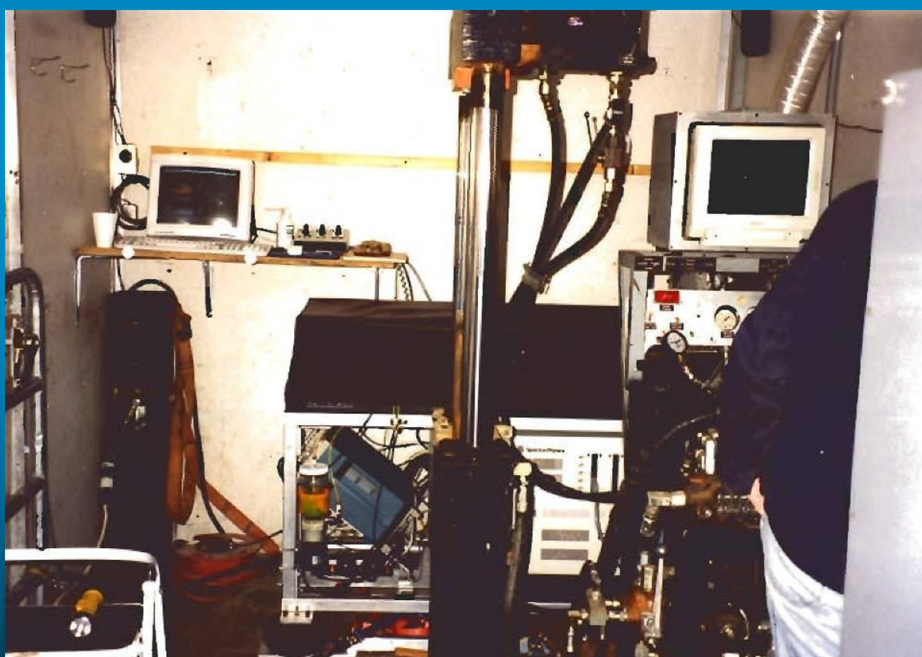
An Introduction and Review:

Laser-Induced Fluorescence (LIF) Technologies

Randy St. Germain, President
Dakota Technologies, Inc.

The personnel at Dakota have been making LIF measurements of PAHs for over 25 years and we've been doing direct push LIF for fuels/oils for 20 years. Our desire is to build equipment that captures world class data – but doesn't have to be operated by a physicist or equipment expert.

ROST, UVOST, TarGOST, and Dye-LIF were designed from the bottom up to do one thing… log state-of-the-art fluorescence information in the subsurface with direct push.



ROST Prototype circa 1991

UVOST 2007

LIF History

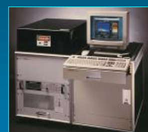
1992

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

1993

Dakota Technologies Incorporates

1994



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

1996

Lockheed Martin sells ROST Fleet to Fugro Geosciences

1997

Dakota Develops Percussion-Capable Probe (SPOC)

1998

Dakota Technologies First Provides Regional "ROST" Service

"Dark Ages"

2003

Dakota Technologies Introduces TarGOST Service

2006

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

2007

Dakota Technologies Introduces UVOST

Dakota's Optical Screening Tools (LIF, Color)

Model	Manufacturer / Providers	Technology / Deployment	Target
ROST - Rapid Optical Screening Tool	Dakota Fugro exclusively	dye laser - 290nm spectral/temporal Percussion & CPT	fuels/oils containing low to moderate PAH
UVOST - Ultra-Violet Optical Screening Tool	Dakota offered by numerous field service providers	XeCl laser - 308nm spectral/temporal Percussion & CPT	fuels/oils containing low to moderate PAH
TarGOST – Tar-specific Green Optical Screening Tool	Dakota Dakota exclusively	Nd:YAG laser - 532nm spectral/temporal Percussion & CPT	coal tars/creosotes containing moderate to heavy PAH
Soil Color	Dakota offered by Dakota and available to providers	broadband white light reflectance Percussion & CPT	Munsell soil color, soil class, ???

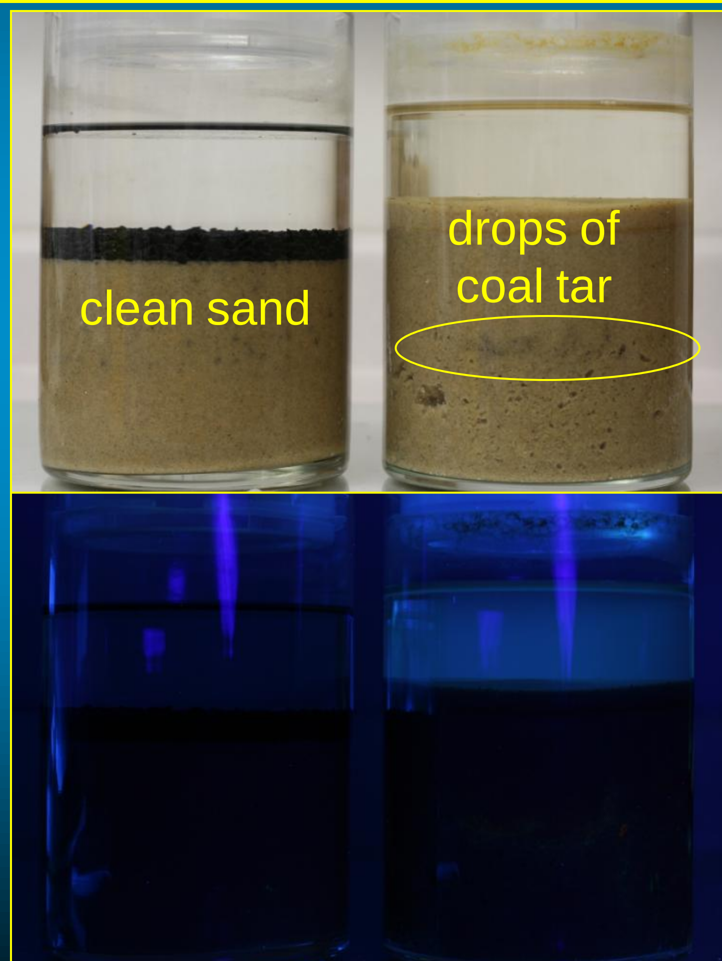
The LIF Site Characterization Concept

Q: why do environmental investigators “chase” NAPLs such as fuels, oils, creosotes, coal tars?

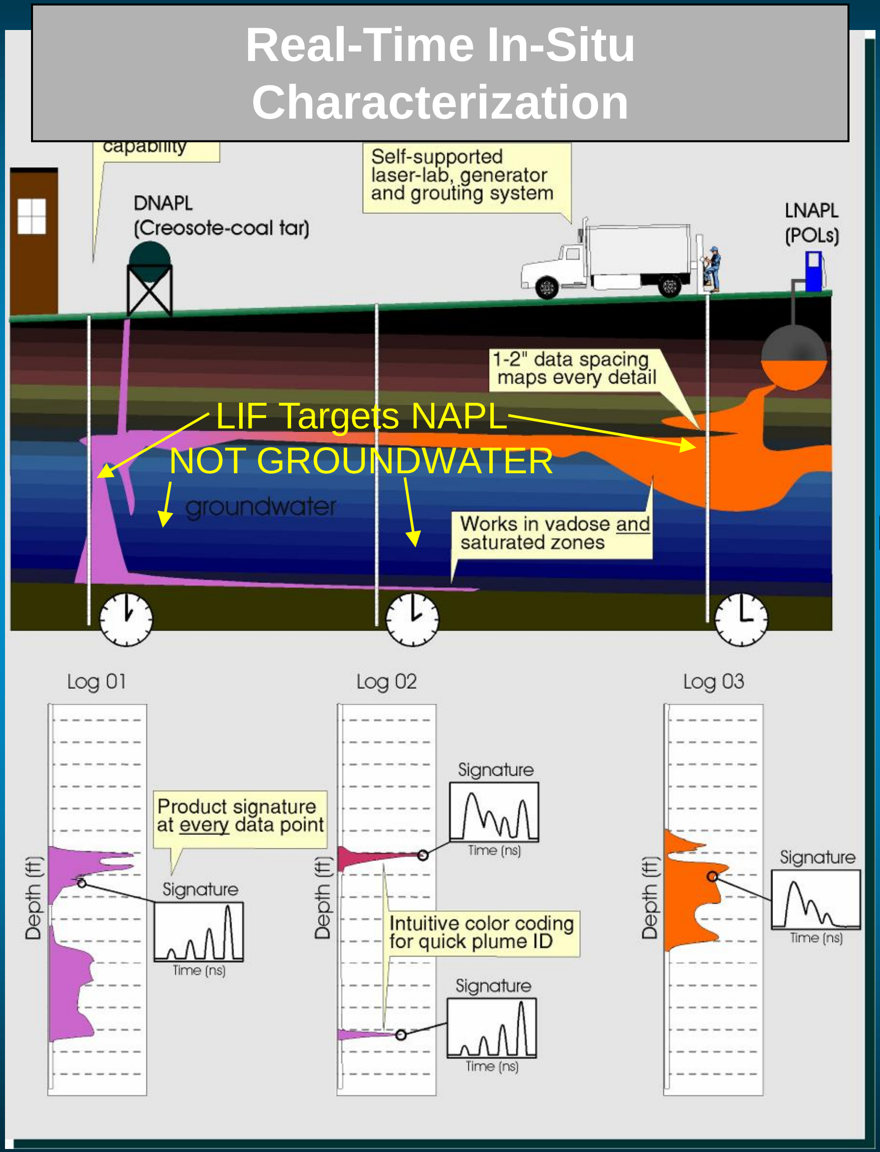
A: they contain bad actors (polycyclic aromatic hydrocarbons)
* ingestion or dermal exposure risk
* **capable of long term sourcing of aromatics to groundwater**

biota from
clean soil/groundwater

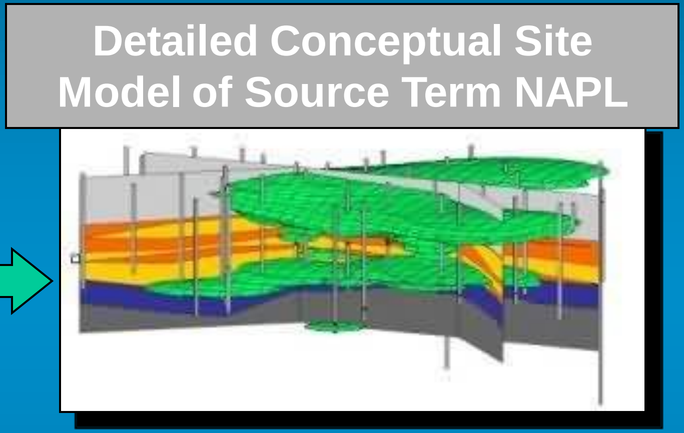
same biota on PAHs!



LIF Method

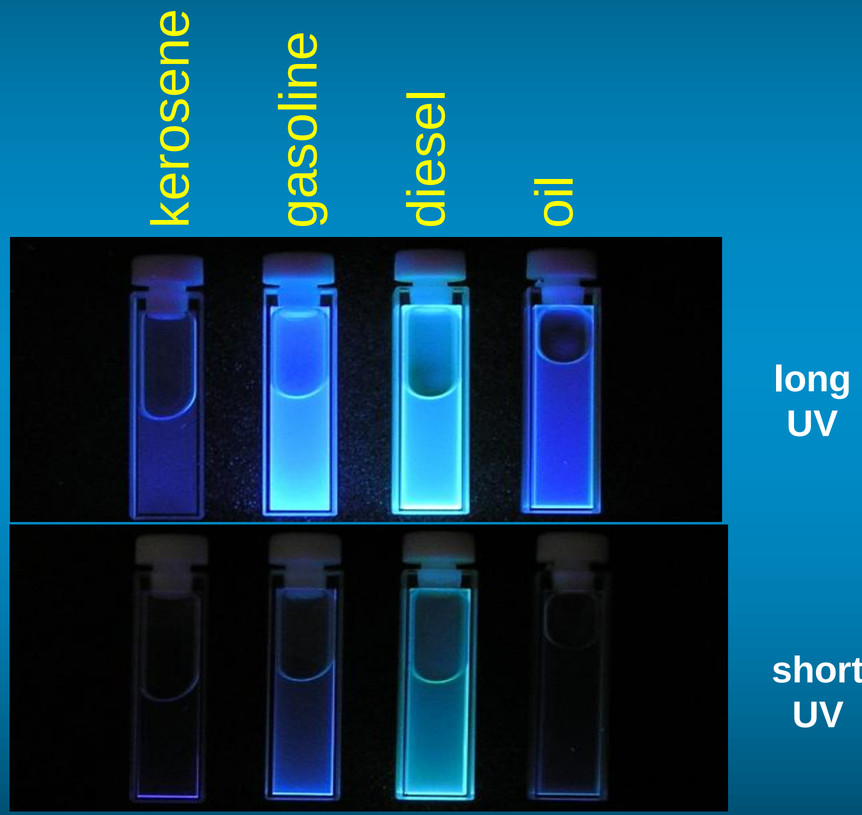


Desired Result



fortunately all PAH non-aqueous phase liquids or NAPLs fluoresce

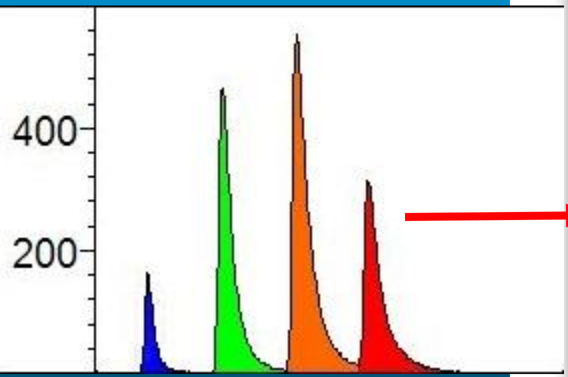
PAH fluorescence is a way to detect them by their "glow"



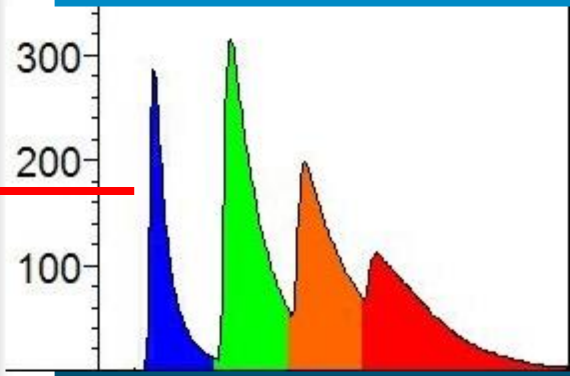
fluorescence

crude oil **diesel**

what LIF "sees"



what LIF "sees"



basics of Optical Screening Tools

(Dakota designed LIF systems)…

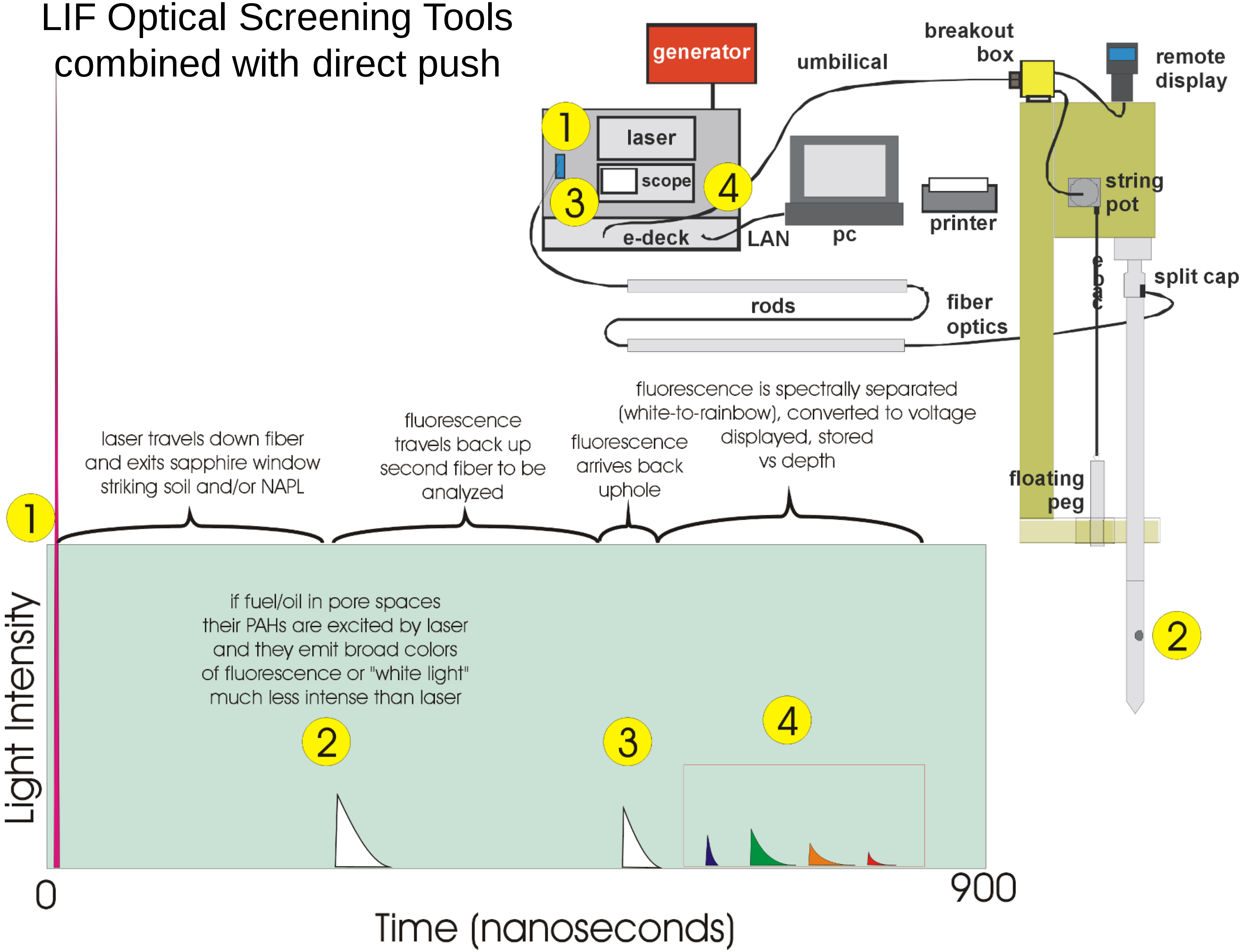
- spectroscopic (light-based)
- sapphire-windowed probe head requires "direct push" delivery
  - dynamic (Geoprobe®/AMS)
  - static (CPT)
- log fluorescence of a fuel's/oil's PAHs vs depth during penetration
- measurements penetrates into formation only as deep as light can (not very far!)

windowed probe - percussion

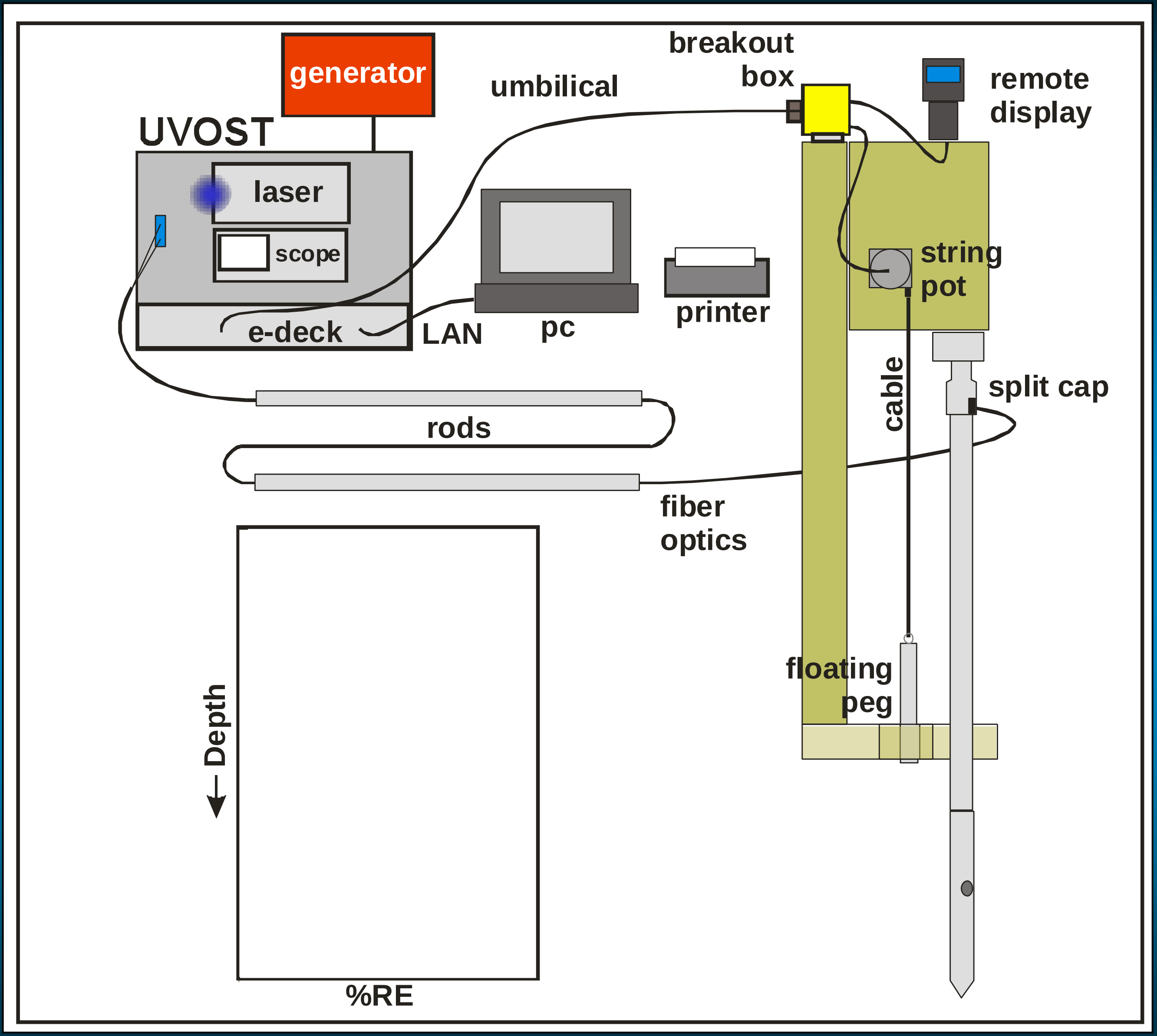
windowed probe – submerged derrick

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)

• dissolved phase PAHs

LIF compatible sites

most PAH-NAPL sites

- Leaking underground storage tanks

- Pipelines
- Refineries
- Fueling areas

- Fire-training facilities
- Automobile service locations (hydraulic fluid, POLs)

- Surface spills

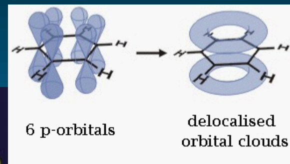
The Spectroscopy Behind LIF

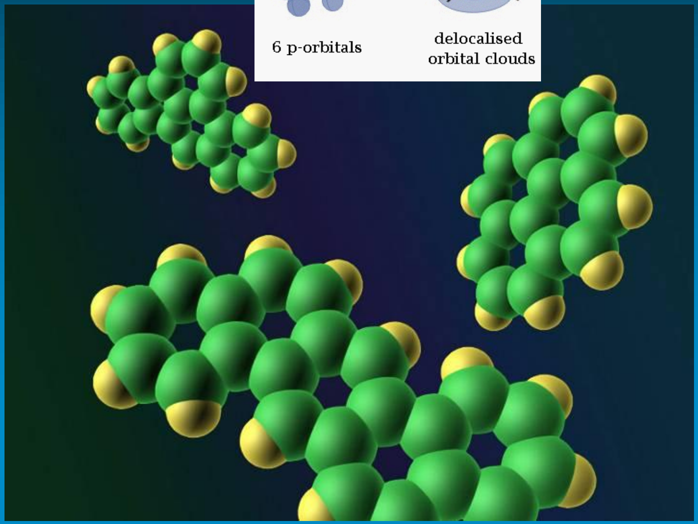
the light interaction behavior of
polycyclic aromatic molecules

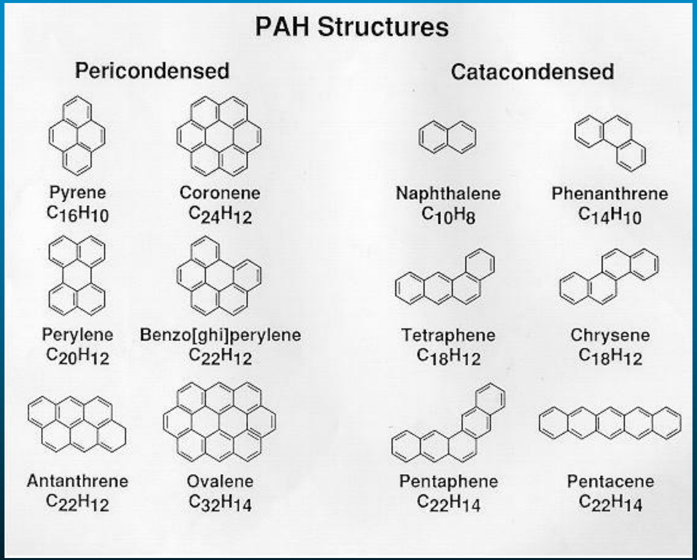
and the non-aqueous phase liquids
(NAPL) in which they dwell

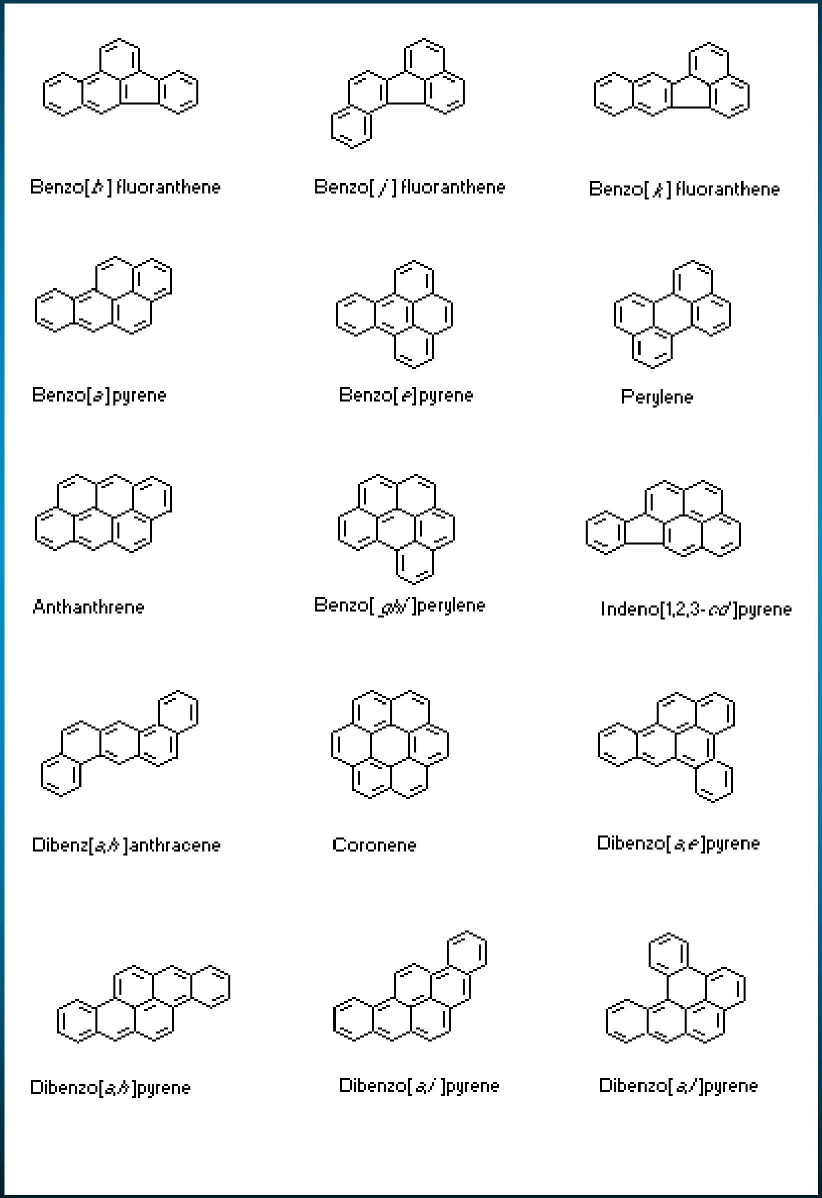
structure of aromatics allows the "magic"

one or more planar sets of six carbon atoms that are connected by delocalized electrons









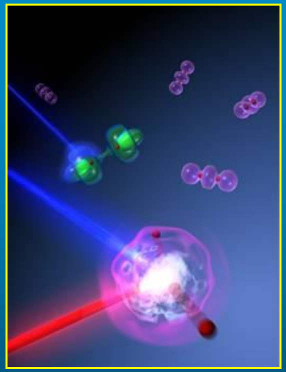
fluorescence spectroscopy

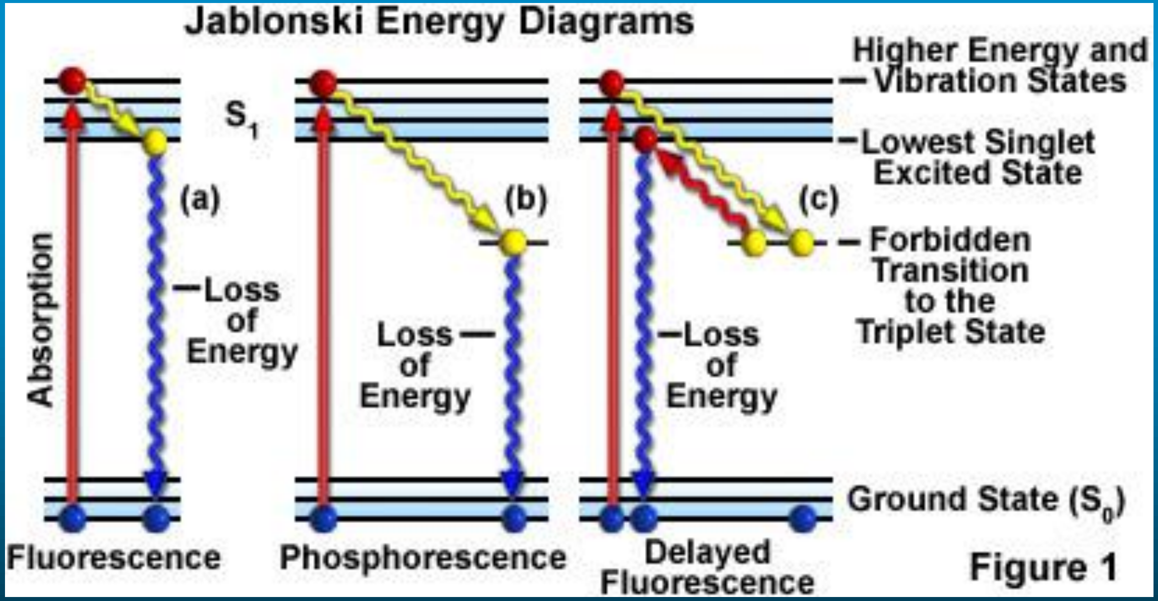
spectroscopy – study the interaction of light with matter

fancy quantum mechanics "stuff" determines behavior
molecules absorb light – might shed that energy by emitting light

aromatic (ring-shaped) molecules excel at this

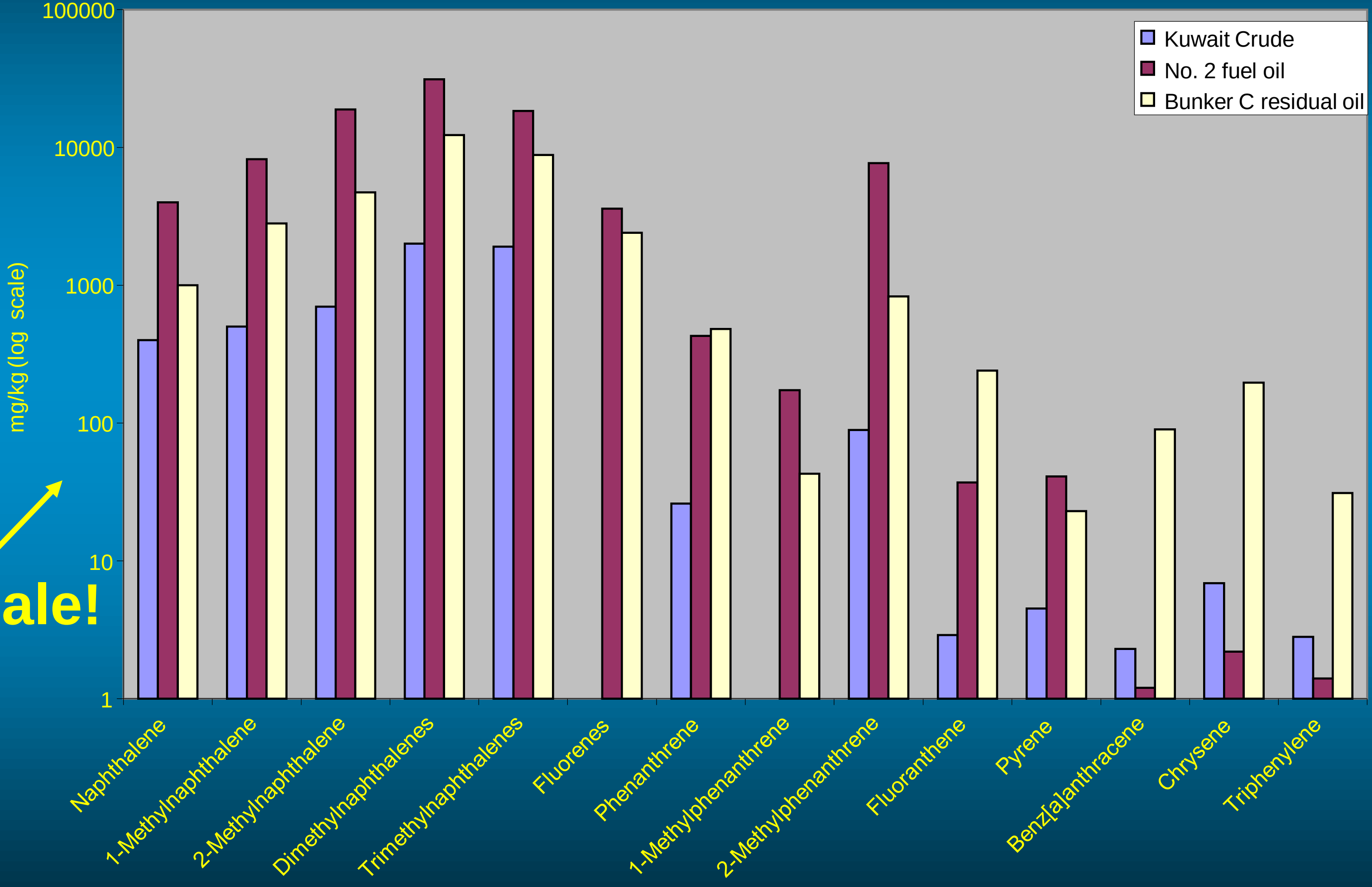
energy (wavelength/frequency/wavenumber) of each photon emitted depends on which energy level it was at prior to "launch" of a photon





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

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

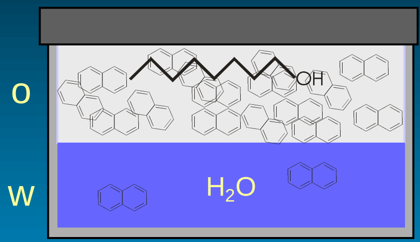


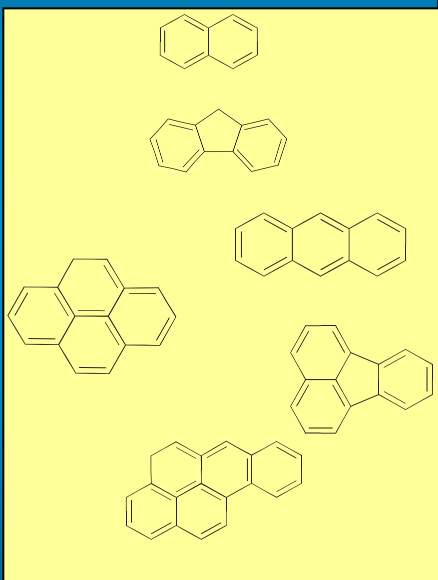
log scale!

