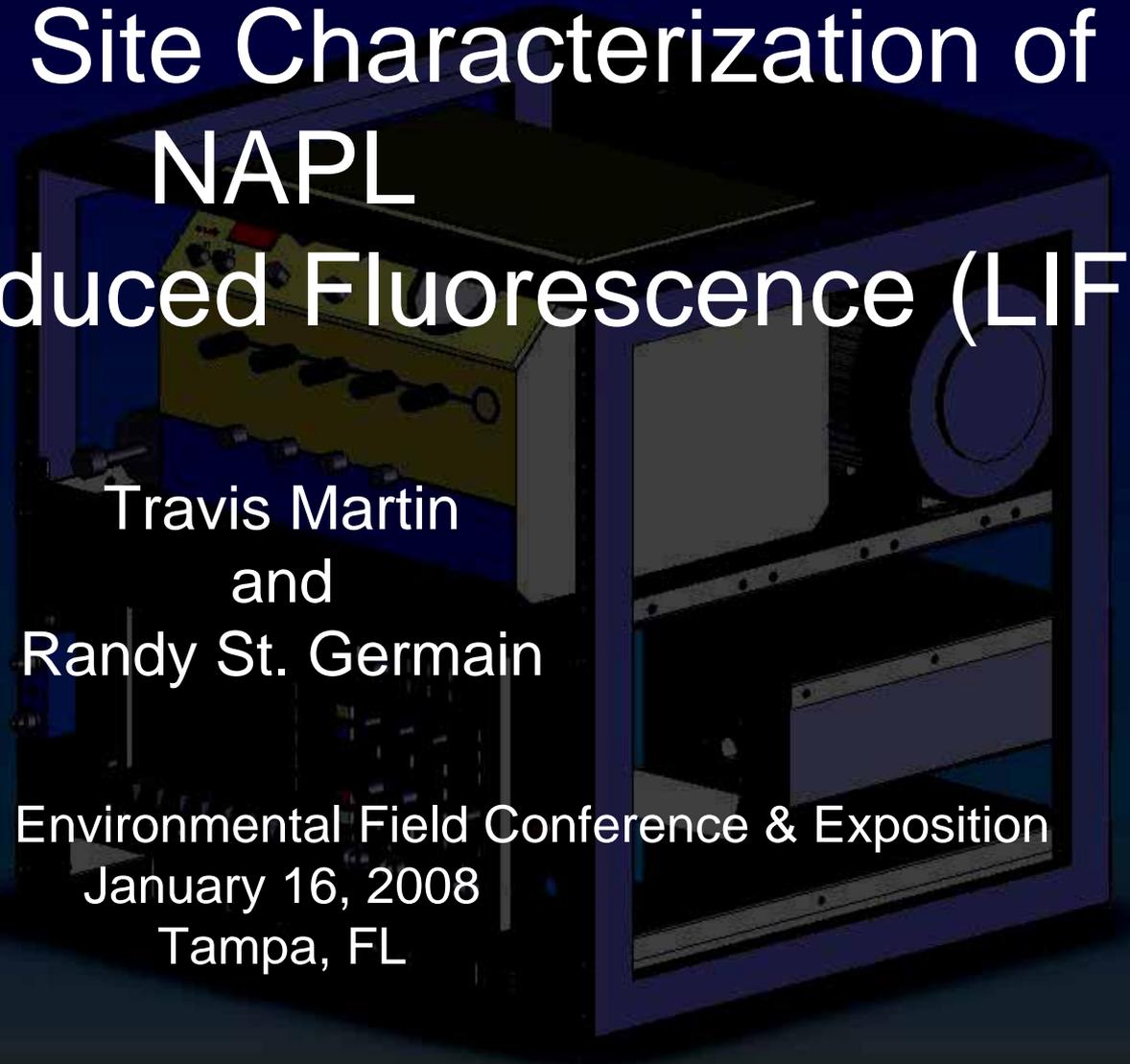


# Direct Push Site Characterization of NAPL with Laser-Induced Fluorescence (LIF)

Travis Martin  
and  
Randy St. Germain

2008 North American Environmental Field Conference & Exposition  
January 16, 2008  
Tampa, FL



# Today's LIF Workshop

- Brief History of LIF
- LIF instrumentation
- Spectroscopy
- Performance
- LIF's Pros/Cons
- Site Investigation Advice
- Example Logs and CSMs
- Real-time demo of UVOST™ and TarGOST®



# LIF detects PAH-containing NAPLs (“source terms”)

## Using UV excitation...

- Gasoline (highly weathered or aviation gas fluorescence yield is very low)
- Diesel
- Jet (Kerosene)
- Motor Oil
- Cutting Fluids
- Hydraulic Fluid
- Crude oil

## Using Visible excitation...

- Coal Tar (MGP waste) – often poor in UV due to self-quenching/intersystem crossing/photon cycling (energy transfer)
- Creosote/Pentachlorophenol (wood treating) – often poor in UV due to self-quenching/intersystem crossing/photon cycling (energy transfer)
- Bunker – often poor in UV due to self-quenching/intersystem crossing/photon cycling (energy transfer)

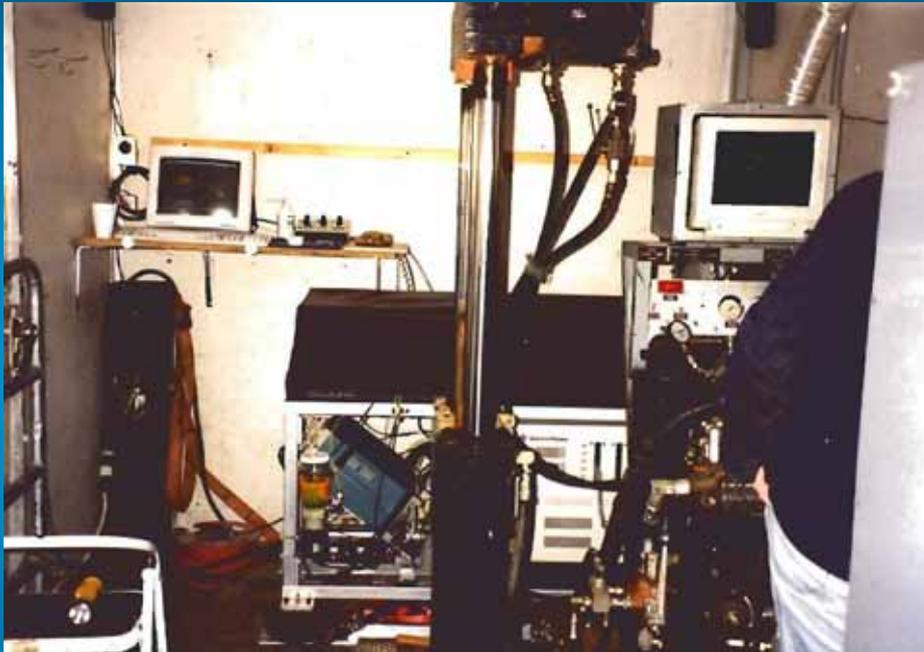
## Never/Rarely...

- 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 rarely respond
- dissolved phase (aqueous) PAHs

# Potential LIF Characterization Sites

- Leaking underground storage tanks
  - Pipelines
  - Refineries
  - Fueling areas
  - Fire-training facilities
- Automobile service locations (hydraulic fluid, POLs)
  - Surface spills
  - Lagoons - waste ponds
- former MGP (coal tar) and creosote (wood treating) sites

# The Past vs. Present



ROST prototype circa 1991



UVOST 2008

# Dakota Technologies' LIF History



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



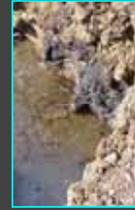
Dakota, Hogentogler, Unisys  
Develop Rapid Optical  
Screening Tool (ROST)



Dakota Develops Percussion-  
Capable Probe (SPOC)



"Dark Ages"



Dakota Technologies Introduces  
TarGOST Service



Dakota Technologies Introduces  
UVOST



1993

1996

1998

2006

1992

1994

1997

2003

2007

Lockheed Martin sells ROST  
Fleet to Fugro Geosciences



Dakota Technologies First  
Provides Regional "ROST"  
Service

Dakota Technologies  
Incorporates



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



# Dakota's LIF Service Totals

(3-4 field operators – part time - since 2000)

## UV LIF (ROST/UVOST™)

Total production: 90,289ft (17 miles)

# Logs: 2683

## Visible LIF (TarGOST®)

Total production: 92,316ft (17.5 miles)

# Logs: 3692

# Sites: 62

# Projects: 83

# Consultants 24

Average Feet/Day: 300-500 ft/day (barge work is obviously slower)

Best ever 10 hour day: 767 feet (TarGOST) November, 2007

# LIF Instrumentation

features a sapphire-windowed probe deployable  
with a wide variety of direct-push platforms

(percussion-based probes can be used when Dakota's SPOC™ sapphire-windowed probe is employed)

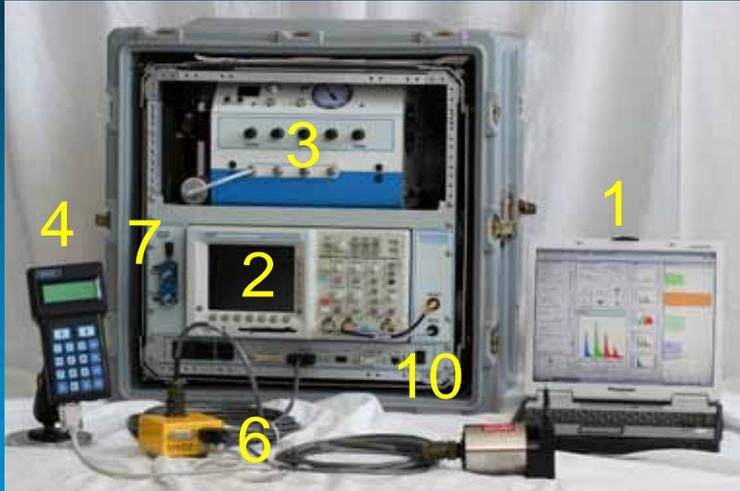


# LIF - a variety of direct-push platforms can be utilized to suit a wide range of site conditions



# LIF Instrument Hardware Basics

(UVOST™ shown here)



1. Control computer
2. Oscilloscope
3. Laser
4. Remote Display
5. Emission/detection module
6. Breakout Box
7. Fiber I/O
8. Launch Assembly
9. Fiber-based Trigger
10. E-Deck



