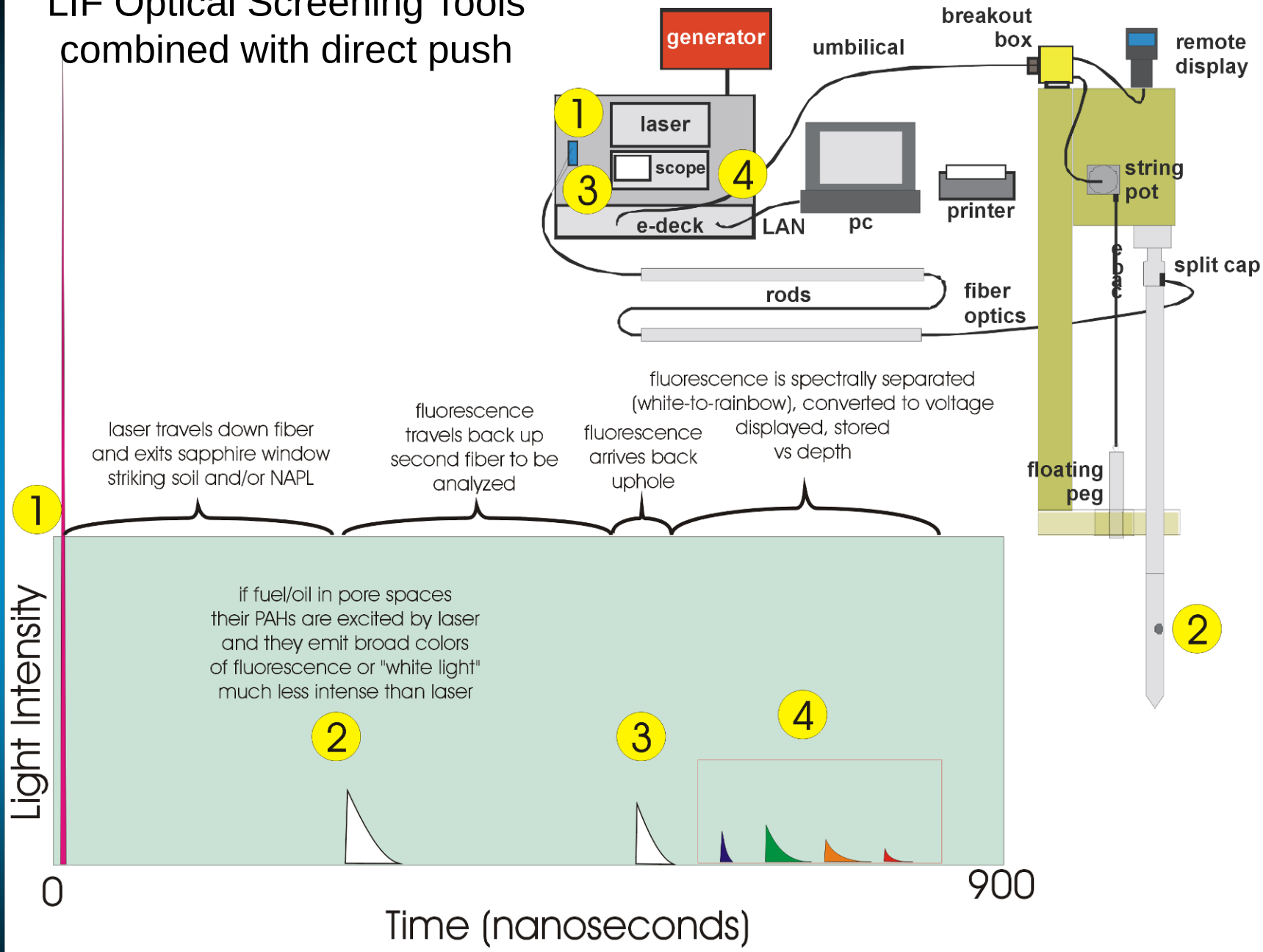
- spectroscopic (light-based)
- sapphire-windowed probe head requires “direct push” delivery
  - dynamic (Geoprobe®/AMS)
  - static (CPT)
- log fluorescence of a fuel’s/oil’s PAHs vs. depth during penetration
- measurement penetrates into the formation only as deep as light can (not very deep!)

windowed probe - percussion

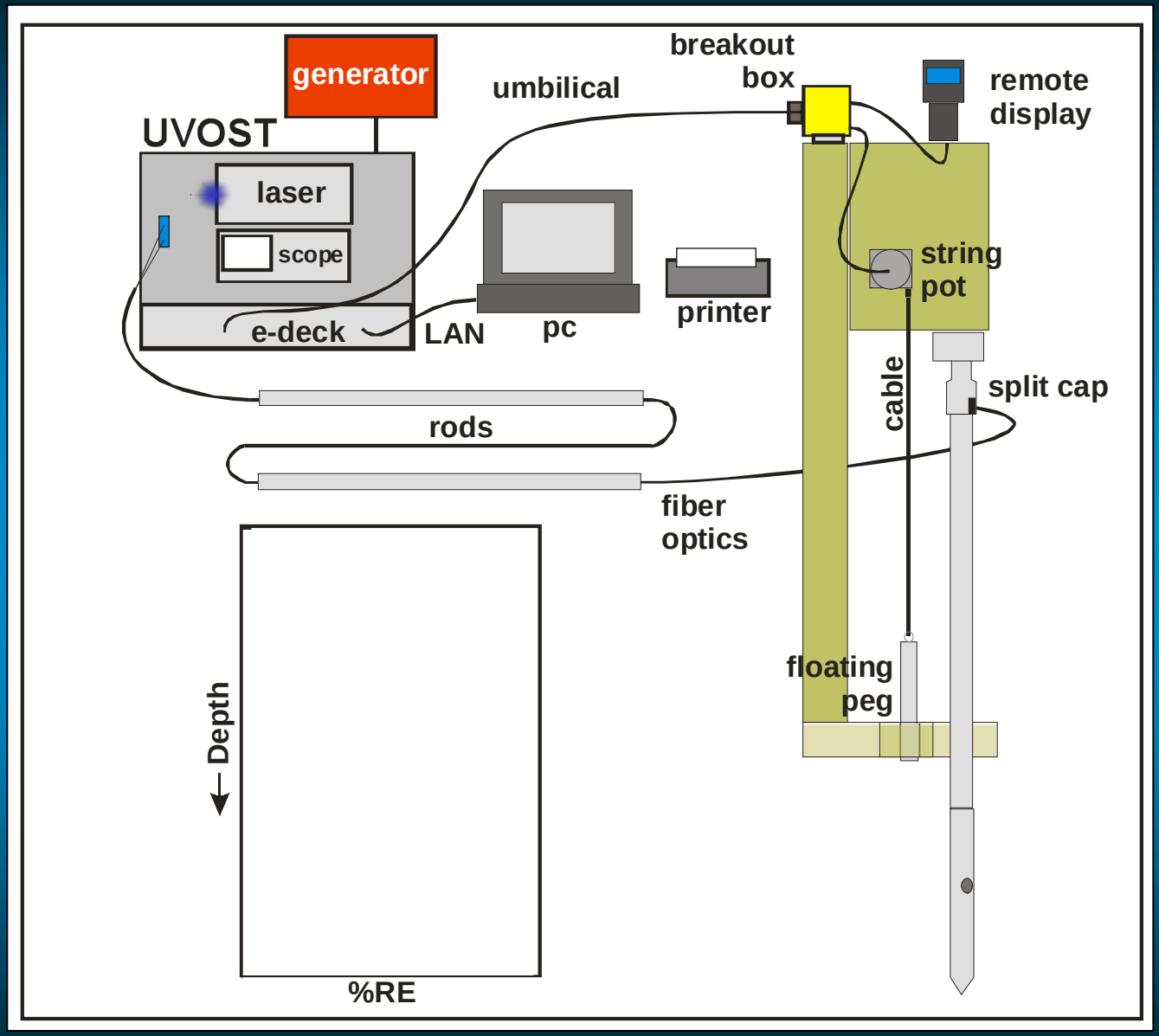
windowed probe – submerged derrick

windowed CPT “sub” above CPT

LIF Optical Screening Tools combined with direct push



LIF Optical Screening Tools and direct push



OSTs are deployable under wide variety of platforms and conditions

- Geoprobe®, PowerProbe, CPT, even drill rigs (in soft materials)
- on-shore, off-shore, ice, bogs, sediments, tar pits, settling ponds
- rain, snow, sleet, sun, wind, hot, cold… with “100 % recovery”

UV LIF (this training's focus) detects…

almost any other PAH-containing NAPL like:

Reliably

- Gasoline (highly weathered and aviation yield is very low)
- Diesel
- Jet (Kerosene)
- Motor Oil
- Cutting Fluids
- Hydraulic Fluid
- Crude oil
- Fuel oils

Occasionally (but NOT predictable enough to employ UVOST with any confidence!)

- Coal Tar (MGP waste) – often poor due to self-quenching/energy transfer
- Creosote/Pentachlorophenol (wood treating) – often poor due to self-quenching/energy transfer
- Bunker – often poor due to self-quenching/energy transfer

Never/Rarely

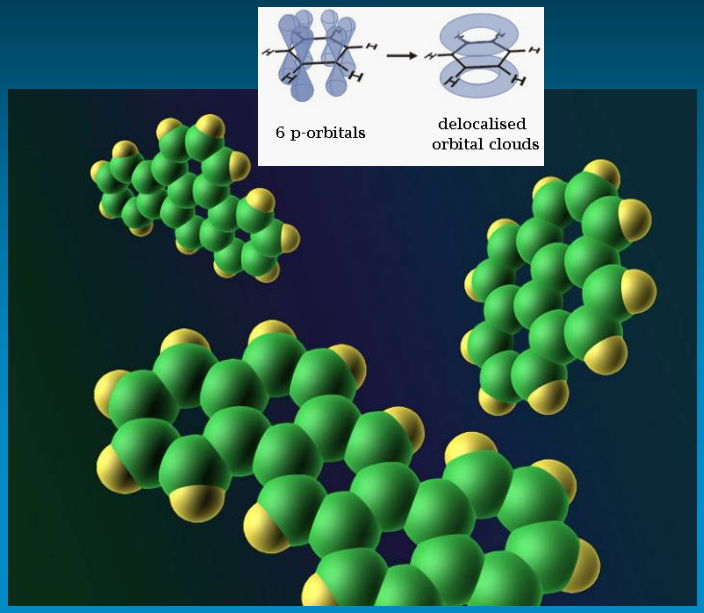
- polychlorinated bi-phenyls (PCB)s – due to internal heavy atom effect
- chlorinated solvent DNAPL – aliphatics lack aromaticity (no ring-shapes) - but co-solvated PAHS can/do respond
- dissolved phase PAHs

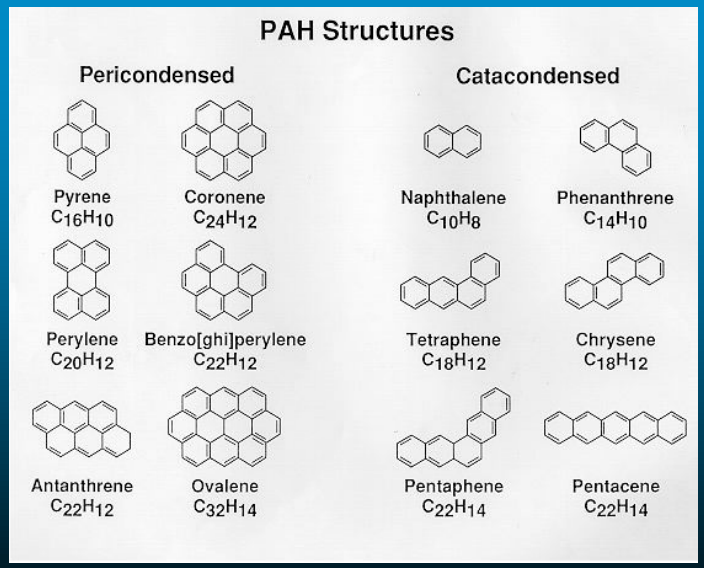
The Spectroscopy Behind LIF

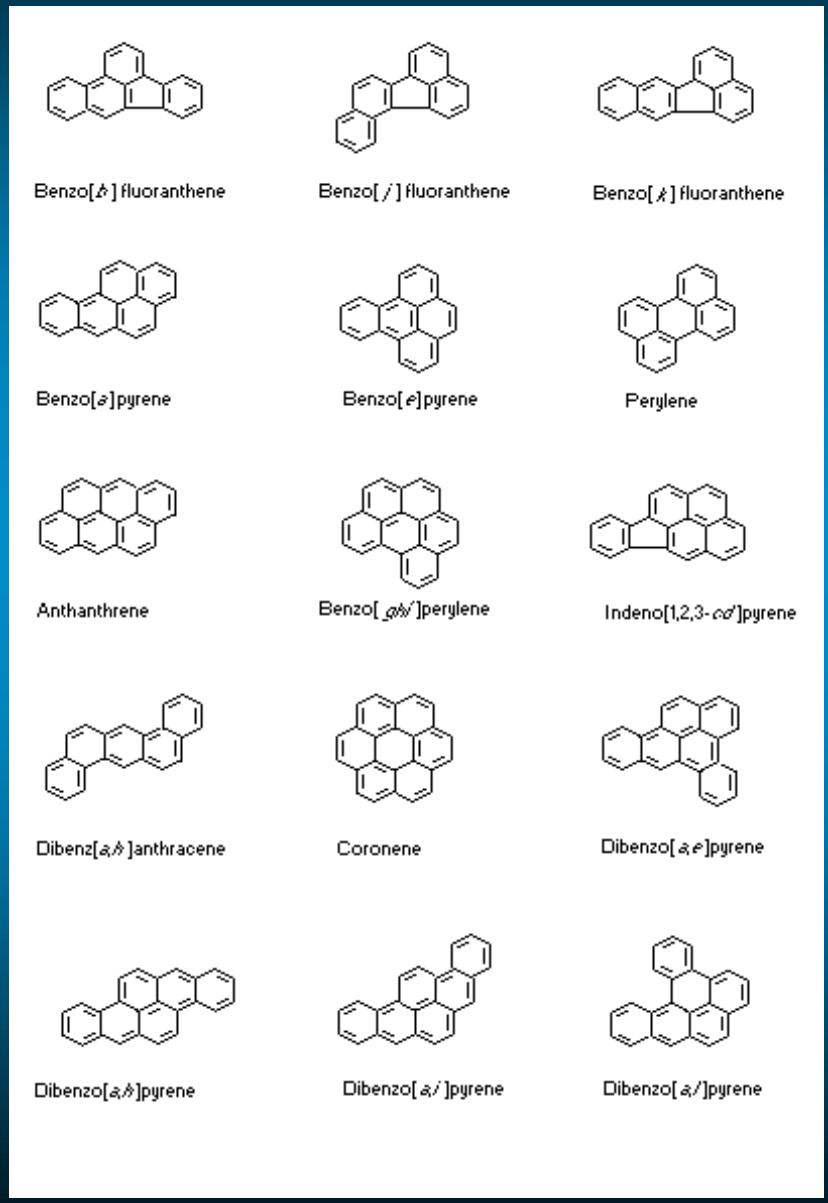
the nature of the molecules that fluoresce and non-aqueous phase liquids (NAPL) in which they dwell

structure of aromatics allows fluorescence

one or more “benzene” rings - planar sets of six carbon atoms that are connected by delocalized electrons







fluorescence spectroscopy

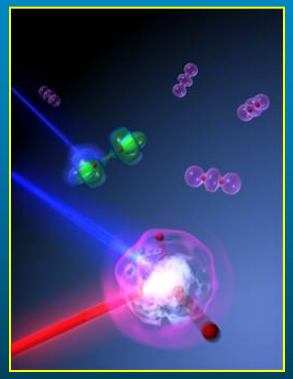
spectroscopy – study the interaction of light with matter

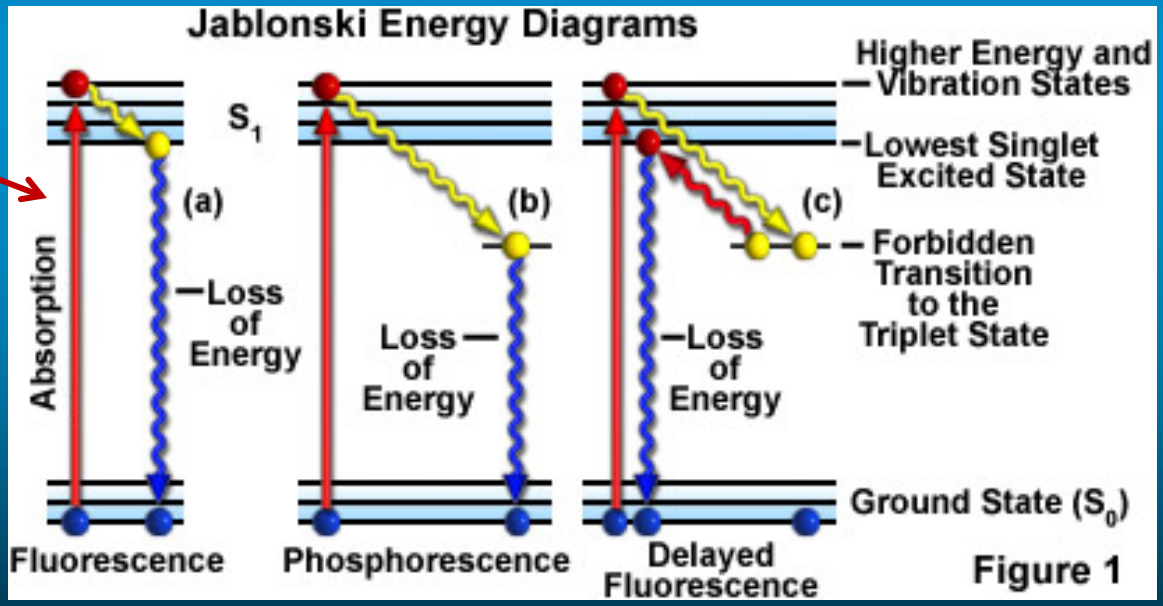
fancy quantum mechanics "stuff" determines behavior
molecules absorb light and excites an electron
later the molecule might "shed" that energy by emitting light

aromatic (ring-shaped) molecules excel at this

energy (wavelength/frequency/wavenumber) of each photon emitted depends on which energy level it was at prior to "launch" of a photon

~1 femtosecond (0.000000000000001 seconds) to occur!



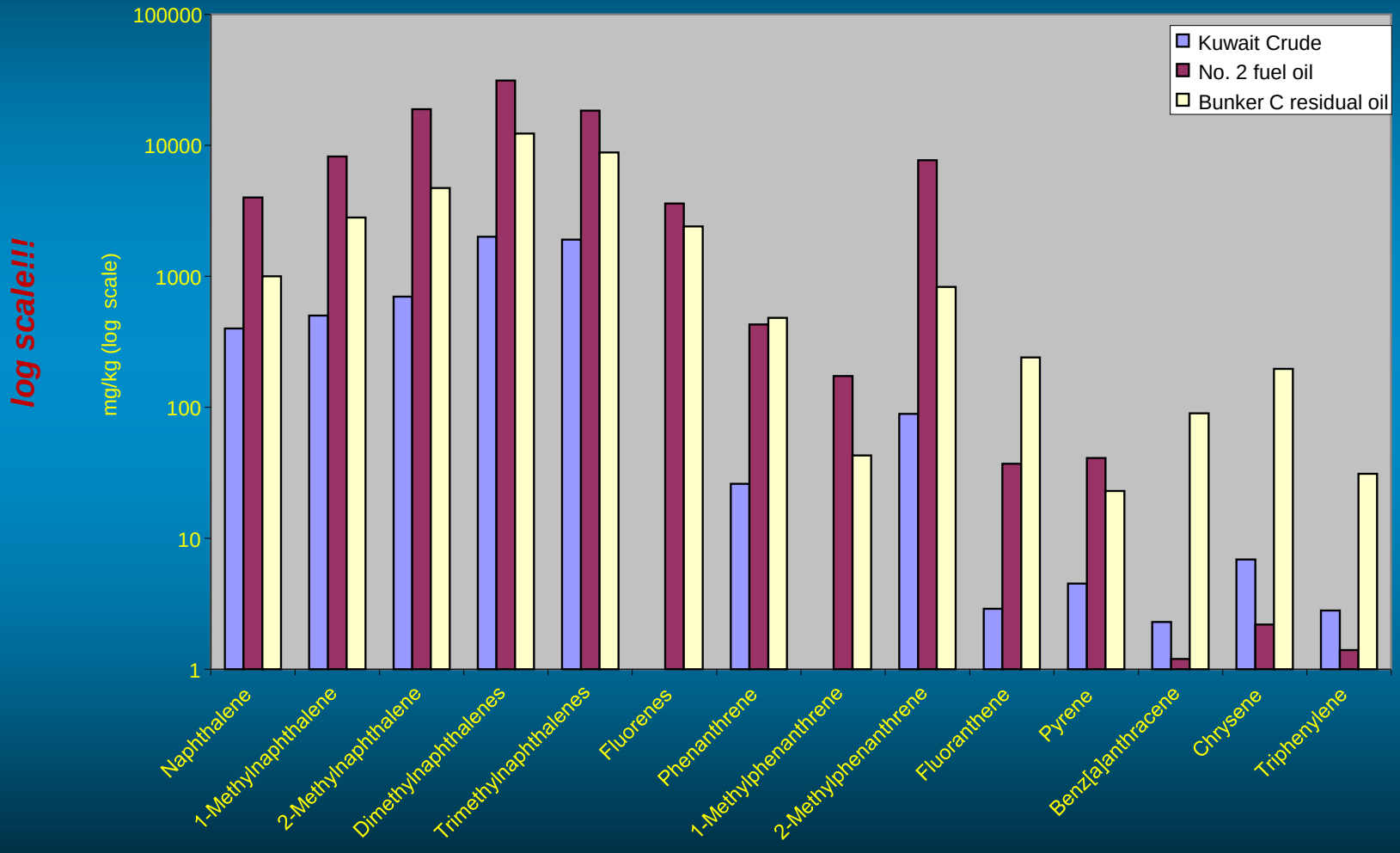


note to "brainiacs": purchase Joseph R. Lakowicz' "**Principles of Fluorescence Spectroscopy**", 3rd Edition

this temporal LIF stuff is FAST!

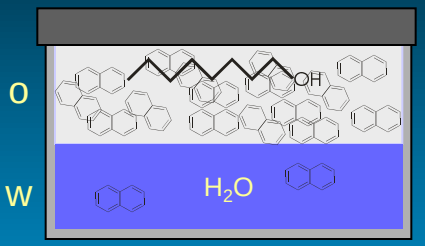
Transition	Time Scale	Radiative Process?
Absorption	10^{-15} s	yes
Internal Conversion	10^{-14} - 10^{-11} s	no
Vibrational Relaxation	10^{-14} - 10^{-11} s	no
Fluorescence	10^{-9} - 10^{-7} s	yes
Intersystem Crossing	10^{-8} - 10^{-3} s	no
Phosphorescence	10^{-4} - 10^{-1} s	yes

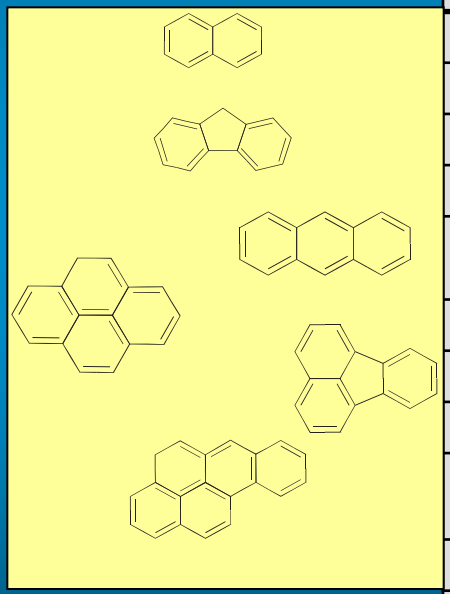
fuels/oils are complex mixtures containing dozens or hundreds of various PAHs dissolved in many non-fluorescent solvent molecules



PAHs want to be in organic solvent much more so than groundwater

size and degree of substitution determine preferential solubility behavior
this is why NAPL is the “source term” of dissolved phase (and a dermal hazard)



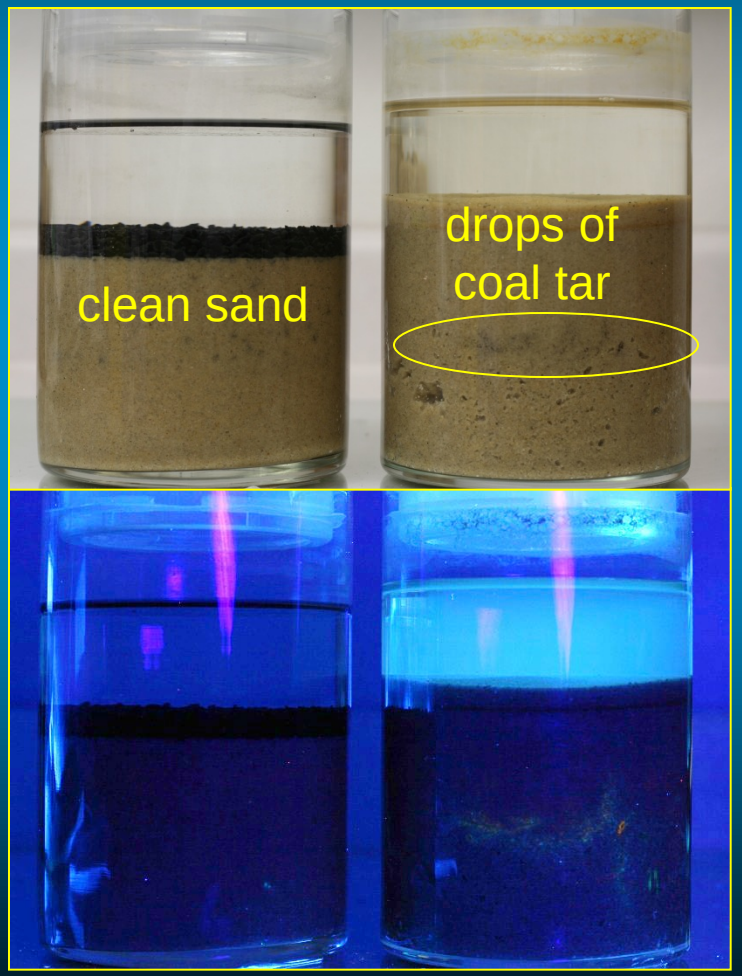


octanol – a straight chain fatty alcohol with eight carbon atoms

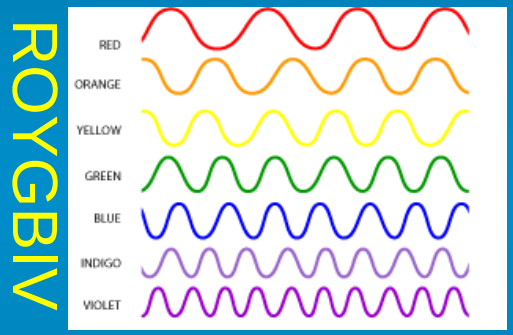
Compound (C.A.S.N°)		Molecular weight	Kow 125 to 1250	log Kow	Water solubility at 25°C (mg/L) B = 1780 T = 535 E = 161 X = 150
naphthalene (91-20-3)	1	128.16	3,162	3.5	31.7
acenaphthene (83-32-9)	1	154.21	19,952	4.33	3.42
fluorene (86-73-7)	1	166	15,136	4.18	1.98
phenanthrene (85-01-8)	1	178.24	31,623	4.5	1.29
anthracene (120-12-7)	1	178.24	31,623	4.5	0.045
pyrene (129-00-0)	1	202.26	79,433	4.9	0.135
fluoranthene (206-44-0)	1	202.26	125,893	5.1	0.26
benz[a]anthracene (56-66-3)	1	228	398,107	5.6	0.0057
benz[a]pyrene (50-32-8)	1, 2	252.32	1,000,000	6.0	0.0038
benzo[b]fluoranthene (205-99-2)	2	252.32	1,148,154	6.06	0.014
benzo[j]fluoranthene (205-82-3)	2	252.32	1,148,154	6.06	
benzo[k]fluoranthene (207-08-9)	2	252.32	1,148,154	6.06	0.0043
indeno[1,2,3-cd]pyrene (193-39-5)	2	276	2,511,886	6.4	0.00053

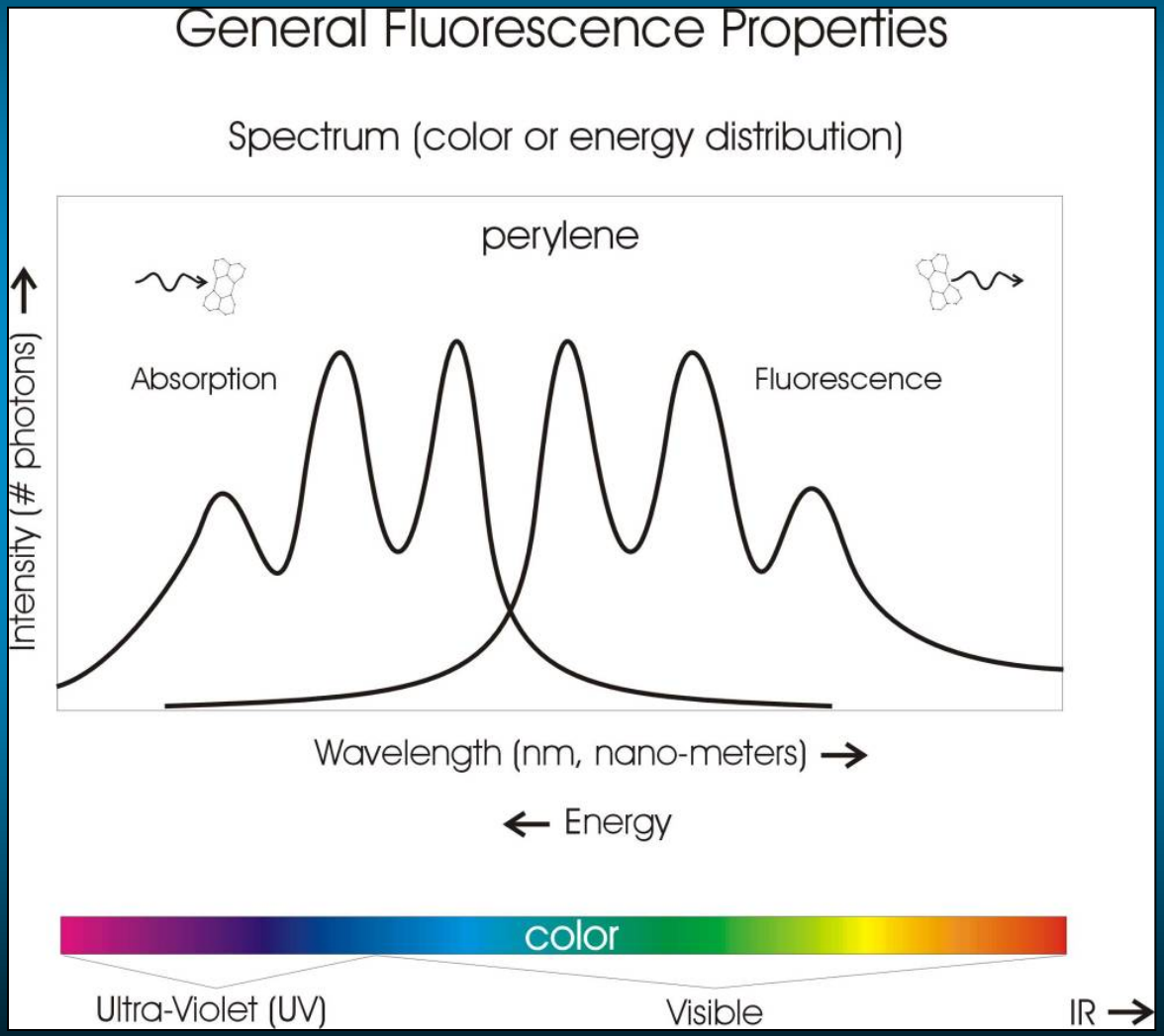
PAHs' great preference to remain in an organic solvent (vs. water) affects its chemistry and environmental behavior

- weathering
- sourcing
- recalcitrance
- analytical results
- fluorescence (PAHs need a solvent to be efficient)



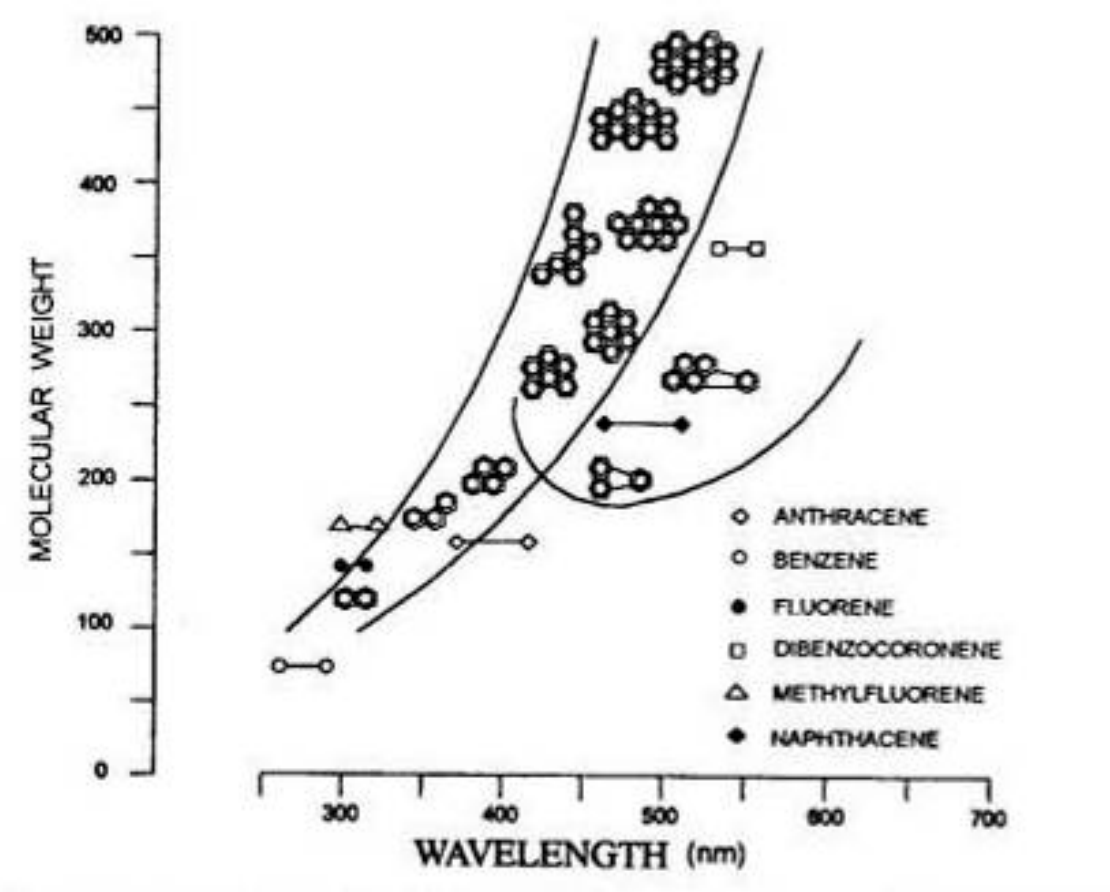
- emission spectrum is unique for each PAH
- fluorescence spectrum does not change with excitation wavelength
- the PAH has no ‘memory’ of how it got excited

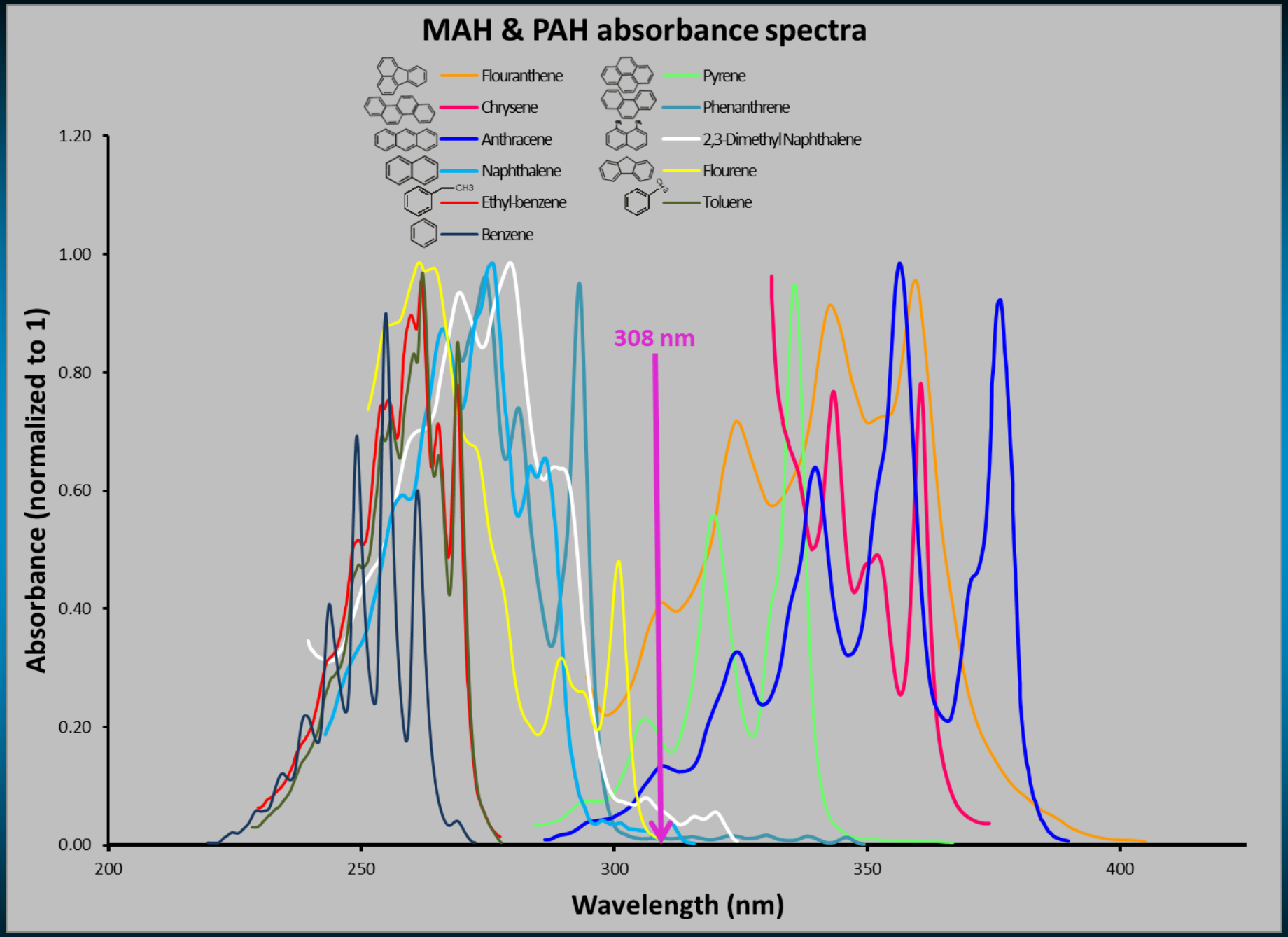


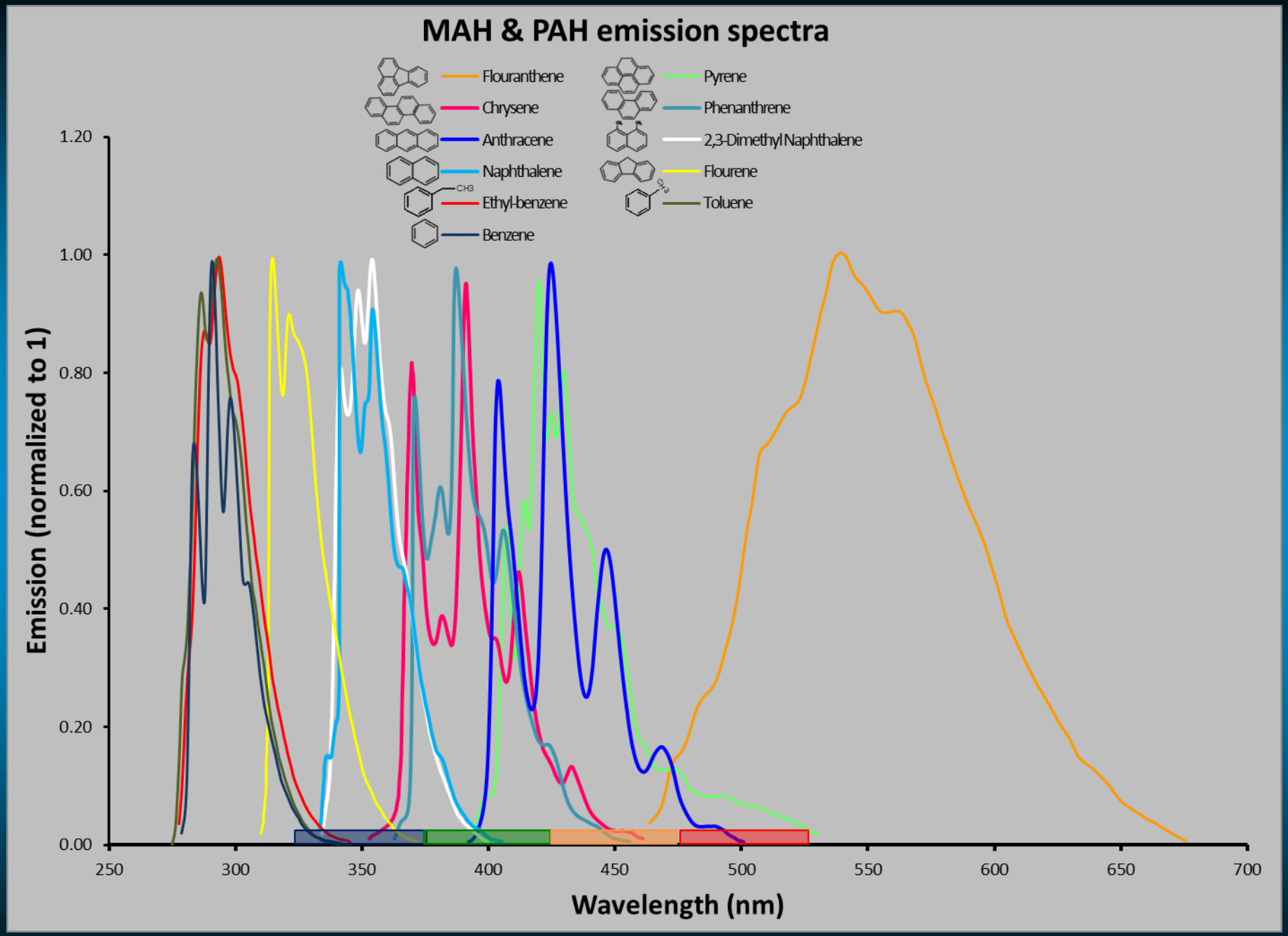


a PAH's size/structure influence the color of light it emits

generally larger (more rings) equates to longer wavelength (lower energy) light being emitted




MAH & PAH absorbance spectra
Flouranthene
Chrysene
Anthracene
Naphthalene
Ethyl-benzene
Benzene
Pyrene
Phenanthrene
2,3-Dimethyl Naphthalene
Flourene
Toluene
CH3
308 nm
Absorbance (normalized to 1)
1.20
1.00
0.80
0.60
0.40
0.20
0.00
200
250
300
350
400
Wavelength (nm)


MAH & PAH emission spectra
Flouranthene
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Pyrene
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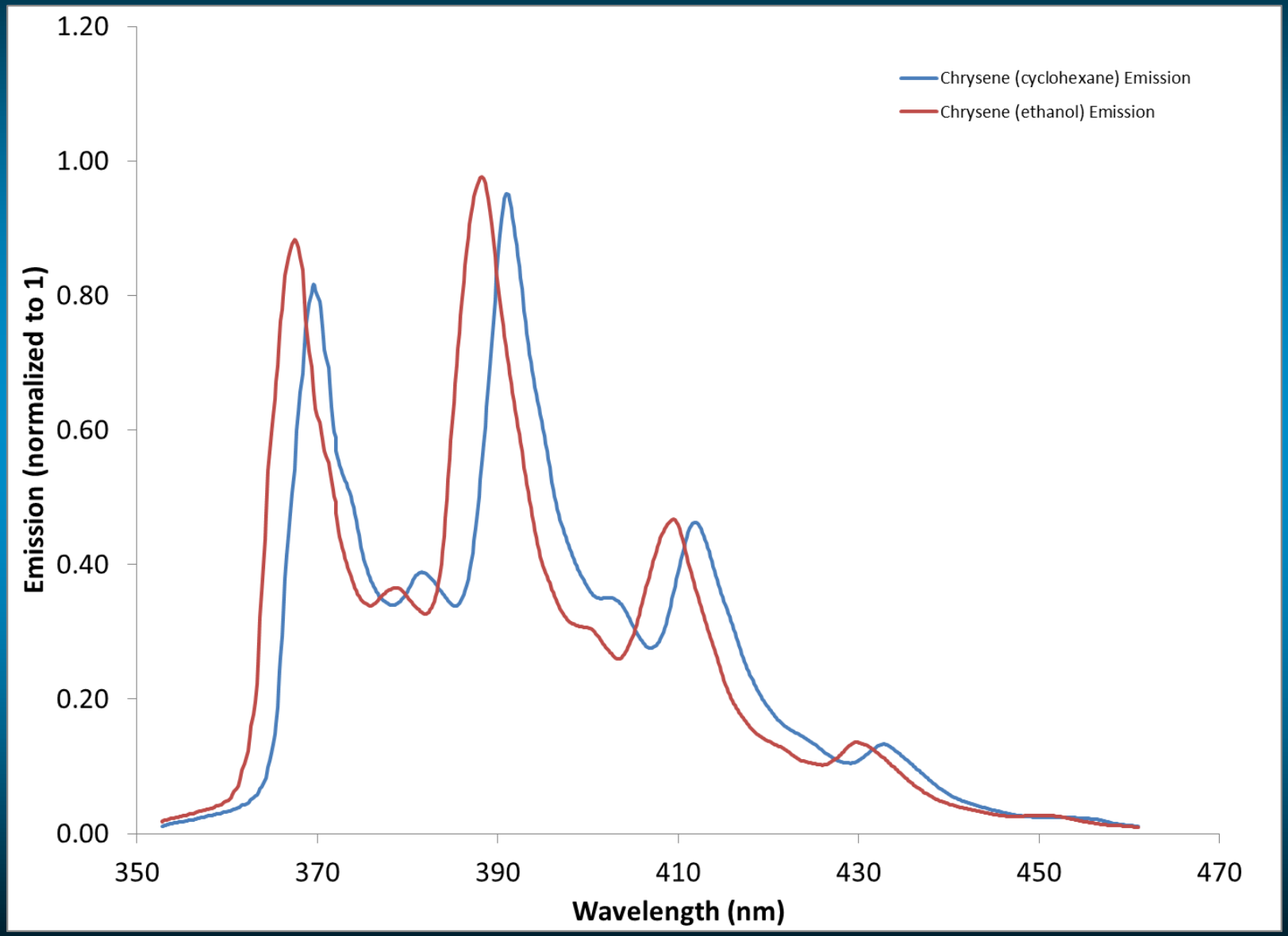
2,3-Dimethyl Naphthalene
Flourene
Toluene
Emission (normalized to 1)
Wavelength (nm)
0.00
0.20
0.40
0.60
0.80
1.00
1.20
250
300
350
400
450
500
550
600
650
700

careful…even the solvent used can shift the emission wavelengths
as you can see there are lots of players and lots of complications in petro fluorescence
fuels are a big mess of dozens or hundreds of these PAHs and solvent issues all mixed together

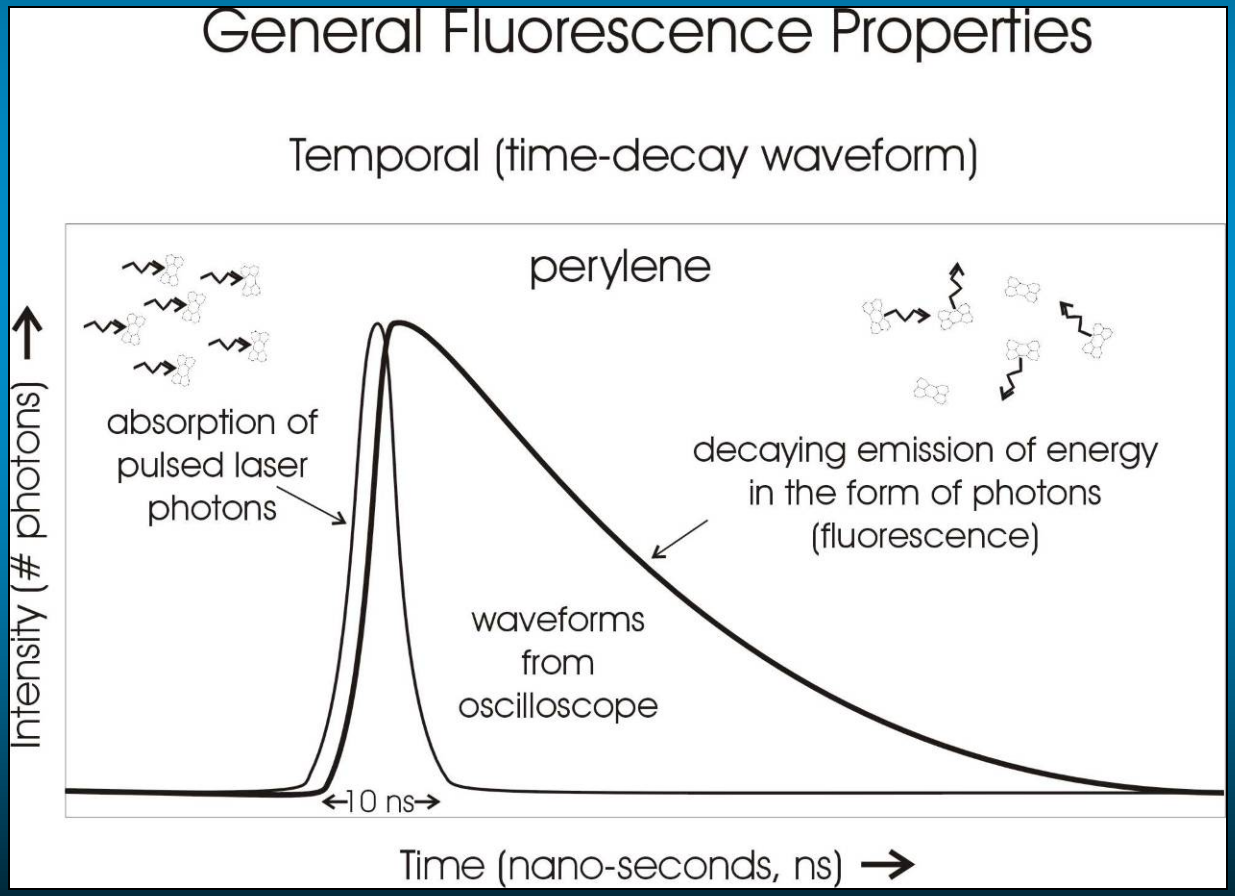


lifetime or fluorescence decay

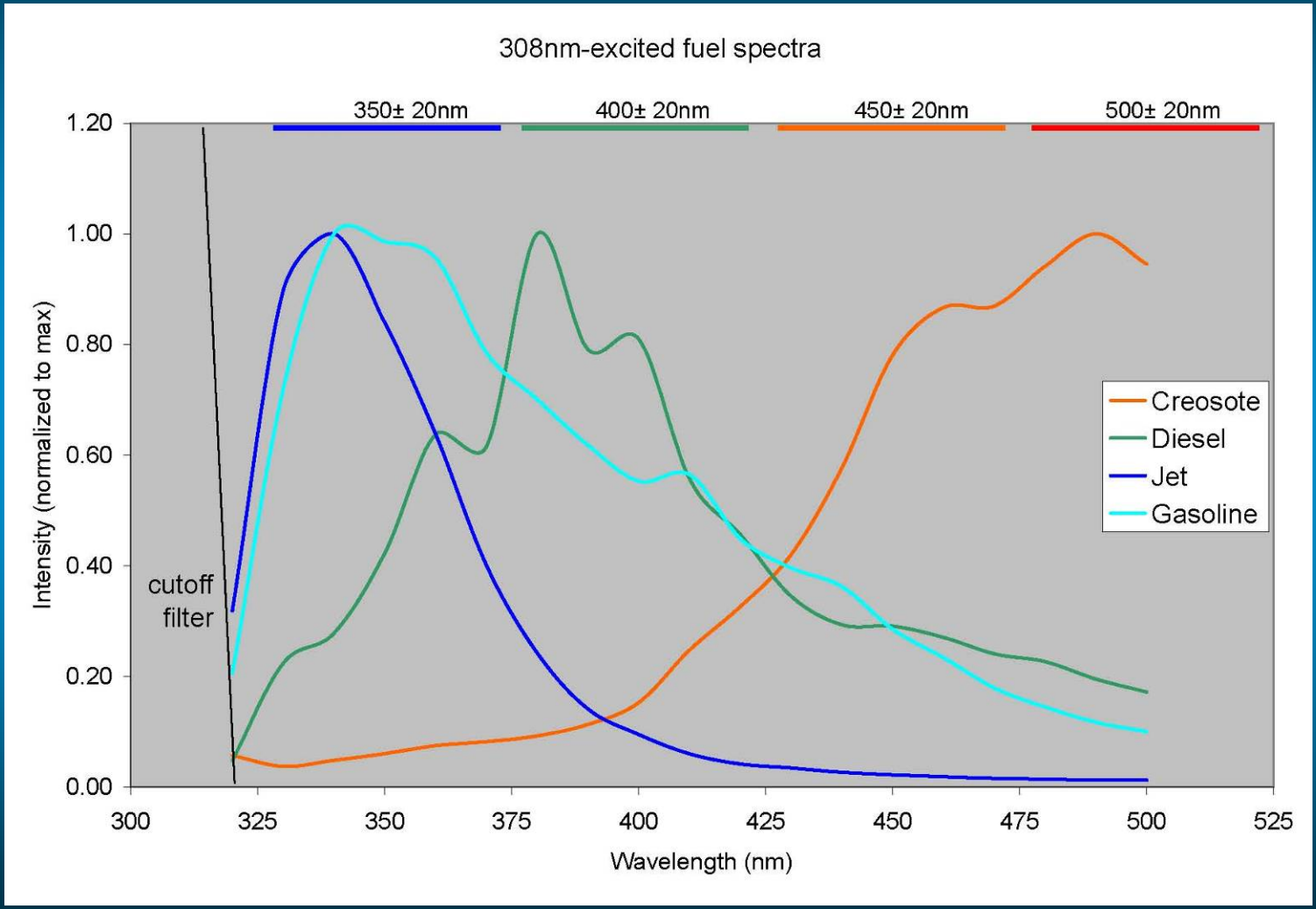
fluorescence dies away with time after being pulsed

this is called the fluorescence lifetime (Greek symbol τ or "tau")

it is the time it takes for 1/e of the population of excited PAH molecules to return to their electronic ground state by fluorescing or otherwise "shedding" the absorbed photon's energy



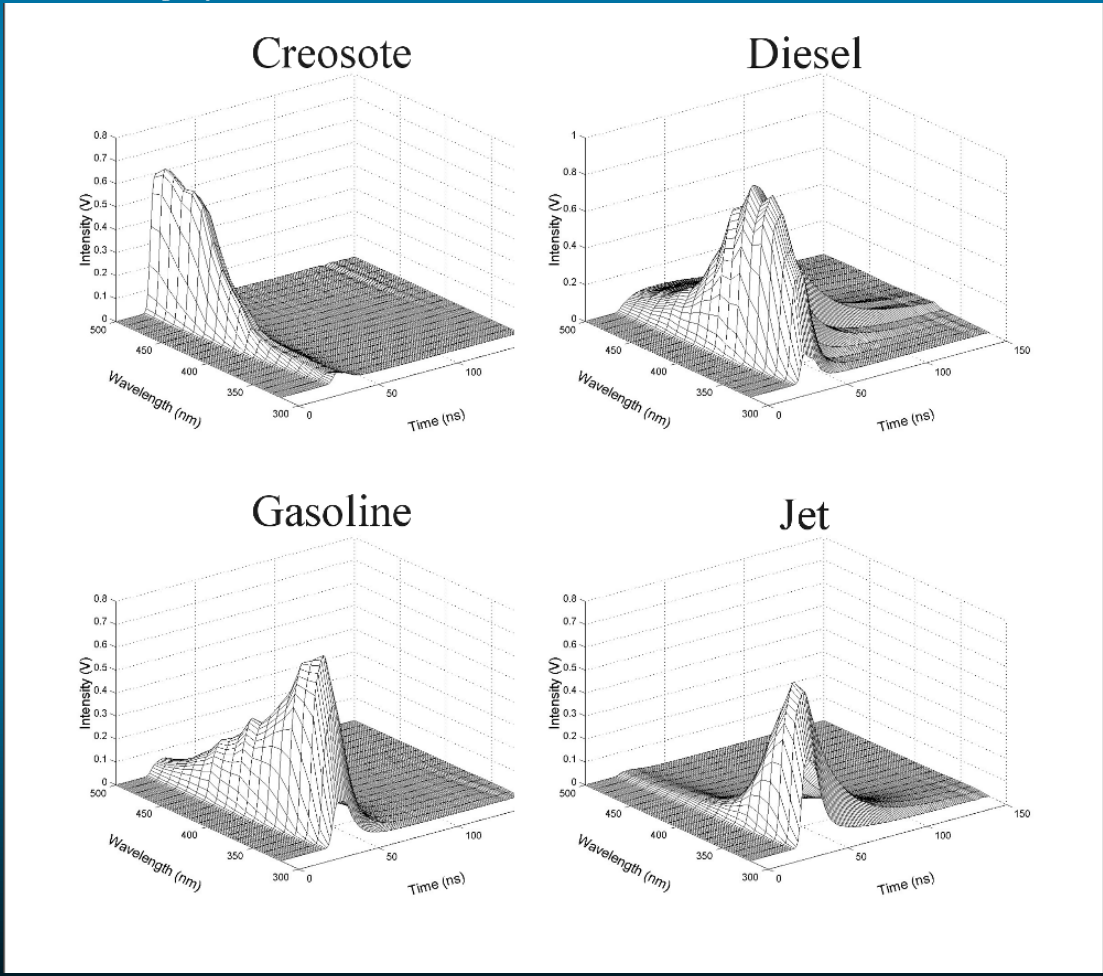
UVOST emission spectra for typical fuels
(note the spacing of your UVOST's filters!)