PAHs prefer NAPL to groundwater

size and degree of substitution determine organic preference

this is why NAPL is the “source term” of dissolved phase and a dermal hazard



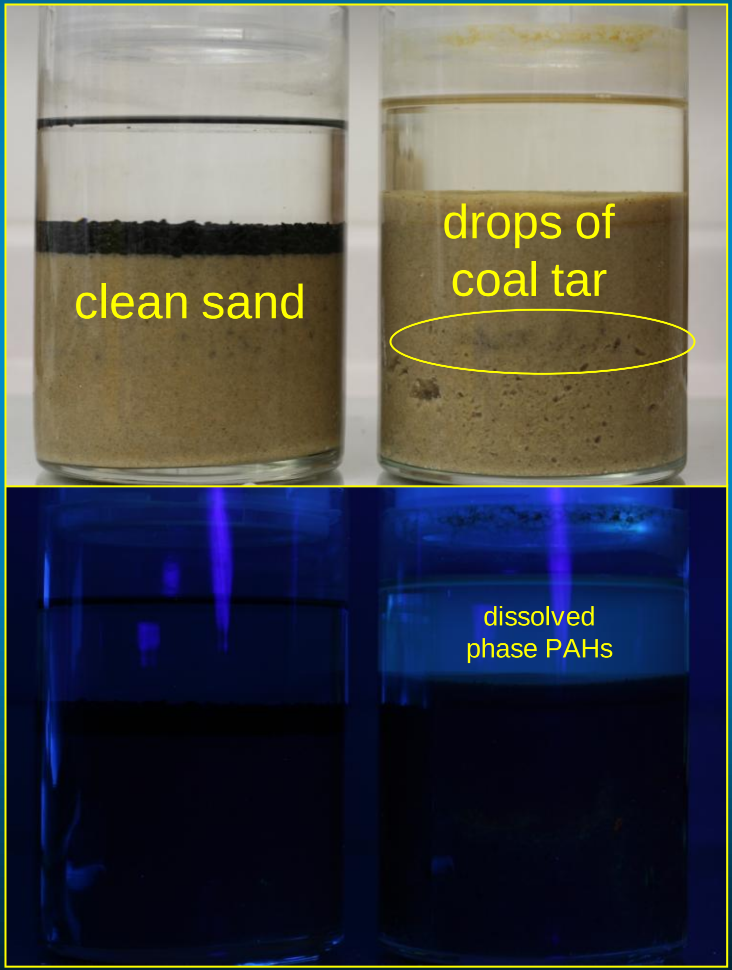


Compound (C.A.S.N°)		Molecular weight	Kow 125 to 1250	log Kow	Water solubility at 25°C (mg/L) B = 1780 T = 535 E = 161 X = 150
naphthalene (91-20-3)	1	128.16	3,162	3.5	31.7
acenaphthene (83-32-9)	1	154.21	19,952	4.33	3.42
fluorene (86-73-7)	1	166	15,136	4.18	1.98
phenanthrene (85-01-8)	1	178.24	31,623	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

octanol – a straight chain fatty alcohol with eight carbon atoms

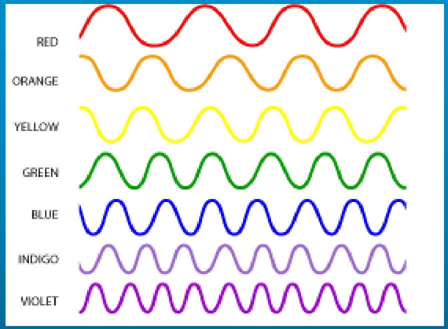
PAH's great preference for organic solvent affects its chemistry and behavior

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

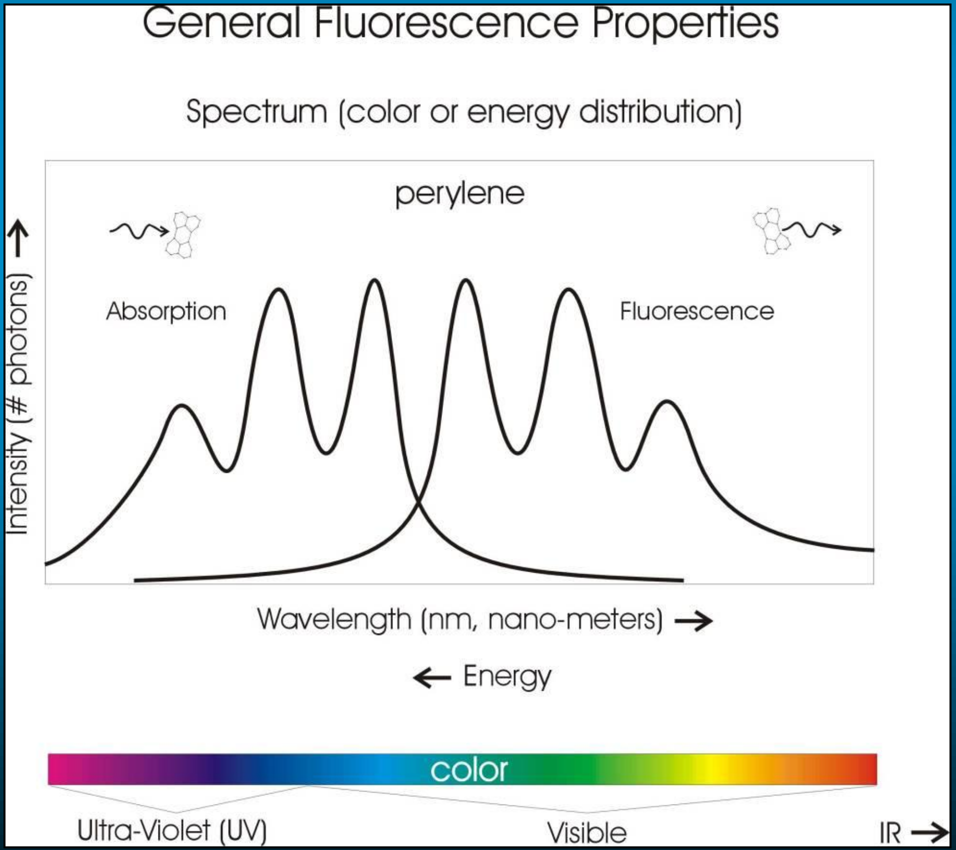


poly-cyclic aromatic hydrocarbons (PAHs) found in all petroleum, oils, lubricants are responsible for their innate fluorescence

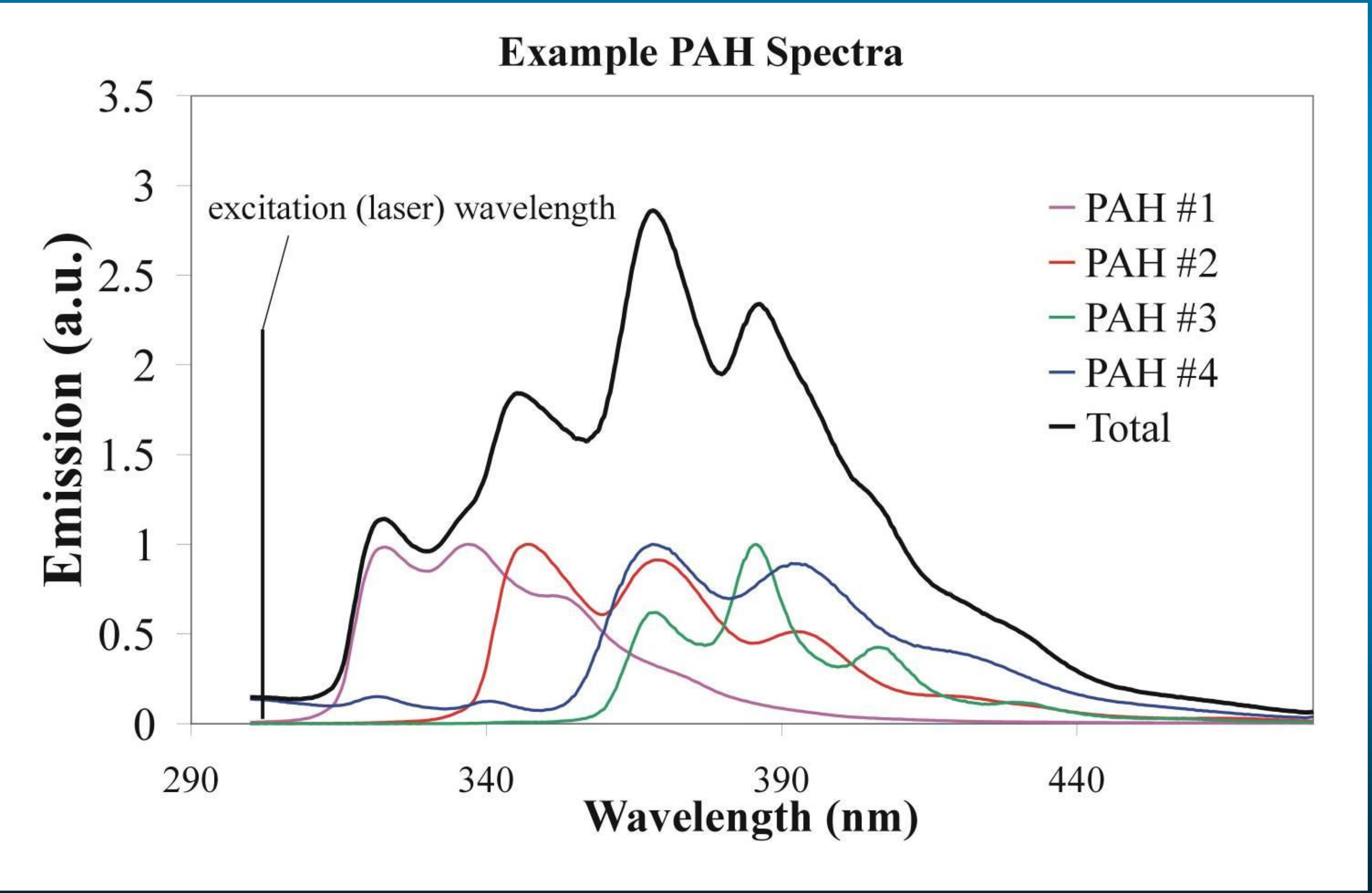
emission spectrum is unique for a pure PAH – spectrum does not change with excitation wavelength because the PAH has no memory of how it got excited, it just fluoresces



ROYGBIV



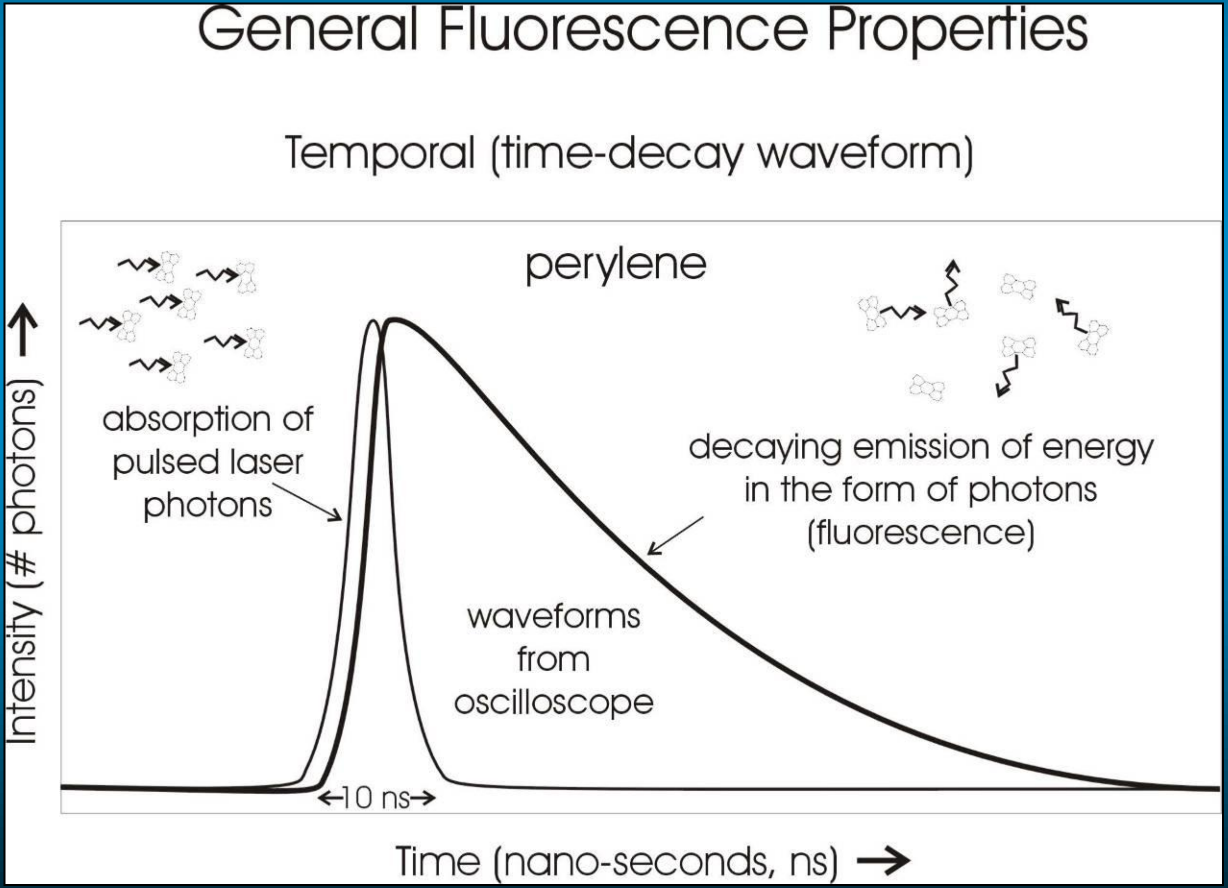
fuels contain 100s of PAHs
their spectra overlap so you lose ability to identify any one PAH
fluorescence spectra can indicate ‘classes’ of fuels though



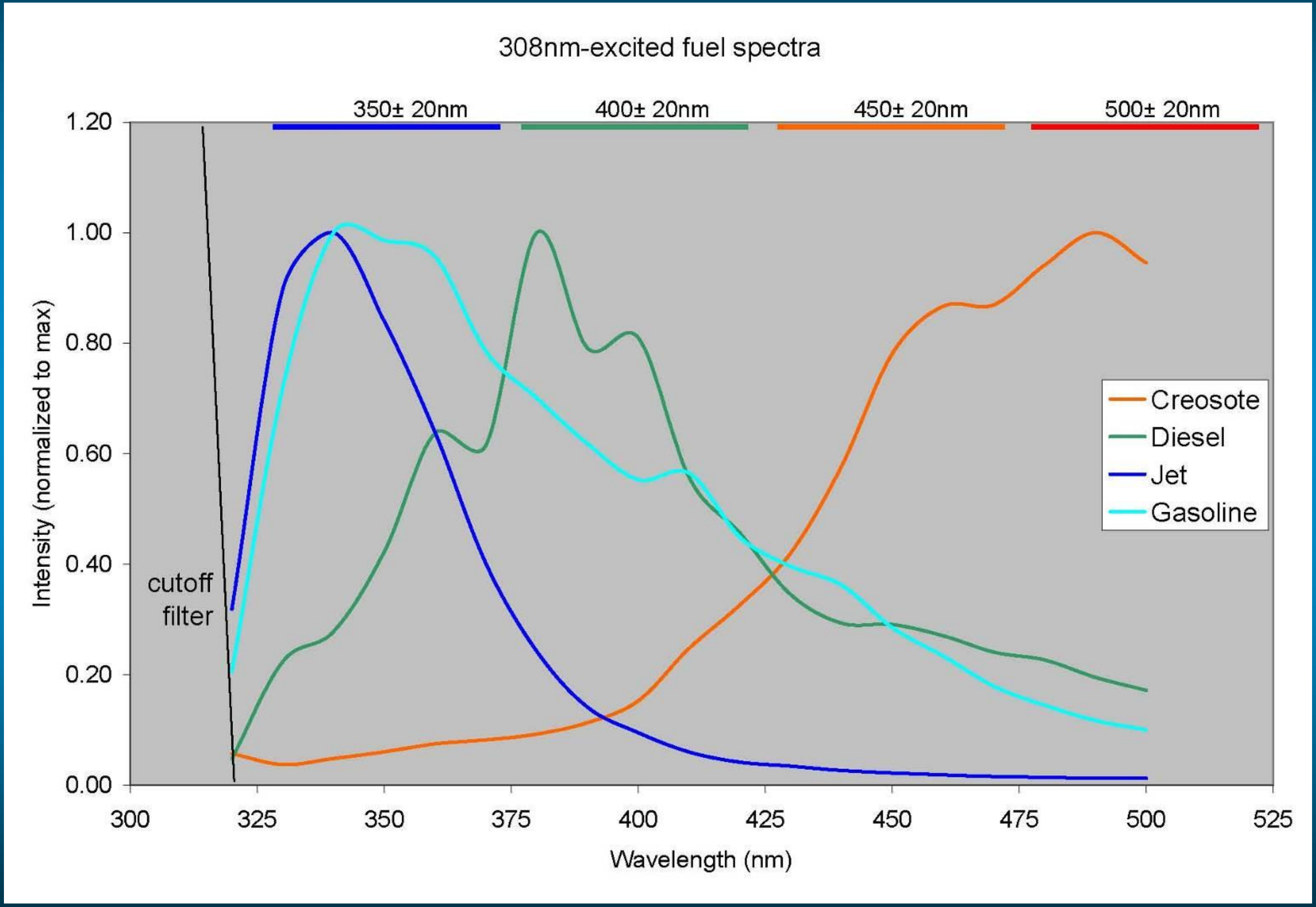
lifetime or fluorescence decay

fluorescence dies away with time after being pulsed

certain wavelengths of light from various fuels have differing lifetimes
that help us differentiate the fuels from each other



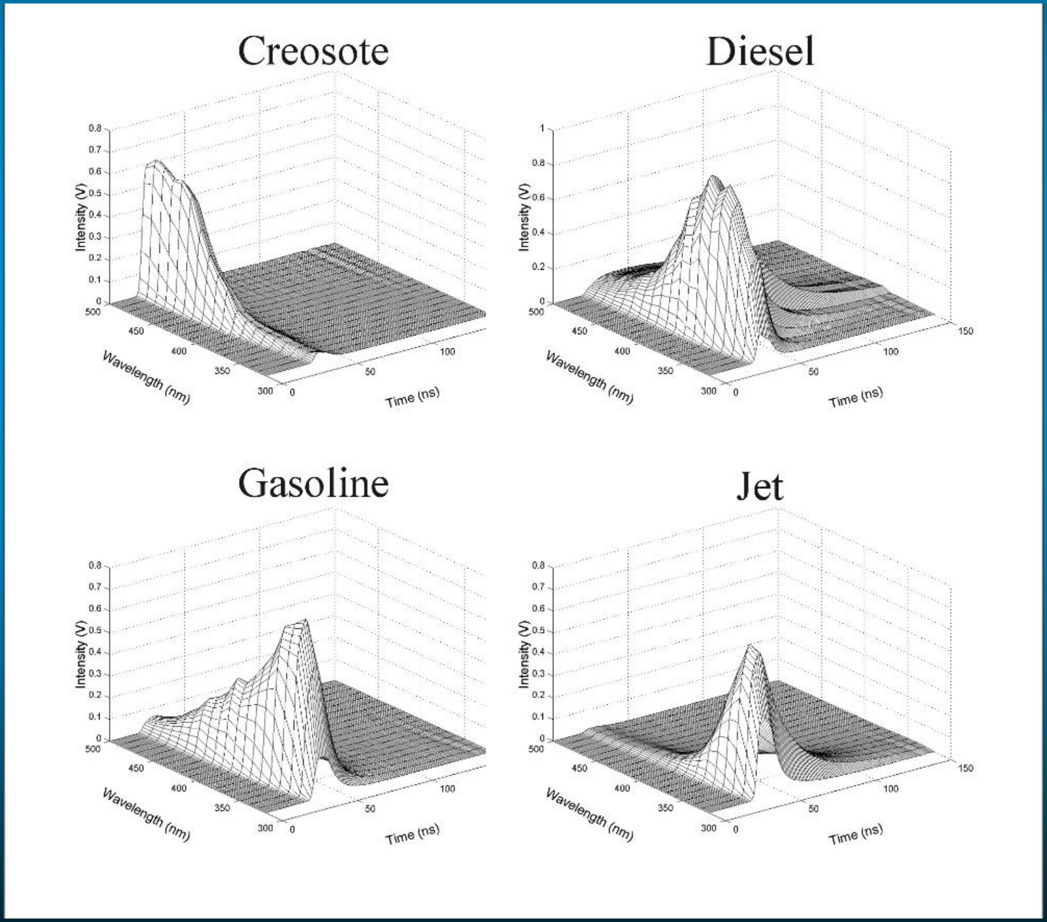
emission spectra for typical fuels
(note the spacing of the 4 UVOST LIF system filters)



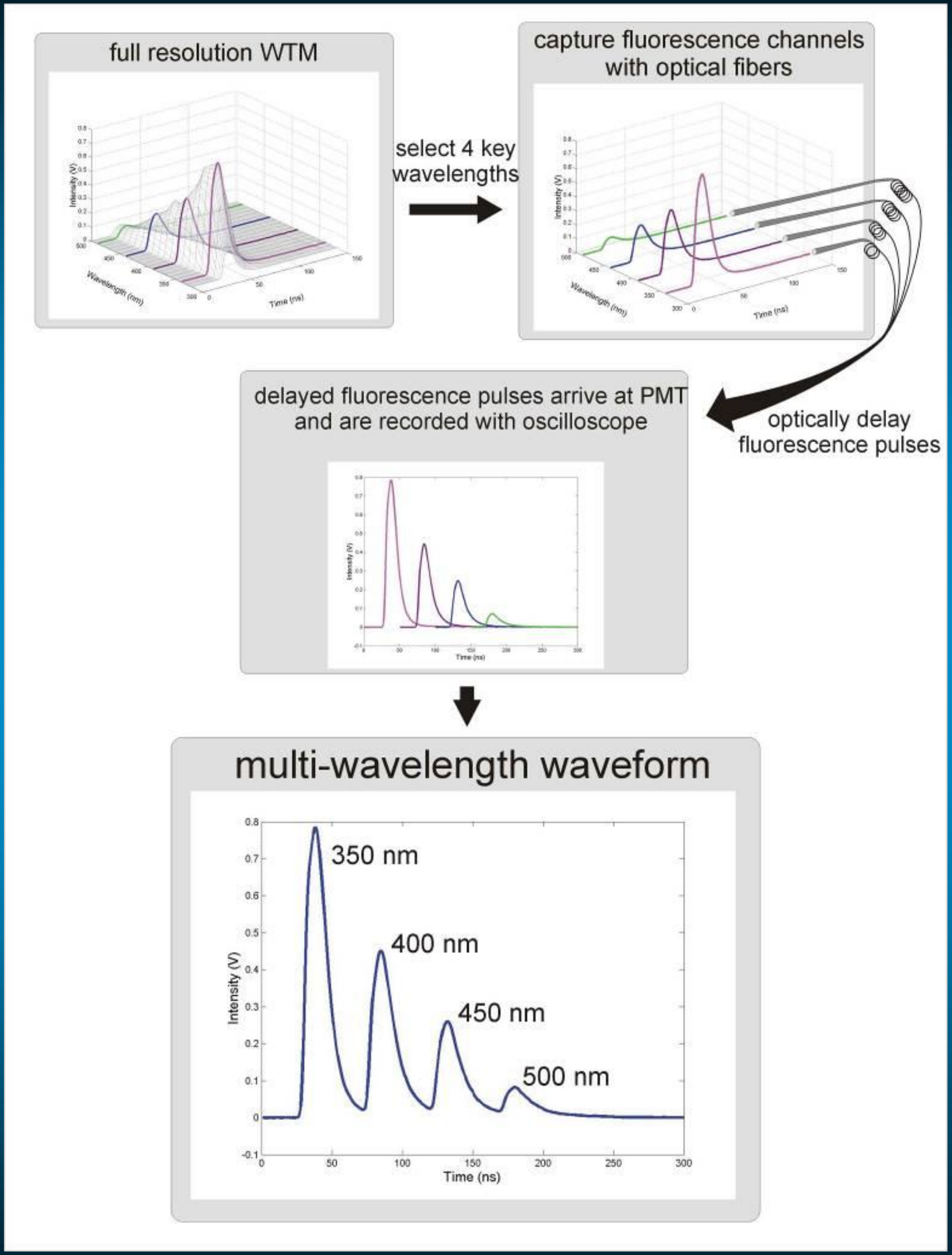
wavelength-time matrices of fuels

each mix of PAHs (and their aliphatic solvent, oxygen concentration, matrix, etc.) yield a fairly unique wavelength/time matrix called the WTM - fuels/oils have a unique and characteristic WTM

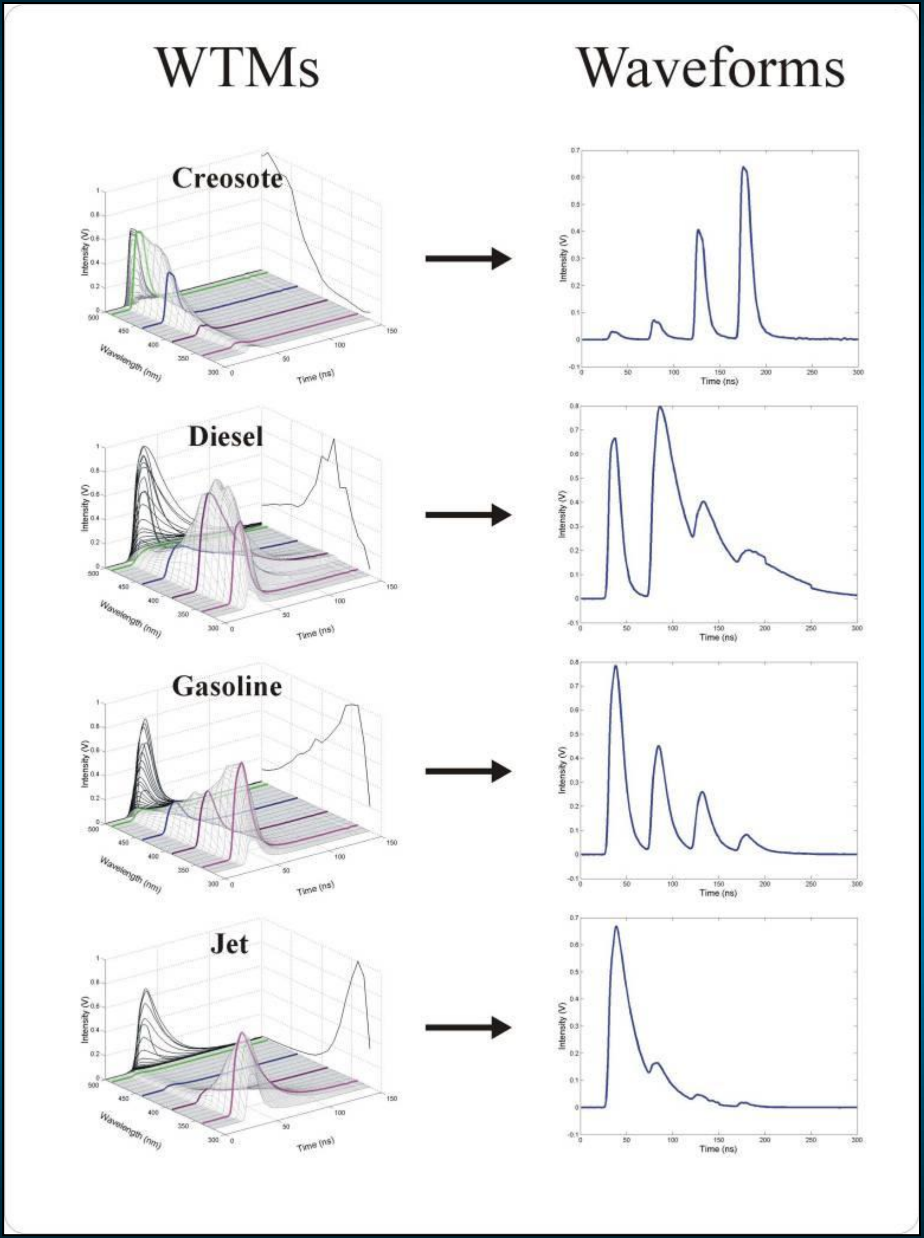
most fuel types look similar to each other under “normal” conditions – so identifying fuels/oils as this or that is usually straightforward… kerosenes (jets) look like other kerosenes, diesels like other diesels, etc.



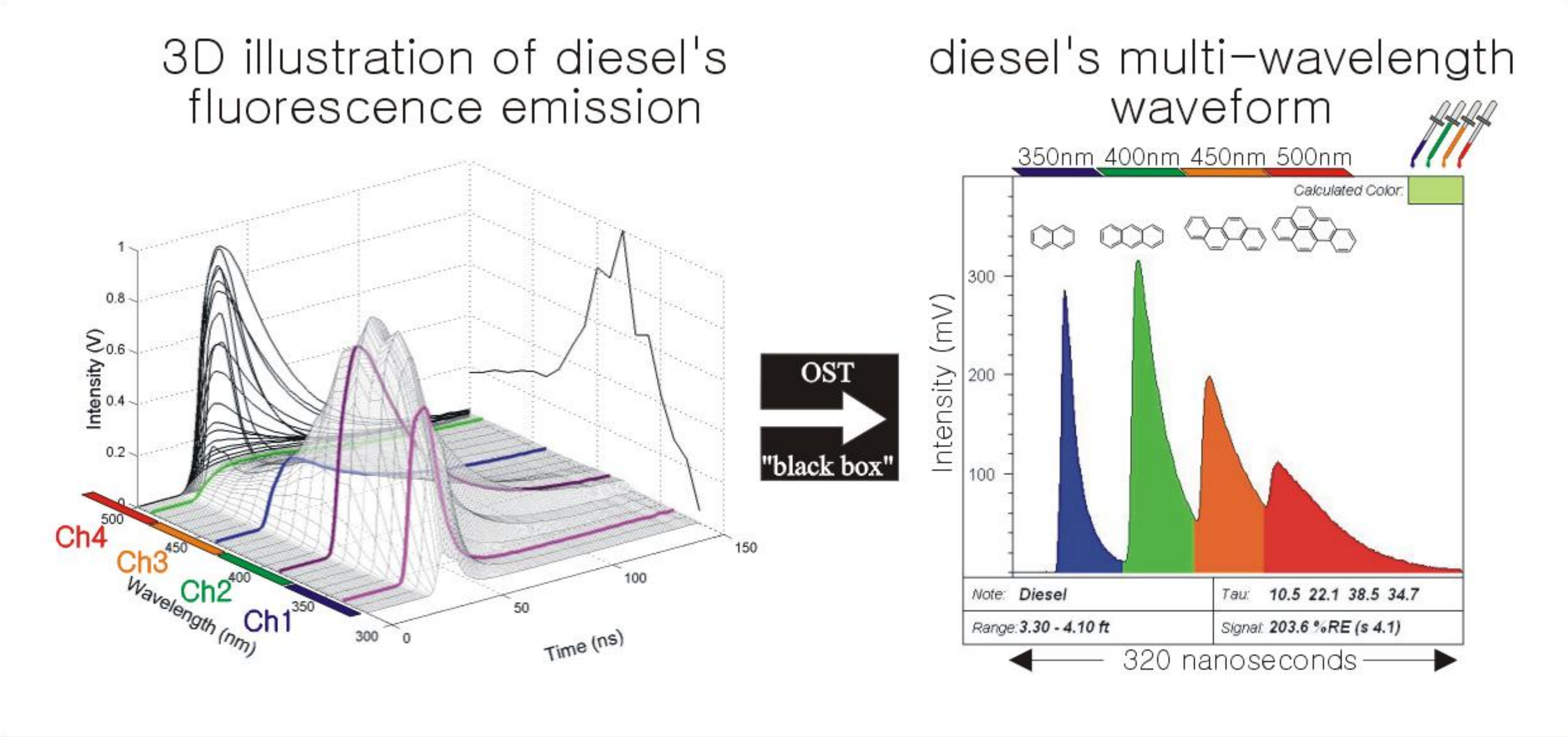
multi-wavelength waveforms of OST systems



multi-wavelength waveforms of common NAPLs



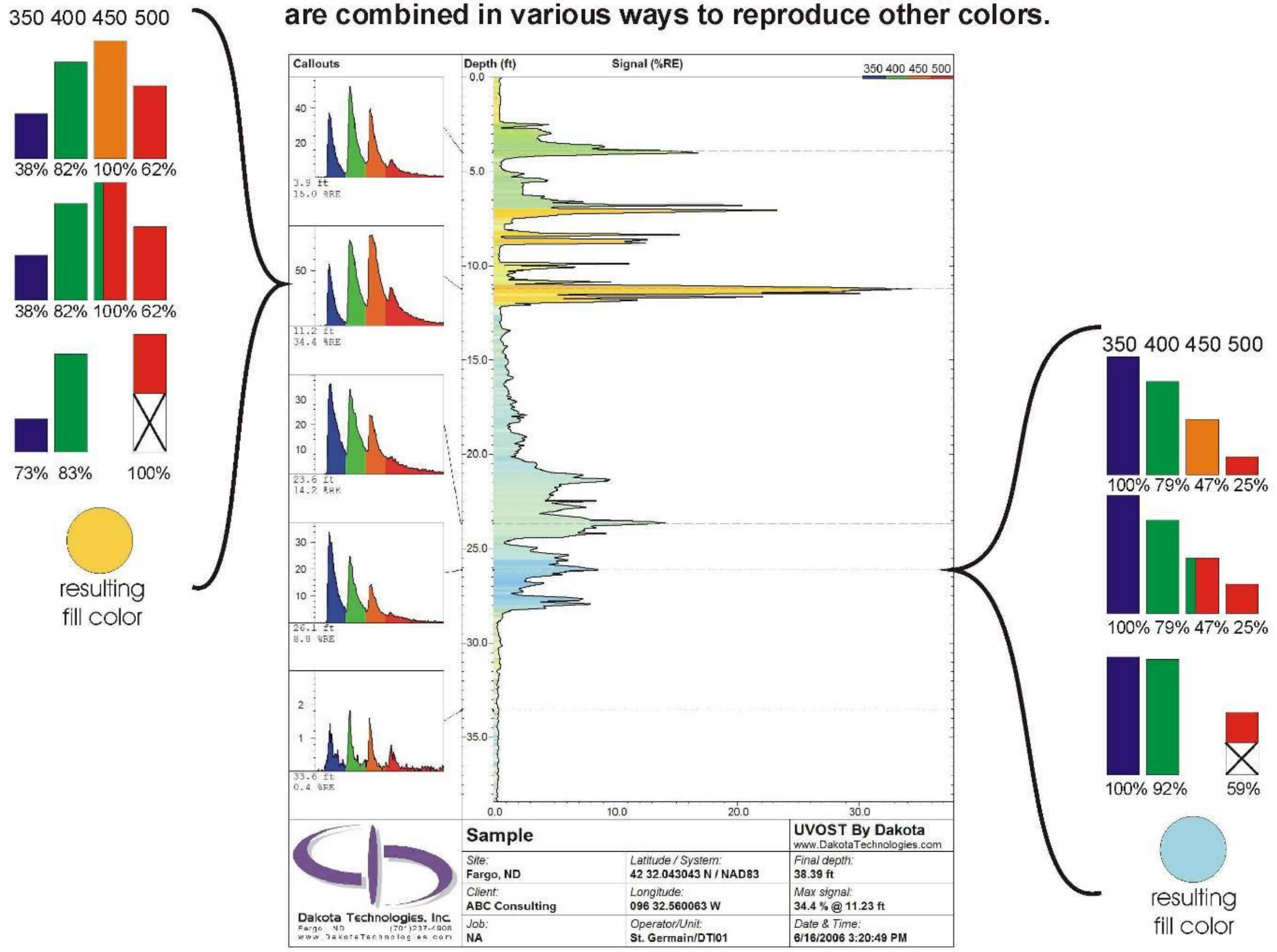
multi-wavelength waveforms
OSTs create “shorthand” version of WTM



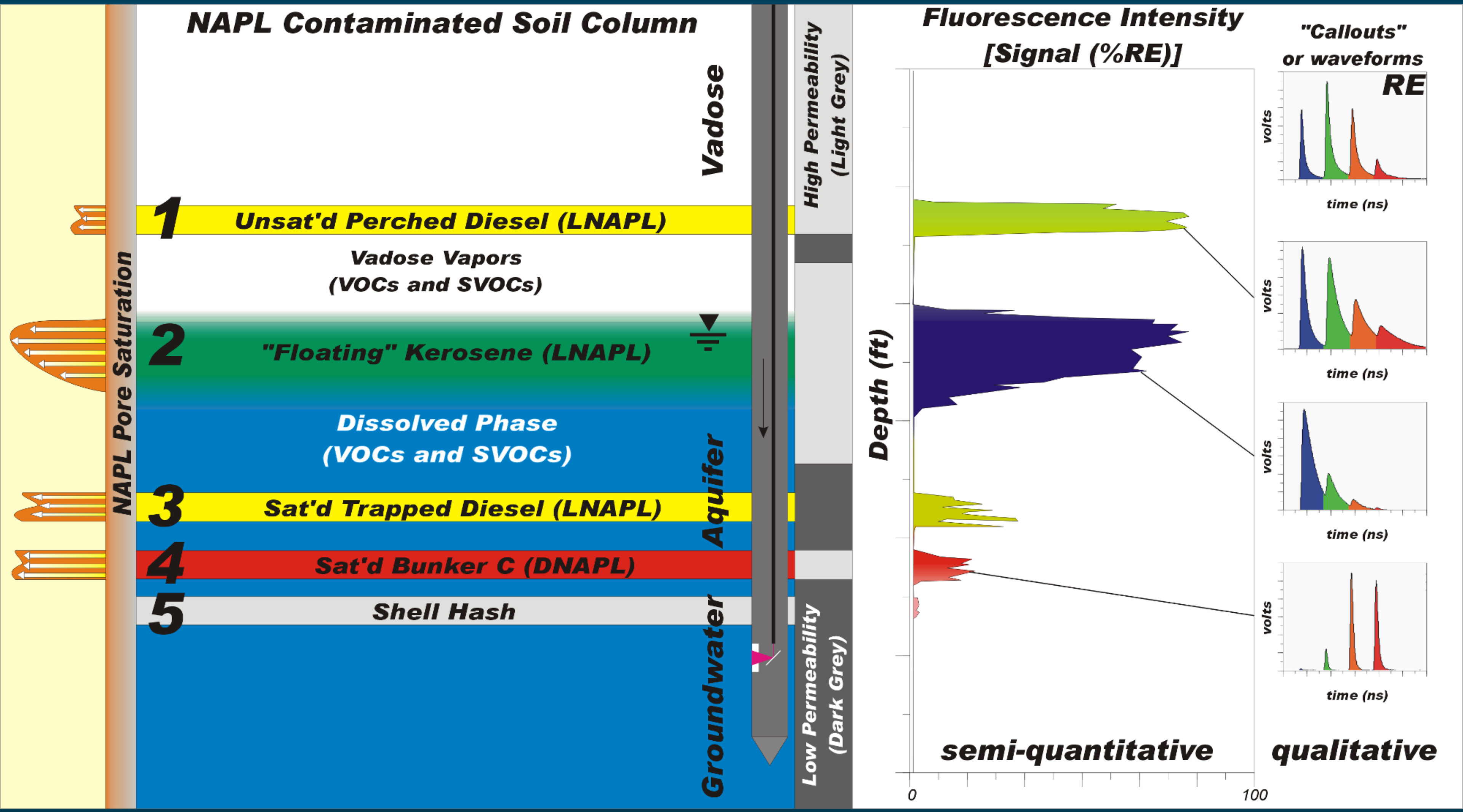
Colorization of UVOST/ROST Waveforms

Dakota's UVOST colorization scheme uses RGB calculations of the relative areas of the 350, 400, 450, and 500 nm channels to generate RGB fill color.

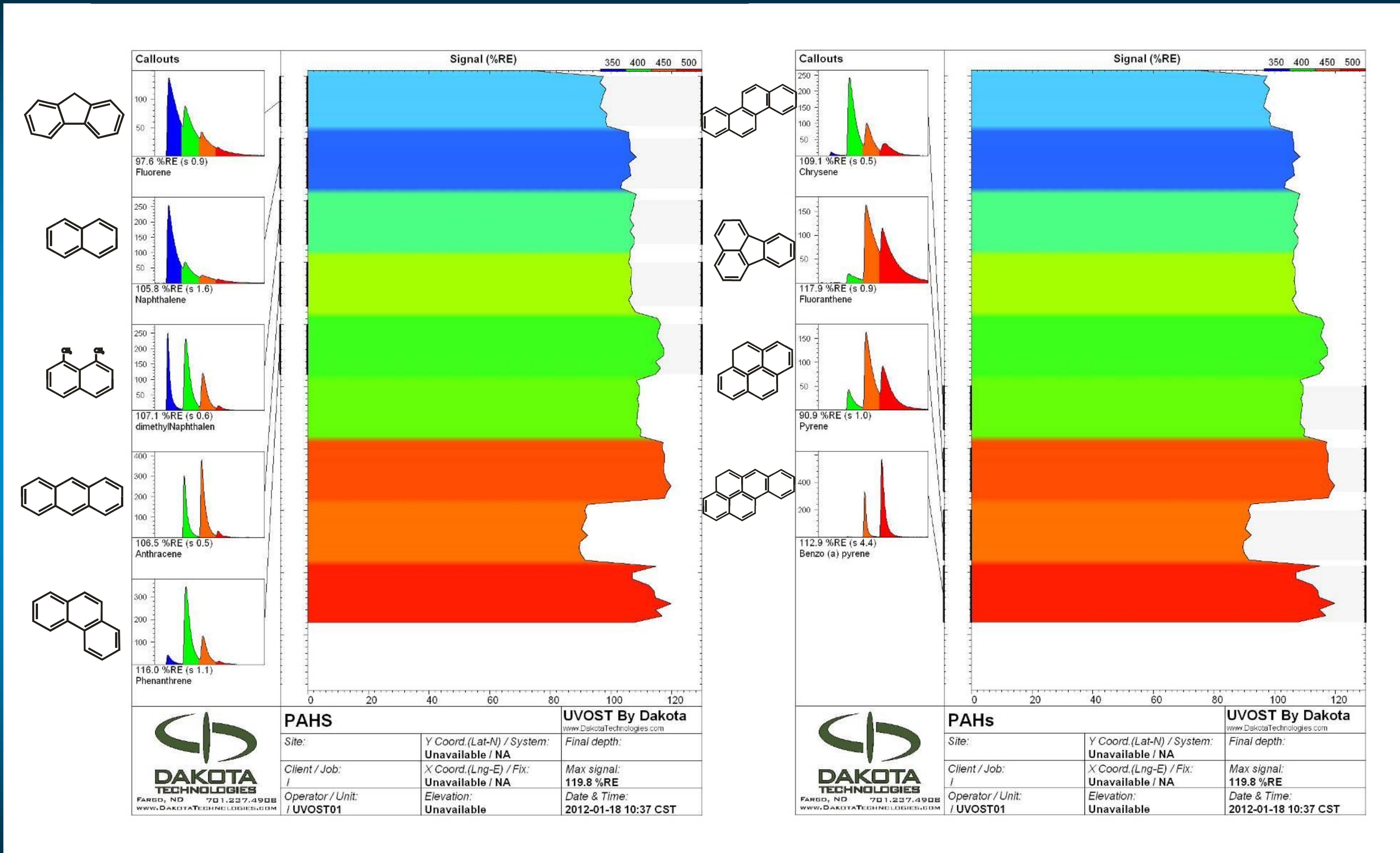
The RGB color model is an additive model in which red, green, and blue are combined in various ways to reproduce other colors.