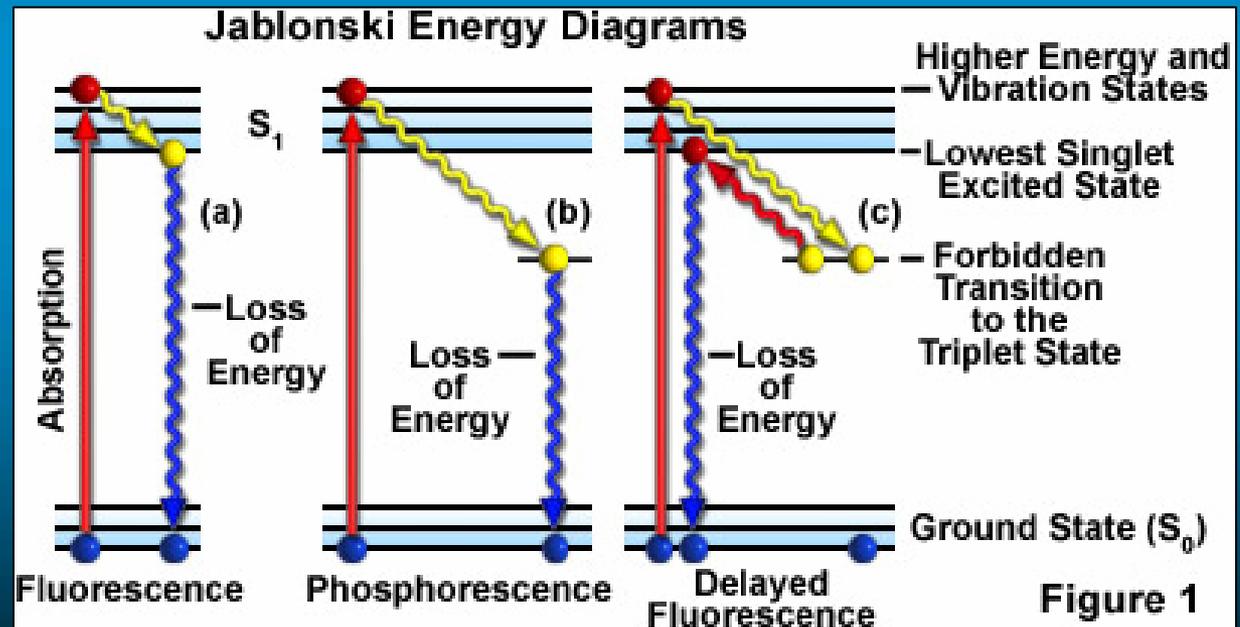
# Fluorescence Spectroscopy

(the “mysterious magic” behind the technology)

spectroscopy = the study the interaction between light and matter

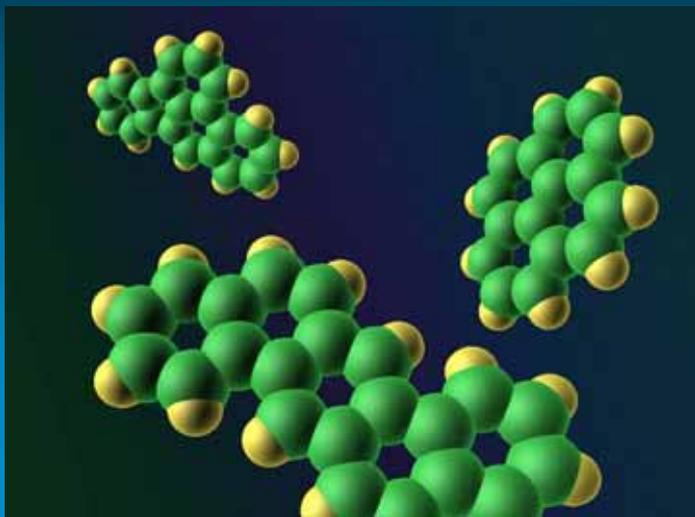
fancy quantum level physics rule the behavior

molecules first absorb light – then *might* rid themselves of that energy by emitting light  
aromatic (ring-shaped) molecules excel at this  
especially polycyclic aromatic hydrocarbons (PAHs)



For details - see Joseph R. Lakowicz' “Principles of Fluorescence Spectroscopy”, 3<sup>rd</sup> Edition

# PAH structures – aromatic rings



## PAH Structures

### Pericondensed



Pyrene  
C<sub>16</sub>H<sub>10</sub>



Coronene  
C<sub>24</sub>H<sub>12</sub>



Perylene  
C<sub>20</sub>H<sub>12</sub>



Benzo[ghi]perylene  
C<sub>22</sub>H<sub>12</sub>



Anthanthrene  
C<sub>22</sub>H<sub>12</sub>



Ovalene  
C<sub>32</sub>H<sub>14</sub>

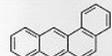
### Catacondensed



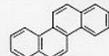
Naphthalene  
C<sub>10</sub>H<sub>8</sub>



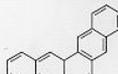
Phenanthrene  
C<sub>14</sub>H<sub>10</sub>



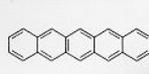
Tetraphene  
C<sub>18</sub>H<sub>12</sub>



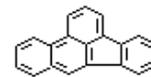
Chrysene  
C<sub>18</sub>H<sub>12</sub>



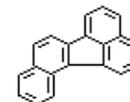
Pentaphene  
C<sub>22</sub>H<sub>14</sub>



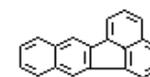
Pentacene  
C<sub>22</sub>H<sub>14</sub>



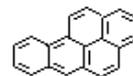
Benzo[a]fluoranthene



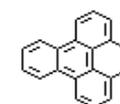
Benzo[b]fluoranthene



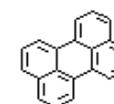
Benzo[k]fluoranthene



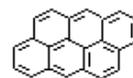
Benzo[a]pyrene



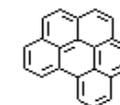
Benzo[e]pyrene



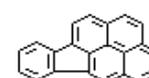
Perylene



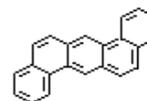
Anthanthrene



Benzo[ghi]perylene



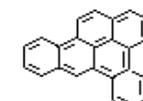
Indeno[1,2,3-cd]pyrene



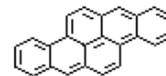
Dibenz[a,h]anthracene



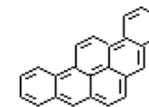
Coronene



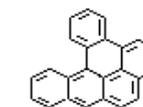
Dibenz[a,e]perylene



Dibenz[a,h]pyrene



Dibenz[o,p]pyrene



Dibenz[a,i]pyrene

# PAH Properties

fuels/oils are “soups” made up of various PAHs  
in an aliphatic “broth”

*PAH concentrations in a crude oil and two distillate fuel oils*  
(From Neff, 1979)

<b>Compound</b>	<b>Kuwait Crude (µg/g)</b>	<b>No. 2 fuel oil (µg/g)</b>	<b>Bunker C residual oil (µg/g)</b>
Naphthalene	400	4000	1000
1-Methylnaphthalene	500	8200	2800
2-Methylnaphthalene	700	18900	4700
Dimethylnaphthalenes	2000	31100	12300
Trimethylnaphthalenes	1900	18400	8800
Fluorenes	<100	3600	2400
Phenanthrene	26	429	482
1-Methylphenanthrene	-	173	43
2-Methylphenanthrene	89	7677	828
Fluoranthene	2.9	37	240
Pyrene	4.5	41	23
Benz[a]anthracene	2.3	1.2	90
Chrysene	6.9	2.2	196
Triphenylene	2.8	1.4	31

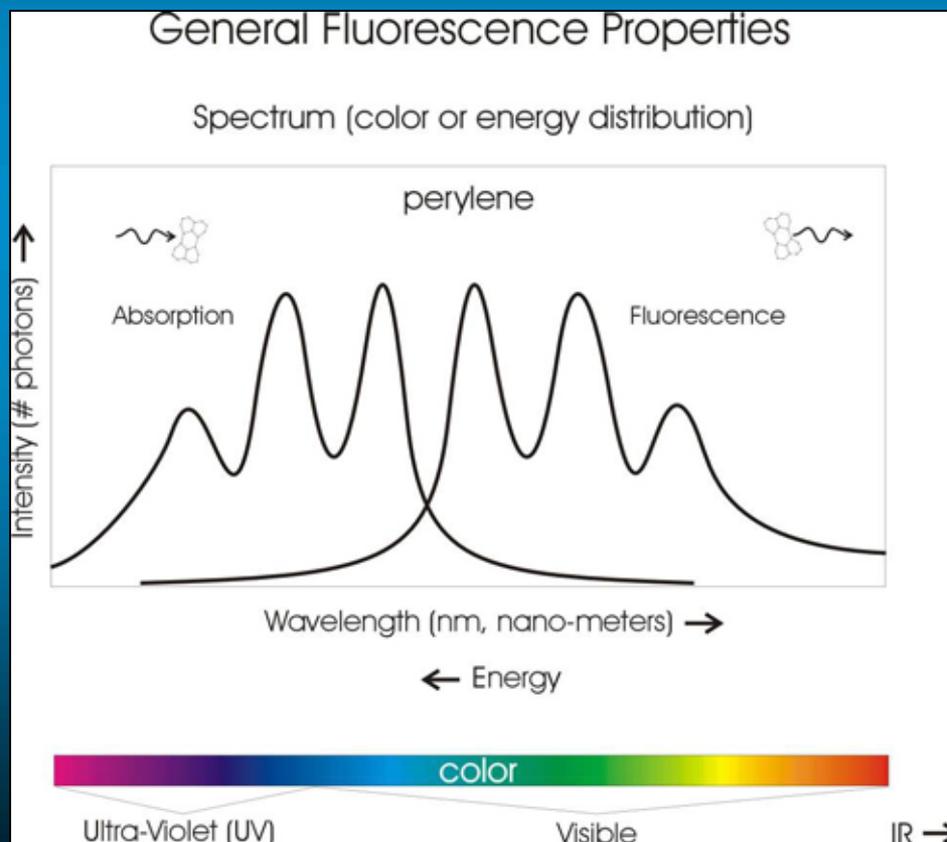
# PAHs... prefer NAPL

Compound (C.A.S.N°)		Molecular weight	log Kow	Water solubility at 25°C (mg/L)	Melting point (°C)	Vapor pressure at 25 °C (mPa)
naphthalene (91-20-3)	1	128.16	<b>3.5</b>	<b>31.7</b>	80.5	11 960
acenaphthene (83-32-9)	1	154.21	<b>4.33</b>	<b>3.42</b>	95	594
fluorene (86-73-7)	1	166	<b>4.18</b>	<b>1.98</b>	116.5	94.7
phenanthrene (85-01-8)	1	178.24	<b>4.5</b>	<b>1.29</b>	101	90.7
anthracene (120-12-7)	1	178.24	<b>4.5</b>	<b>0.045</b>	216	25
pyrene (129-00-0)	1	202.26	<b>4.9</b>	<b>0.135</b>	156	91.3 x 10 <sup>-6</sup>
fluoranthene (206-44-0)	1	202.26	<b>5.1</b>	<b>0.26</b>	111	1328
benz[a]anthracene (56-66-3)	1	228	<b>5.6</b>	<b>0.0057</b>	162	14.7 x 10 <sup>-3</sup>
benz[a]pyrene (50-32-8)	1,	252.32	<b>6.0</b>	<b>0.0038</b>	179	0.37 x 10 <sup>-6</sup>
benzo[b]fluoranthene (205-99-2)	2	252.32	<b>6.06</b>	<b>0.014</b>	168	0.13 x 10 <sup>-5</sup> to 0.133 at 20°C
benzo[j]fluoranthene (205-82-3)	2	252.32			166	
benzo[k]fluoranthene (207-08-9)	2	252.32	<b>6.06</b>	<b>0.0043</b>	217	2.8 x 10 <sup>-9</sup>
indeno[1,2,3-cd]pyrene (193-39-5)	2	276	<b>6.4</b>	<b>0.00053</b>	164	1.3 x 10 <sup>-5</sup>

# Laser-Induced Fluorescence (LIF)

it's the poly-cyclic aromatic hydrocarbons (PAHs) found in all petroleum, oils, lubricants (POLs) that are responsible for their innate fluorescence