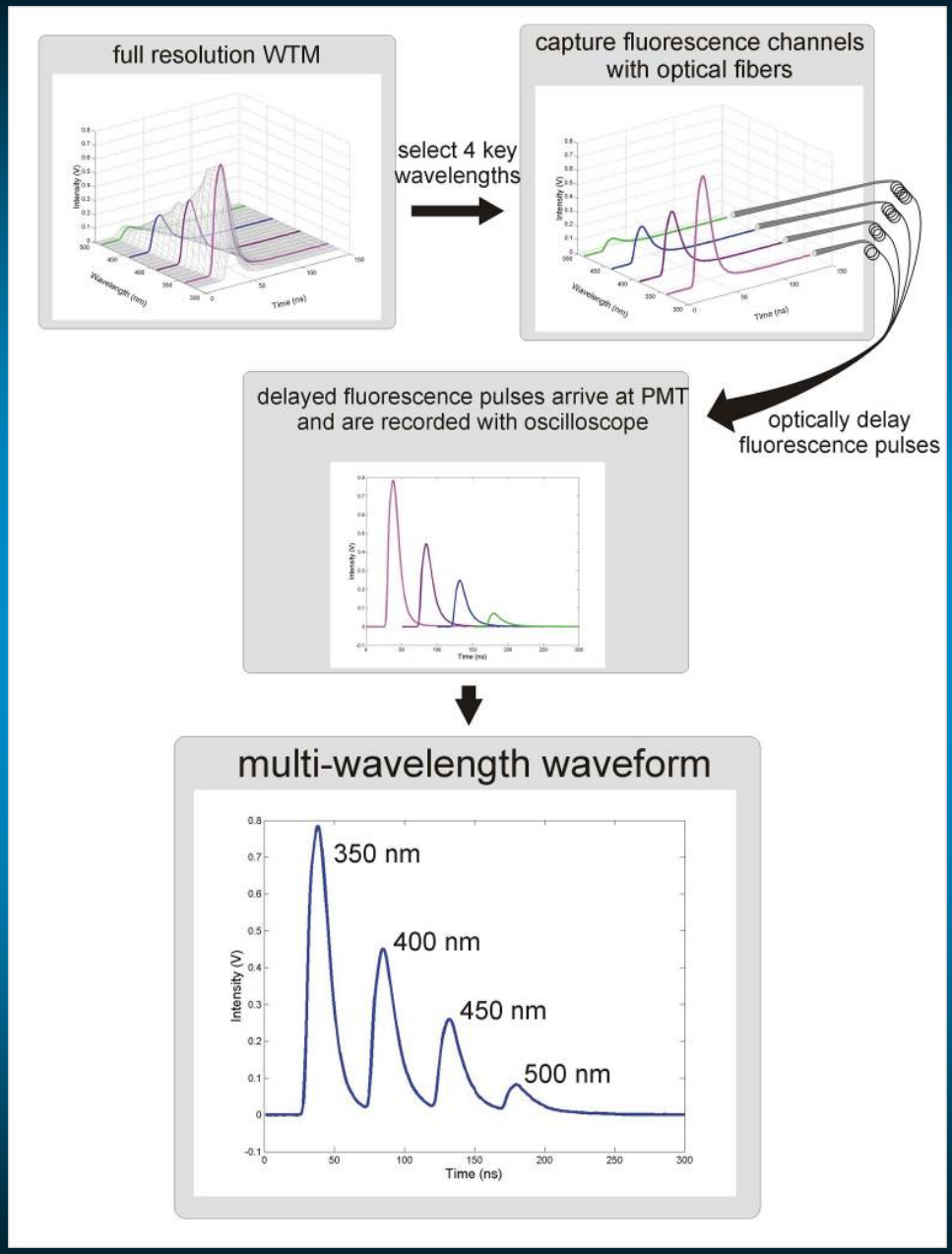
wavelength-time matrices of fuels

each mix of PAHs (and their aliphatic solvent, oxygen concentration, matrix, etc.) yield a fairly unique wavelength/time matrix or WTM

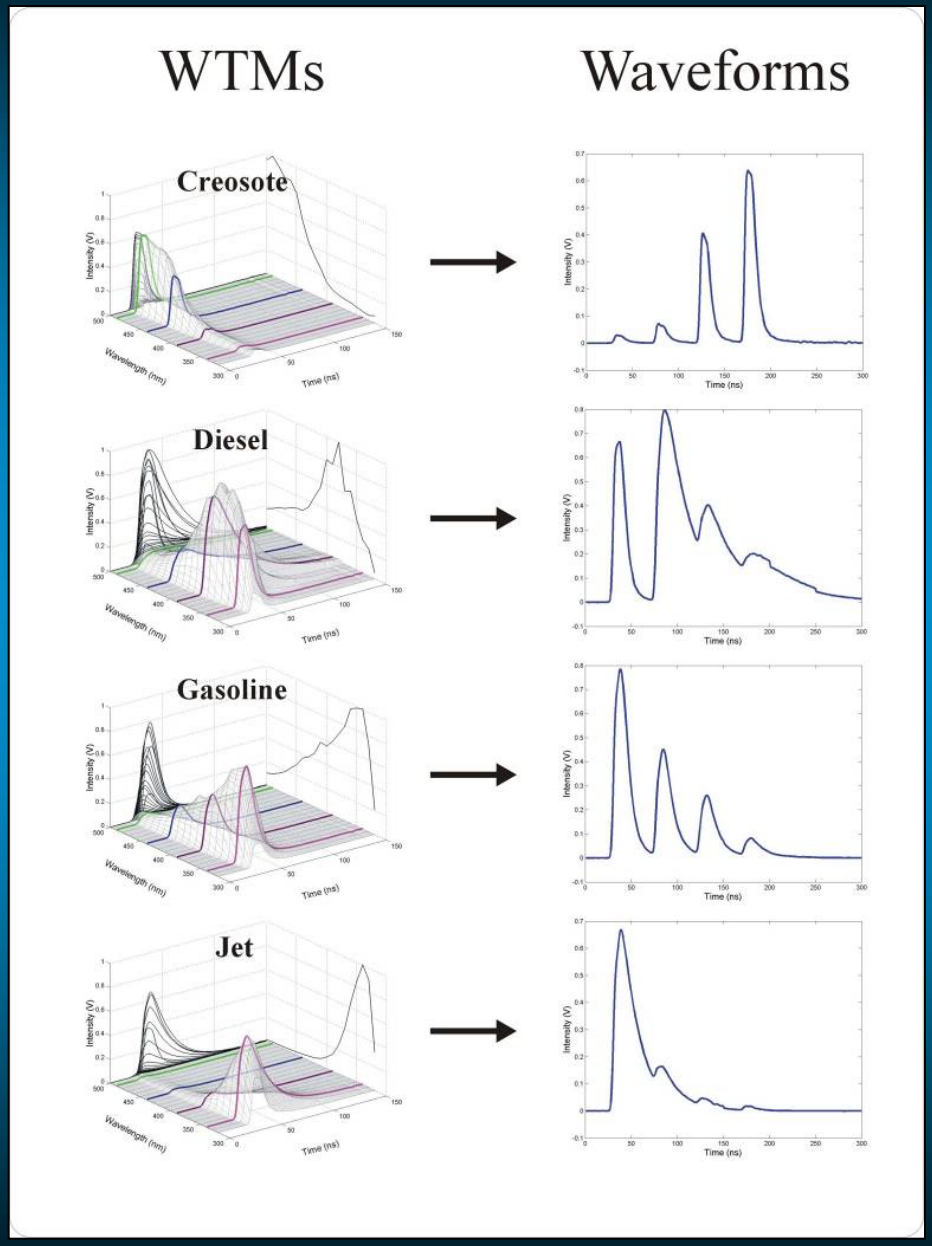
- fuels/oils have a “characteristic” WTM
- most fuel types look similar to each other under “normal” conditions
- so identifying fuels/oils as this or that is usually straightforward
- kerosene (jet) looks like other kerosene, diesel like other diesel, etc.



multi-wavelength waveforms – how UVOST acquires WTMS really really really fast!

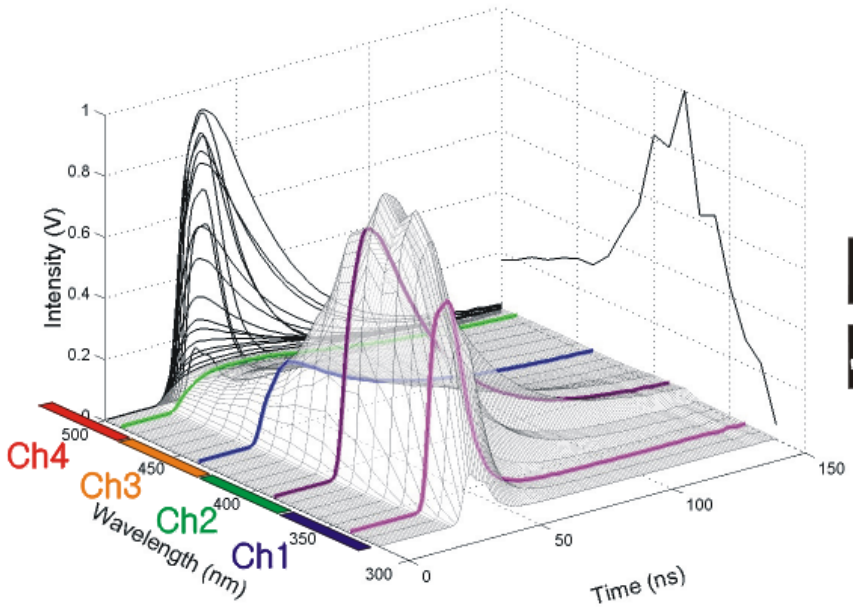


multi-wavelength waveforms



multi-wavelength waveforms
OSTs create “shorthand” version of WTMs

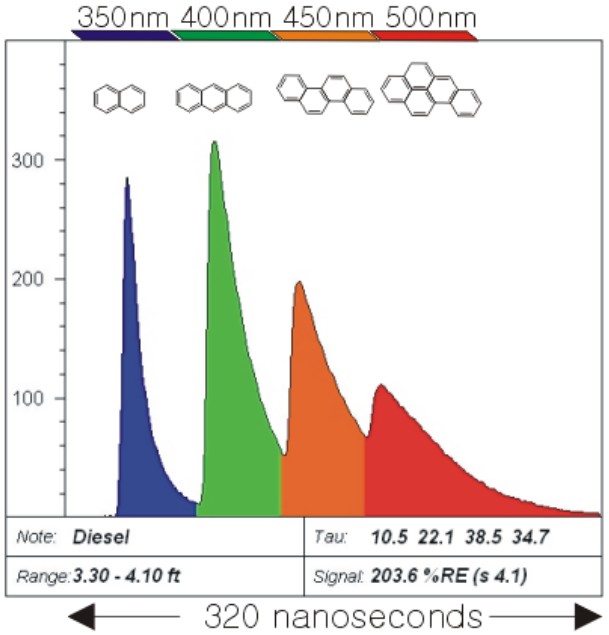
3D illustration of diesel's fluorescence emission



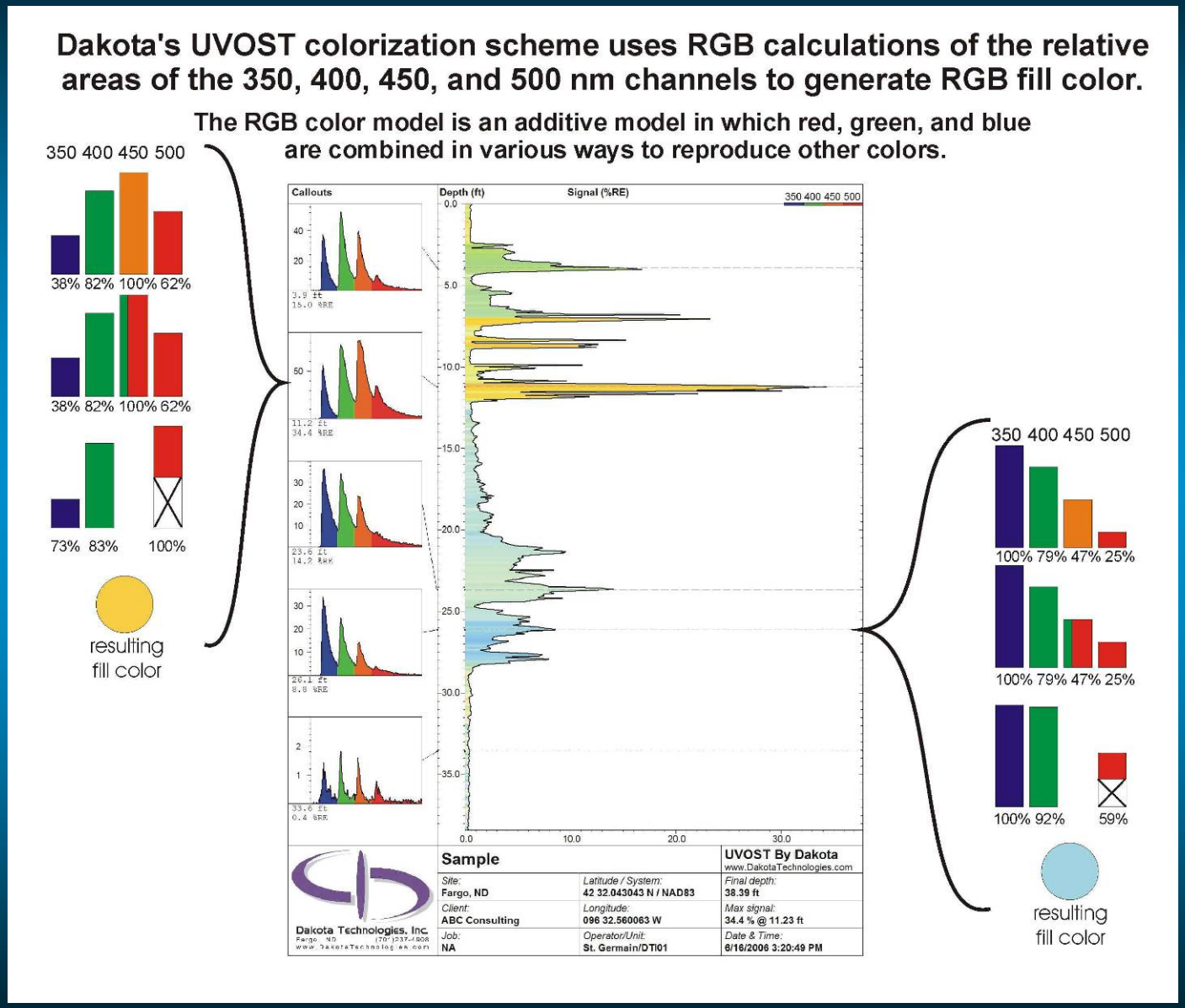
OST

"black box"

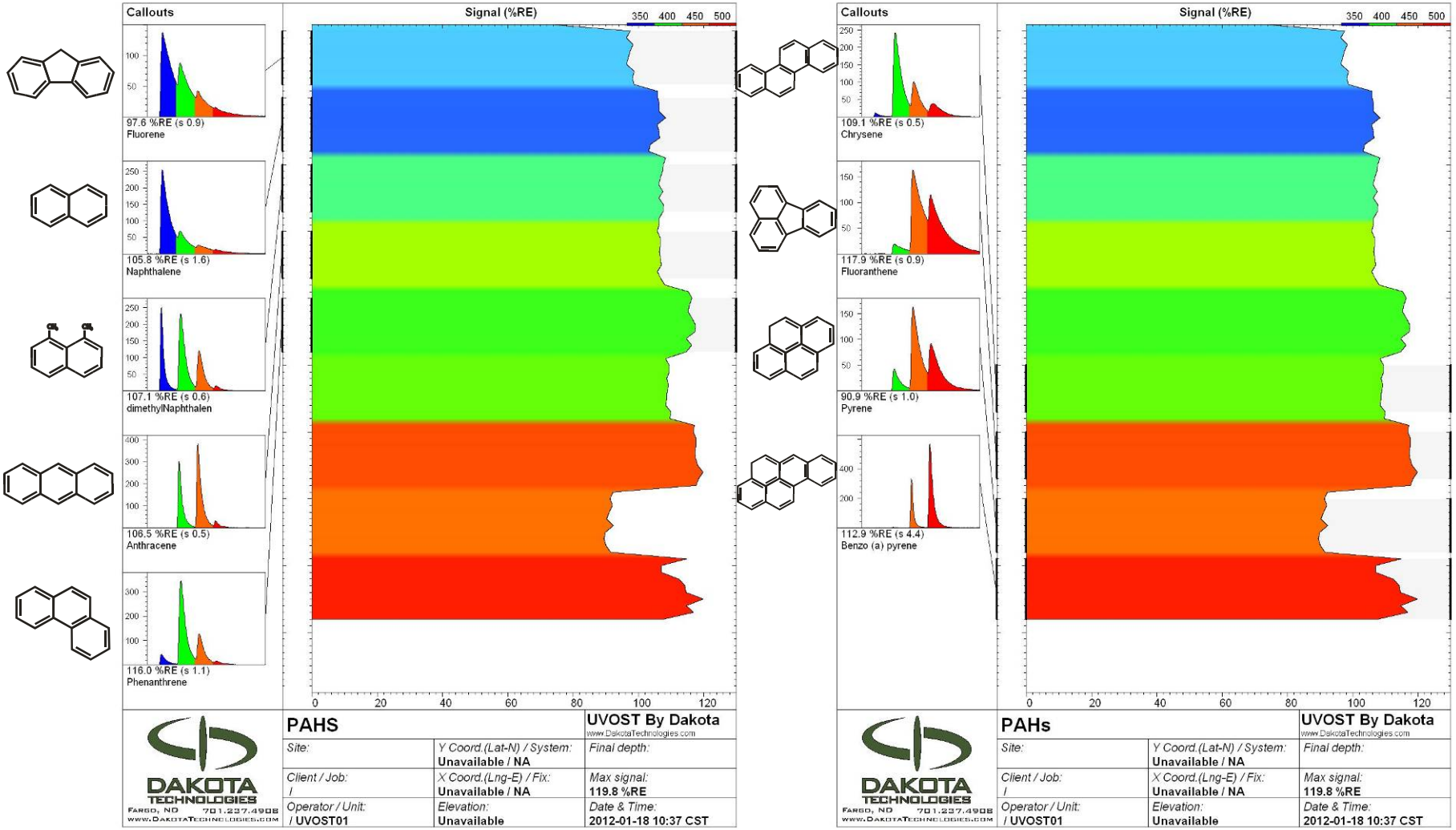
diesel's multi-wavelength waveform

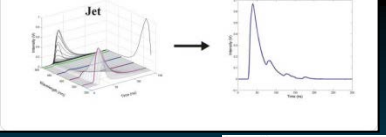


colorization of UVOST/ROST waveforms

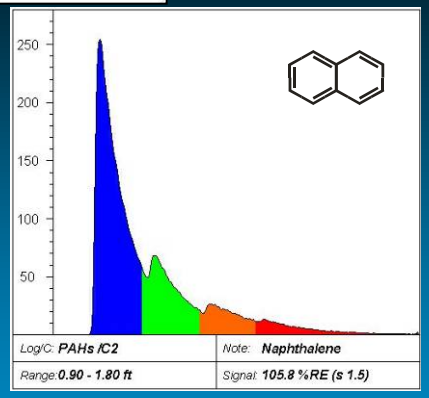


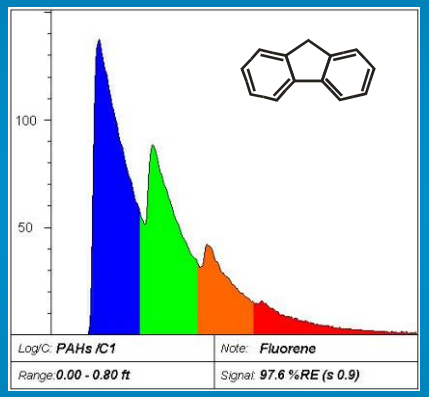
Pure PAHs on UVOST

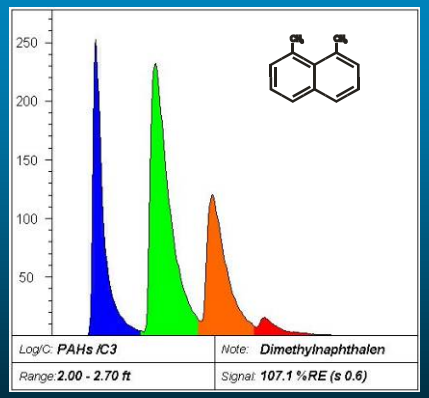


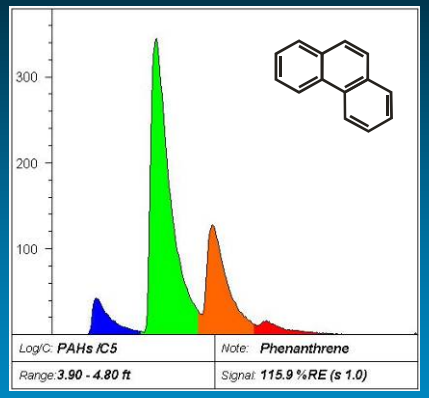


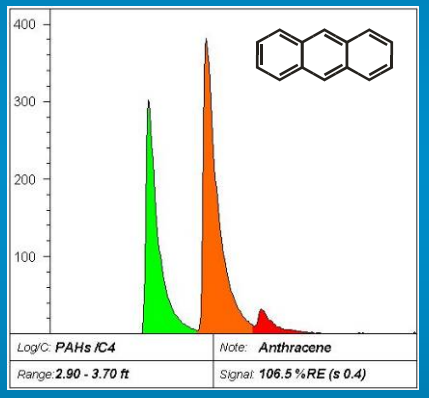
PAHs on UVOST

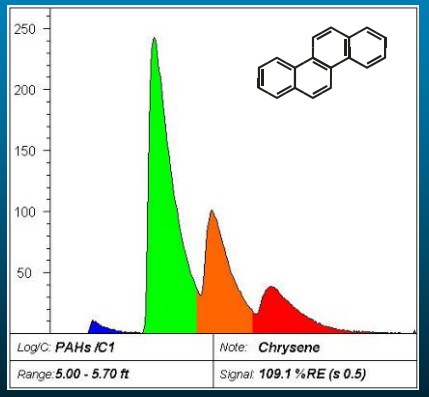


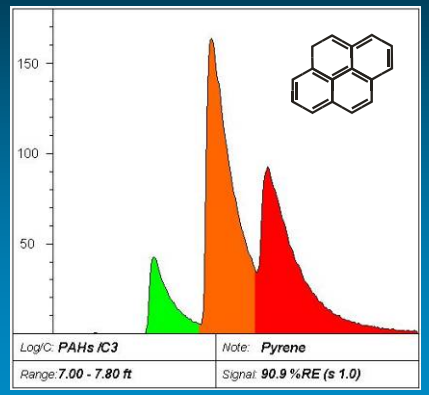


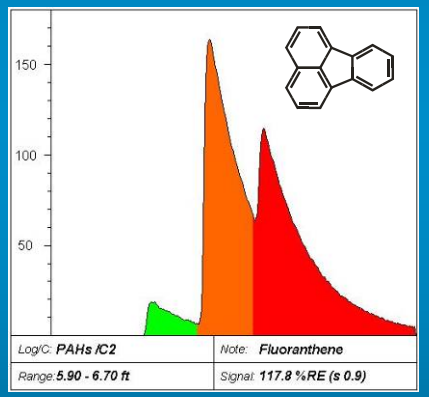


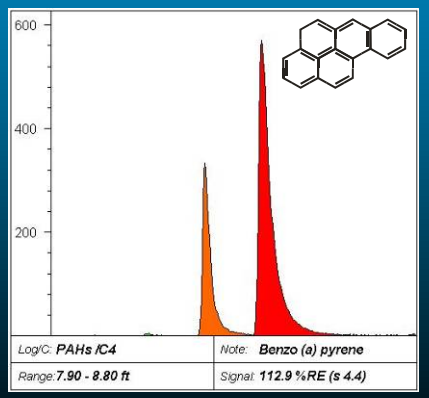








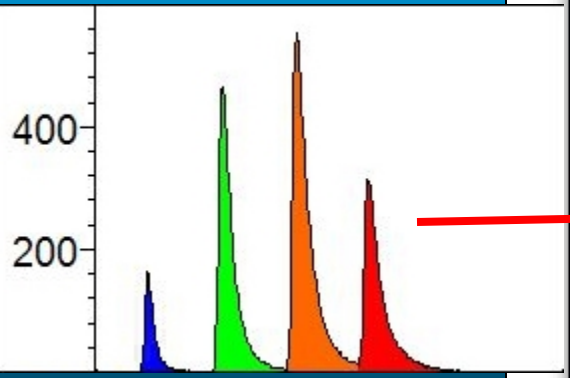


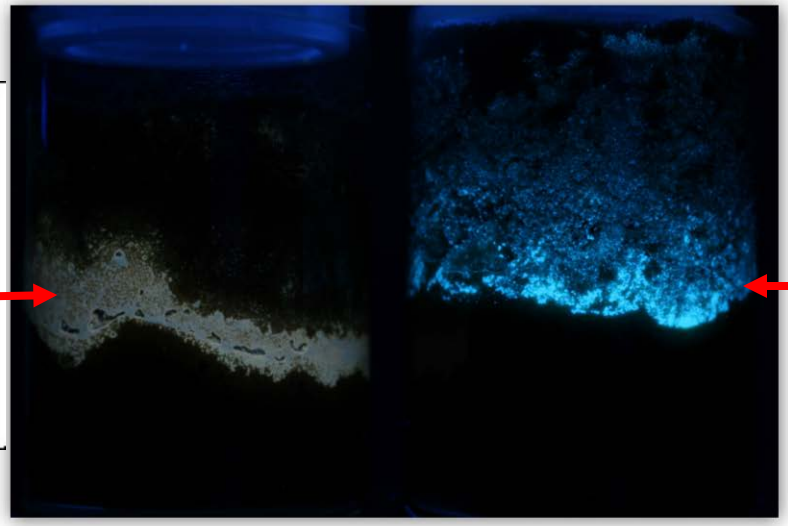


so…. does this slide make sense now?

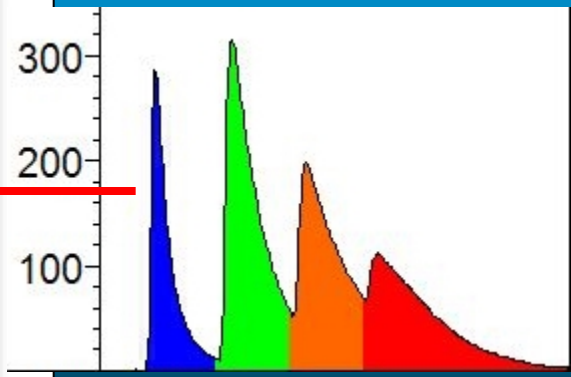
crude oil **diesel**

what LIF "sees"





what LIF "sees"

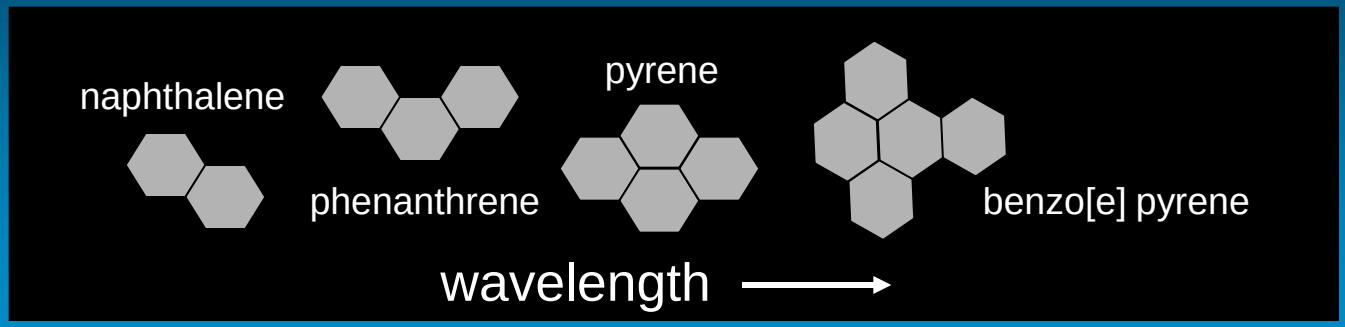


Qualitative nature of fuel and oil fluorescence (PAH mixtures)

general PAH fluorescence trends once again

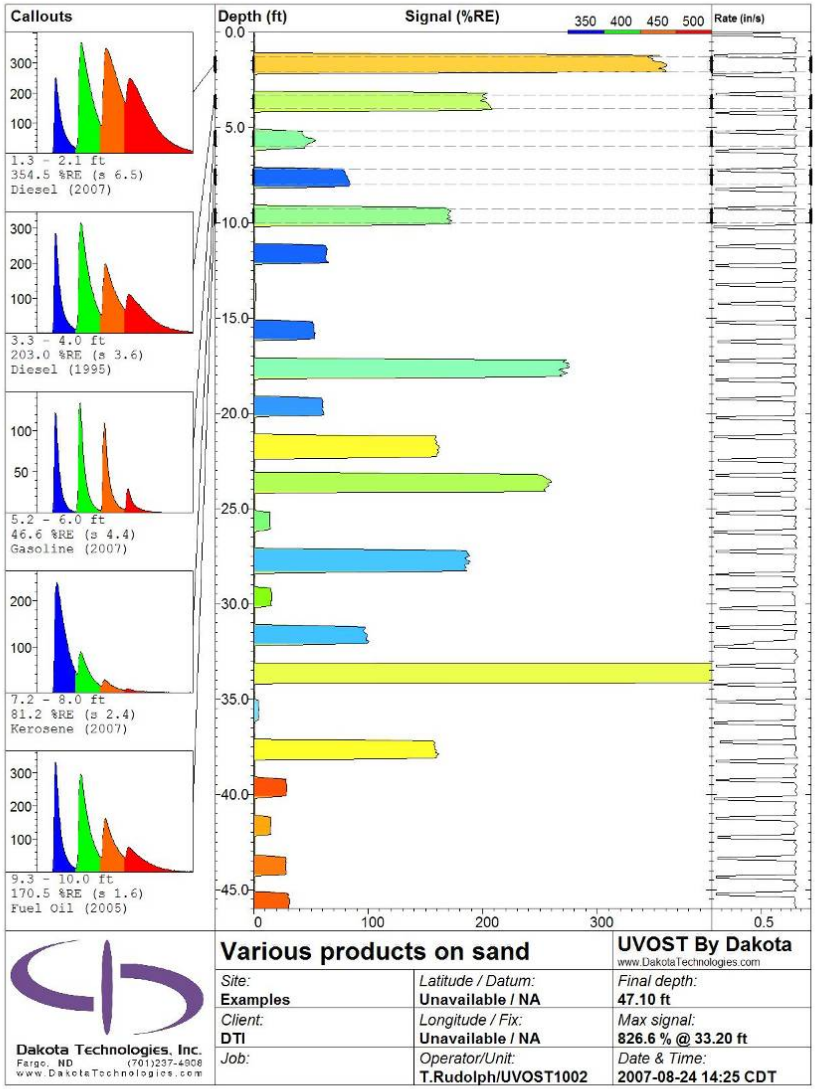
PAH fluorescence emission generally trends with # rings and degree of substitution

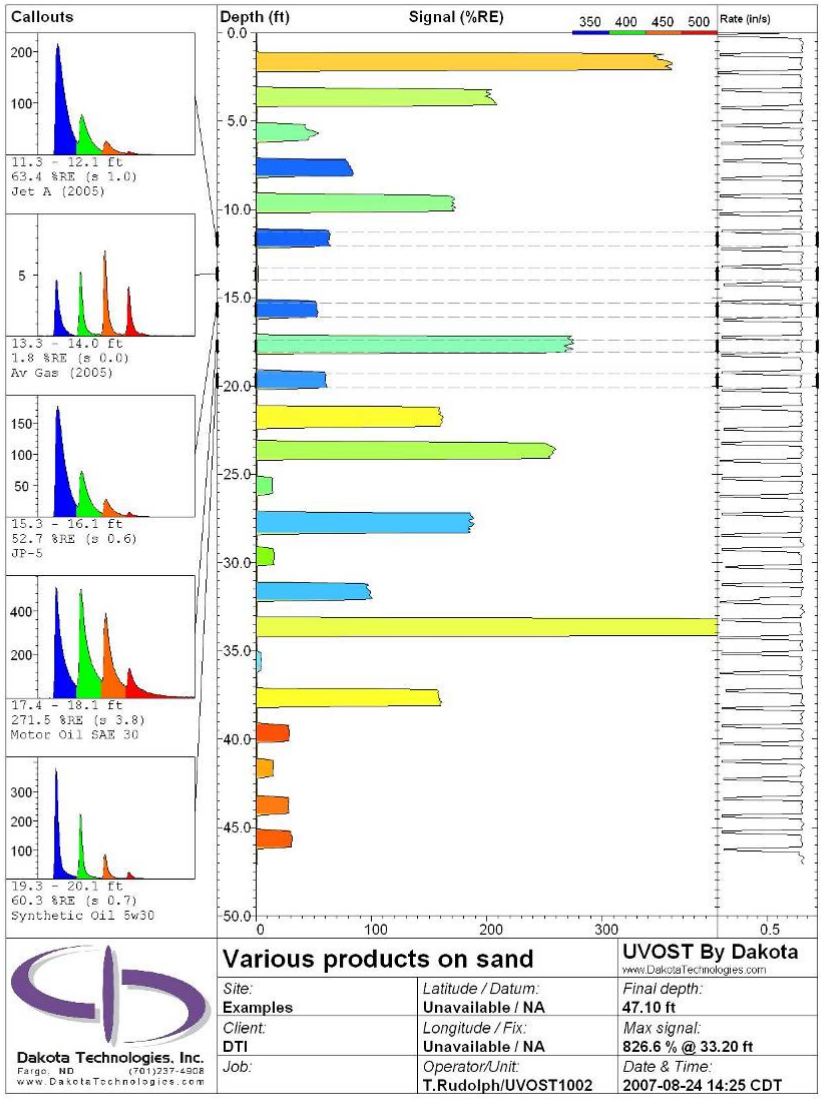
the larger and more complex the PAH the longer wavelength its absorbance and emission spectra



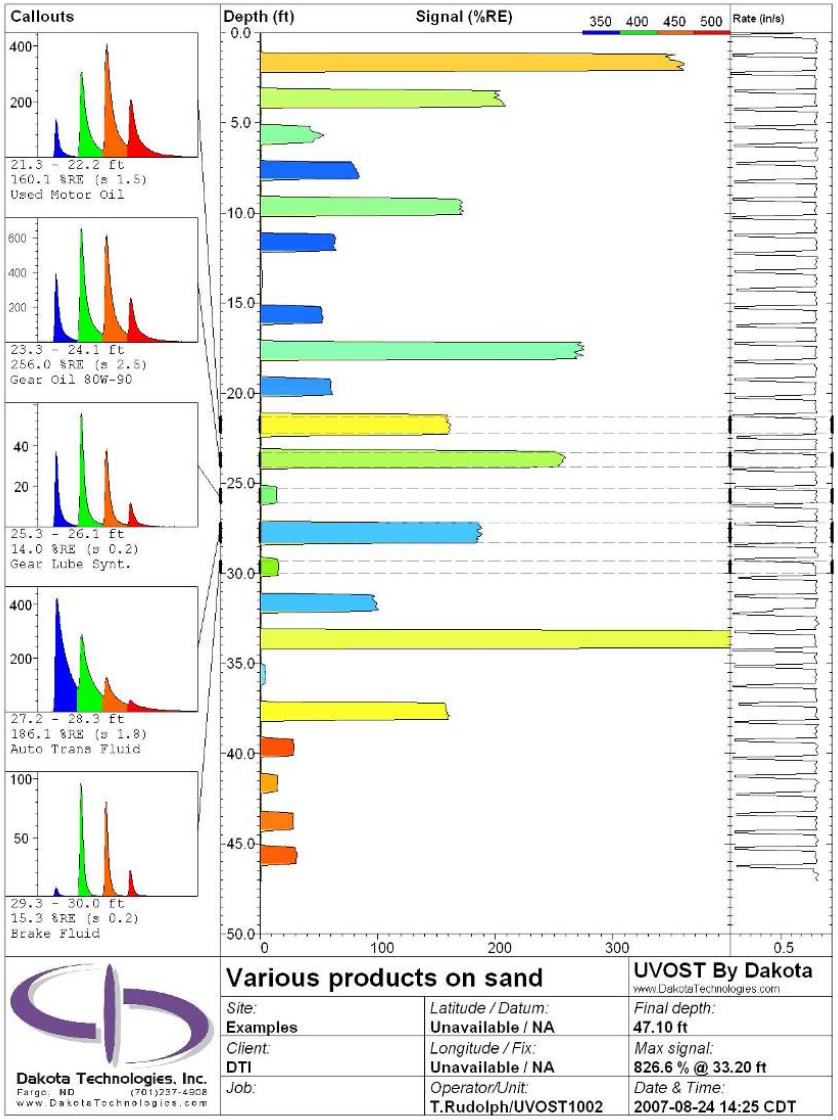
UVOST waveforms of various NAPLs

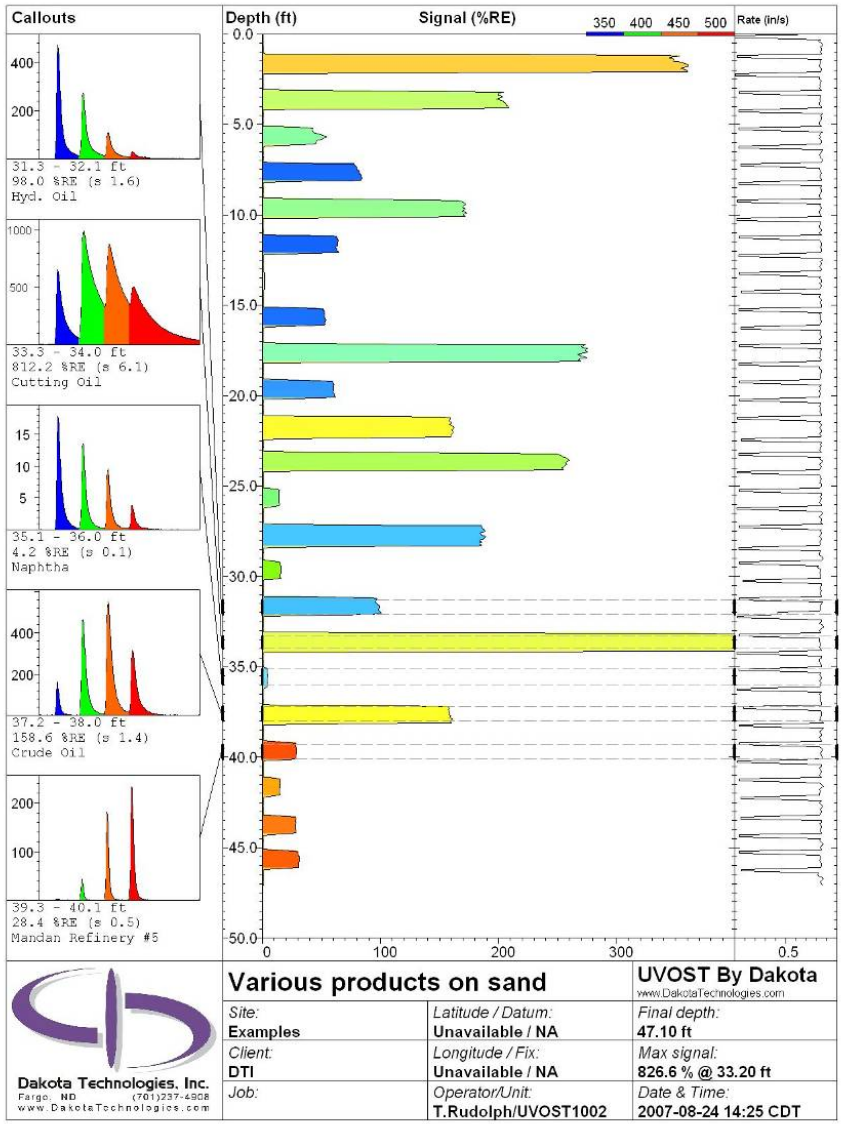
wet Fisher sea sand saturated with various NAPLs



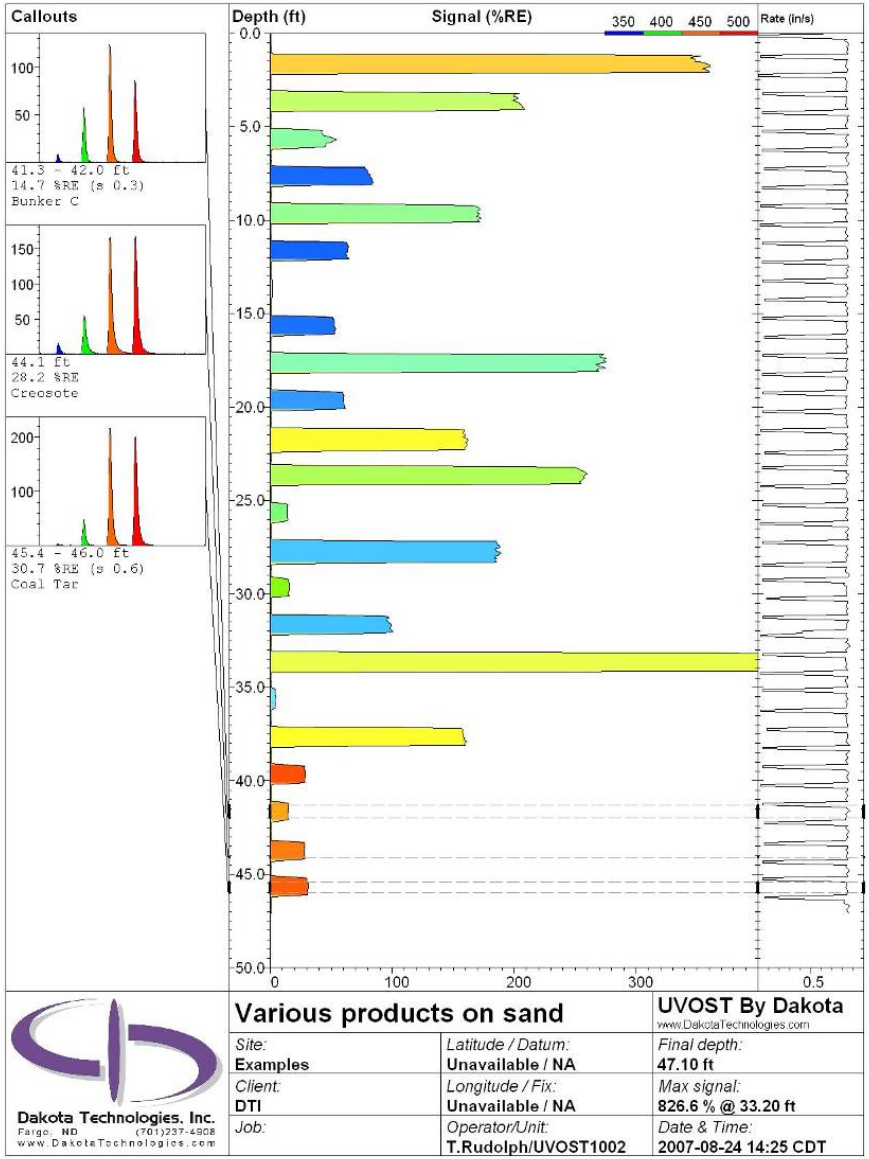


UVOST waveforms of various NAPLs





UVOST waveforms of various NAPLs



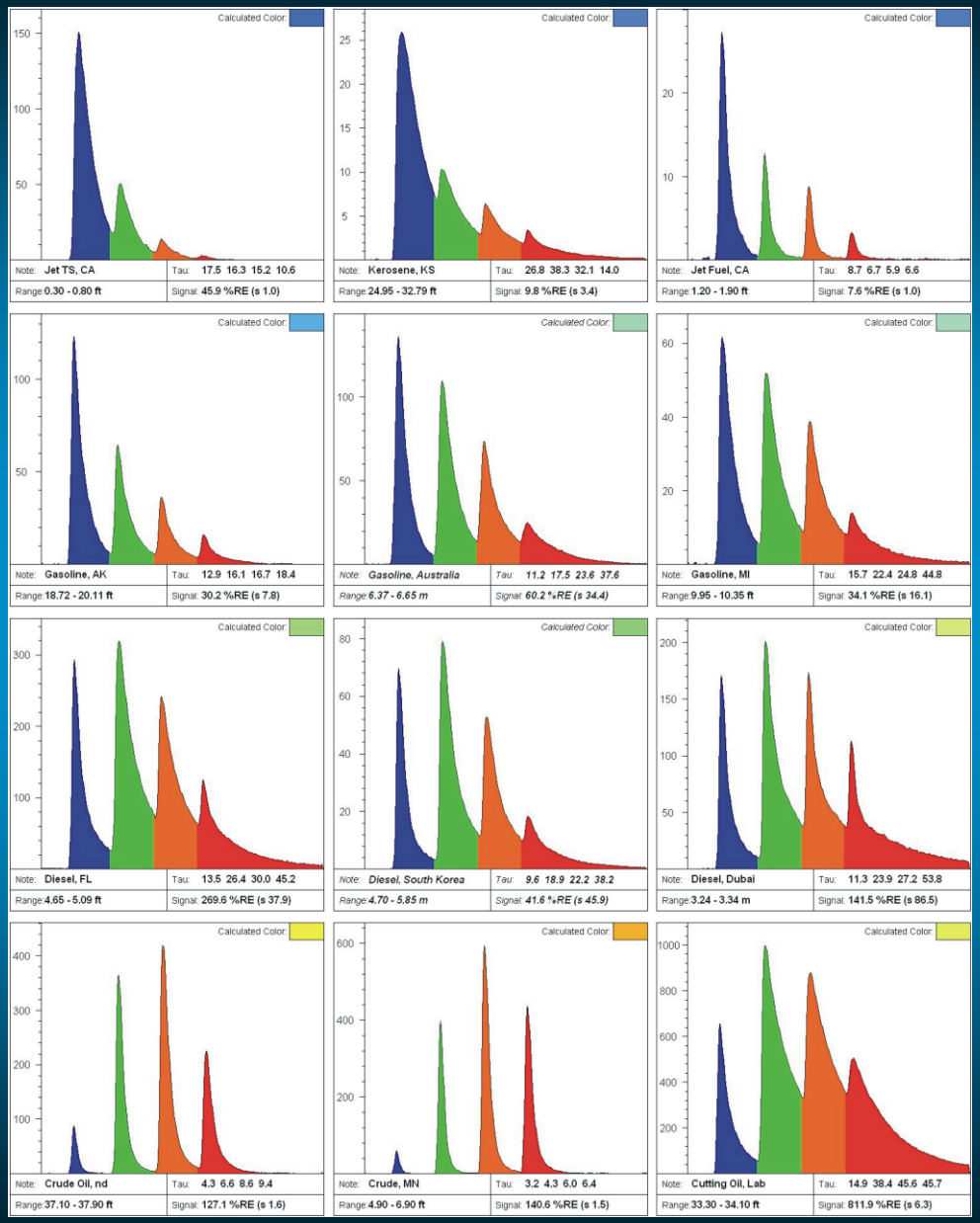
UVOST waveforms of various NAPLs

Jet/Kerosene

Gasoline

Diesels

Oils



“Semi-Quantitative” Nature of fuel and oil fluorescence

LIF calibration

Dakota's systems calibrated with a known reference material
(single point calibration)
similar to calibrating a photo-ionization detector (PID) with 100ppm isobutylene

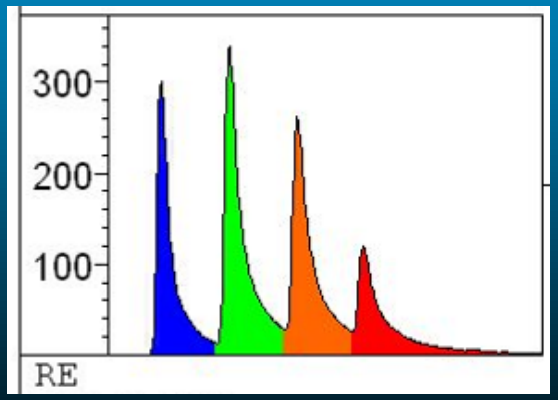
Dakota has used same "reference emitter" (RE) material since 1994

RE is placed on window just before each/every sounding
all subsequent readings are normalized by the reference emitter response
(data is ultimately displayed as %RE)

this corrects for change in optics, laser energy drift, window, mirror, etc.

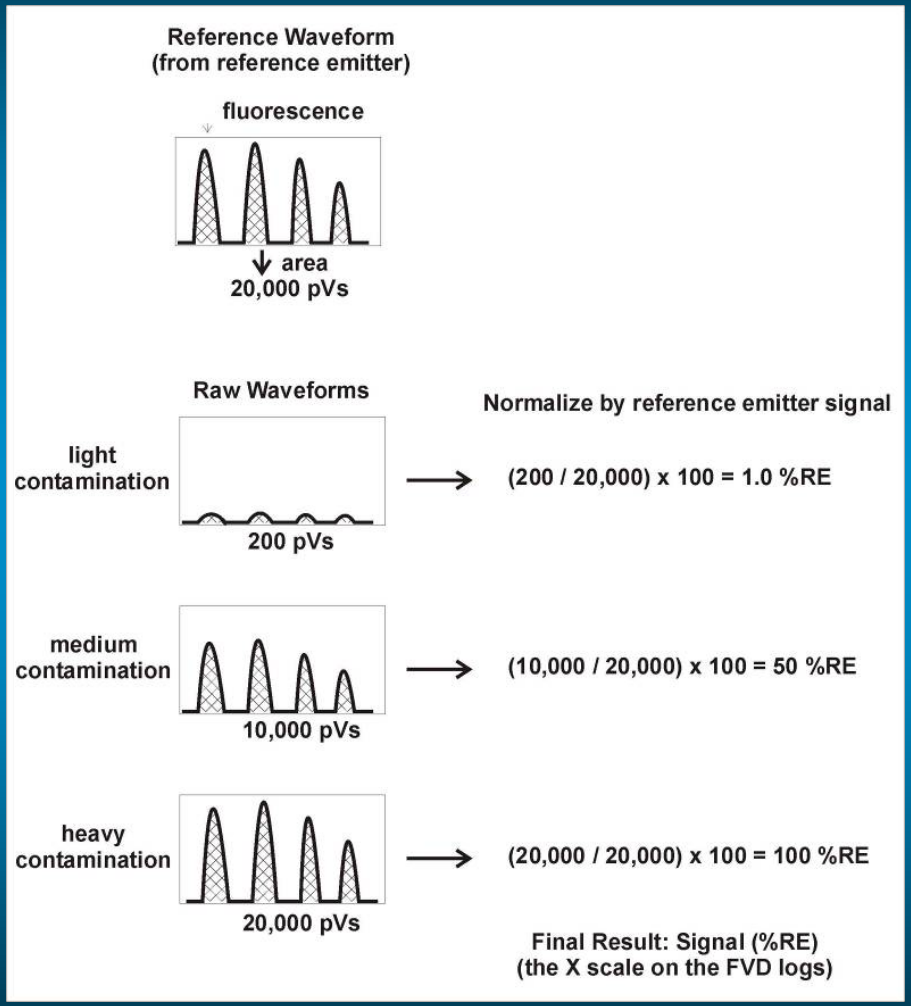
RE approach is used by all ROST and UVOST providers globally

the correct shape of waveform also allows checking the qualitative aspect of the fluorescence



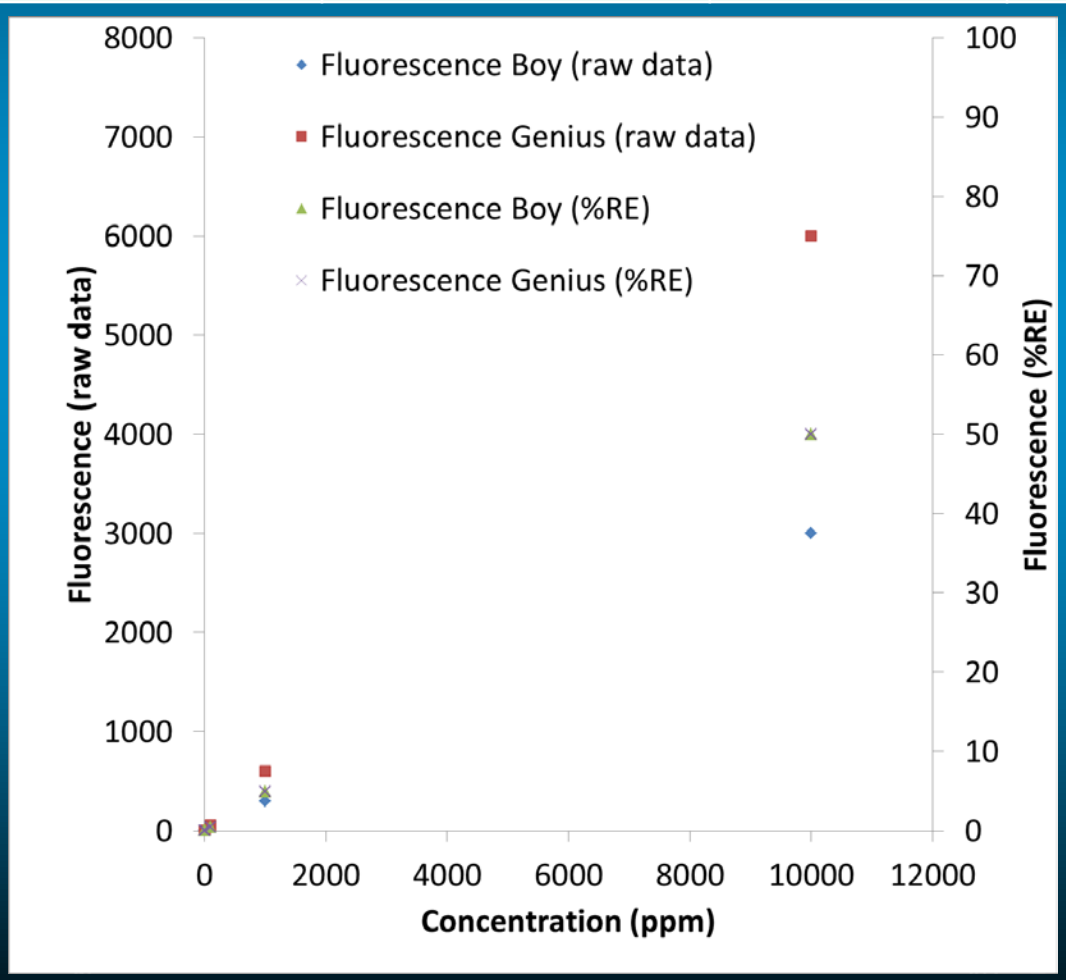
UVOST's Reference Emitter or RE
(RE does NOT stand for REflectivity!)