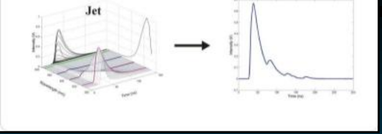
UVOST/ROST Logs vs NAPL/Location

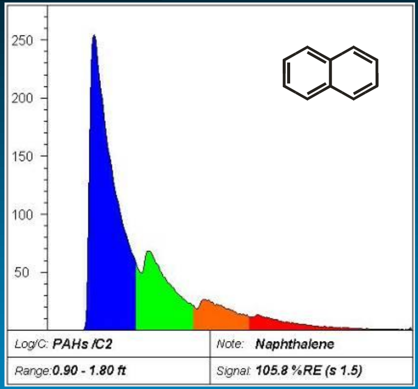


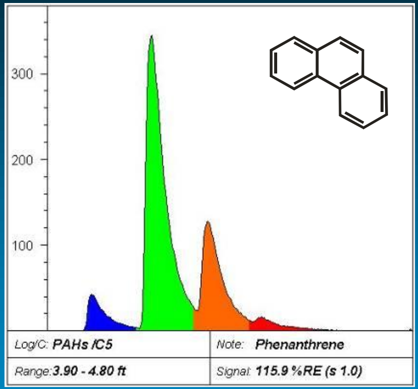
Pure PAHs on UVOST

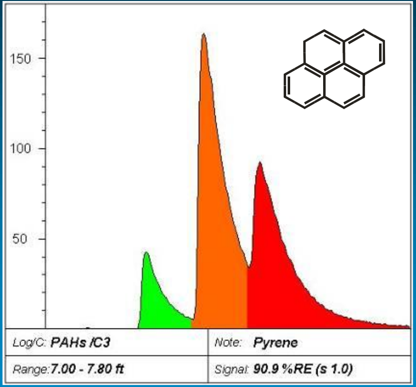


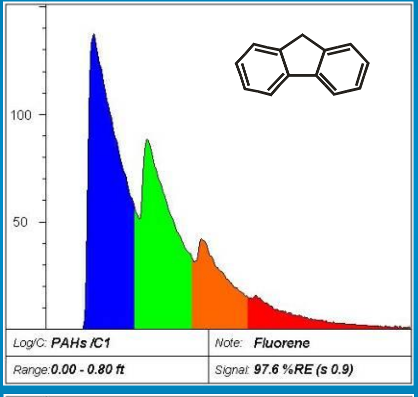
PAHs on UVOST

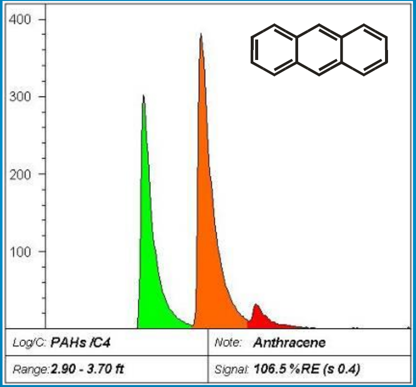


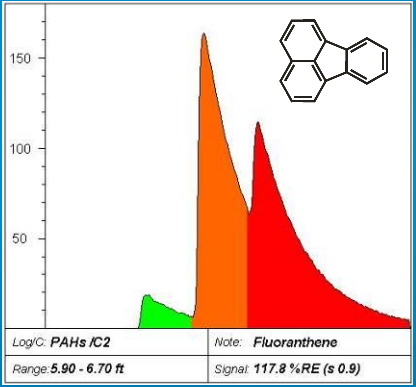


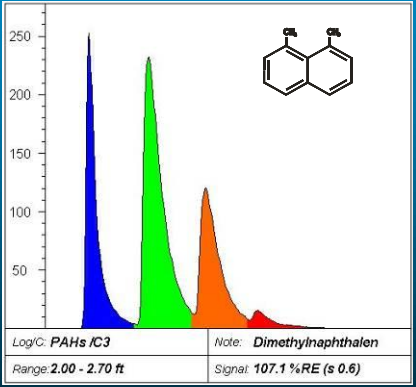


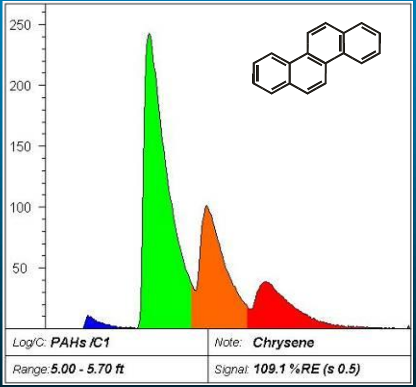


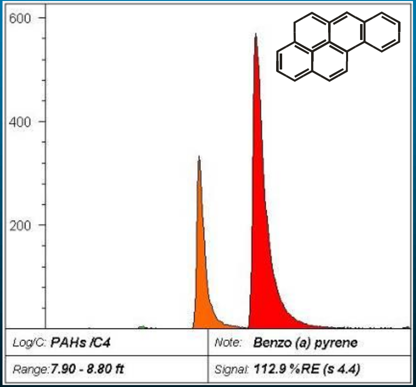






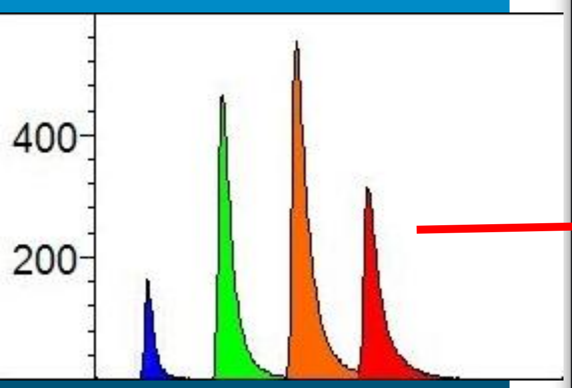


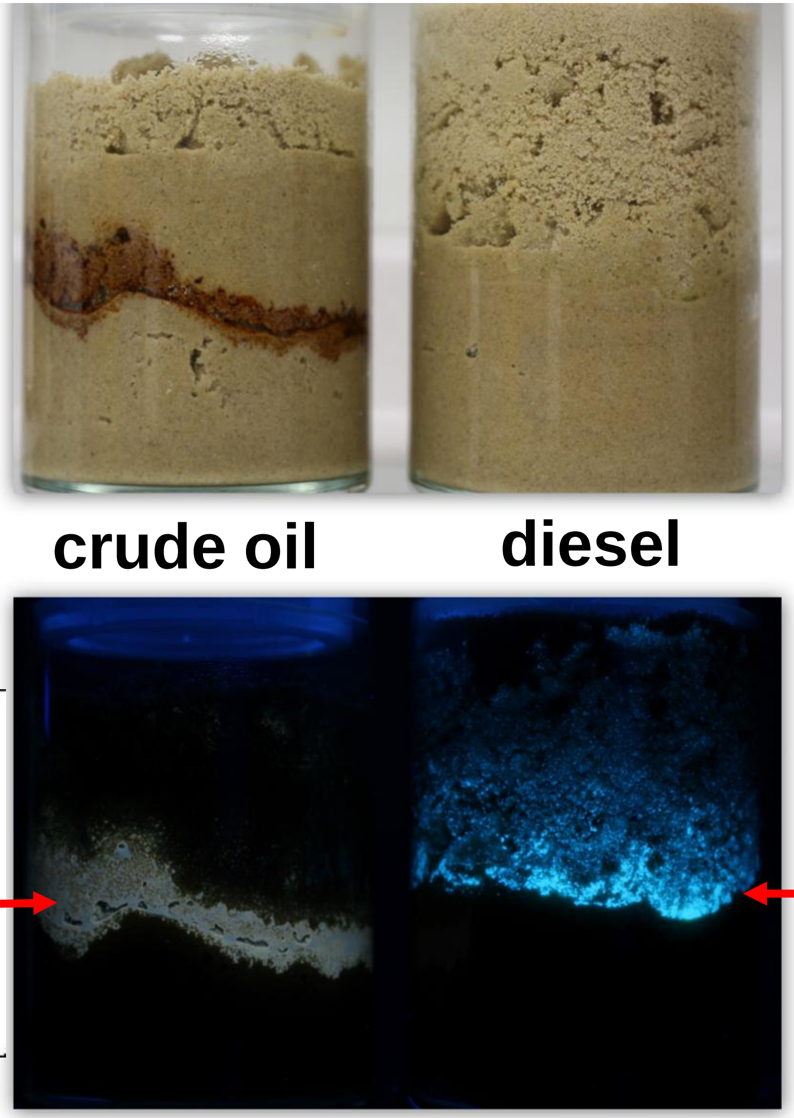




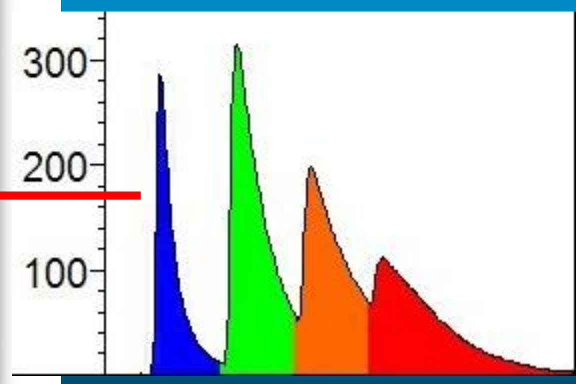
so…. this slide maybe makes better sense now?

what LIF “sees”





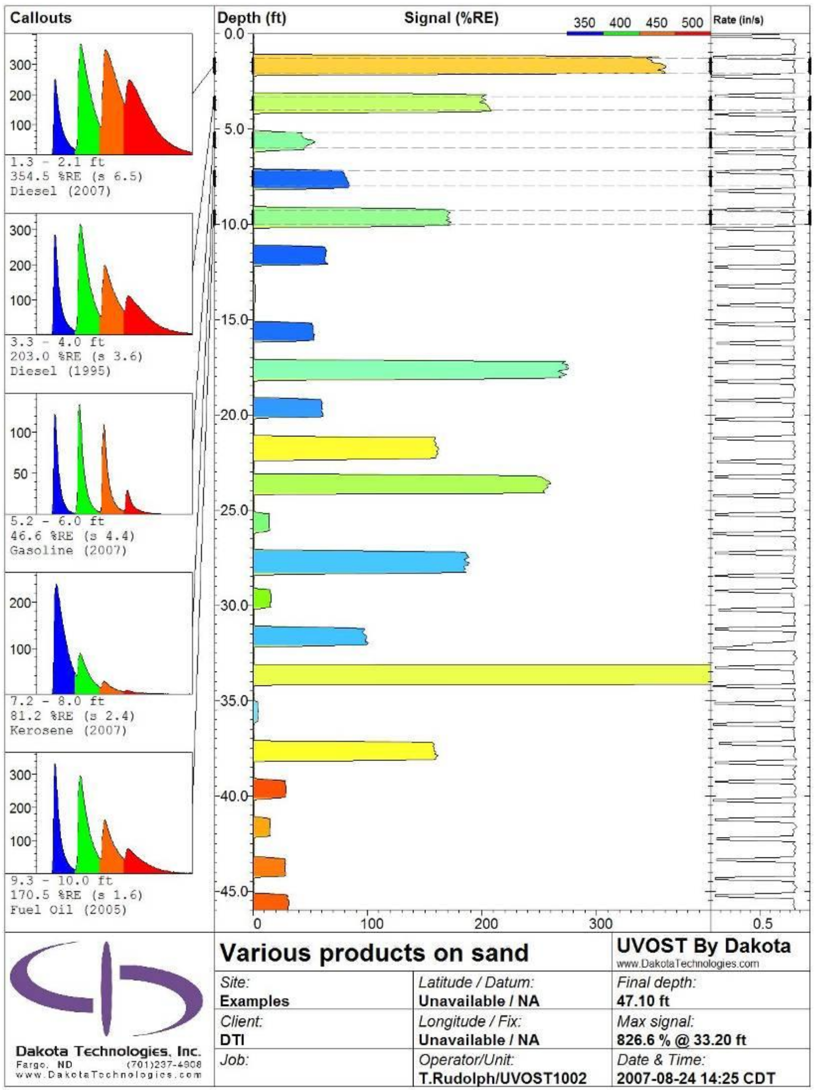
what LIF “sees”

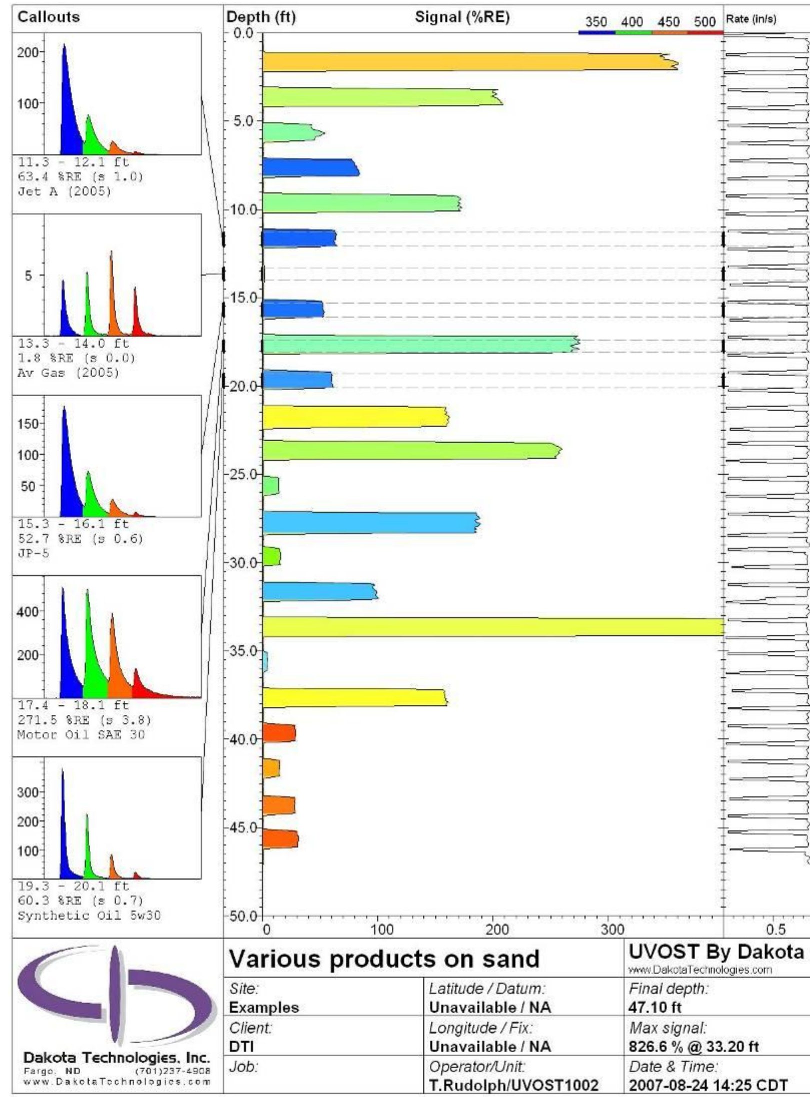


Qualitative nature of fuel and oil fluorescence (PAH mixtures)

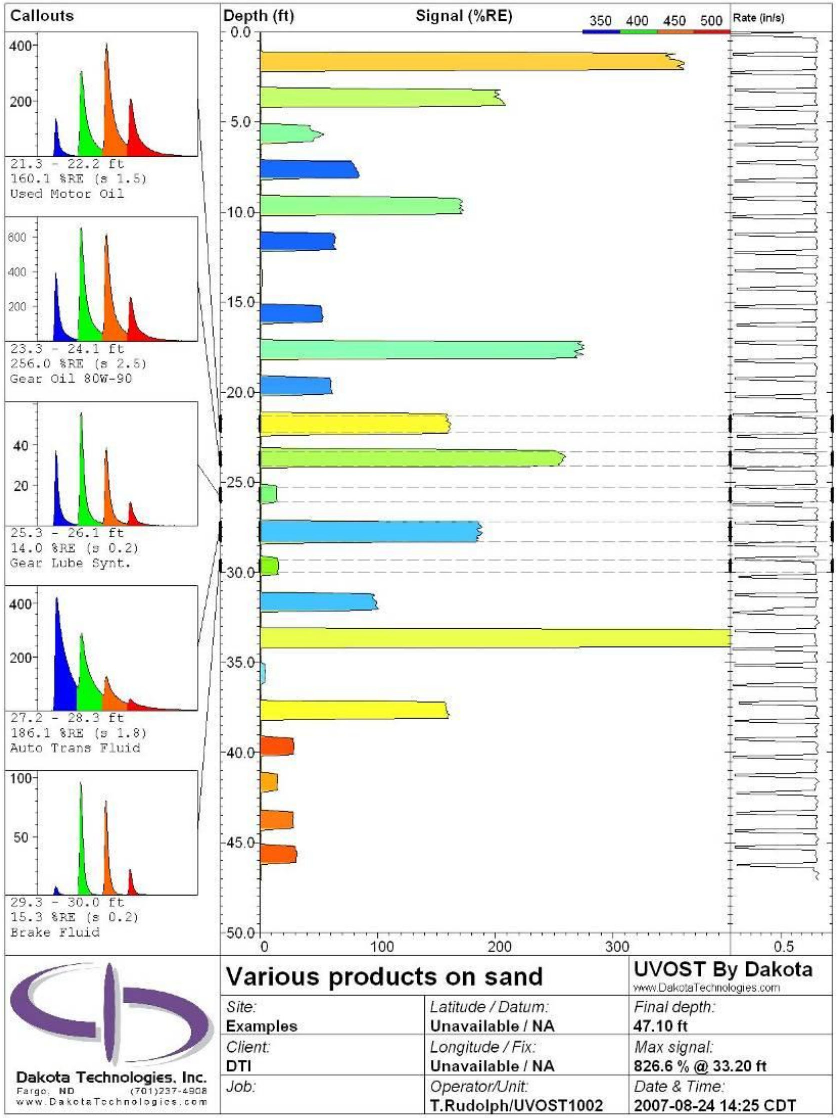
UVOST waveforms of various NAPLs

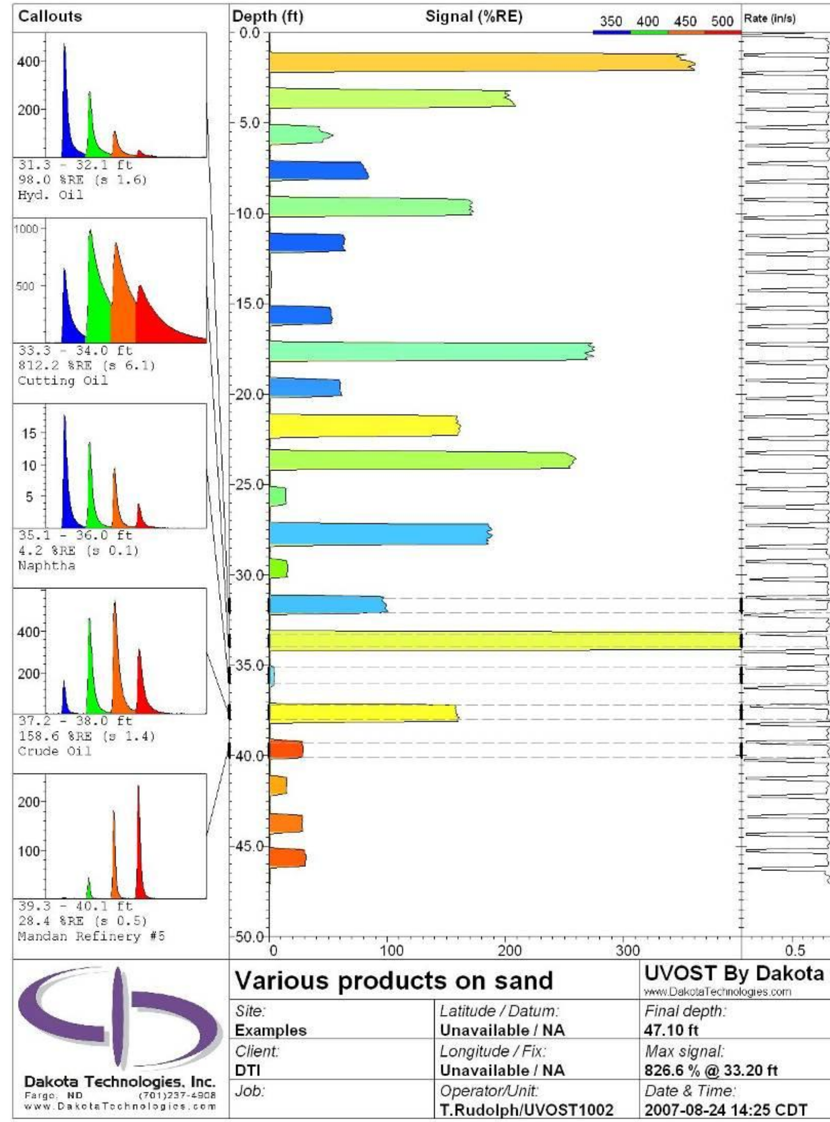
wet Fisher sea sand saturated with various NAPLs



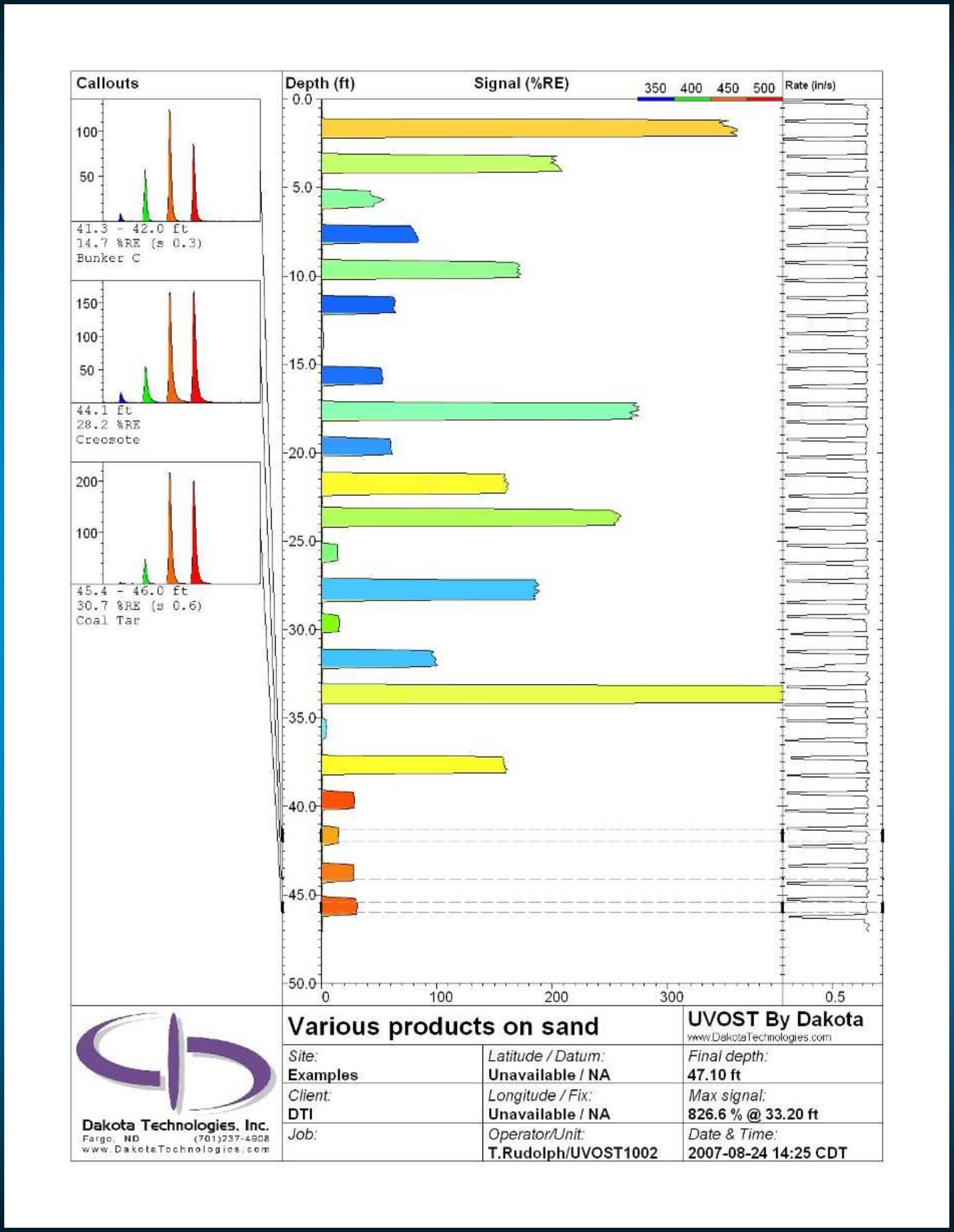


UVOST waveforms of various NAPLs





UVOST waveforms of various NAPLs



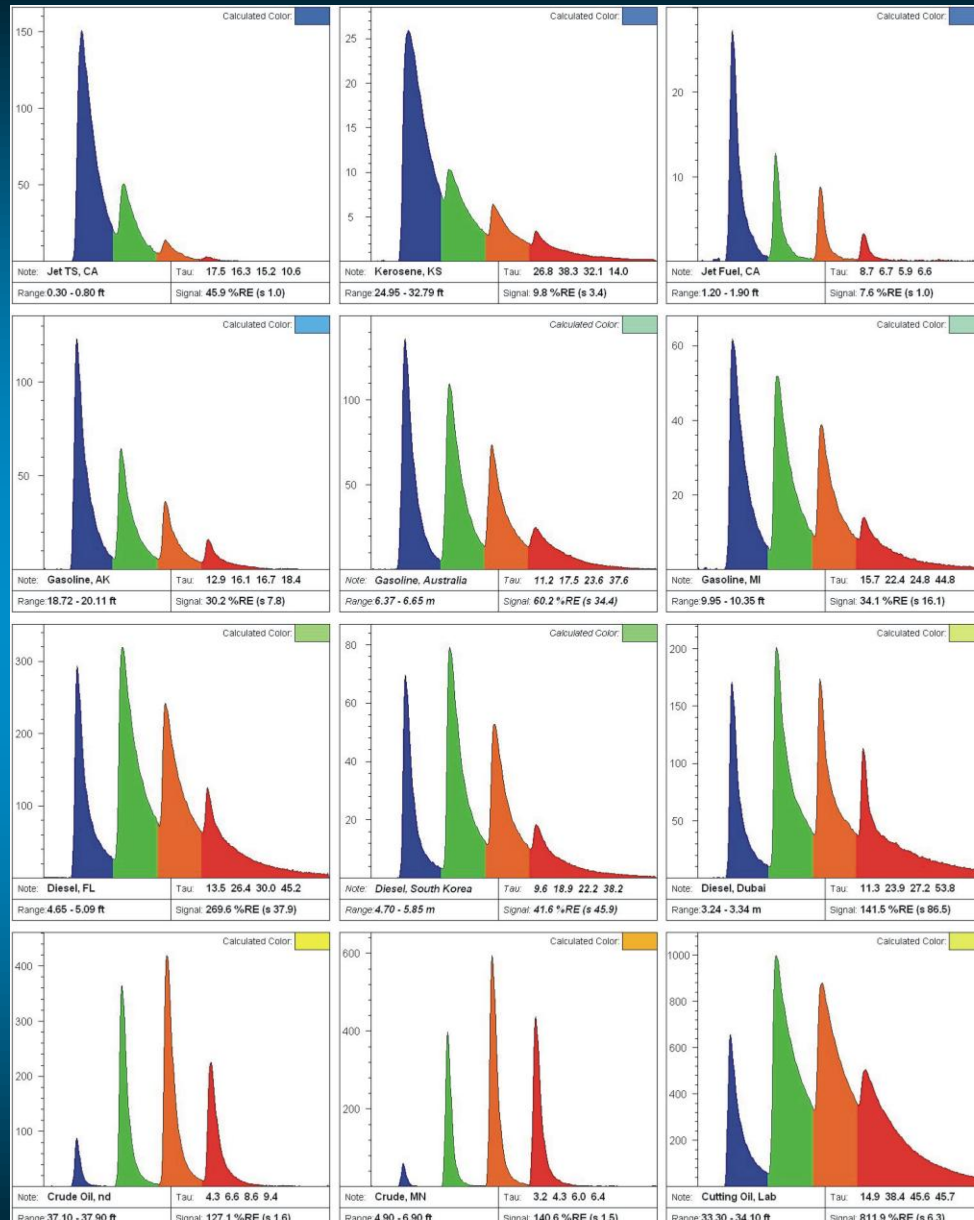
UVOST waveforms of various NAPLs

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

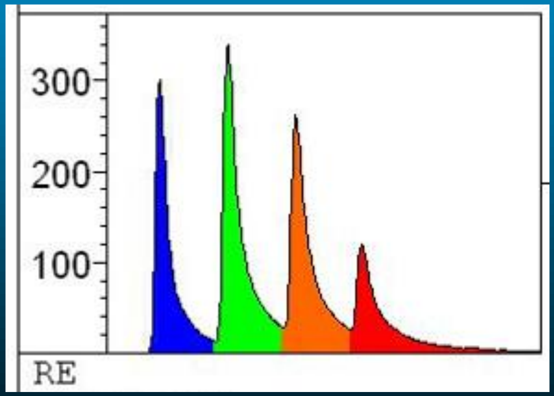
Dakota has used same "reference emitter" (RE) material since 1994

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

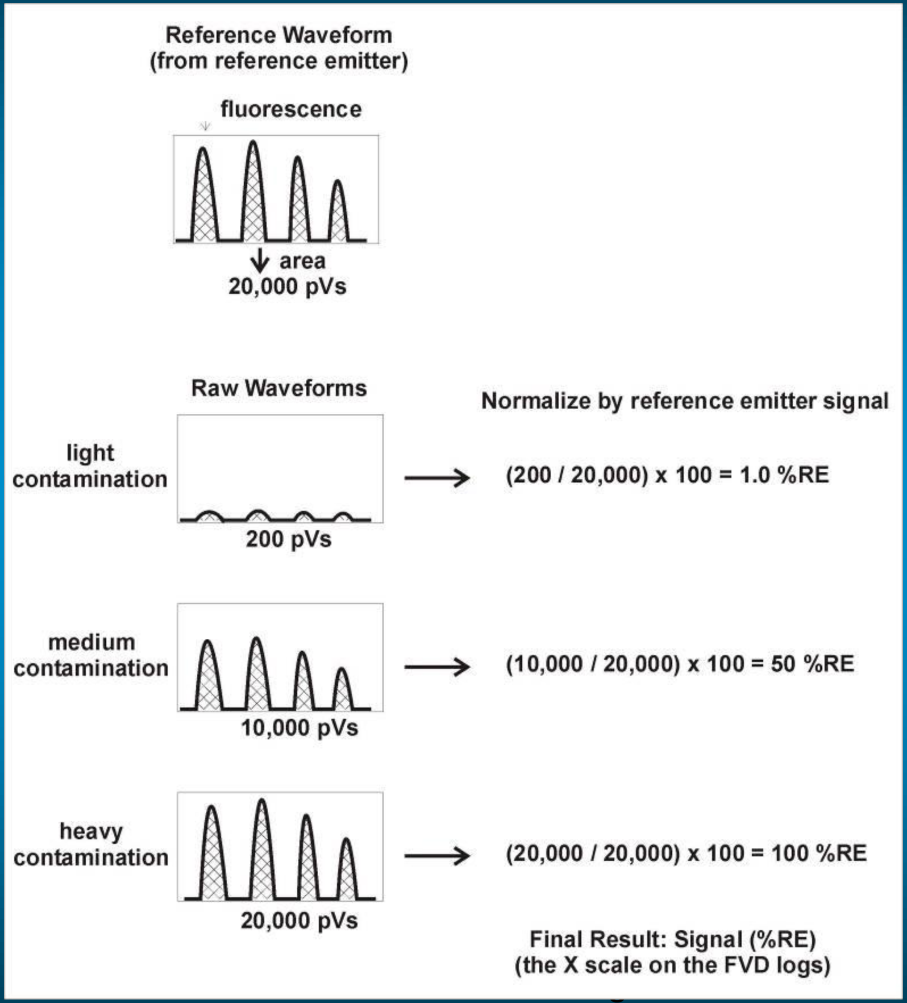
the correct shape of waveform also allows checking the qualitative aspect of the fluorescence



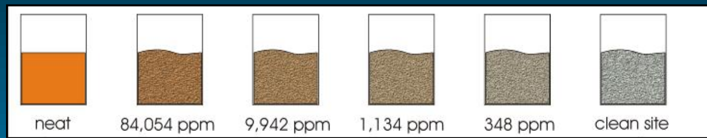
UVOST's Reference Emitter or RE

(RE does NOT stand for REflectivity!)

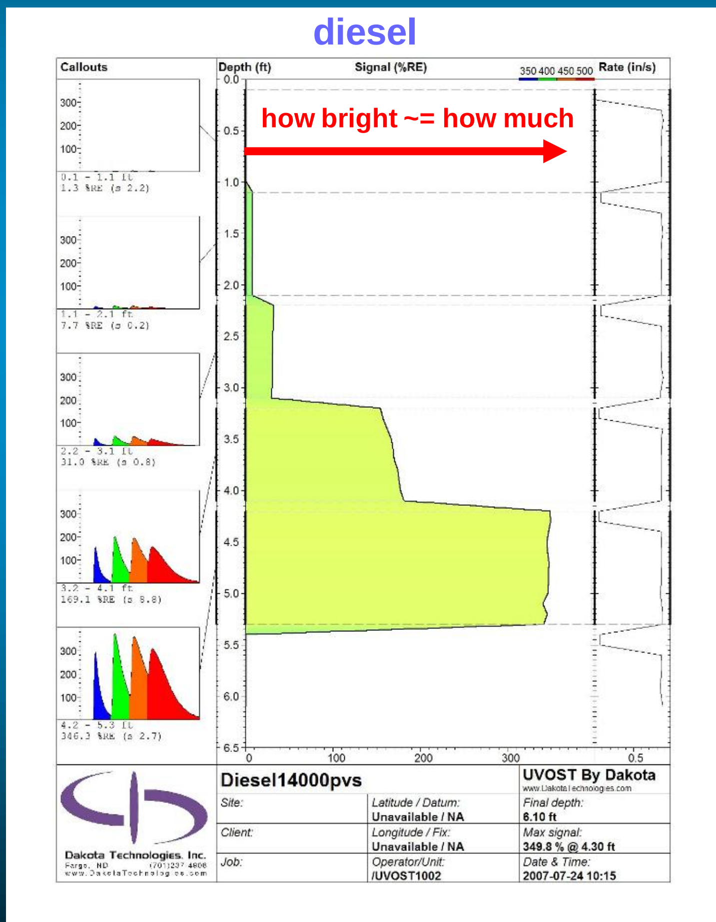
- think of RE just as you would of the 100 ppm isobutylene used to calibrate a PID
- the RE normalizes the response for laser energy changes, fiber optic cable length, detector aging, etc.
- the same RE solution is used by all UVOST and ROST providers
- Dakota has a large stockpile of the material which 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



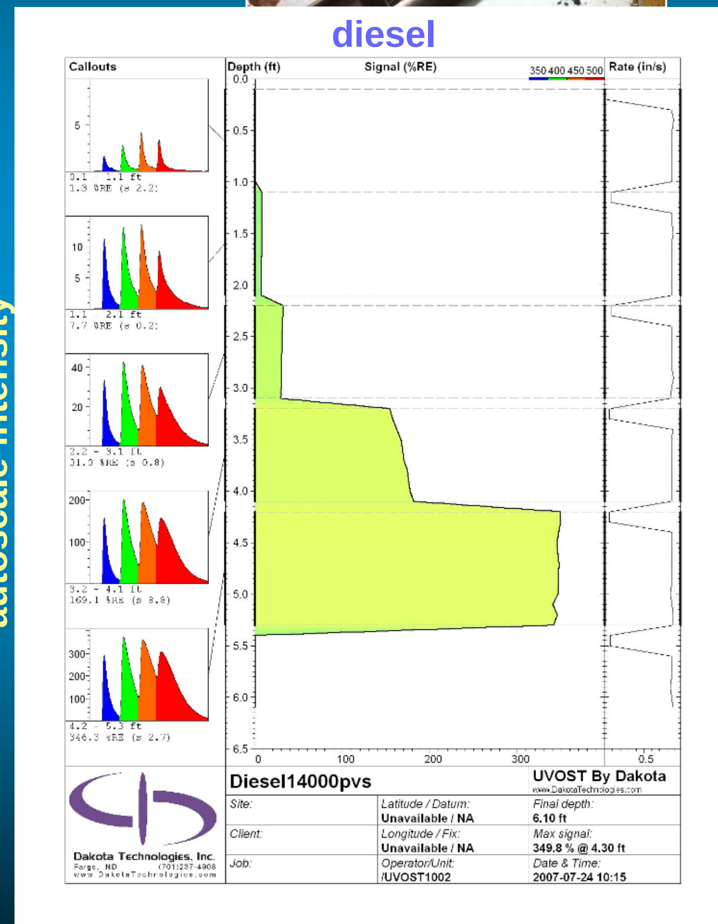
lab studies: mix fuels with soils to demonstrate how LIF yields 'semi-quantitative' data



fixed scale intensity

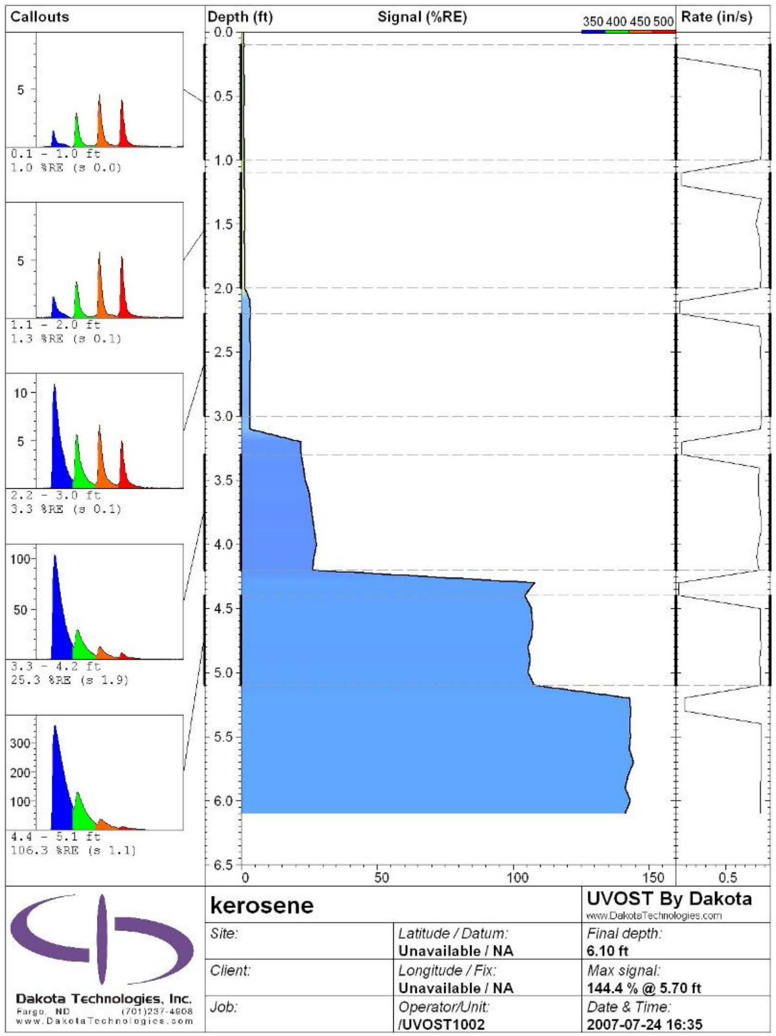


autoscale intensity

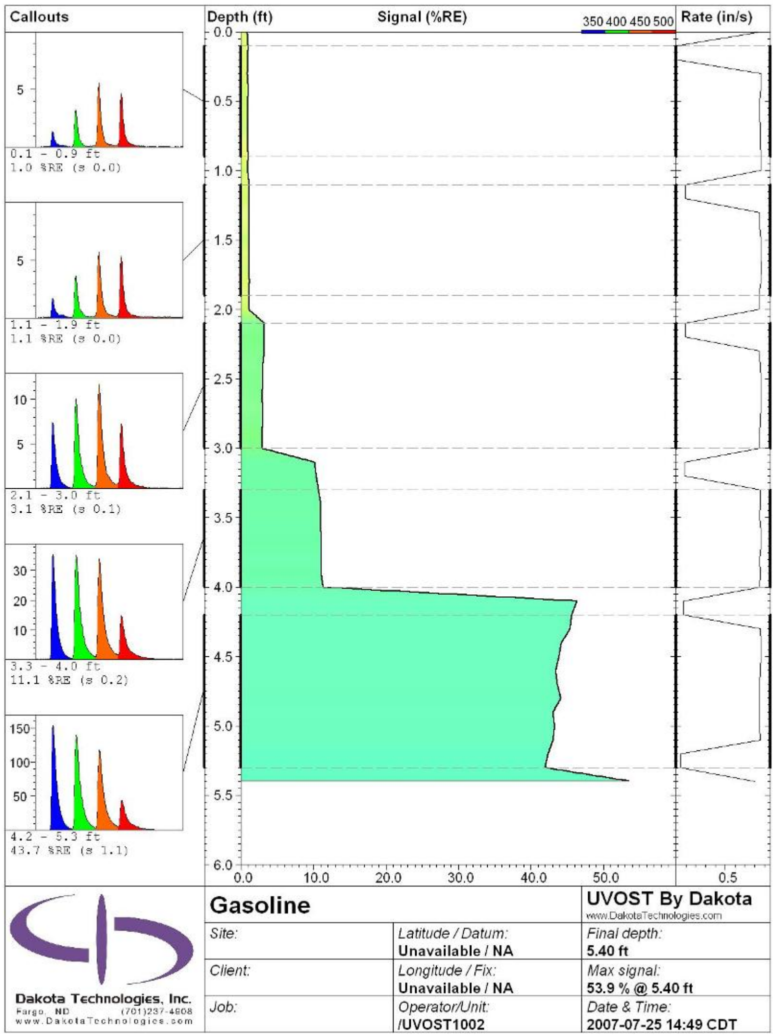


LIF contains both quantitative (how much) and qualitative (what kind) of data

kerosene (jet fuel)