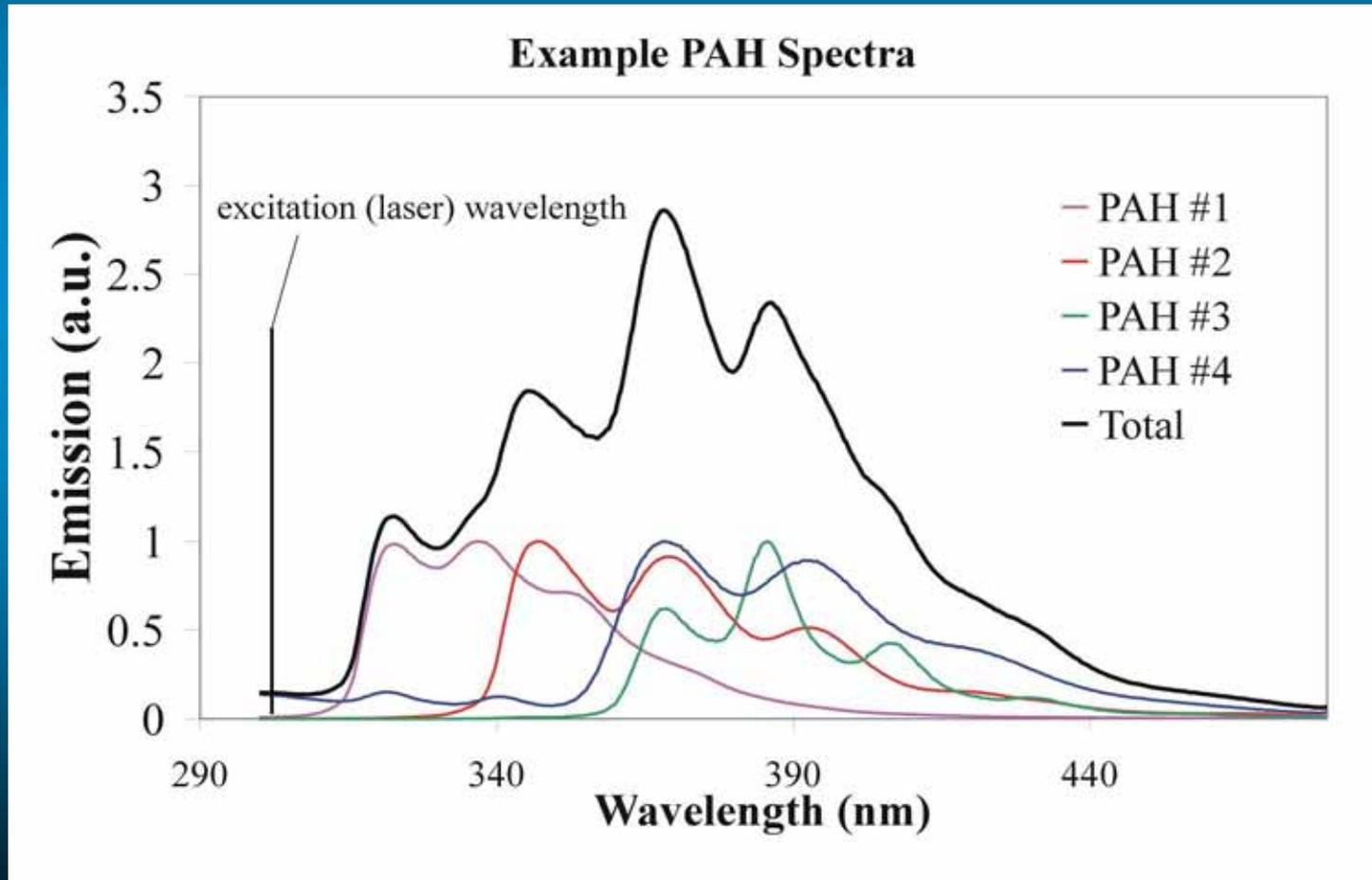
emission spectrum is unique for each PAH – does not change with excitation wavelength



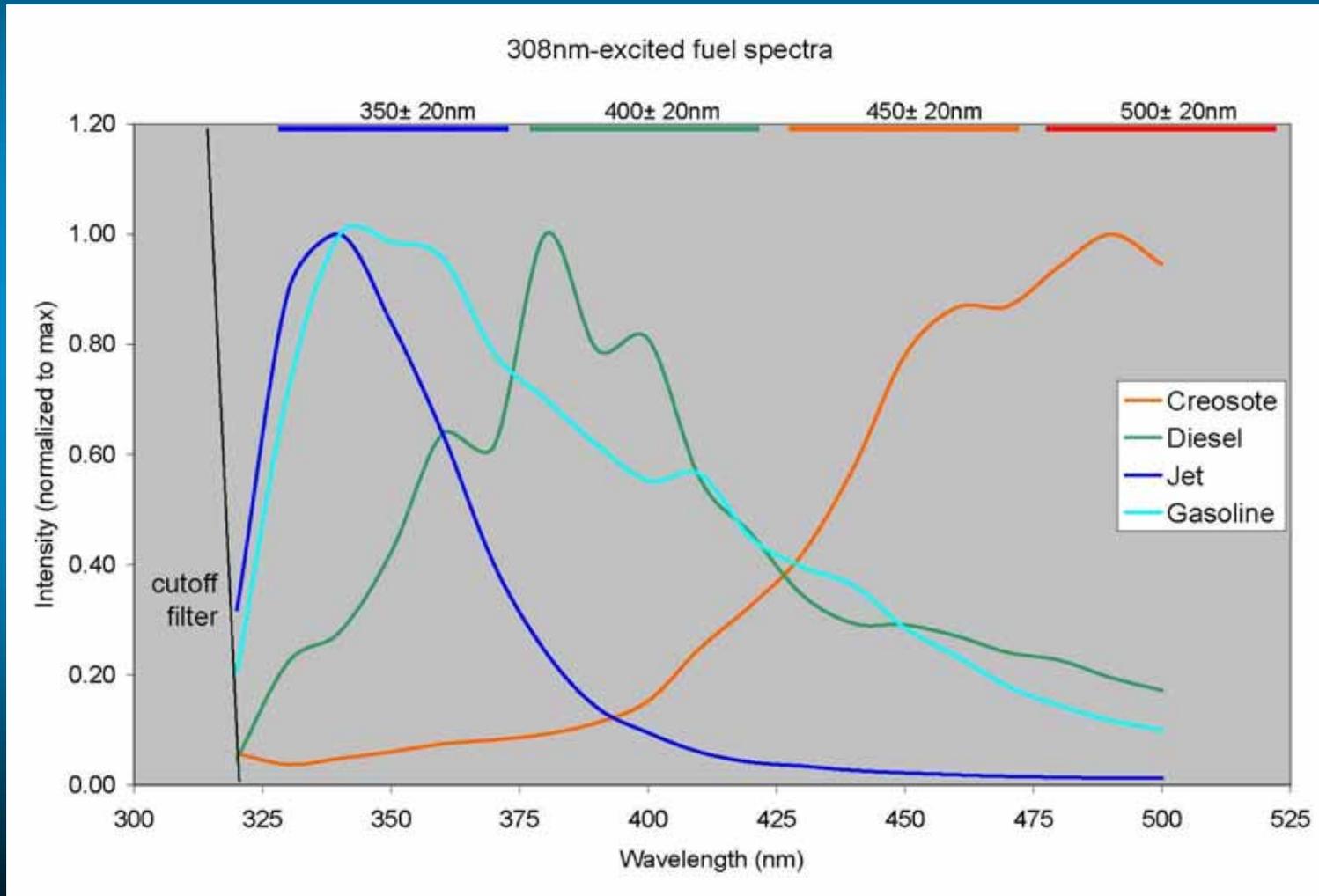
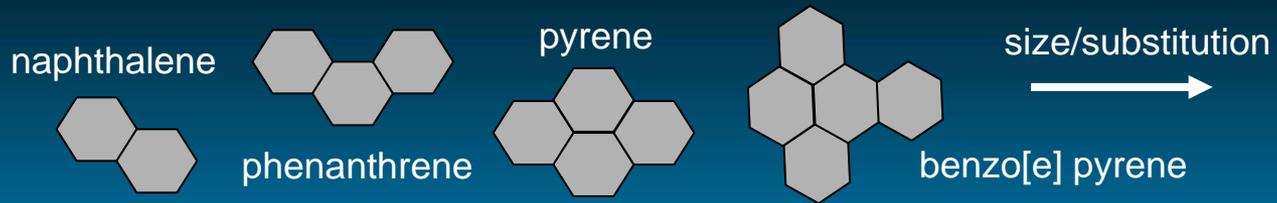
# Laser-Induced Fluorescence (LIF) Concepts

in fuels there is a mix of many PAHs  
their spectra overlap and you lose ability to identify any one PAH – just classes at best  
emission spectrum is still unique for each PAH BUT...

varying the excitation wavelength for PAH mixtures DOES cause a change in overall emission spectrum