- think of RE just as you would of the 100 ppm isobutylene used to calibrate a PID
- the RE normalizes the response for laser energy changes, fiber optic cable length, detector aging, etc.
- the same RE solution is used by all UVOST and ROST providers
- Dakota has a large stockpile of the material which was prepared from standard ingredients
- the relationship between RE and the concentration of NAPL
- it depends on the fuel/oil, some simply glow brighter than others

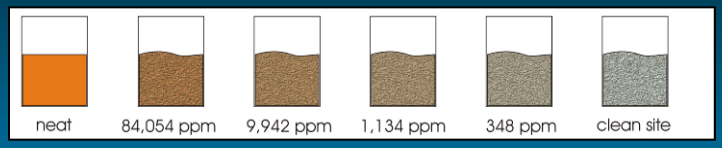


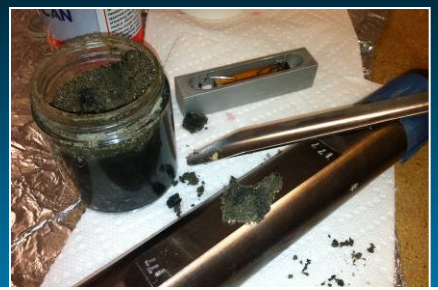
why RE?

Concentration (ppm)	Fluorescence Boy (raw data)	Fluorescence Genius (raw data)	Fluorescence Boy (%RE)	Fluorescence Genius (%RE)
0	1	2	0.02	0.02
10	3	6	0.05	0.05
100	30	60	0.50	0.50
1000	300	600	5.00	5.00
10000	3000	6000	50.00	50.00
RE	6000	12000		



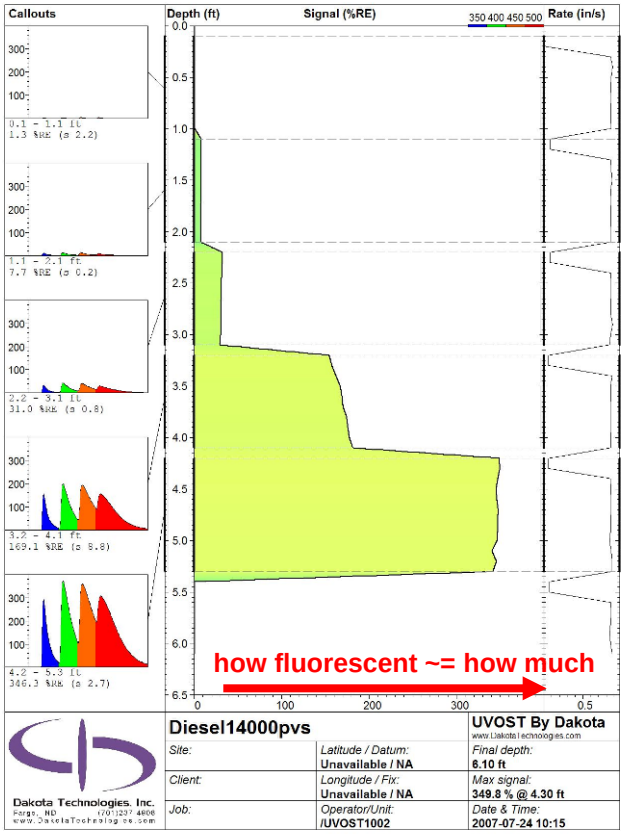
lab studies: mix fuels with soils to demonstrate how LIF yields 'semi-quantitative' data





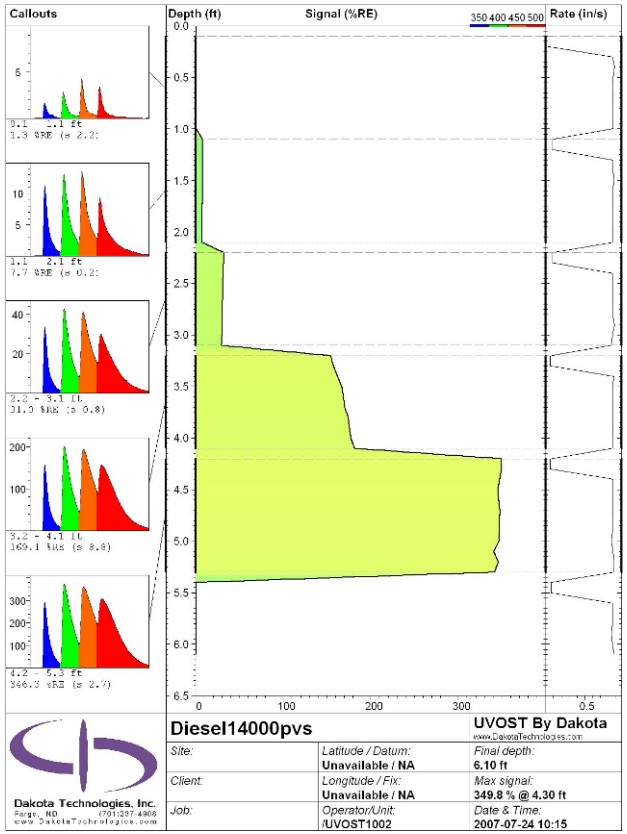
fixed scale intensity

diesel



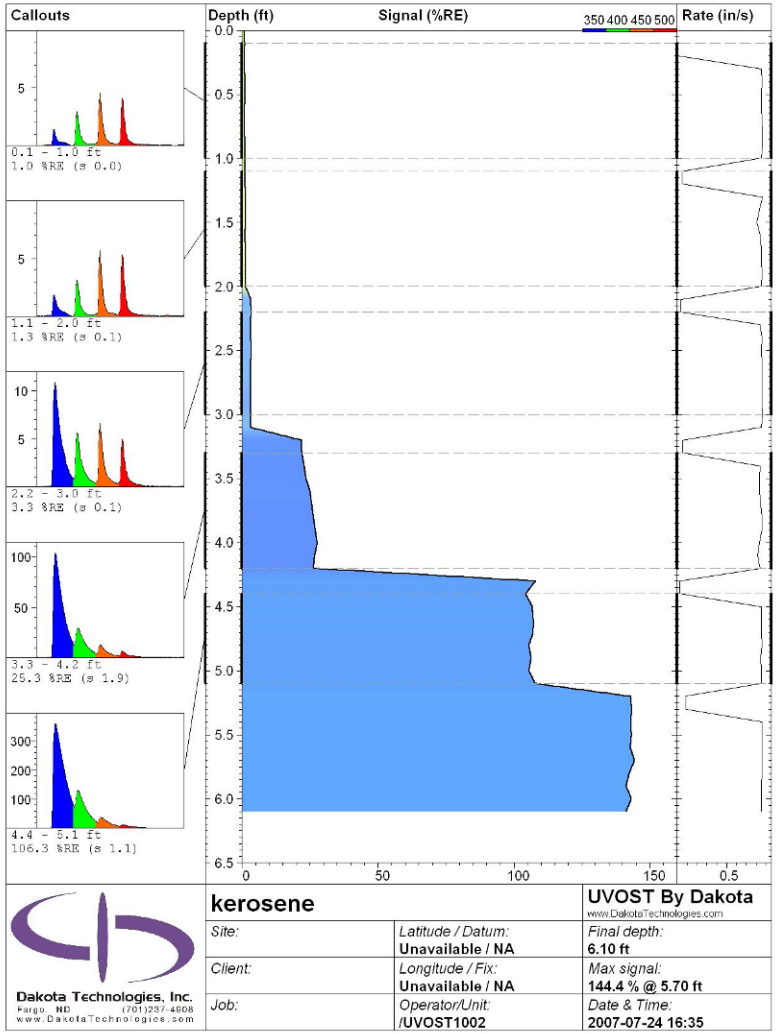
auto-scale intensity

diesel

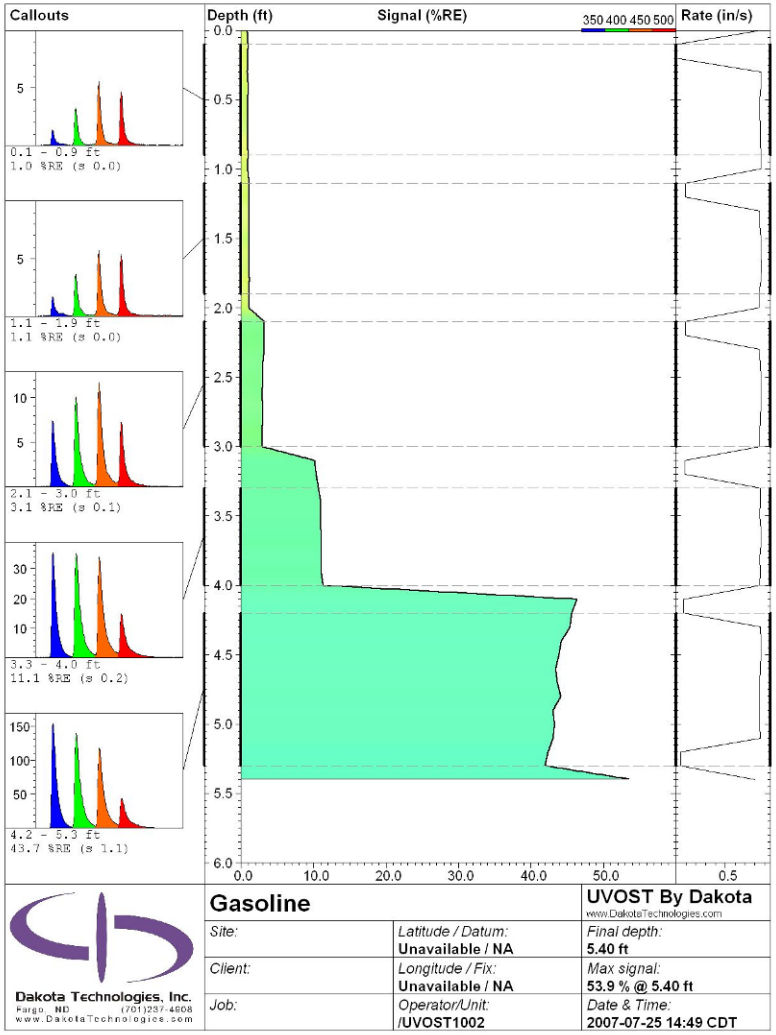


LIF contains both quantitative (how much) and qualitative (what kind) of data

kerosene (jet fuel)



gasoline

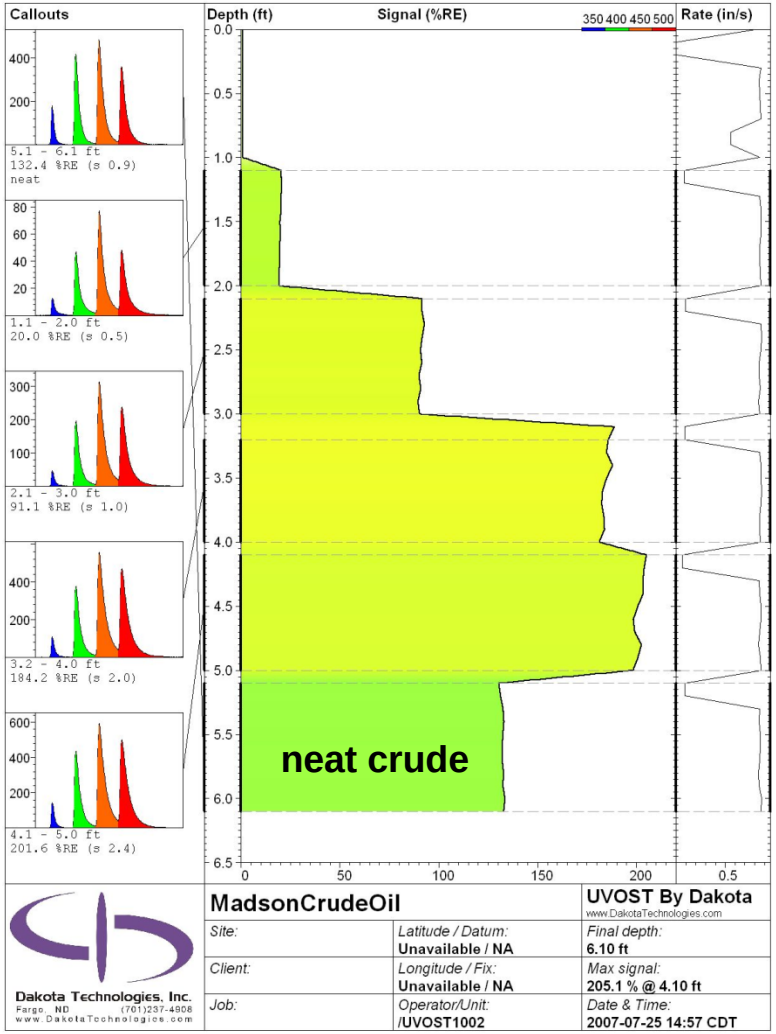


more lab studies

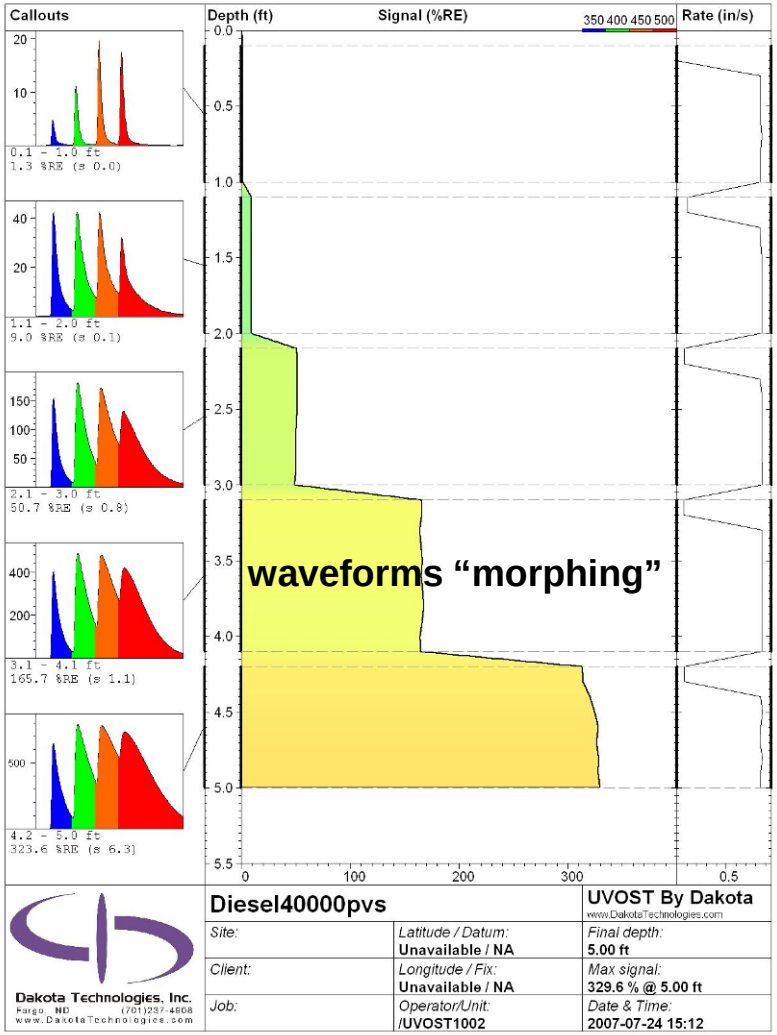
crude oil “rollover”

too much fluorescence (saturation)

crude oil

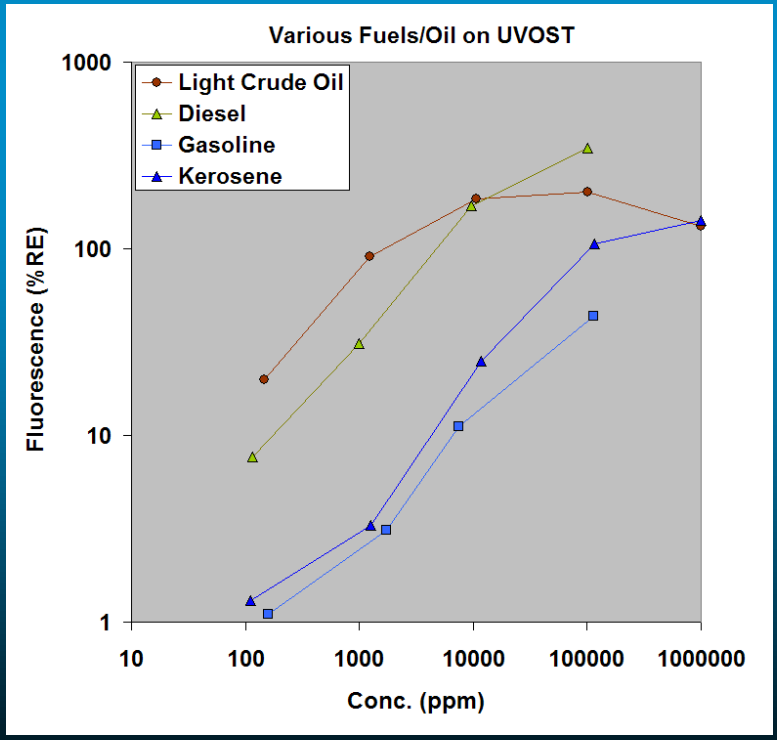


diesel



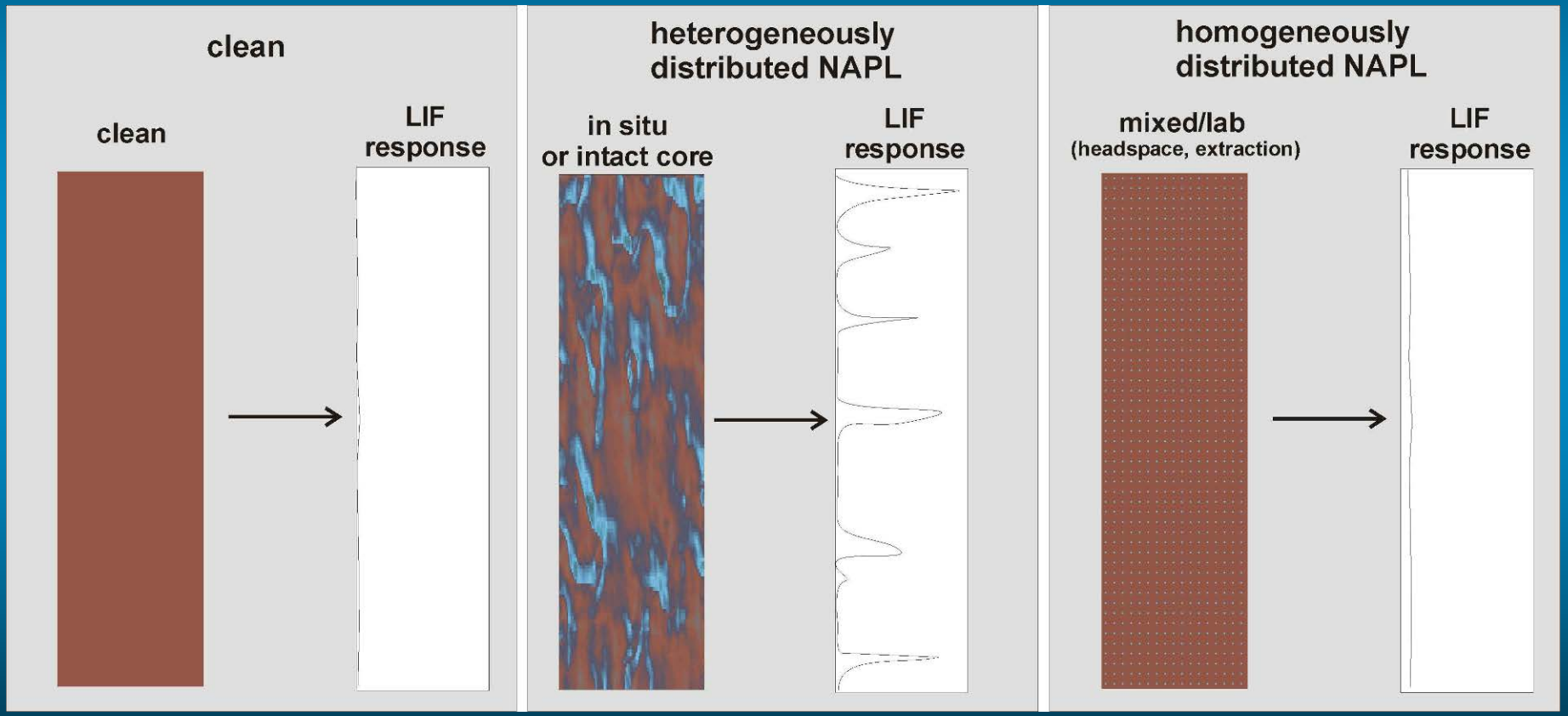
UVOST's "semi-quantitative" performance

- typically 10-1,000 ppm (TRPH) limit of detection (LOD) on petroleum fuels/oils - statistically in a controlled experiment – up/down from there depending on heterogeneity
- gasoline is difficult – it evaporates in jars and during pipetting, etc. and simply glows "weaker" than others
- semi-linear response over several orders of magnitude on fuels/POLs (depends on soil/fuel/conditions)
- note the non-monotonic response of crude – due to high PAH content and resulting signal "rollover"
- variability has been seen across gasolines, kerosenes (jets), crudes, diesels (two fuels of same type)
- generally speaking diesel is best behaved – gasoline and kerosene can be 10-fold lower
- these lab experiments "underestimate" practical field sensitivity because in downhole NAPL is mottled, these lab soils were mixed/equilibrated so NAPL coats ALL sand grains equally, this doesn't often occur in nature as one will hit globules/seams/mottling, even on very small scales (marbling/blebs)
- note that the LOD for PAHs themselves (mg/kg) is much lower than it seems at first glance – since we're measuring total fuel mass here (mostly aliphatics) – not PAH mass



in-situ
vs.
lab or “homogenized” samples

natural heterogeneity often allows “better” detection of NAPL vs. homogenized lab samples
lab-based LODs are typically conservative estimate of in-situ LOD



Organoleptic (smell/site) observations accepted without hesitation by many stakeholders
But has its flaws (really no great alternative though)

Matrix affects the organoleptic approach.
Dakota has mixed dozens and dozens of spiked sample sets for research and application to field studies in last 20 years.

Experiment to try:
hand an experienced geologist a 1,000 ppm NAPL-spiked clean sand and a 1,000 ppm NAPL-spiked dark fine clay and you will get 2 **wildly** different estimations of “NAPL impact” (think about floor dry or kitty litter)

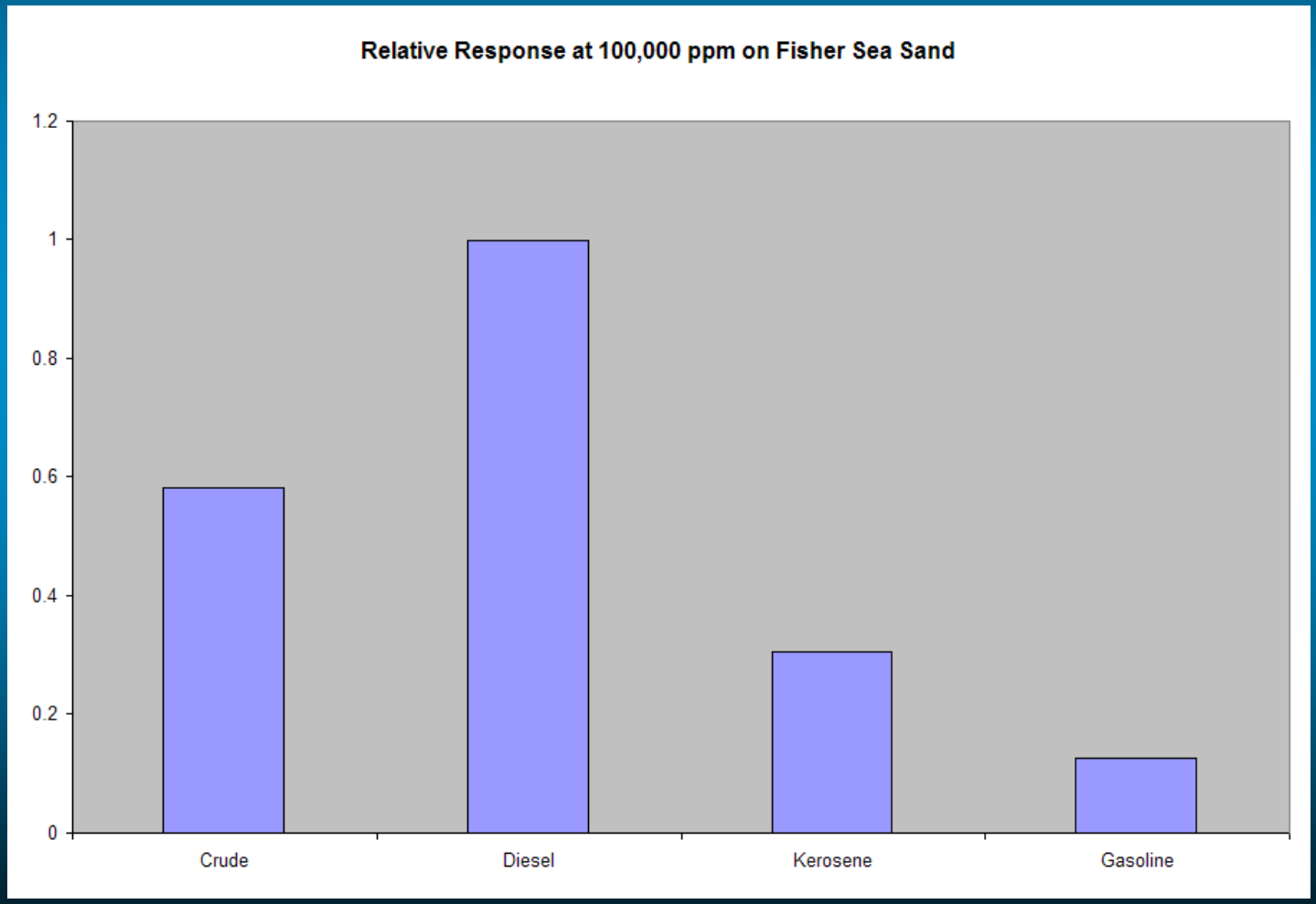
Simple Fact: Fine soils hide NAPL while clean sands and gravels flaunt it

“sheens” are NAPLs that are observable at amazingly low conc’s!

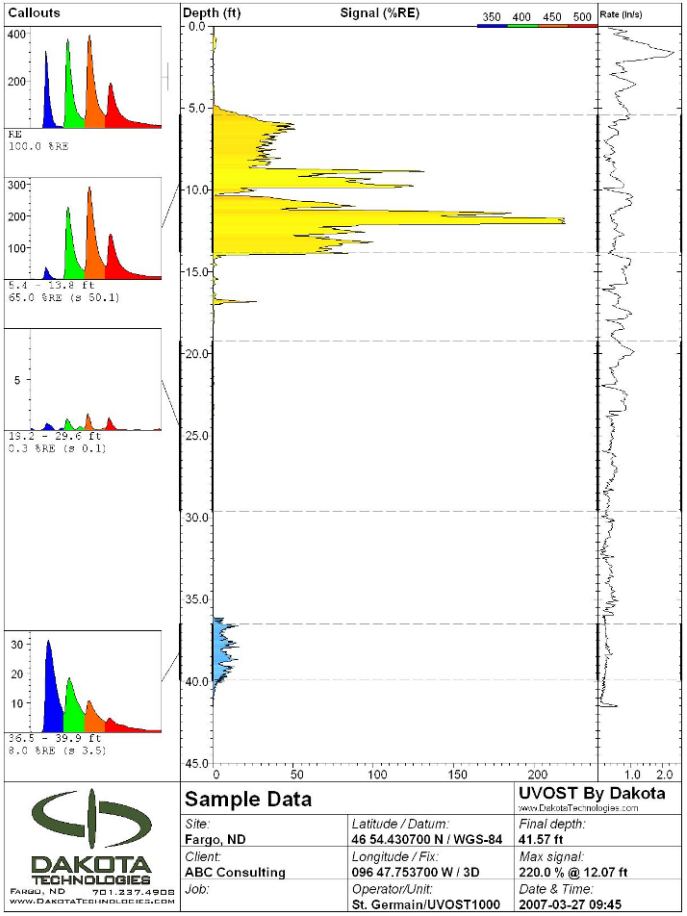
LIF's semi-quantitative performance

these are the result of **one series** of randomly acquired fuels and crude oil – product "brightness" can vary

- Gasoline is typically 32% aromatic – but mostly single ring aromatics (BTEX) that UVOST "can't see"
- Diesel is typically 38% aromatics
- Kerosene or jet fuel is 23% aromatics (limited to prevent smoke) – nearly all naphthalenes



what does this quantitative variation mean for field logs?

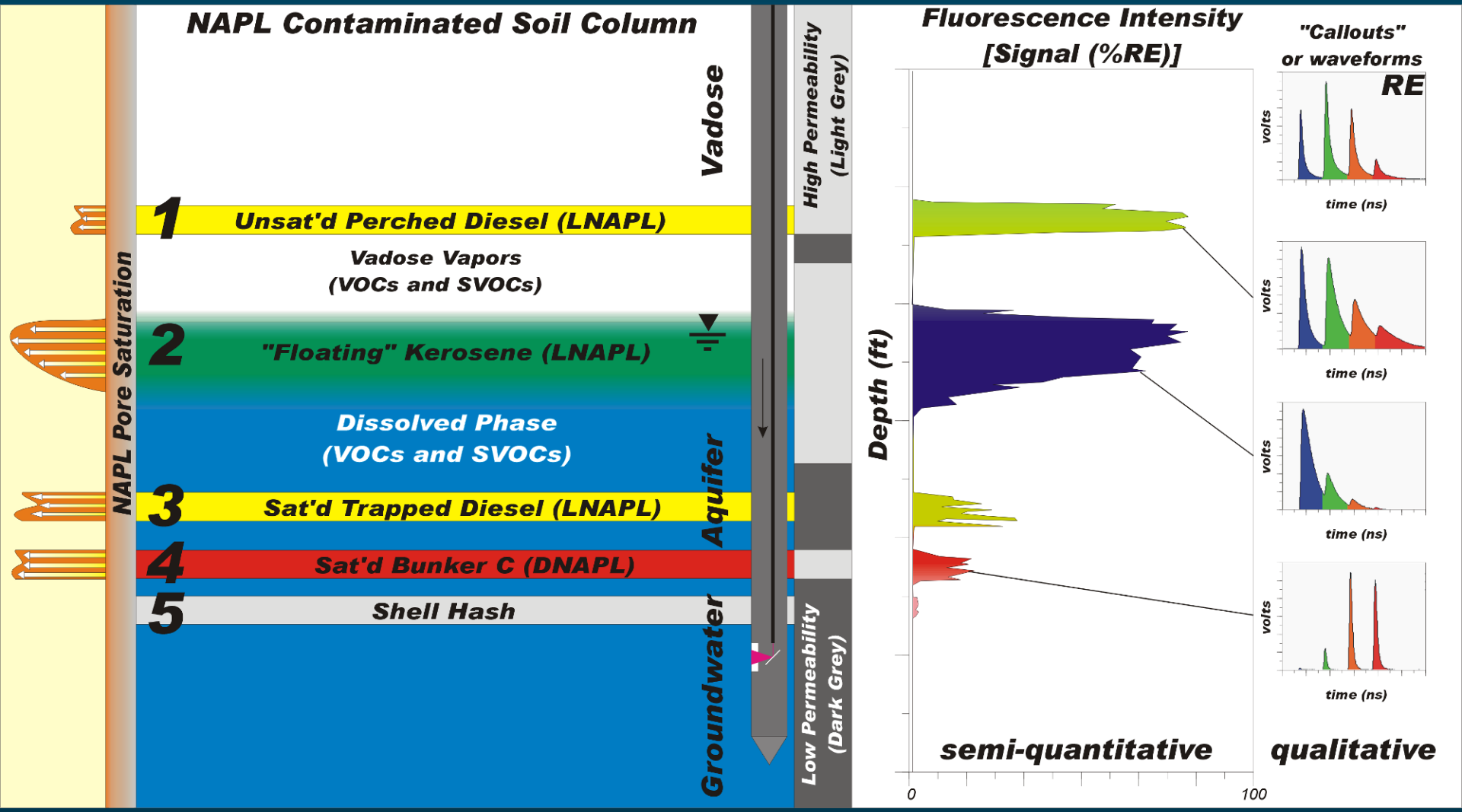


MN – Service Station - 2 NAPLS
(oil or weathered gas on top.... intact gasoline bottom)

LIF is fairly quantitative when it comes to one NAPL type at a simple site with simple geology, but multiple products under complex geology… there's going to be differences in response

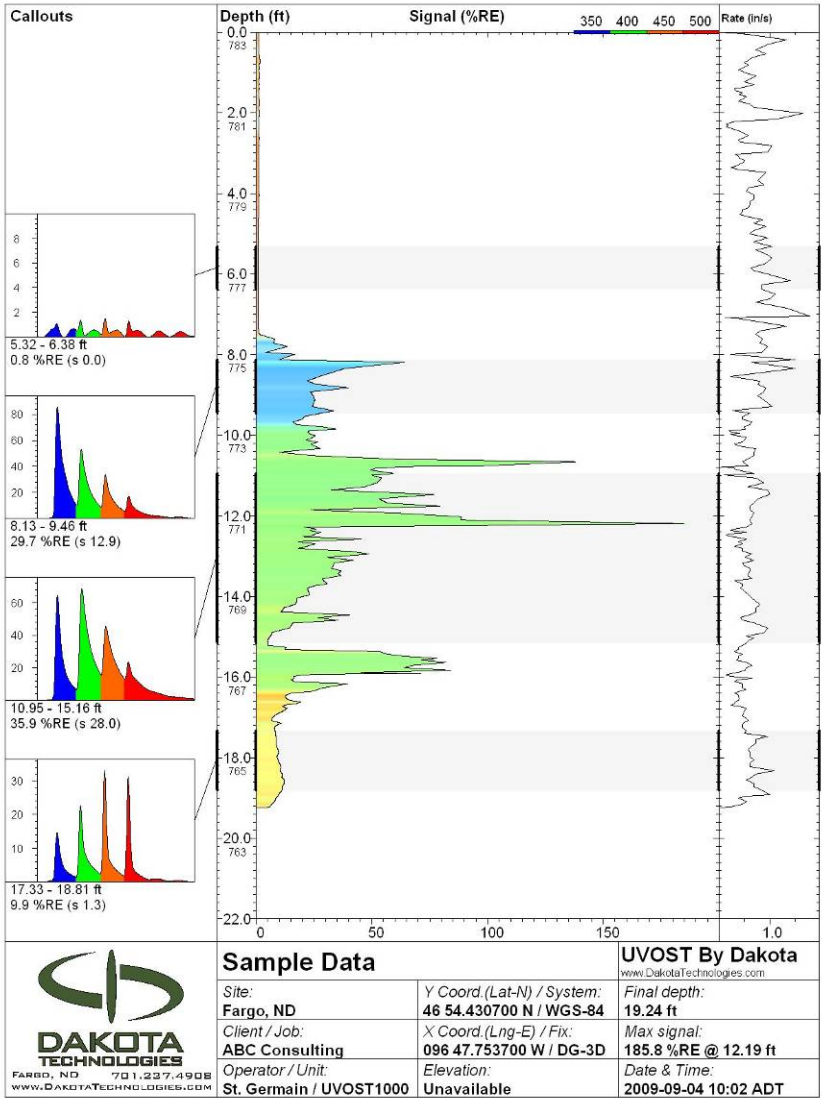
but same is true for geologist who can spot NAPL in sand much better than fines… test yourself

UVOST/ROST logs vs. NAPL and its location



field log example

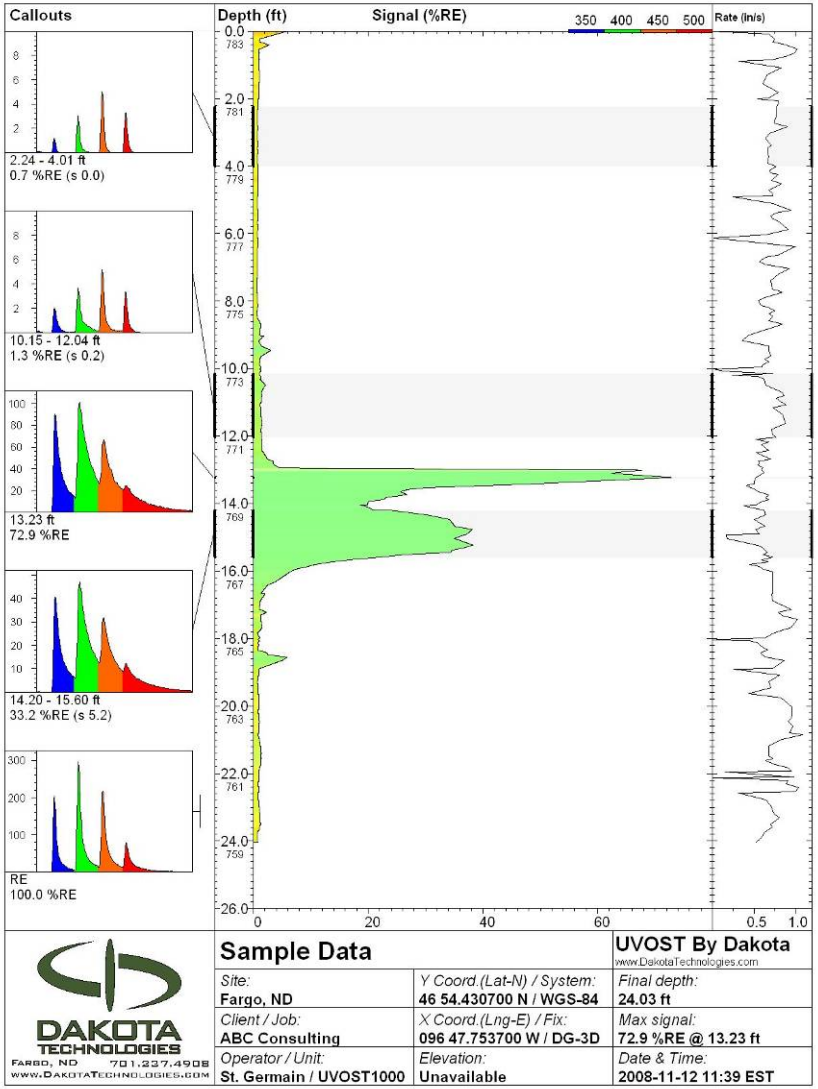
variation top to bottom
= heterogeneous product
or
strange weathering pattern



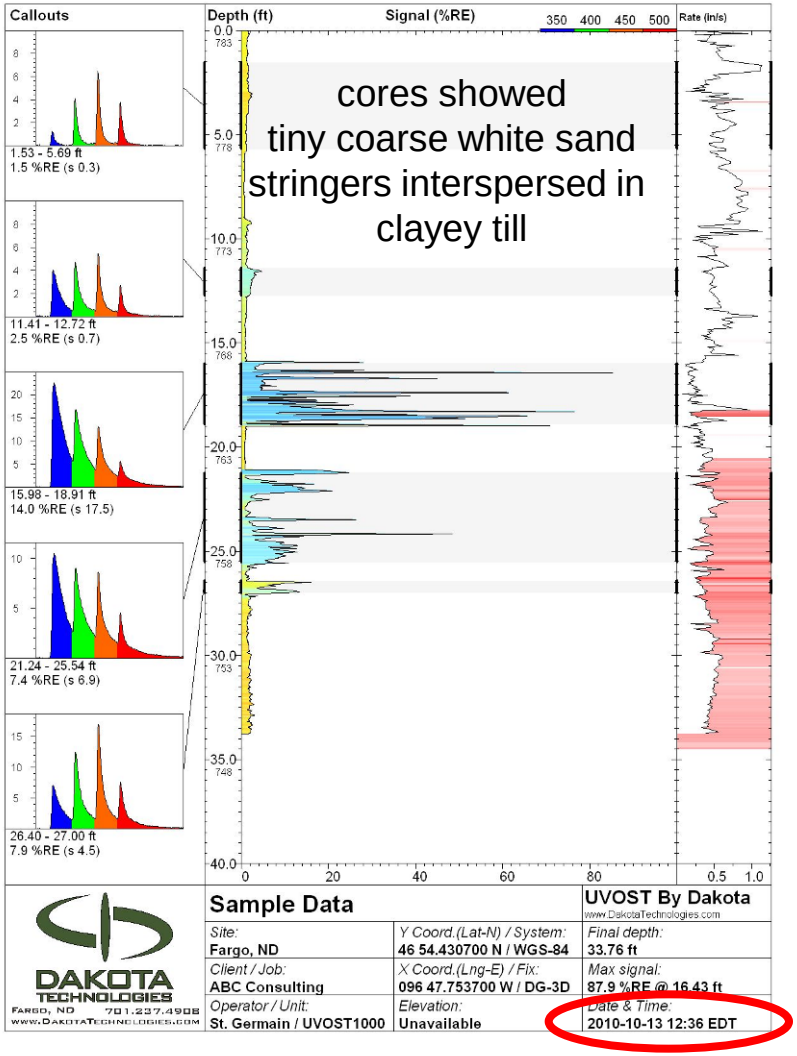
this type of “confetti” color pattern is very common in bulk handling facilities where many products spilled over long periods

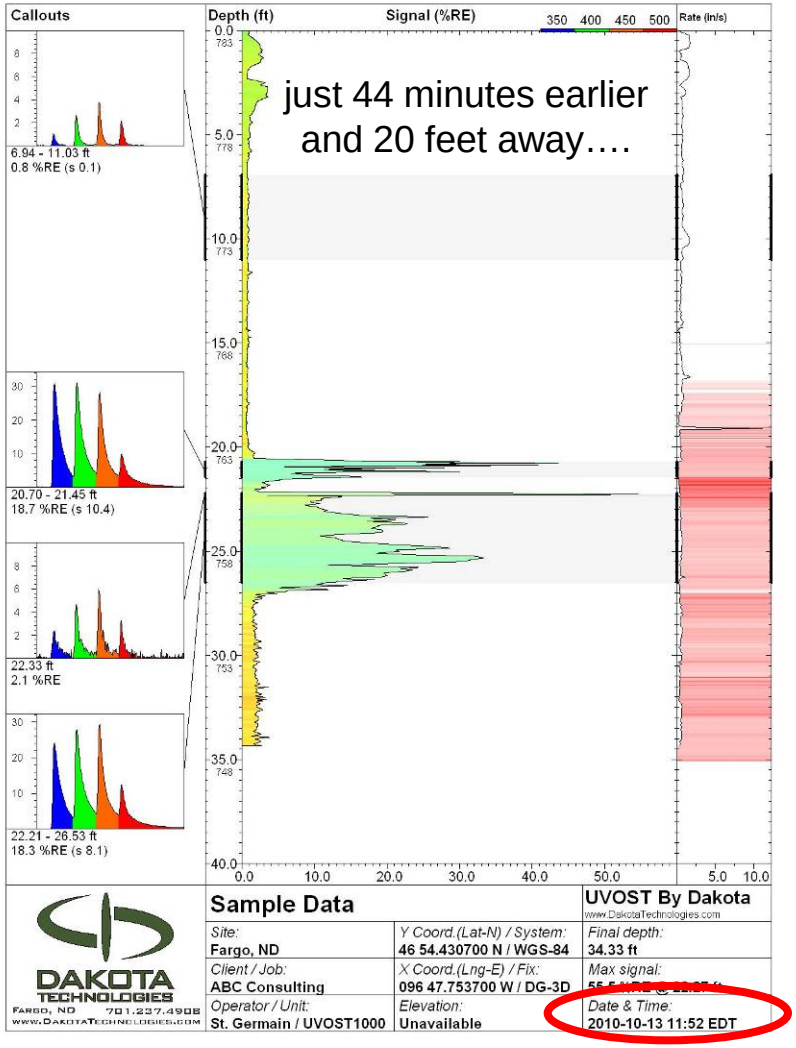
field log example

consistent top to bottom
= homogeneous product



is this a sandbox geology with floating pancake “shark’s fin”? not so for log at left… these two logs tell you a LOT about geology





Limitations of UV LIF

soil type (pore spaces) affect the LIF response

UVOST's response depends on "optically available" NAPL pressed against the sapphire window. Response decreases as particle size and soil color decreases. Tiny particles (high surface area) help "hide" the NAPL and dark soils help "sink" any resulting fluorescence.

There can easily be a **10-fold** difference in response due solely to soil matrix!

- **Enhanced responses in:**
  - **course "clean" sands with open pore spaces**
  - **light colored soils help reflect resulting emission back into window**

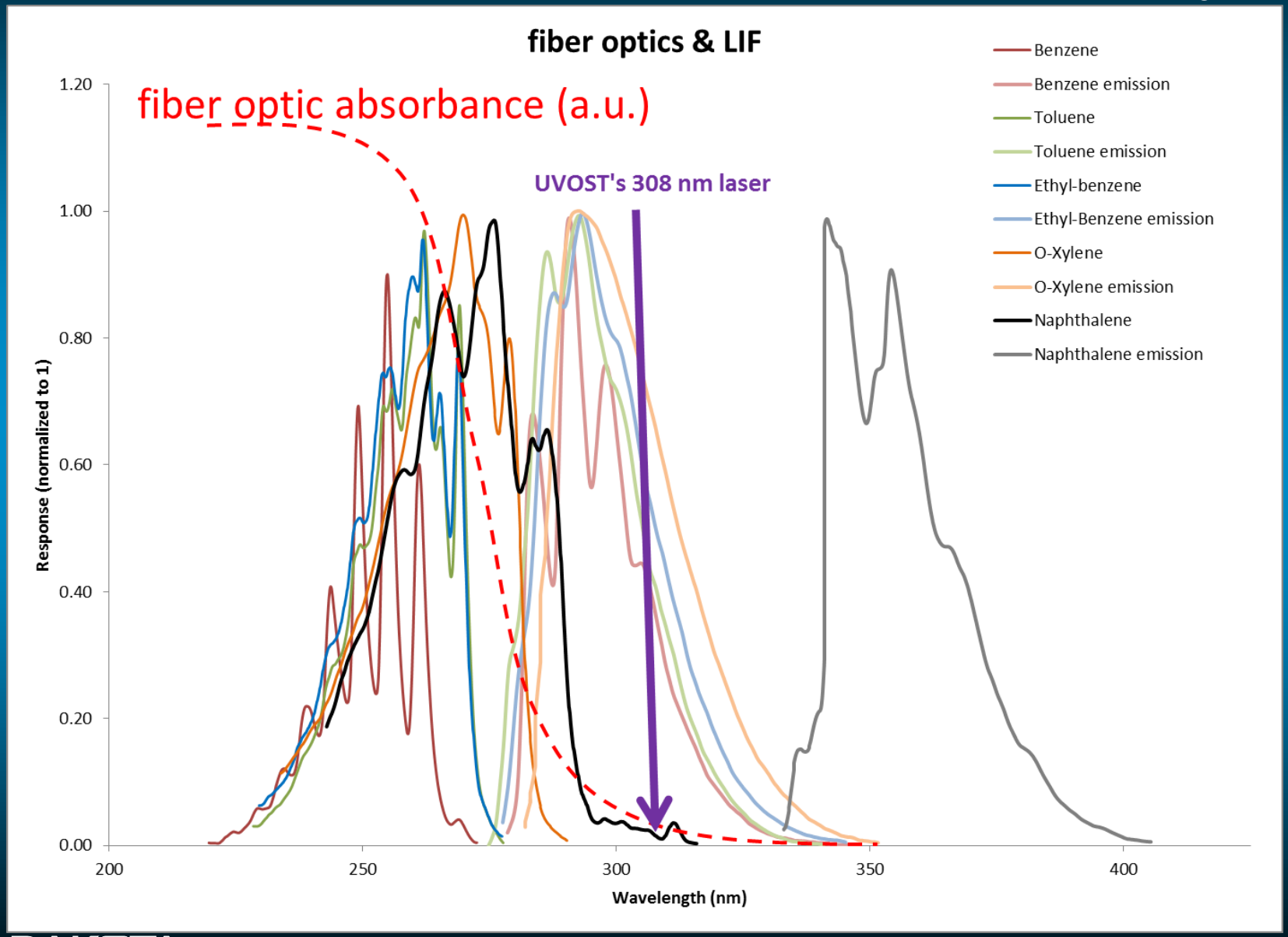
- **Degraded responses in:**
  - **fines/clays**
  - **dark colored soils absorb resulting emission**

soils pore spaces saturated with diesel
various soil types have various fluorescence intensity

can UVOST detect BTEX?

no… it can't - due to fiber optic absorbance of BTEX excitation wavelengths

UVOST would use Nd:YAG 4th harmonic 266nm laser **if** fibers didn't absorb that wavelength



dissolved phase experiment

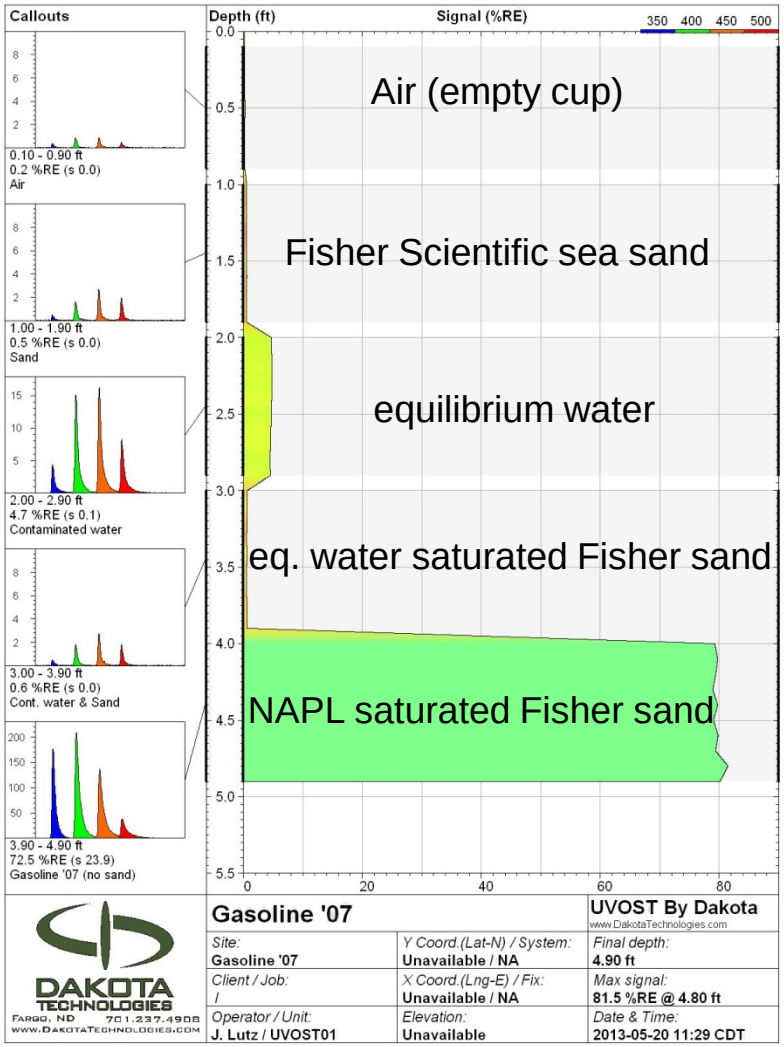
1. combine NAPLs and water in jars
2. let sit for 4 days
3. extract water that has “equilibrated” with NAPL
4. examine clean sand, contaminated water, cont’d water/sand mixture, and NAPL/sand mixture with UVOST

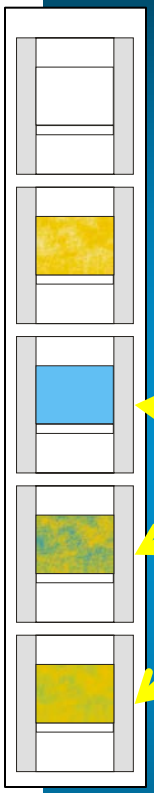
experiment cont'd

experiment cont'd

insert samples into sapphire window bottomed "cups" at exact same geometry as LIF probe window