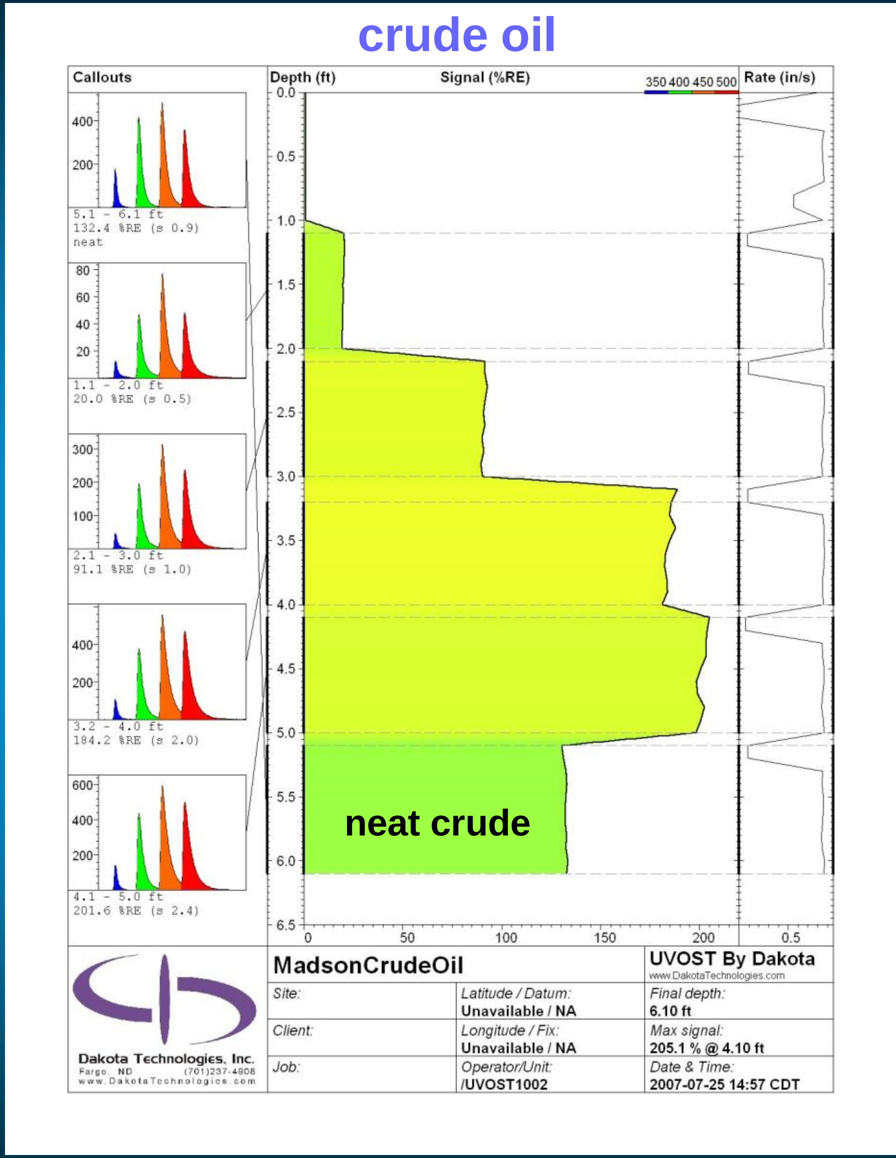


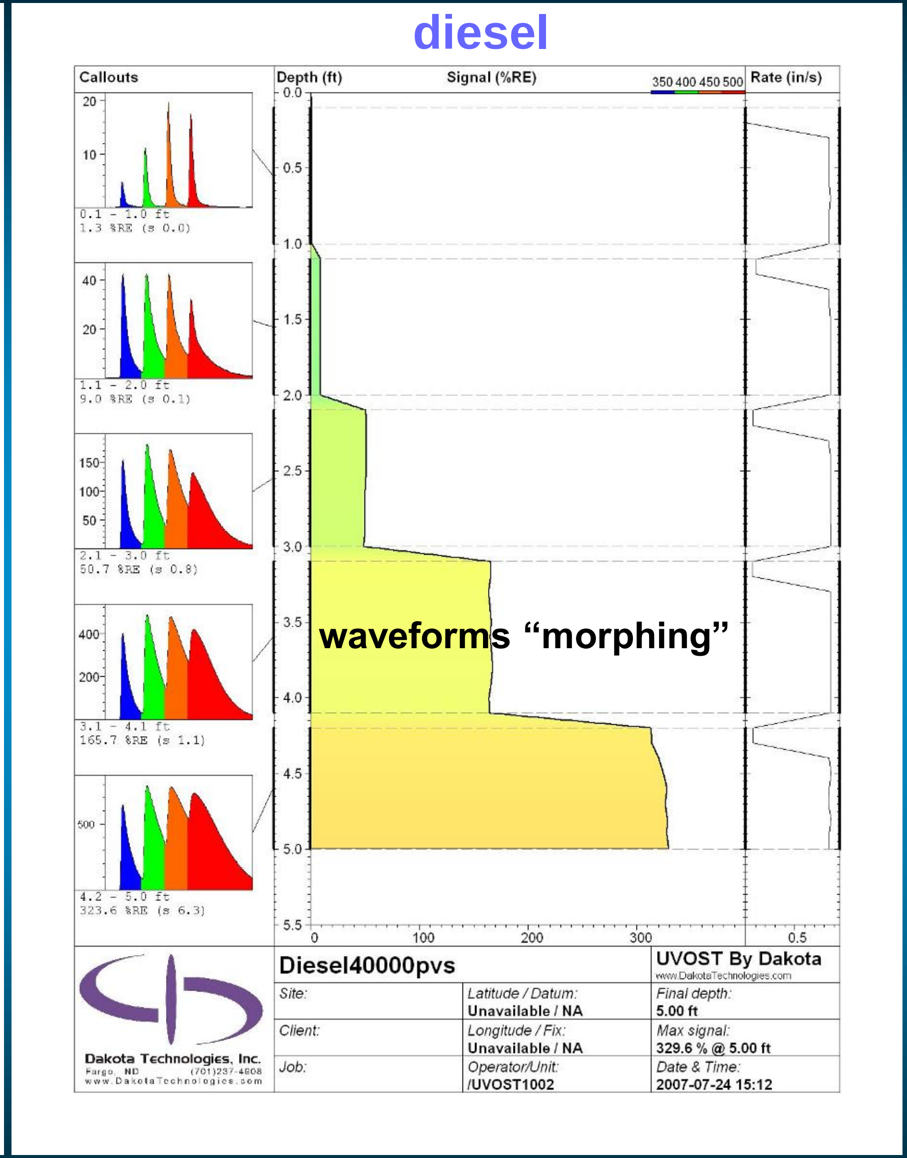
gasoline



more lab studies

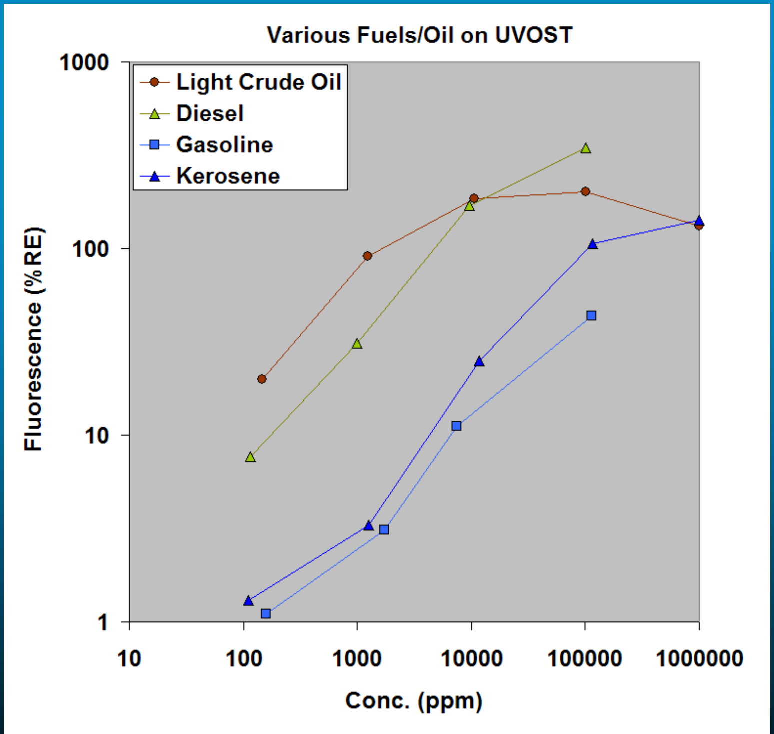
crude oil "rollover" | **too much fluorescence (saturation)**





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



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!

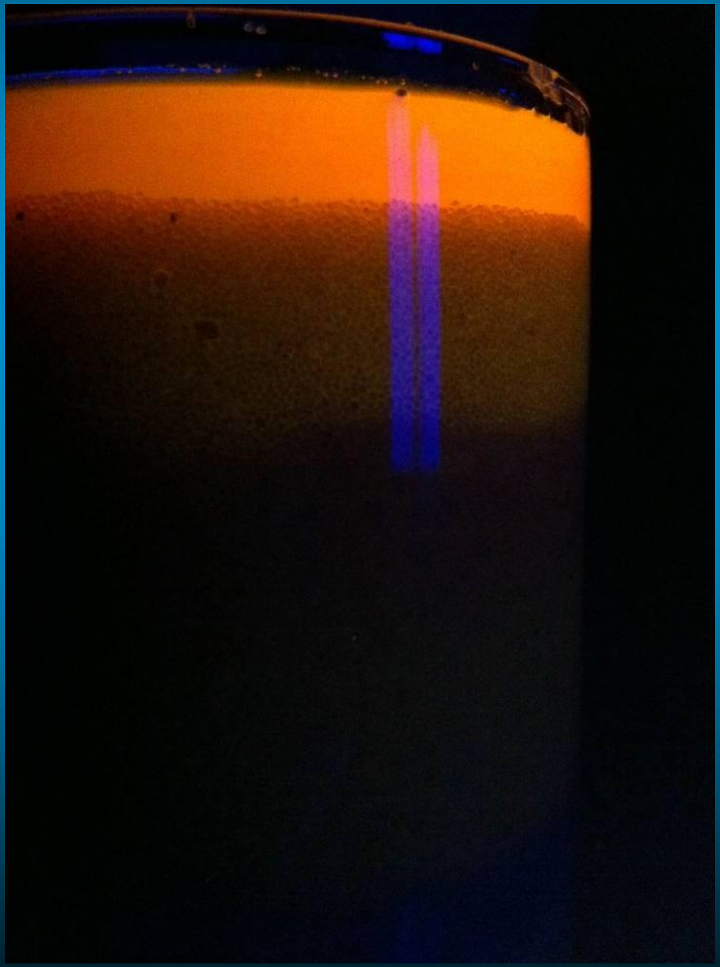
- **Enhanced responses in:**
  - **course "clean" sands with open pore spaces**
  - **light colored soils help reflect resulting emission back into window**

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

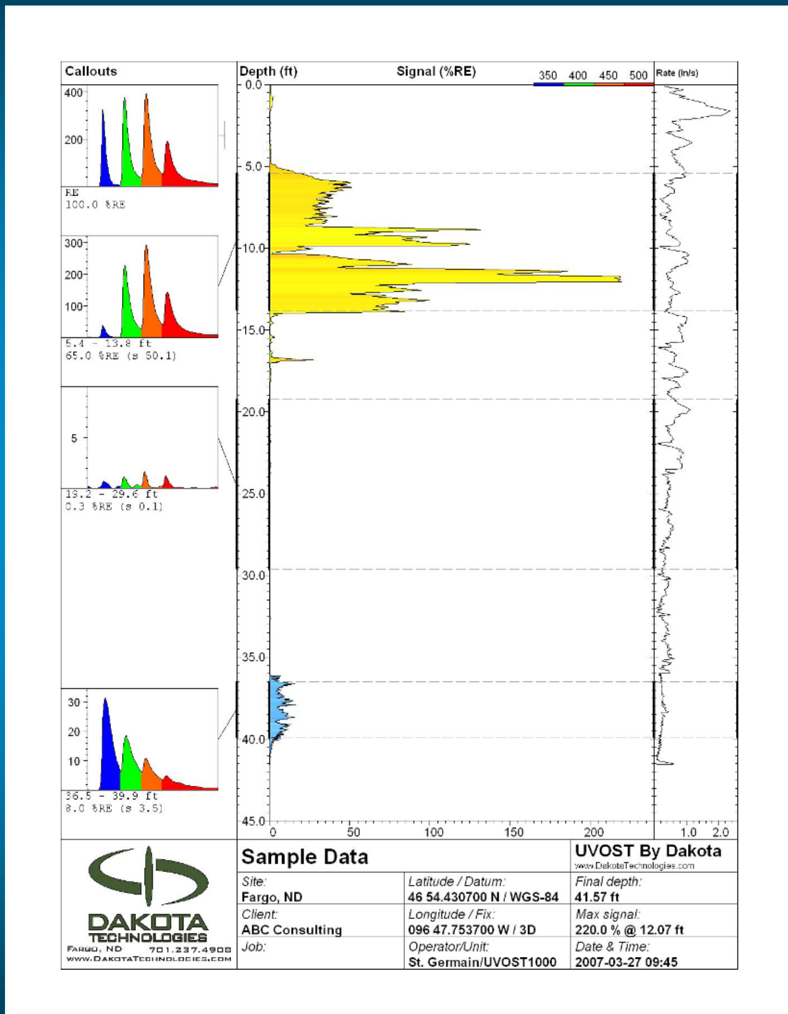
soils pore spaces saturated with diesel
various soil types have various fluorescence intensity

soil matrix effects
varies the fluorescence intensity

it's simply the optics of soil grains and pore spaces
big pores make more dye (PAH) available to the light and to the camera's lens
(same with fluorescence of fuel/oil)



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 <u>one</u> NAPL type at a <u>simple</u> site with simple geology, but multiple products under complex geology… <u>there's going to be differences in response</u>

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

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]

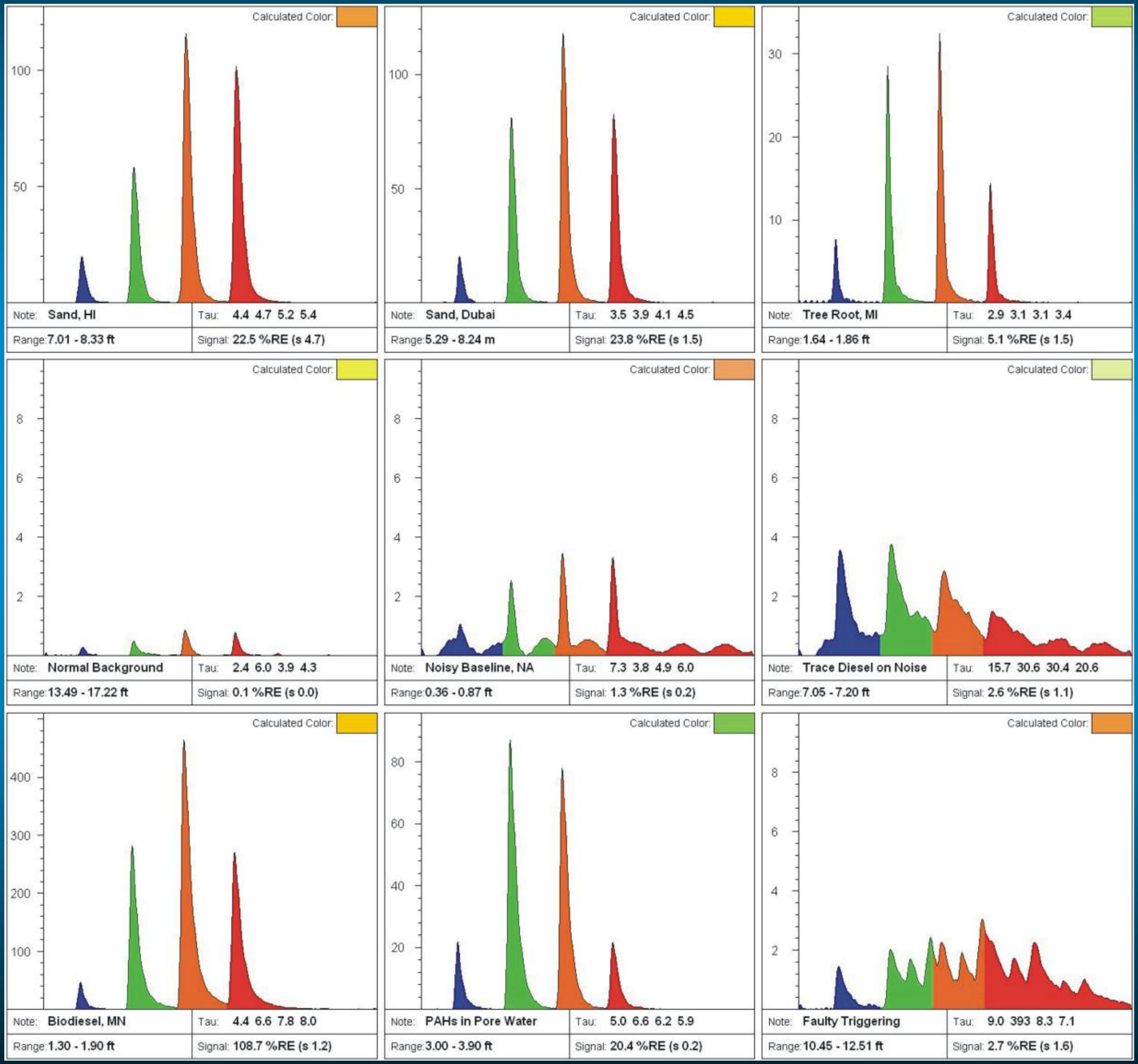
sea shells (weak-strong)
paper (medium-strong)
peat/meadow mat (weak)
calcite/calcareous sands (weak-strong)
asphalt (very weak)
stiff/viscous tars (weak)
certain soils (weak)
tree roots (weak-medium)
sewer lines (medium-strong)
coal (very weak to none)
quicklime (weak)

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)

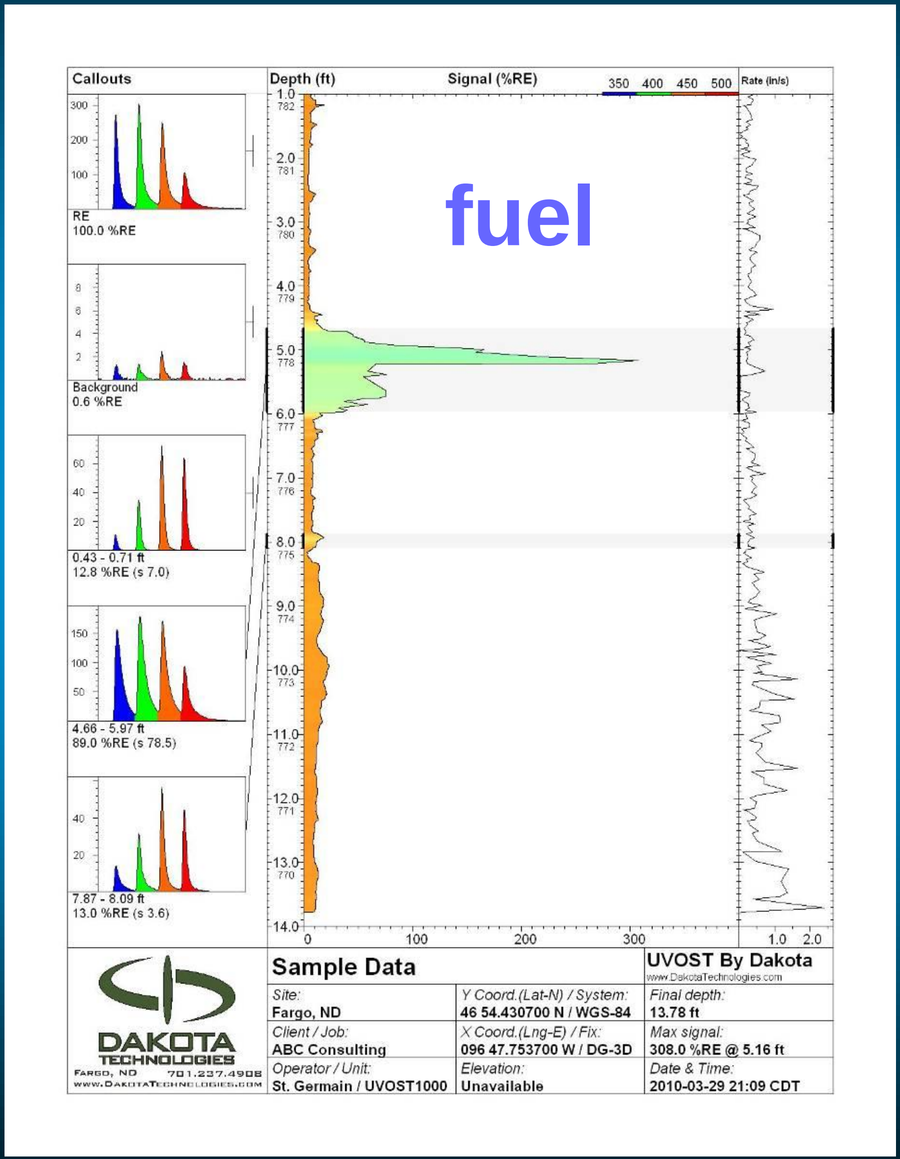
false positives/negatives

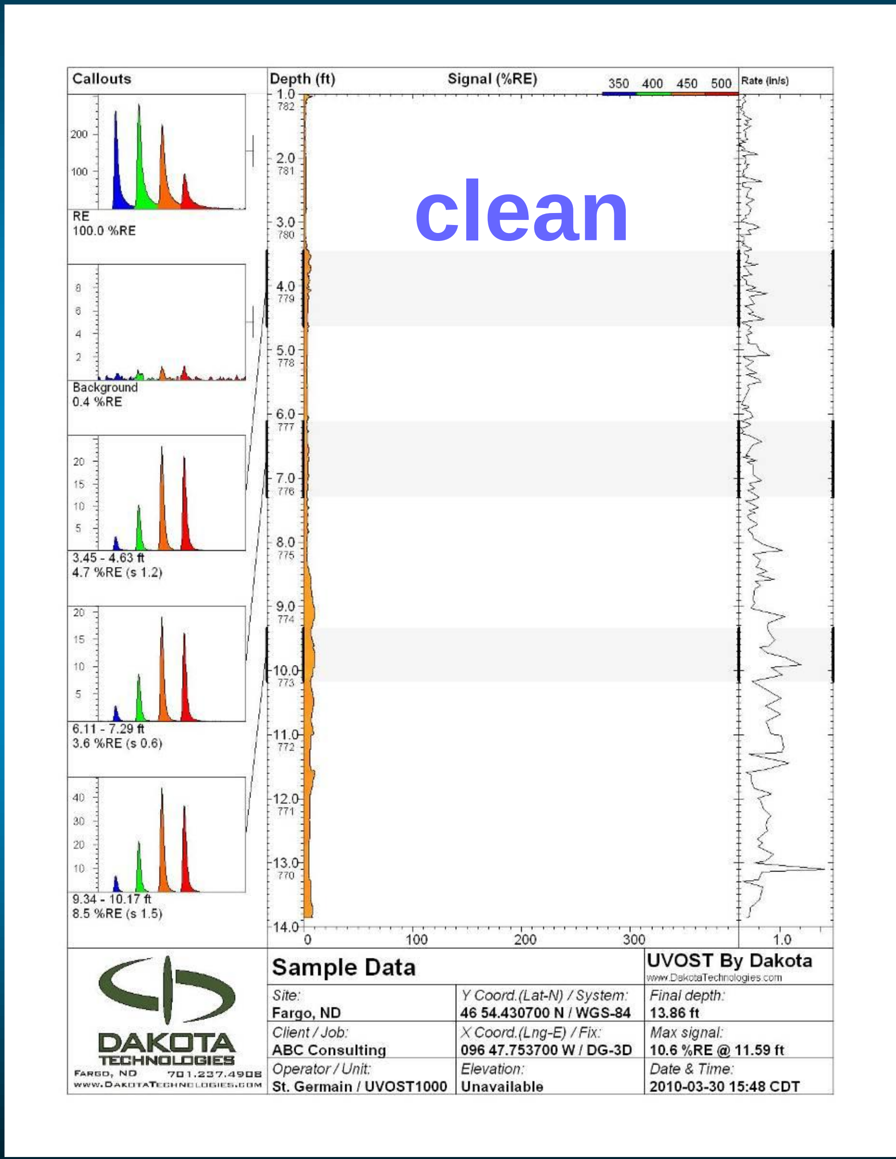
most have short lifetimes and look “odd” vs target fuel/oil



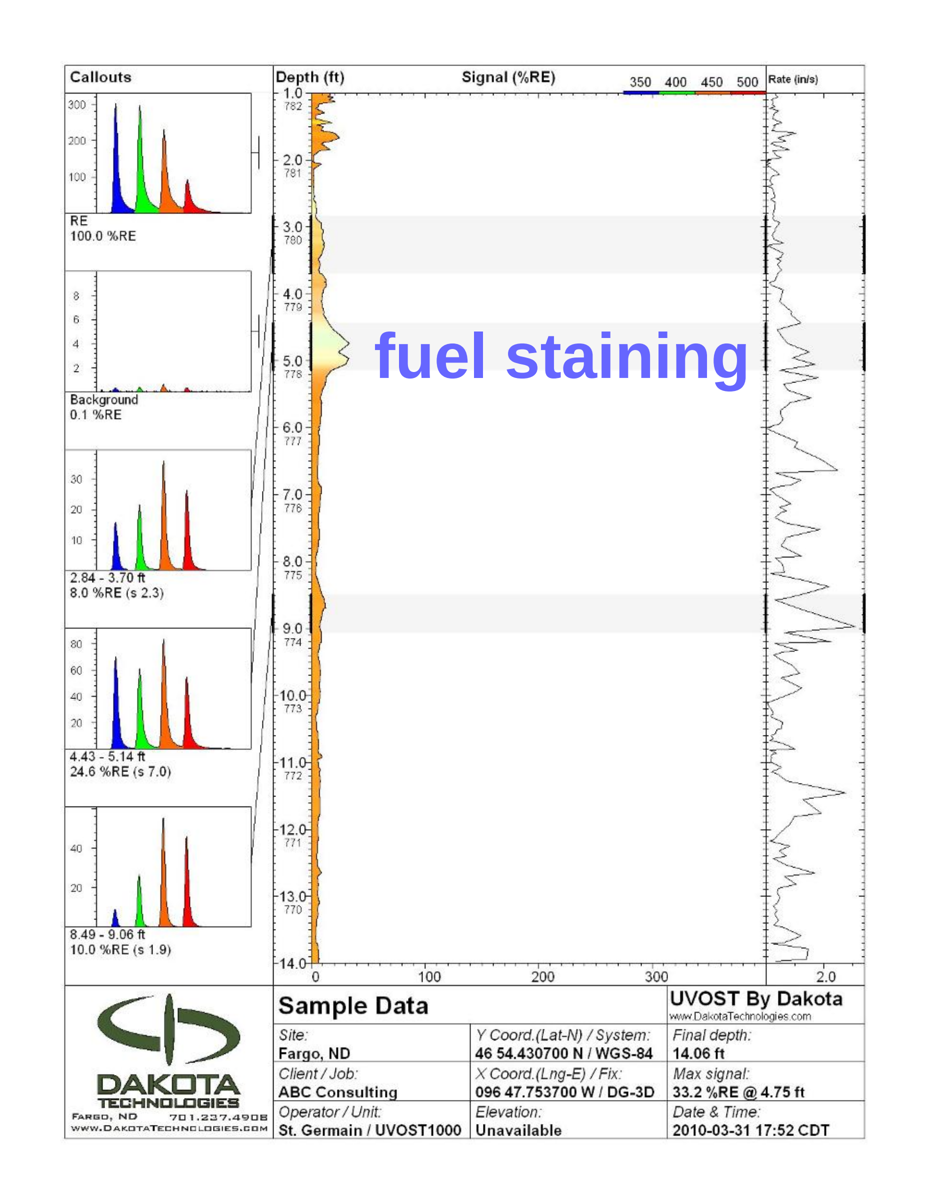
false positive – calcareous sands

often context of the site or entire log helps "make the call"





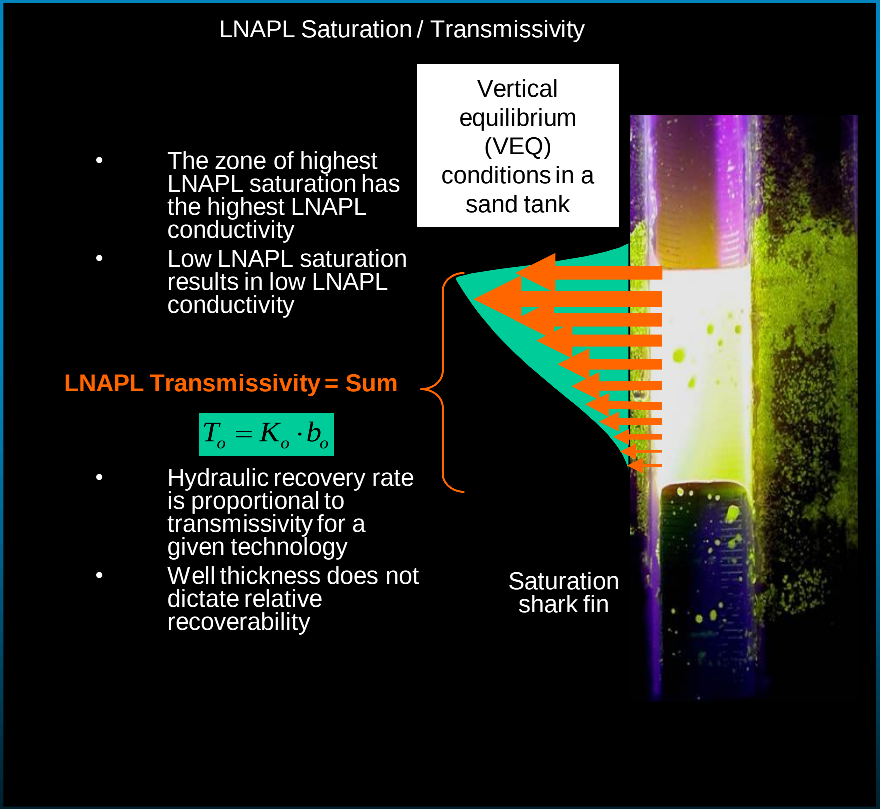
logs from previous slide (calcareous sands) help solve this “head scratcher”



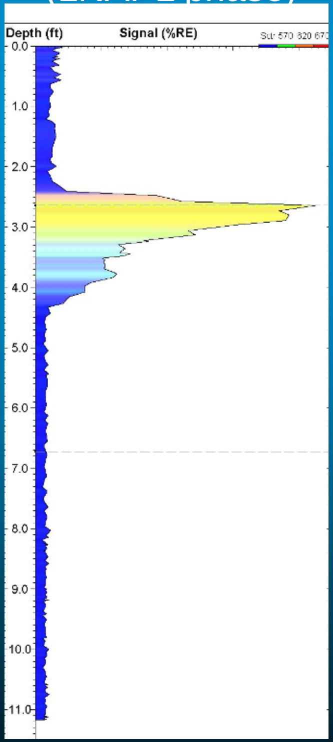
the "shark's fin" in a "sand box"

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

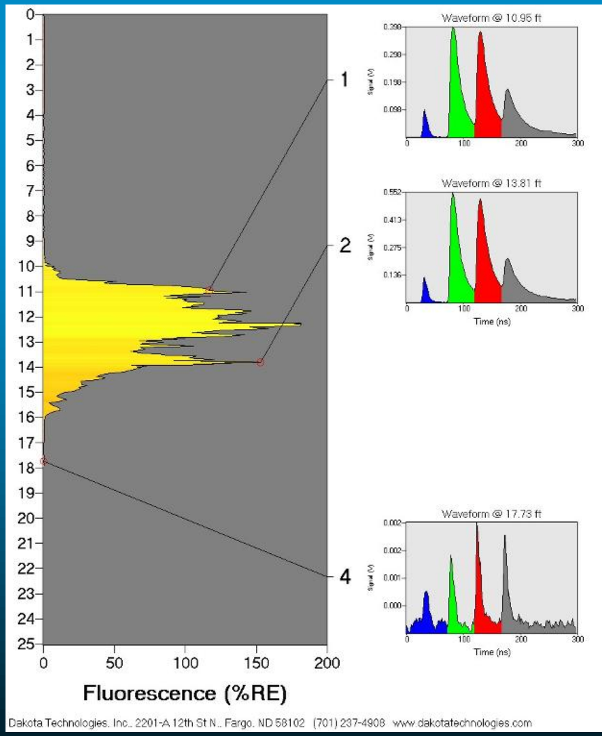
- http://www.clu-in.org/conf/itrc/iuLNAPL/
- http://www.clu-in.org/conf/itrc/LNAPLcr/
- http://www.dnr.mo.gov/env/hwp/docs/lnaplbasics.pdf



Coal Tar (LNAPL phase)

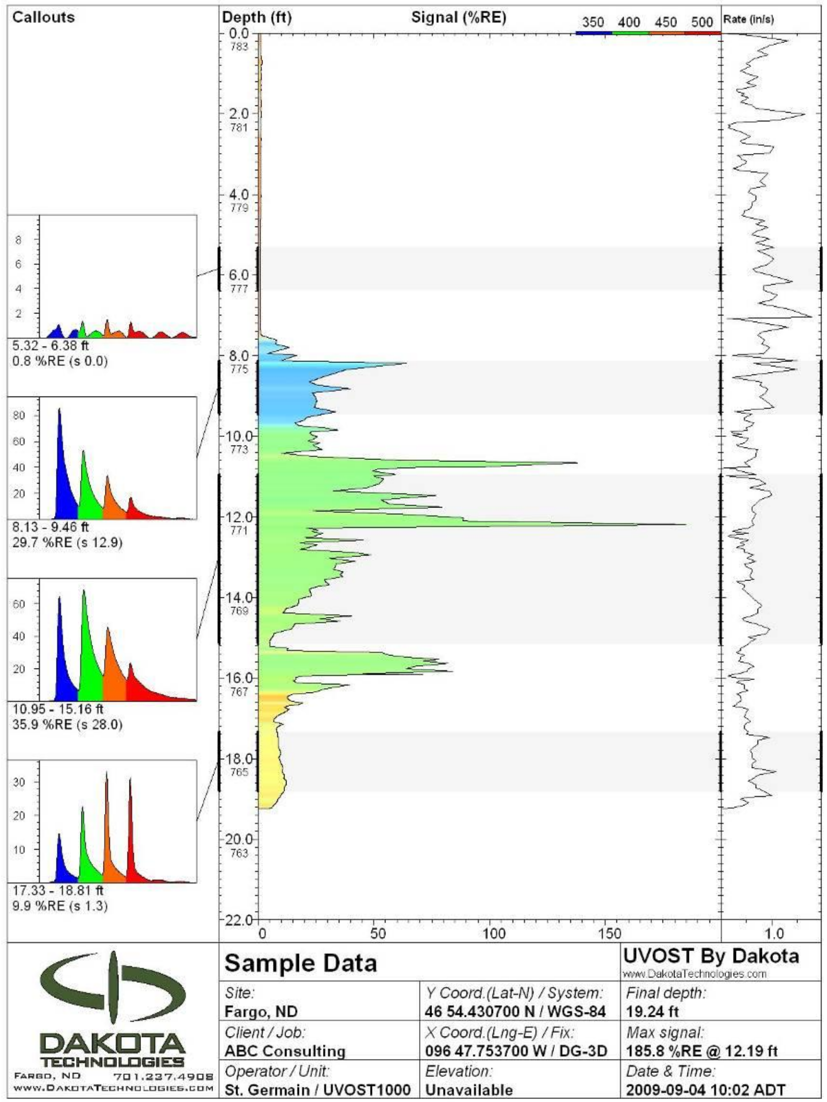


Diesel



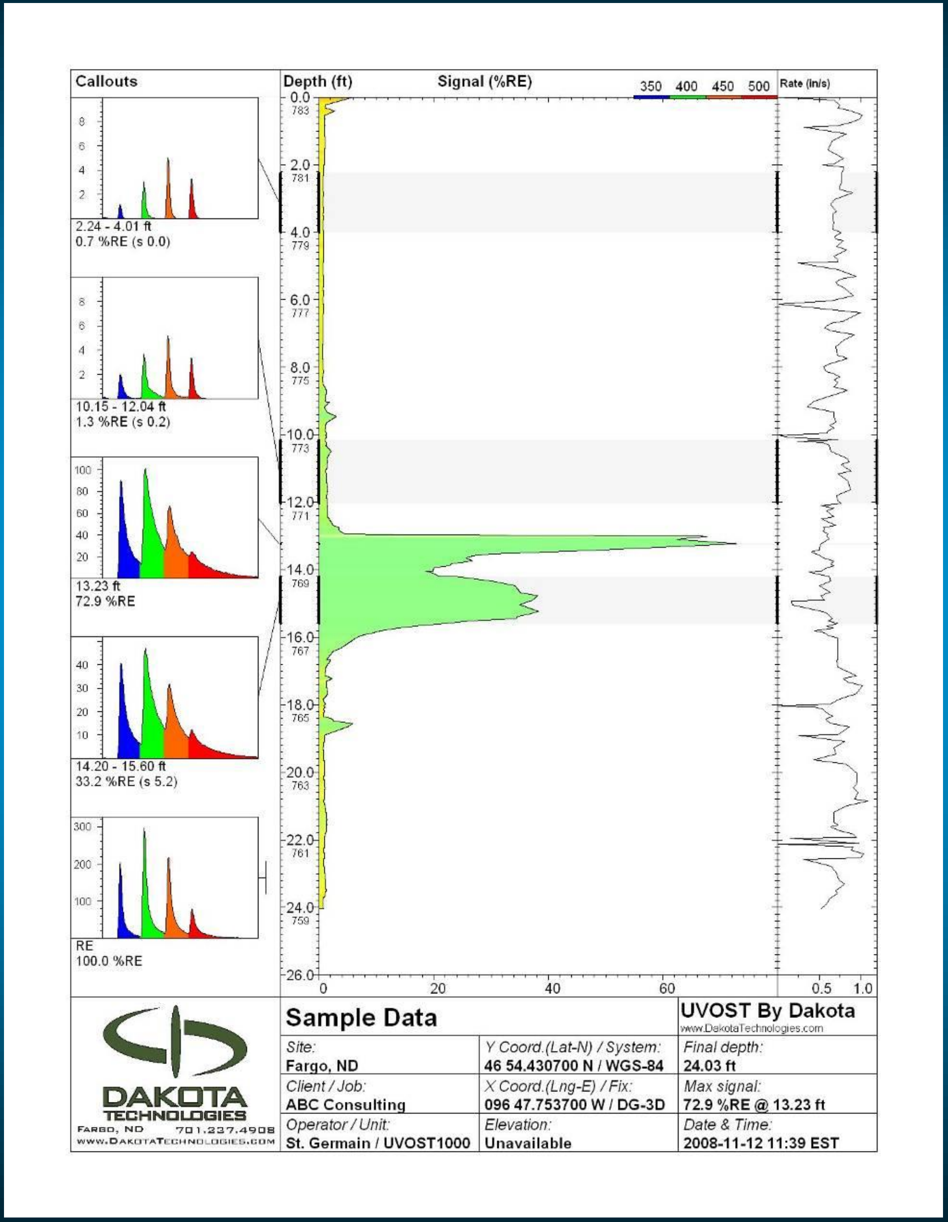
field log example

variation top to bottom
= heterogeneous product
or
strange weathering pattern



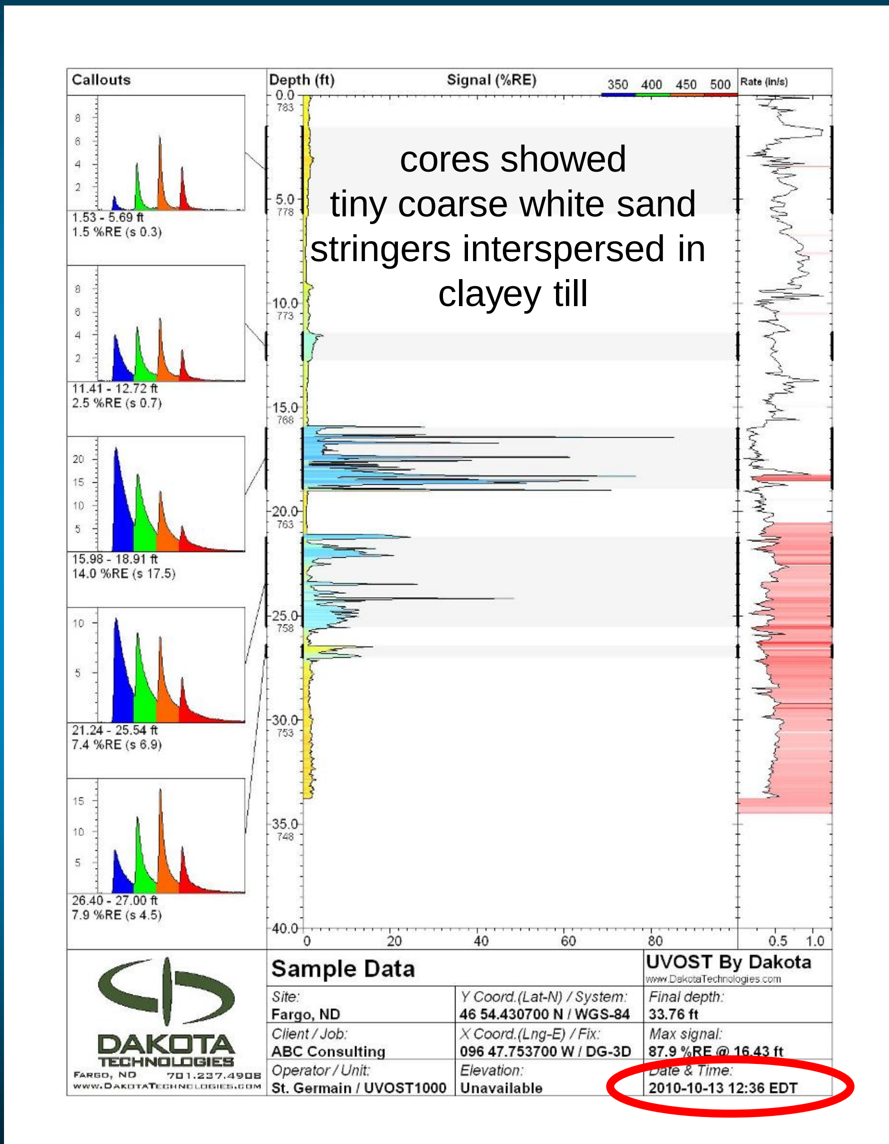
this type of “confetti” color
pattern is very common
in bulk handling facilities
where many products
spilled over long periods