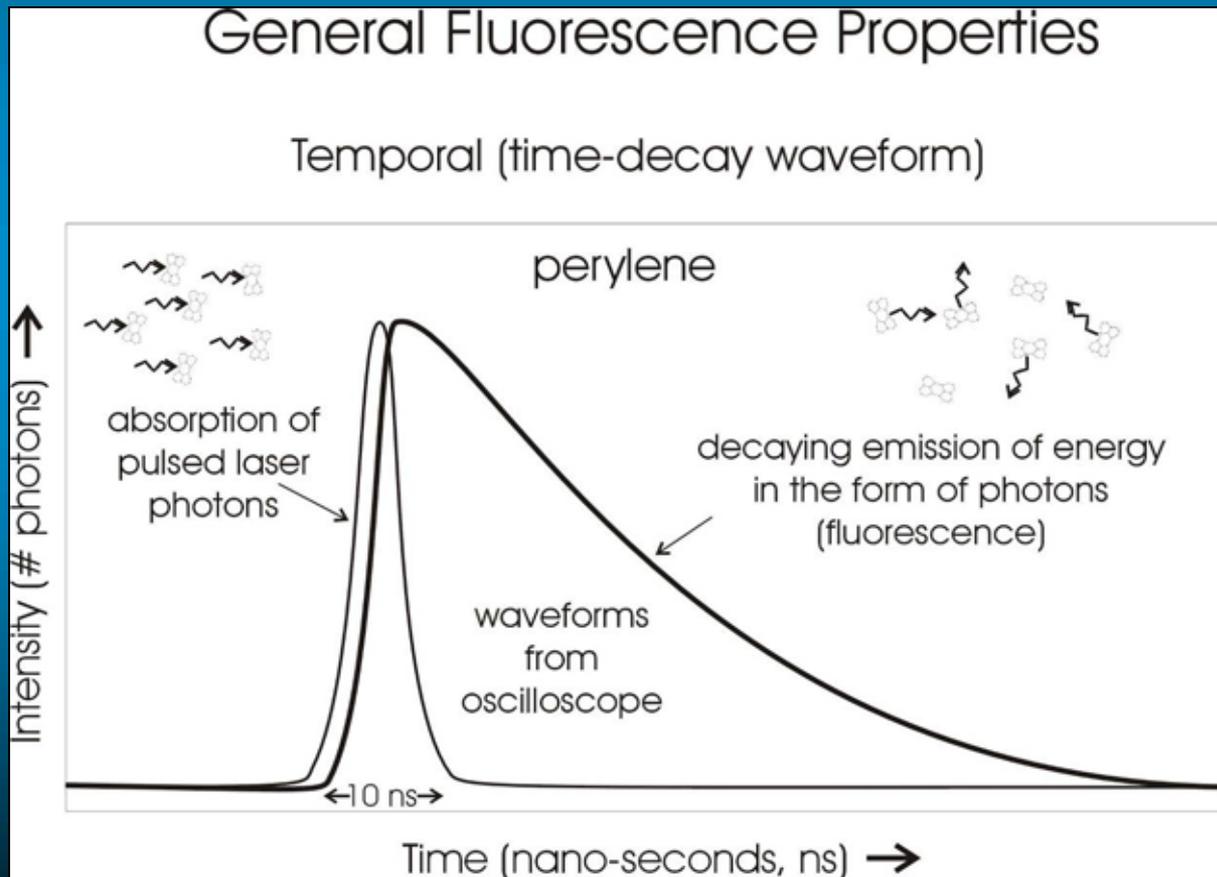


# UVOST emission spectra for typical fuels



# Laser-Induced Fluorescence (LIF) Concepts

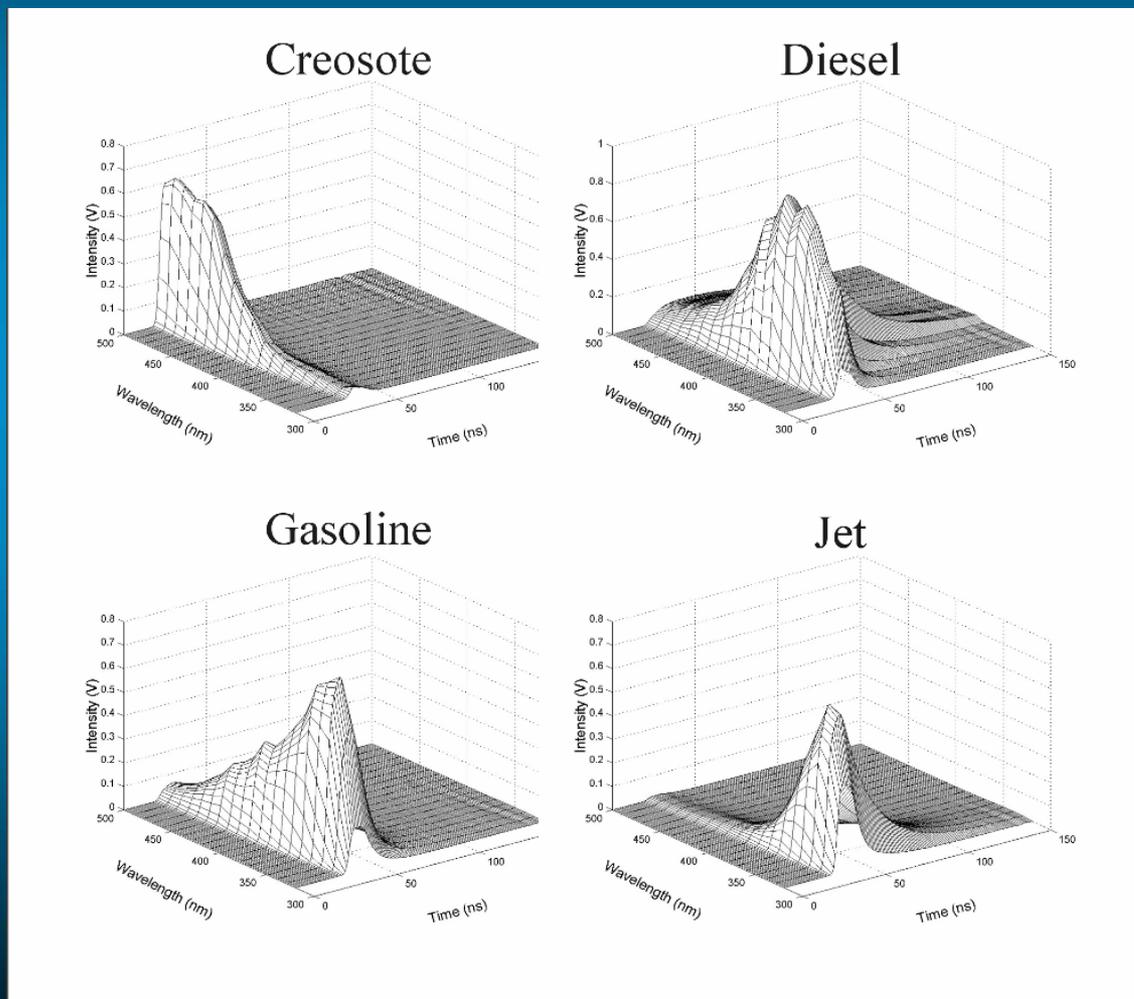
there is a 3<sup>rd</sup> dimension to fluorescence that most people don't know (or care) about  
it involves time over which a population of excited PAHs fluoresce  
Dakota's LIF systems with fast-pulsed lasers make extensive use of this property



# Laser-Induced Fluorescence (LIF) Concepts

each mix of PAHs (along with the aliphatic solvent, oxygen concentration, matrix, etc.) yield a fairly unique wavelength/time matrix or “WTM”

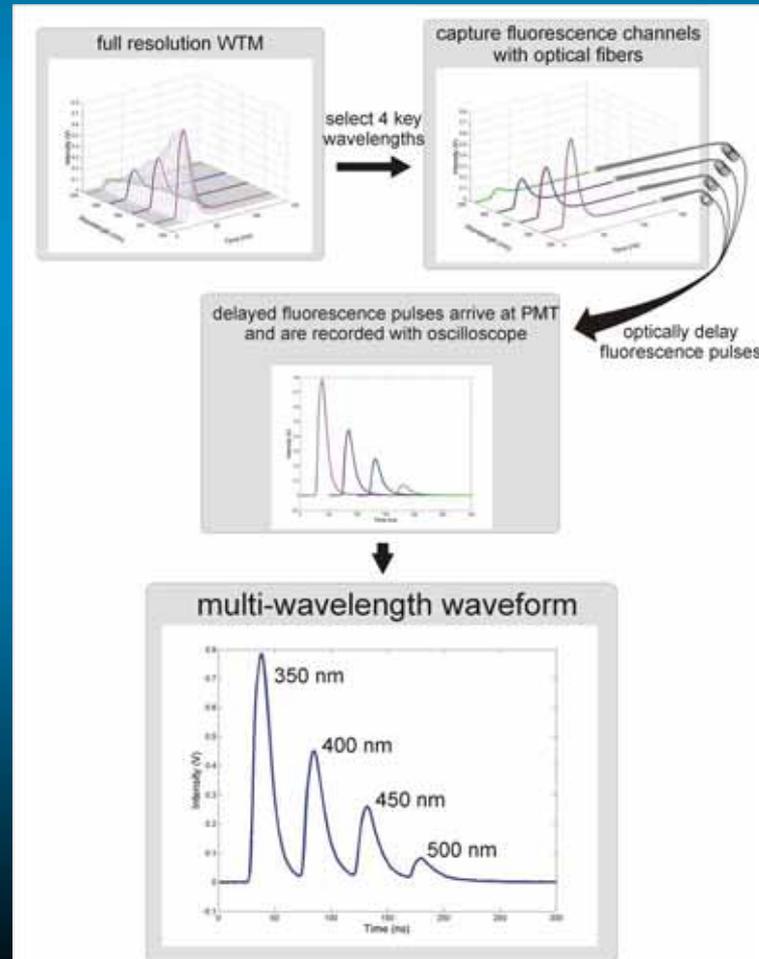
all “classes” of fuels/oils have a characteristic WTM



# Laser-Induced Fluorescence (LIF) Concepts

WTMS are powerful – but they couldn't be obtained “on the move” and folks sometimes wanted them every foot or so! (back in ROST's early days – mid 90's)

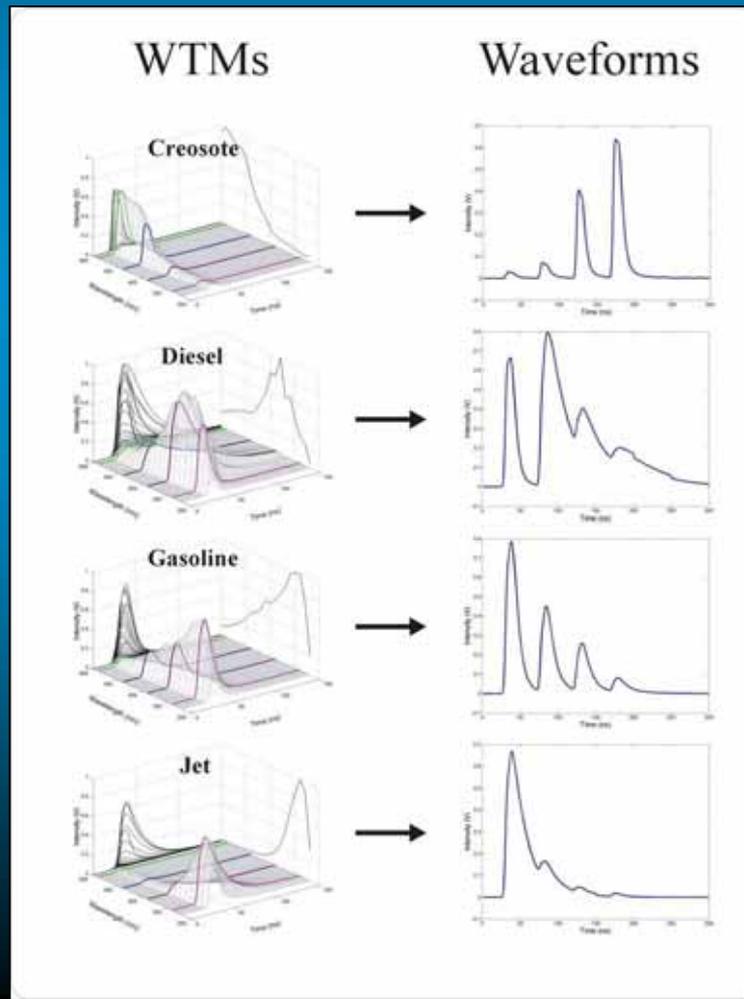
so we were forced to get “clever” and design a solution...  
time delayed fluorescence “channels” solve this



# Laser-Induced Fluorescence (LIF) Concepts

with time delay you combine both the spectral (wavelength/color) and temporal (lifetime) fluorescence information that's being emitted by the NAPL

so for fast simultaneous quantitative and qualitative information – a multi-wavelength waveform is “tough to beat”

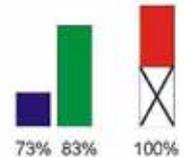
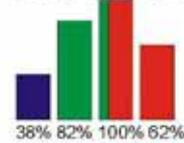
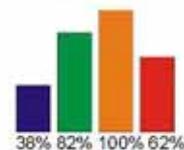


# Colorization of UVOST Waveforms

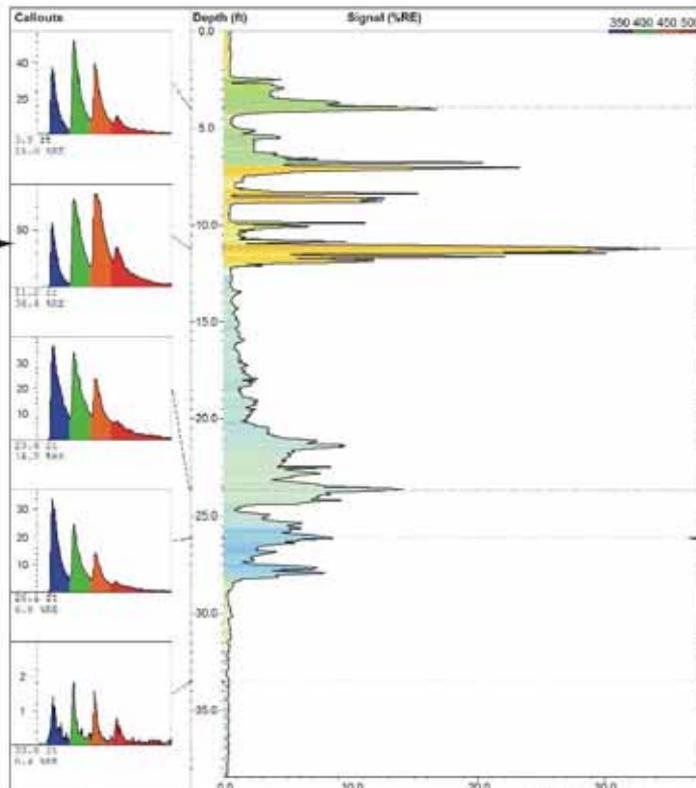
Dakota's UVOST colorization scheme uses RGB calculations of the relative areas of the 350, 400, 450, and 500 nm channels to generate RGB fill color.