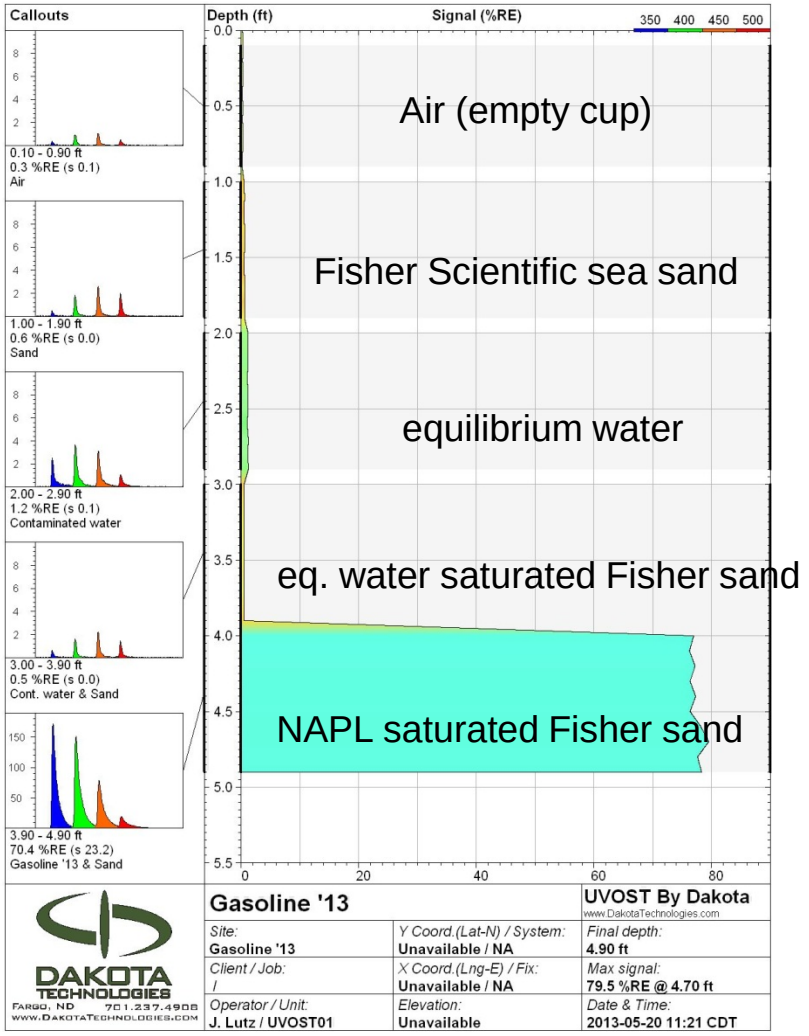
2007 gasoline

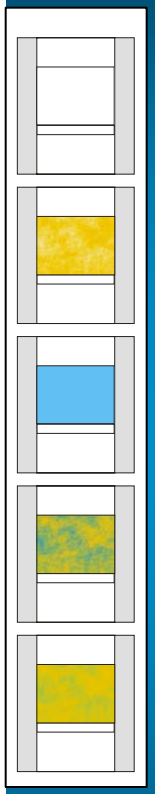




experiment cont'd

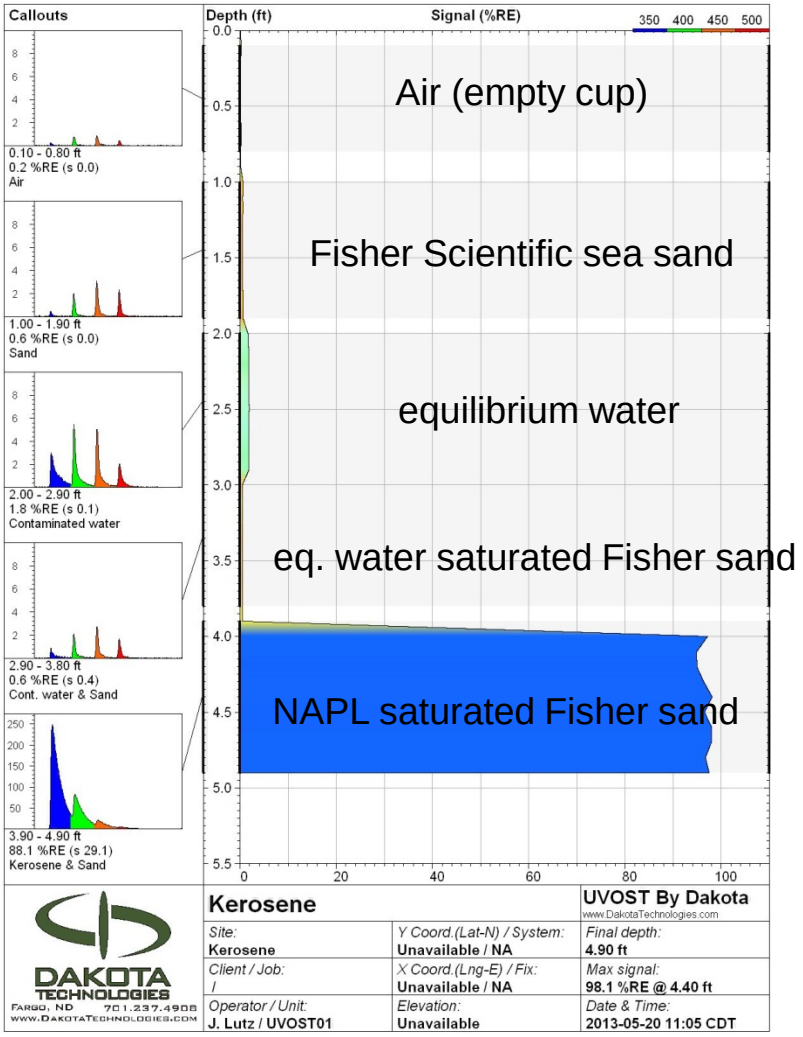
2013 gasoline

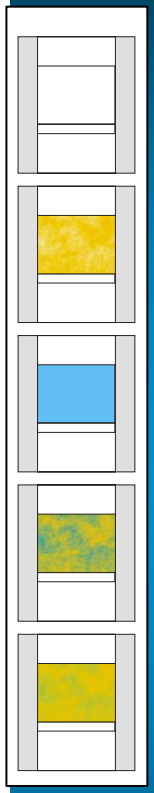




experiment cont'd

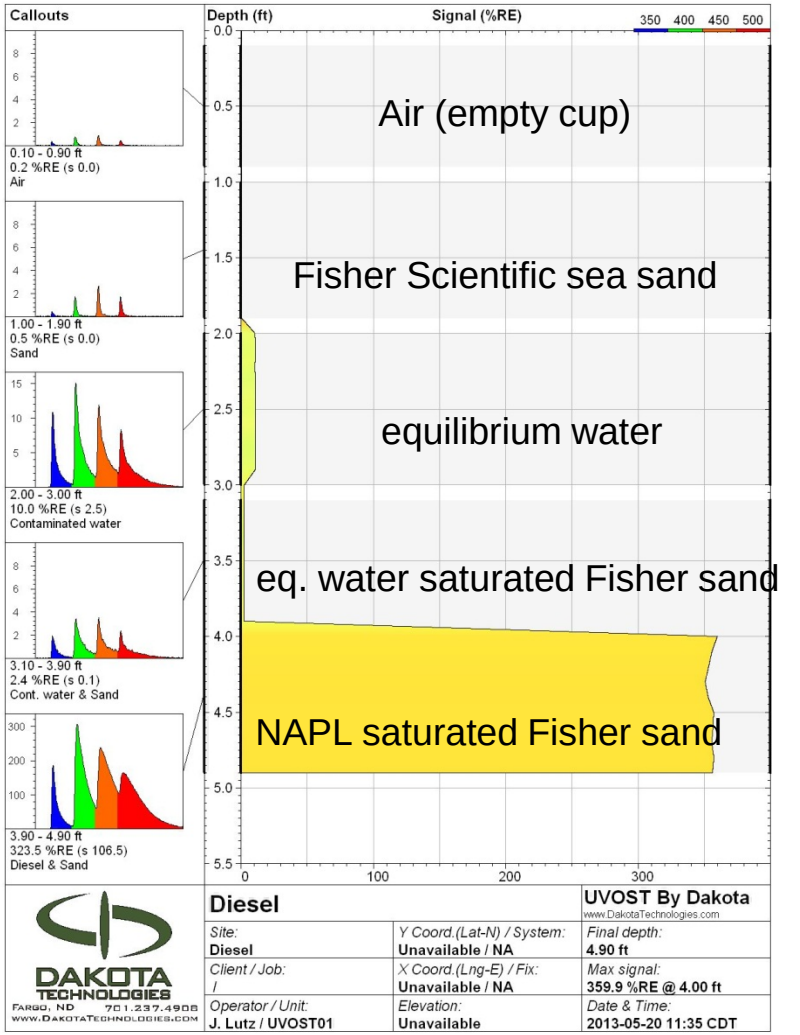
kerosene





experiment cont'd

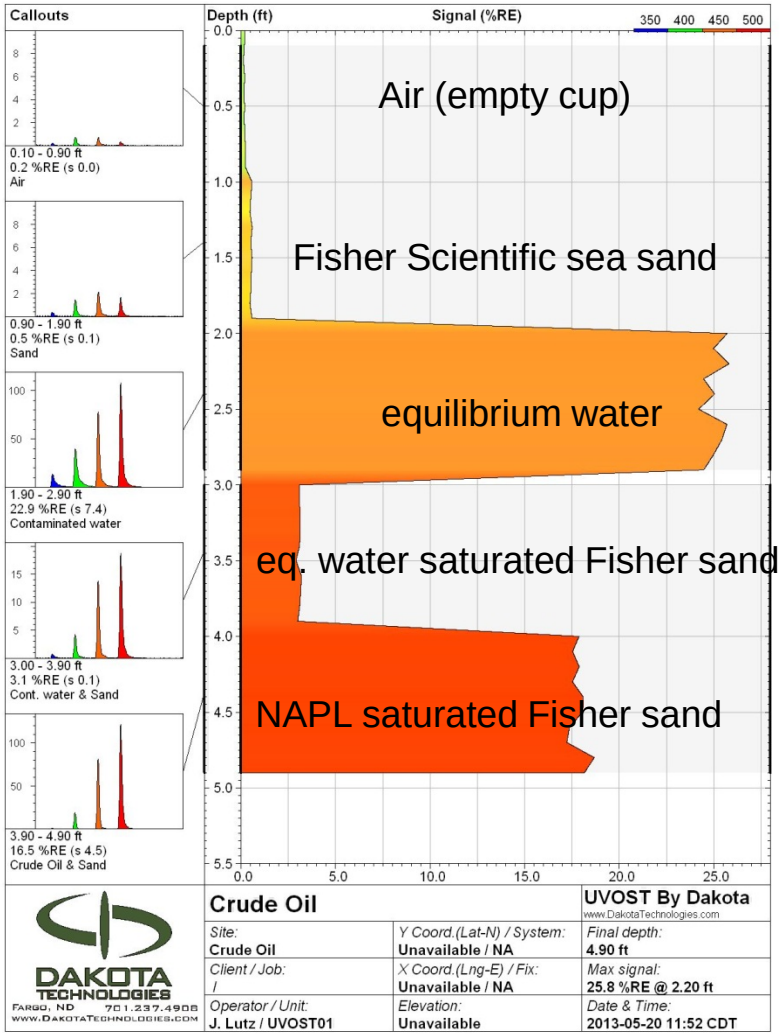
diesel

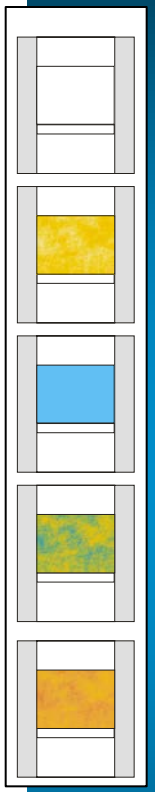


experiment cont'd

??? dissolved looks like the "heavy"!

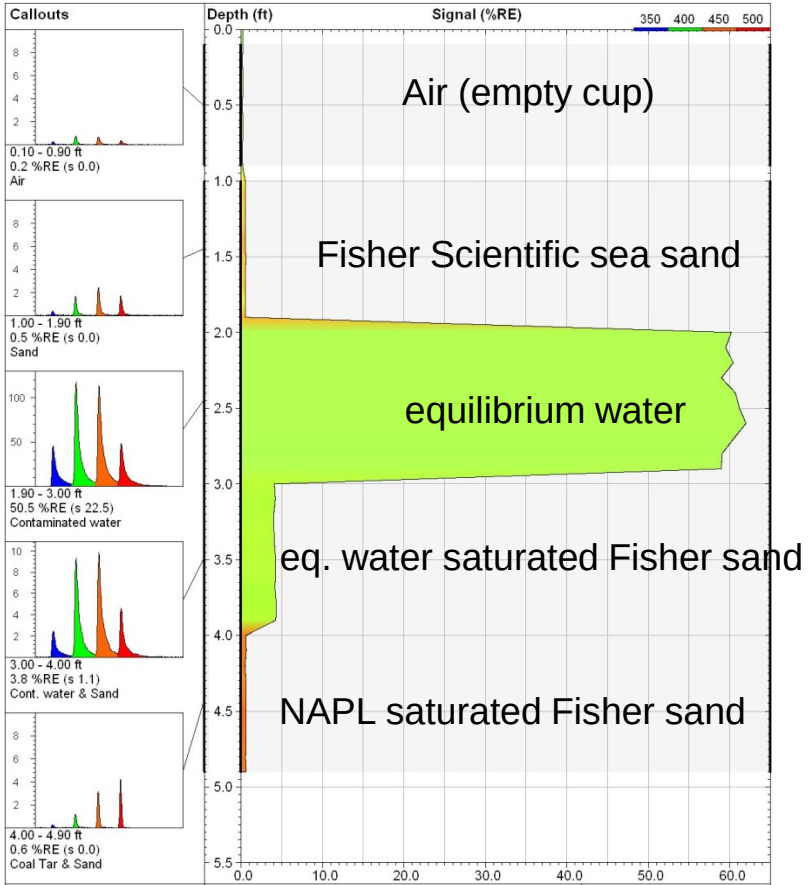
heavy crude (#5)

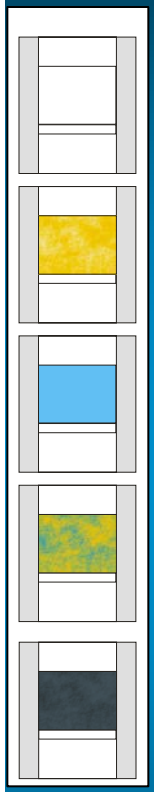




experiment cont'd

coal tar





false positives/negatives

most have short lifetimes and look “odd” vs. target fuel/oil

Previously observed positives [weak 1-3% RE, medium 3-10% RE, strong >10% RE]

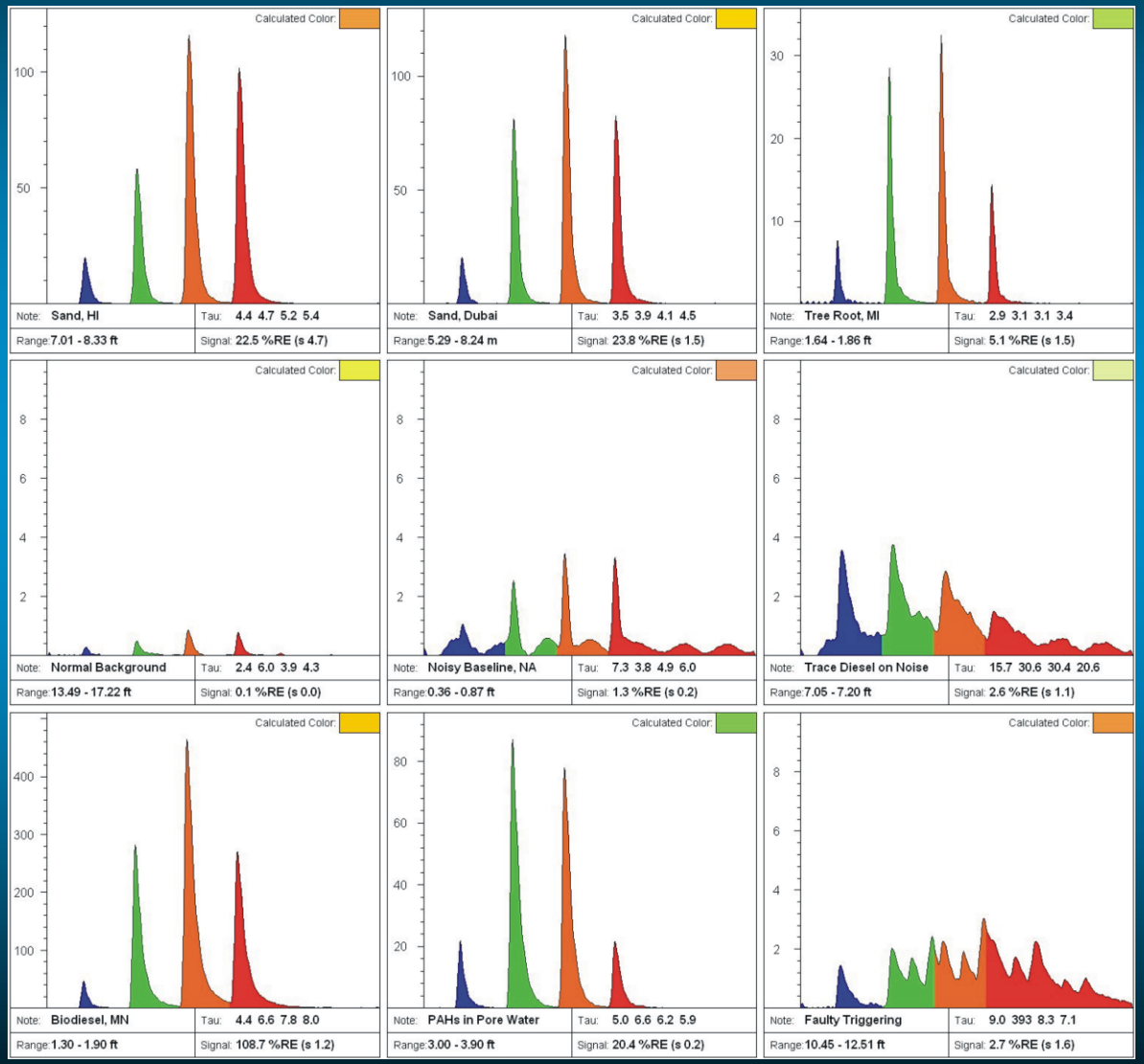
sea shells (weak-strong)
paper (medium-strong)
peat/meadow mat (weak)
calcite/calcareous sands (weak-strong)
asphalt (very weak)
stiff/viscous tars (weak)
certain soils (weak)
tree roots (weak-medium)
sewer lines (medium-strong)
coal (very weak to none)
quicklime (weak)

Previously observed negatives

extremely weathered fuels (especially gasoline)
aviation gasoline (weak)
coal tars (most)
creosotes (most)
“dry” PAHs such as aqueous phase, lamp black, purifier chips, “black mayonnaise”
most chlorinated solvents
benzene, toluene, xylenes (relatively pure)

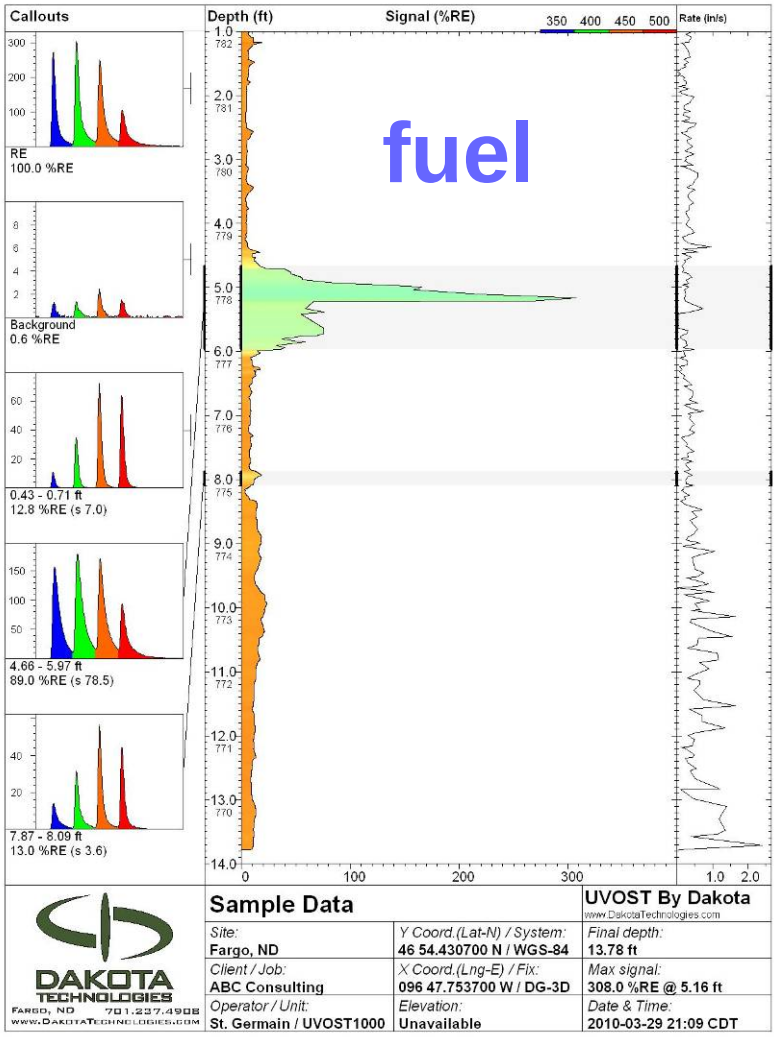
false positives/negatives

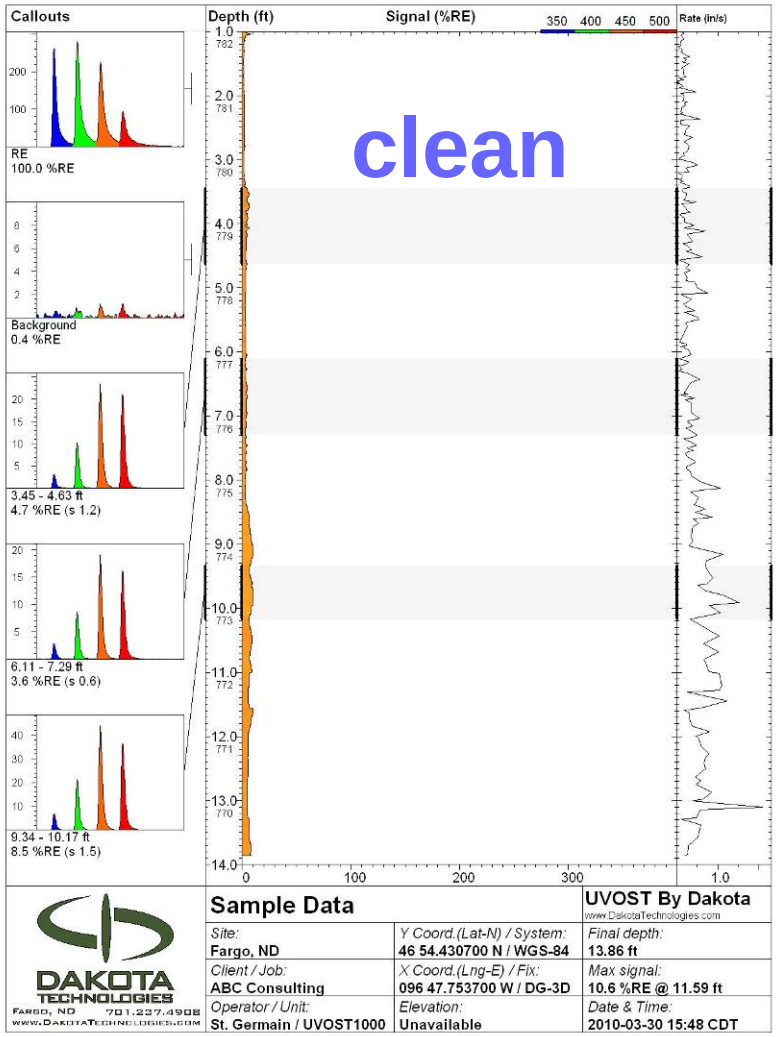
most have short lifetimes and look “odd” vs. target fuel/oil



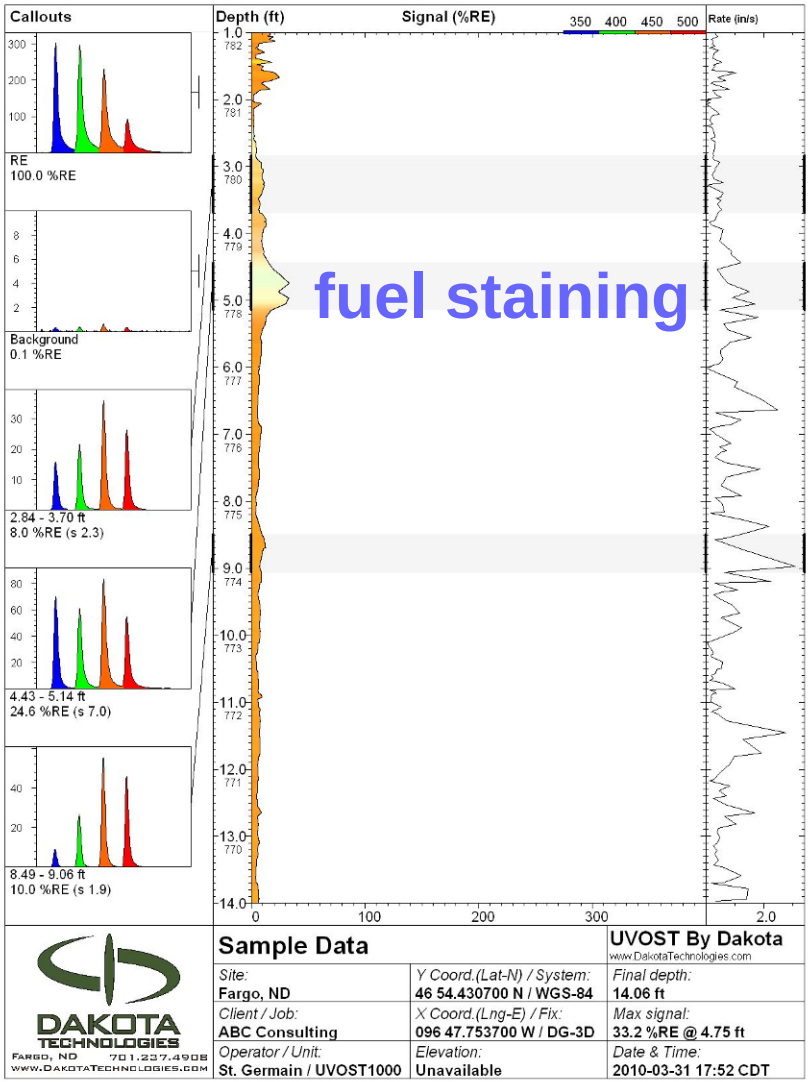
false positive – calcareous sands

often context of the site or entire log helps “make the call”





logs from previous slide (calcareous sands) help solve this “head scratcher”



MIP vs. LIF?

(truth is, they aren't really competitors)

Membrane Interface Probe (MIP)

- designed for **VOCs** (which LIF can't detect usefully)
- "sticky" semi-VOCs often cause transfer line/carryover issues
- difficult to find "bottom" of NAPL due to carryover and resulting lag time, especially if multiple layers
- chlorinated sites make up dominant portion of MIP market

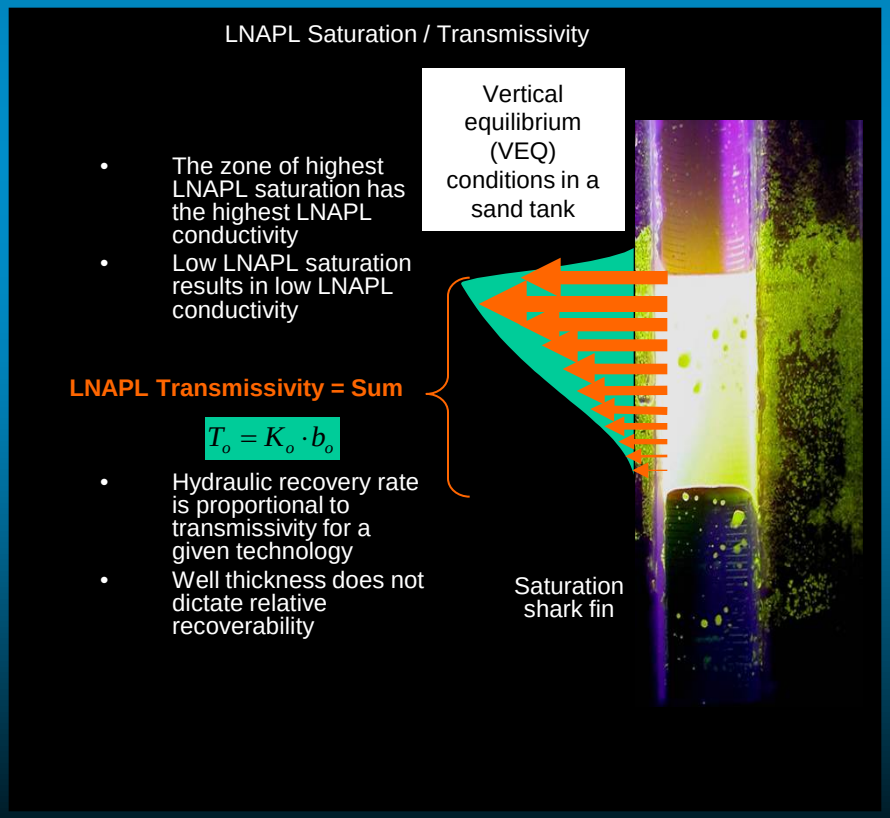
LIF

- Designed specifically for **NAPL delineation and only NAPL**
- smooth/hard sapphire window is "slick" like Teflon – resists carryover
- nearly instantaneous rise/fall - and 100% reversible response
- LIF does NOT see any useful levels of response to dissolved phase
- LIF shows intimate (inch scale) detail of NAPL distribution (relative to MIP)
- LIF provides readily interpreted "spectral" information in real time
- LIF is blind to chlorinated DNAPL dissolved phase (but Dye-LIF will see DNAPL itself)

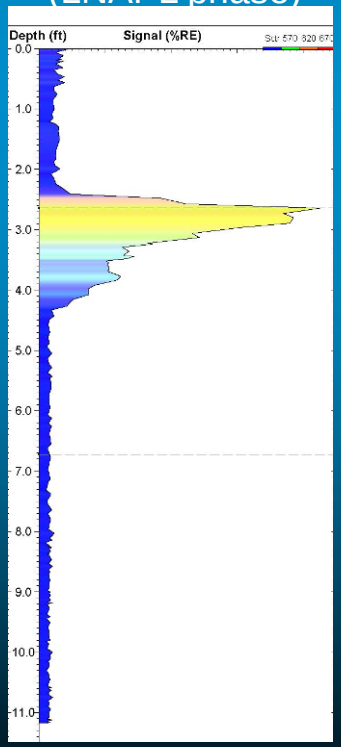
the “shark’s fin” in a “sand box”

recent LNAPL saturation/recovery theory reflects what LIF logs (**in homogeneous lithology**) have shown for years

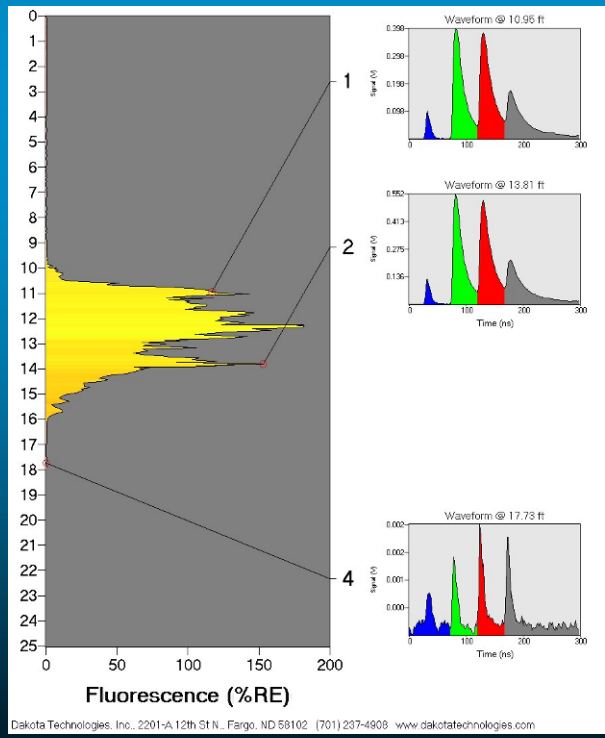
- http://www.clu-in.org/conf/itrc/iuLNAPL/
- http://www.clu-in.org/conf/itrc/LNAPLcr/
- http://www.dnr.mo.gov/env/hwp/docs/lnaplbasics.pdf



Coal Tar (LNAPL phase)



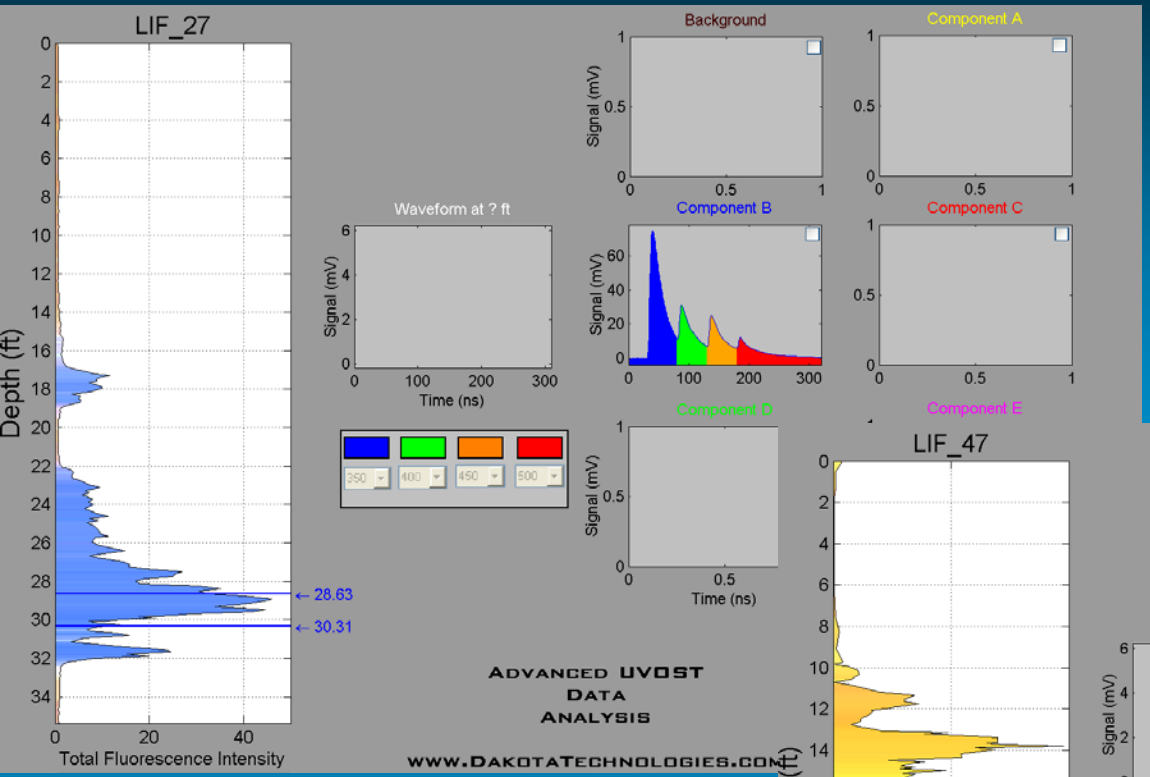
Diesel

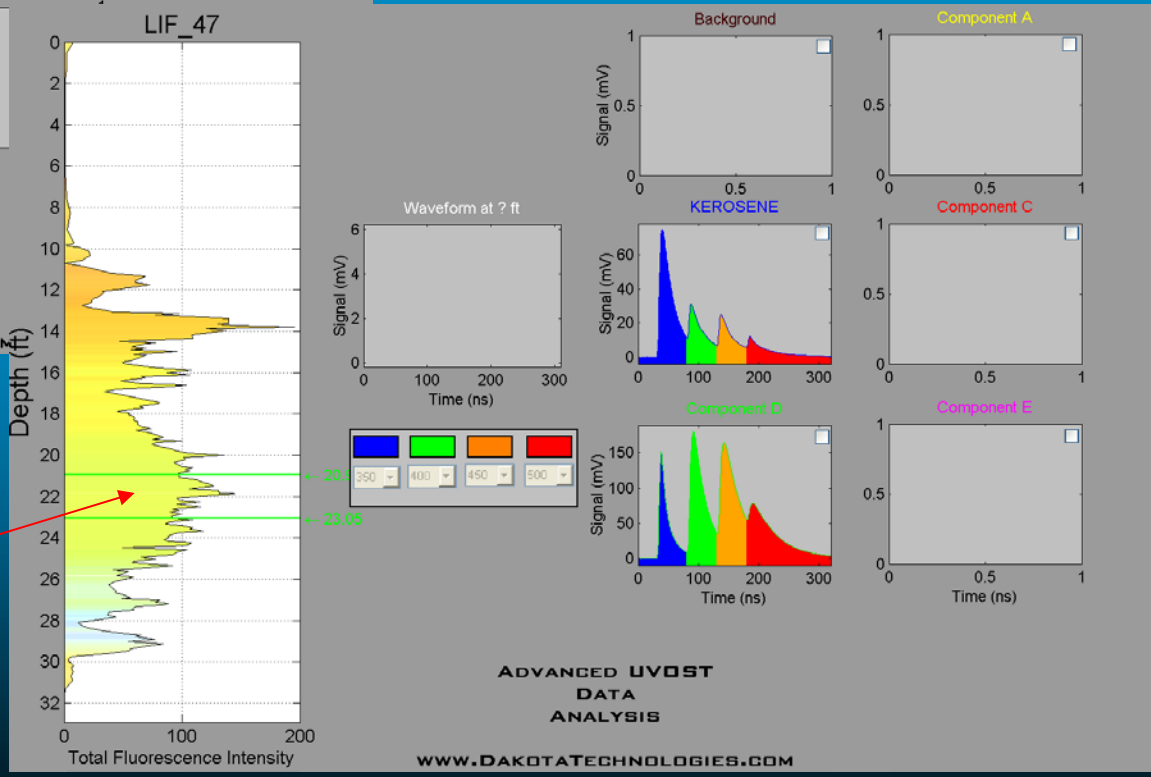


NNLS (non-negative least squares) fitting

- takes full advantage of waveforms/lifetimes
- does things that color-coding can’t
- numerical file output easily incorporated into CSM visualization

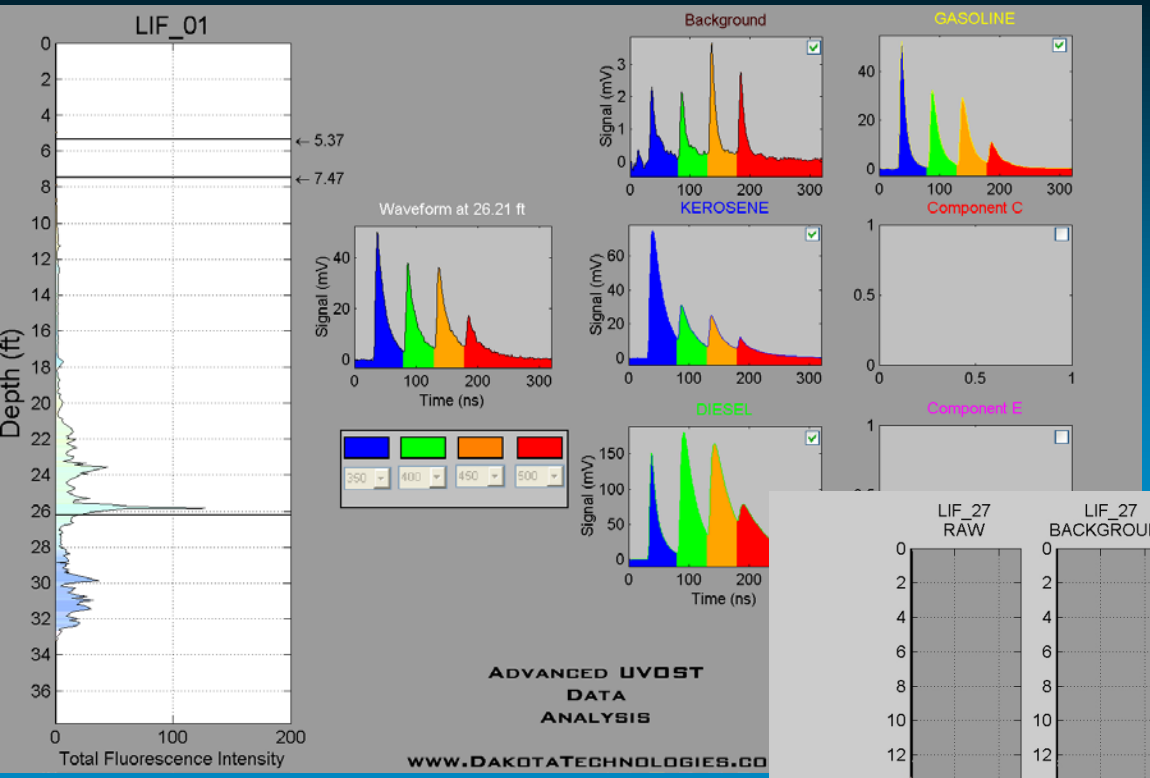
NNLS field example

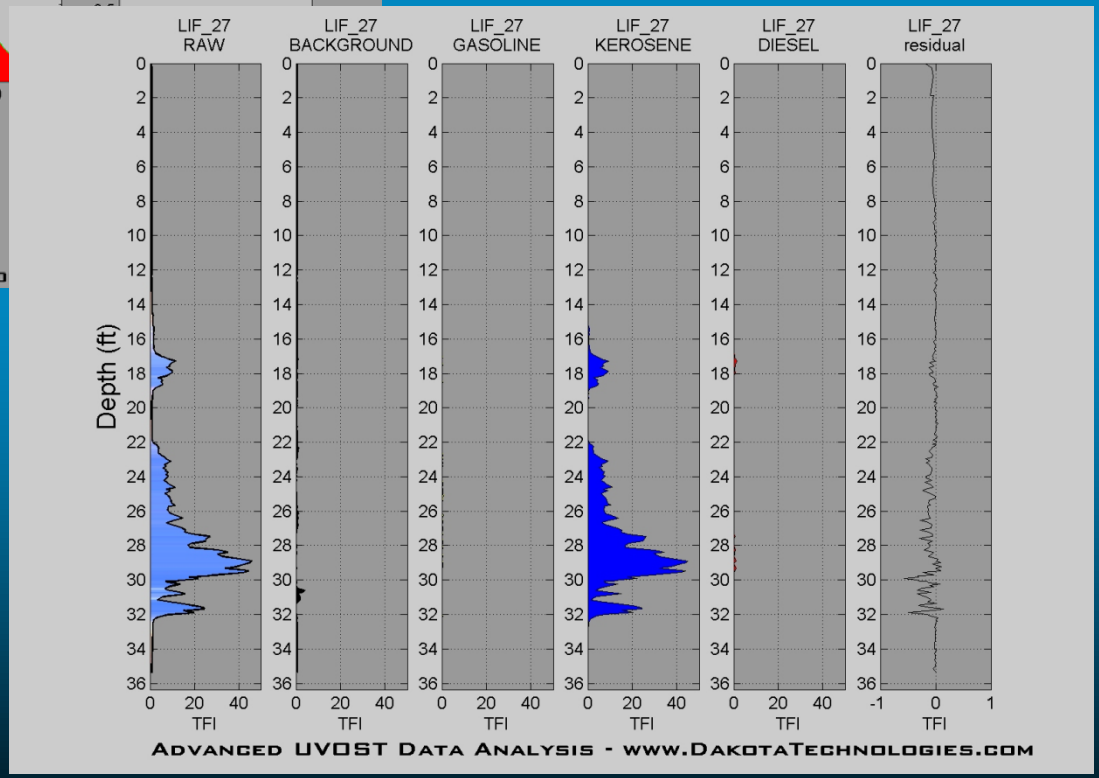




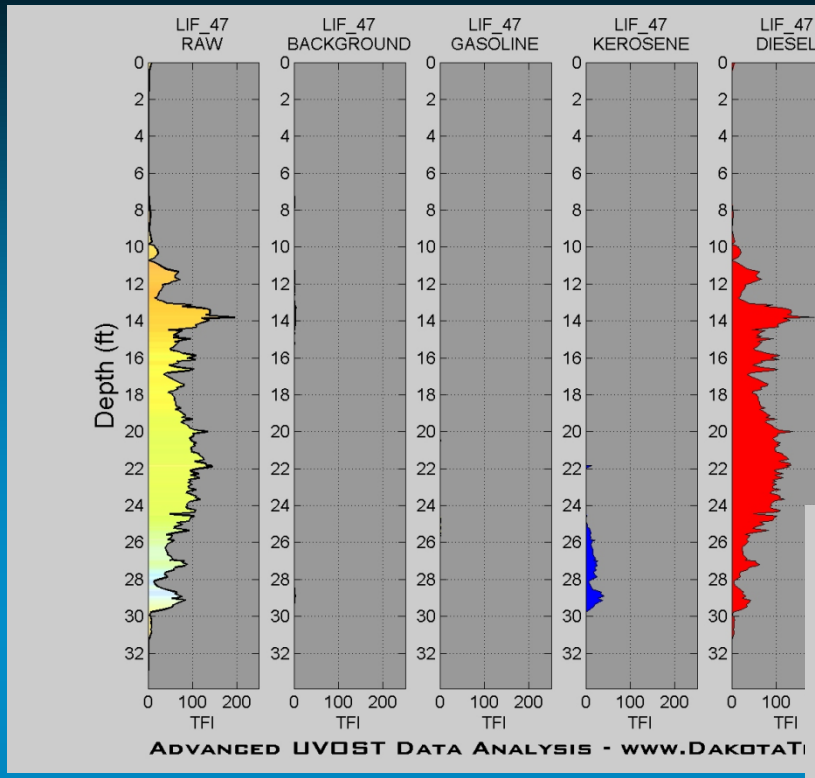
poor harvest area…
no choice though

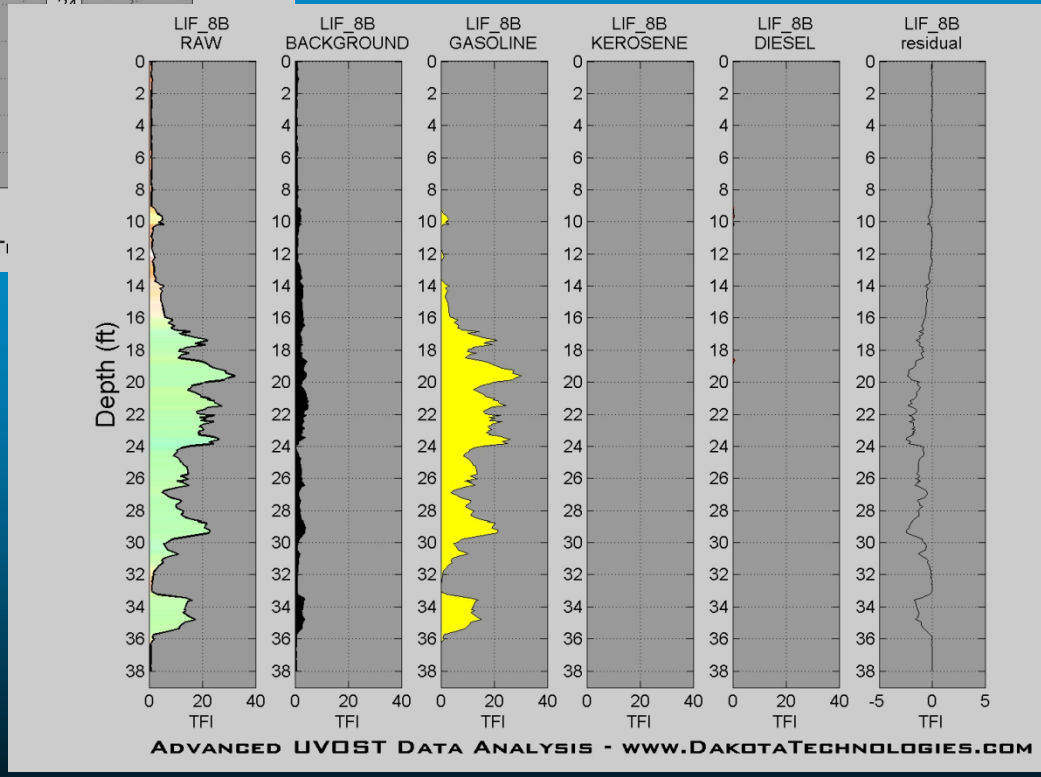
NNLS field example



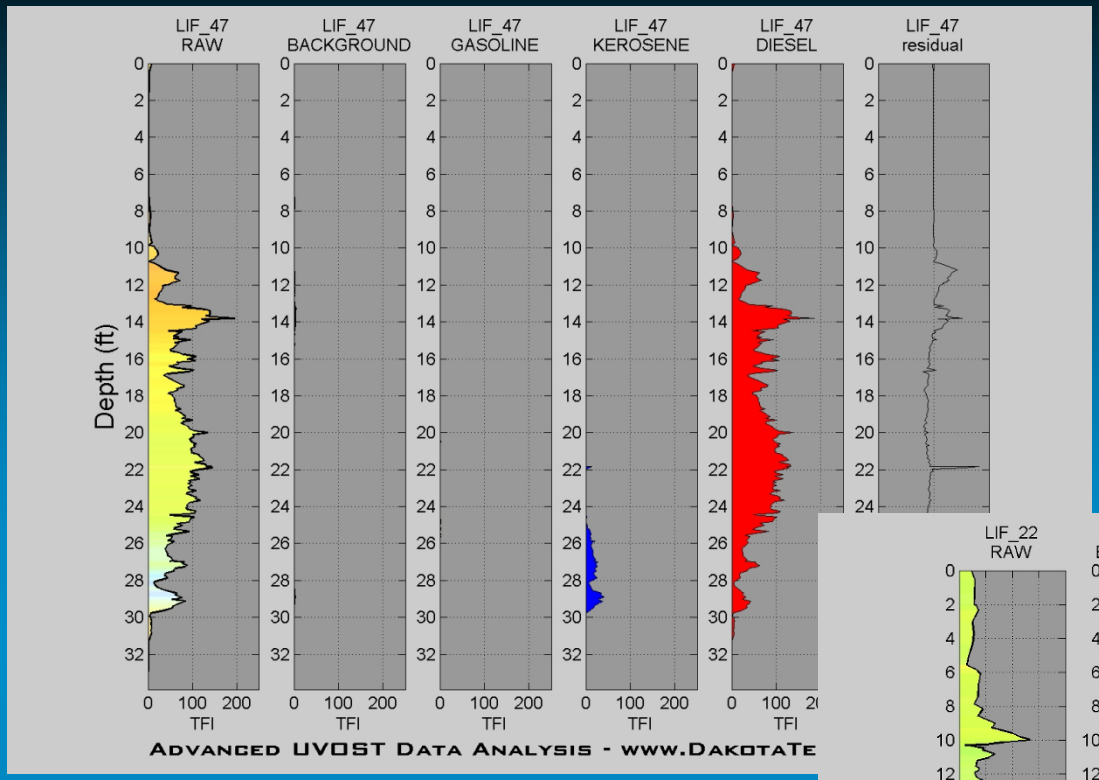


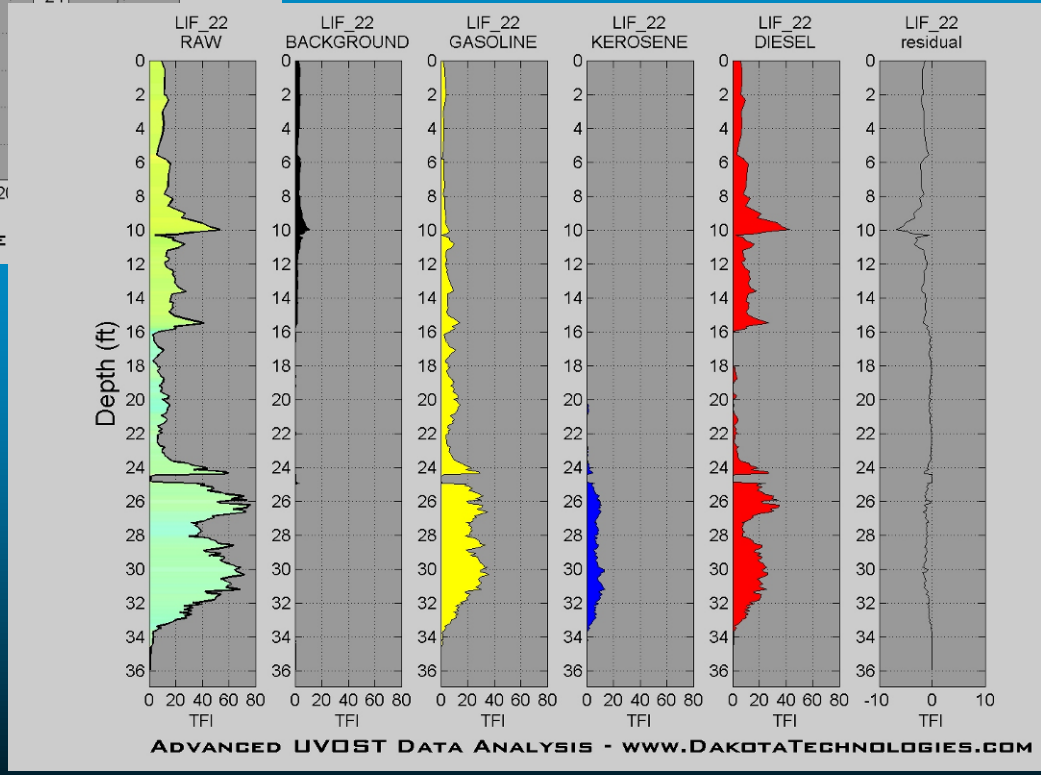
NNLS field example





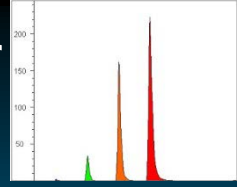
NNLS field example

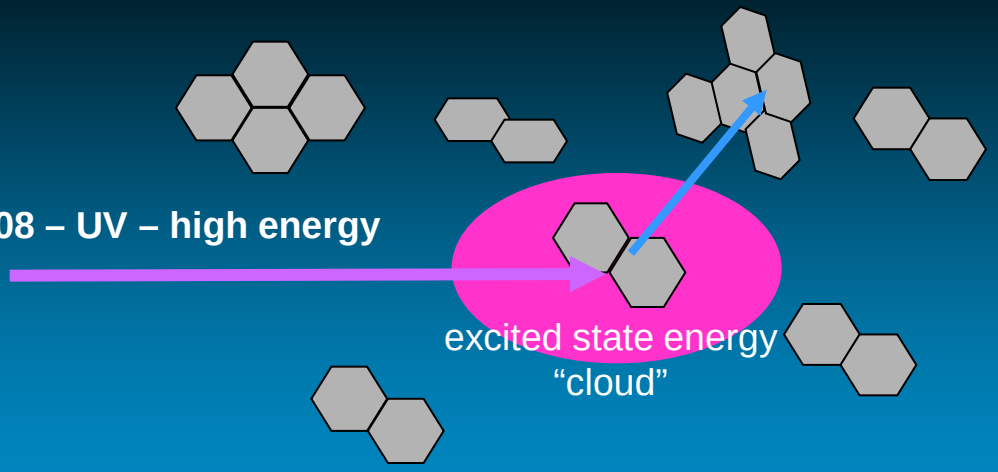




“heavies”… where things start to fall apart for ultraviolet LIF’s semi-quantitative behavior

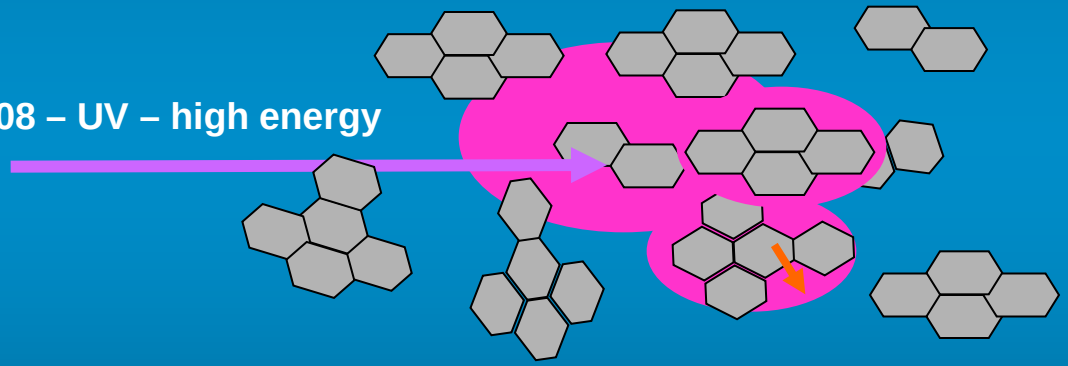
PAHs, Excitation Wavelength, and Energy Transfer





Dilute PAHs, High Concentration
Straight chains etc.
(fuels and light oils)

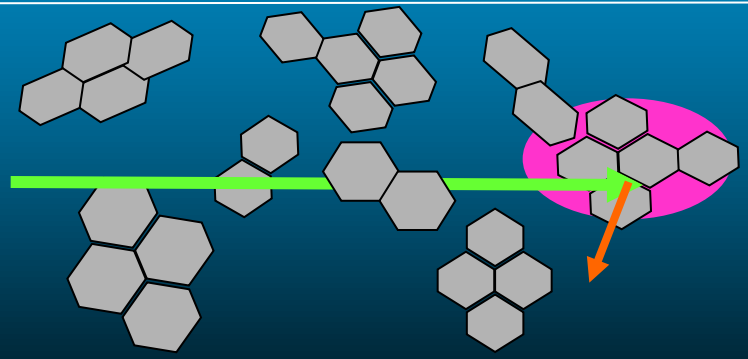
strong absorbance by smaller PAHs
low chance of energy transfer
few neighboring large PAHs
strong fluorescence



Heavier LNAPL exhibiting larger and higher concentration PAHs

strong absorbance by smaller PAHs
high chance of energy transfer
many neighboring large PAHs
weak, if any, fluorescence