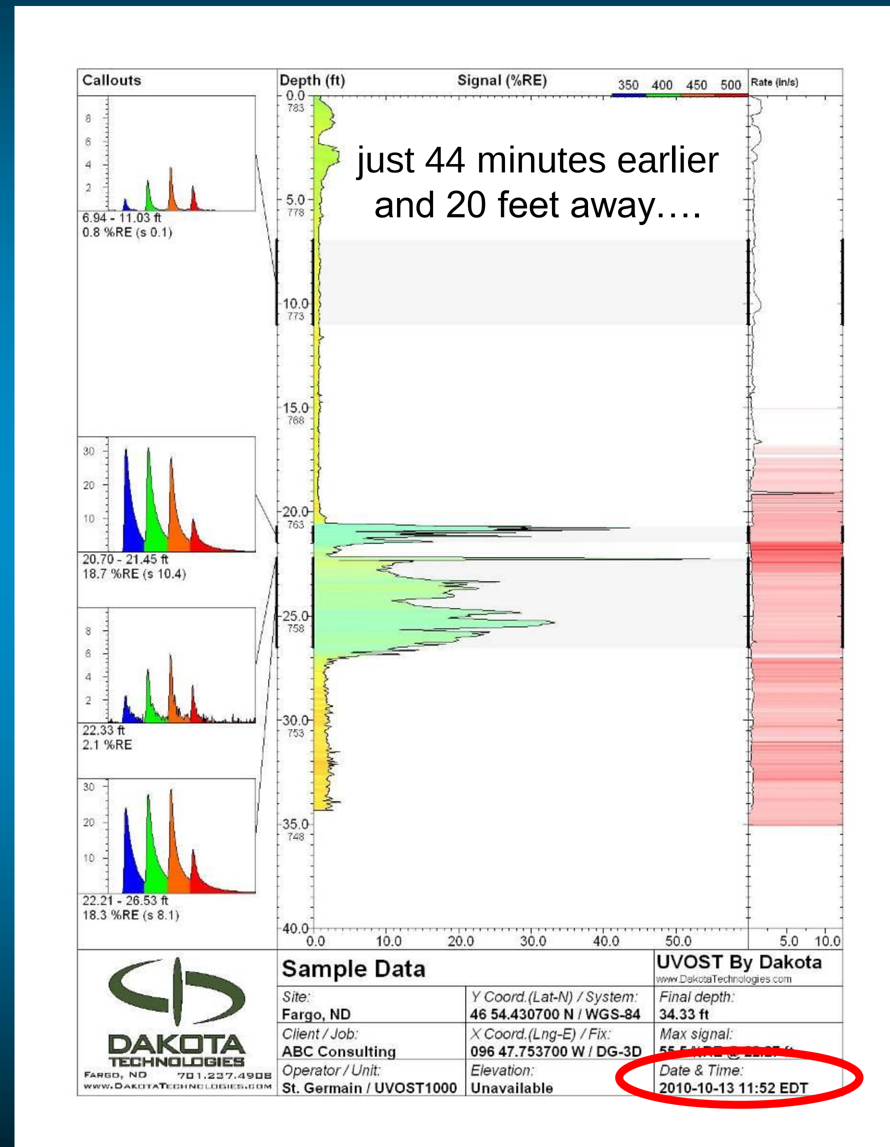
field log example



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





Advanced Topics

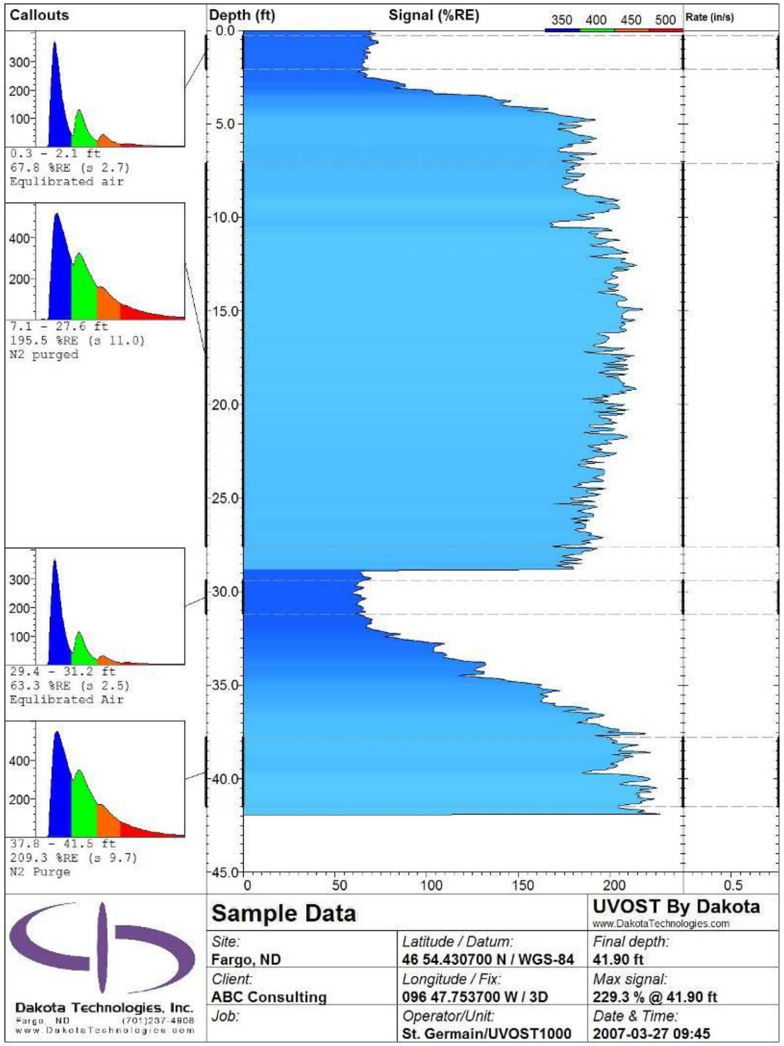
- limitations/compications
- LIF’s role in NAPL distribution theory
- site investigation basics
- UV LIF’s struggle with “heavies”

(coal tars and creosotes)

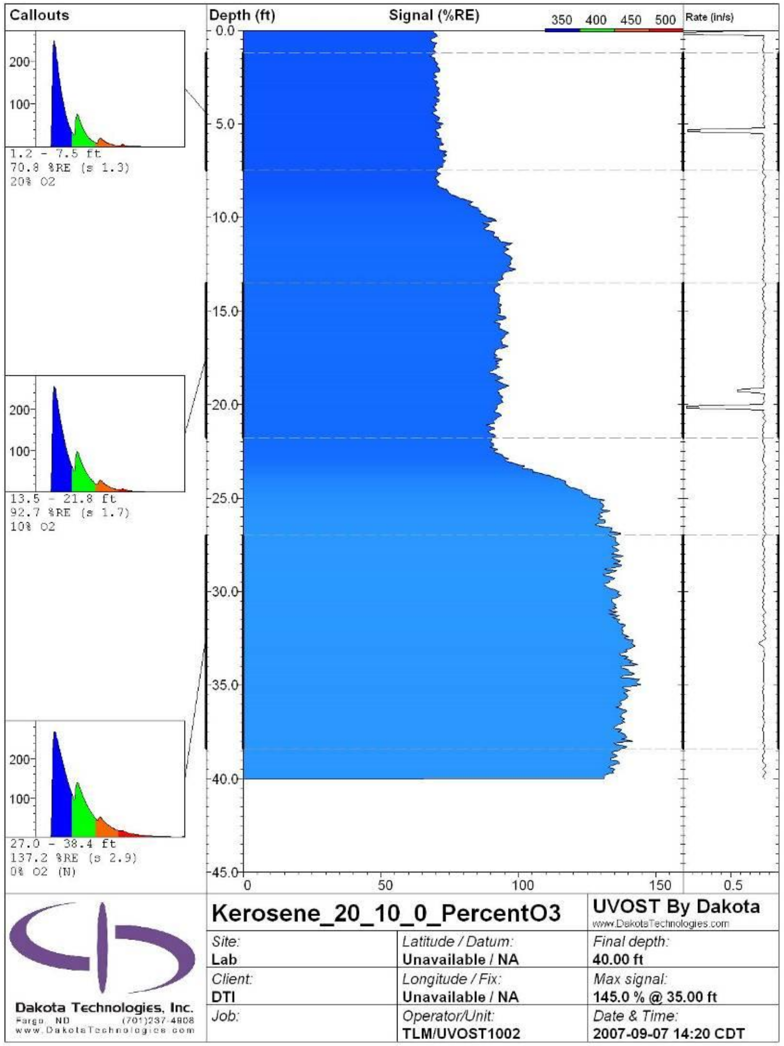
Oxygen’s role in LIF waveform and response

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

different product waveform? – no - O2 quenching

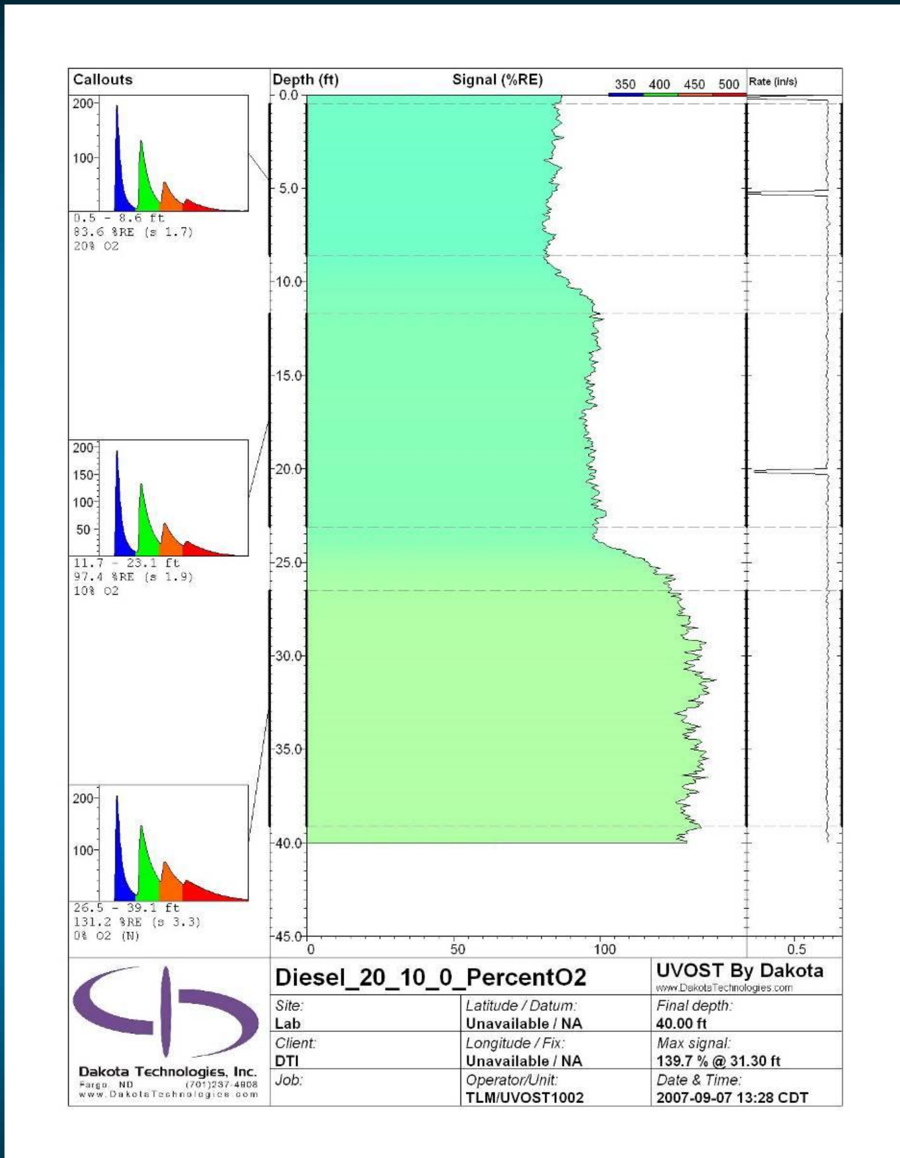


customer's NAPL from a well - 2005

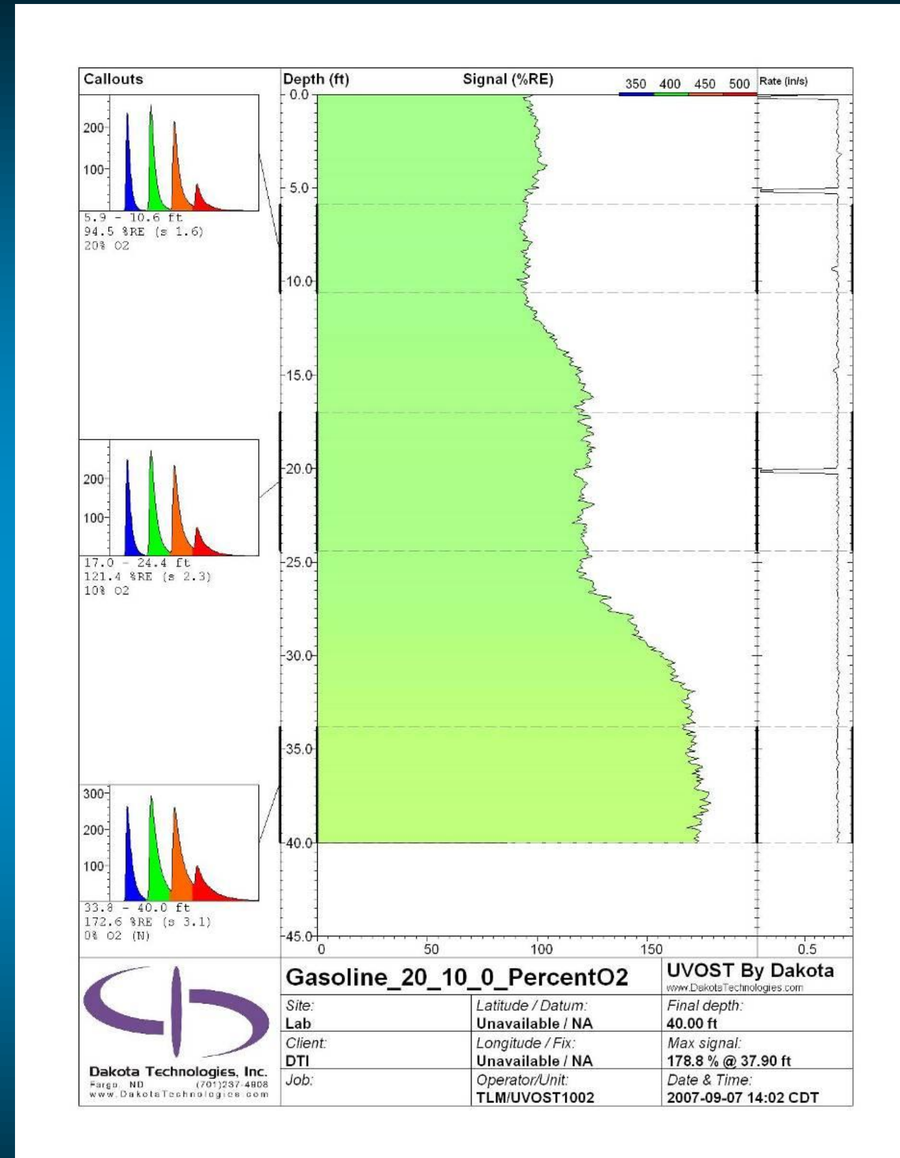


kerosene from pump

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



diesel from pump



gasoline from pump

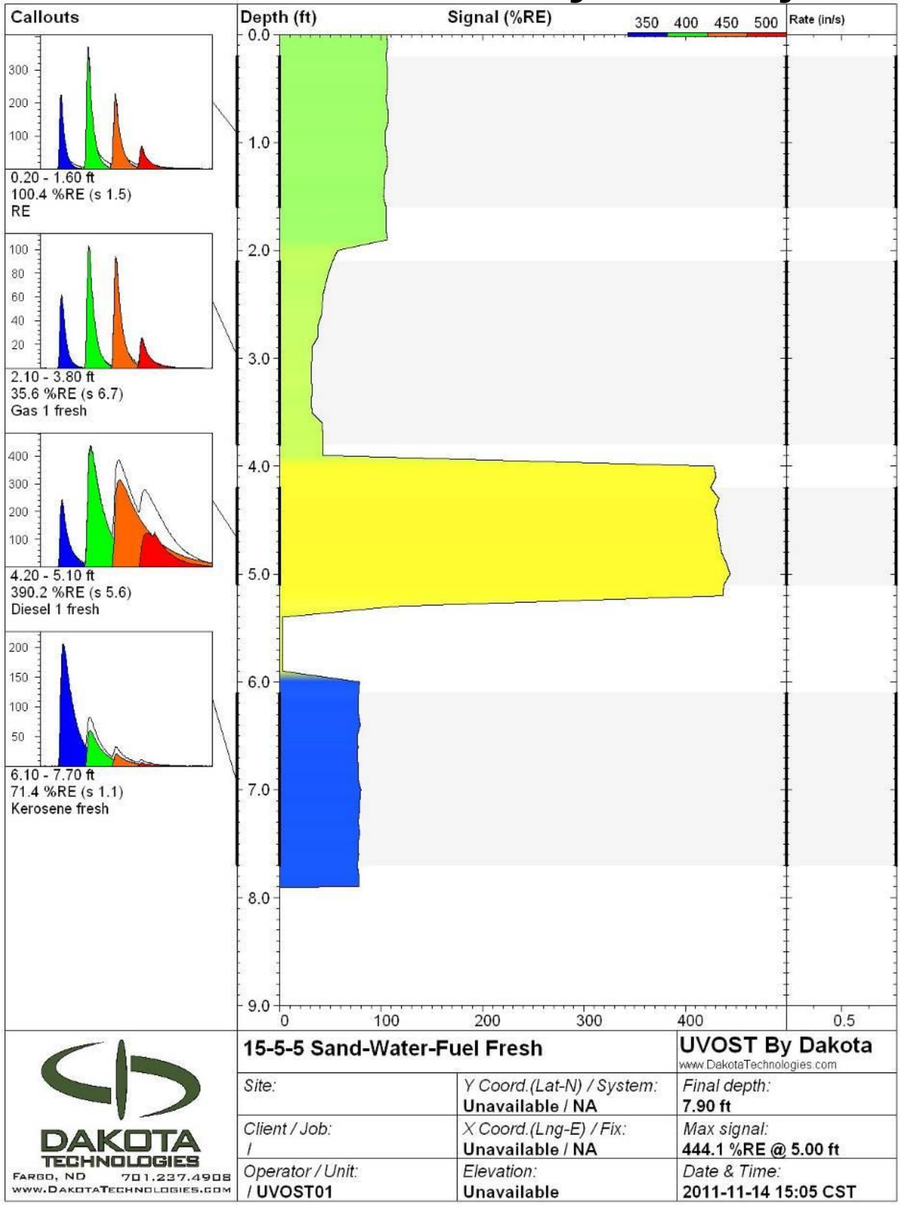
weathering (NAPL’s nemesis)

starring “The Chameleon” of LIF… gasoline

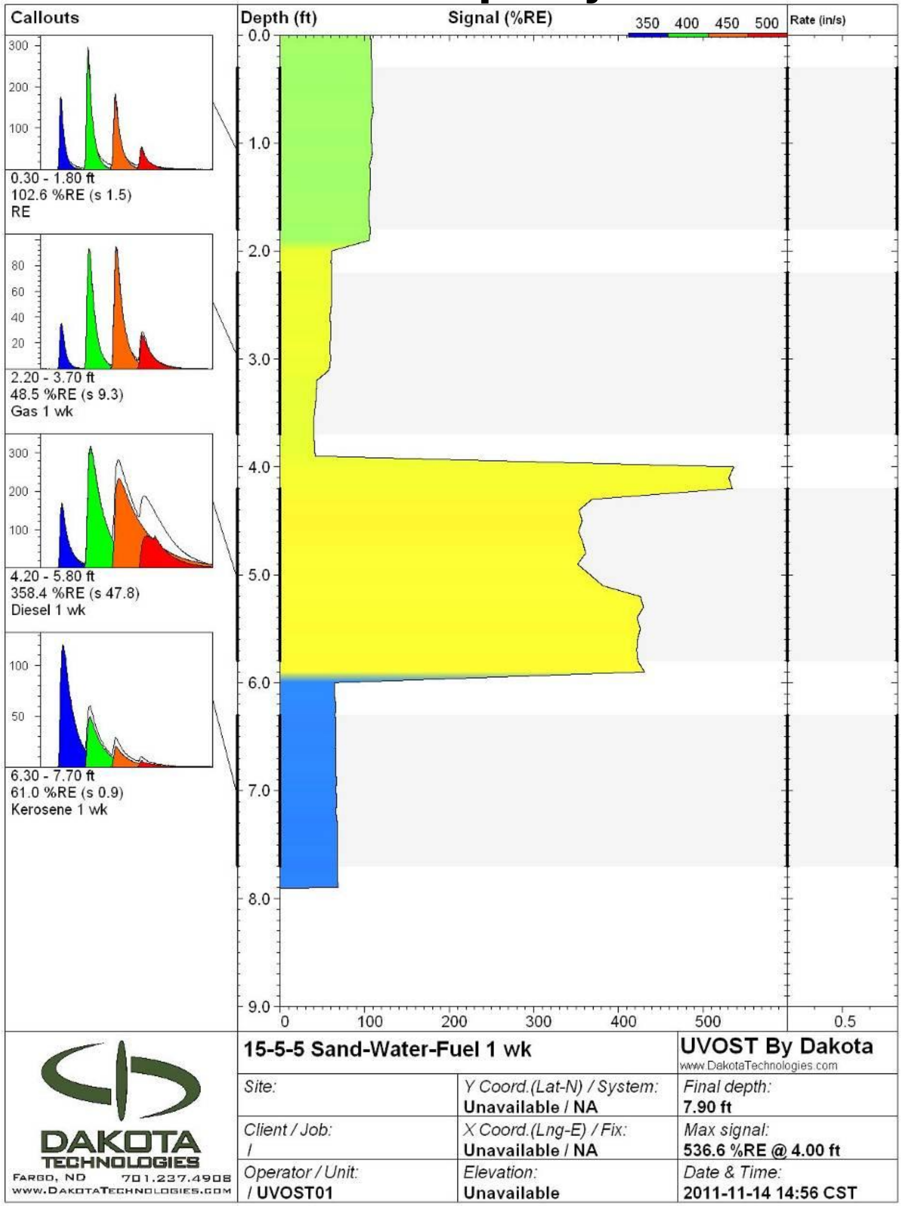
why is gasoline the chameleon?

• starting out low on PAHs
• very volatile and ‘solvent’ easily lost

fresh fuels in wet sandy soil in jars



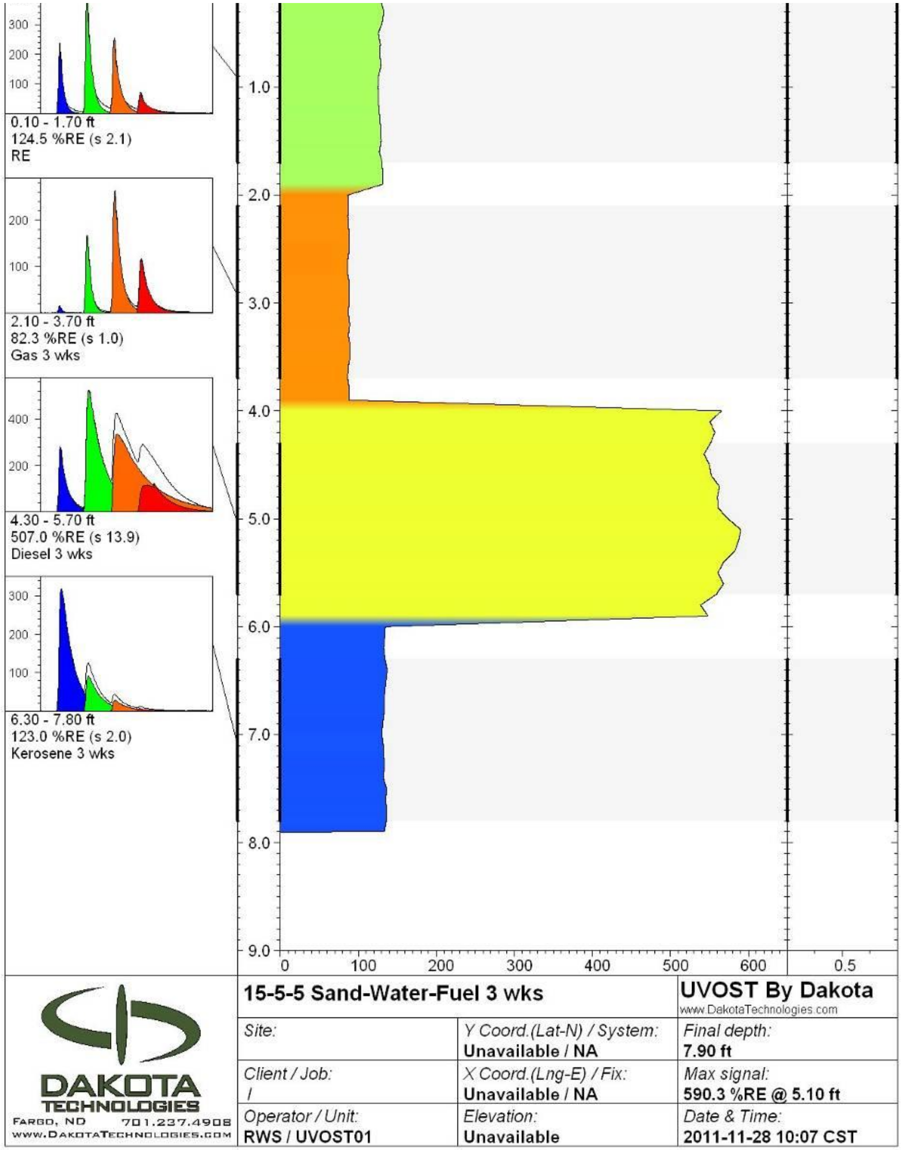
1 week of open jars



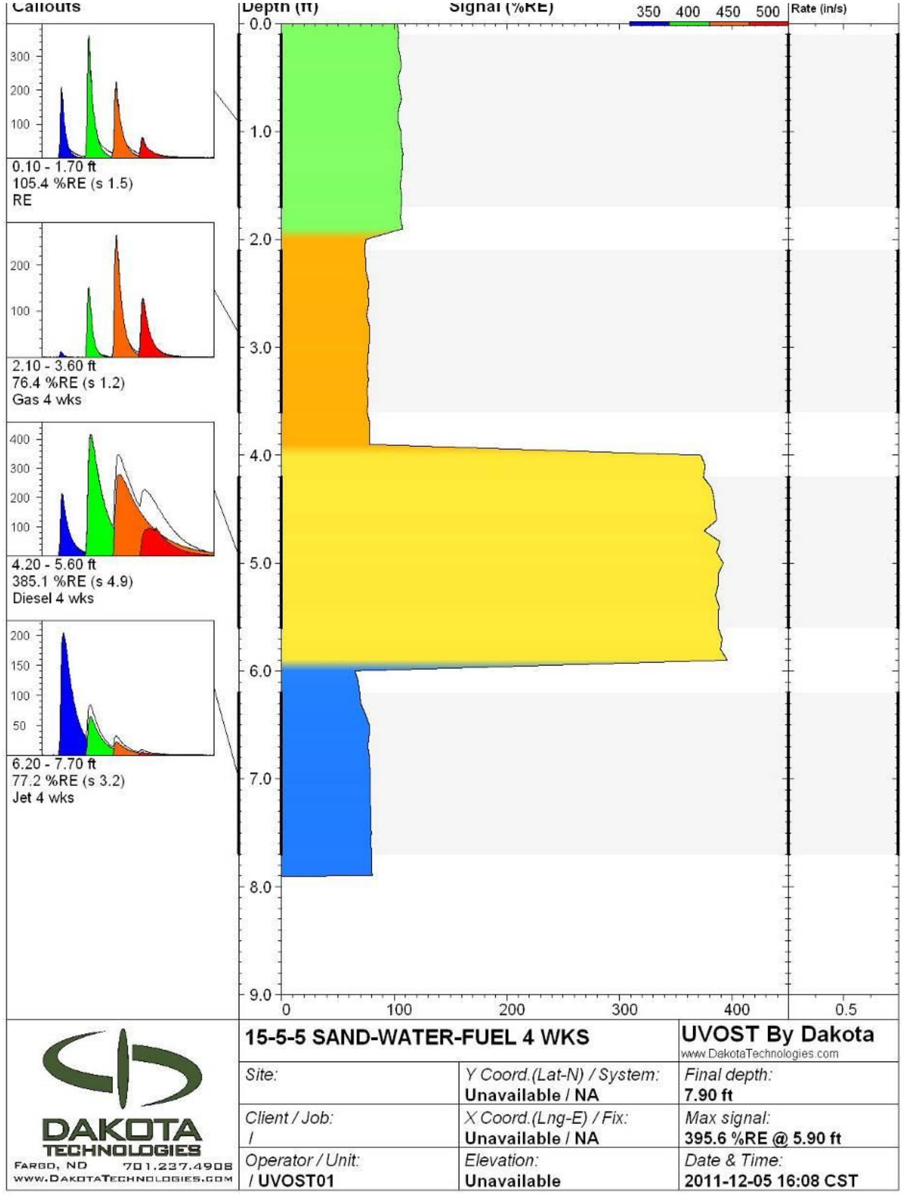
3 weeks of open jars

extreme conditions!!