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

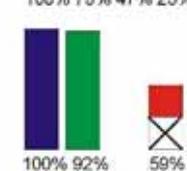
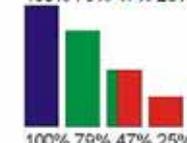
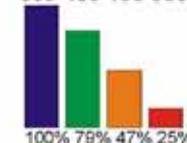
350 400 450 500



resulting fill color



350 400 450 500



resulting fill color



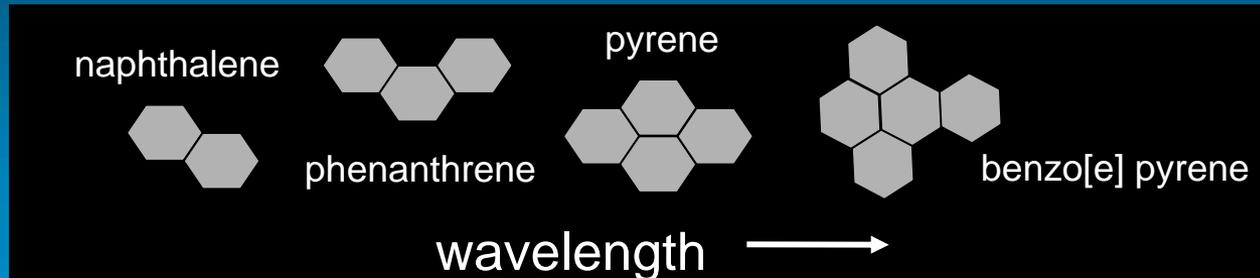
Dakota Technologies, Inc.  
Fargo, ND 58103  
www.dakotatech.com

Sample		UVOST By Dakota www.DakotaTechnologies.com	
Site:	Fargo, ND	Latitude / System:	42 32 043043 N / NADE3
Client:	ABC Consulting	Longitude:	096 32.569063 W
Job:	NA	Operator/Unit:	St. Germain/DT101
		Final depth:	38.39 ft
		Max signal:	34.4 % @ 11.23 ft
		Date & Time:	8/16/2008 3:23:49 PM

# general NAPL fluorescence trends

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

in general the larger the PAH – the longer its absorbance and emission wavelengths

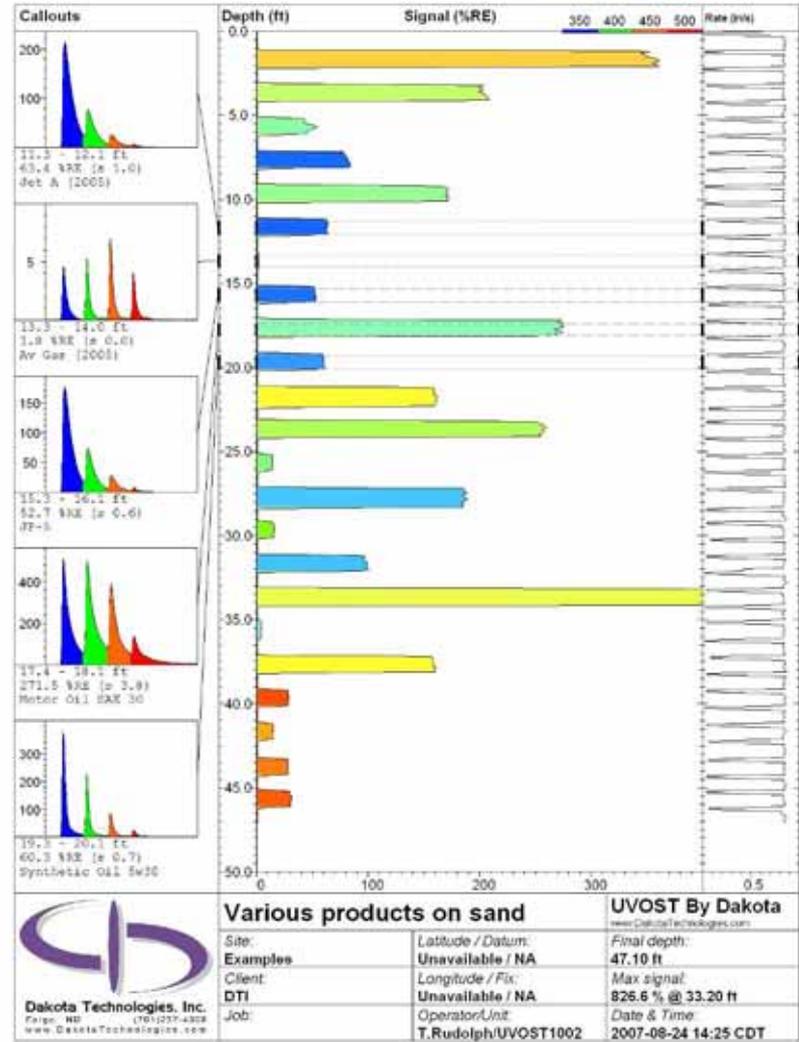
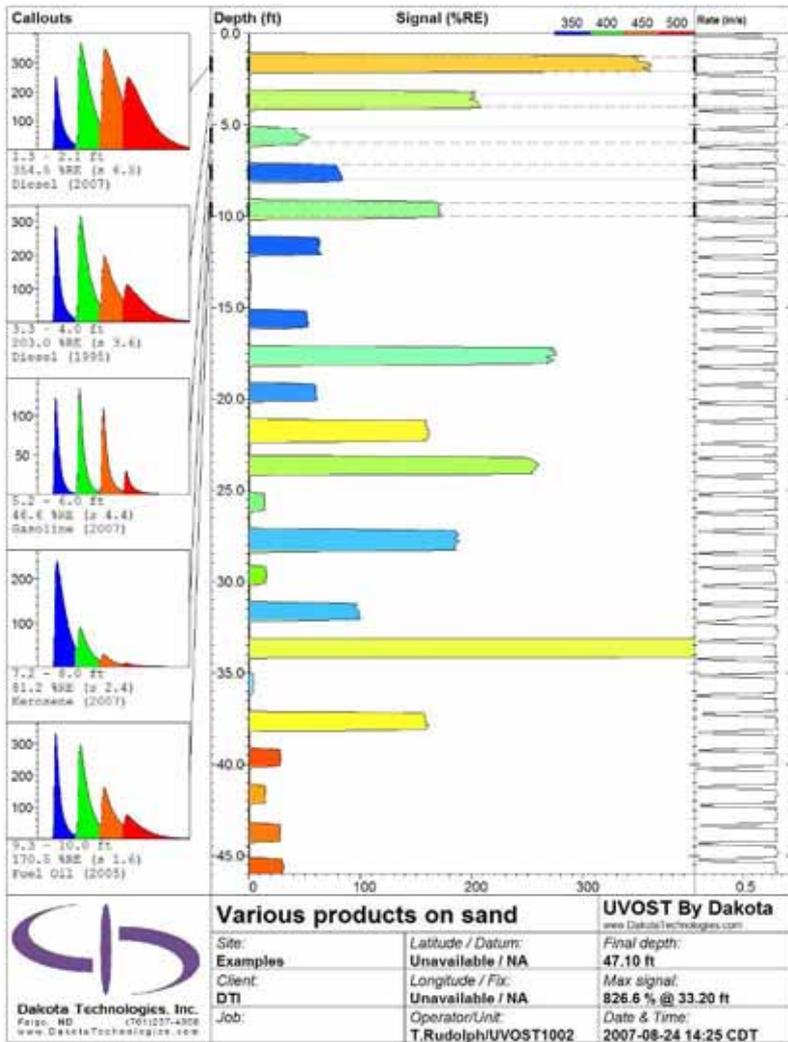


**so what effect does this have on fluorescence waveforms?**

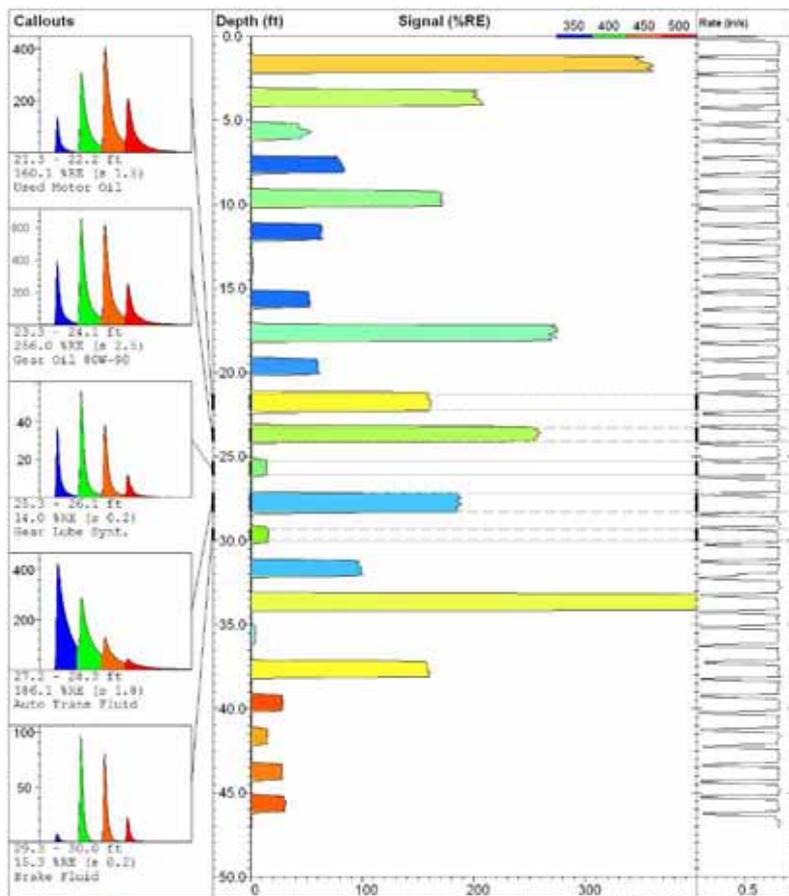
- fuels/NAPLs with predominantly smaller PAHs fluoresce in left-most channels of the waveform
- mid-range fuels/oils fluoresce “across the board” (in all 4 channels)
- “heavies” like coal tar, bunker fuels, etc. fluoresce predominantly in the right-most channels (longer wavelength) – not because they only contain large PAHs, but the large PAHs “rob” smaller PAH’s absorbed energy – more about that later

# UVOST Response for Various NAPLs

[wet Fisher sea sand - saturated with NAPL]