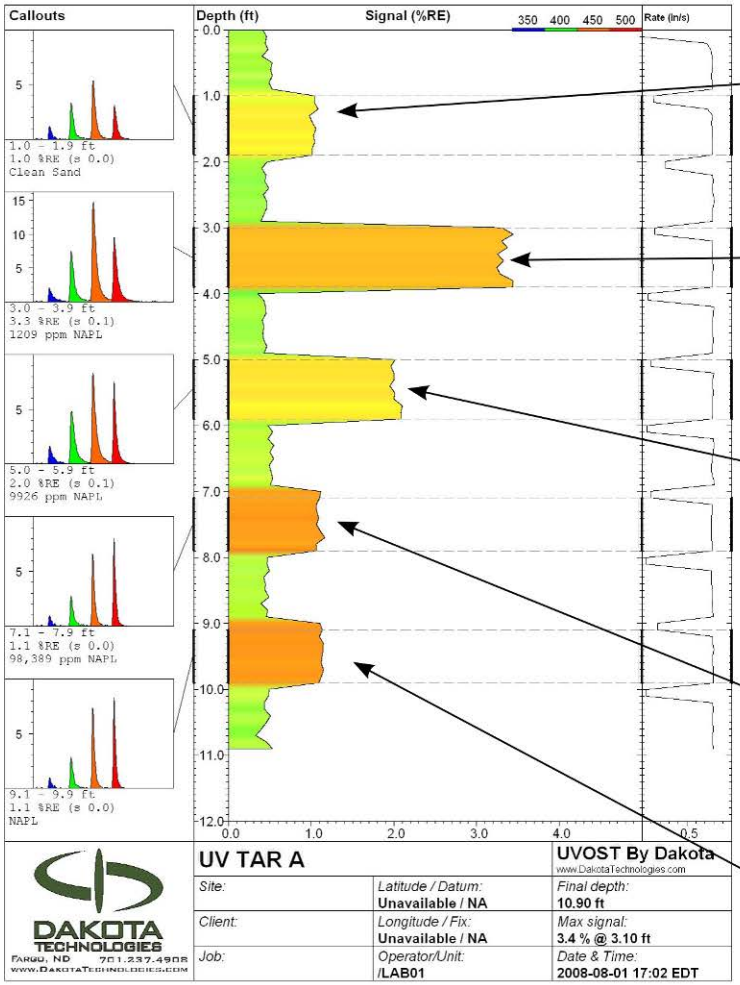
532nm – visible - low energy

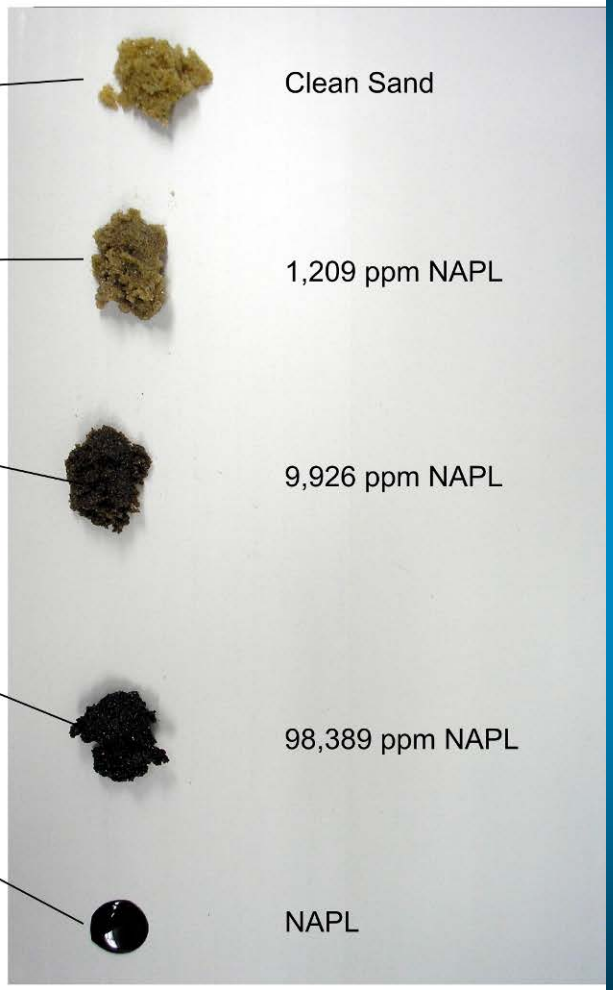


conc’d “close packed” PAHs
(tars, creosotes, heavy crude)

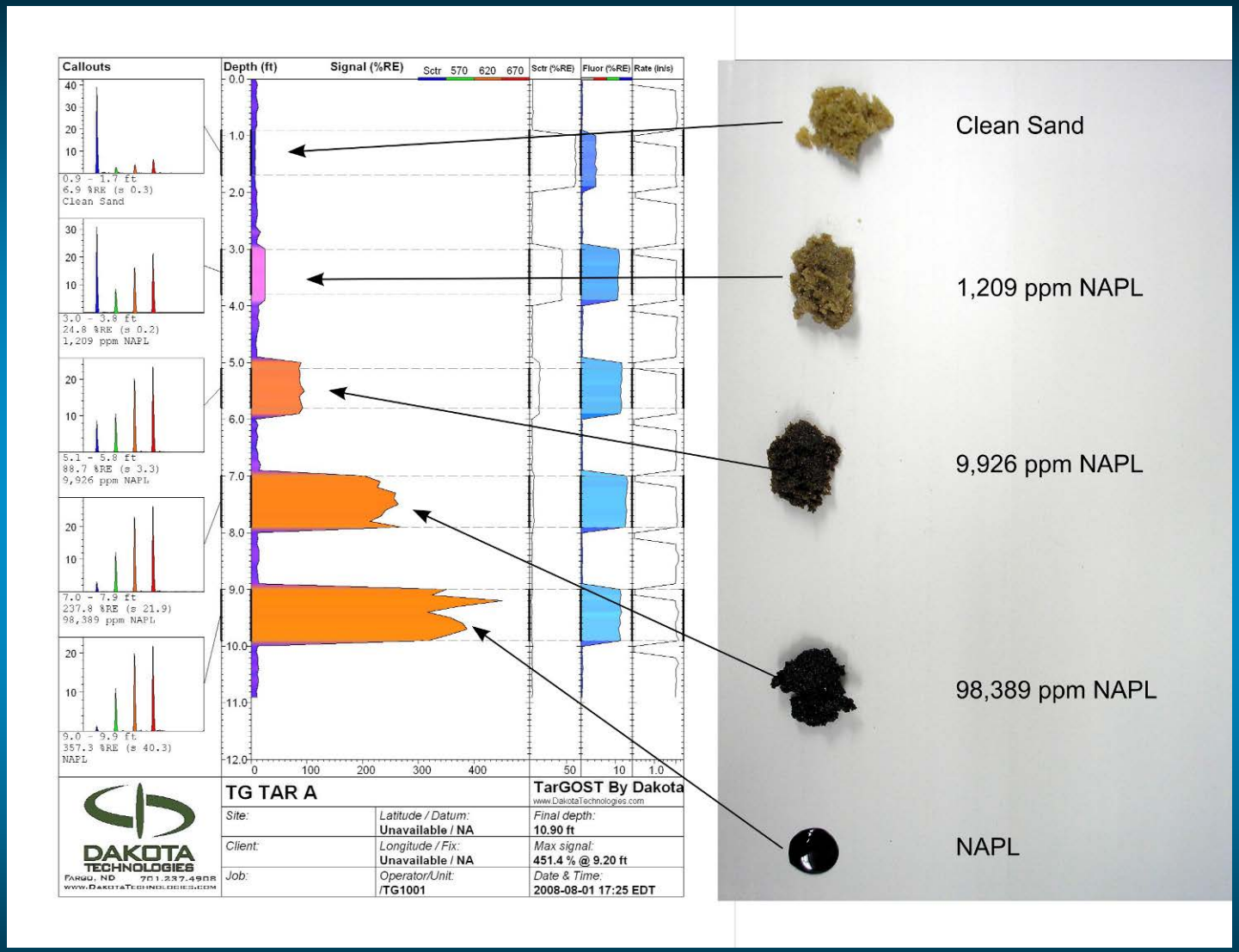
no absorbance by smaller PAHs
direct excitation of large PAHs
low chance of energy transfer
moderate fluorescence

typical MGP coal tar on UV LIF



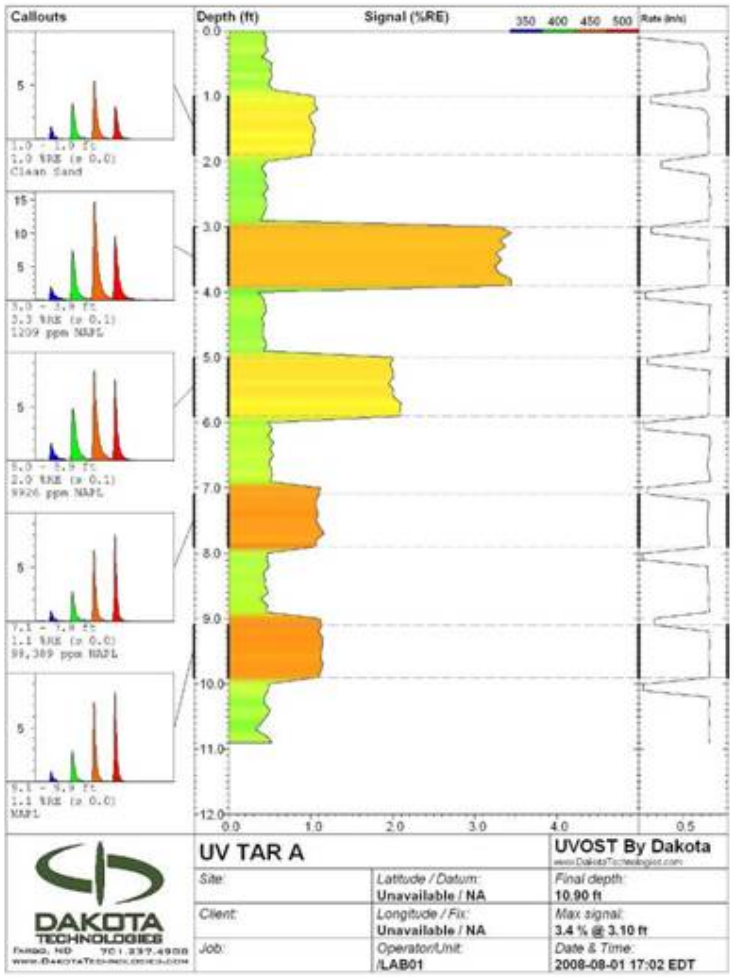


typical MGP coal tar on TarGOST

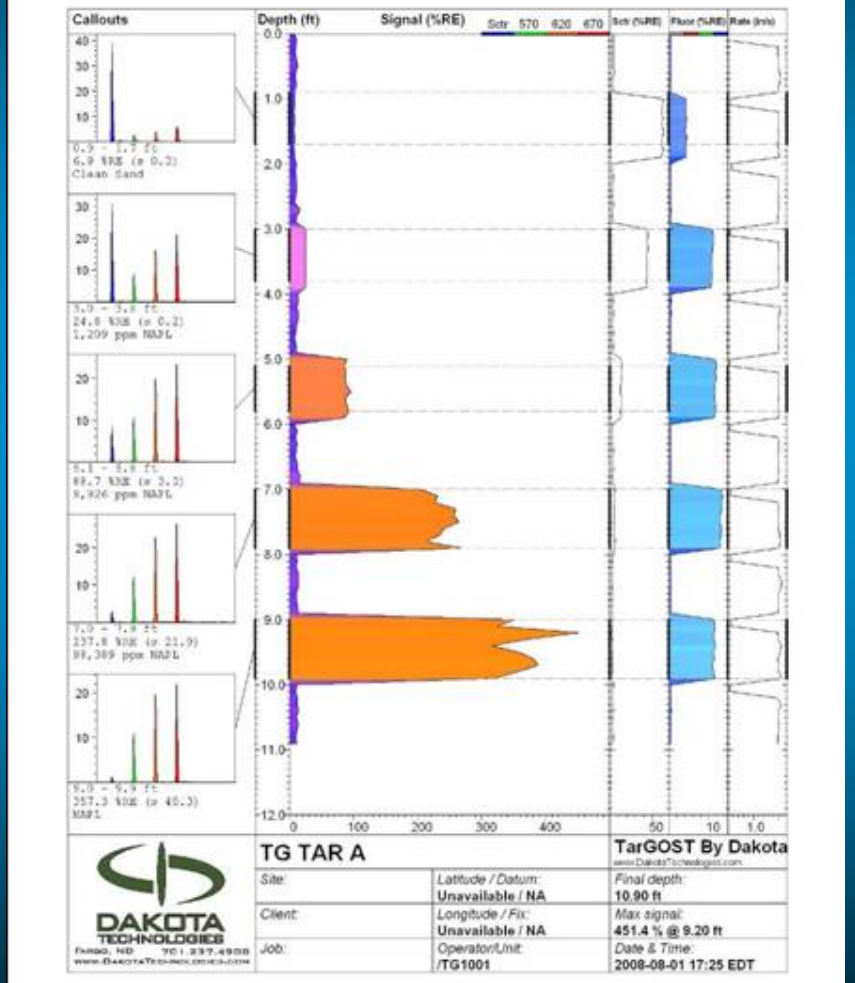


typical MGP coal tar on UV LIF vs. TarGOST

UVOST

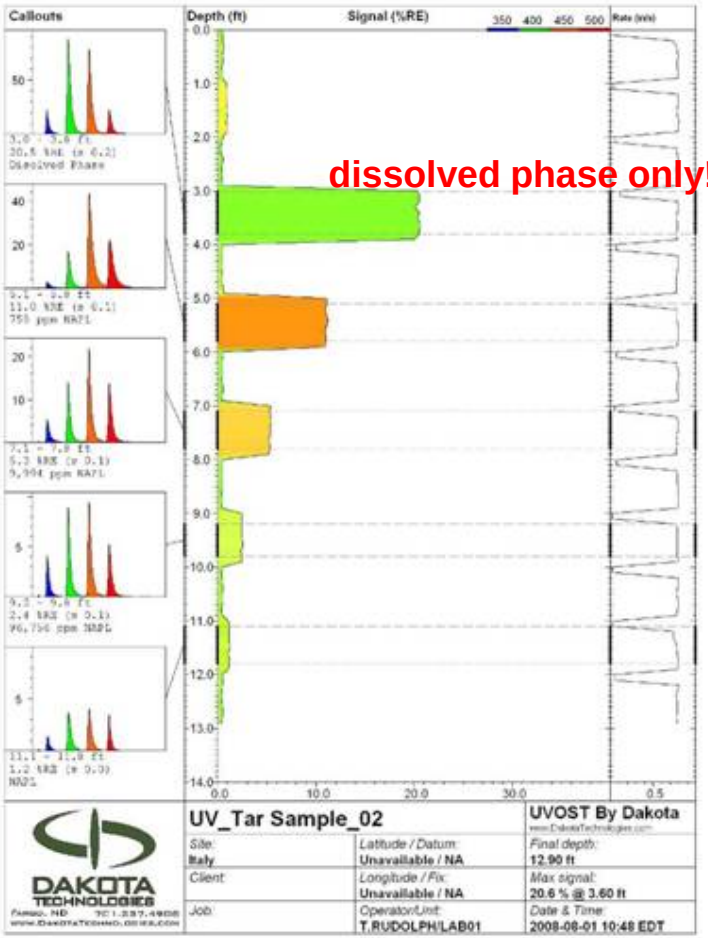


TarGOST

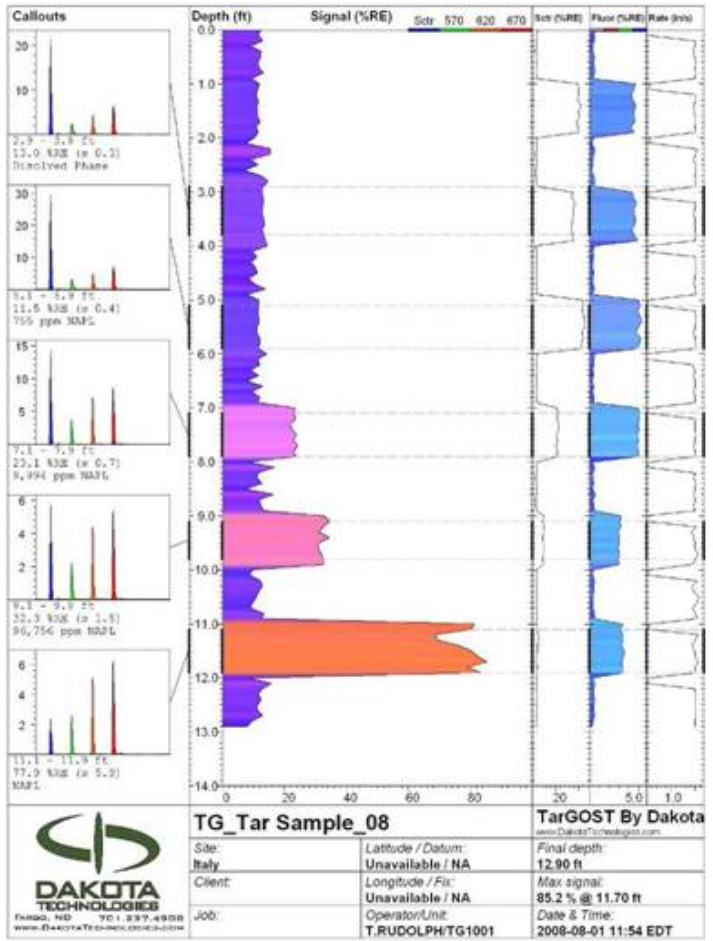


pitchy coal tar on UV LIF vs. TarGOST

UVOST

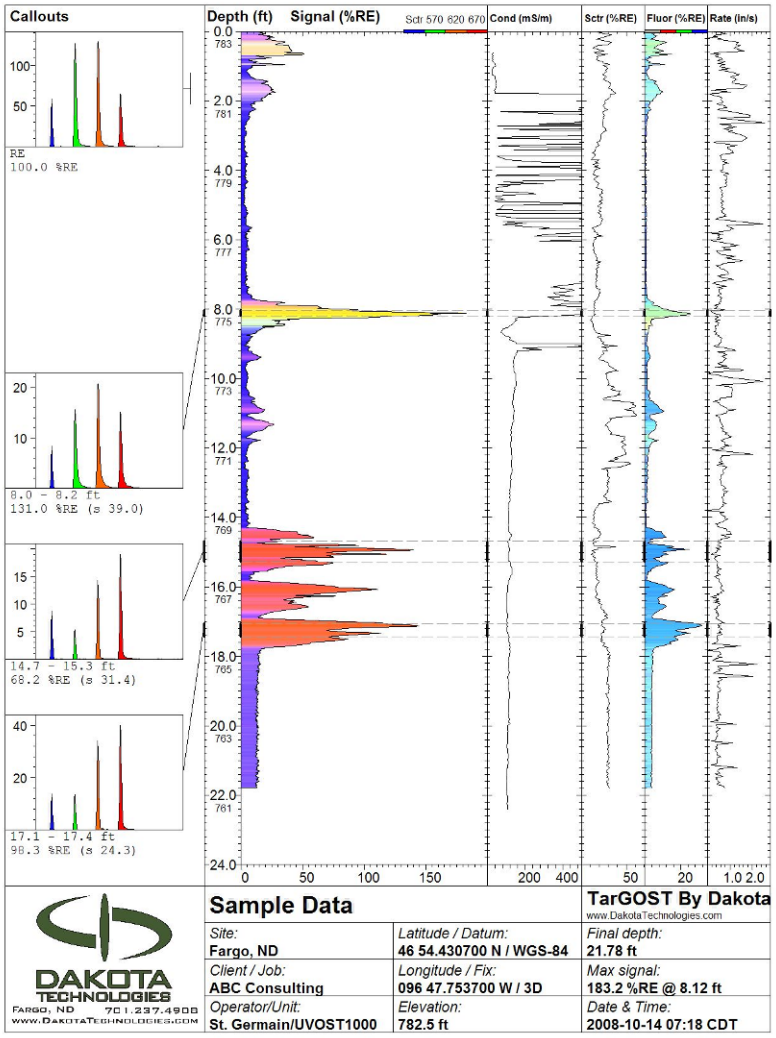


TarGOST

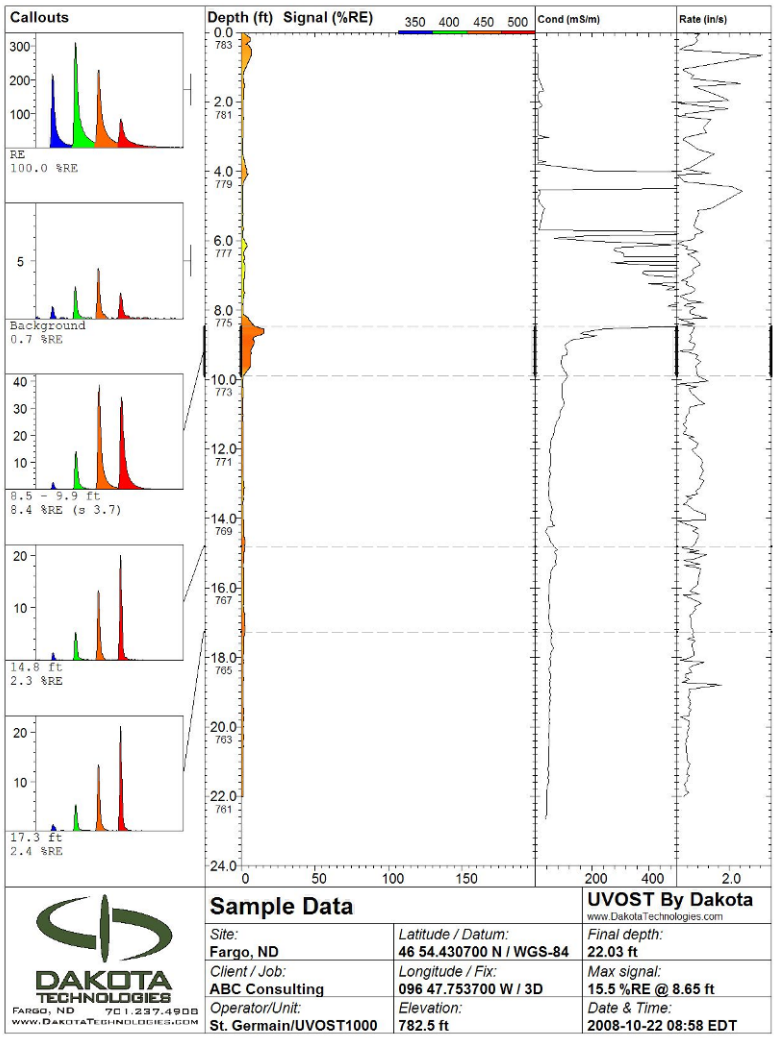


coal tar – former MGP – duplicate logs

TarGOST

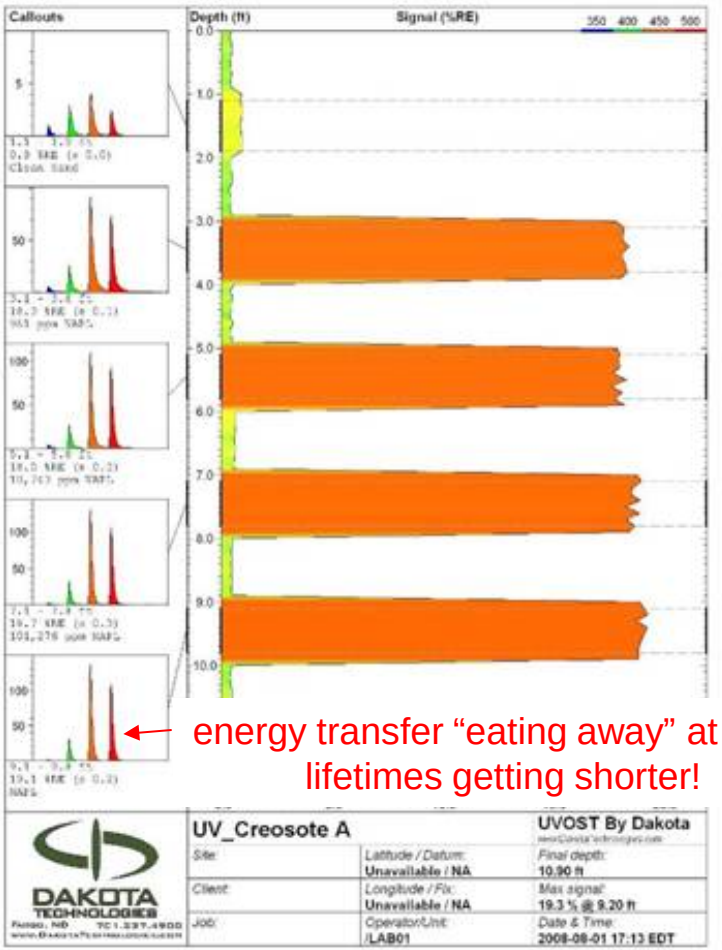


UVOST

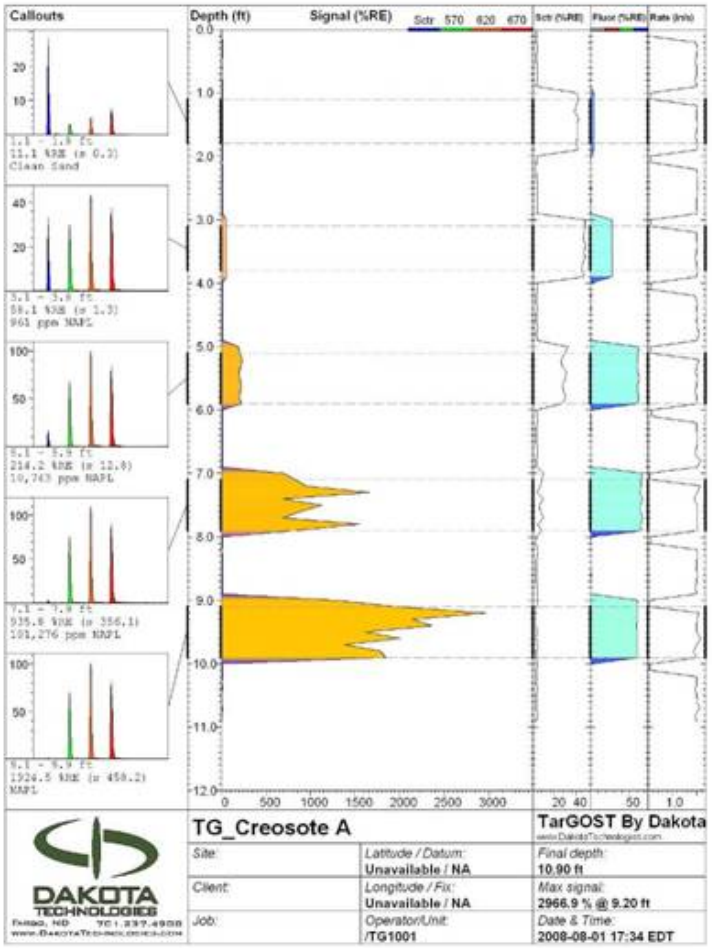


a “UV-friendly” creosote on UV LIF vs. TarGOST (many creosotes behave like coal tar)

UVOST



TarGOST

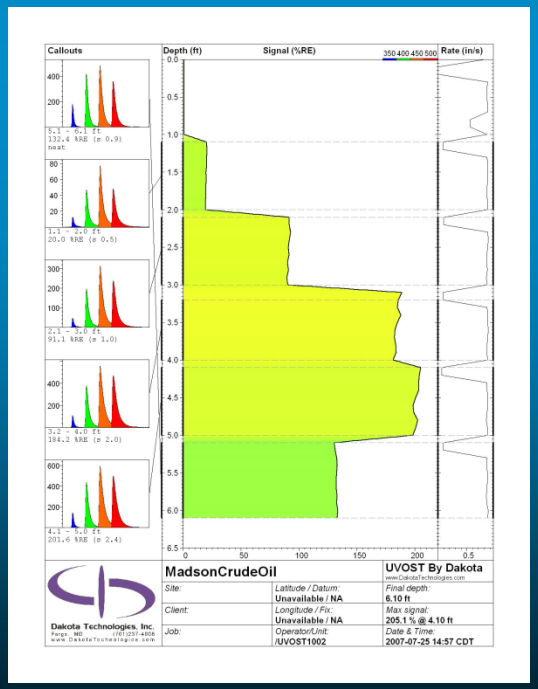


“Heavies” are incompatible with UV LIF

Dakota has found the following materials ‘misbehave’ in the UV:

- Coal tar
- Coking tar/pitch
- Creosote
- bunker B-C or other “heavy fuel oils”

Notice that crude oil is not in the “heavies” list. The majority of crude oils that Dakota has examined were found to behave monotonically in the UV at low-to-mid concentrations, only “rolling over” at the very high to neat concentrations. This is acceptable behavior since “a lot of NAPL is a lot of NAPL”.



crude

Dakota's Stance on Screening for High-PAH Content NAPLs (aka "heavies") with UVOST

Dakota desires to limit our potential legal exposure should litigation result from UVOST characterization of a coal tar or creosote site. Legal risk is your reason to take this matter seriously and avoid getting yourselves involved in a "heavy" NAPL site investigation with UVOST.

For this reason, DAKOTA HEREBY OFFICIALLY DIVORCES ITSELF OF ANY/ALL DATA RESULTING FROM **PURPOSEFUL** APPLICATION OF UVOST ON A COAL TAR, CREOSOTE, OR OTHER SITE KNOWN TO CONSIST OF THESE OR SIMILARLY BEHAVED HIGH PAH CONCENTRATION NAPLS (heavies). In order to maintain the UVOST product's exceptional reputation for quality, Dakota insists that all UVOST service providers abstain from conducting UVOST investigations where "heavies" are the target NAPL.

Dakota's TarGOST System History

TarGOST® services since 2004 (in the petroleum LNAPL logging business for 20 years)

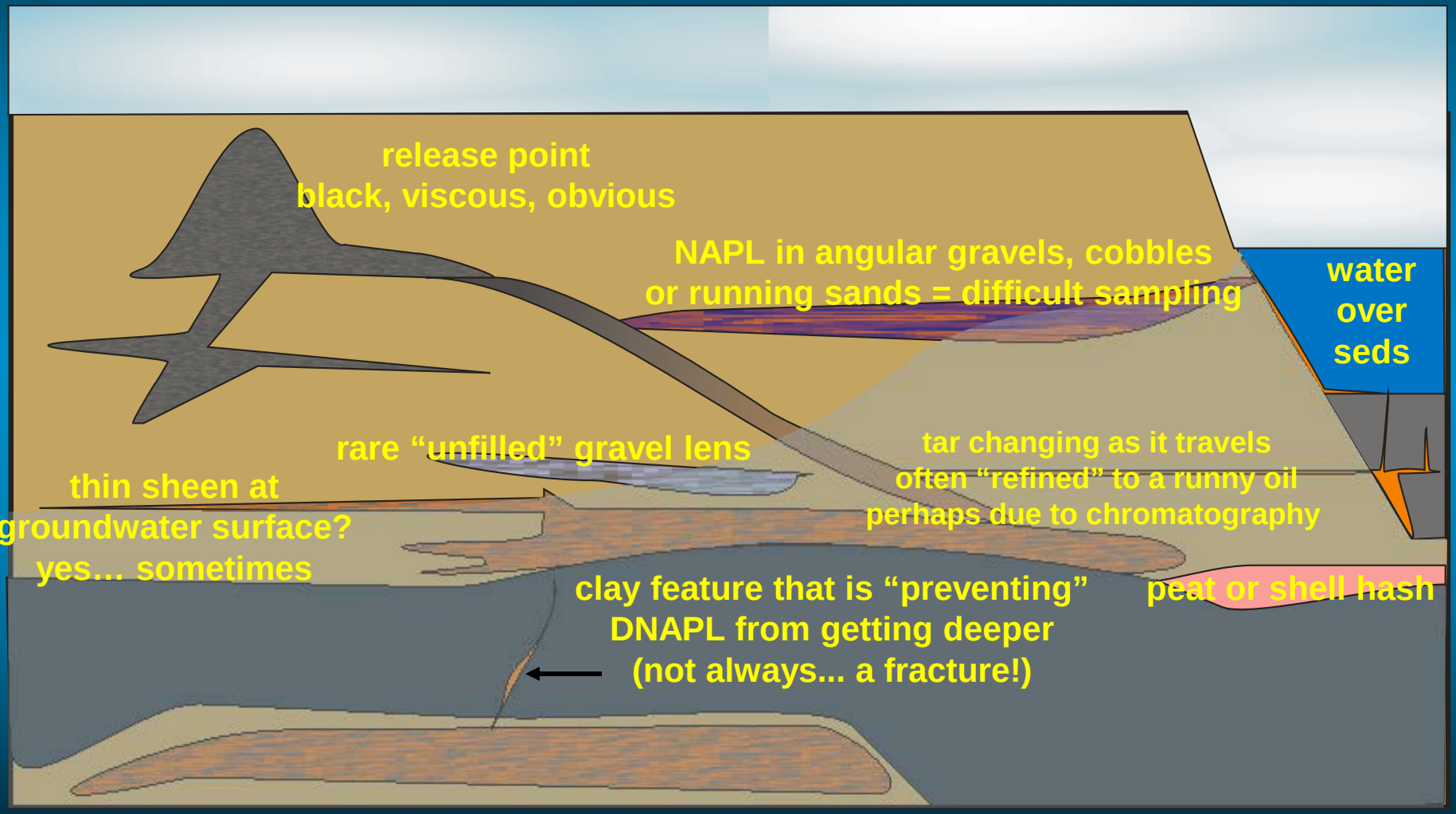
tar/creosote logging to date:	**259776 ft (49.2 miles)**
# Logs:	**10,848**
# Investigations:	**233 [some on sites visited more than once]**

Properties of Coal Tars (and Creosotes)

- Density barely greater than water - so tar can fraction into LNAPL and (most often) a DNAPL (near “zero gravity”)
- Tars/creosotes can sink, float, or both (common)
- Tremendous “penetration” capabilities
  (think penetration oil’s ability to loosen bolts)
- Viscosity ranges from solids to runny oils
- Most near-surface and surface coal tars and creosotes are NOT representative of the sub-surface material (lost VOCs)
- Not at all fun to handle/decon!
- Will have you smelling like your grandma’s sweater drawer in no time

MGP Sites

Sooty Creek Gas Co., Former MGP, TypiVille, USA



MGP NAPL Characterization Tools

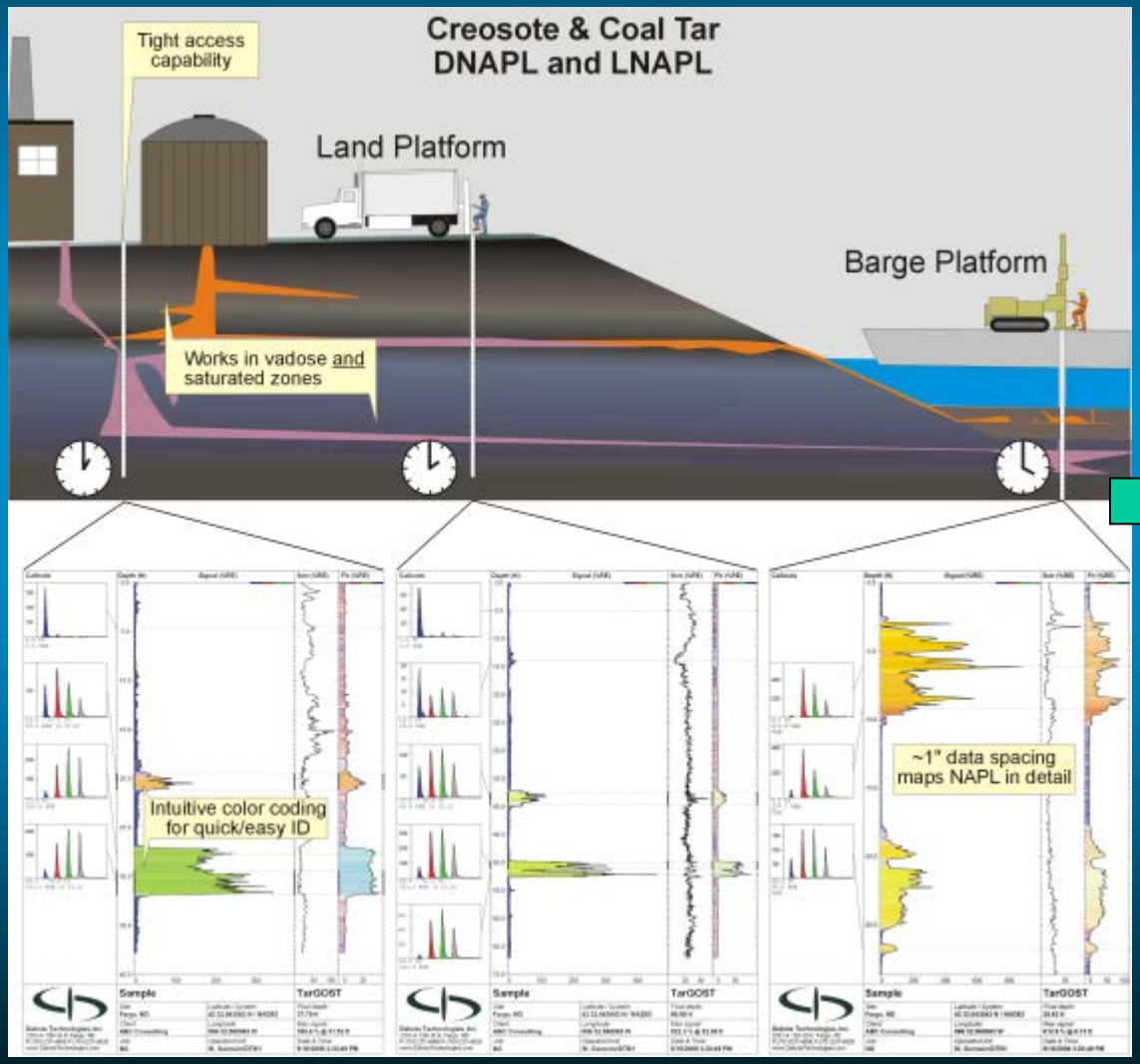
Traditional Sampling/Analysis

obtaining soil samples

- back hoe
- hollow stem auger
- direct push (Geoprobe/AMS)
- sonic
- hand tools

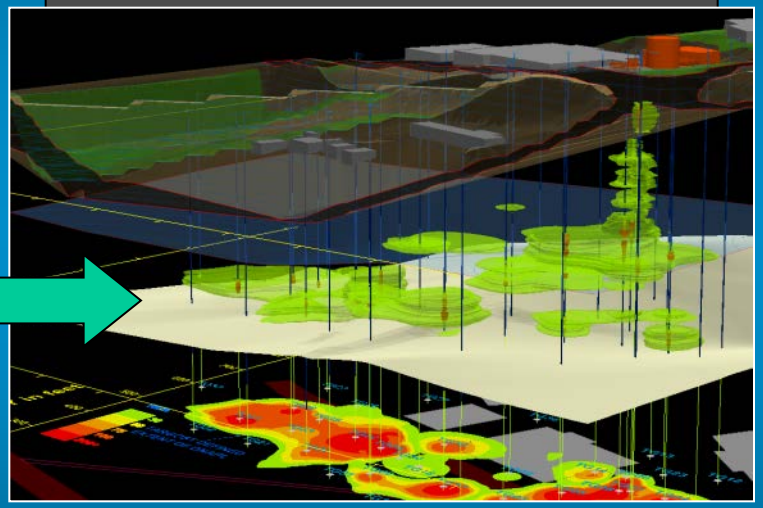
TarGOST® (a specific form of laser-induced fluorescence or LIF)

real time logging of tar in-situ



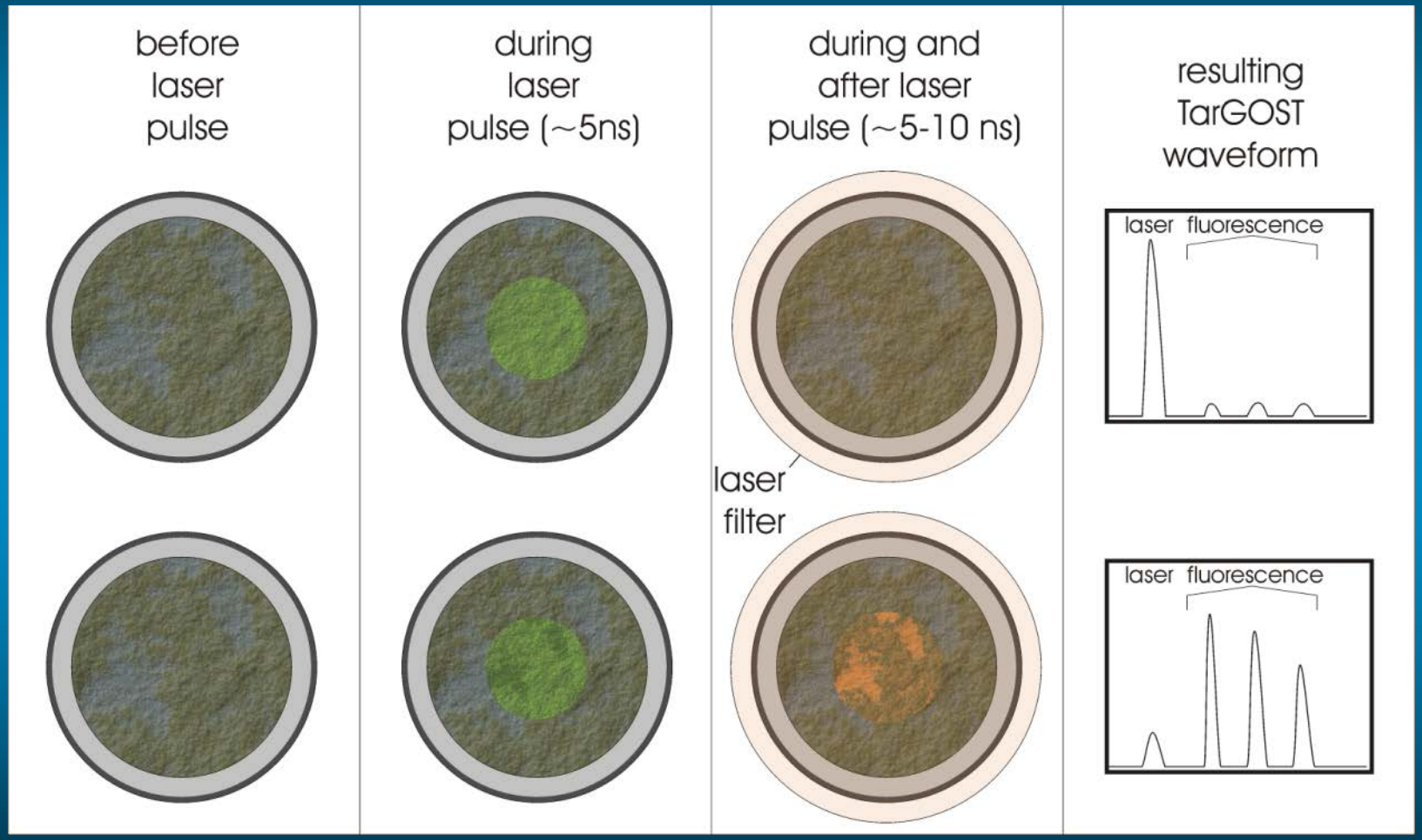
higher density information
for better engineering/decisions

Detailed Conceptual Model

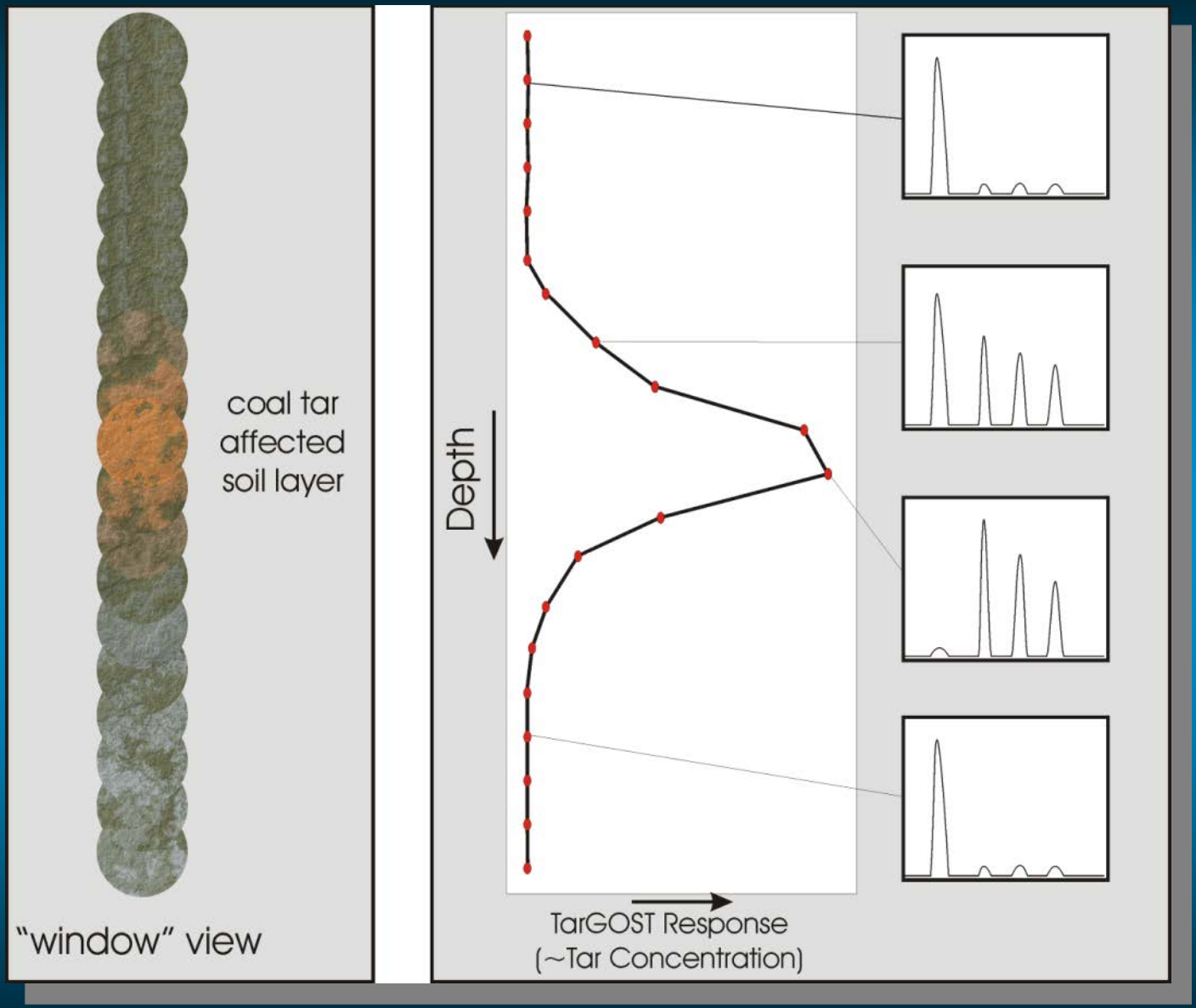


so how does TarGOST "see" tar?….

here's a conceptual view of what it would look like
if we were inside probe – looking out sapphire TarGOST window



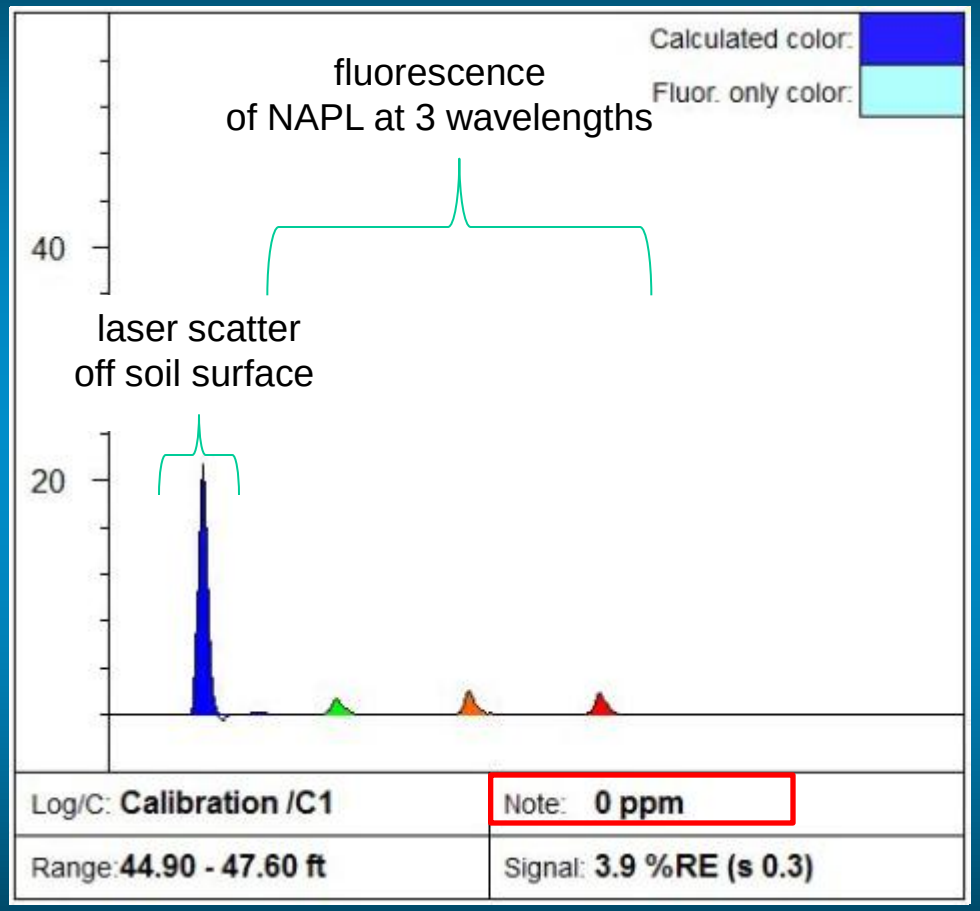
so how does TarGOST “see” tar?….



DAKOTA TECHNOLOGIES

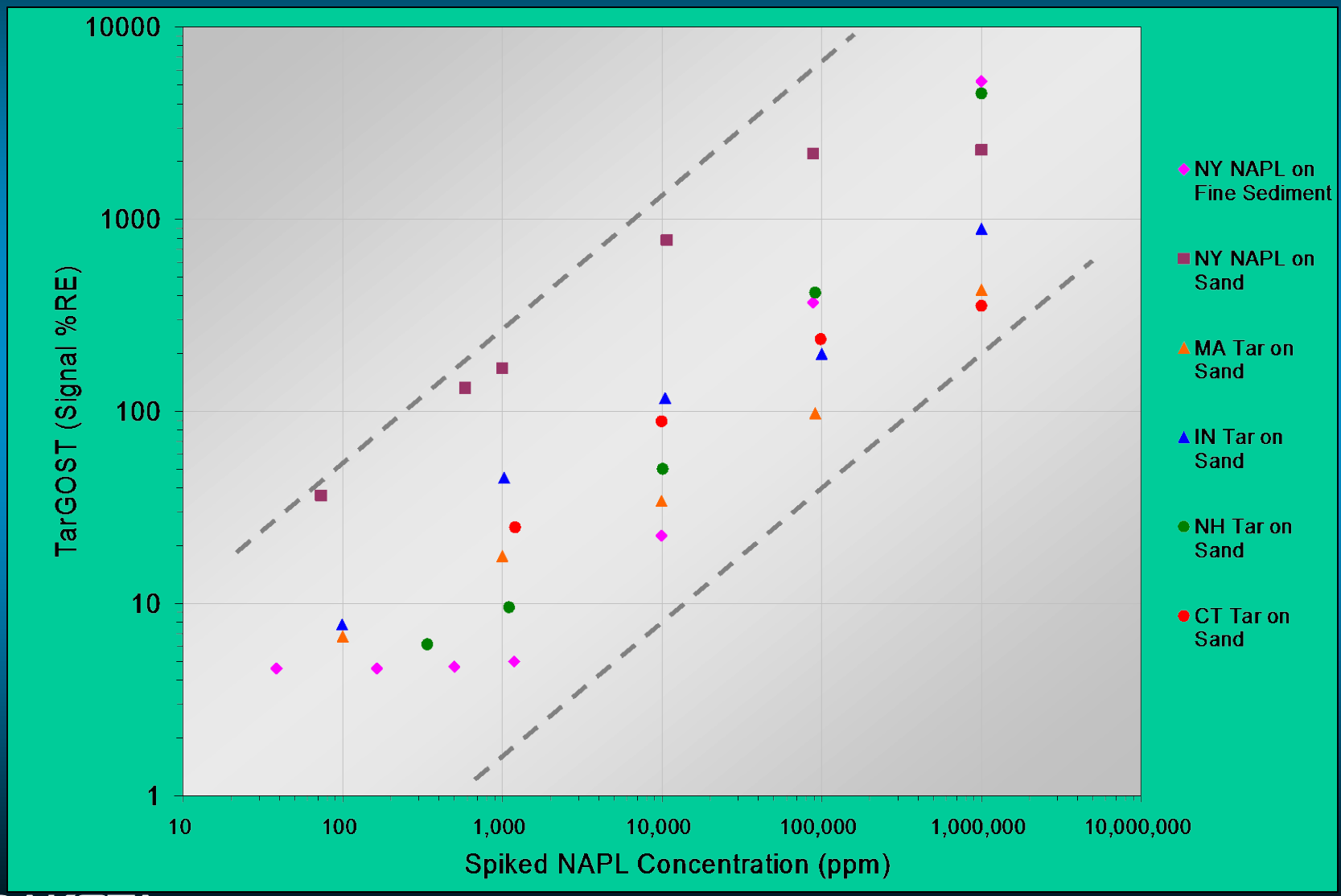
waveforms vs. NAPL saturation

fluorescence grows and scatter shrinks with increasing NAPL saturations



Semi-quantitative response to NAPL

varies with “brightness” of fluorescence of NAPLs and soil matrix – fine being less responsive than coarse



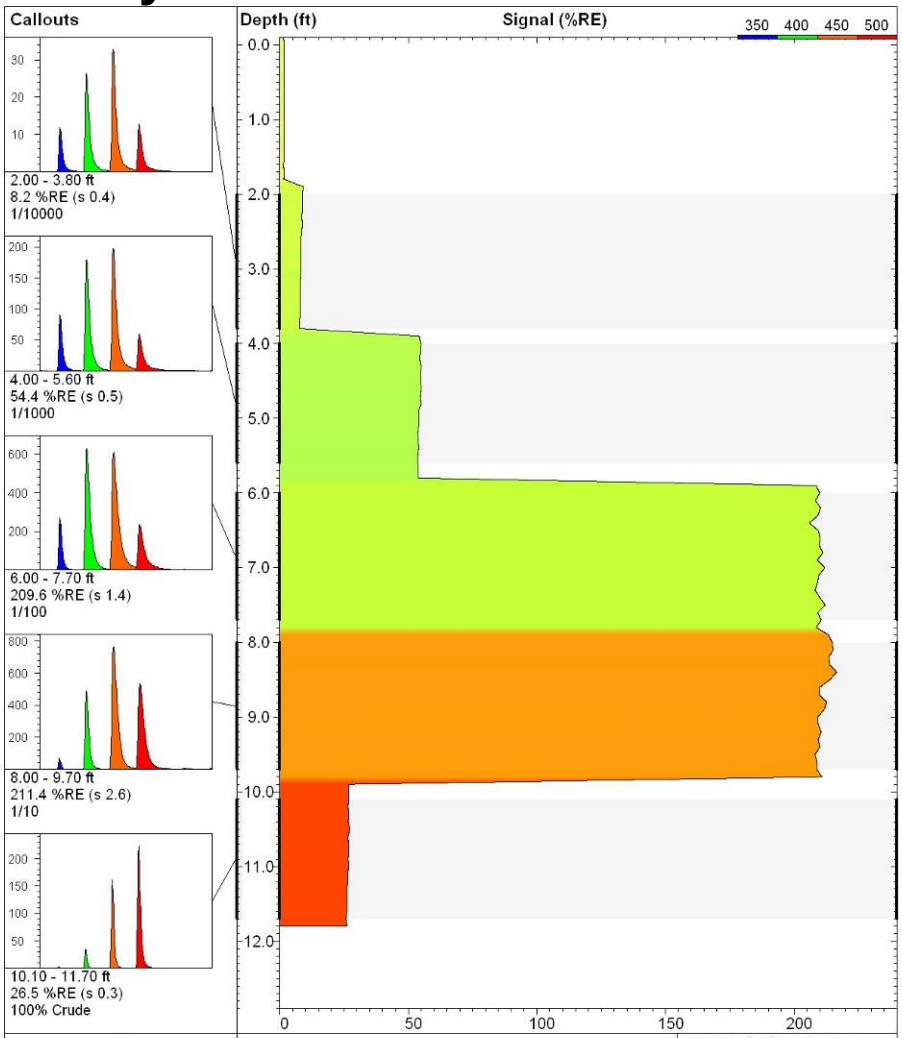
So… UV fluorescence struggles with heavies

how can Dakota prove the energy transfer is the key to the problem with UV fluorescence?