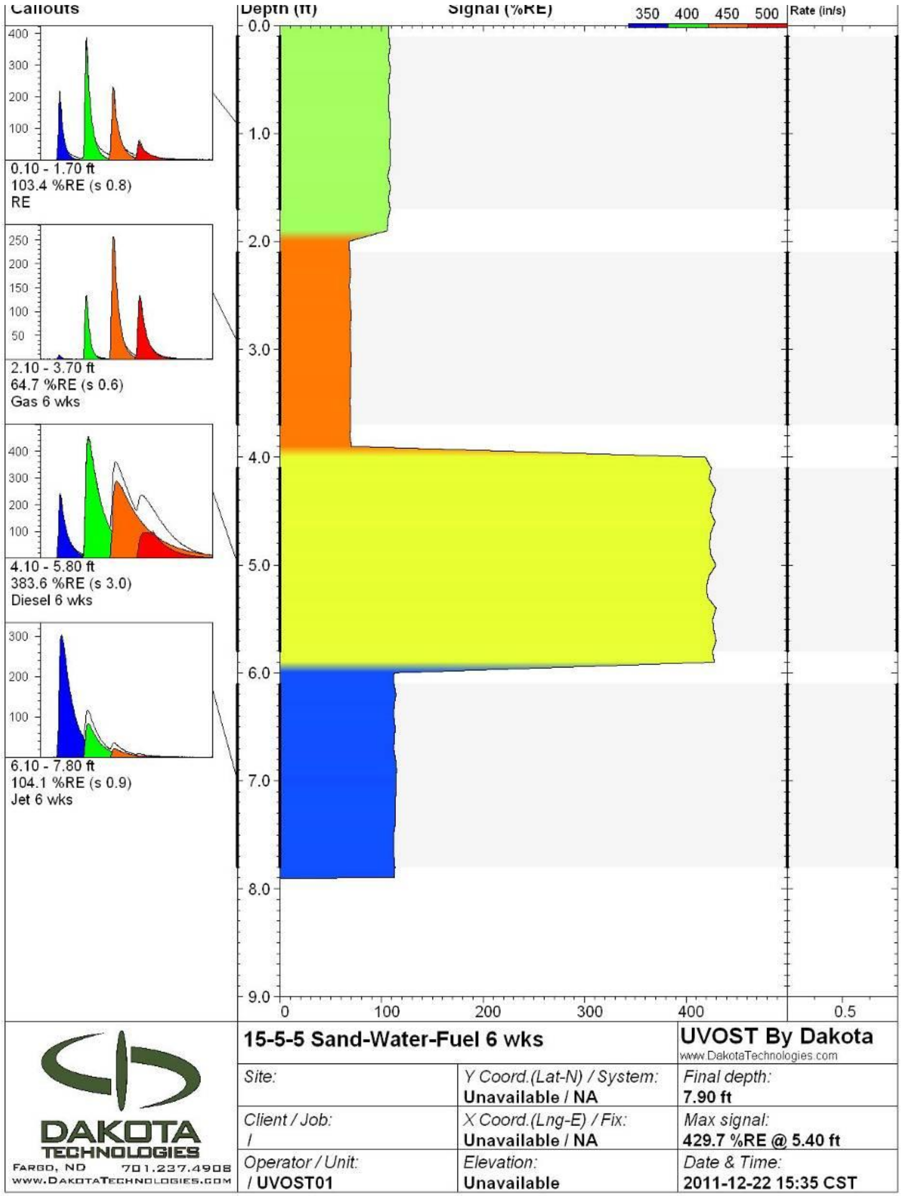
(gasoline jar went dry and had to be rewetted)



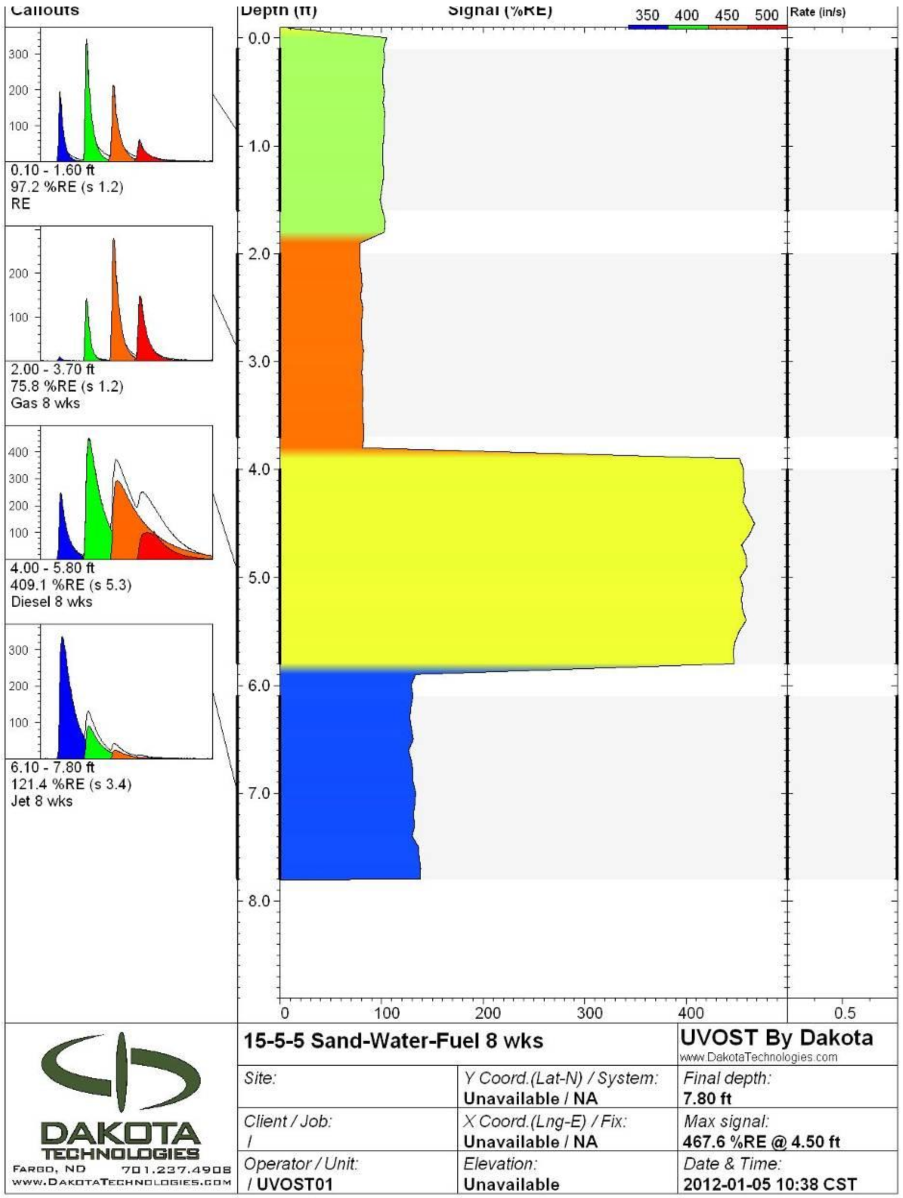
4 weeks of open jars

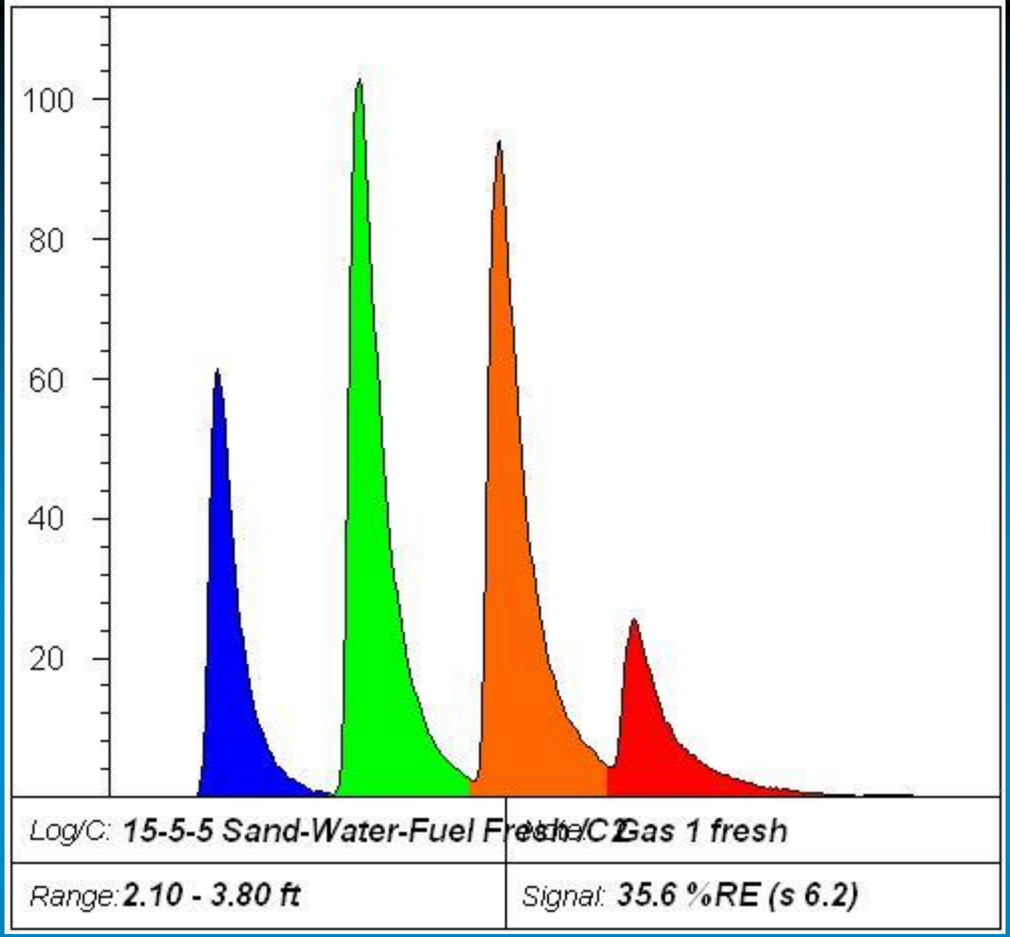


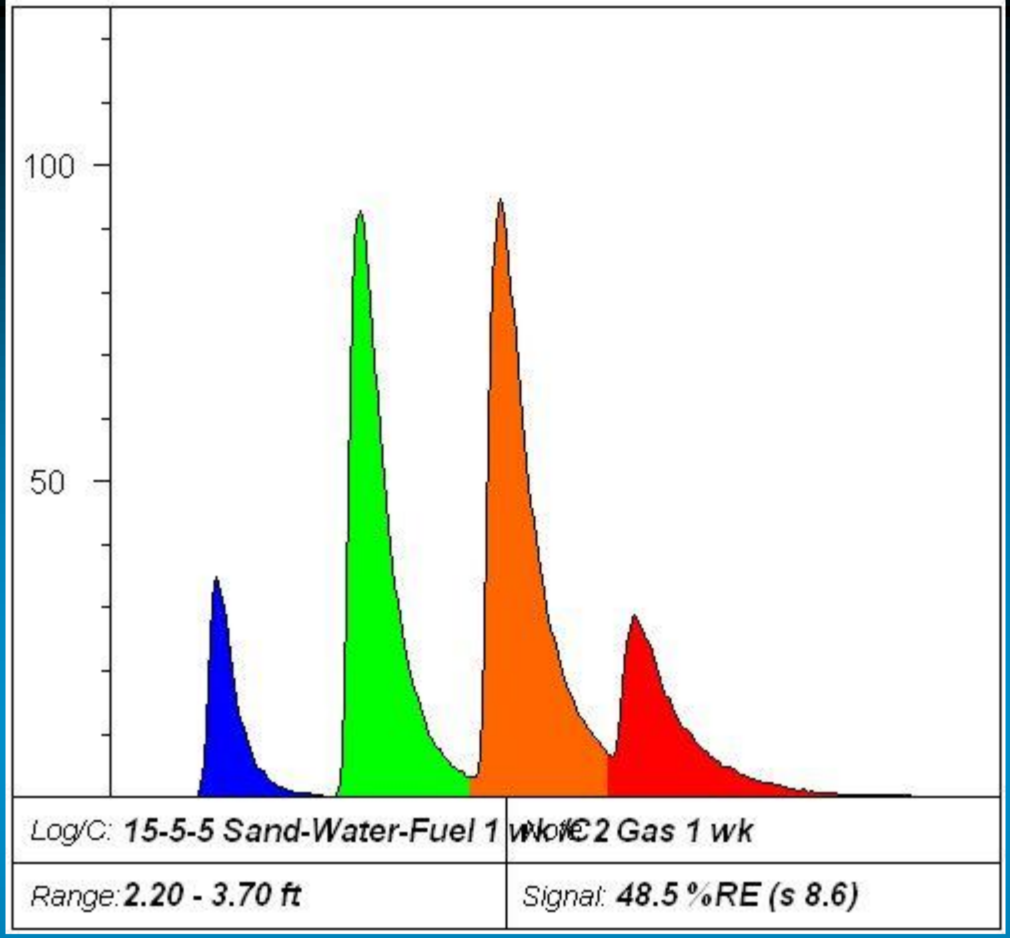
6 weeks of open jars

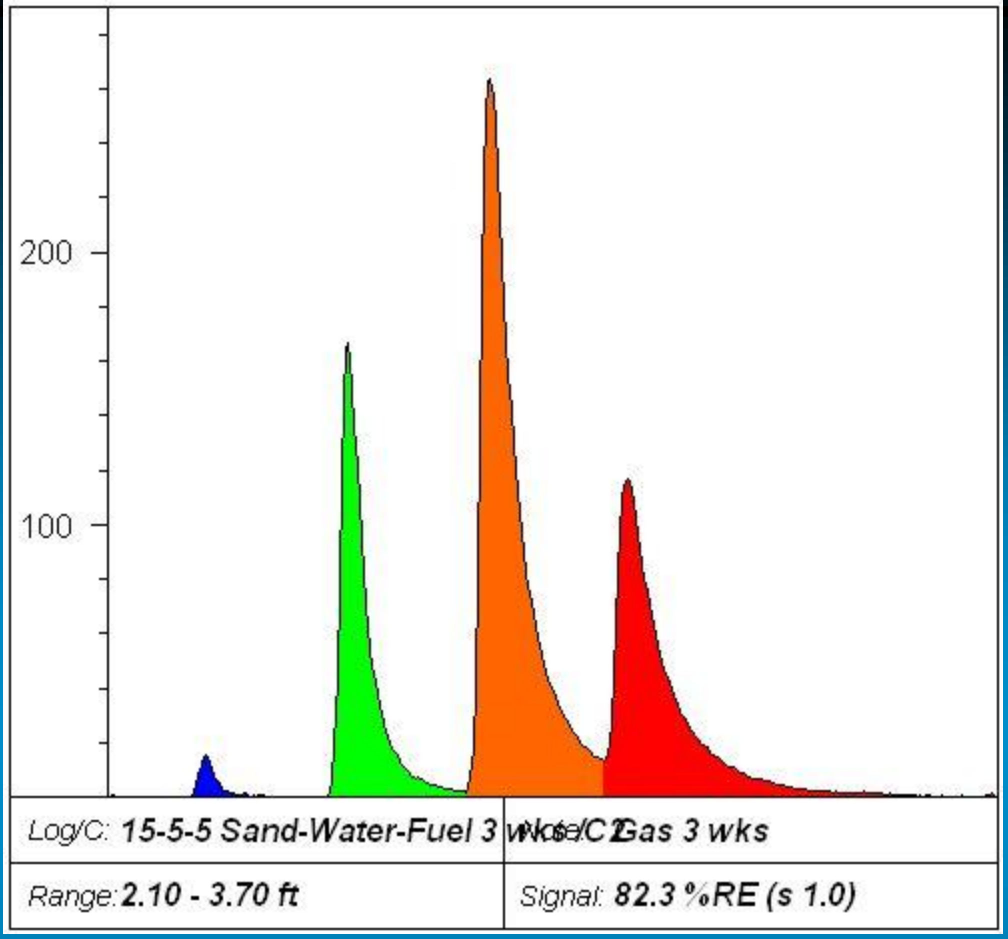


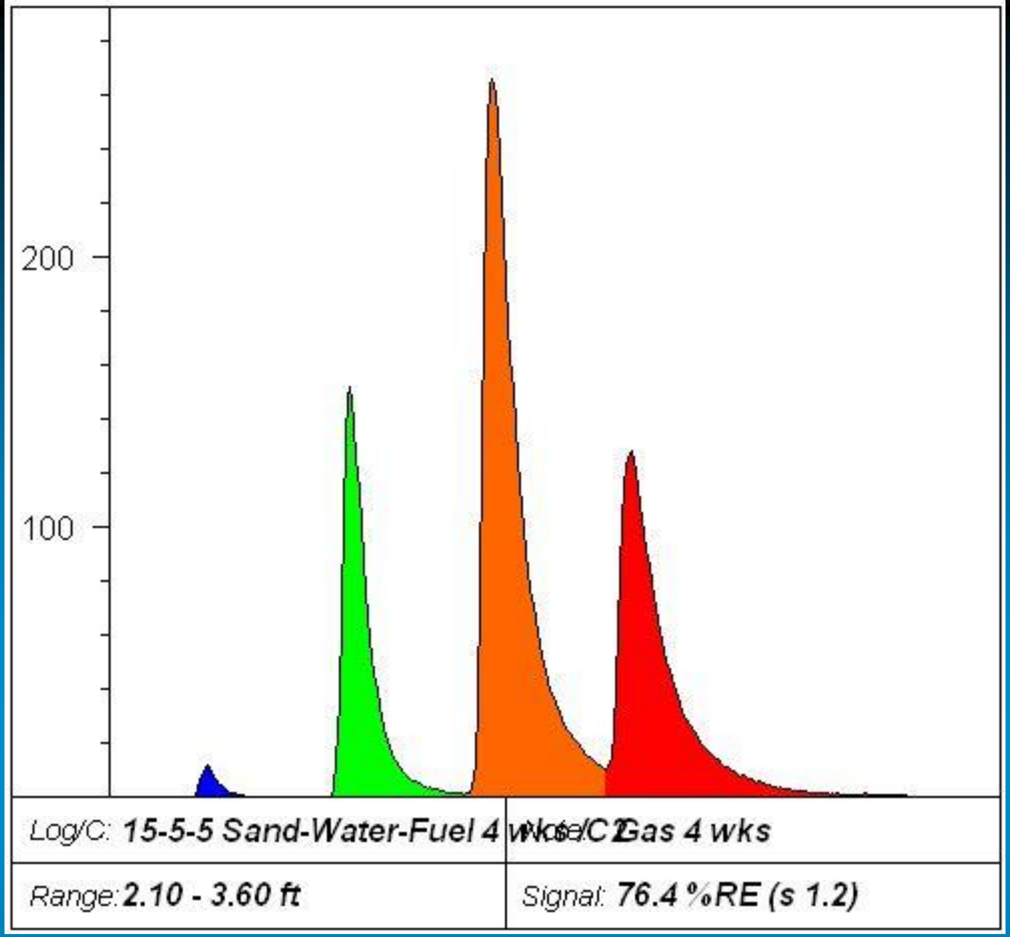
8 weeks of open jars



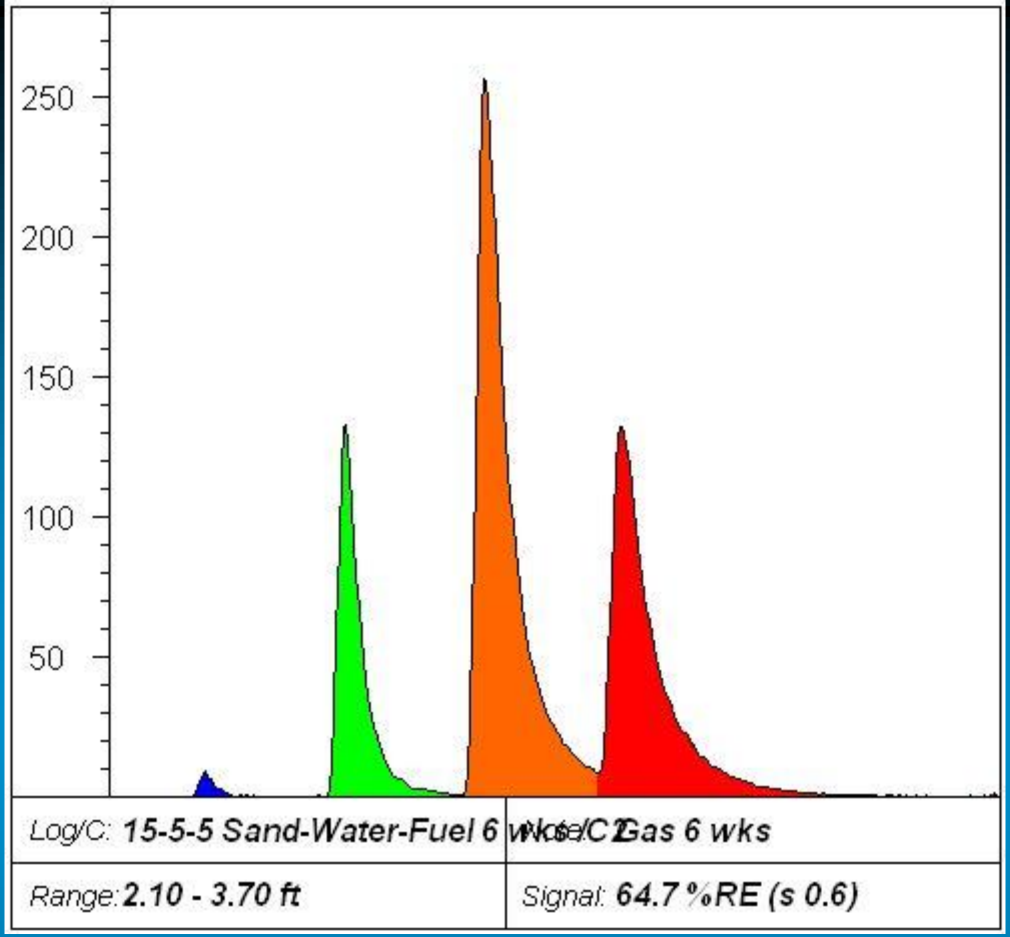

100
80
60
40
20
Log/C: 15-5-5 Sand-Water-Fuel Fresh Note/C2 Gas 1 fresh
Range: 2.10 - 3.80 ft
Signal: 35.6 %RE (s 6.2)

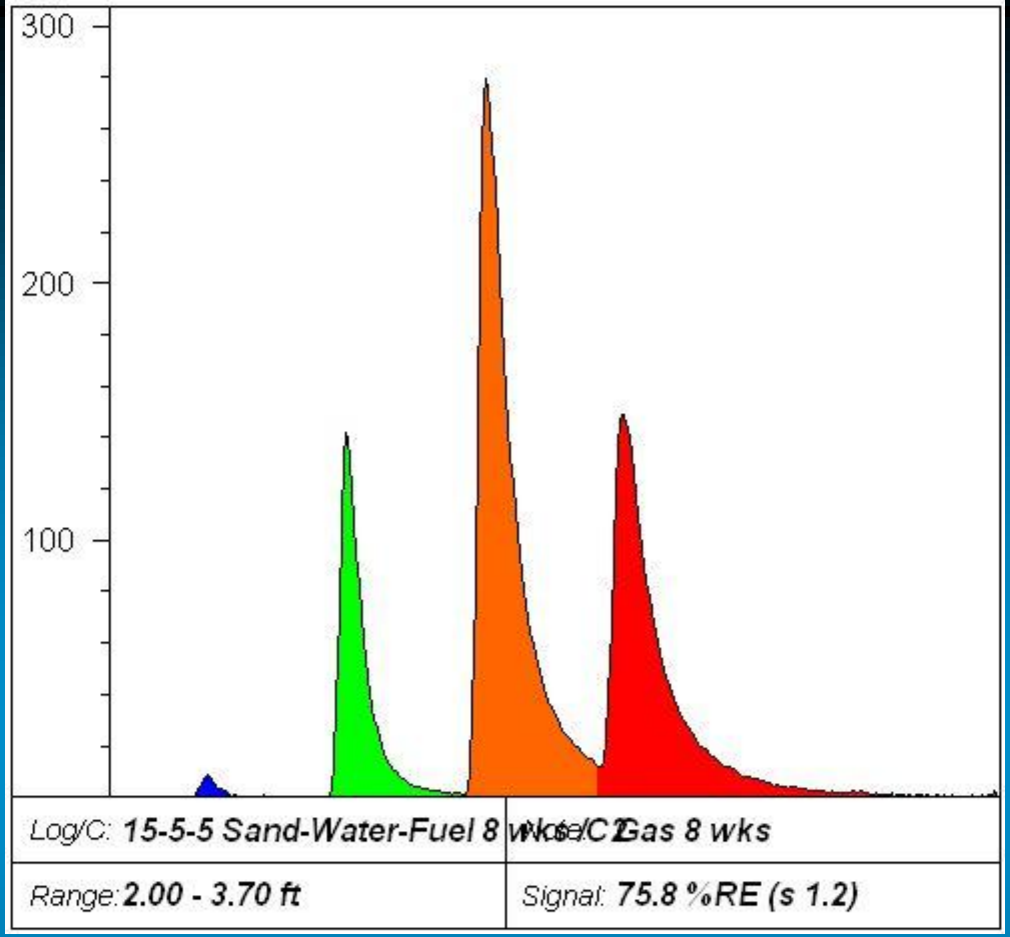

100
50
Log/C: 15-5-5 Sand-Water-Fuel 1 wk
Gas 1 wk
Range: 2.20 - 3.70 ft
Signal: 48.5 %RE (s 8.6)


200
100
Log/C: 15-5-5 Sand-Water-Fuel 3 wks
Note/C2: Gas 3 wks
Range: 2.10 - 3.70 ft
Signal: 82.3 %RE (s 1.0)



200
100
Log/C: 15-5-5 Sand-Water-Fuel 4 wks
Note: C2 Gas 4 wks
Range: 2.10 - 3.60 ft
Signal: 76.4 %RE (s 1.2)


250
200
150
100
50
Log/C: 15-5-5 Sand-Water-Fuel 6 wks
Note/C2: Gas 6 wks
Range: 2.10 - 3.70 ft
Signal: 64.7 %RE (s 0.6)



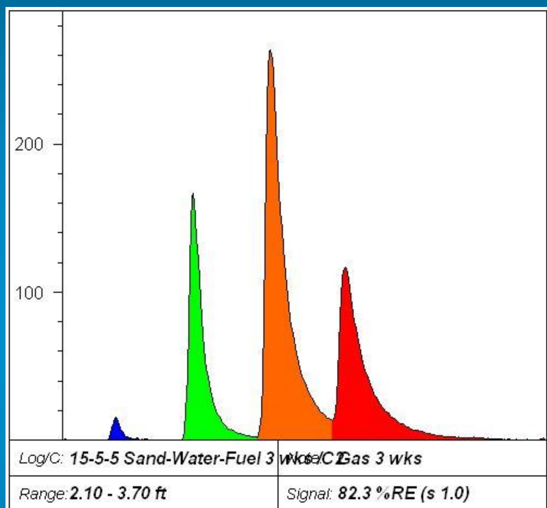
how would this beat up, waxy, low VOC gasoline rate on the TPH(GRO) chart??

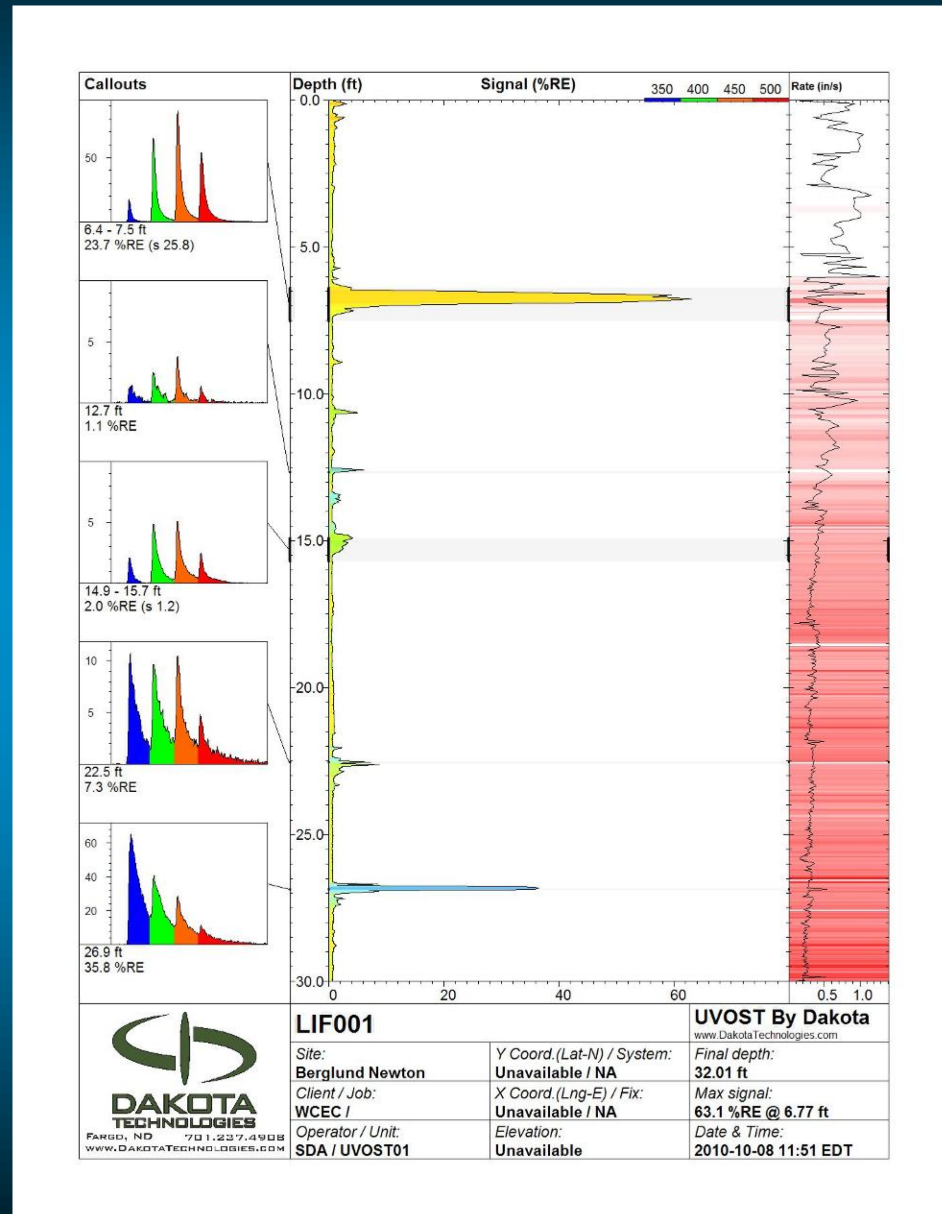
not so high – chemically it is not strictly gasoline any longer, and LIF reflects that

is this test realistic? probably not, too extreme – but maybe accurate of desert SW?

former gasoline station in MN in 2010

can you find me in the log at right?





what has LIF revealed about
LNAPL distribution
in the last 20 years?

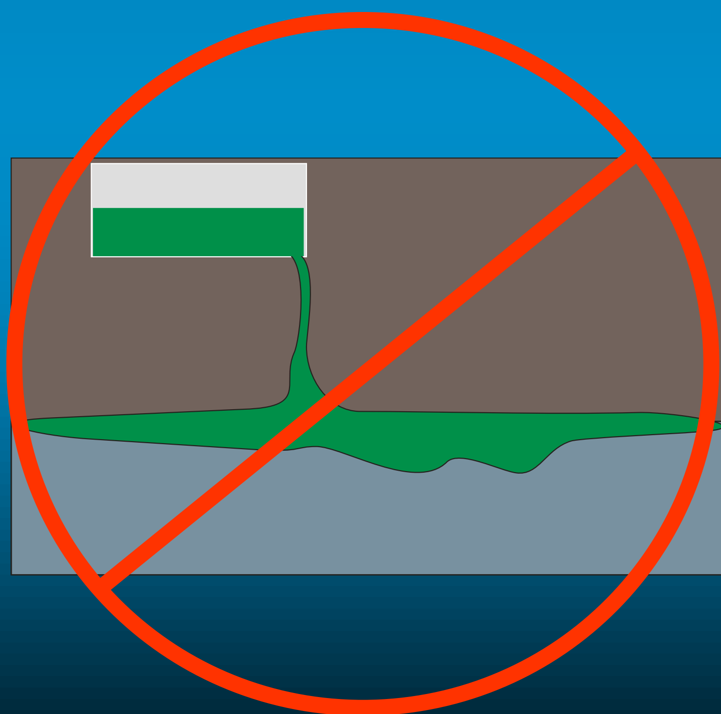
we can't eliminate PAH exposure risk <u>until the LNAPL is removed or neutralized</u> – either by us or nature (treating just the groundwater is a short term 'fix')

you can't design remedy for problem LNAPL without knowing where it is

groundwater tools (wells) lack necessary qualities, specificity, and coverage

wells are for measuring SYMPTOMS – not the disease

zombie-like adherence to the "LNAPL floats on the groundwater's surface" 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

so the diagrams are (necessarily) simple

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

So who died and crowned you a NAPL Know-It-All?

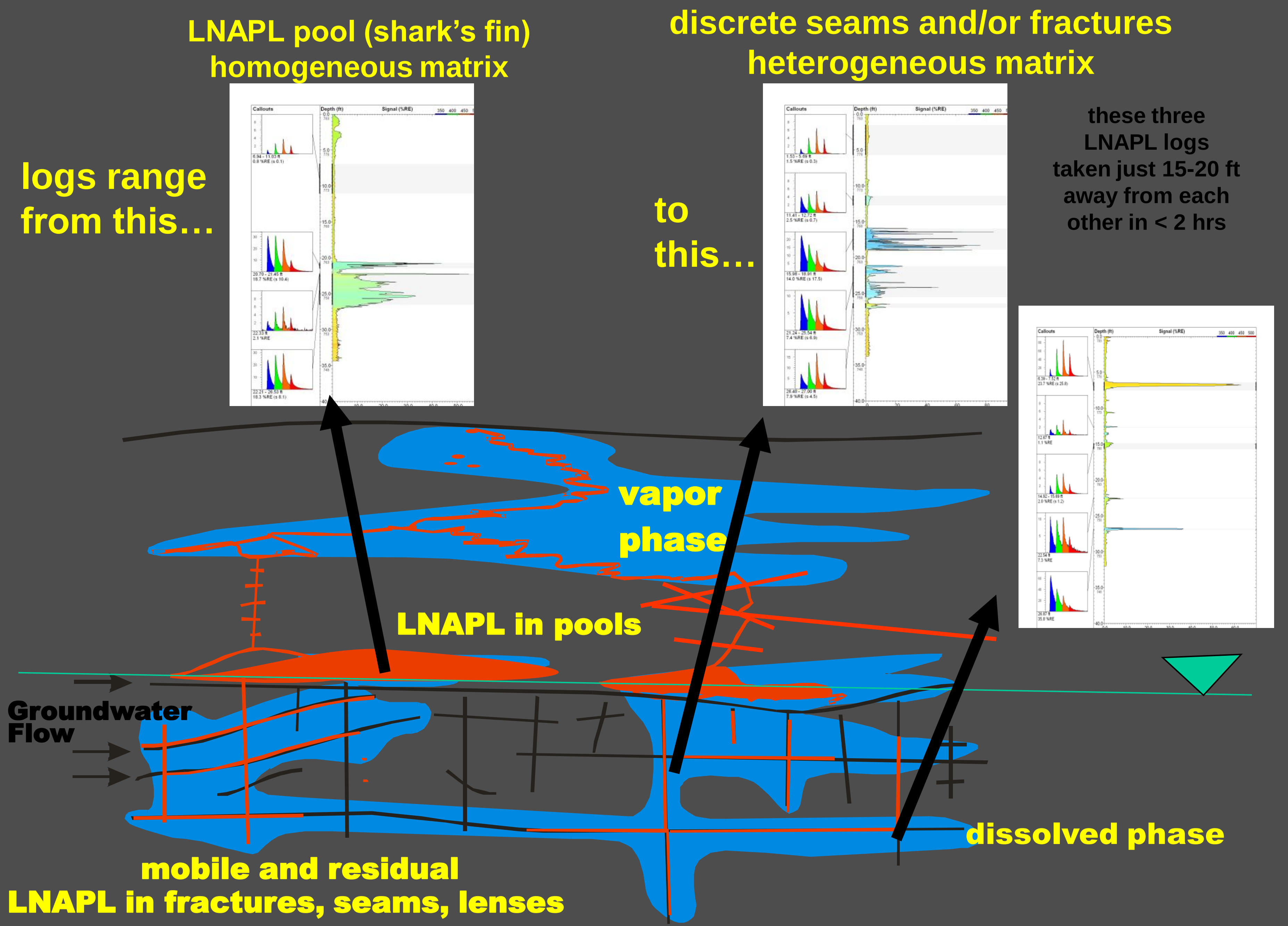
Simple… I've cheated, a LOT!

20 years of logging NAPL with LIF…

(today's focus) →

- 100s of miles of LNAPL logging with ultraviolet LIF (ROST, UVOST)
- 43 miles of DNAPL (known to be sneaky) logging with LIF: >200 sites (coal tar, etc.)

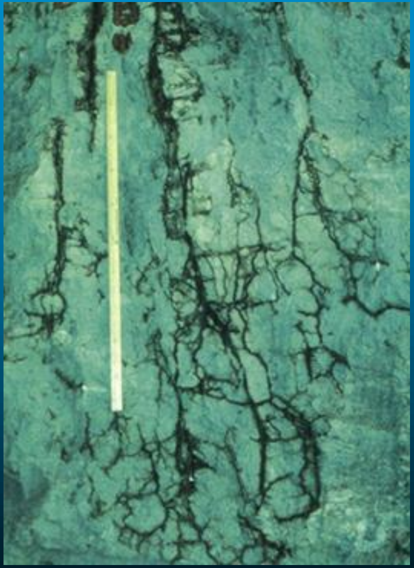
at some sites the LNAPL is more accurately depicted by classic DNAPL diagrams!



LIF has ability to prevent LNAPL CSM 'mistakes' or at least provide an autopsy of why the previous CSM was so misleading

- focuses on the LNAPL, not the symptoms (dissolved phase)
- productive (300-500 ft/day)
- LIF logs continuously
- results available immediately
- productivity allows side-by-sides (co-located logs)
- easy to add logs, go deeper, explore
- dismisses with confusing logging jargon like "odor", "affected soil", "potentially impacted", "product"
- LIF maps the site geology in many cases because LNAPL prefers to travel in sand/gravel/fractures while avoiding clays and other fines (unless fractured)

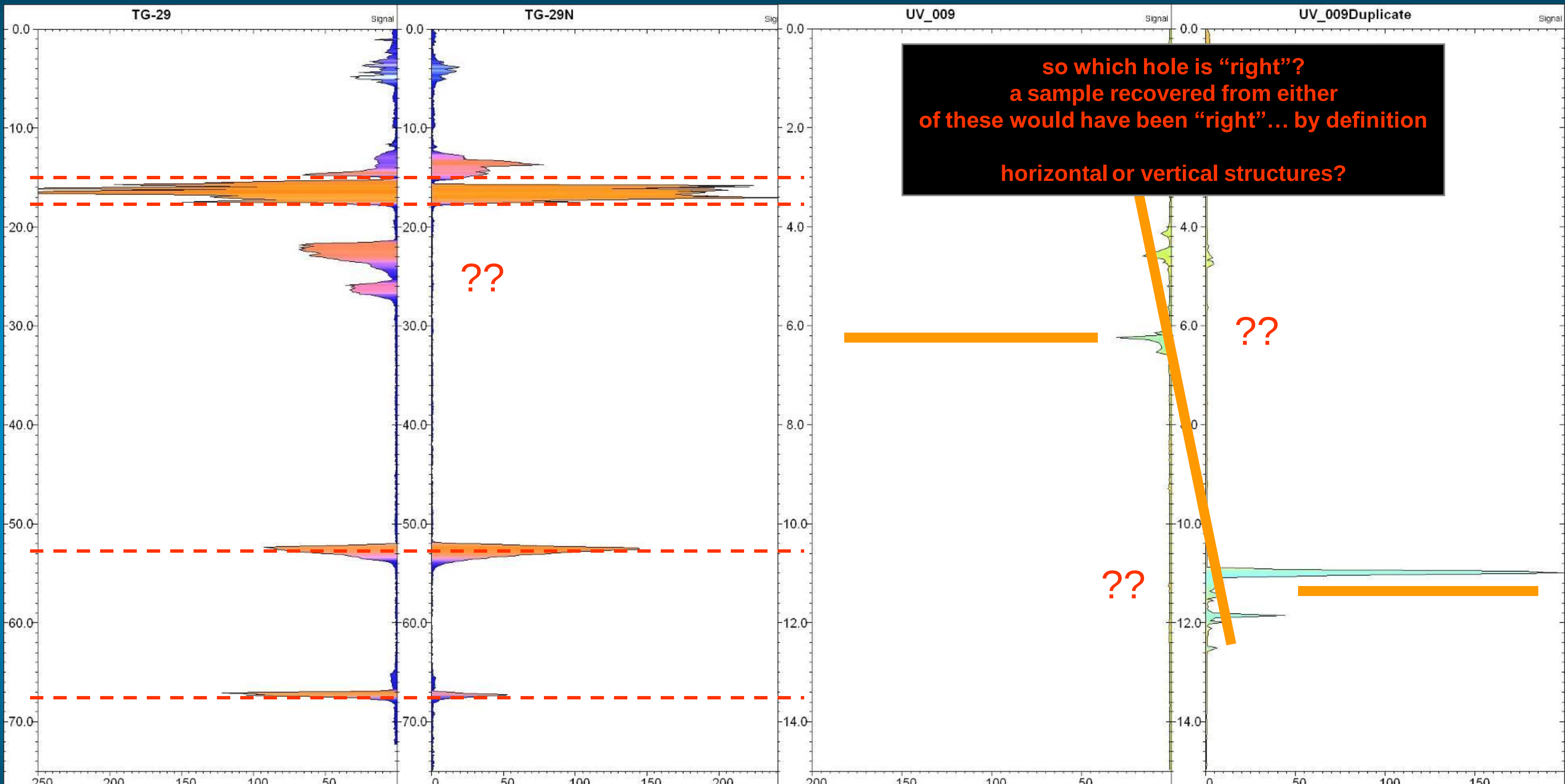
why has the NAPL distribution often been so difficult to delineate using traditional tools?



- 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
- NAPL 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 <u>water</u>, not LNAPL – they simply can’t be trusted for LNAPL

measuring localized heterogeneity with LIF

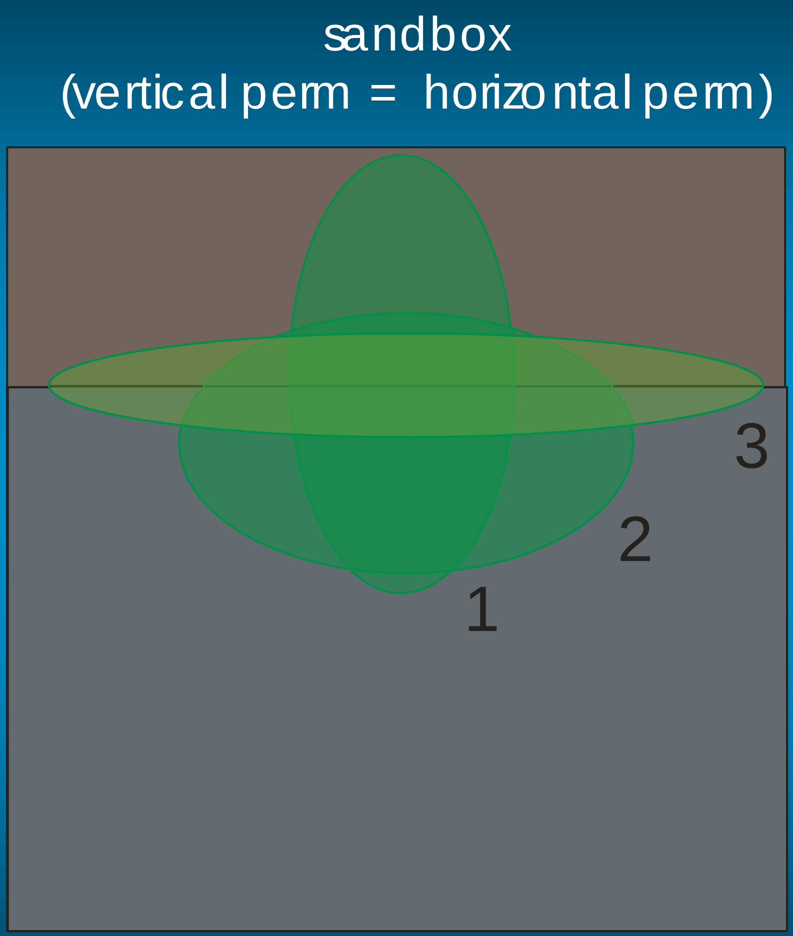
do you ever continuously core/sample two locations side-by-side? why not?
we encourage our clients to do so at every site and results are very insightful

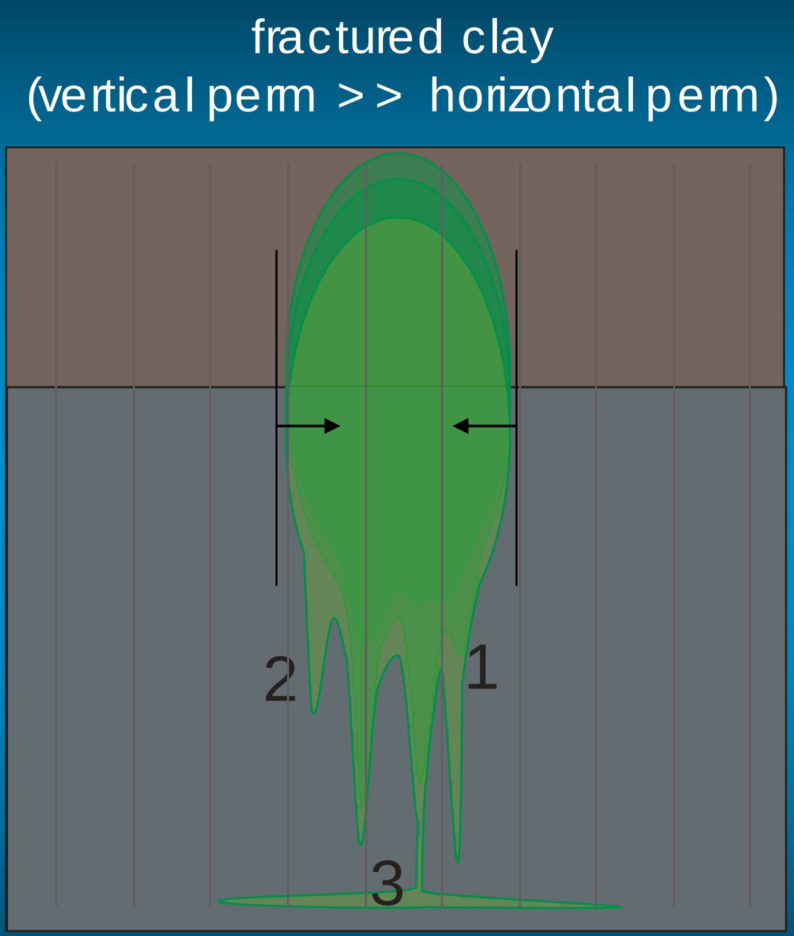


localized coal tar "layers" confirmed
[TarGOST data]

NOT "layers" of gasoline
[UVOST data]

LNAPL far below groundwater **potentiometric** surface?





fuel free to flow laterally….