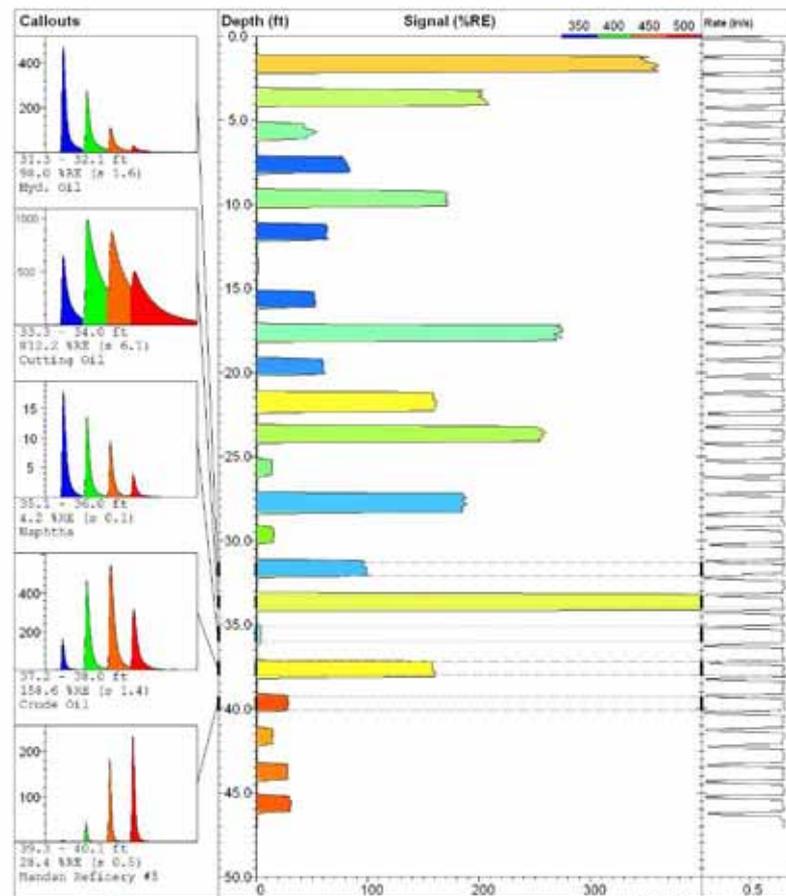


# UVOST Response of Various NAPLs



## Various products on sand

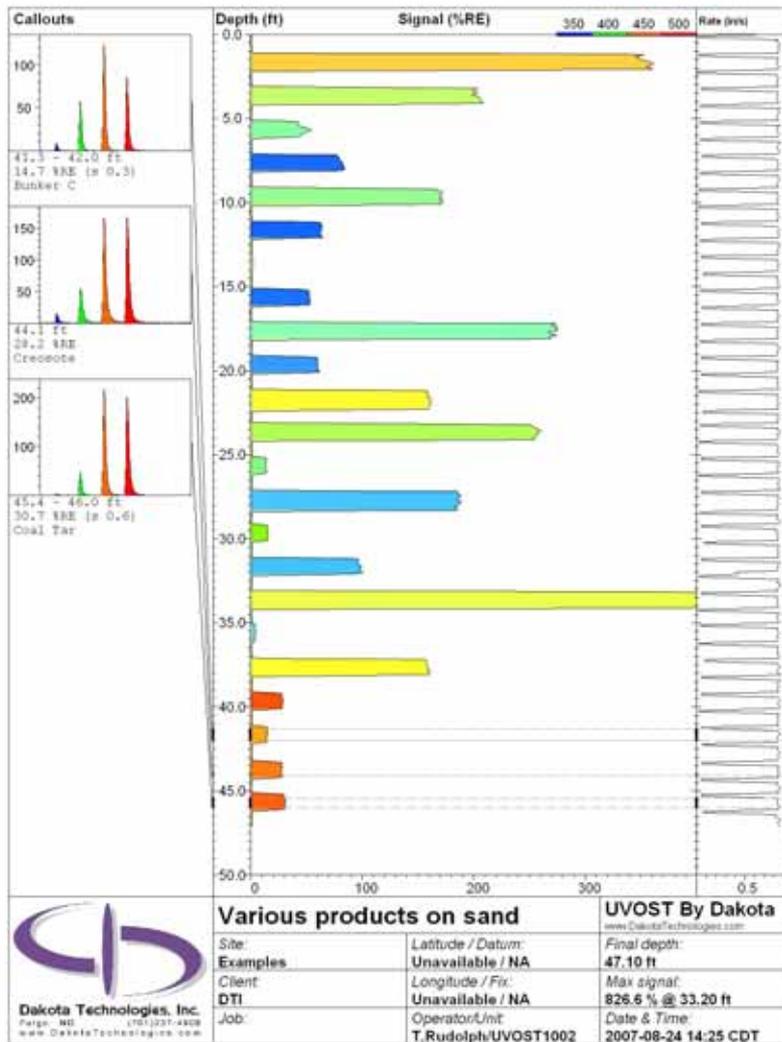
		<b>UVOST By Dakota</b> <small>www.DakotaTechnologies.com</small>
Site:	Latitude / Datum:	Final depth:
Examples	Unavailable / NA	47.10 ft
Client:	Longitude / Fix:	Max signal:
DTI	Unavailable / NA	826.6 % @ 33.20 ft
Job:	Operator/Unit:	Date & Time:
	T.Rudolph/UVOST1002	2007-08-24 14:25 CDT



## Various products on sand

		<b>UVOST By Dakota</b> <small>www.DakotaTechnologies.com</small>
Site:	Latitude / Datum:	Final depth:
Examples	Unavailable / NA	47.10 ft
Client:	Longitude / Fix:	Max signal:
DTI	Unavailable / NA	826.6 % @ 33.20 ft
Job:	Operator/Unit:	Date & Time:
	T.Rudolph/UVOST1002	2007-08-24 14:25 CDT

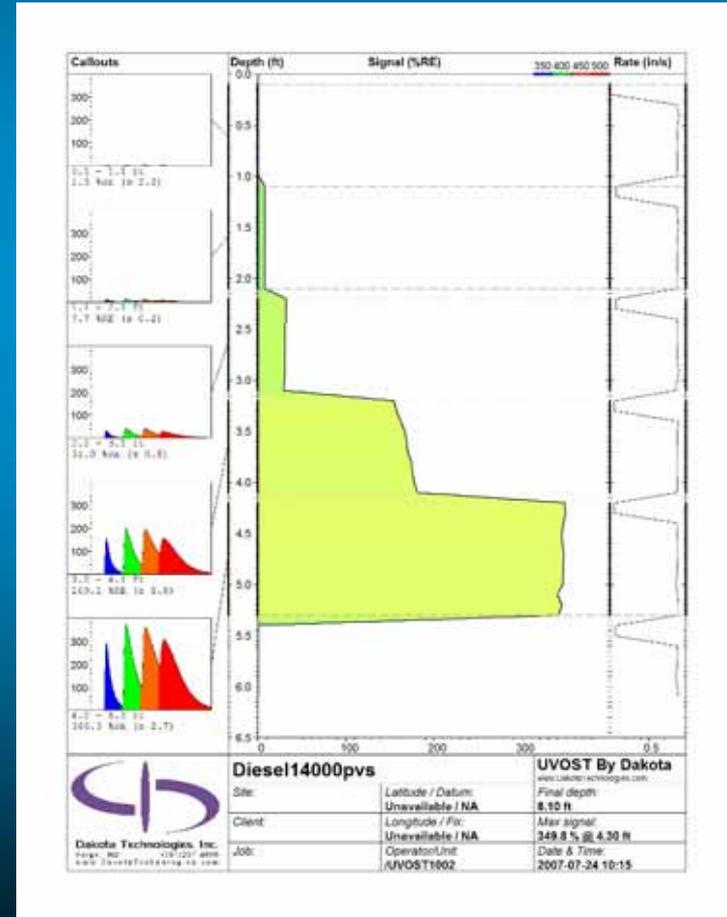
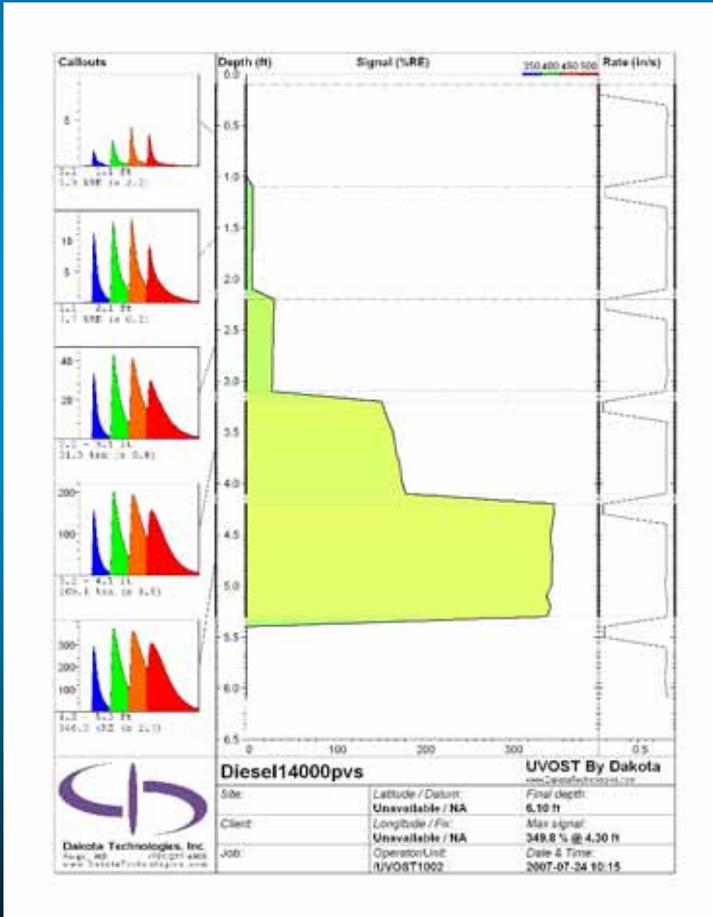
# UVOST Response of Various NAPLs



# Lab study – let's examine quantitative aspect of LIF

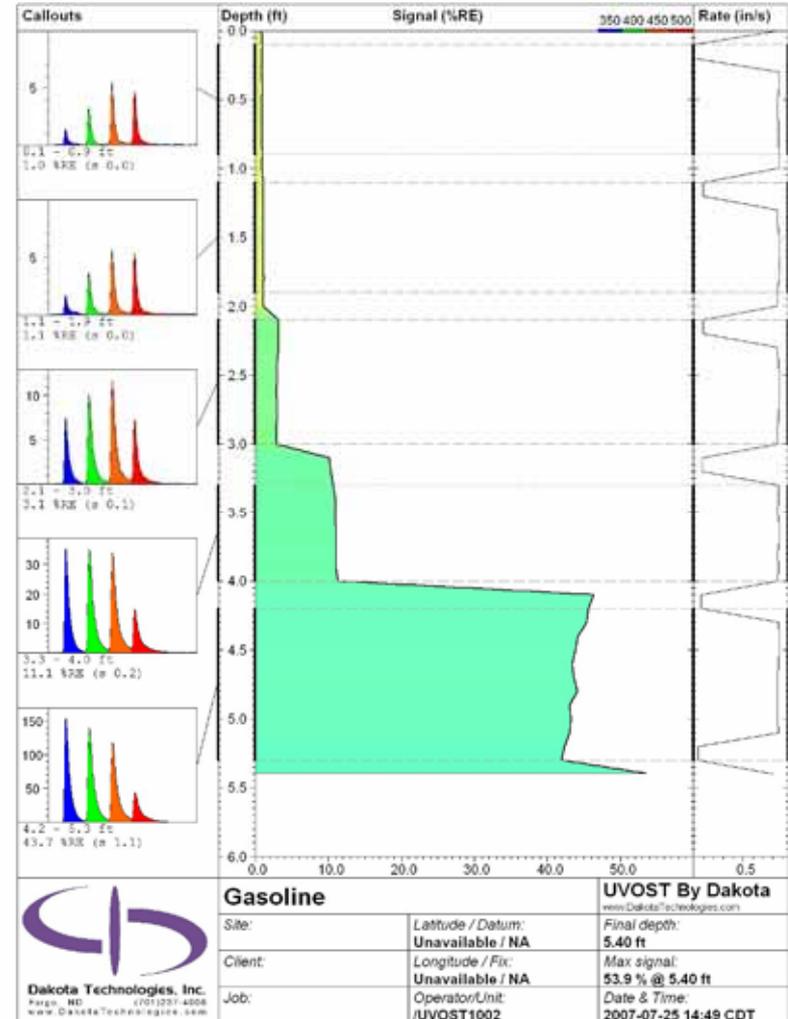
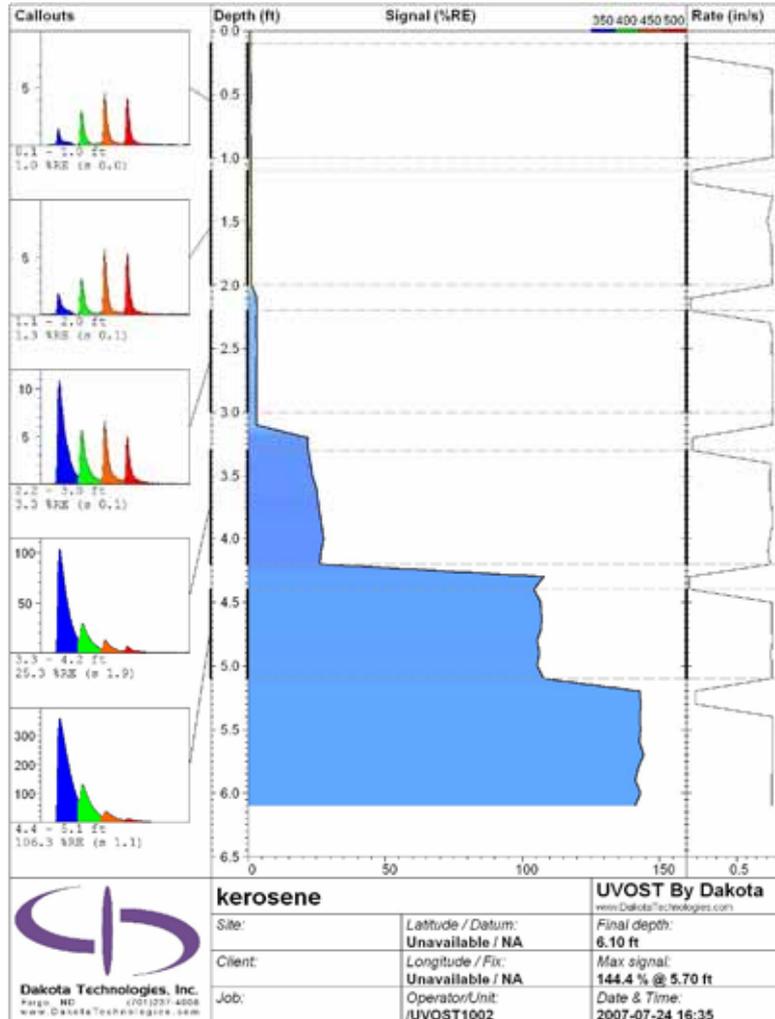


decade series dilutions (100, 1000, 10000, 100000 ppm)