Well… what if we gave them more room?
(a bigger pool in which to act out their water ballet without crashing into each other)

we can do this by diluting with a non-fluorescent alkane

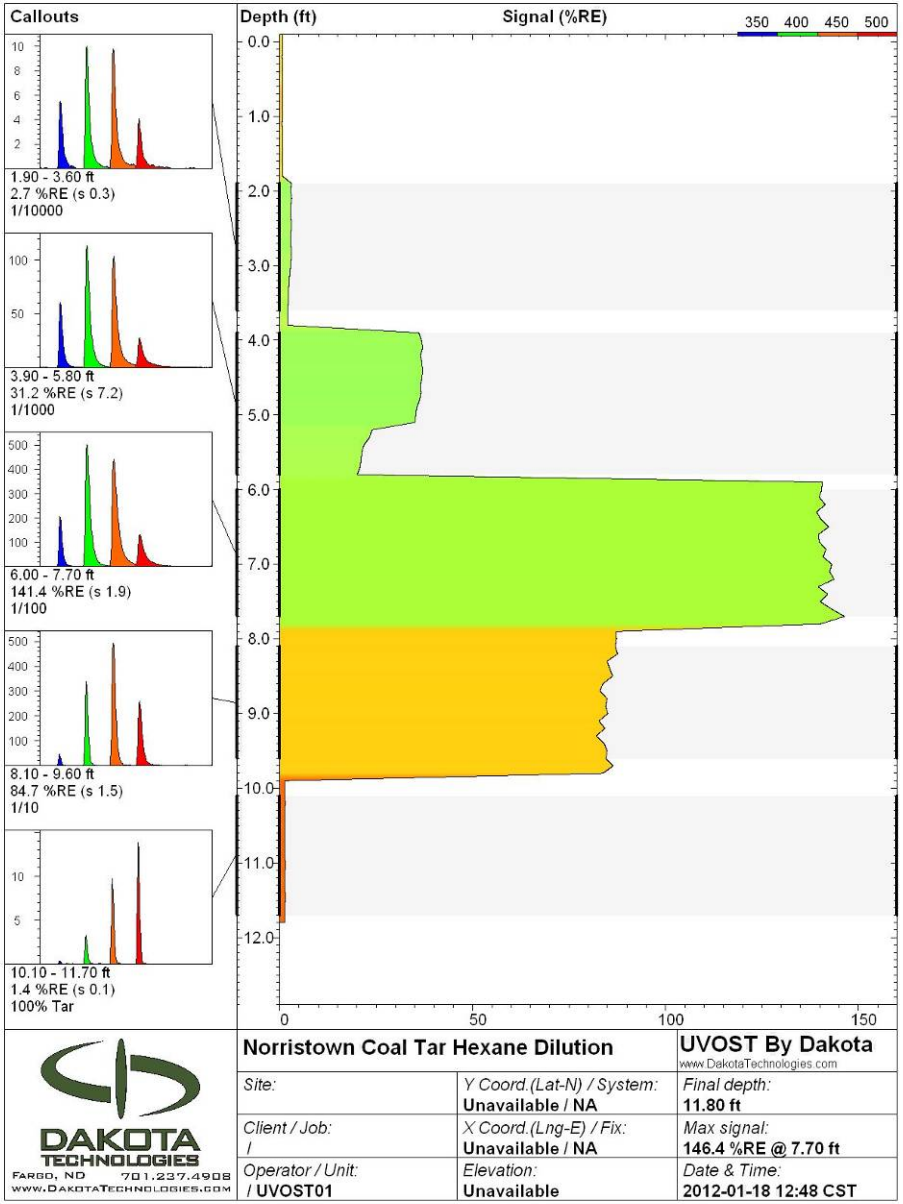
heavy crude diluted with hexane



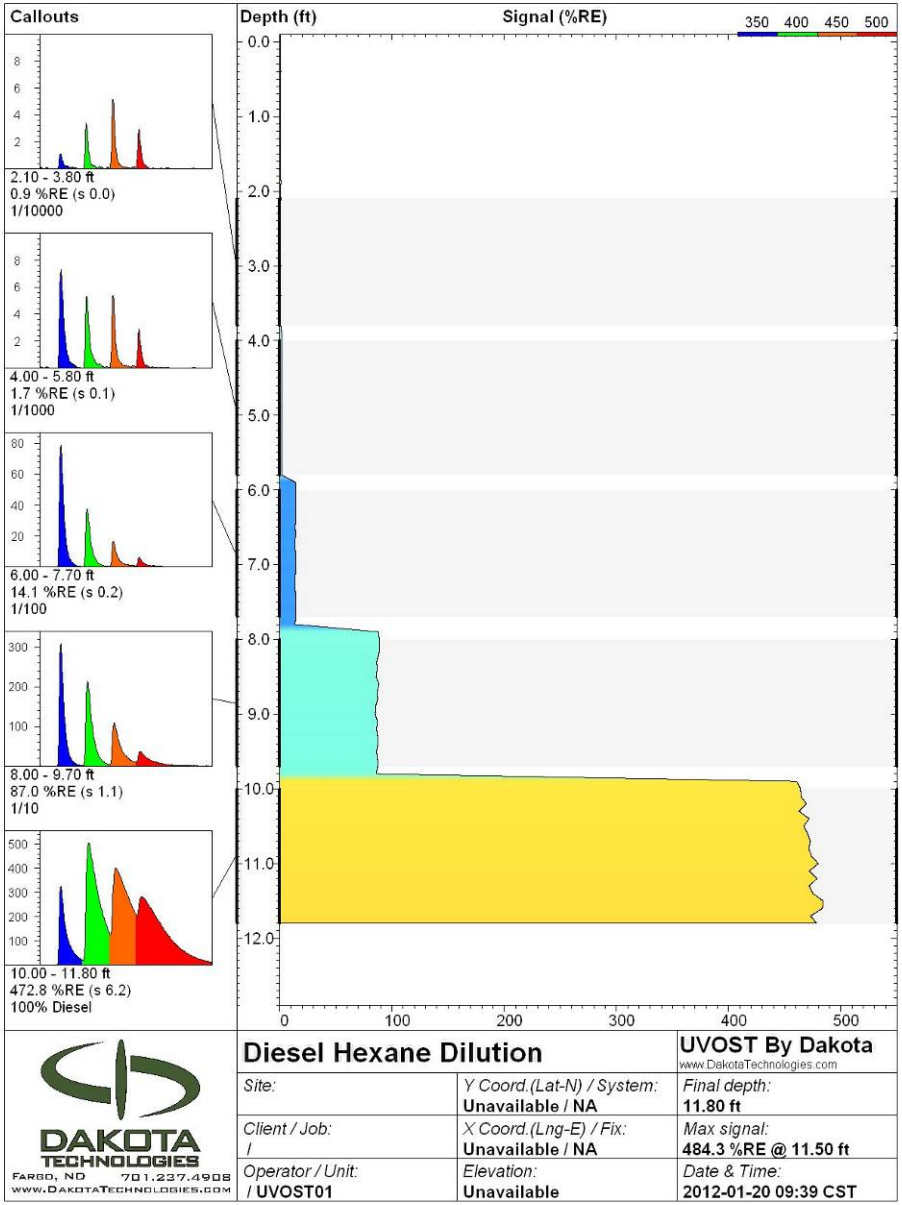
DAKOTA TECHNOLOGIES
FARGO, ND 701.237.4908
WWW.DAKOTATECHNOLOGIES.COM

Mandan Crude Hexane Dilution		UVOST By Dakota www.DakotaTechnologies.com
Site:	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **11.80 ft**
Client / Job: **/**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **216.5 %RE @ 8.40 ft**
Operator / Unit: **/ UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2012-01-20 09:21 CST**

coal tar diluted with hexane



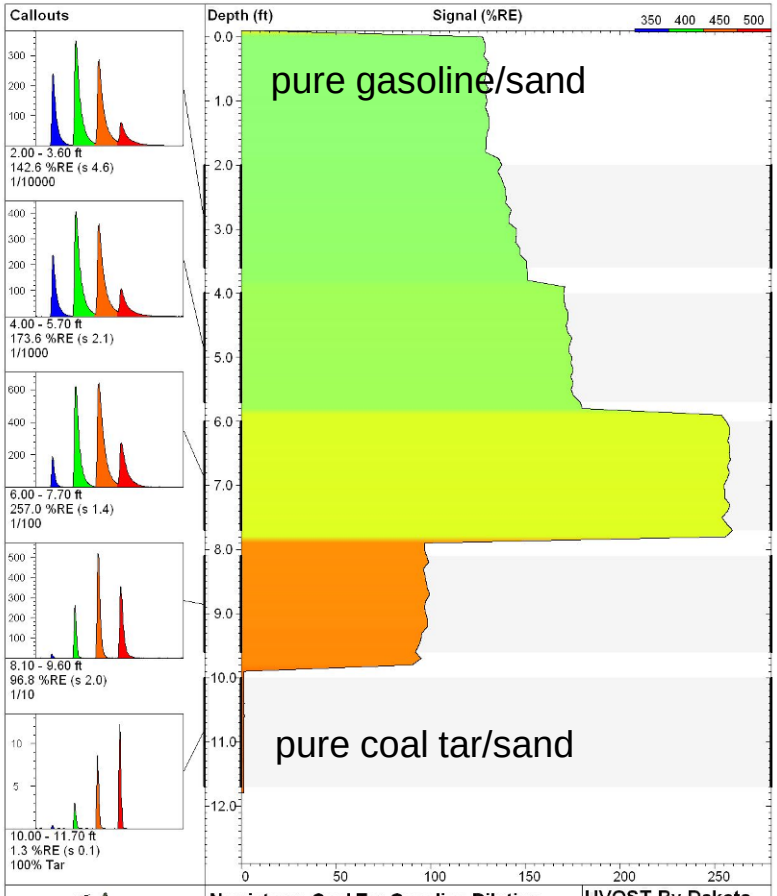
diesel diluted with hexane



secondary lesson again

UV LIF: heavies dominate light fuels when they mix

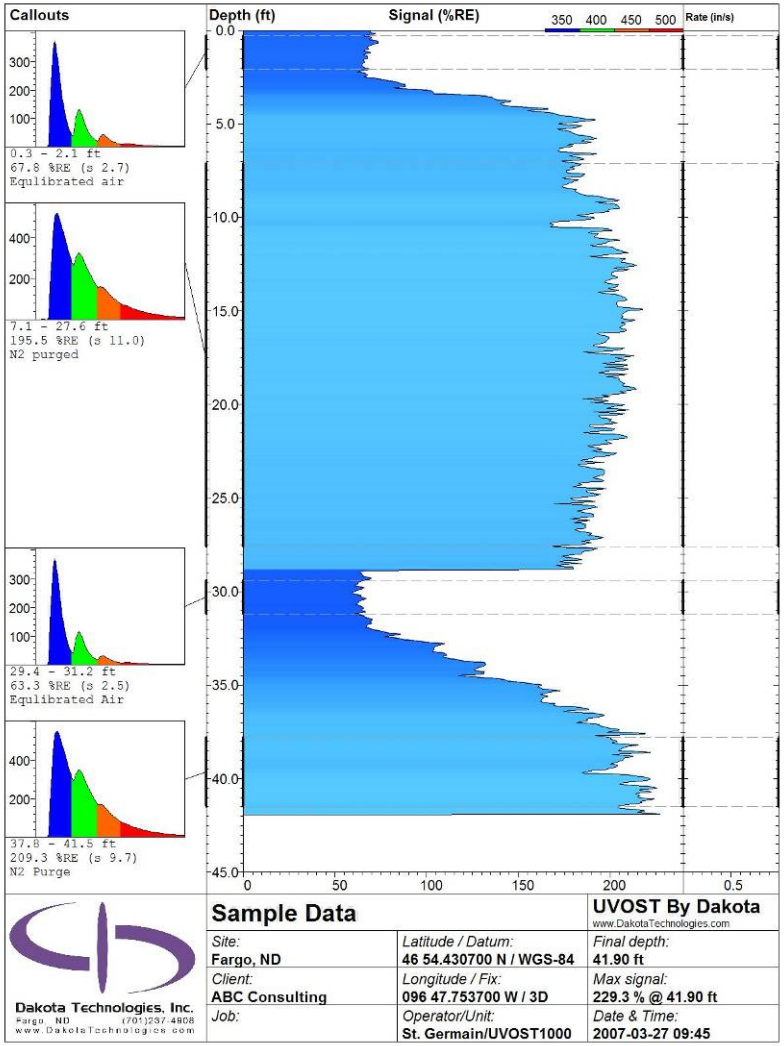
coal tar diluted with gasoline



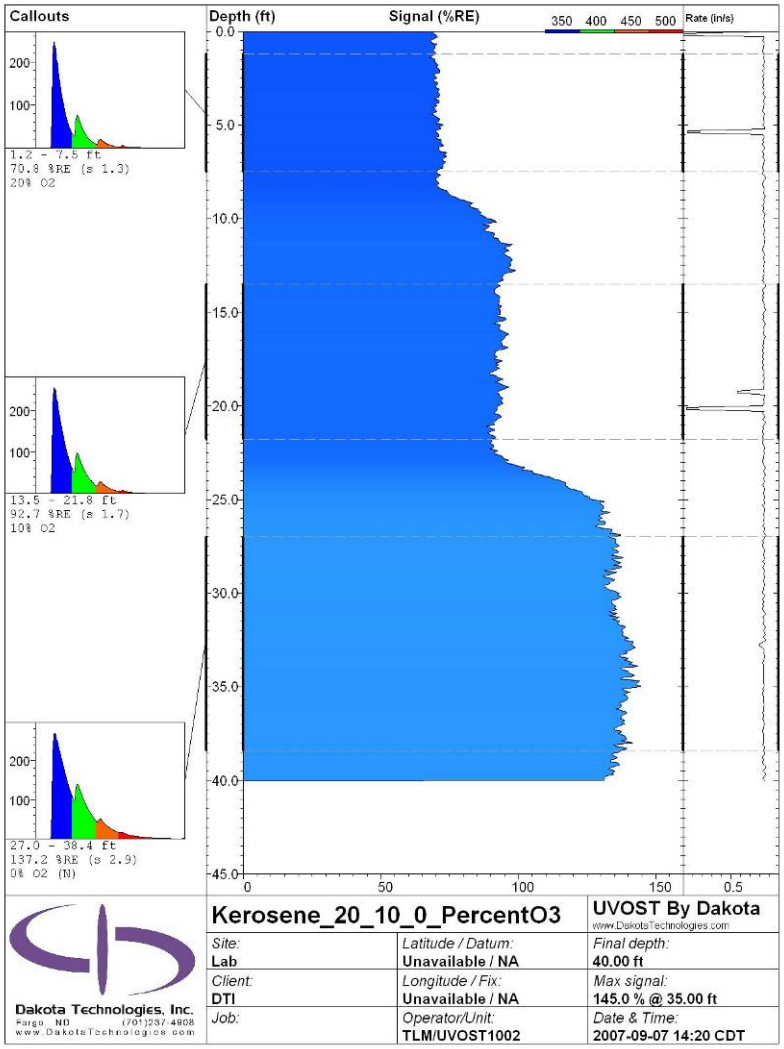
Oxygen’s role in LIF waveform and response

examples of oxygen quenching for common fuels
technique: bubble N/O2 mix through neat fuel in cuvette

different product waveform? – no - O2 quenching

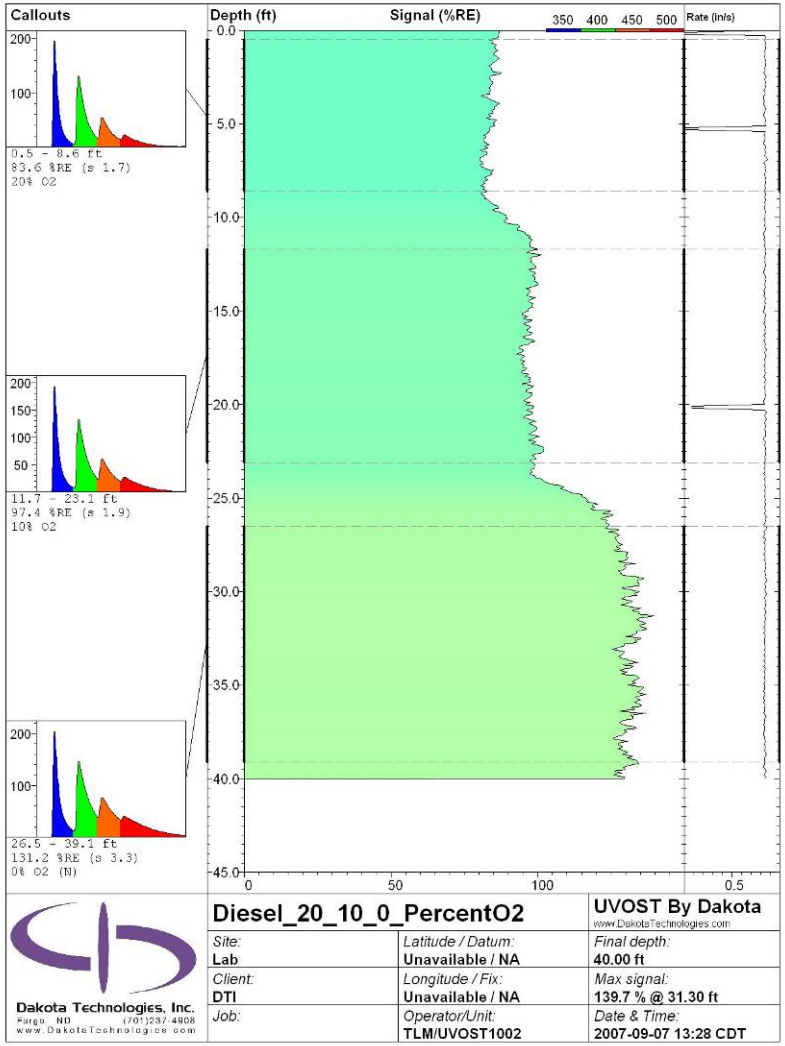


customer's NAPL from a well - 2005

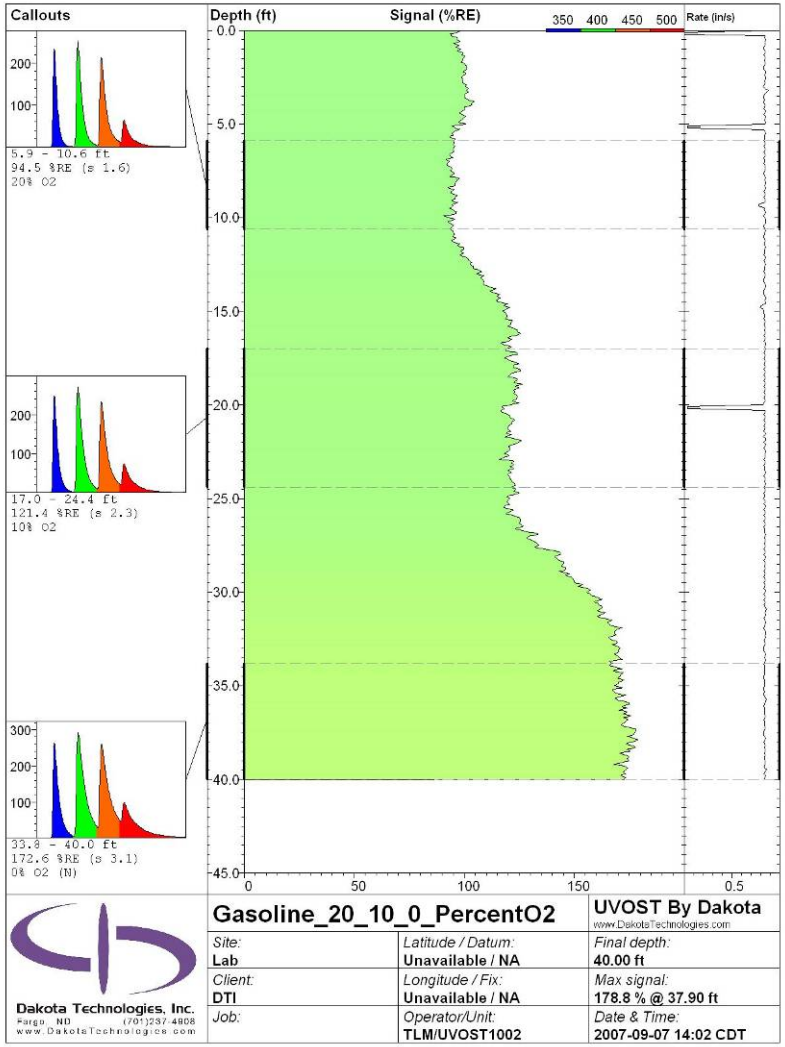


kerosene from pump

examples of oxygen quenching for common fuels
technique: bubble N/O2 mix through neat fuel in cuvette



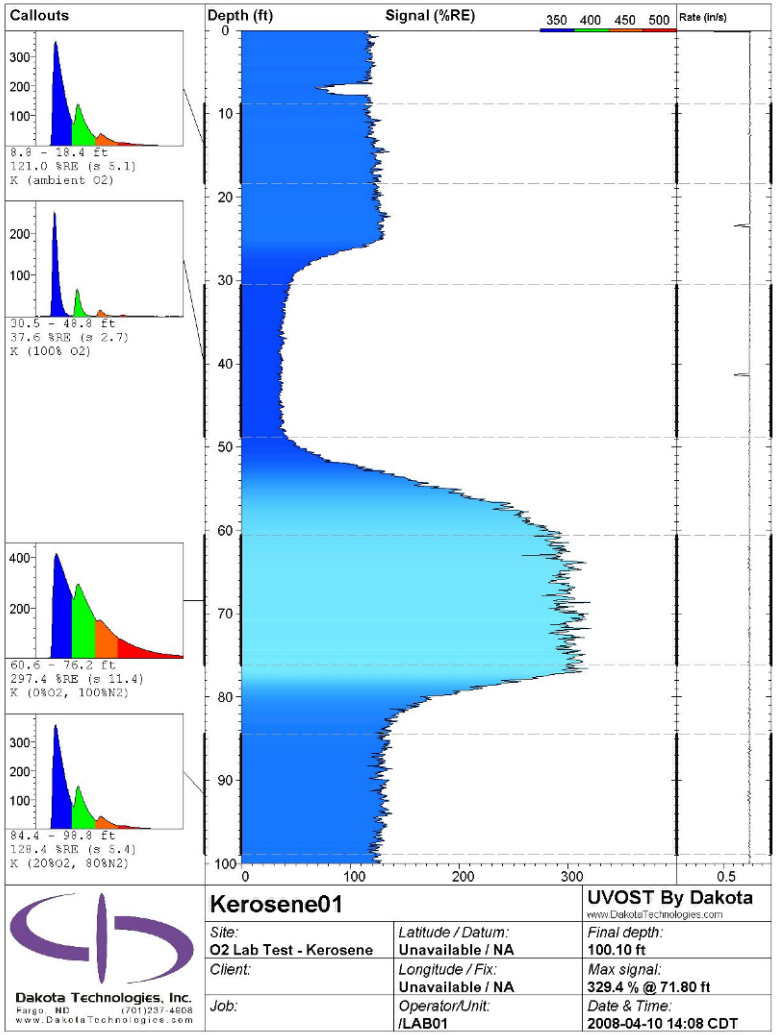
diesel from pump



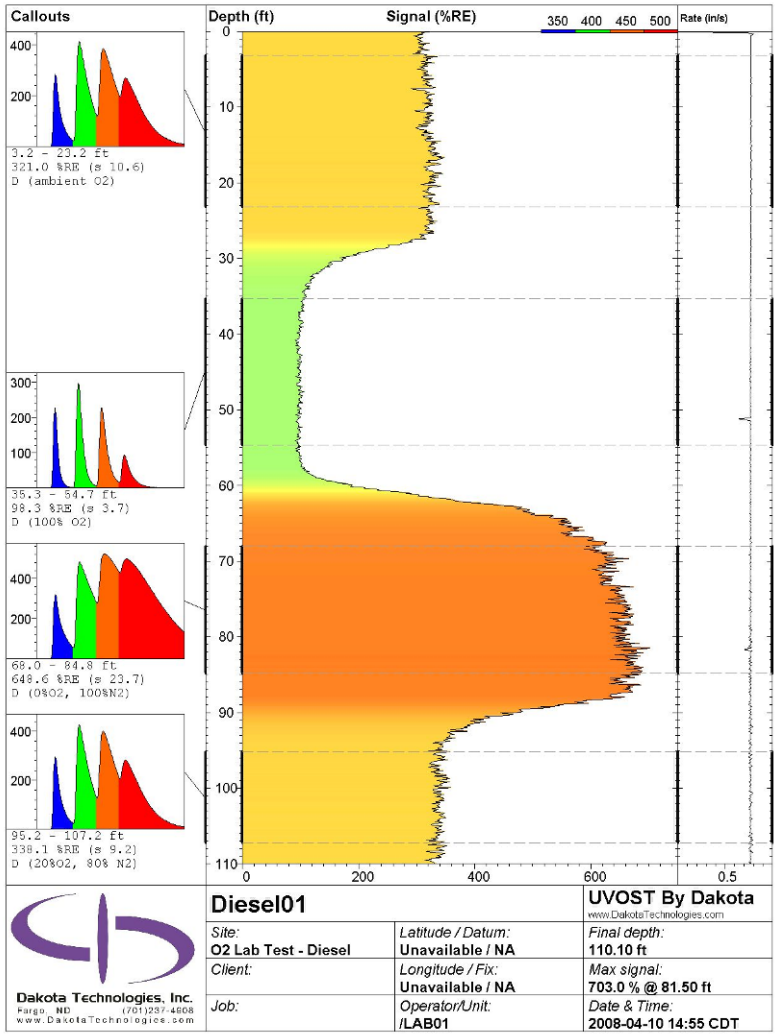
gasoline from pump

EXTREME examples of oxygen quenching for common fuels

technique: bubble N/O2 mix through neat fuel in cuvette – adding extra O_2!



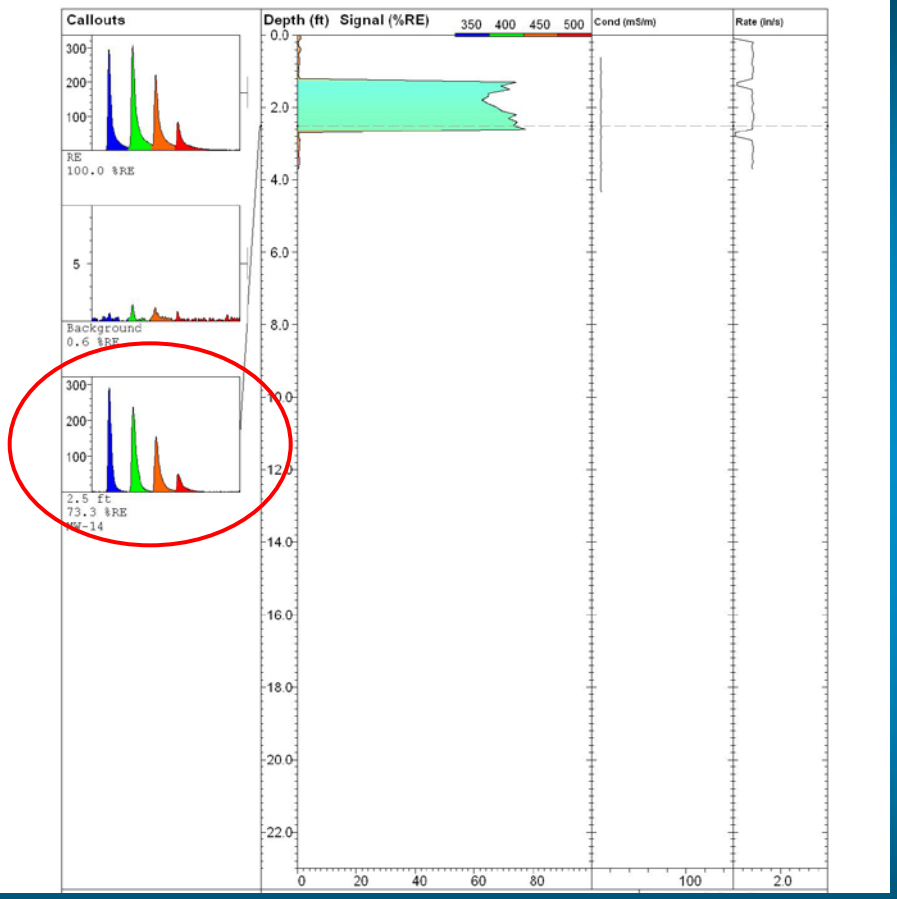
kerosene



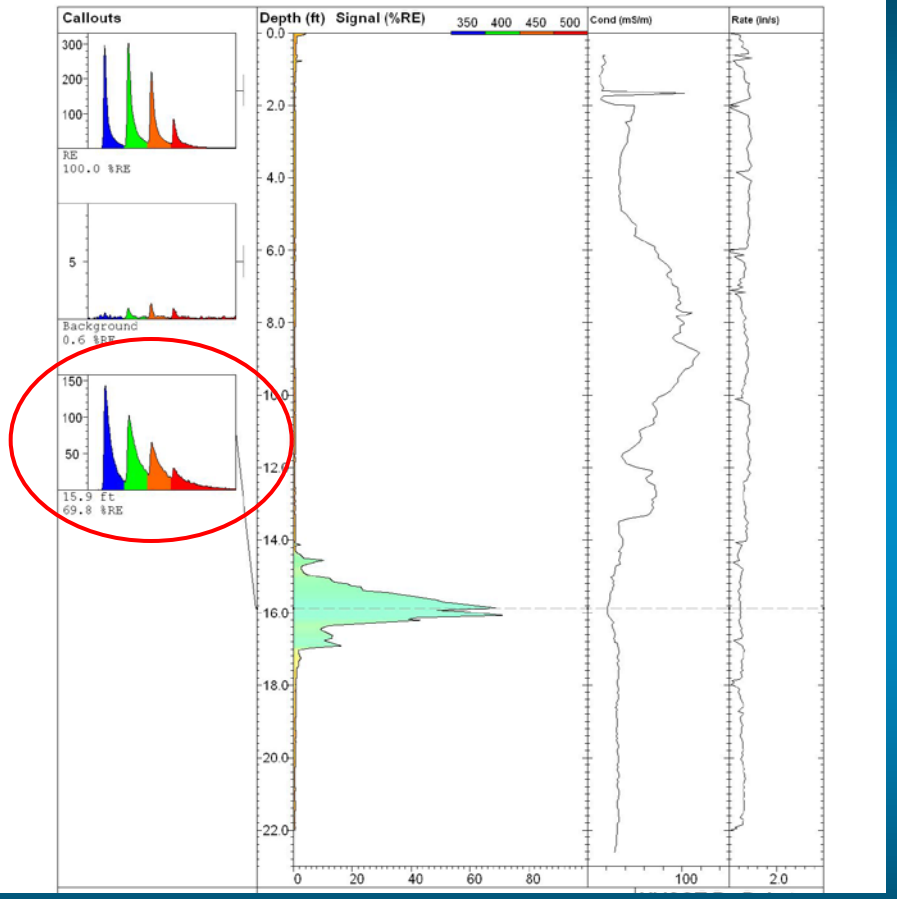
diesel

textbook field data example

uphole “lab test” (can’t keep oxygen out!)

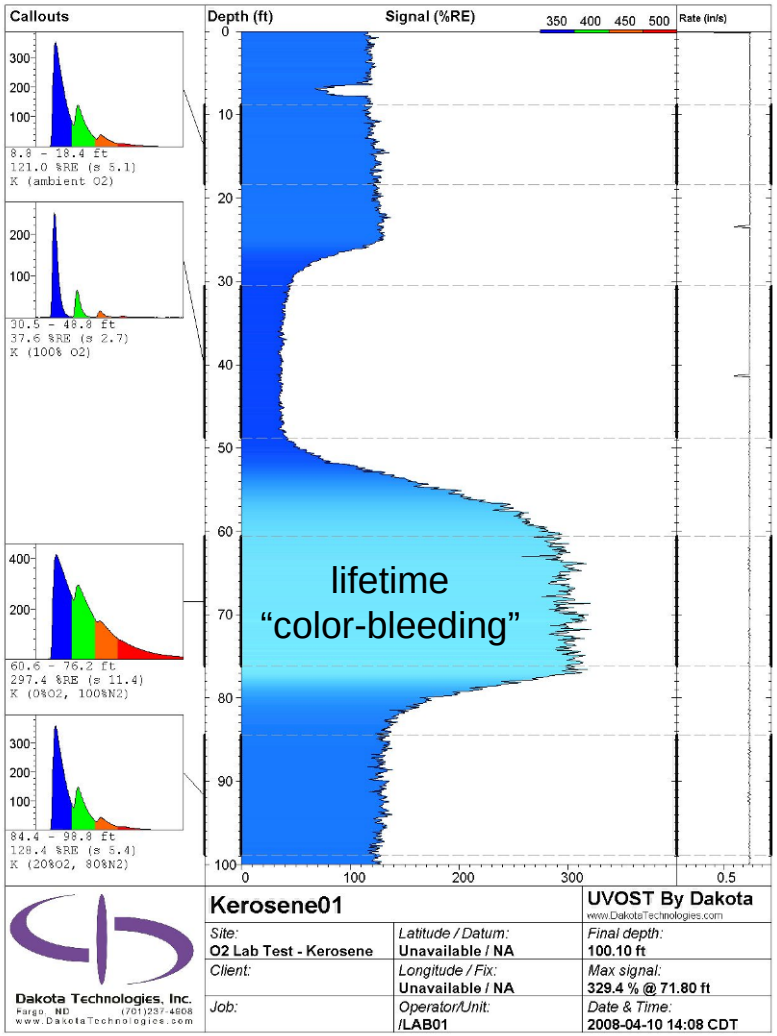


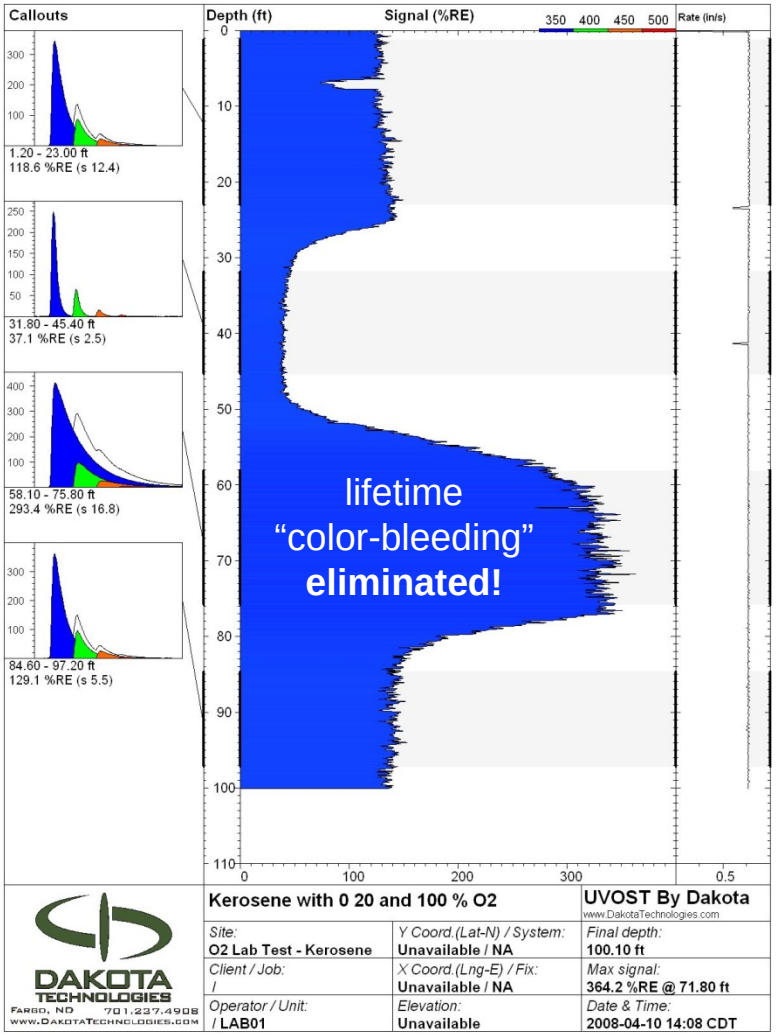
downhole test of same NAPL!



good time to look at long lifetime's negative affect on colorization!

newest OST code can generate lifetimes for each and every channel and each and every depth!





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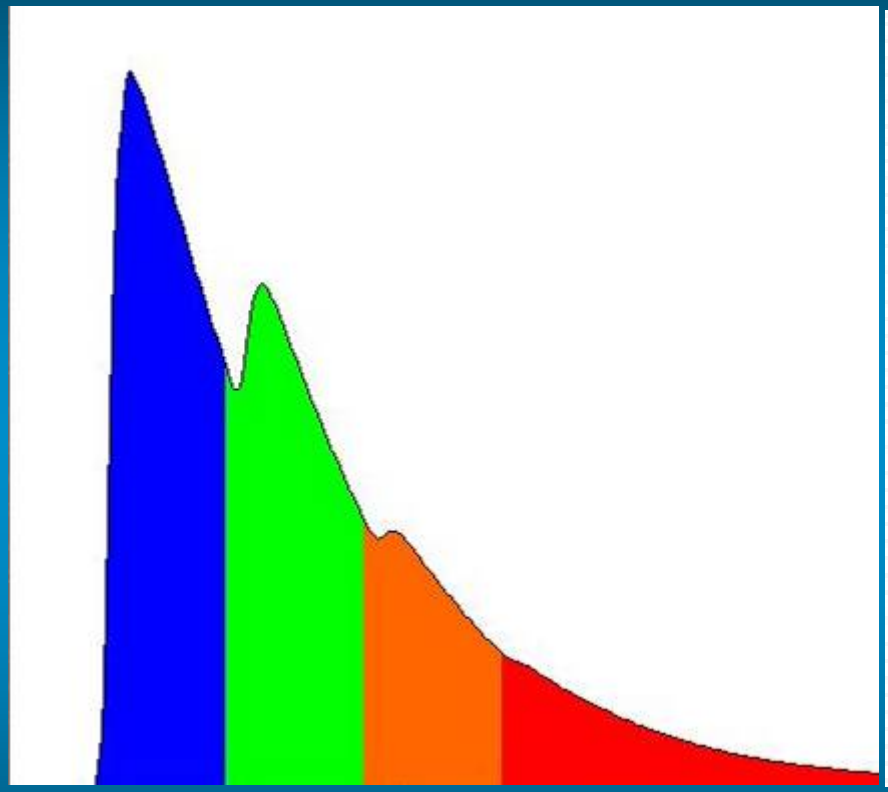
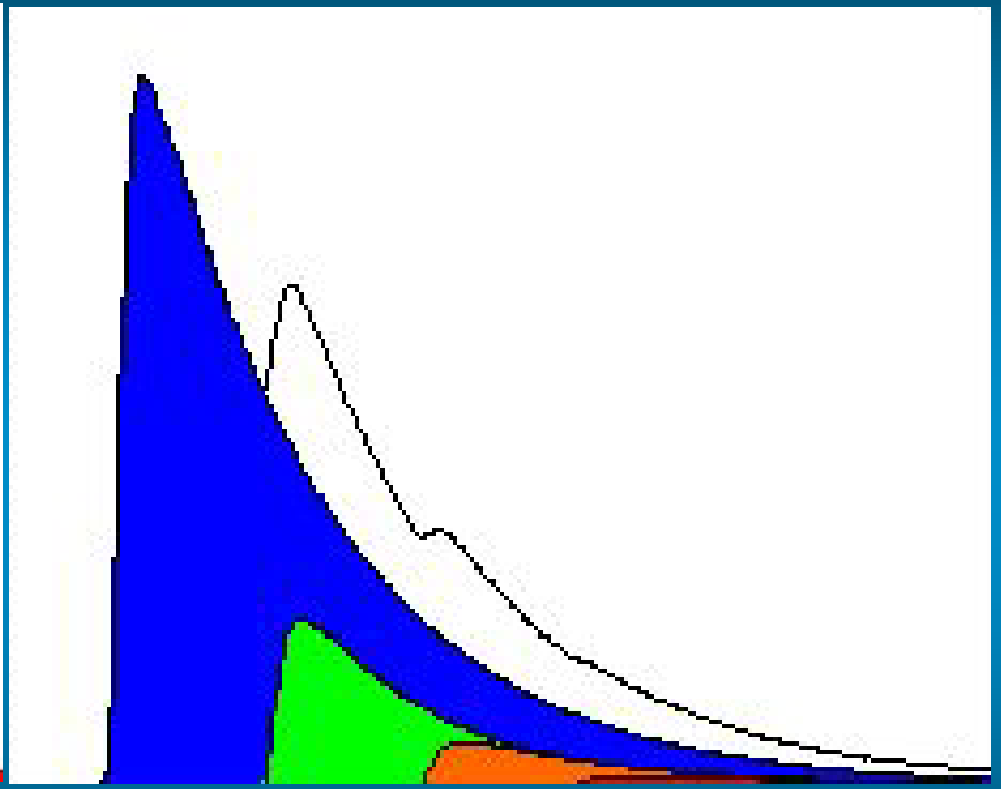
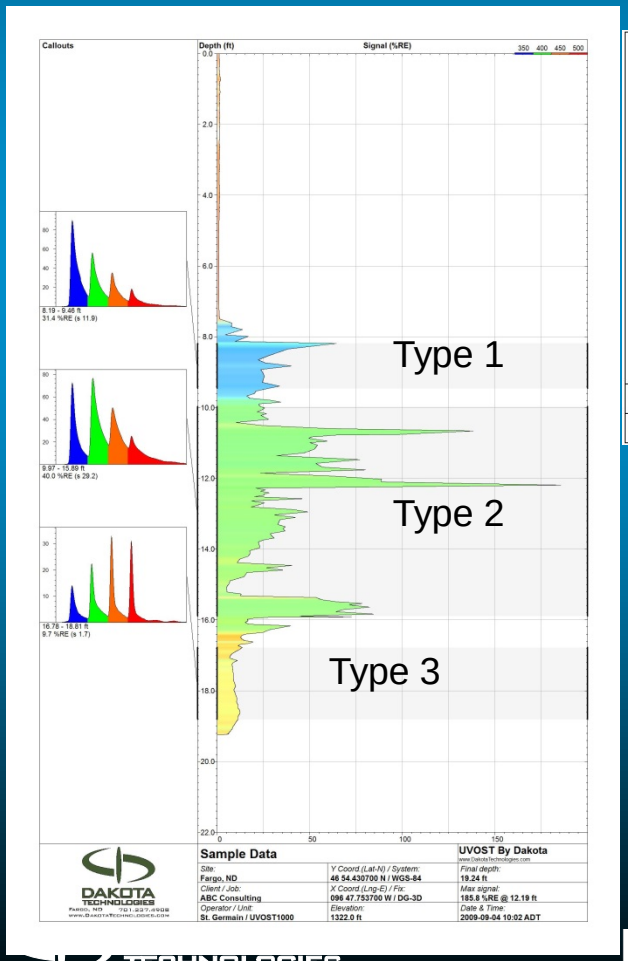
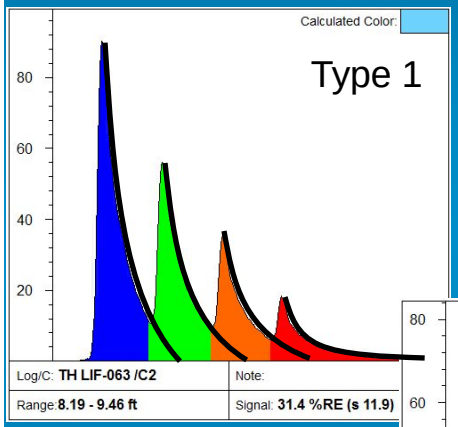


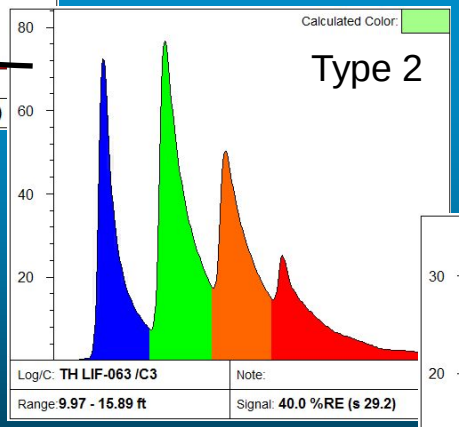


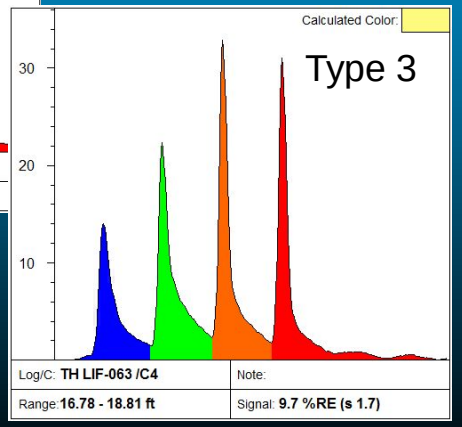
waveform lifetime fitting

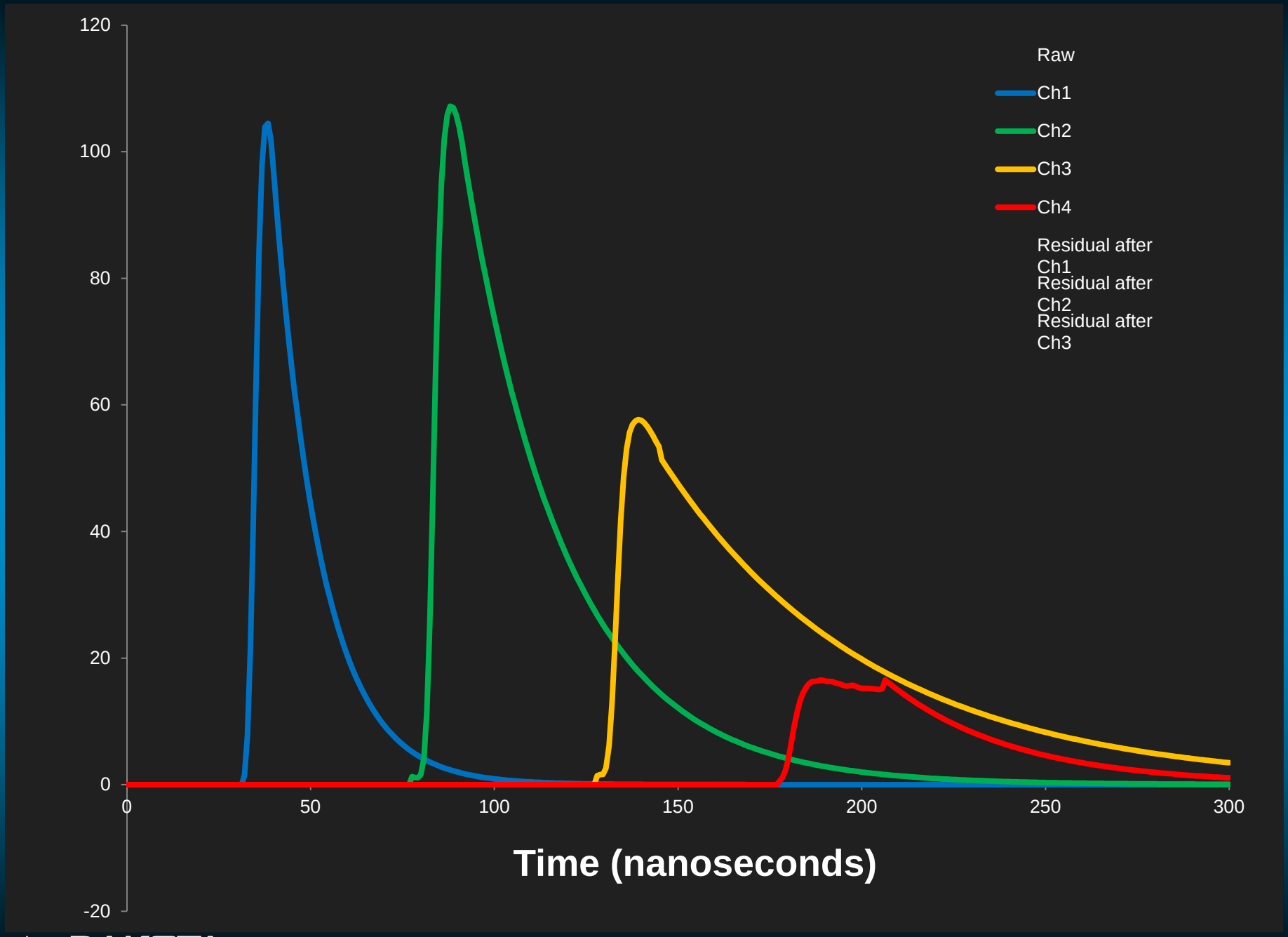
- waveforms change with product chemistry
- chemistry differences are due to the NAPL source or weathering
- pulsed laser excitation yields four pulses of fluorescence [350nm (blue), 400nm (green), 450nm (orange), and 500nm (red)]
- these pulses “bleed” into each other affecting colorization and our ability to accurately determine each individual channel’s fluorescence contribution
- OST software module calculates exponential decays – breaking down the multi-wavelength waveforms into separate wavelength fluorescence decay pulses





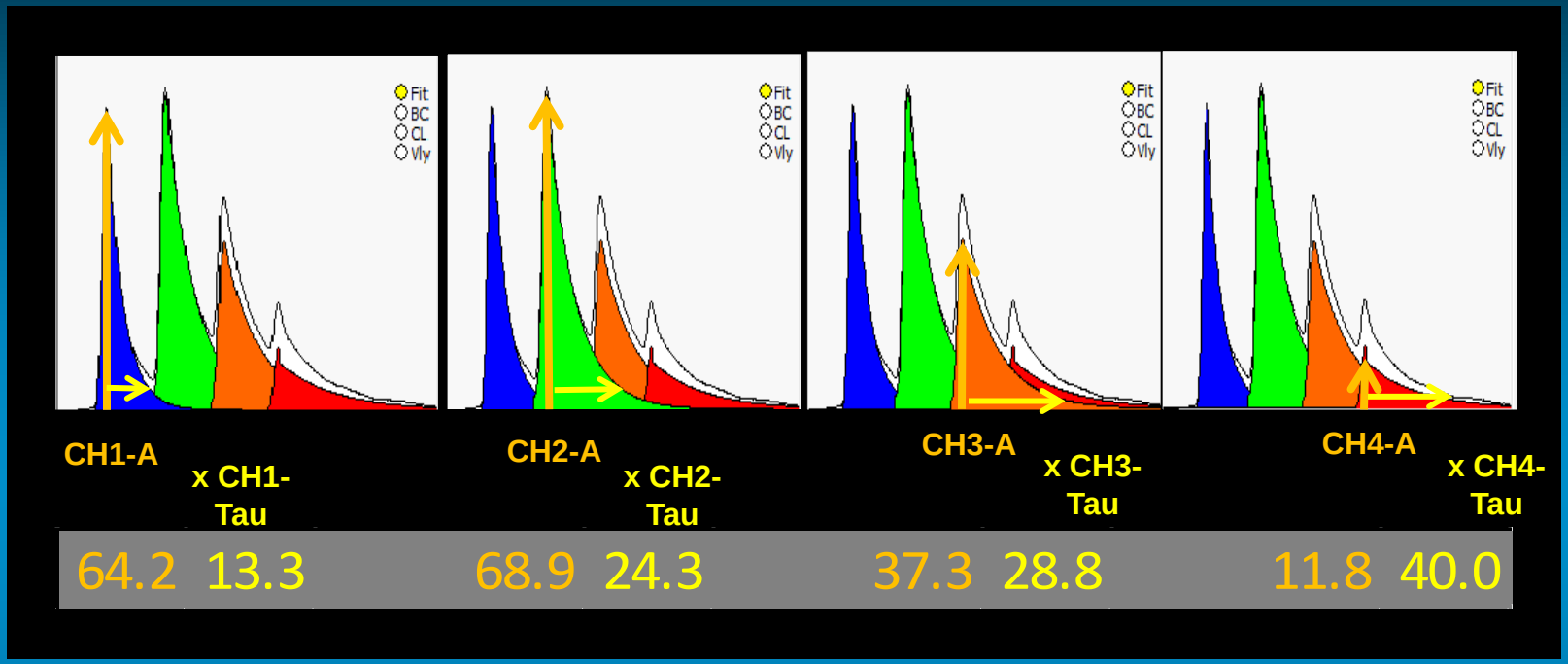





120
100
80
60
40
20
0
-20
0
50
100
150
200
250
300
Time (nanoseconds)
Raw
Ch1
Ch2
Ch3
Ch4
Residual after Ch1
Residual after Ch2
Residual after Ch3

fitting is done on all waveforms vs. depth creating four channel amplitudes (A) and four lifetimes (tau) for each depth (ca. every inch)

Depth	RE_Norm	RE_Fit	CH1-A	CH1-Tau	CH2-A	CH2-Tau	CH3-A	CH3-Tau	CH4-A	CH4-Tau	<Tau Avg>
0	-1.96E-04	5.32E-02	0.144993	2.209021	0.516585	1.92089	0.747119	0.364631	0.175115	1.730564	1.192102
0.002	0.121793	0.131715	0.370273	3.927942	0.339334	6.286537	0.408429	2.765036	0.332677	6.510731	4.74452
0.008	7.48E-02	0.11055	0.372983	3.900043	0.412072	5.131155	0.66537	1.893293	0.180275	2.56165	3.244371
0.01	0.183006	0.163036	0.384	5.539474	0.929661	4.619411	0.841712	4.44419	0.370378	4.970337	4.752359
0.099	6.31E-02	8.47E-02	0.350459	5.384068	0.392606	3.452472	0.376737	1.828101	0.178557	0.271204	3.06502
0.135	0.052401	6.59E-02	0.320573	7.189041	0.616781	1.63781	0.407034	2.372973	0.184439	2.18404	3.063451
0.527	0.131327	0.100379	0.127157	11.26302	0.469778	5.377861	0.42247	4.483602	6.20E-02	8.17012	5.880556
0.609	8.58E-02	0.103687	0.409208	7.298145	0.224081	7.386196	0.666631	2.720192	0.321246	1.010917	4.181978
0.693	4.07E-02	7.19E-02	0.154508	10.52414	0.401555	3.502514	0.668307	2.147111	4.65E-02	0.351963	3.528088
0.754	0.10817	0.119839	0.307301	6.277873	0.490208	2.825852	0.583898	3.276093	0.206438	1.031408	3.4262
0.819	5.52E-02	8.68E-02	0.206024	10.4313	0.206687	5.732303	0.679603	2.76388	0.221619	2.263245	4.34863
0.882	6.08E-02	0.074304	0.262538	6.294797	0.197394	7.341428	0.431102	4.142846	0.139575	1.189173	4.903648
0.941	7.93E-02	0.117918	0.189485	7.427971	0.461678	5.00646	0.693461	2.809827	0.272009	1.466933	3.752482
0.998	5.33E-02	8.77E-02	0.416452	3.73898	0.455151	3.571277	0.464001	1.925876	0.16889	3.387341	3.089592
1.054	8.45E-02	9.45E-02	0.325132	7.695514	0.246809	4.872951	0.654129	3.247154	0.262408	2.497813	4.356295
1.112	7.55E-02	9.99E-02	0.183161	4.557147	0.461284	5.052697	0.634335	3.250693	0.432473	3.149602	3.850726
1.171	5.58E-02	9.19E-02	0.246414	5.885895	0.394366	3.980593	0.514486	5.023301	0.203368	2.372928	4.480363


Fit
BC
CL
Vly
CH1-A
x CH1-Tau
CH2-A
x CH2-Tau
CH3-A
x CH3-Tau
CH4-A
x CH4-Tau
64.2 13.3
68.9 24.3
37.3 28.8
11.8 40.0

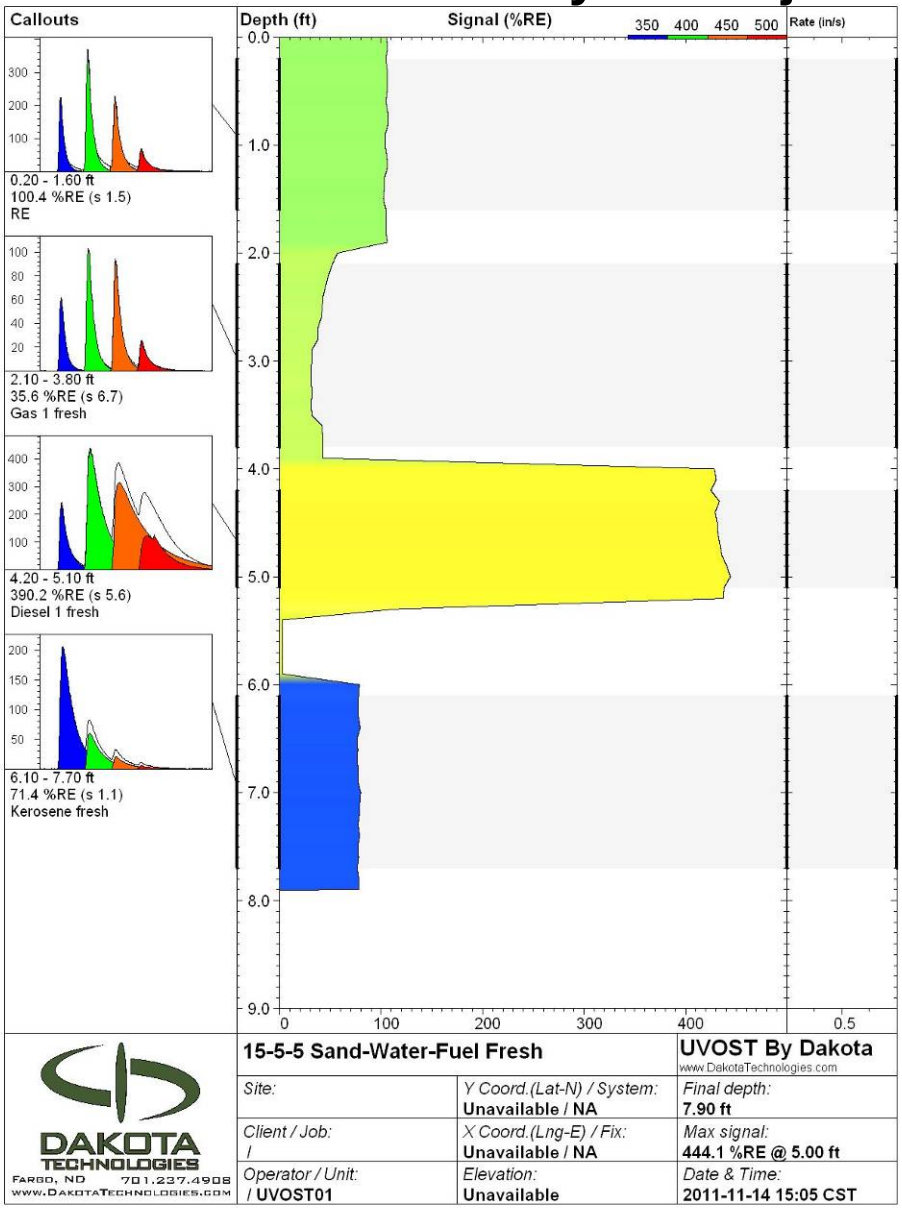
weathering (NAPL's nemesis)

starring "The Chameleon" of LIF… gasoline

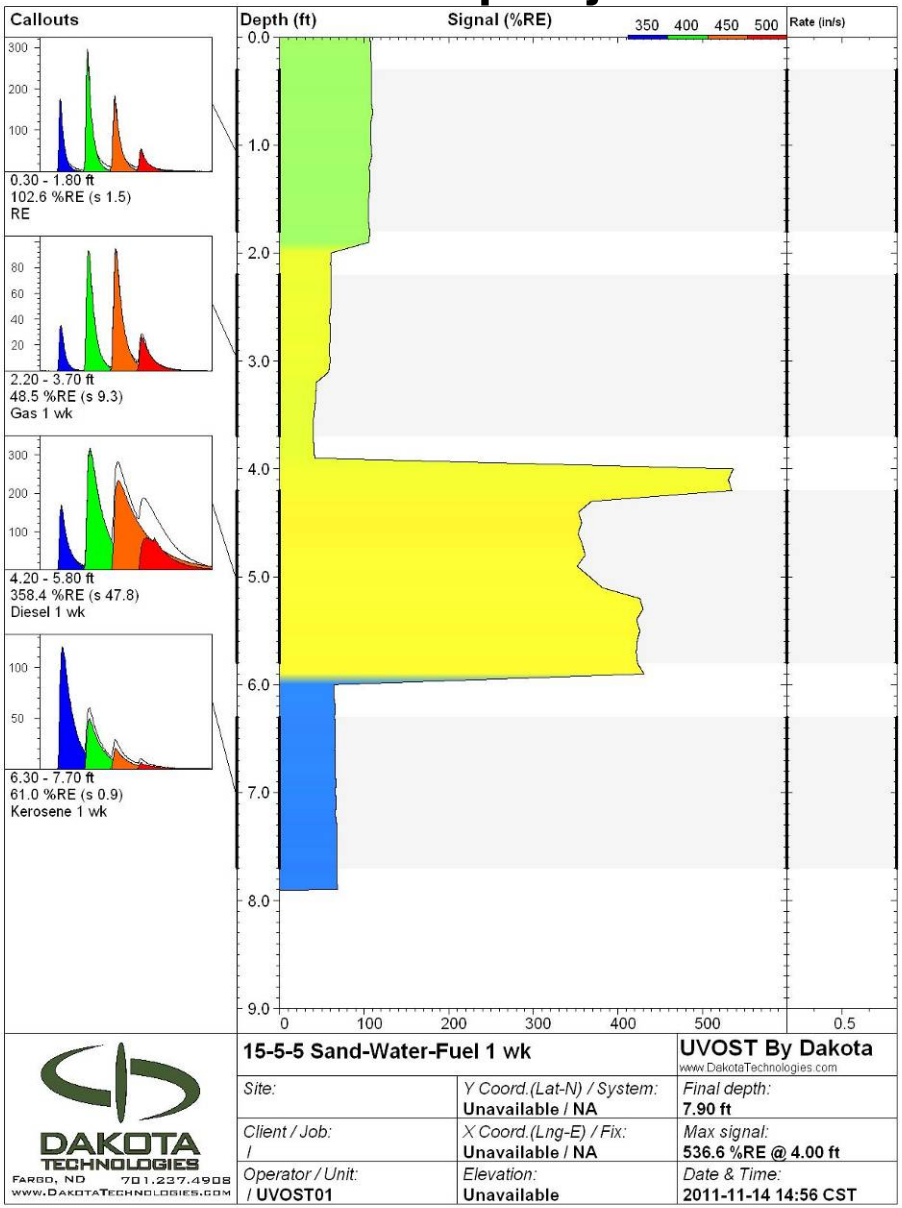
why is gasoline the chameleon?