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

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

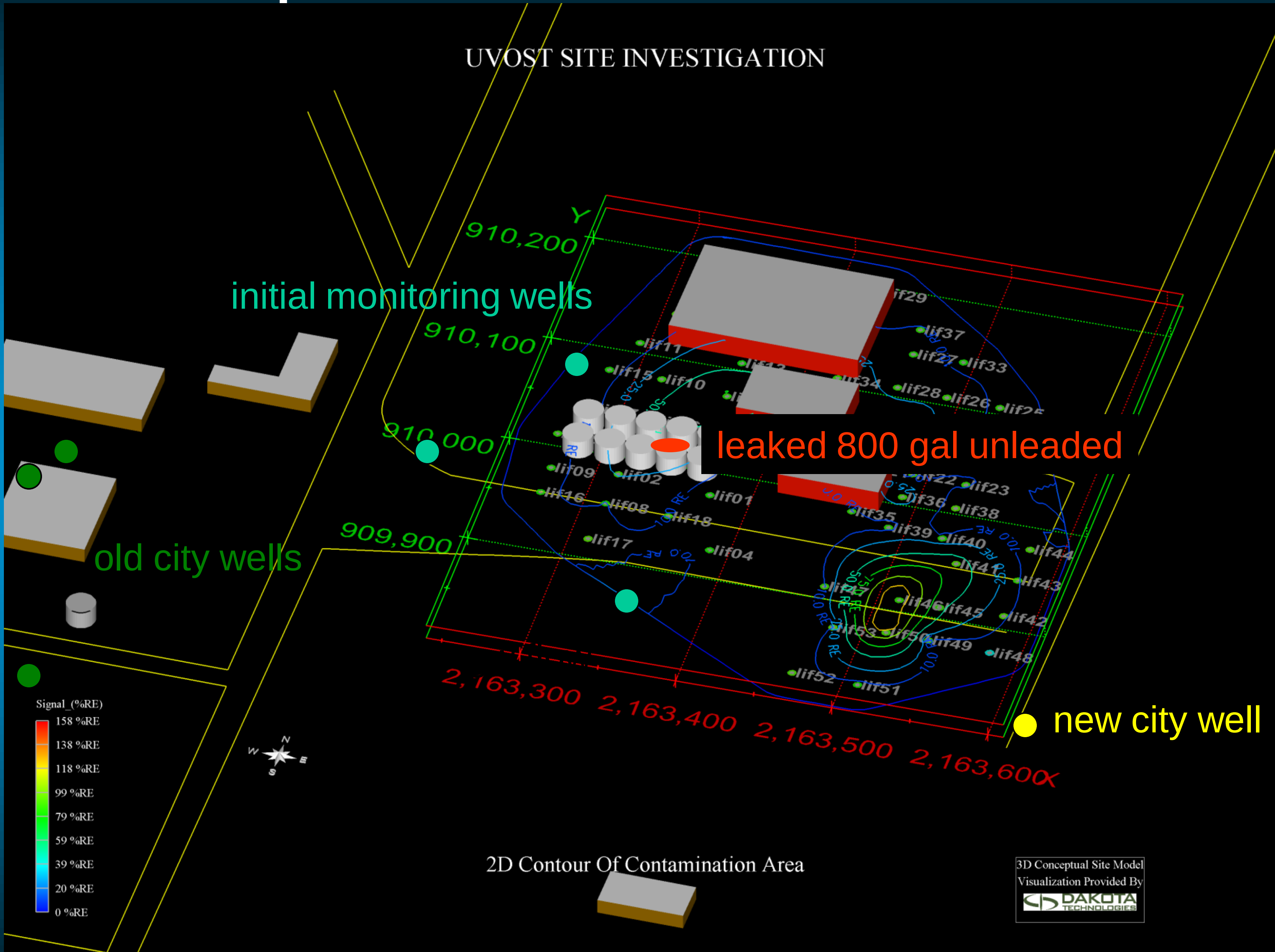
- site was closed 1997 – monitoring wells were pulled
- in 2000 - new high-capacity city supply well installed 300-500 ft away

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

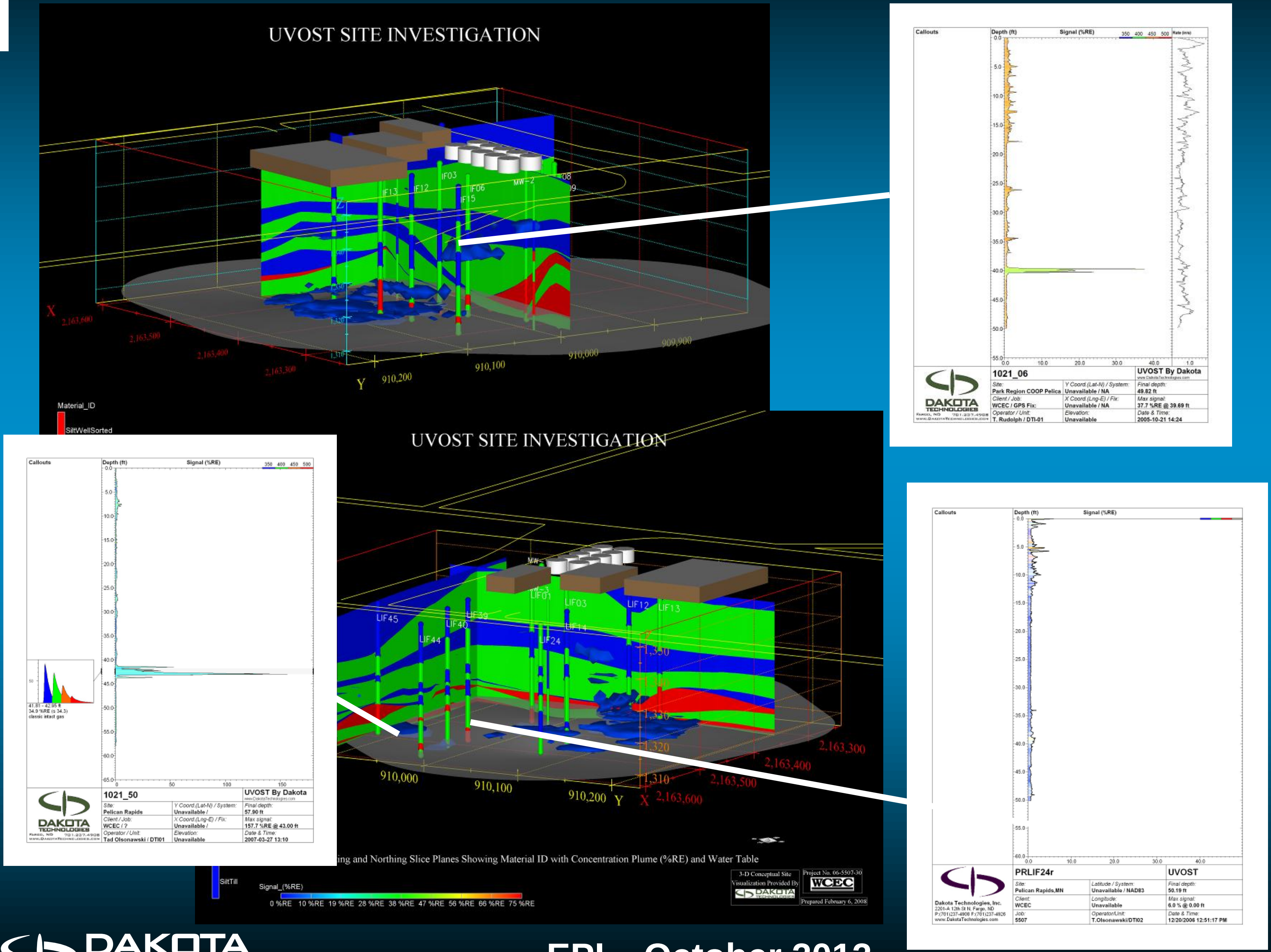
- new monitoring wells installed… still confusing, no NAPL in them!

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

example LNAPL misbehavior #1

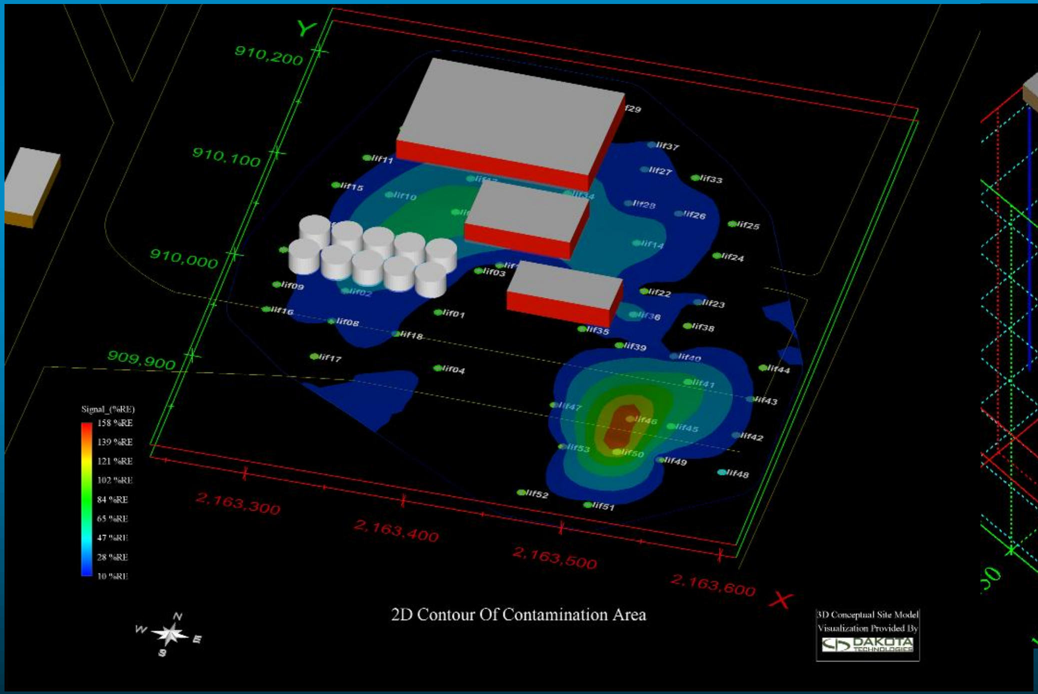


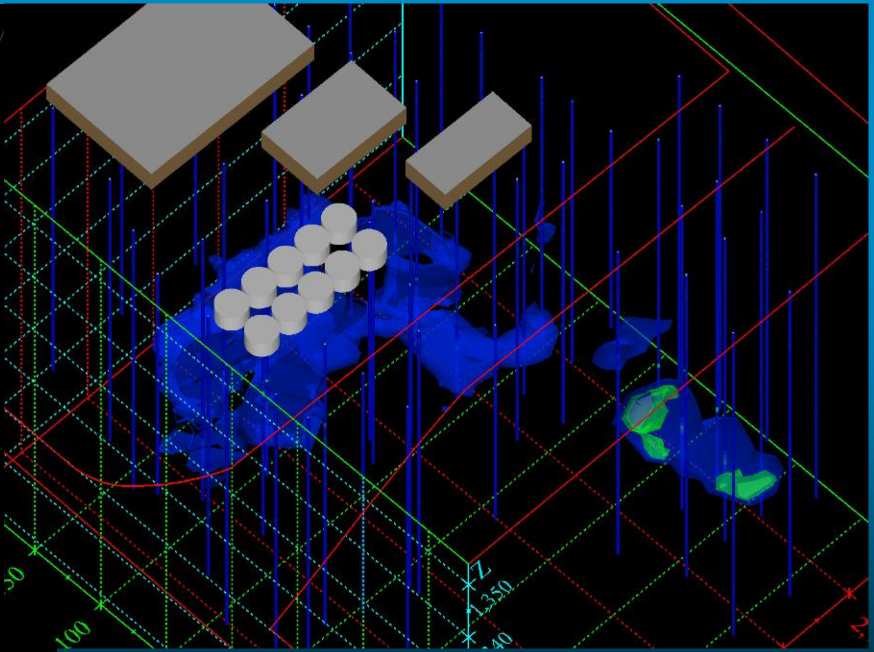
50 LIF (UVOST) borings ~ 4 days work



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 – <u>no well has measurable LNAPL</u>! 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

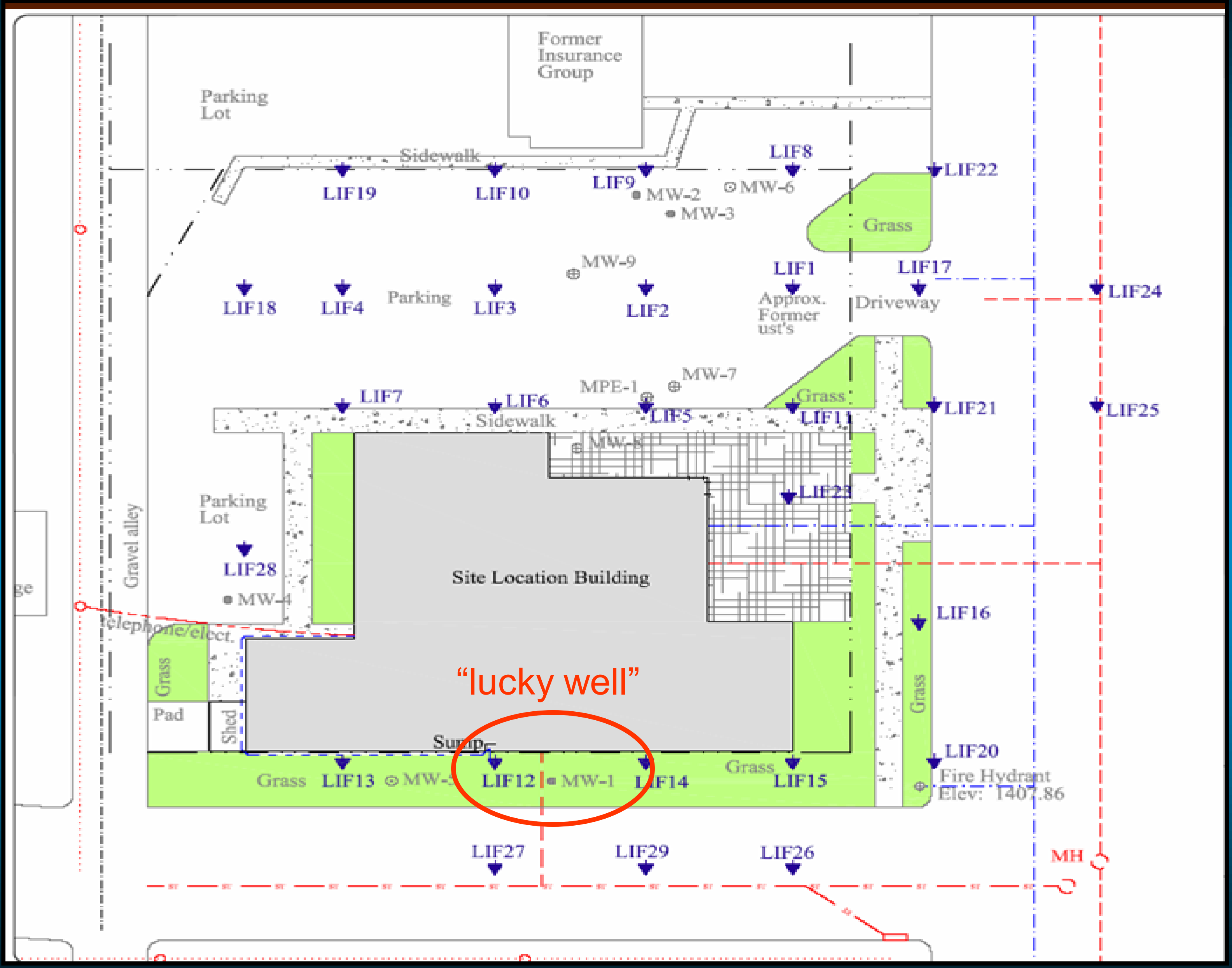
- fuel release site
- tanks were removed – no sign of significant release
- one mandatory well was inadvertently screened 18-28 feet <u>which is 5-6 feet below groundwater surface</u>
- only this “wrongly constructed” well detected LNAPL!

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

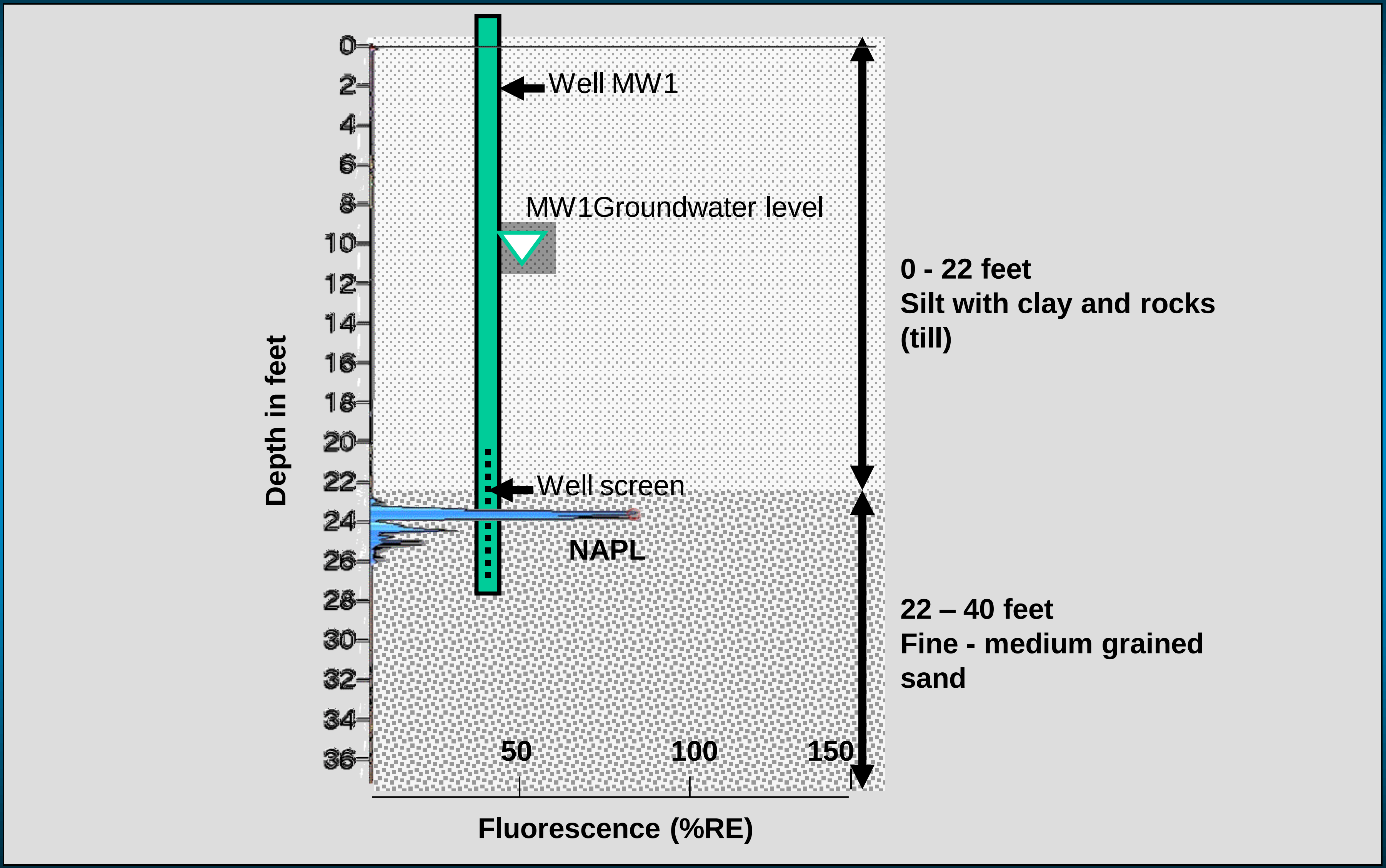
if fuel was released, it’s got to float and show up… right?

so what’s going on?....

example LNAPL misbehavior #2

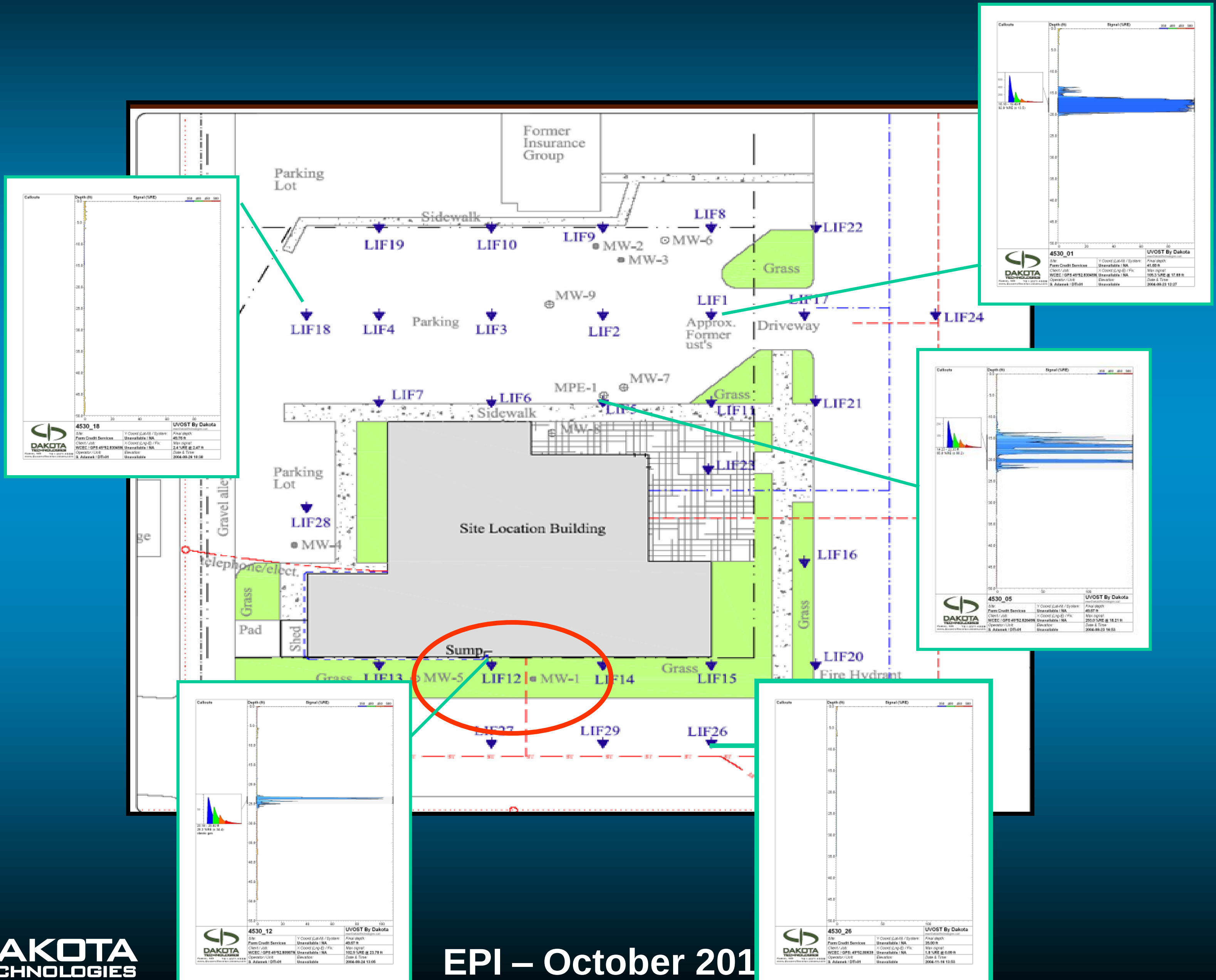


“lucky” well

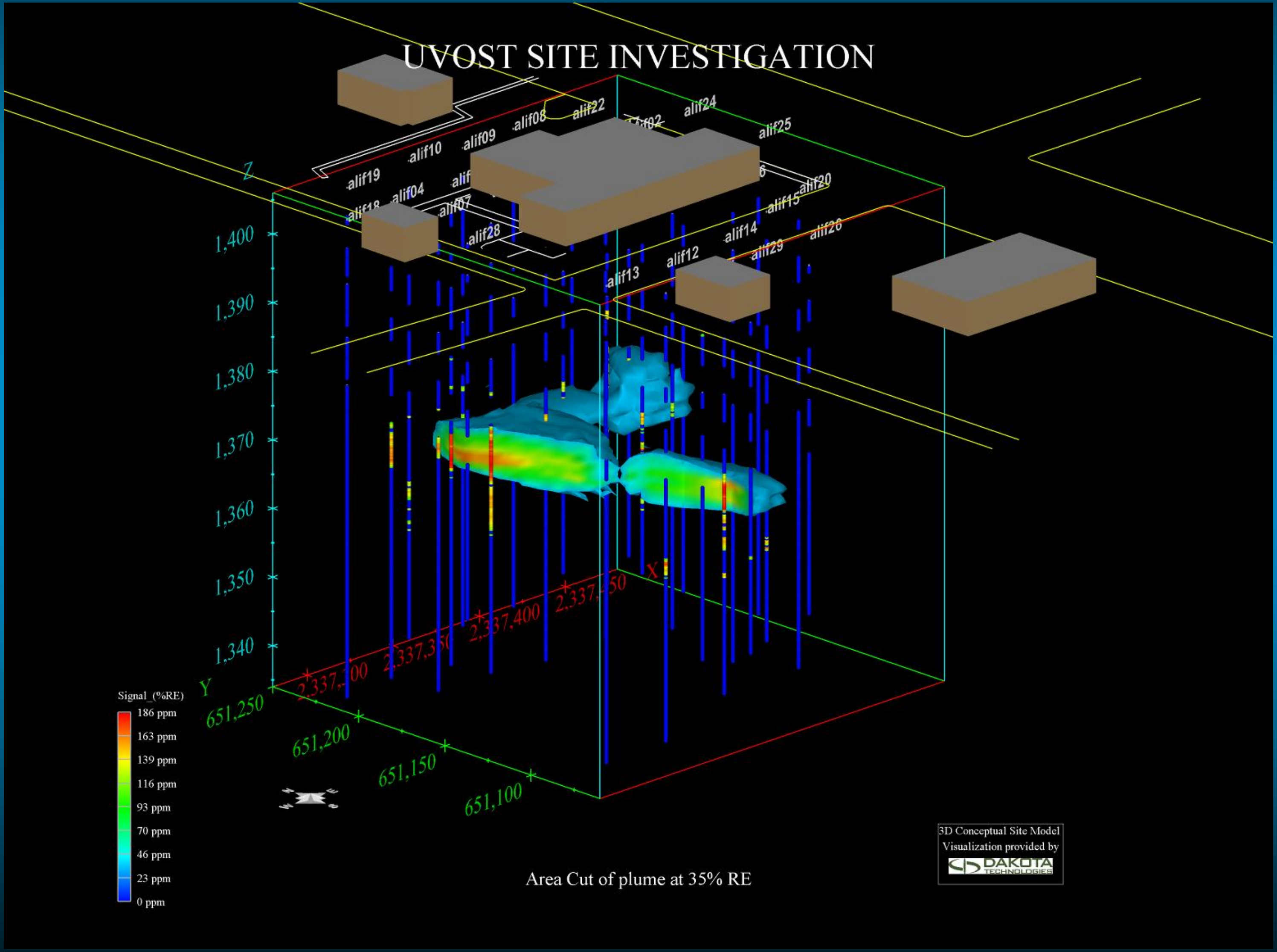


Depth in feet
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
Well MW1
MW1Groundwater level
Well screen
NAPL
50
100
150
Fluorescence (%RE)
0 - 22 feet
Silt with clay and rocks
(till)
22 – 40 feet
Fine - medium grained
sand

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

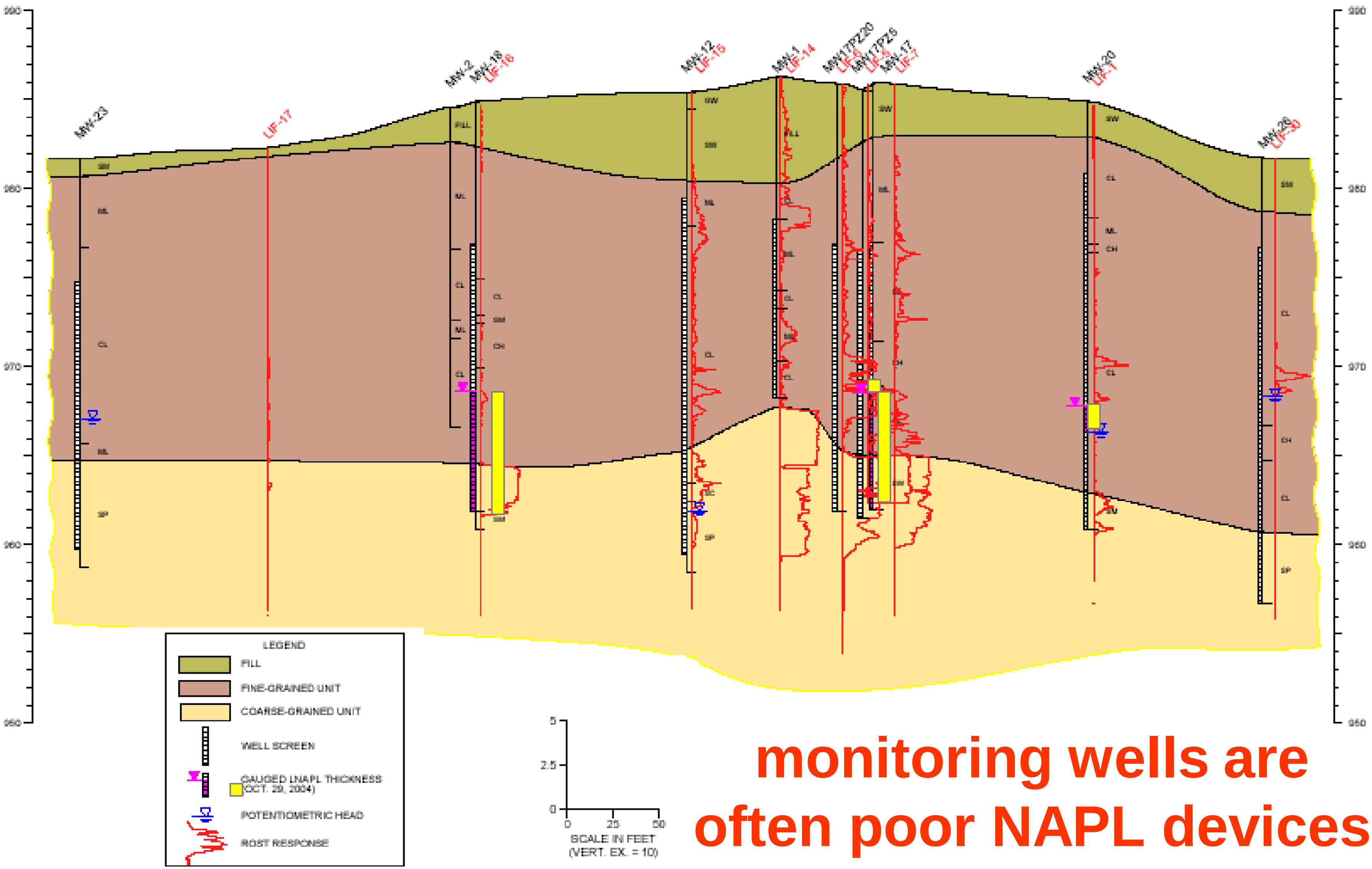


a very large "sunken" gasoline body was located with LIF somehow the gasoline (via pressure/head) had filled the porous sand unit under the clay/silt



example NAPL misbehavior #3

wells show little if any correlation with LNAPL distribution defined by single LIF transect!



monitoring wells are often poor NAPL devices

Example LNAPL misbehaviors # 4, 5, 6….

L.U.S.T.LINE

New England Interstate Water Pollution Control Commission
Bulletin 68
June 2011

Paul Stock is a hydrologist with the Minnesota Pollution Control Agency, Petroleum Remediation Program. Paul can be reached at paul.stock@state.mn.us.

Where's the LNAPL?
How about Using LIF to Find It?

by Paul Stock

The Minnesota Pollution Control Agency (MPCA) Petroleum Remediation Program (PRP) routinely uses data from laser-induced fluorescence (LIF) probes to target petroleum light non-aqueous phase liquids (LNAPLs) when remediation is necessary. Given our experience in using LIF, PRP staff had gained a great deal of insight on LNAPL behavior and found themselves nodding their heads in agreement during the Interstate Technology Regulatory Council's (ITRC) internet-based training on LNAPL behavior when it first became available in March 2009.

A couple of months ago, several PRP technical staff were invited to attend a dry run of the ITRC's LNAPL Classroom Training in order to provide the ITRC's LNAPL Team with feedback. The LNAPL Team has developed a set of excellent classroom training modules that lay out the latest understanding of LNAPL behavior using a multiple lines of evidence approach—LNAPL science. if you will. This science is consistent with and provides a much deeper understanding of what PRP staff have observed about LNAPL behavior using LIF. The LNAPL Classroom Training also includes a process for selecting the appropriate remedial technology to address specific LNAPL concerns using an LNAPL science-based site conceptual model (SCM). You may have guessed by now that one of the first things one needs know is: where's the LNAPL?

The PRP has found that LIF data can reliably answer the question: where's the LNAPL? Moreover, LIF data can also help lead to answers for many other important questions about site-specific LNAPL behavior and its remediation. After more than a decade using LIF, we have concluded that its strategic application results in cost-effective use of limited resources. The word must be getting out. More frequently over the past couple of years, we have been contacted by regulators, consultants, contractors, and even some responsible parties from other states inquiring about the PRP's use of LIF. Recently, a regulator from another state invited PRP staff to train their staff on how to interpret LIF data. The following discussion has been designed to address some of these questions.

NOTE: I should explain that, as we became more aware of what LIF was telling us about the behavior of petroleum products released in the subsurface, we began to abandon the term "free product" in favor of LNAPL. We believe that LNAPL is more scientifically accurate and descriptive, and less prone to past and existing misconceptions about free product. However, I will occasionally use the term "free product" in the following discussion when historically appropriate.

What Is LIF?

Folks working the oil patch have long used ultraviolet light to induce fluorescence when examining drill cuttings for the presence of petroleum hydrocarbons. That basic principle can be applied to the down-hole environment. As a probing tool is advanced to depth, ultraviolet light is directed through a transparent window on to the immediately adjacent soil and whatever fluid occupies the soil pores. A sensor detects and records any florescent light returning through the window.

Essentially, the more petroleum present in the pores adjacent to the window, the stronger the recorded fluorescent response. Because different chemical compounds predictably fluoresce at varying wavelengths and decay times, even more information can be gleaned from further analyses of the light returning to the sensor. In addition, filters can be used to eliminate or reduce unwanted responses.

I am aware of two companies that design and produce commercially available field sensors using ultraviolet light to induce fluorescence of aromatic hydrocarbons for detecting petroleum LNAPLs in the subsurface: Vertek, a division of Applied Research Associates, Inc., out of Randolph, Vermont; and Dakota Technologies, Inc. (DTI), out of Fargo, North Dakota. Information on Vertek's and DTI's respective sensors can be found at *www.vertekcpt.com* and *www.dakotatechnologies.com*.

These sensors are designed to detect lighter and heavier petroleum-based fuels, oils (including crude and lubricants), and/or creosote and tar. The main output is in the form of a graph, typically called a log, of fluorescent response versus depth for each probing location. When a laser is used to generate the ultraviolet light, the technology is generically referred to as laser-induced fluorescence, or LIF for short. Figure 1 shows a sample LIF log.

The Ins and Outs of LIF

It is important to note that induced fluorescence data must be integrated with all available standard site data, including site history, present land use, geology, and soil and groundwater contamination, to develop an SCM using multiple lines of evidence. Moreover, considering typical geological heterogeneity and consequential LNAPL behavior, the benefits of viewing side-by-side LIF and geology data can hardly be overstated.

The induced fluorescent tools are typically deployed with Cone Penetrometer Testing (CPT) or Electrical Conductivity (EC) sensors. These sensors allow collection of side-by-side, high resolution, geologic data. CPT and EC often provide a more objective and complete data set than obtained from typically limited geologic descriptions of physical soil samples collected during routine site investigations.