# Lab studies

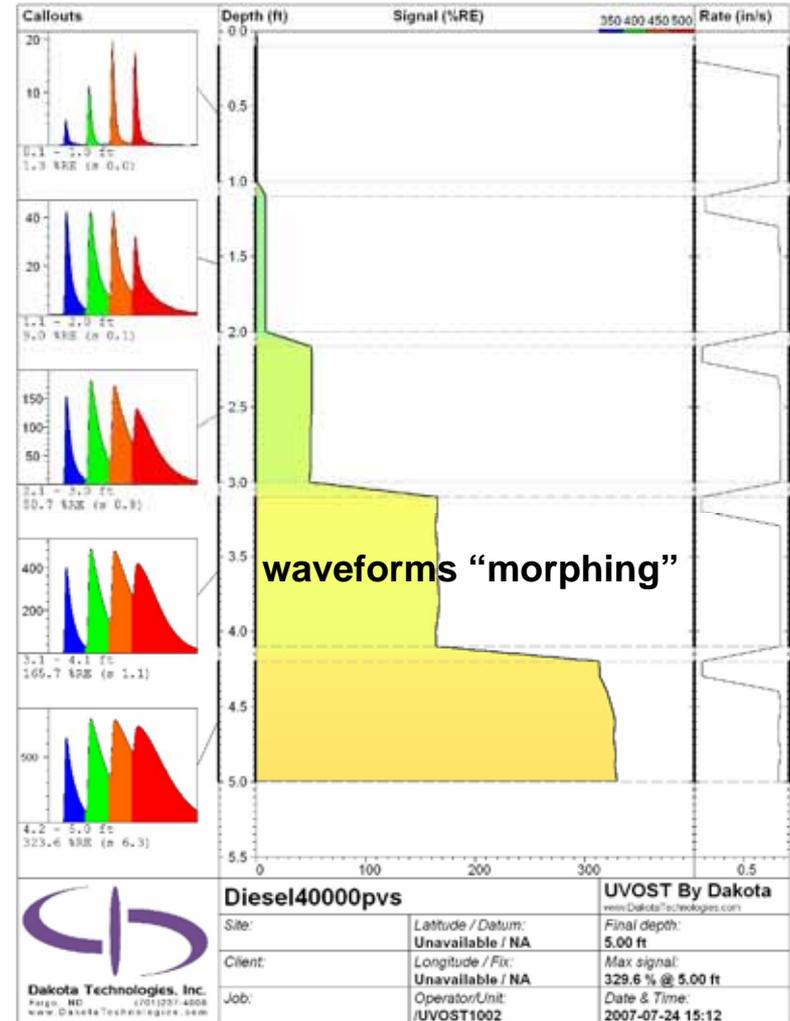
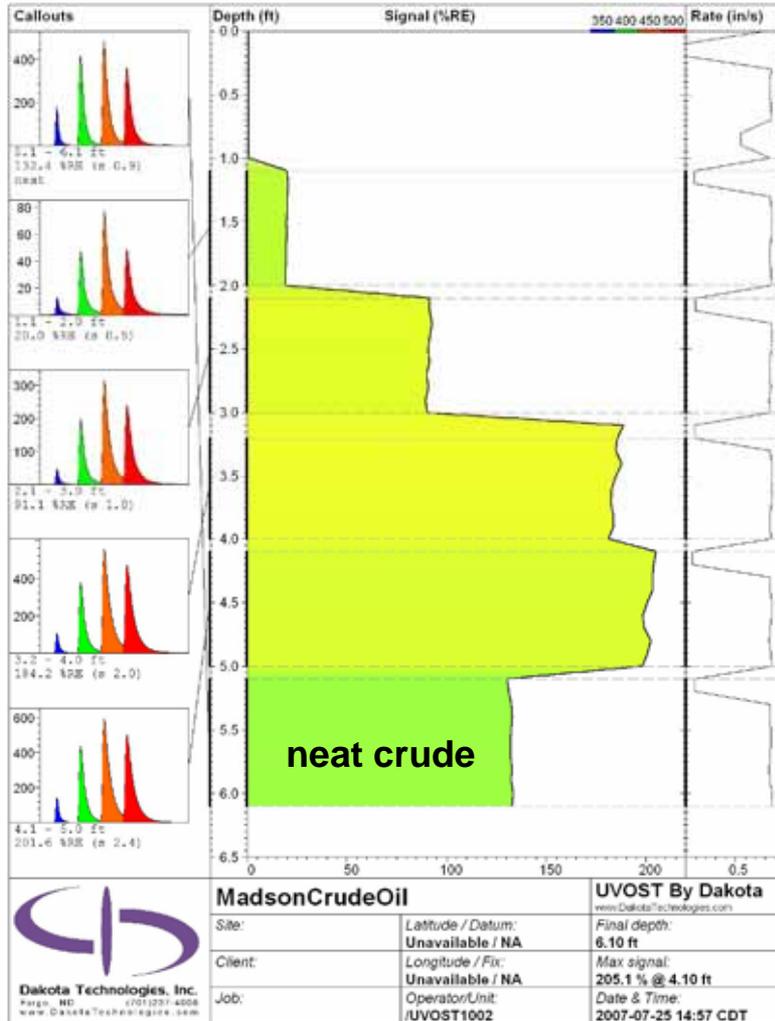
LIF provides both “semi-quantitative” and qualitative data



# more lab studies

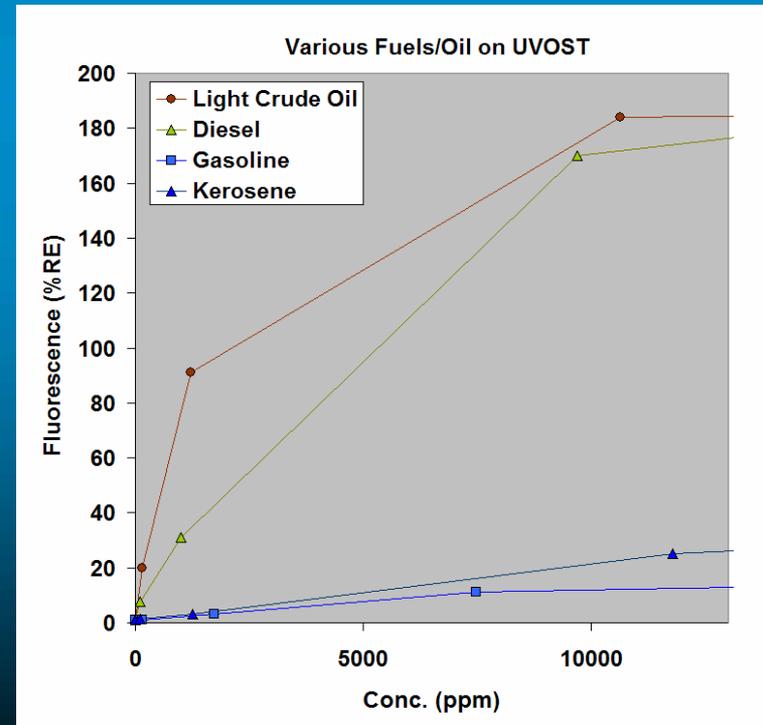
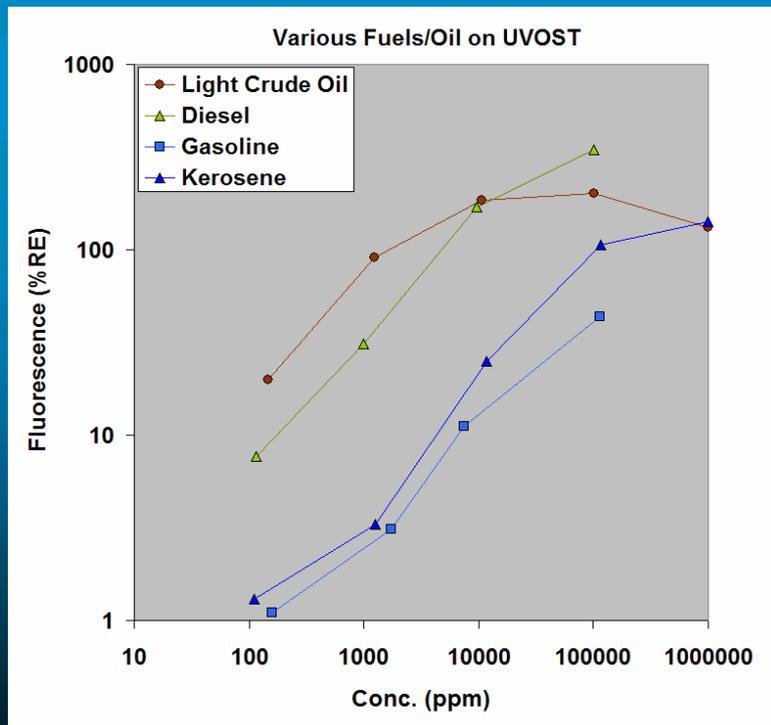
crude oil “rollover” – note colors – energy transfer

too high RE (electronics saturation – note colors)



# LIF's "semi-quantitative" performance

- typically 10-500 ppm (TRPH) limit of detection (LOD) for common petroleum fuels/oils - statistically in a controlled experiment – up or down from there depending on heterogeneity
- semi-linear (at least monotonic) response over several orders of magnitude on fuels/POLs
- generally speaking diesel is best behaved – gasoline and kerosene can be 10-fold lower
- lab studies can “under-estimate” field LODs – in downhole NAPL is mottled – the sandy samples used here 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) – UVOST sees these ‘blebs’ easier than homogeneous sheen
- note that the LOD for actual **PAHs** is actually lower than 10-500ppm, since PAHs often make up only fraction of fuel/oil



# Dakota's Reference Emitter ("RE")

(RE does NOT stand for REflectivity!!)

speaking of quantitative information ("how much NAPL?") – how does the waveform relate to the amount of NAPL?