- starting out low on PAHs
- very volatile and 'solvent' easily lost

fresh fuels in wet sandy soil in jars



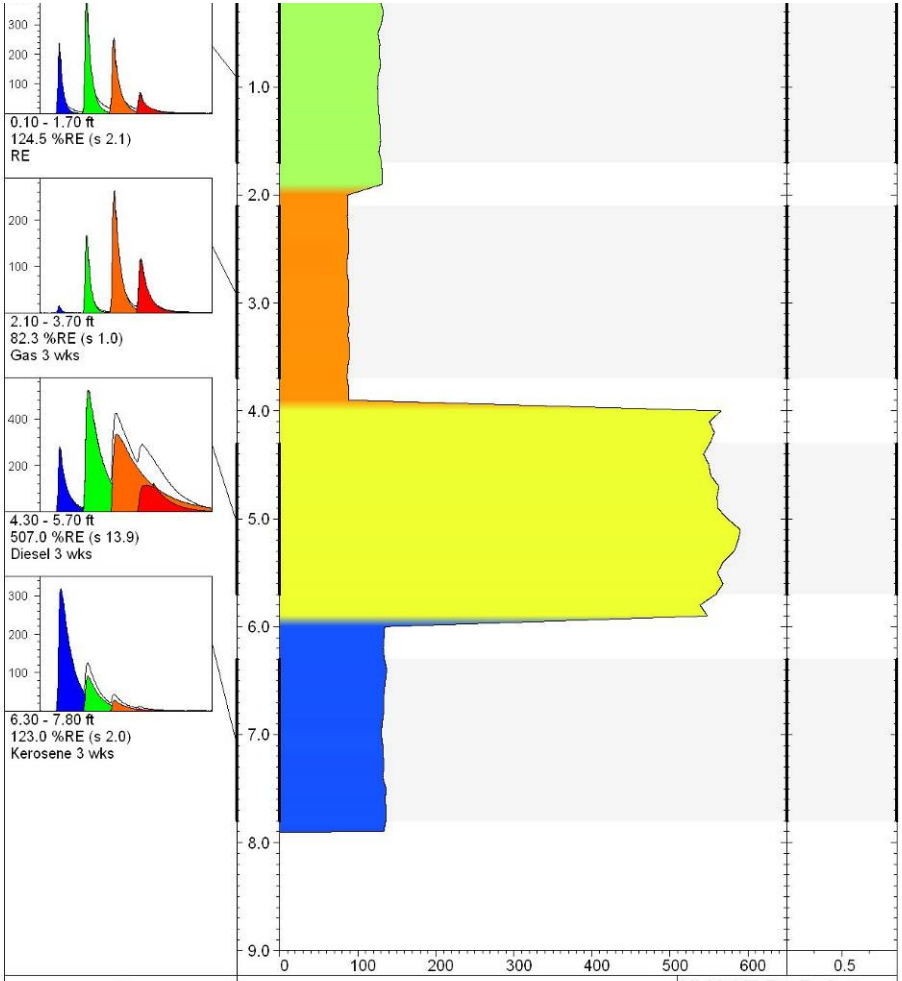
1 week of open jars



extreme conditions!!

3 weeks of open jars

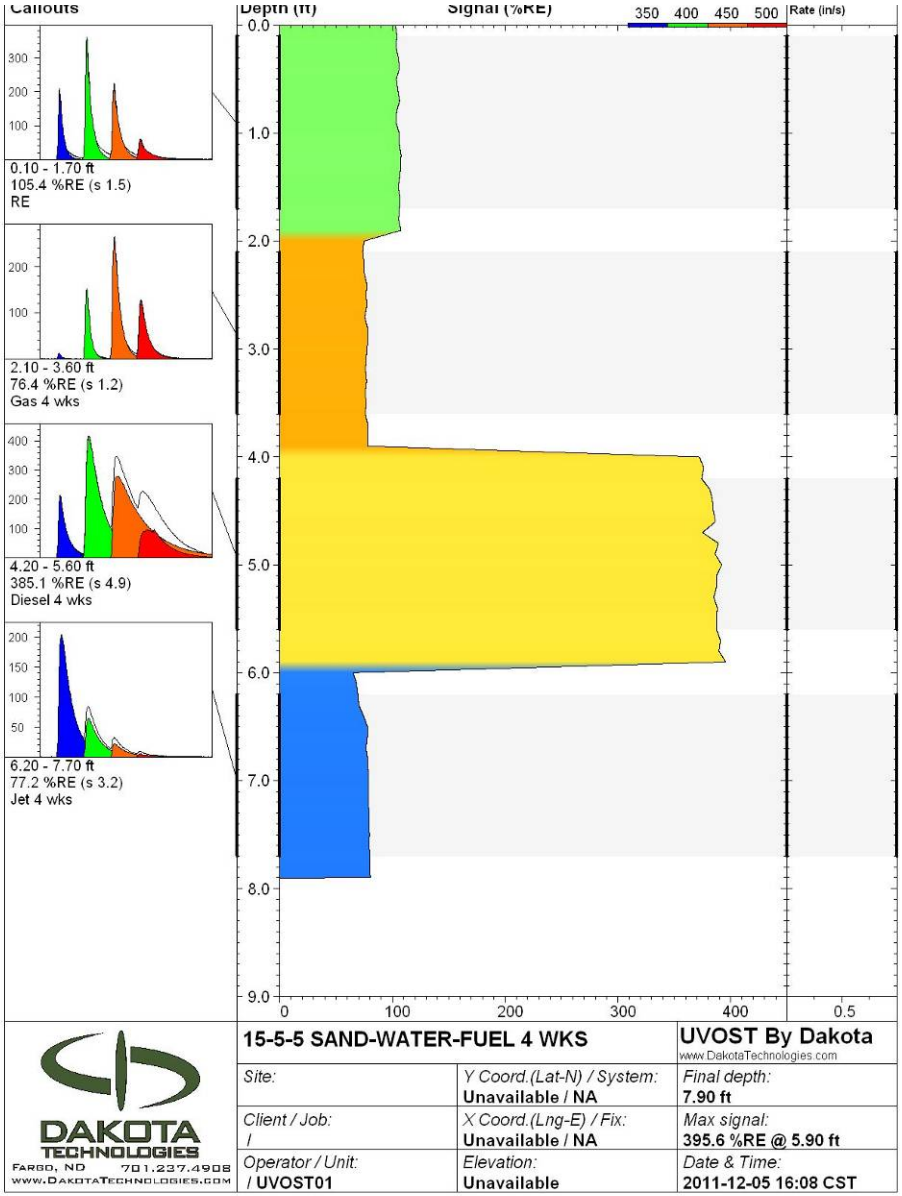
(gasoline jar went dry and had to be rewetted)



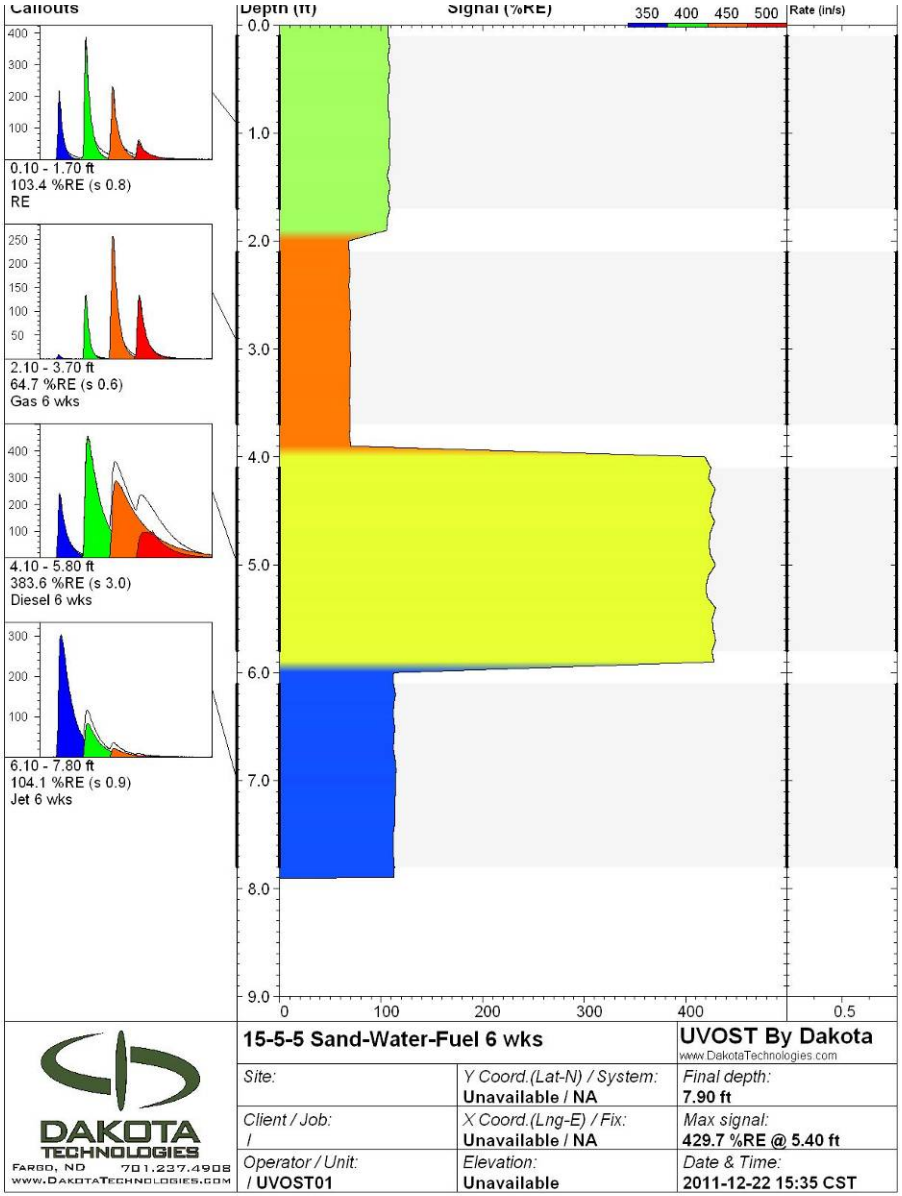
DAKOTA TECHNOLOGIES
FARGO, ND 701.237.4908
WWW.DAKOTATECHNOLOGIES.COM

15-5-5 Sand-Water-Fuel 3 wks		UVOST By Dakota www.DakotaTechnologies.com
Site:	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **7.90 ft**
Client / Job: /	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **590.3 %RE @ 5.10 ft**
Operator / Unit: **RWS / UVOST01**	*Elevation:* **Unavailable**	*Date & Time:* **2011-11-28 10:07 CST**

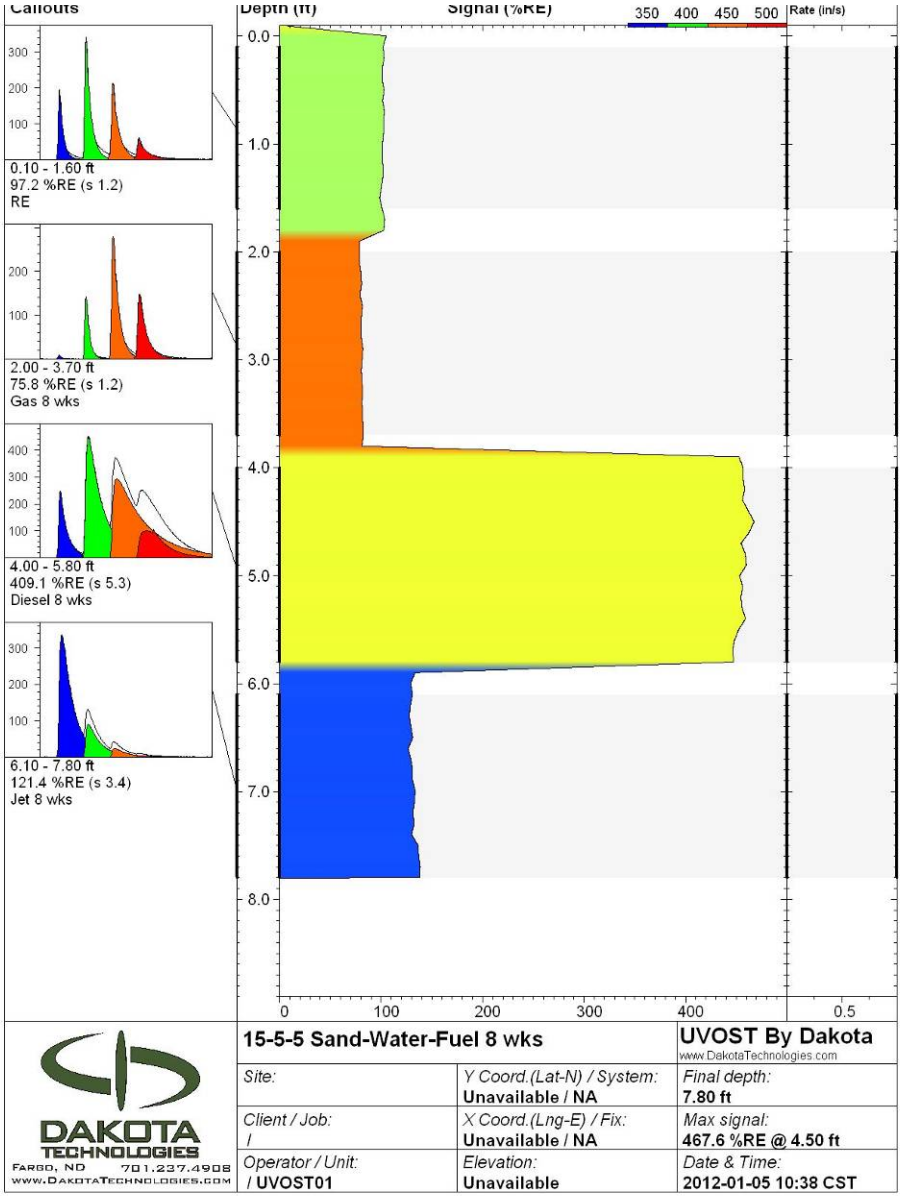
4 weeks of open jars



6 weeks of open jars

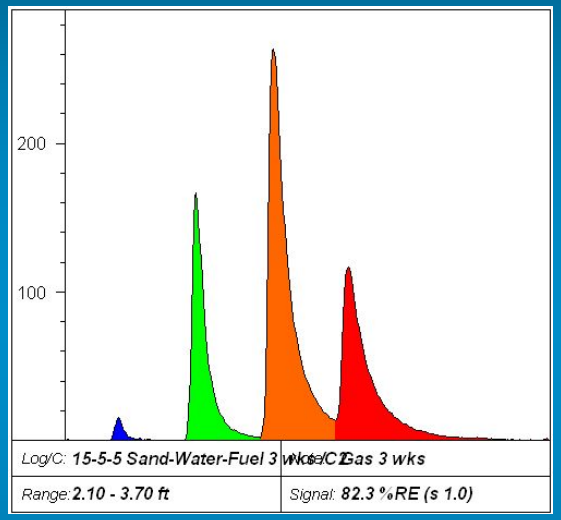


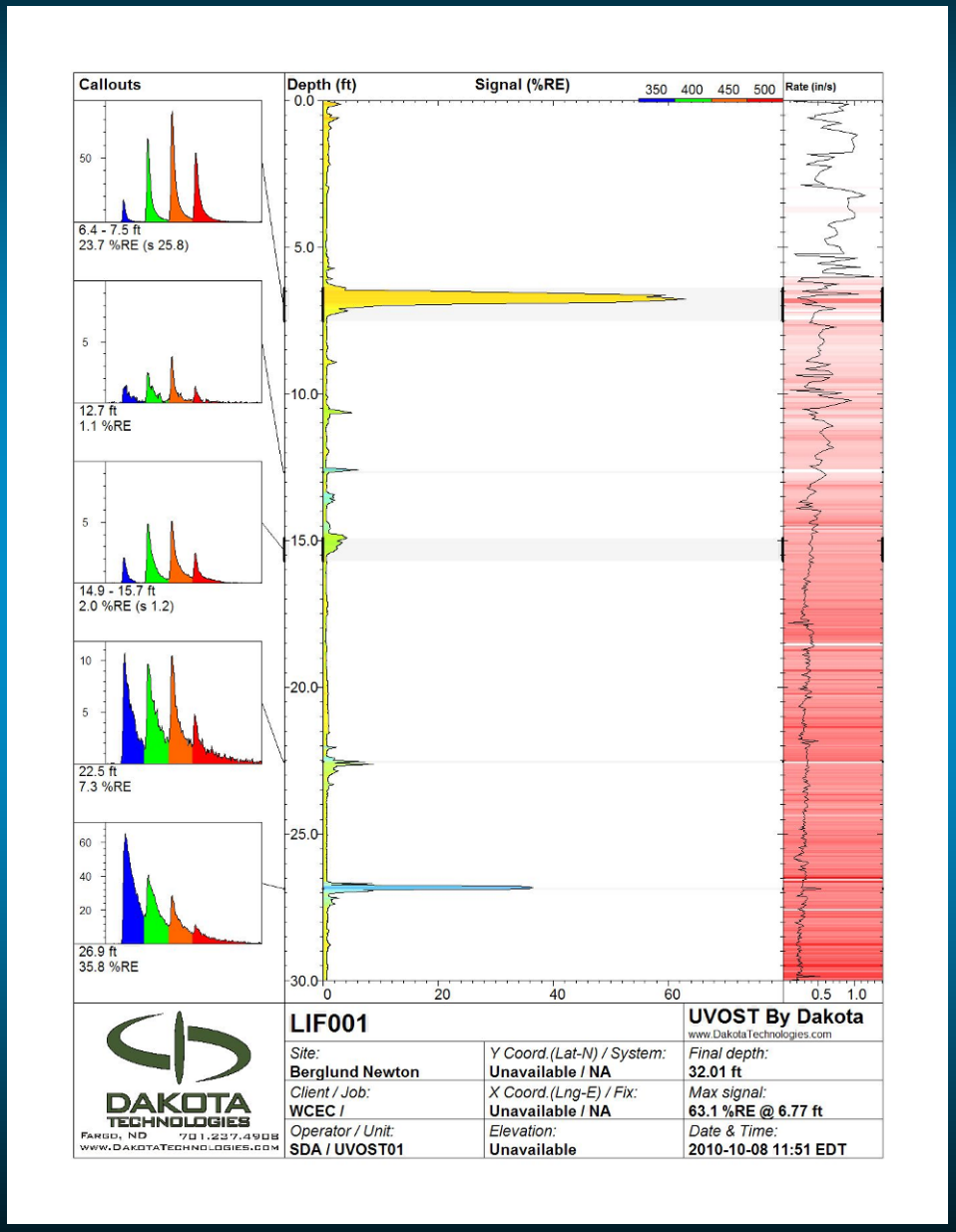
8 weeks of open jars



former gasoline station in MN in 2010

can you find me in the log at right?





Data QA/QC

Check list of key items that lead to quality UVOST data:

- Proper RE intensity – RE waveform same size and shape as the factory (+- 10%)
- Low Background levels – Background waveform does not exceed 5mV ands is correct shape
- Consistent triggering – software helps – but low laser level or damaged fiber/cable are possible
- Proper penetration speed – going too fast can blur/skip significant response – best to error slow
- Rational and consistent callouts – random or obscure callouts confuse client and clutters plot
- Elimination/control of fogging – fogging will absolutely corrupt a log which corrupts client's project
- Proper depth encoding – a dirty/bad pot or bad wiring can cause misleading depths
- Review logs generated by "rookies" – OST software allows review of RE, background, etc.
- Let the LIF speak for itself – never oversell or over promise results – set expectations and relax
- DON'T let confirmation sampling (the "gold standard") create doubt – if operated properly and there is/was fluorescent NAPL in front of the window, UVOST **will** see it – heterogeneity simply happens – A LOT
- Always insist on examining non-typical NAPLs prior to offering to log it for your client
- Back up the UVOST data ASAP
- Transfer data to client ONLY if you're confident in the data quality – when in doubt redo that location

NAPL heterogeneity and its affect on site investigations

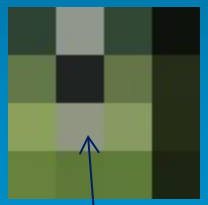
site heterogeneity affects…

- LIF log-to-log repeatability
- validation sampling and correlation
- remediation design
- conceptual site models
- attitudes/confidence toward remediation
- i.e. darn near everything on NAPL sites

Some example “sister logs” follow…

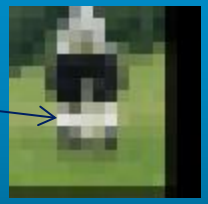
NAPL nature/extent

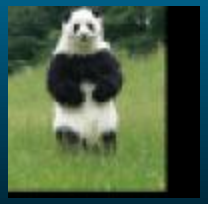
They are simply choices we have to make and financial realities investigators need to face



Maybe you just want to know if there is anything white in the photo?

goal achieved





spent <u>way</u> too much $$!

Data density is key to understanding what the object of our curiosity looks like!

Sampling density will determine greatly what your objects looks like (and your site's CSM)

How far you need to take sample density depends greatly on the end-game

If simply removing the panda-like object then we are done.

If deciding real or fake panda, we were not done!

MGP and Wood Treater Sites

tar/creosote is easy to see but we still suffer from poor NAPL CSMs! WHY?

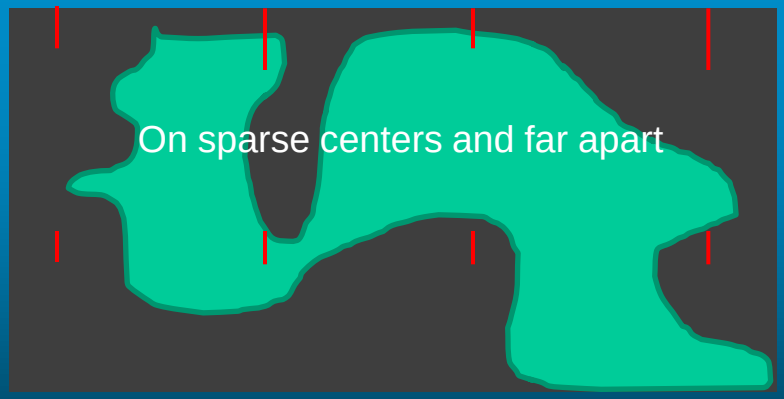
- MGP NAPL can exit as **EITHER** LNAPL and DNAPL (nature can't use density to "herd cats")
- **time** – tar has had decades to get where it's at
- some fraction stays behind (sorbed) while a sub-fraction of the body moves
- geologic features – **any** available crack, fracture, or seam, even small ones, are potential conduit for large volumes given the amount of time available for travel
- complex geological settings (glacial till for example) where "nothing makes sense", every mobilization results in new theory, need for more samples
- what lab tests are useful?.. can we even rely on lab chemistry to tell us how much NAPL? Do you care if 48.7 ppm naphthalene, 12.4 ppm fluorene, etc.?
- usually it falls back to the organoleptic approach (look at and even smell soil samples) and recorded observations
- intimate/detailed/expensive "brainiac" chemistry simply not very practical for a comprehensive site-wide NAPL survey

Sampling for coal tar can run the extremes

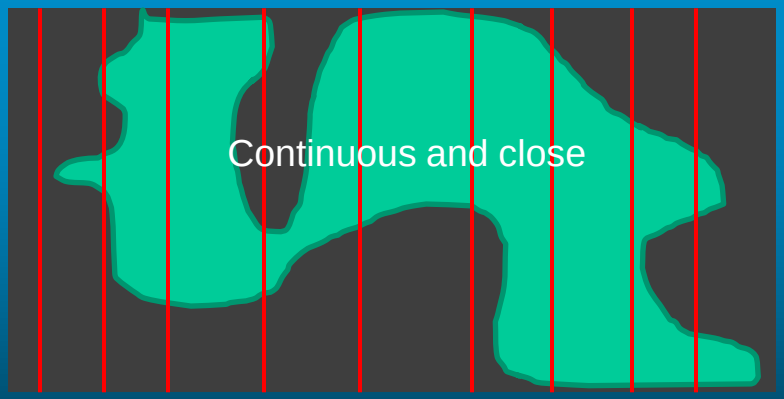
from “as little as my client has to spend according to the regulator”

to “let’s figure this out because we’re about to spend big $20,000,000 on a fix and we want it to be successful!”

Sampling density cross sections

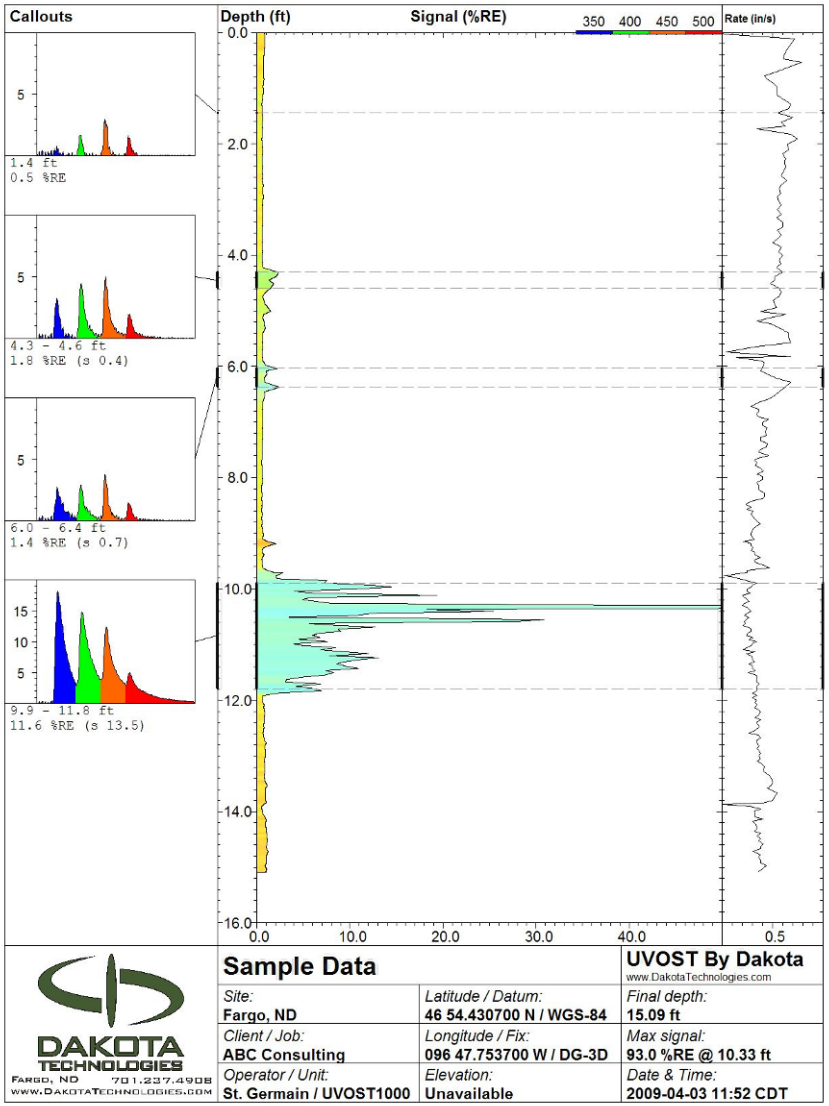


even if highest quality analytical is used
the engineer is doomed to a poor CSM



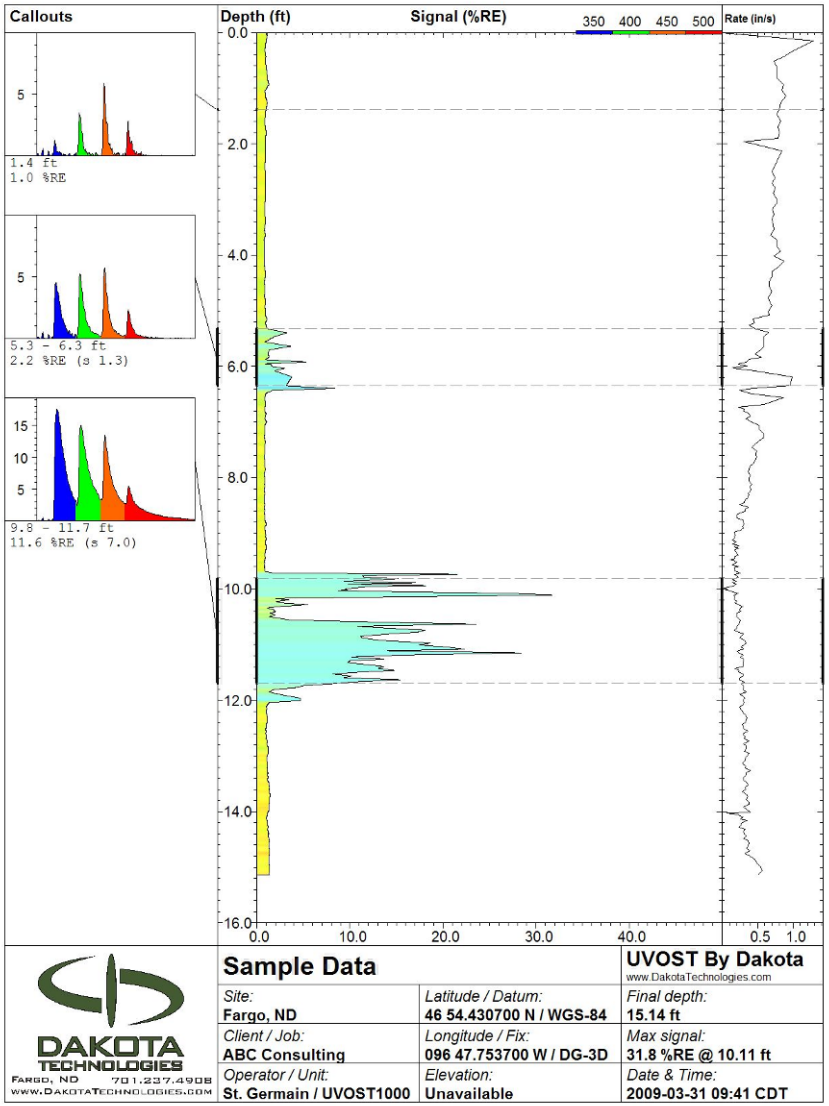
even if modest quality analytical
the engineer will have decent CSM

heterogeneity



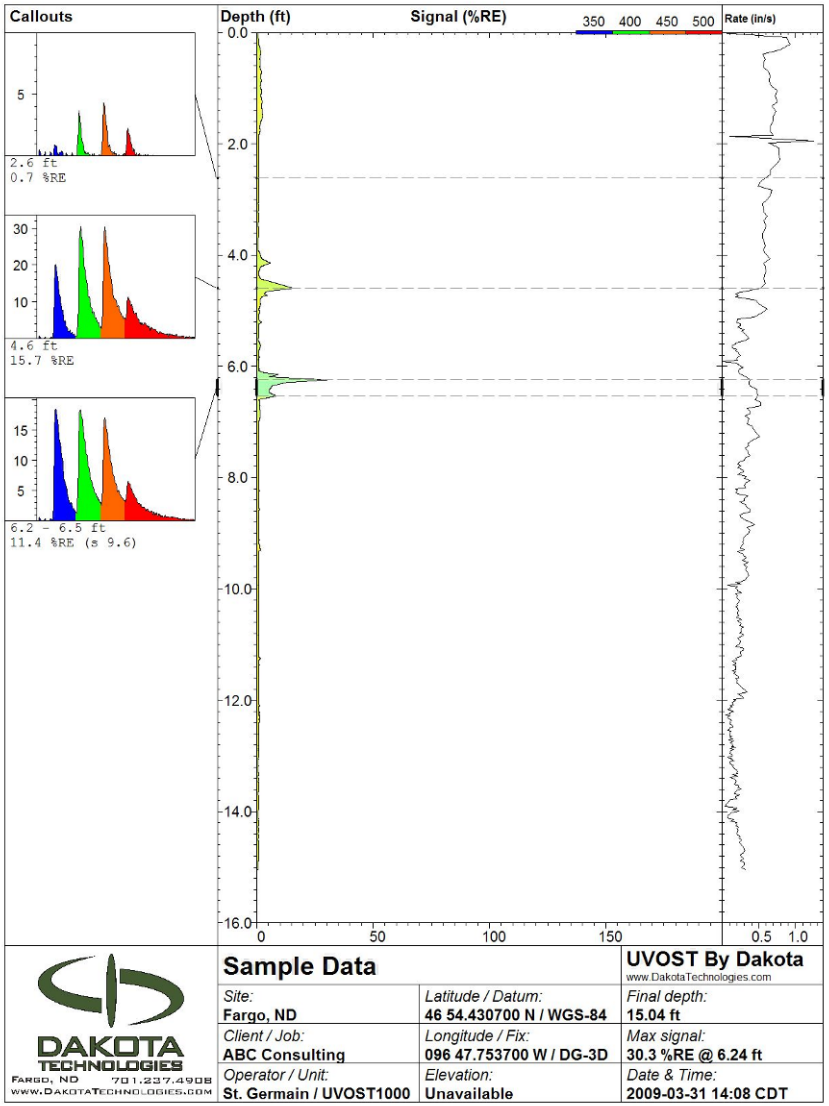
versus…

UVOST (good)



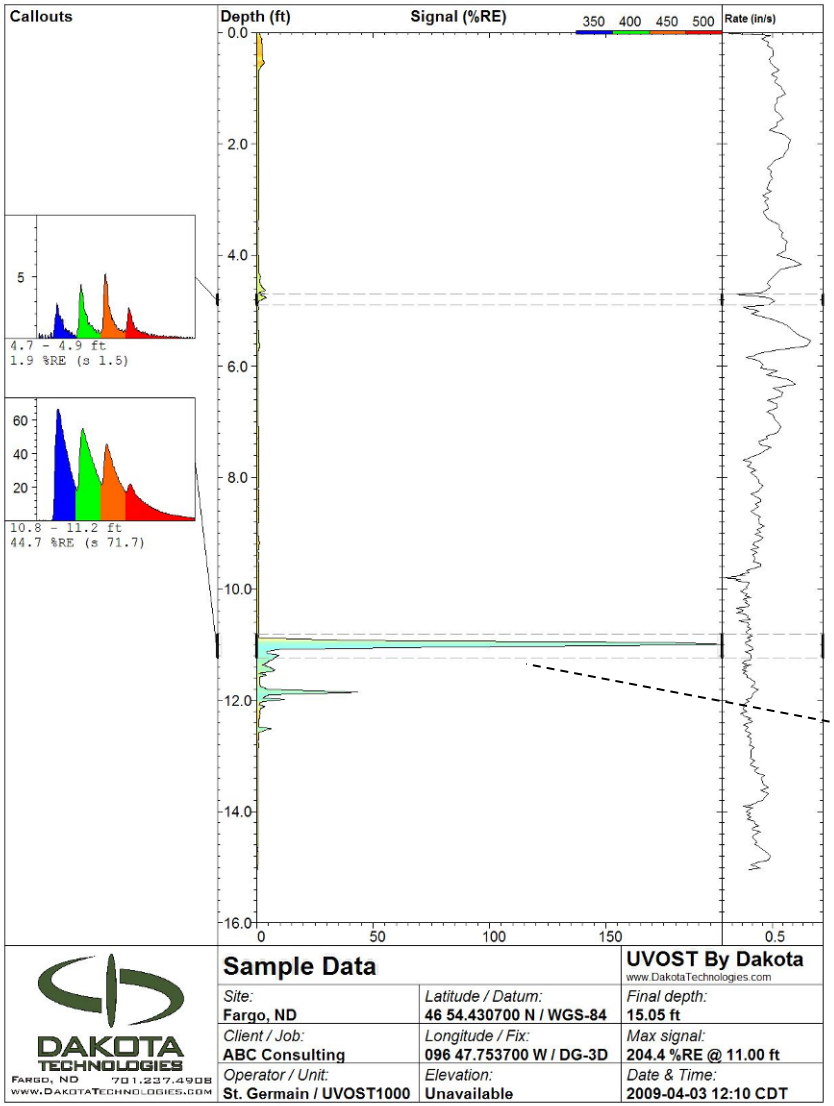
versus…

UVOST



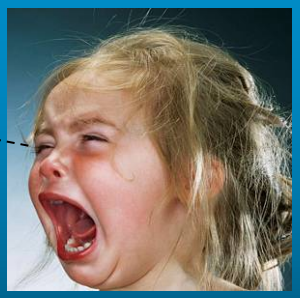
versus…

UVOST (bad)



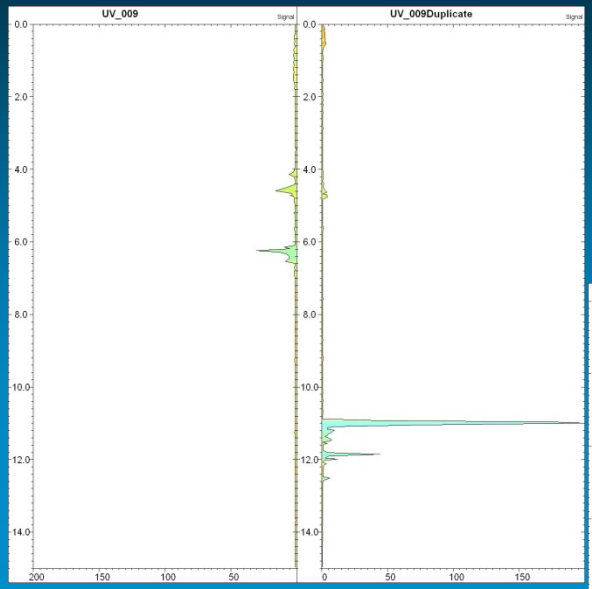
This also happens all the time with sampling/coring but nobody recognizes/realizes it due to expense/time of doing twins.

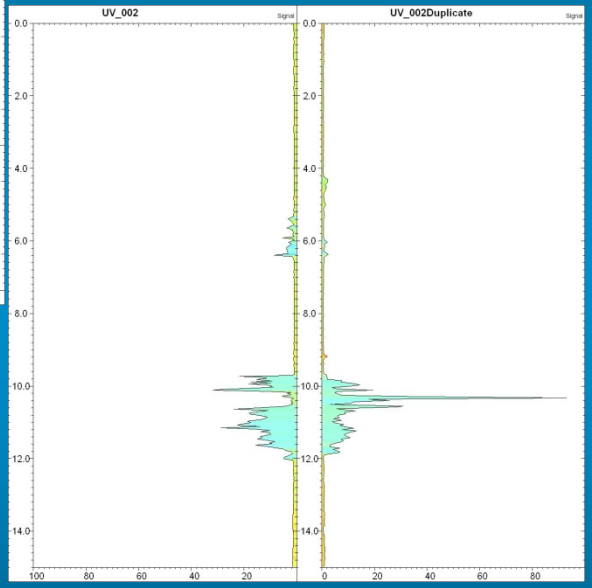
versus…

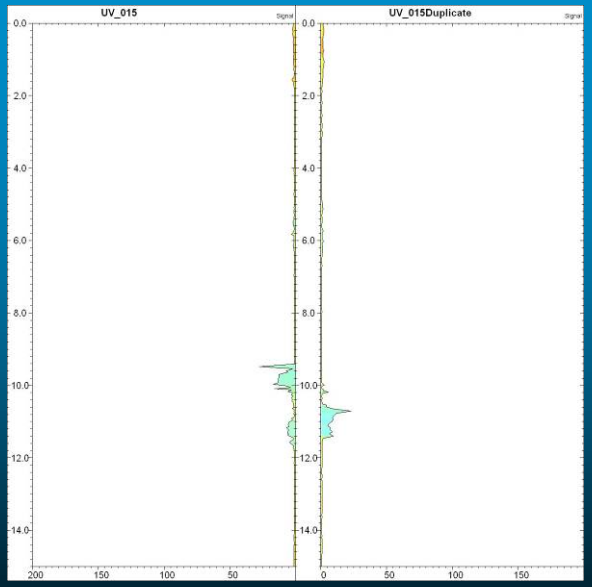


reaction of young consultant who was "hornswoggled" into using new-fangled UVOST – which "can't perform consistently"

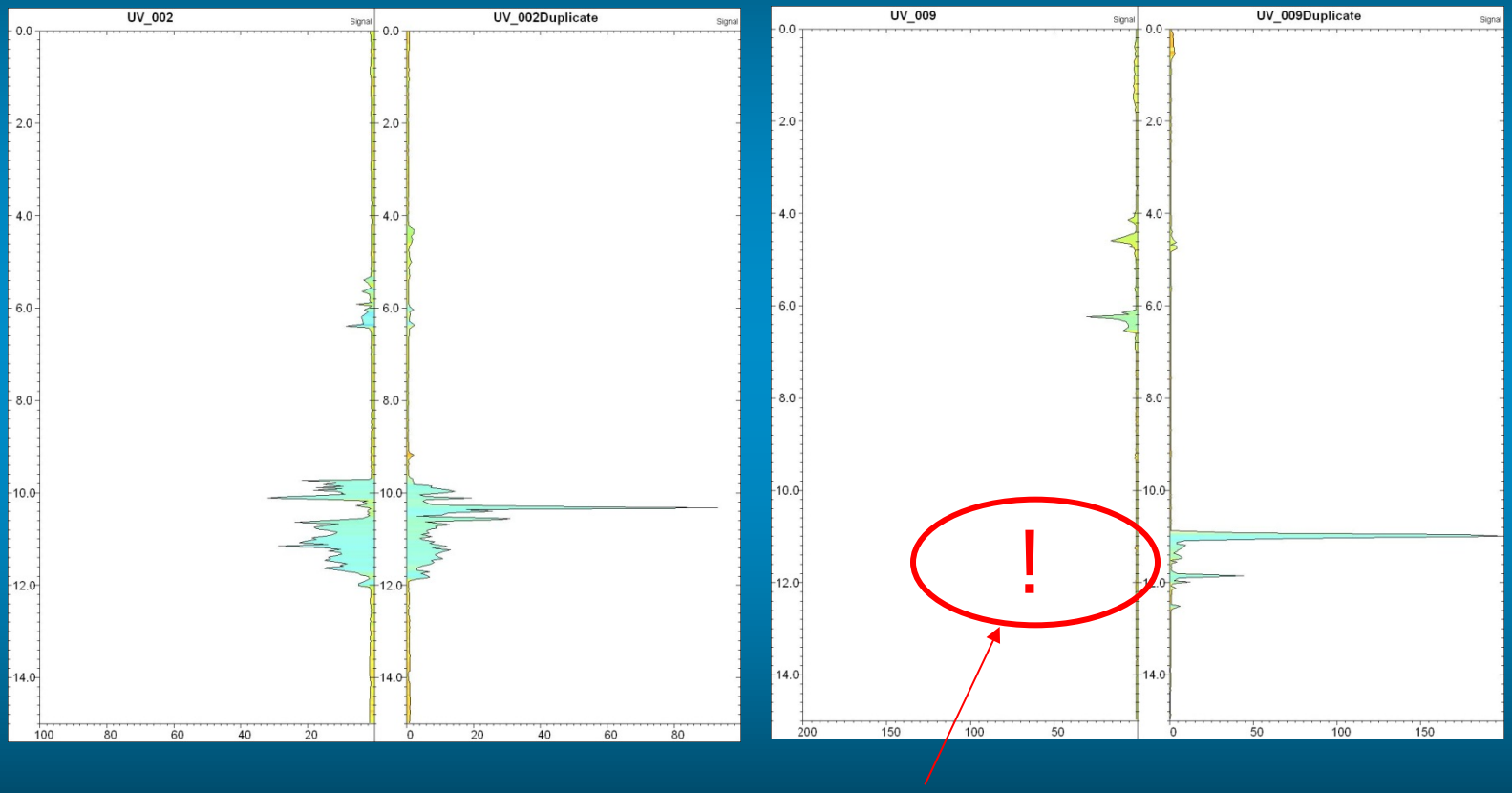
three butterflies from a gasoline spill
trapped gasoline (above and below water table)





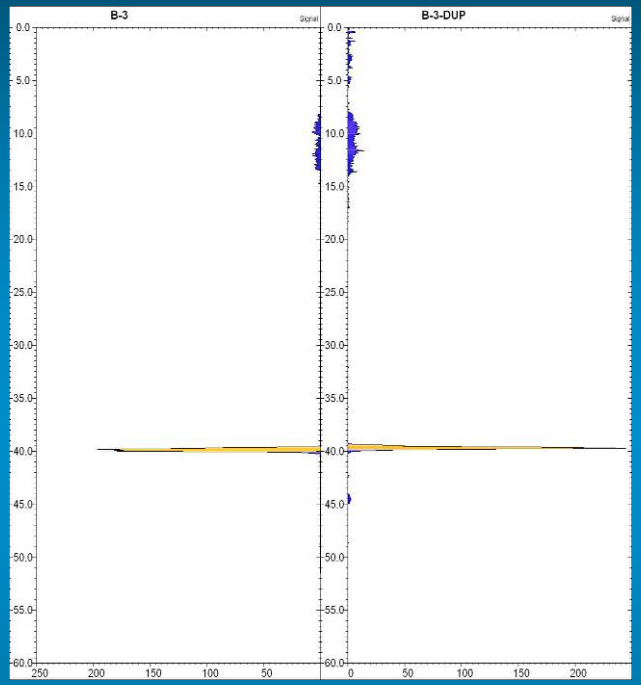


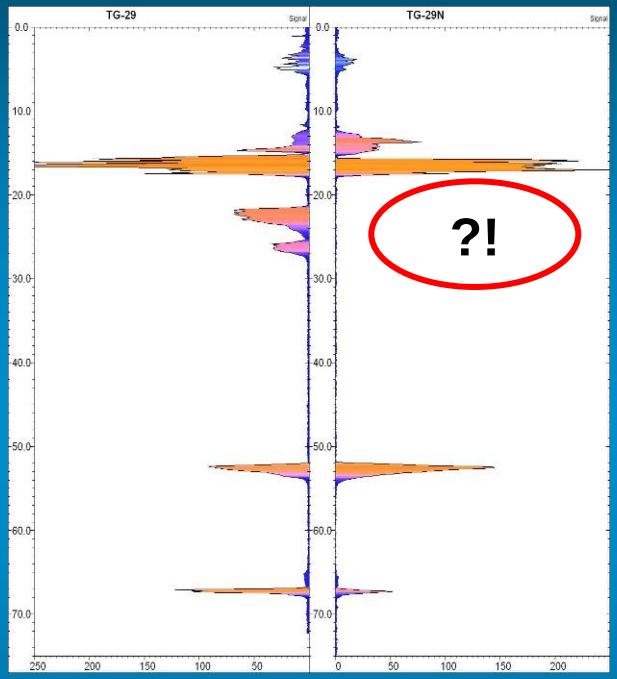
butterfly plots of UVOST logs

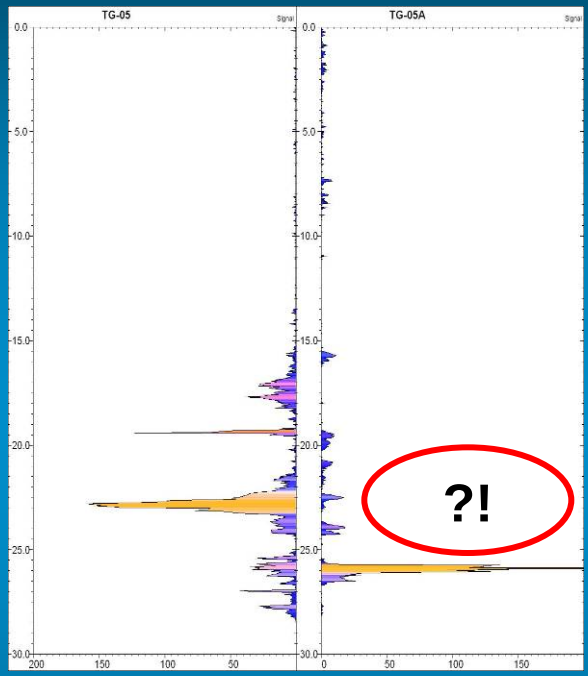


What if this was the "confirmation" sampling borehole? Which boring was "right"?

duplicate butterflies (various sites)







what if the second LIF log was a sampling event, not a second LIF log?