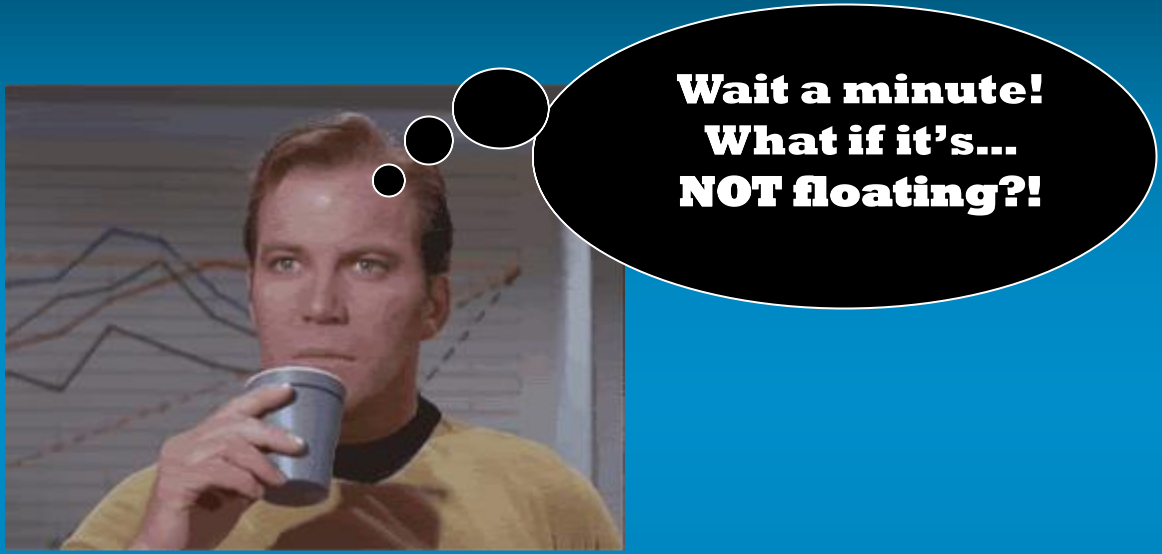
LIF detects polycyclic aromatic hydrocarbon (PAH) molecules (e.g., naphthalene, perylene, anthracene) that fluoresce efficiently when present in an aliphatic solution like typical petroleum LNAPLs composed of gasoline, diesel, heating oil, kerosene, jet fuel, and so on. We have also used LIF to delineate heavier

▪ *continued on page 14*

http://www.neiwpcc.org/lustline/lustline_pdf/lustline_68.pdf

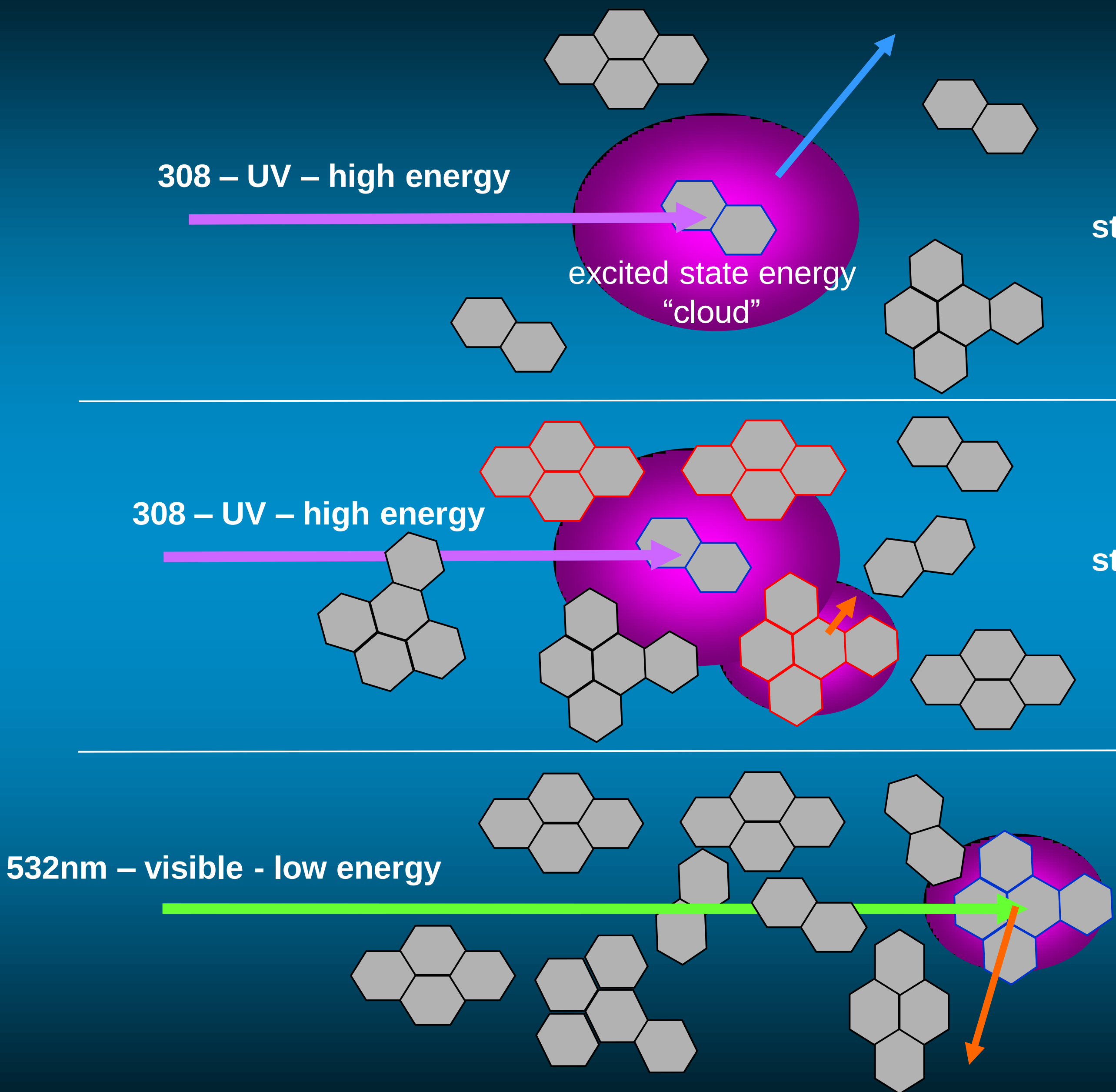
suggestion

next time your LNAPL site is confusing you, consider this…



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

PAHs, Excitation Wavelength, and Energy Transfer



dilute PAHs
(fuels and light oils)

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

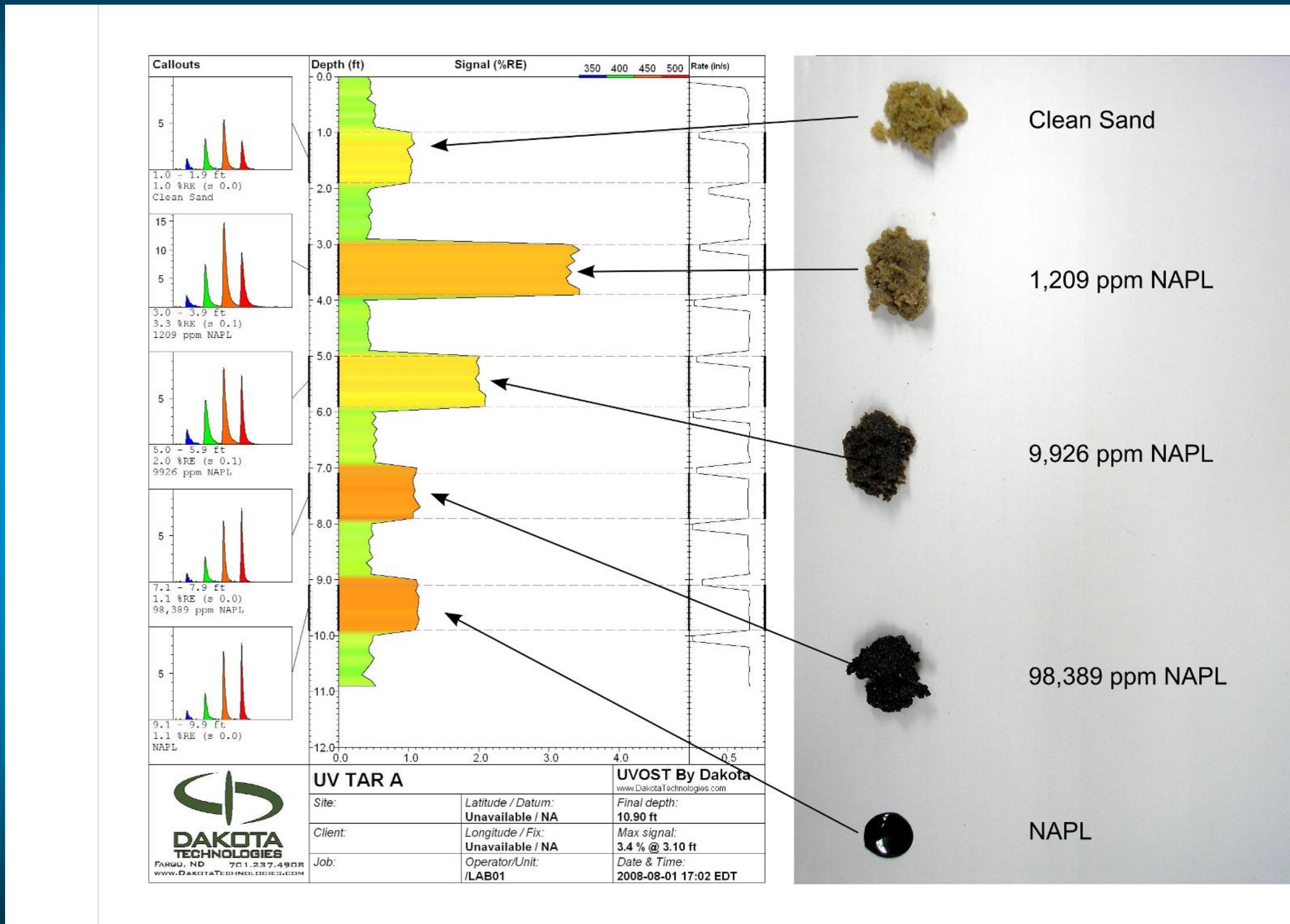
conc'd "close packed" PAHs
(tars, creosotes, heavy crude)

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

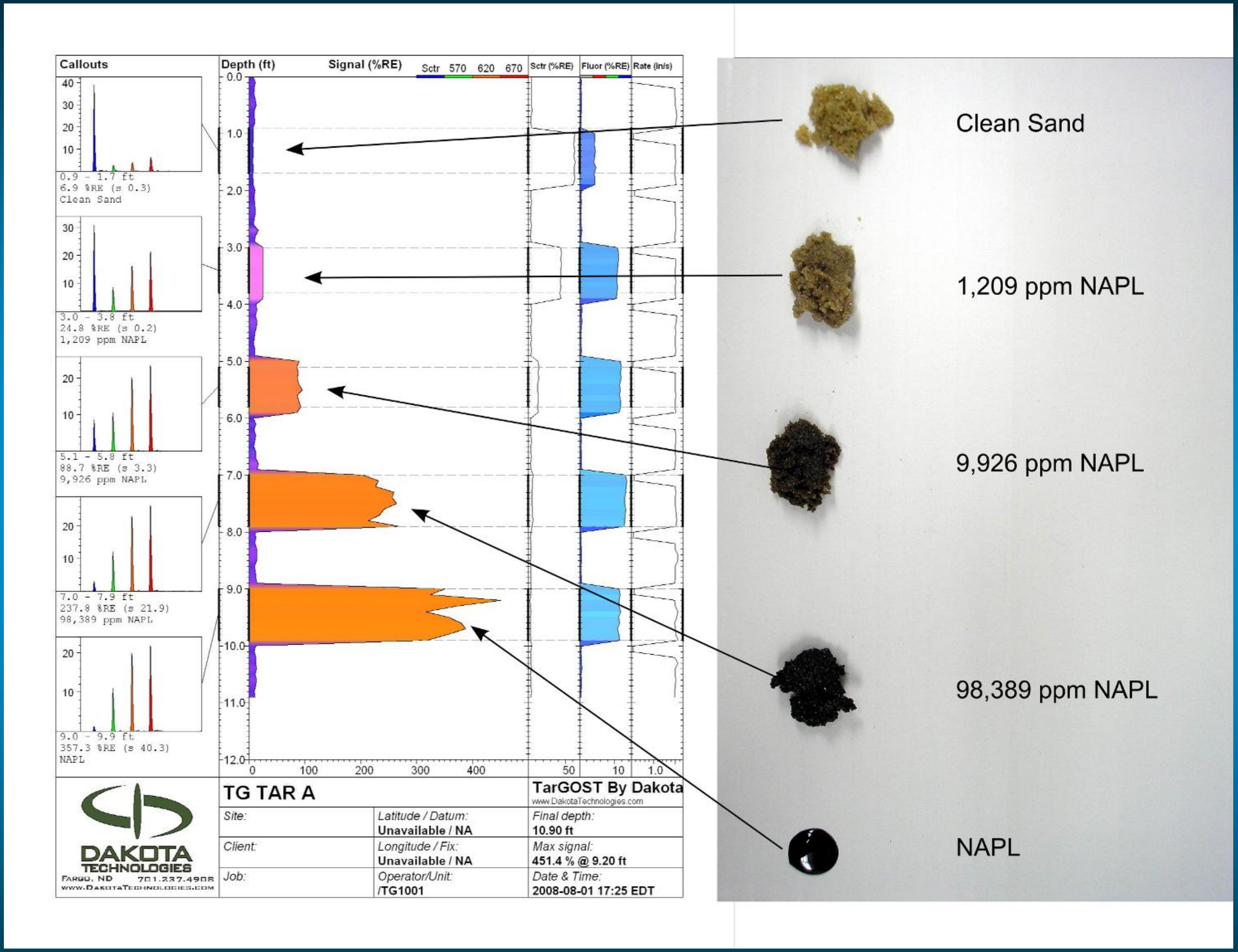
conc'd "close packed" PAHs
(tars, creosotes, heavy crude)

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

typical MGP NAPL (coal tar) on UV LIF



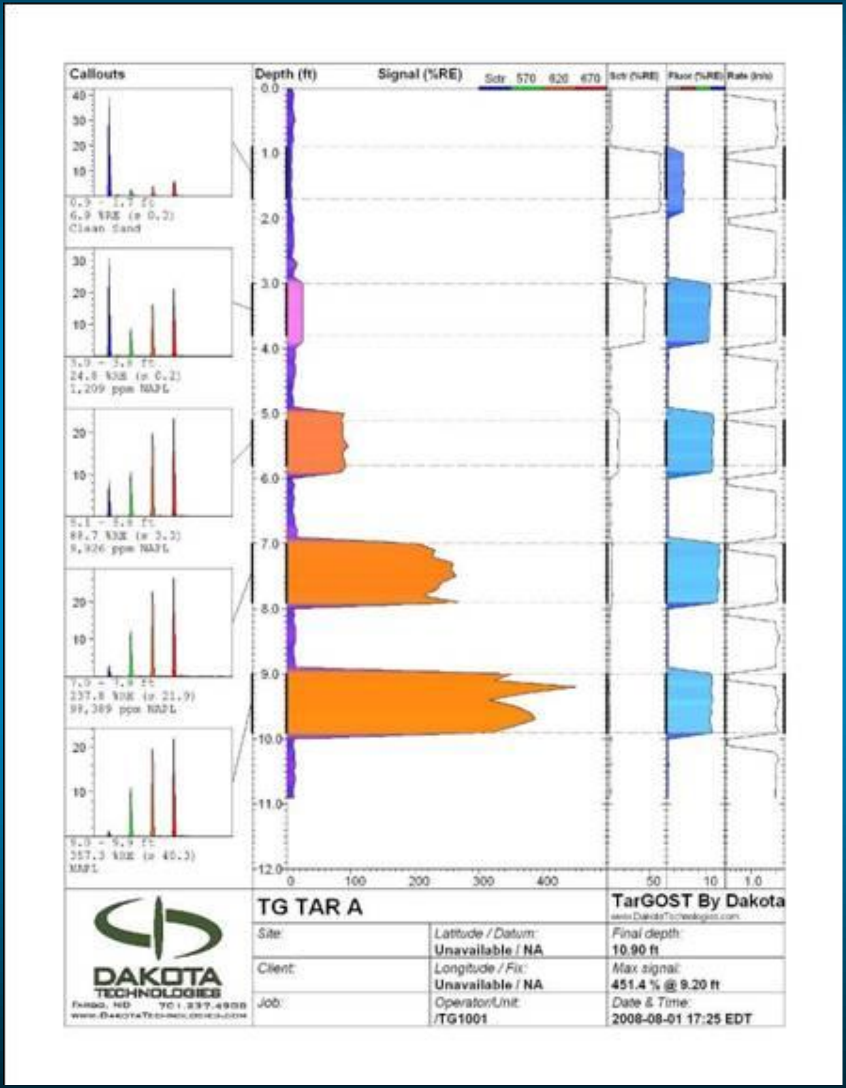
typical MGP coal tar on TarGOST



typical MGP coal tar on UV LIF vs TarGOST

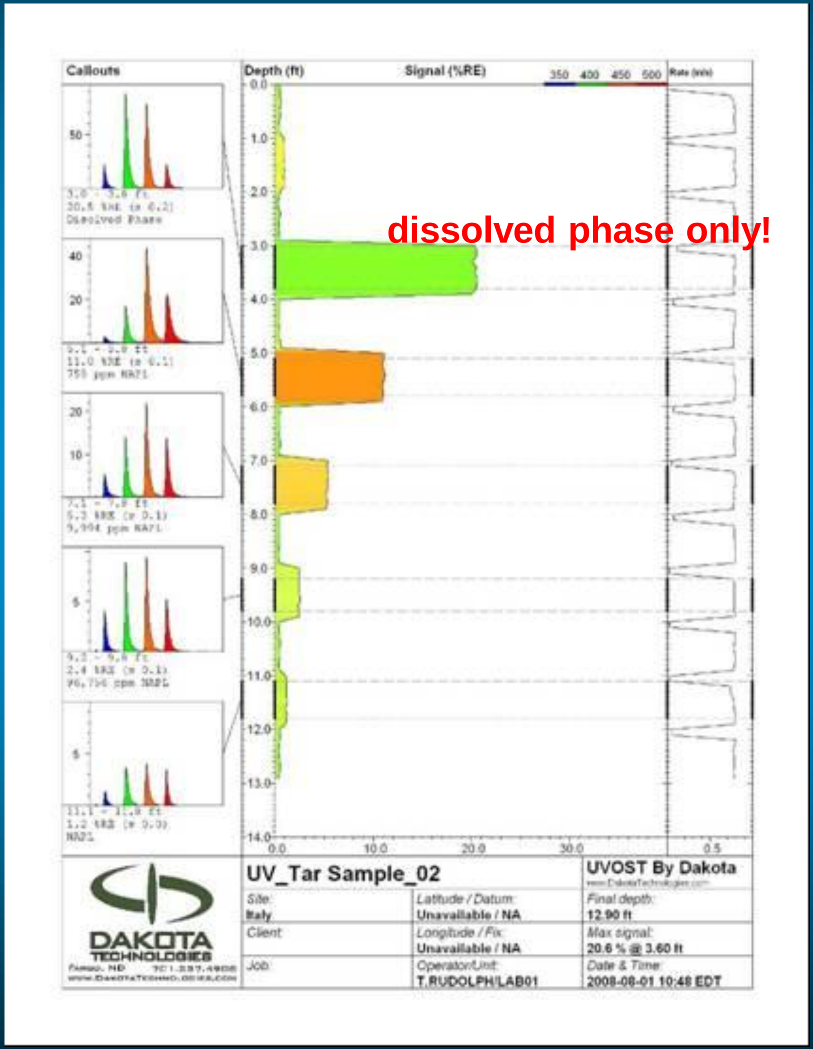
UVOST

TarGOST

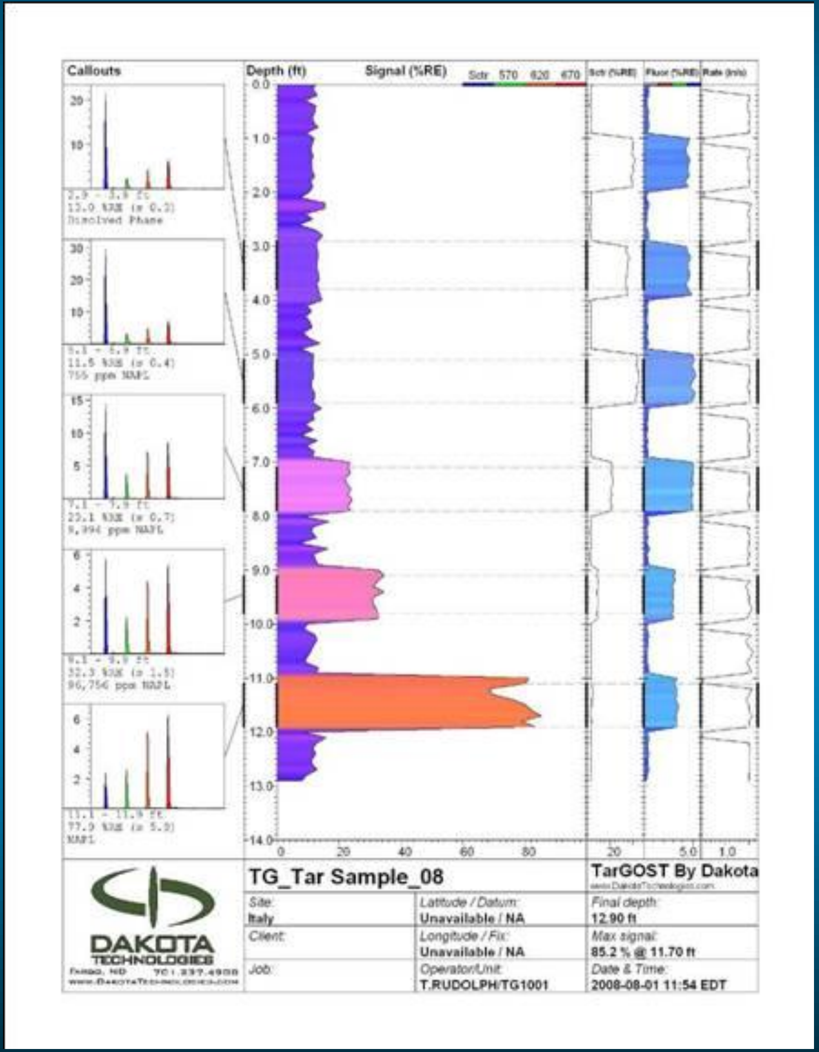


pitchy coal tar on UV LIF vs. TarGOST

UVOST

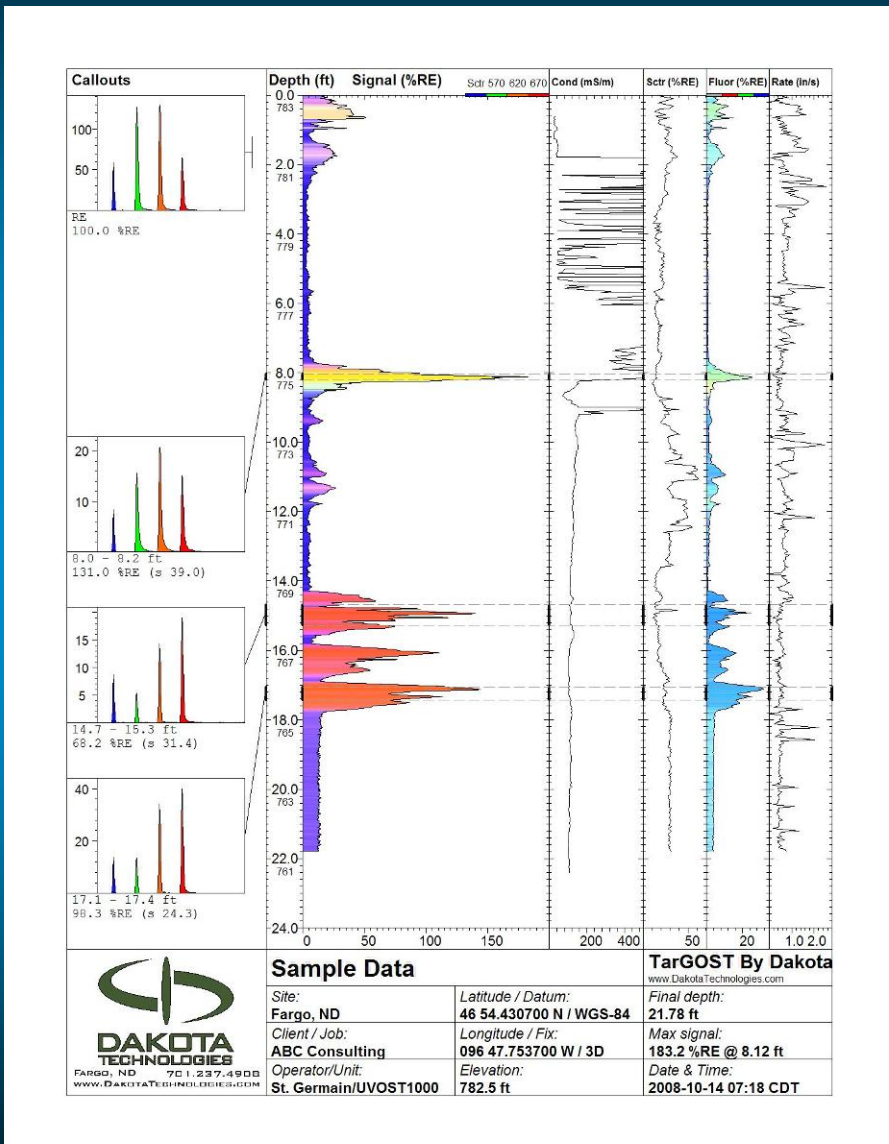


TarGOST

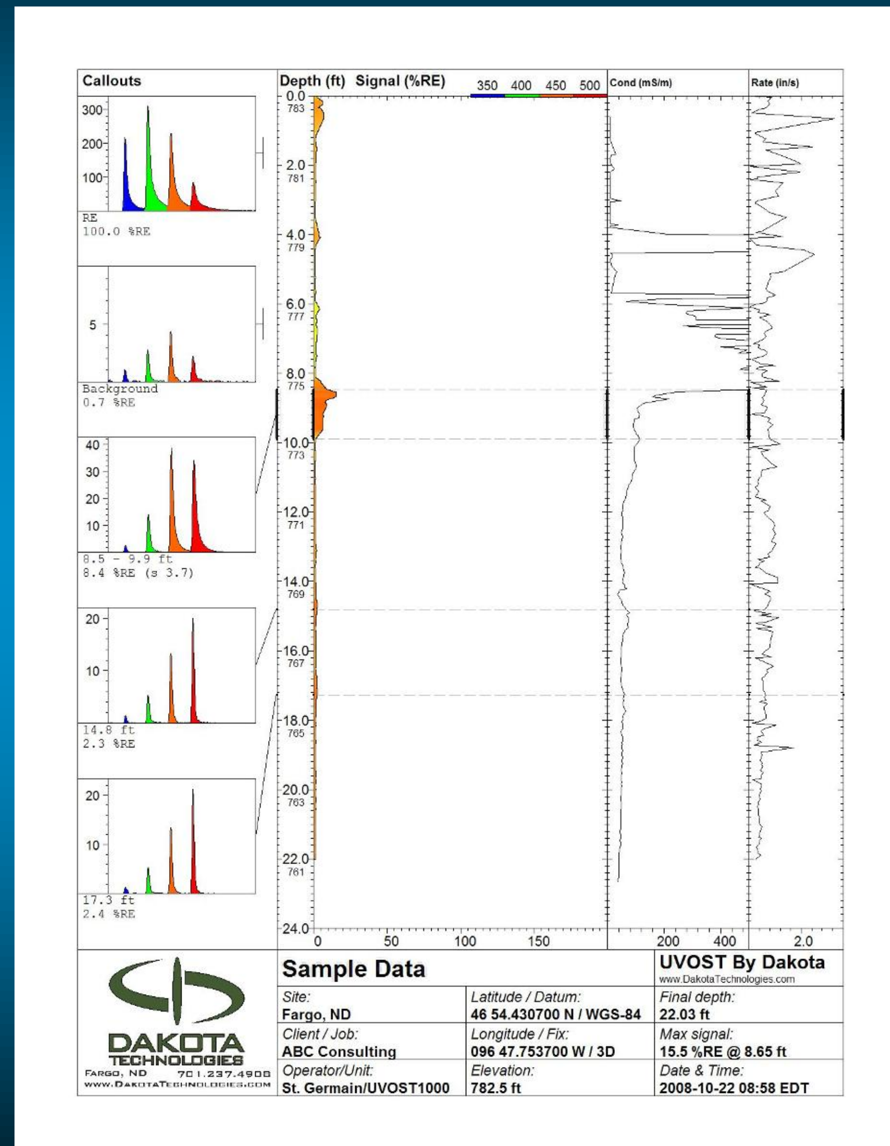


coal tar – former MGP – duplicate logs

TarGOST



UVOST

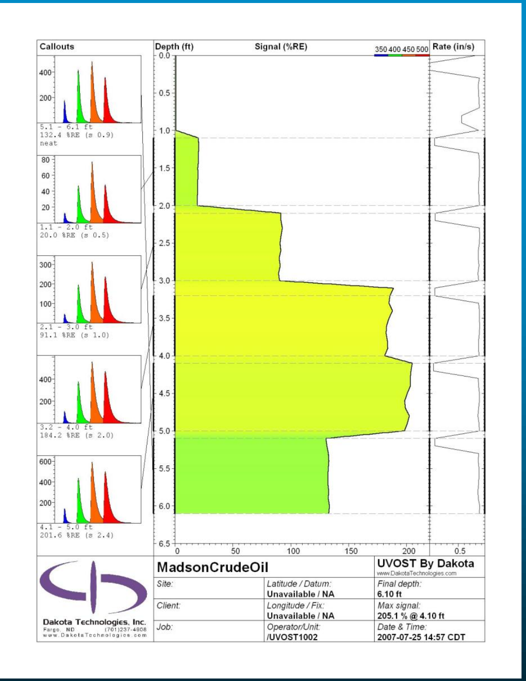


“Heavies” are incompatible with UV LIF

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

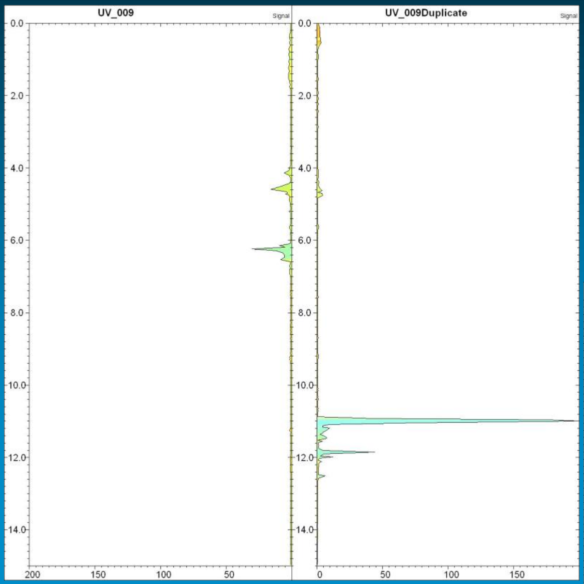
Dakota's Stance on Screening for High-PAH Content NAPLs (aka "heavies") with UVOST

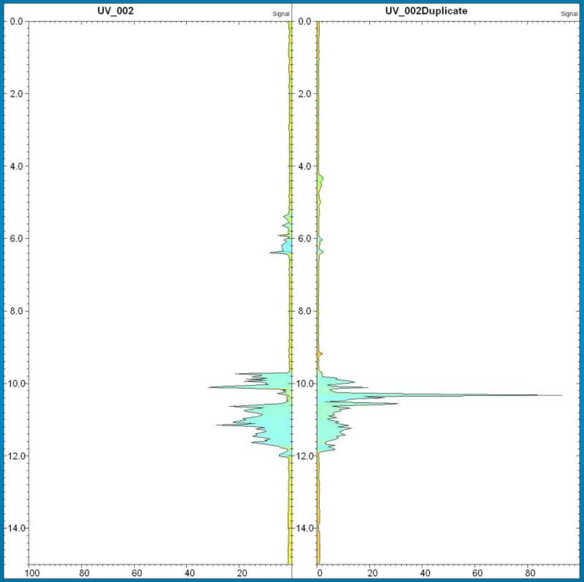
Dakota desires to limit our potential legal exposure should litigation result from UVOST characterization of a coal tar or creosote site. Legal risk is your reason to take this matter seriously and avoid getting yourselves involved in a "heavy" NAPL site investigation with UVOST.

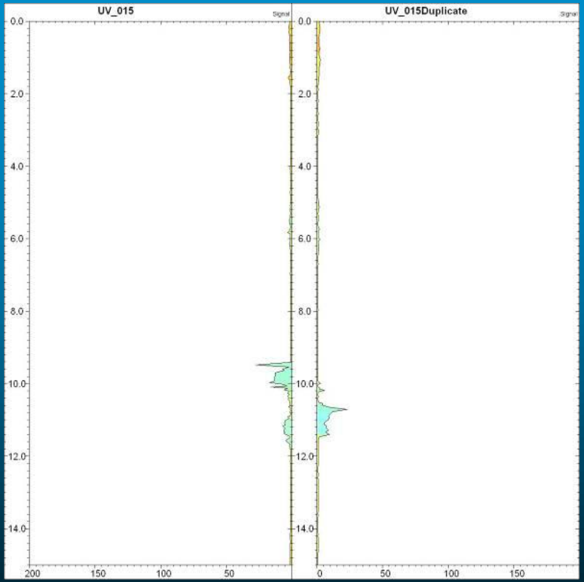
For this reason, DAKOTA HEREBY OFFICIALLY DIVORCES ITSELF OF ANY/ALL DATA RESULTING FROM **PURPOSEFUL** APPLICATION OF UVOST ON A COAL TAR, CREOSOTE, OR OTHER SITE KNOWN TO CONSIST OF THESE OR SIMILARLY BEHAVED HIGH PAH CONCENTRATION NAPLS (heavies). In order to maintain the UVOST product's exceptional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

localized heterogeneity readily demonstrated with LIF duplicate locations

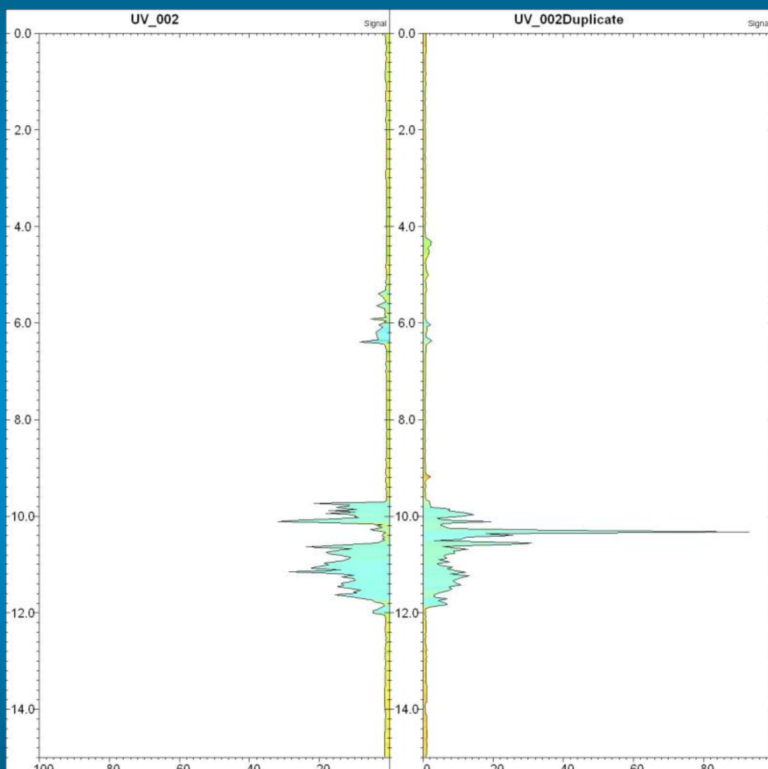
three butterflies from a gasoline spill
trapped gasoline (above and below water table)

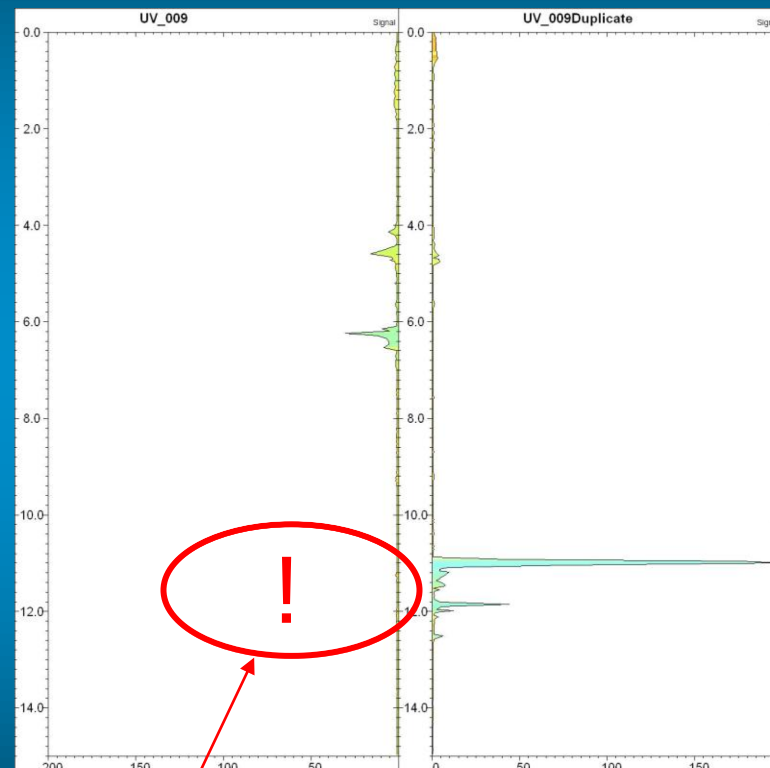






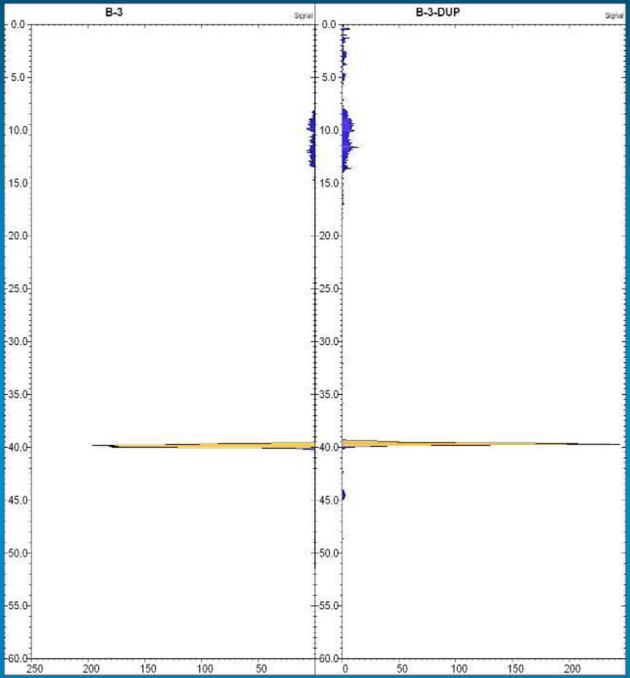
butterfly plots of UVOST logs

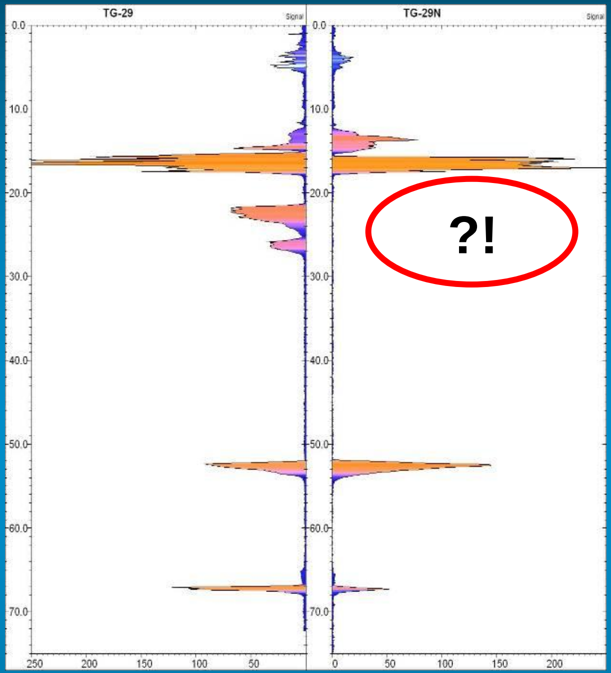


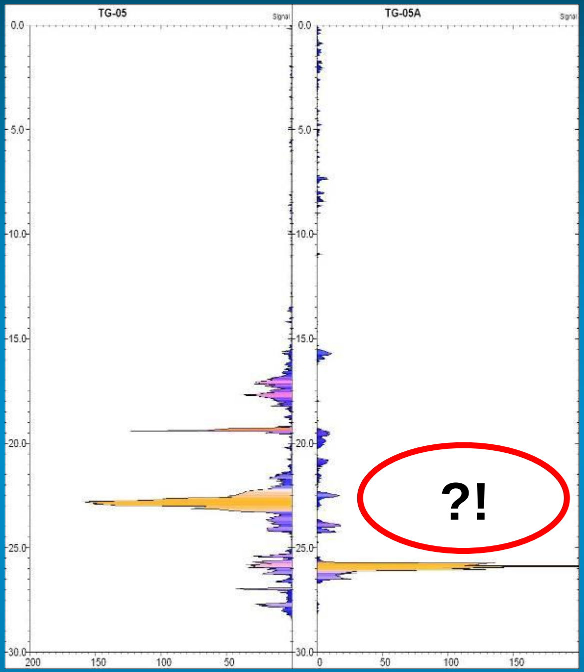


What if this was the "confirmation" sampling borehole? Which boring was "right"?

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!

and finally…some NAPLs are distributed like "floating pancakes"

(data generated for Don Lundy, ES&T)

Re-Delineation of Oil Body in May 2011