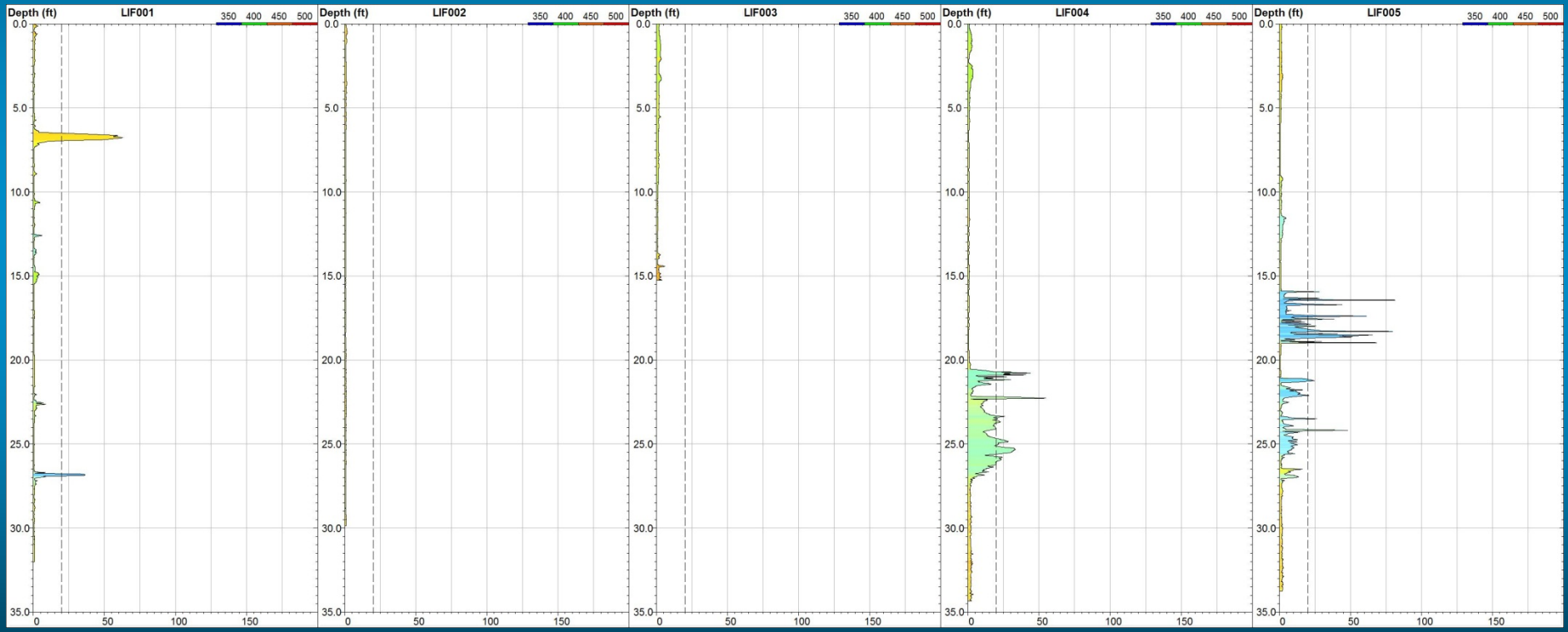
how often do you duplicate sample to see if your samples are consistent?

duplicate LIF only takes 20-40 minutes, but yields tremendous insight!

site-wide NAPL heterogeneity

when are duplicates useful?

When every log seems different than the last and “validation” is planned
(where will we gather “representative” samples at this site???)

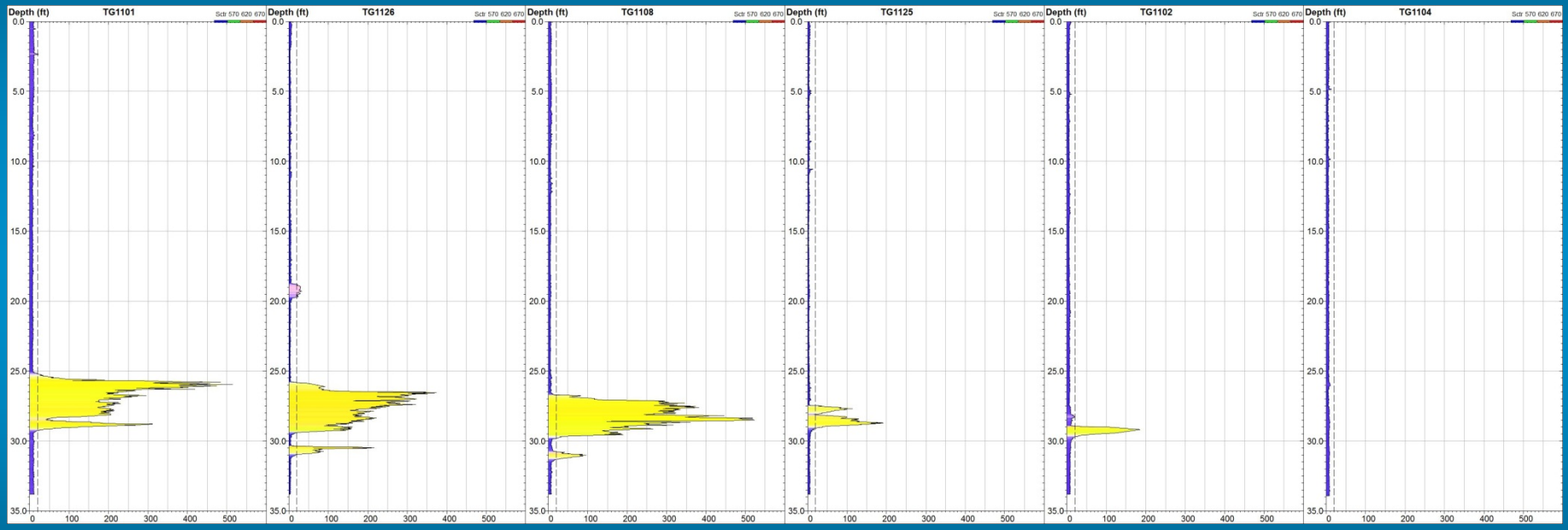


small gasoline service station in glacial till

site-wide NAPL heterogeneity

when are duplicates useful?

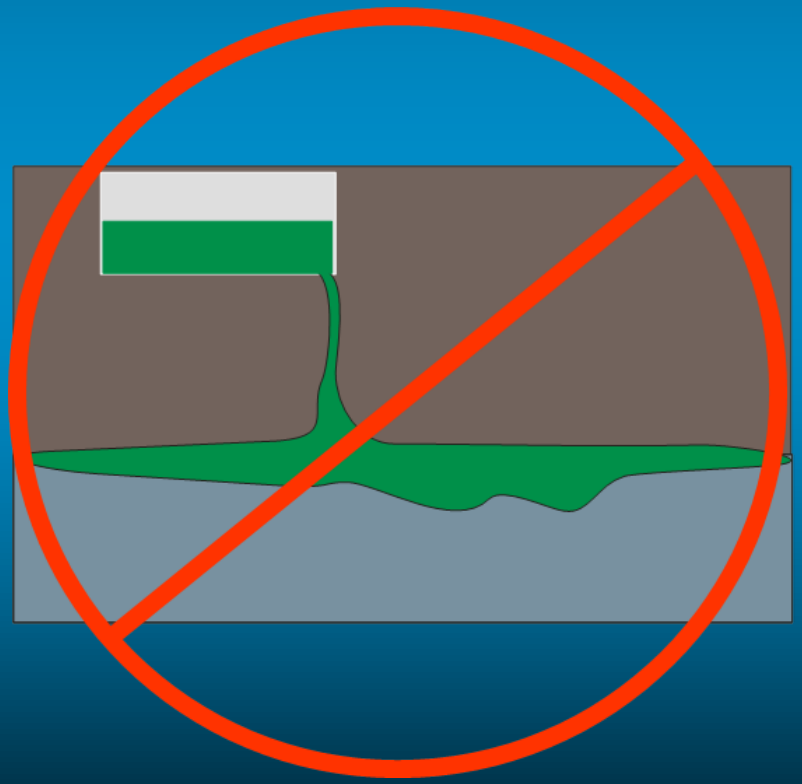
NOT SO MUCH when every log is similar to the last – no real driver exists since heterogeneity appears limited and behavior seems ideal



the pregnant pancake

it's an overly simplistic model (by necessity)

it certainly can/does exist "in the broad picture"
but ANY geology complication = NAPL distribution complication



zombie-like adherence to the "LNAPL floats on the groundwater's surface" or "pancake" model has cost the industry HUGE sums of money, time, and discouragement over the decades

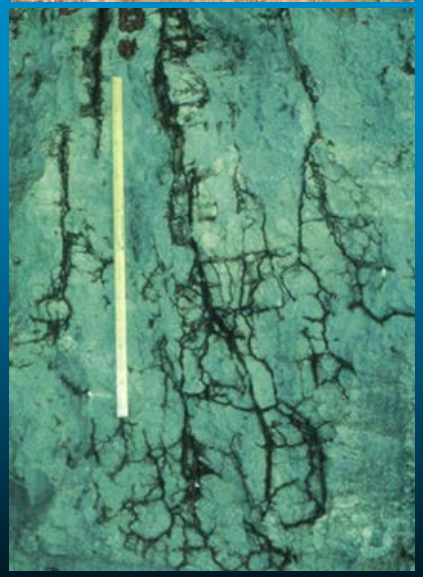
we know why these diagrams are used – to convey simple concepts like "LNAPL is lighter than water" so it floats"

BUT unfortunately they stick in people's minds as illustrating where LNAPL ends up at all LNAPL sites

when it isn't where they think it should be they stop looking or are frustrated by how "it changes every sampling event"

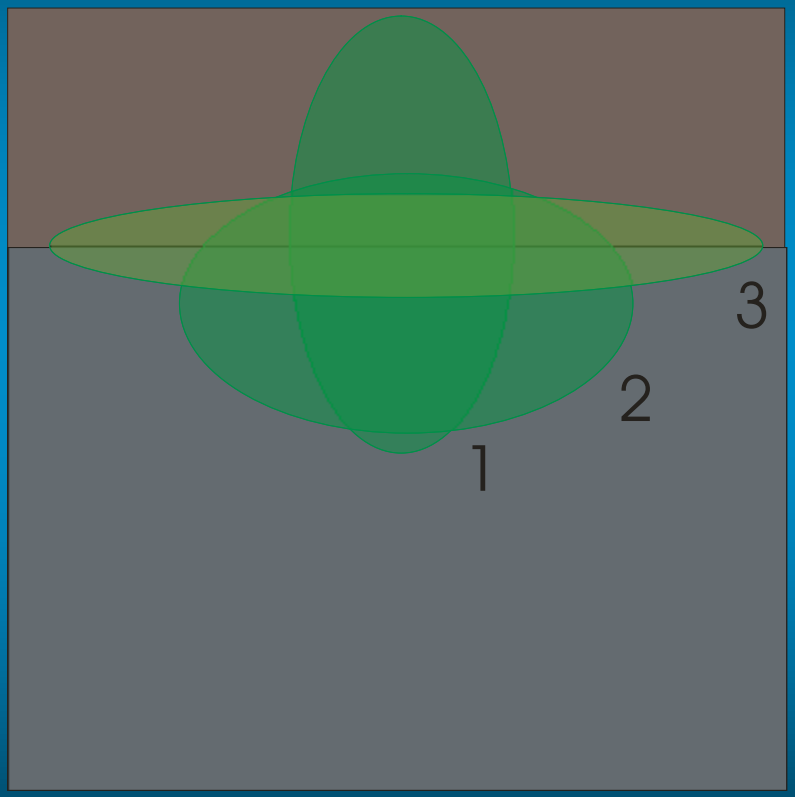
DAKOTA TECHNOLOGIES

- LNAPL can suspend, perch, dive, or float (or all three)
- LNAPL is often found trapped below groundwater surface (sometimes WAY below) - if vertical features (lenses, seams, fractures) dominate then LNAPL can be pushed down – or water table fluctuation and clay
- LNAPL often relies more on **geology** than the density difference between it and water to distribute
- conventional wisdom has us looking in wrong places
- the subsurface is often a **very** complex place – not the fairly homogeneous matrix most guidance documents are “forced” to portray
- we sample a tiny fraction of the site (what is the mass sampled vs. site mass?)
- monitoring wells are designed to monitor water, not LNAPL – they simply can’t be trusted for LNAPL



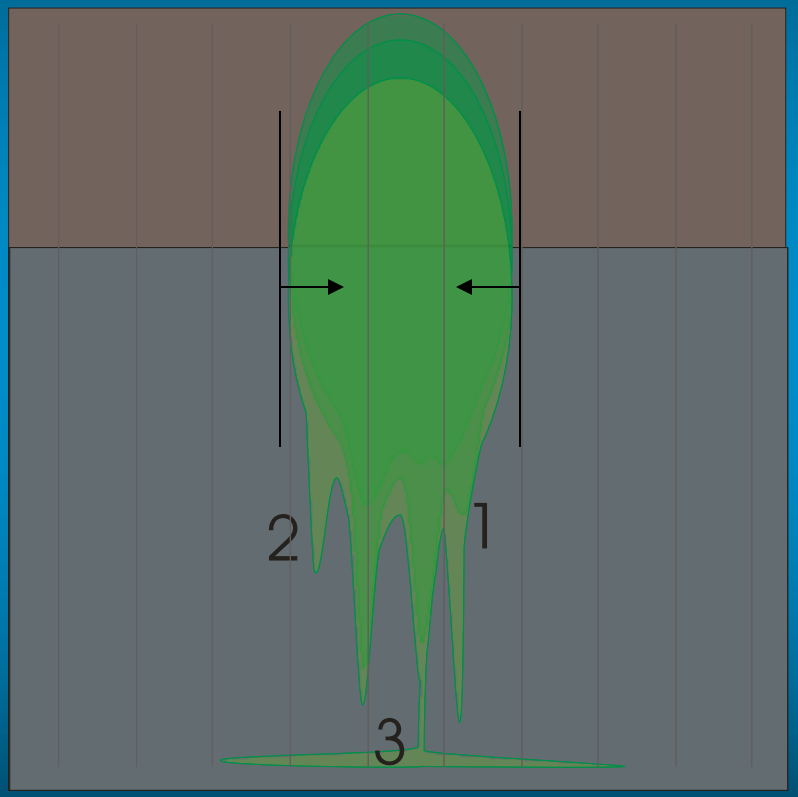
LNAPL far below the groundwater **potentiometric** surface?

sandbox
(vertical perm = horizontal perm)



fuel free to flow laterally….

fractured clay
(vertical perm >> horizontal perm)



fuel can't flow laterally…
like an iceberg it's driven down vertically
where it often finds lateral freedom (wells too)

DAKOTA TECHNOLOGIES

example LNAPL misbehavior case #1

"comeback" site in Minnesota

- above ground tank found with leak in 1995
- tank was replaced – no significant fuel observed in soil
- monitoring wells installed west, east, south - no CoCs in wells

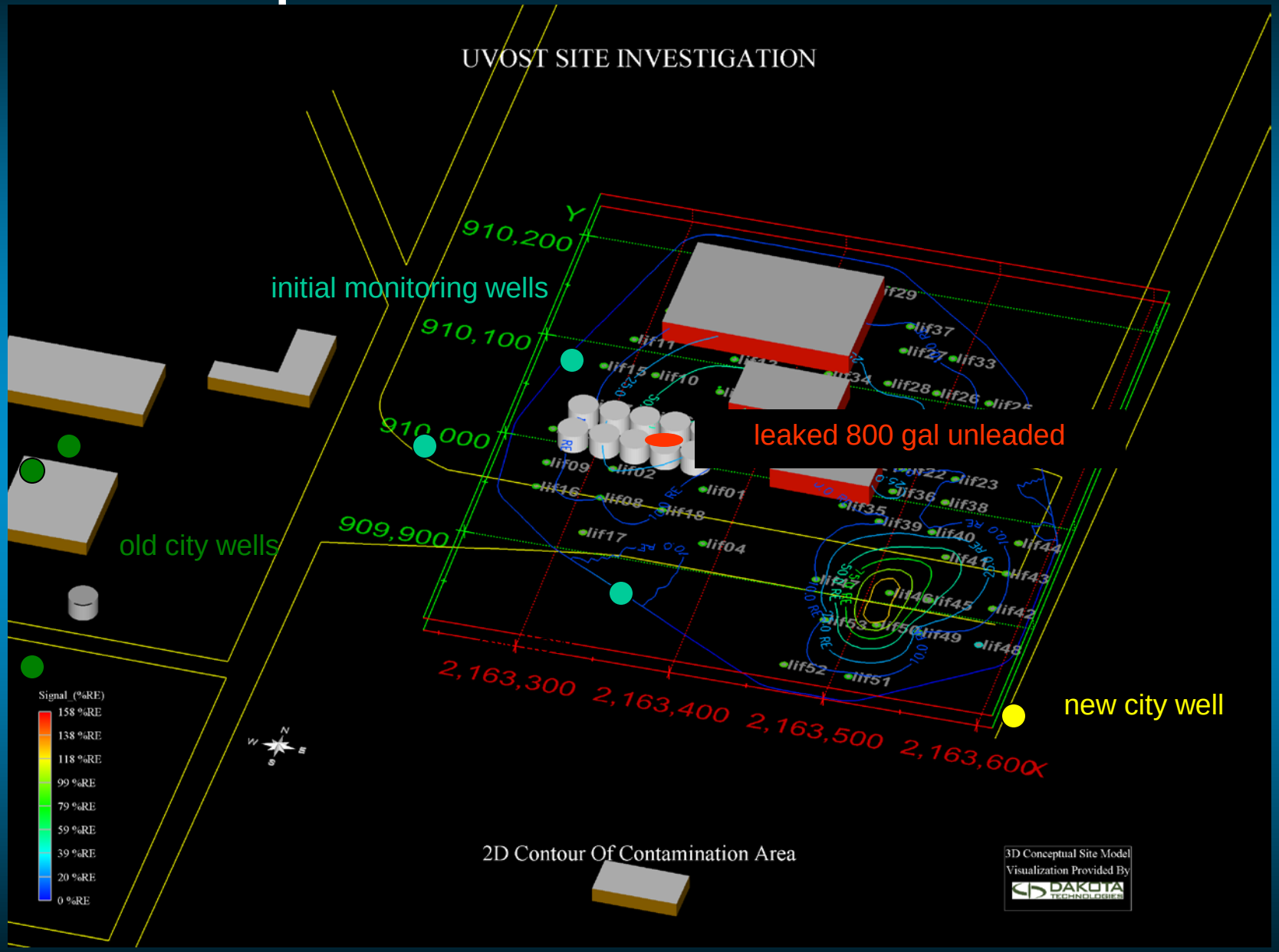
- site was closed 1997 – monitoring wells were pulled
- in 2000 - new high-capacity city supply well installed 300-500 ft away

- 2003 - benzene found in new well - knocking well out of service so the site "comes back" onto the books

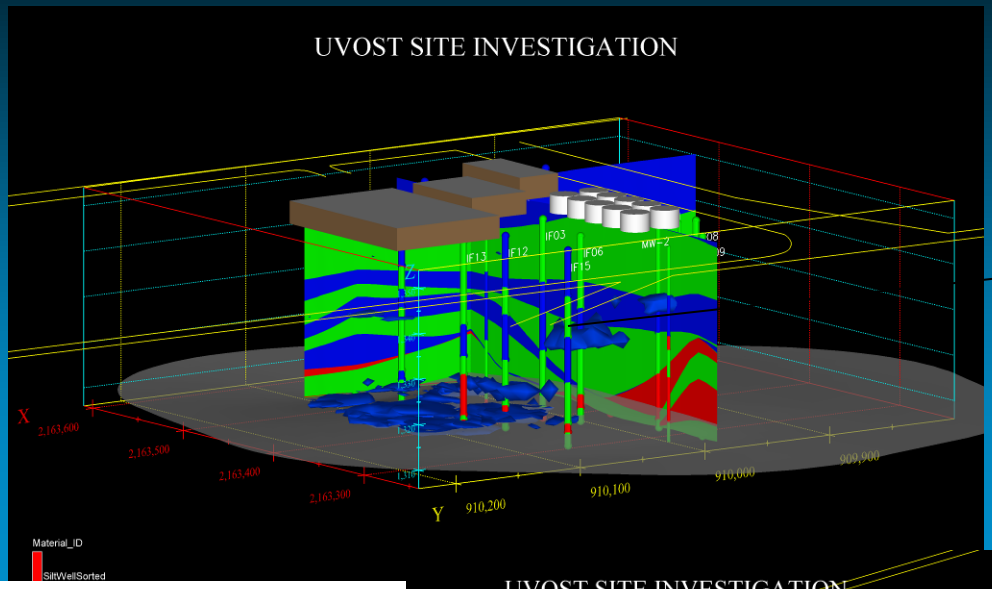
- new monitoring wells installed… still confusing, no NAPL in them!

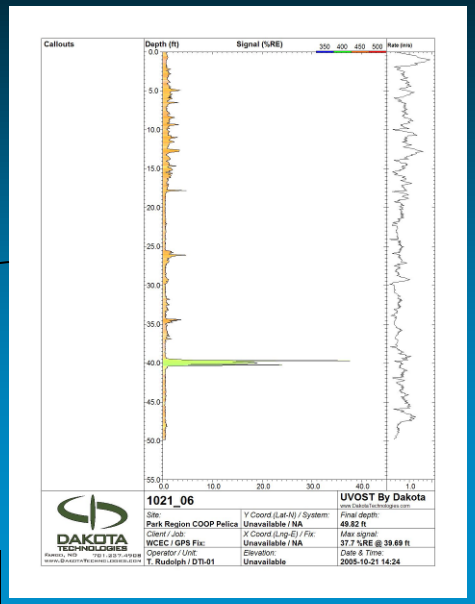
so what's going on?!....

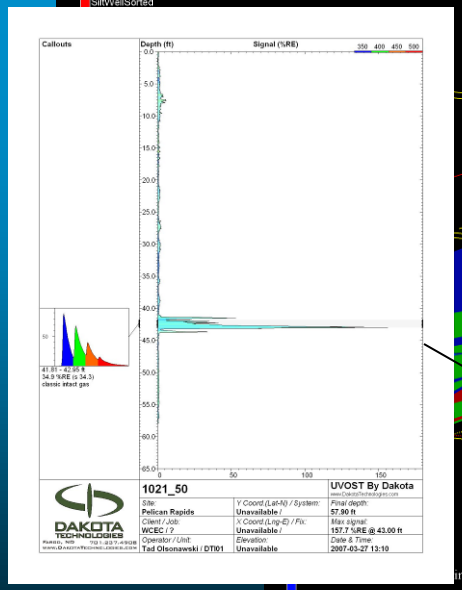
example LNAPL misbehavior #1

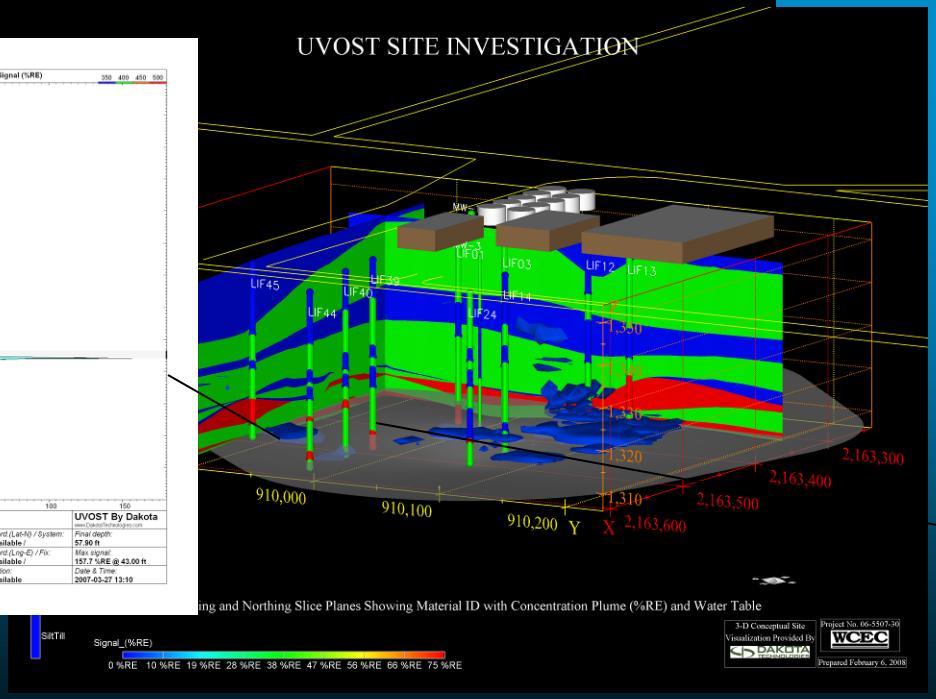


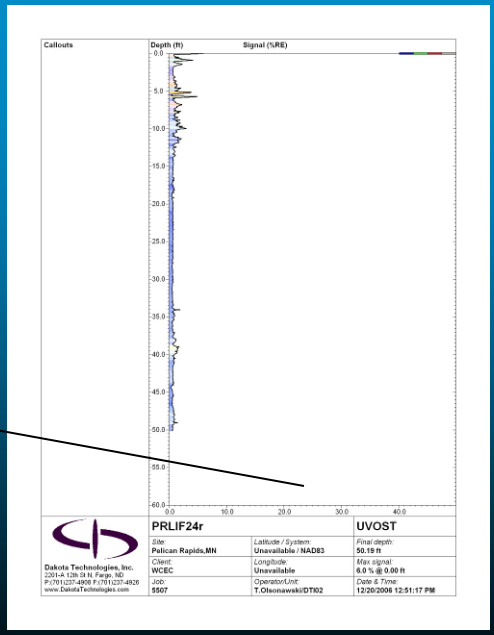
50 LIF (UVOST) borings ~ 4 days work







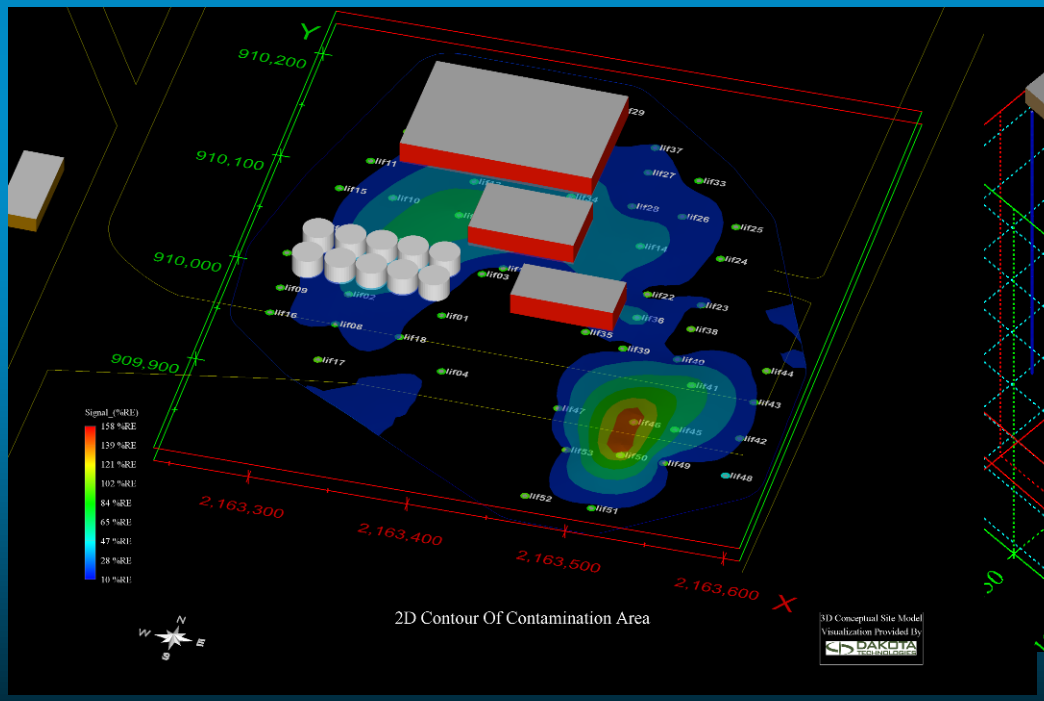


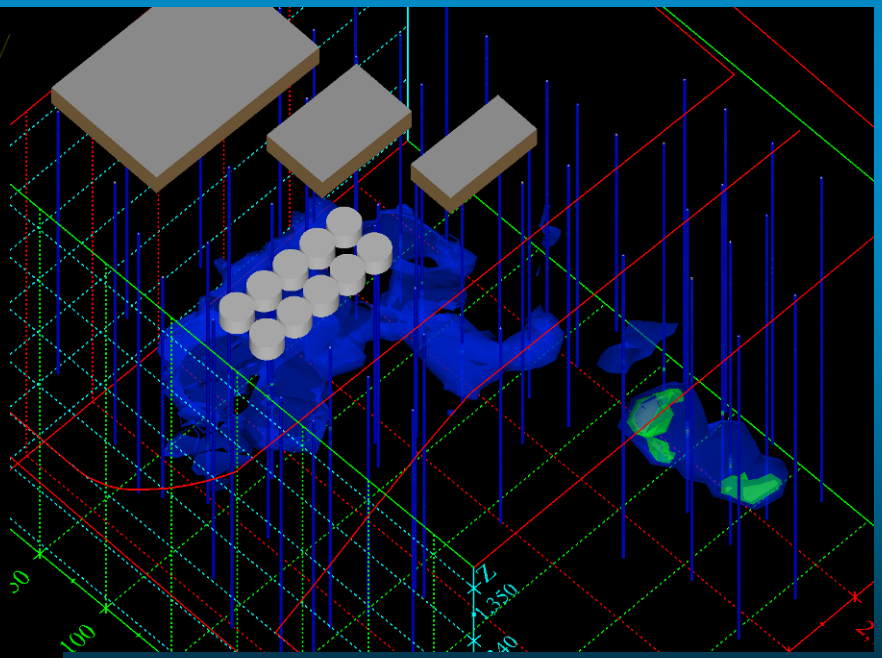


DAKOTA TECHNOLOGIES

the ‘autopsy’ results via LIF

- LNAPL headed north – opposite of groundwater gradient and under a building - rolling down a sloped clay formation
- gasoline then found pathway down past the clay and cascaded to groundwater and moved SW to create highest concentration in a SE “arm”
- one of the first set of 3 wells would likely have detected dissolved BTEX in time
- to date – no well has measurable LNAPL! Just a ‘sheen’ in the well in heart of the “arm”!
- all nearby city wells sealed off – replaced city wells with deep well 1 mile away
- dissolved phase is now stable – currently monitored natural attenuation





example LNAPL misbehavior #2

“lucky well” site in Minnesota

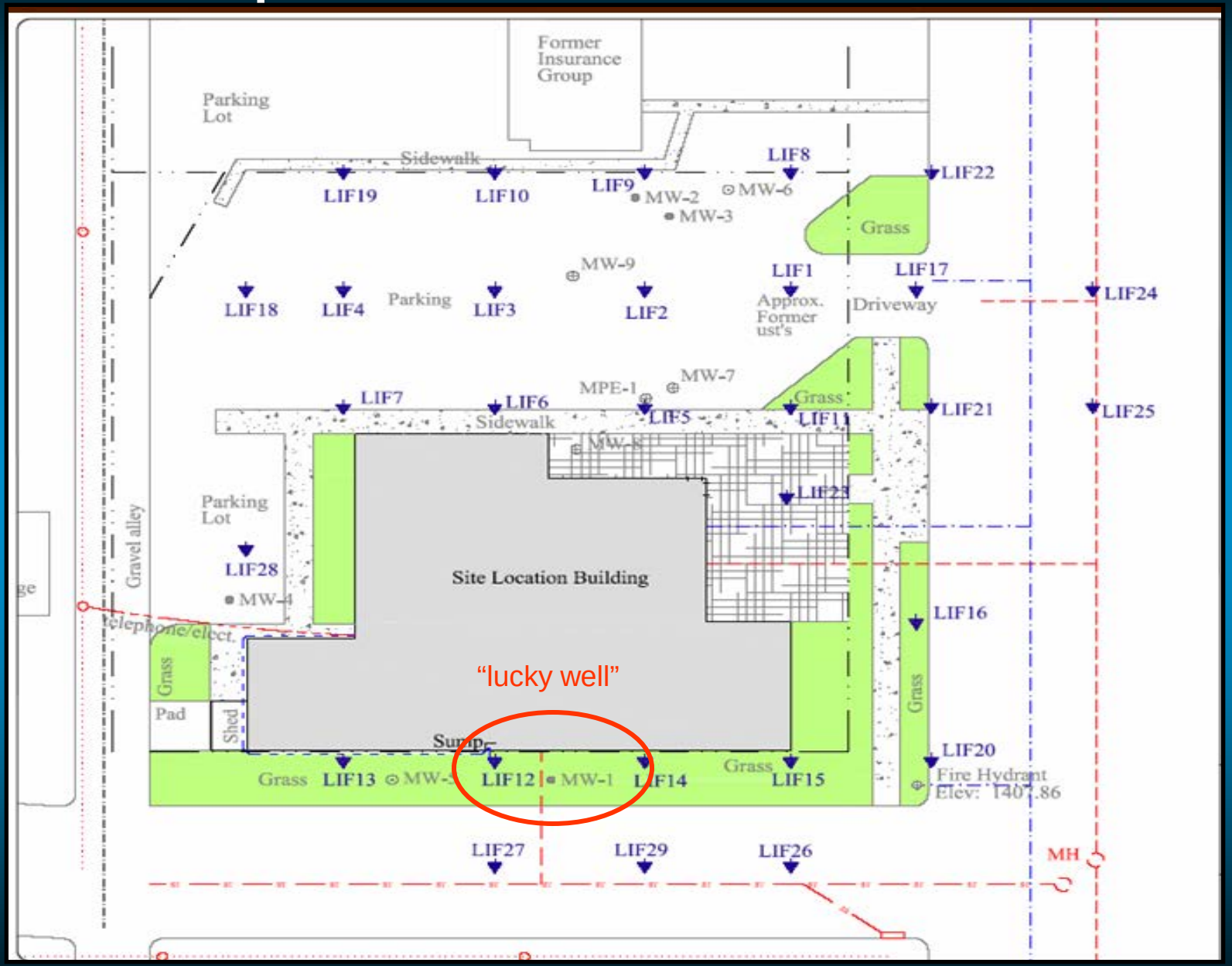
- fuel release site
- tanks were removed – no sign of significant release
- one mandatory well was inadvertently screened 18-28 feet which is 5-6 feet below groundwater surface
- only this “wrongly constructed” well detected LNAPL!

- consultant was dead sure someone spiked the well couldn’t explain lack of fuel in any other wells or tank hole

if fuel was released, it’s got to float and show up… right?

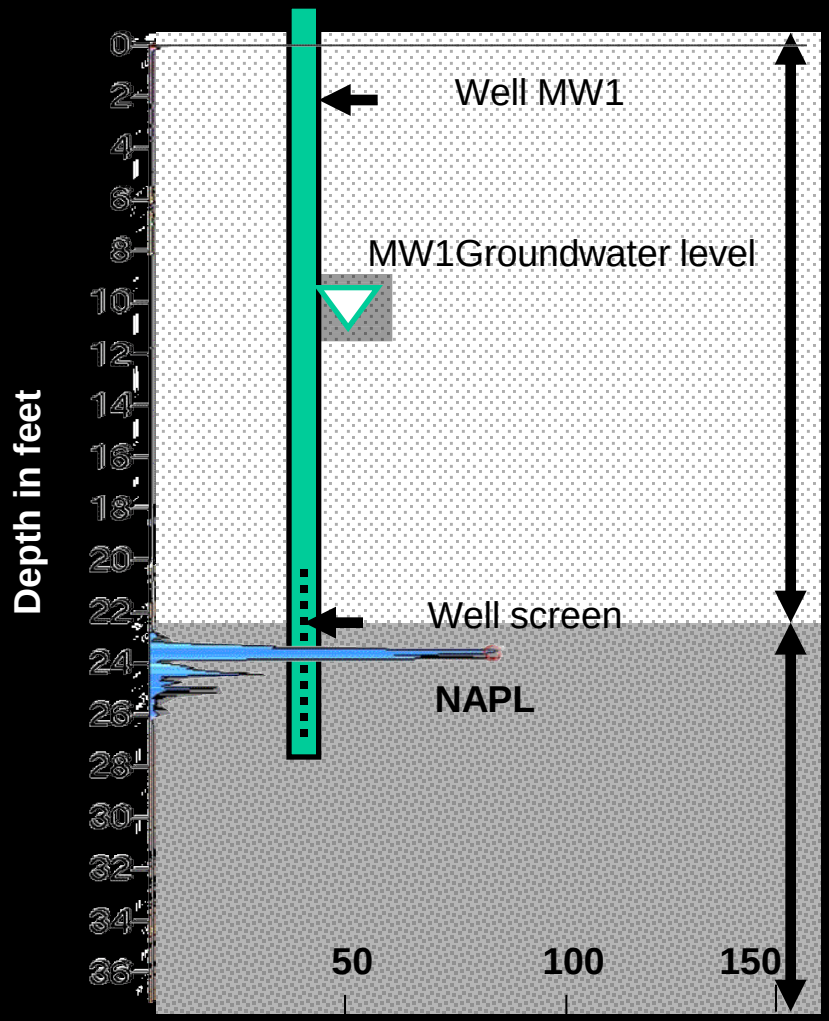
so what’s going on?....

example LNAPL misbehavior #2



DAKOTA TECHNOLOGIES

“lucky” well

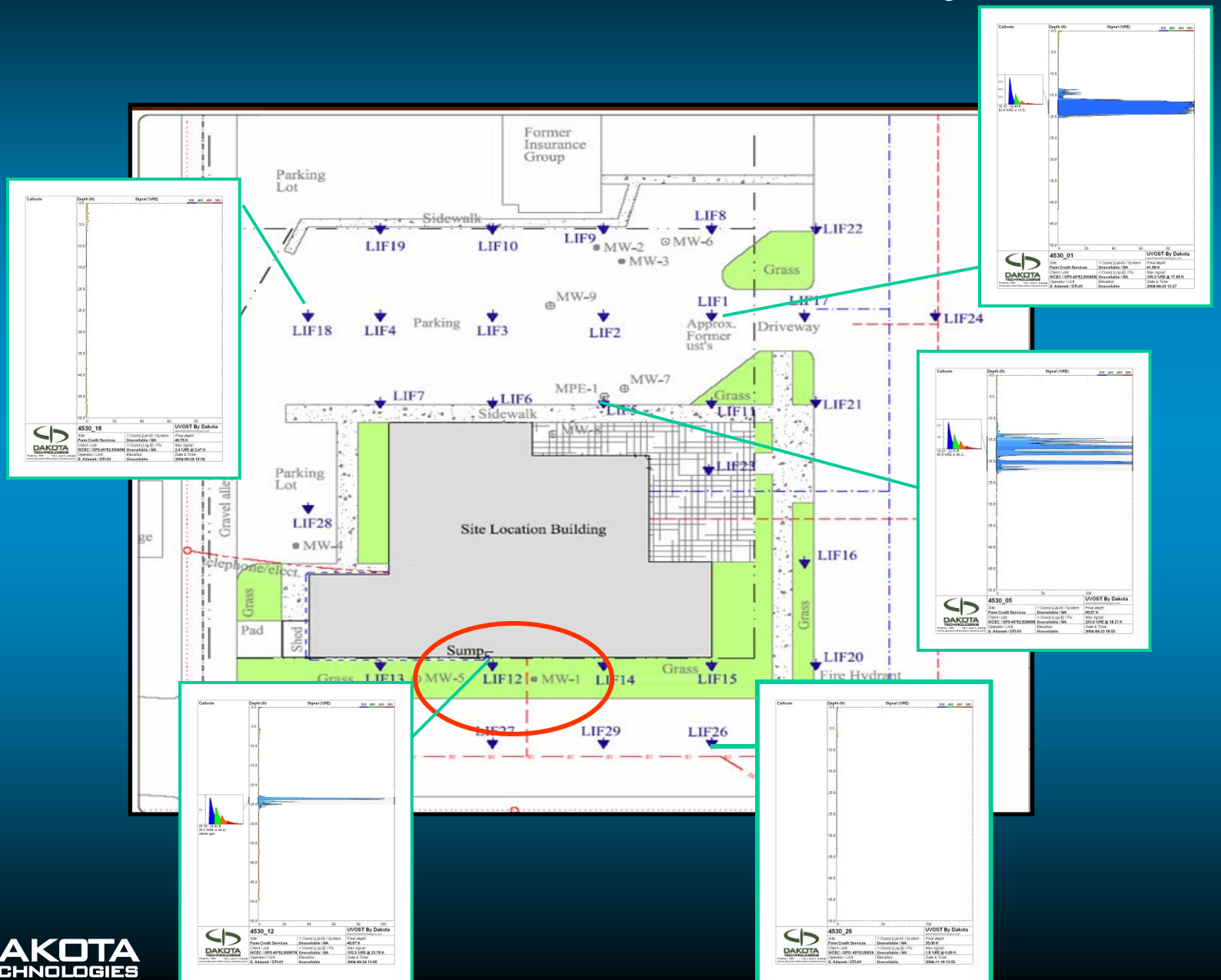


0 - 22 feet
Silt with clay and rocks (till)

22 – 40 feet
Fine - medium grained sand

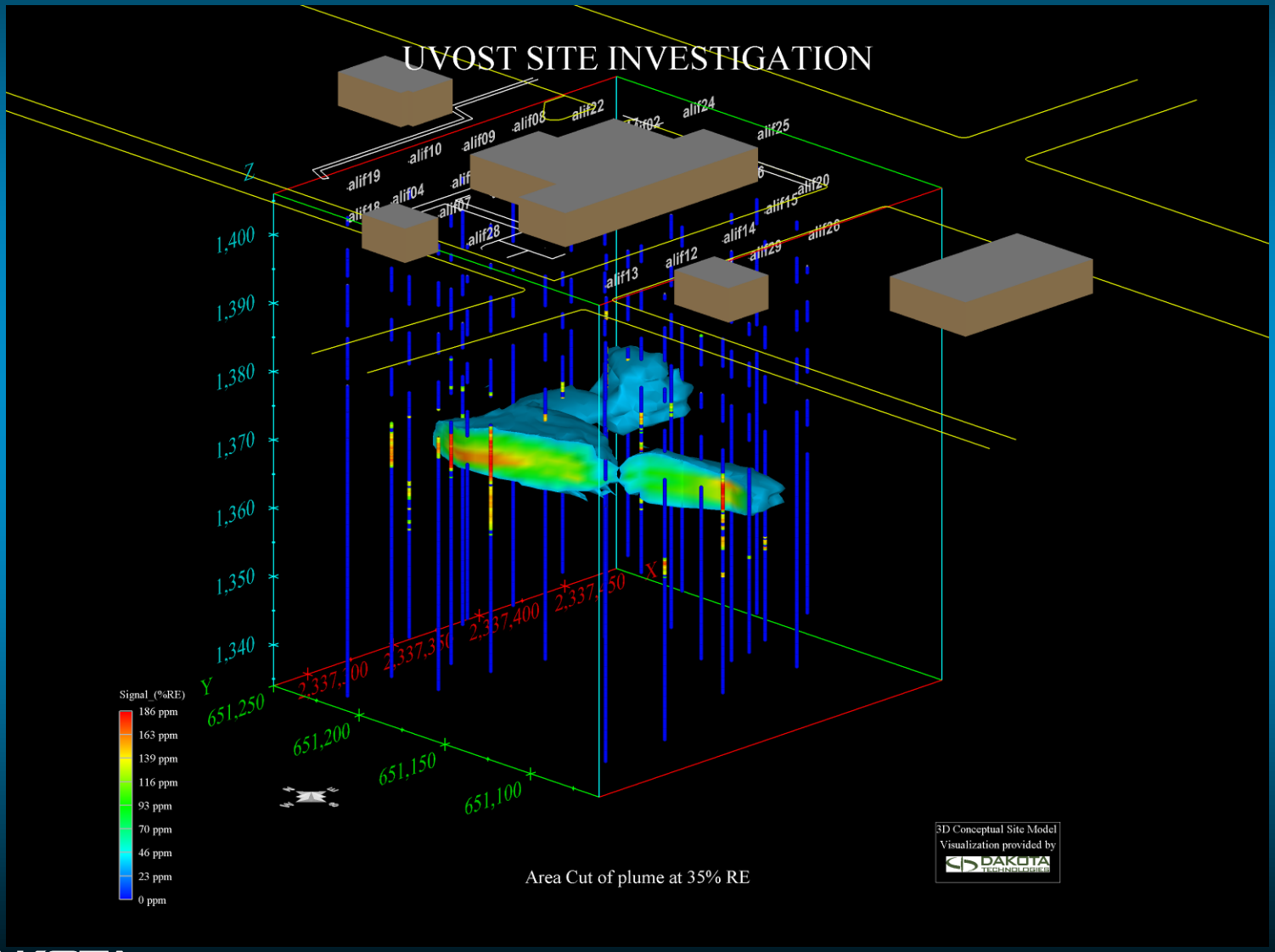
DAKOTA TECHNOLOGIES

so LIF was brought in to “settle the matter”
30 UVOST locations ~ 3.5 days



DAKOTA TECHNOLOGIES

a very large “sunken” gasoline body was located with LIF somehow the gasoline (via pressure/head) had filled the porous sand unit under the clay/silt



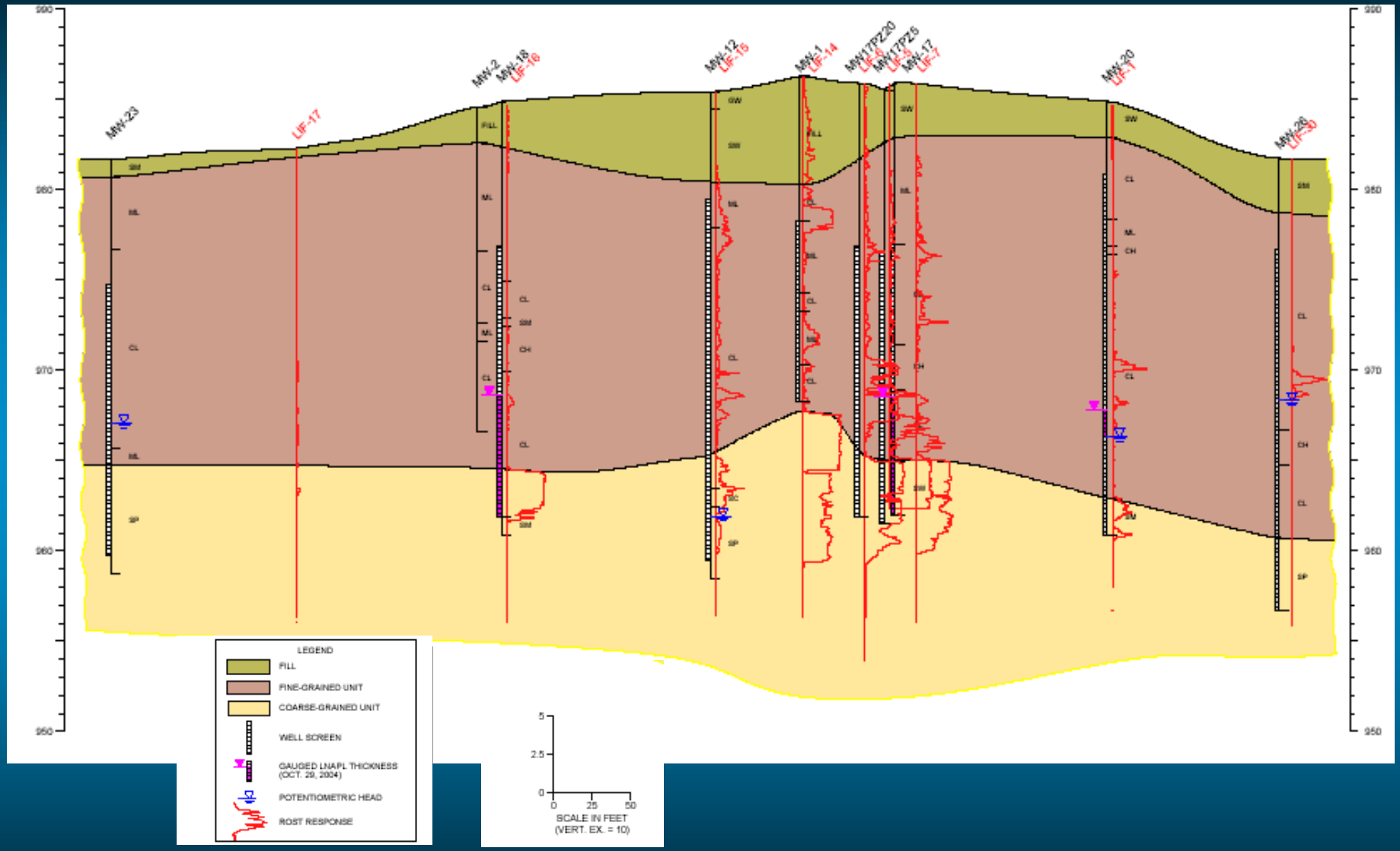
Battelle AECOM

Limitations of Laser Induced Fluorescence Technology

Andrew J. Kirkman, P.E.
AECOM
St. Paul, MN

June 29, 2011

LNAPL Site Conceptual Model

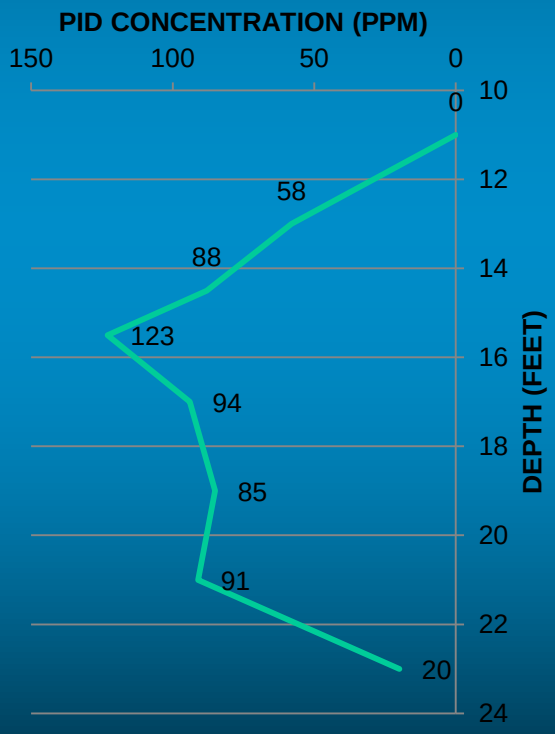


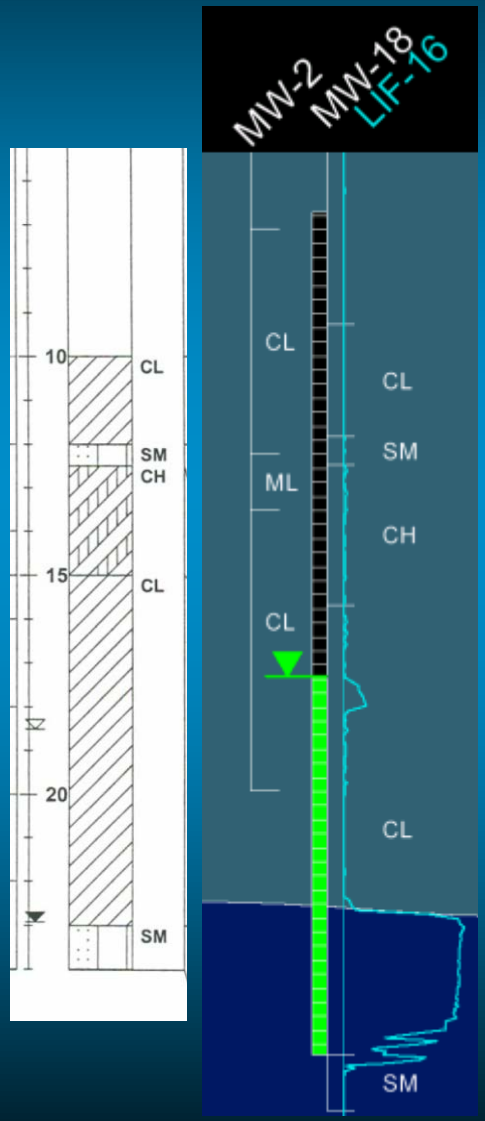
LNAPL in wells had **very poor** correlation with LNAPL in adjacent formation

PID Fails to Discriminate – LIF Domination Has Arrived

Battelle

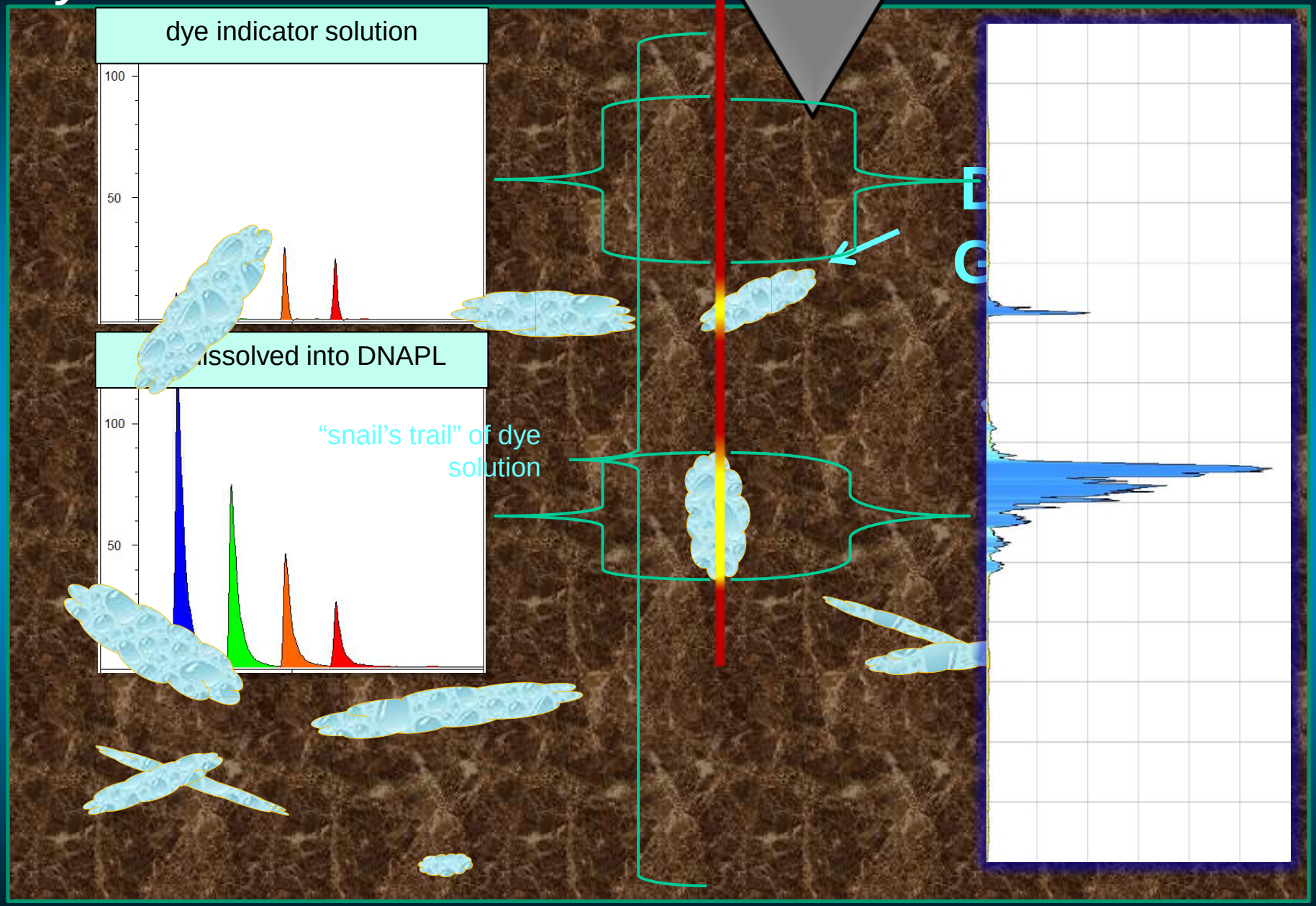
AECOM





LIF provides the foundation for LNAPL Site Conceptual Model (LSCM) and basis for refuting gauged LNAPL thickness as a metric for impact magnitude

Dye-LIF Probe in Action



Thank you!

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