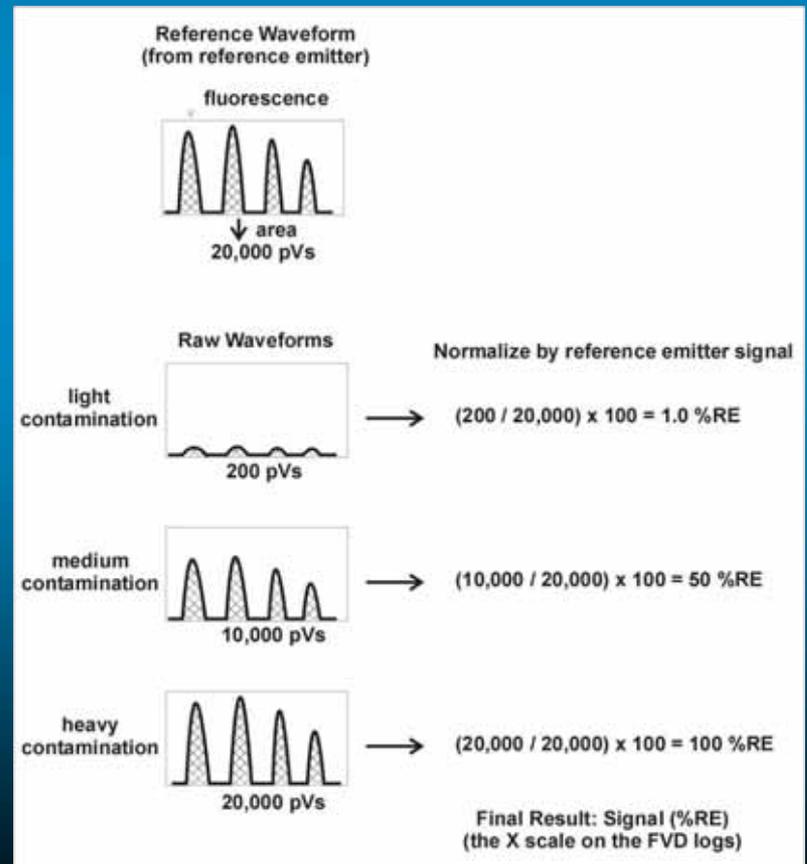
the diagram below illustrates how the software determines fluorescence intensity as %RE – RE stands for Reference Emitter

RE is a standard Dakota-provided NAPL that you calibrate UVOST/TarGOST with prior to every sounding – think of RE as you would the tank of 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 is used by all UVOST service providers worldwide

the relationship between %RE and the concentration of NAPL depends on the fuel – some simply glow brighter than others

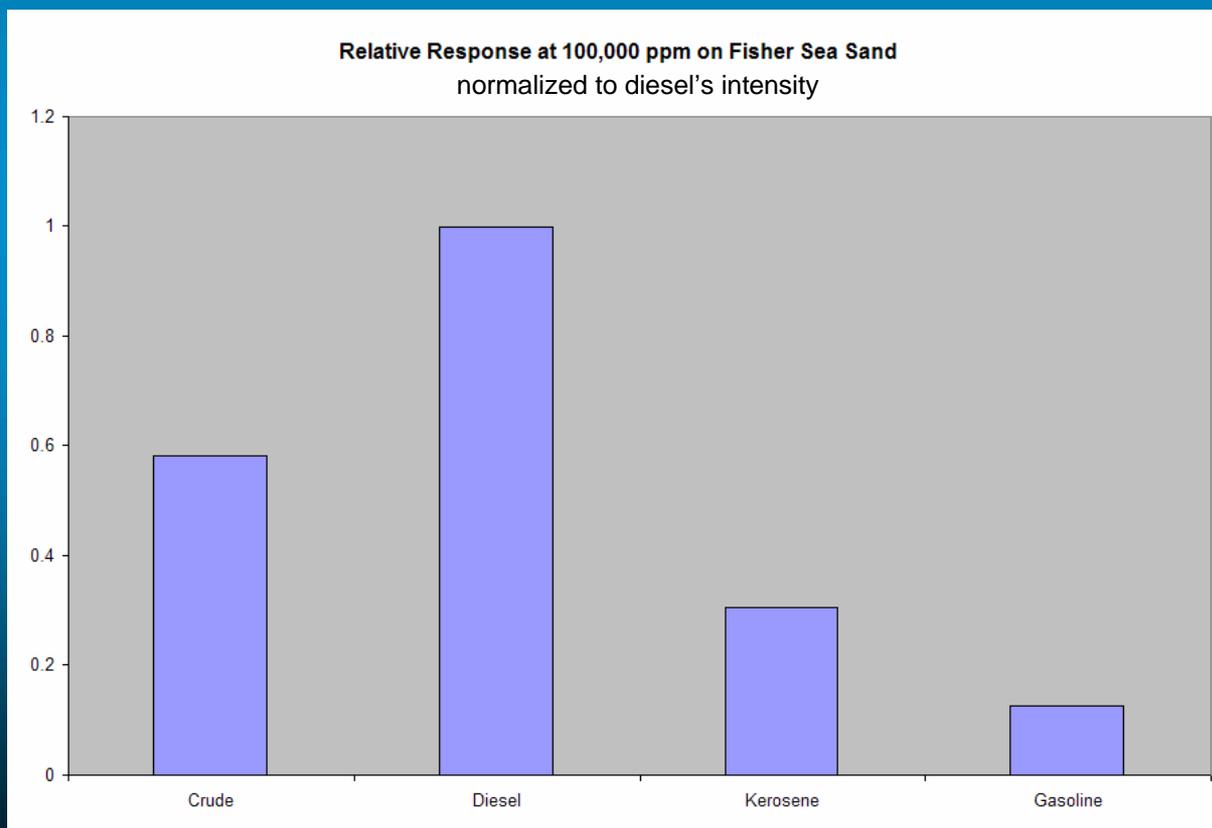
[Note that "M1" is Dakota's former name for RE]



# UVOST's semi-quantitative performance

Previous slides were results from just **one set** of randomly acquired fuels and a crude oil  
– product “brightness” can vary, so your results may differ depending on source, age, makeup of NAPL

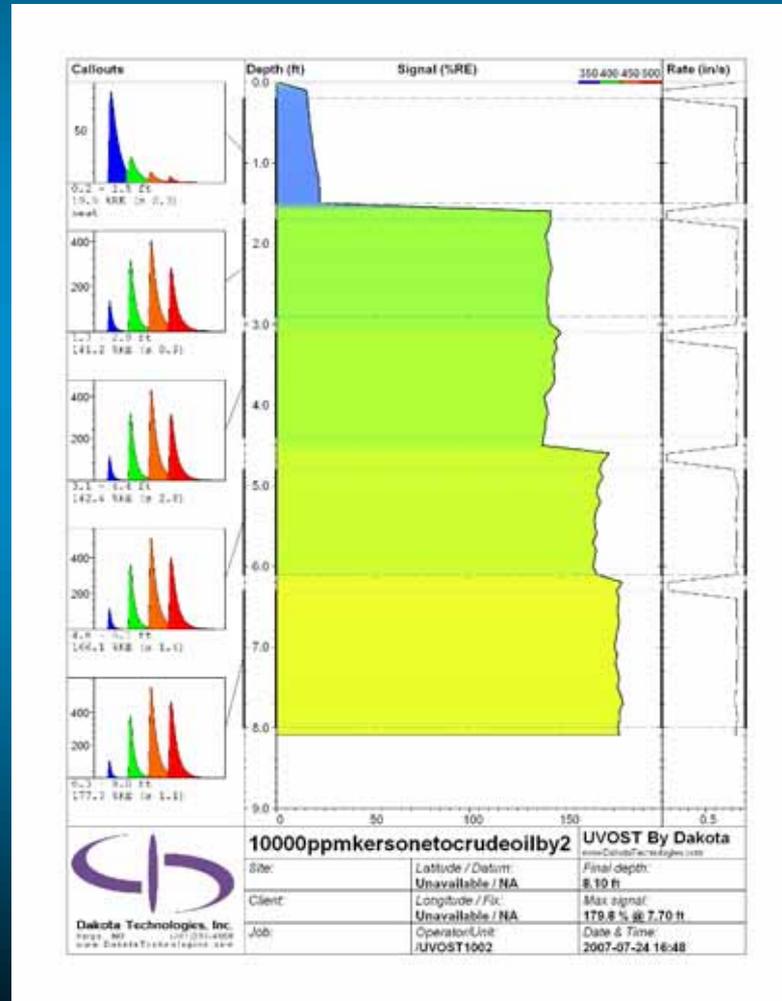
- Gasoline is typically 32% aromatic – but mostly mono-aromatics (BTEX) that UVOST “can’t see” but gasoline **still** contains sufficient PAHs to respond to UV LIF
- Diesel is typically 38% aromatics – mostly PAHs, so it “glows” nicely
- Kerosene (jet fuel) is as much as 23% aromatics – nearly all naphthalenes so it does fluoresce sufficiently in UV



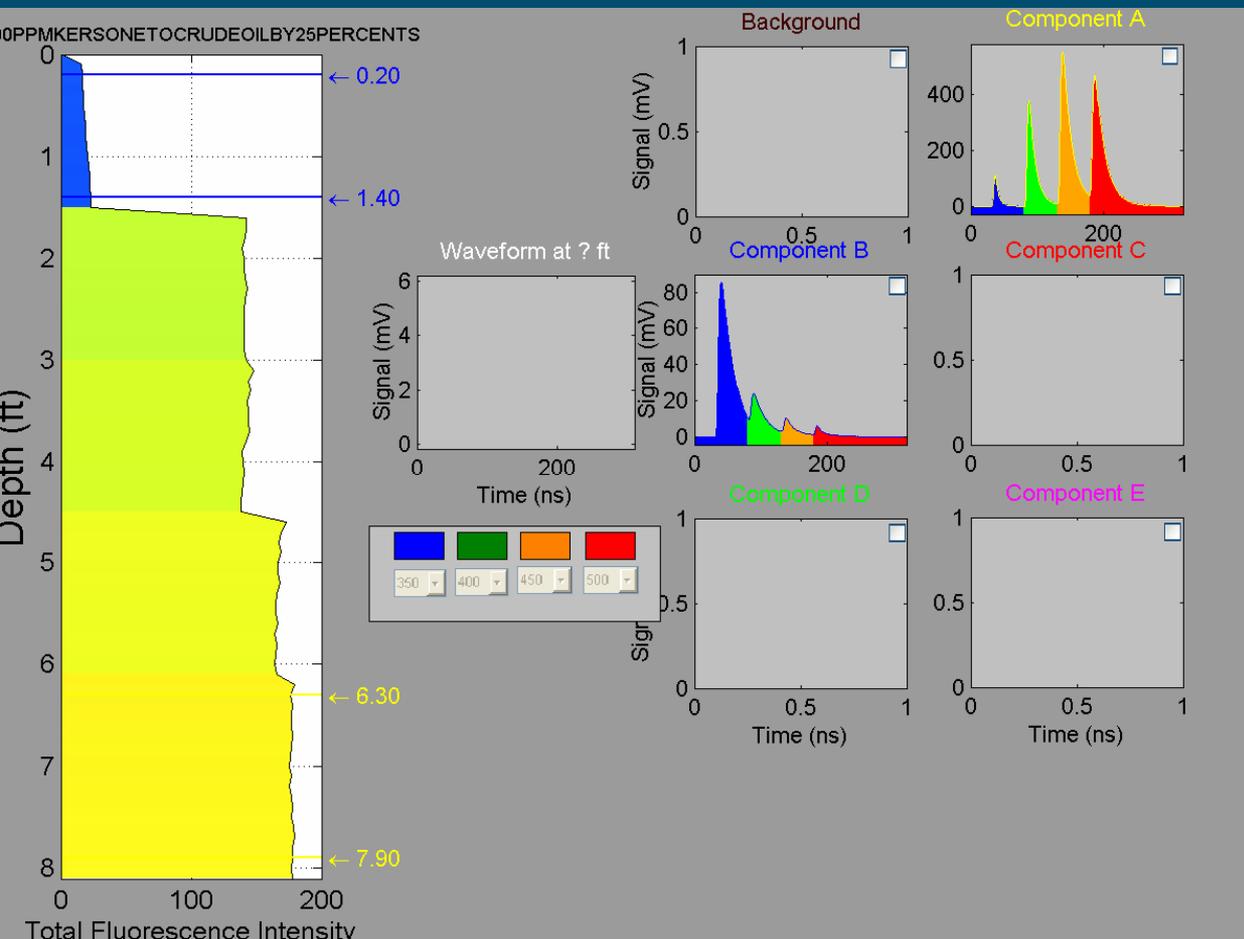
# UVOST's qualitative performance

The fluorescence of various products are quasi "additive" – in other words, mixtures of products have waveforms that are combinations of the separate product's waveforms added together. This isn't always linear or "perfect", but waveform analysis can be used to separate the various products.

Example experiment: Mix up some 10,000 ppm kerosene and crude on sand. Log below starts out with 10,000 ppm kerosene – then 25% replacement of kerosene with crude until we reach 10,000 ppm crude oil.



# Advanced Waveform Analysis

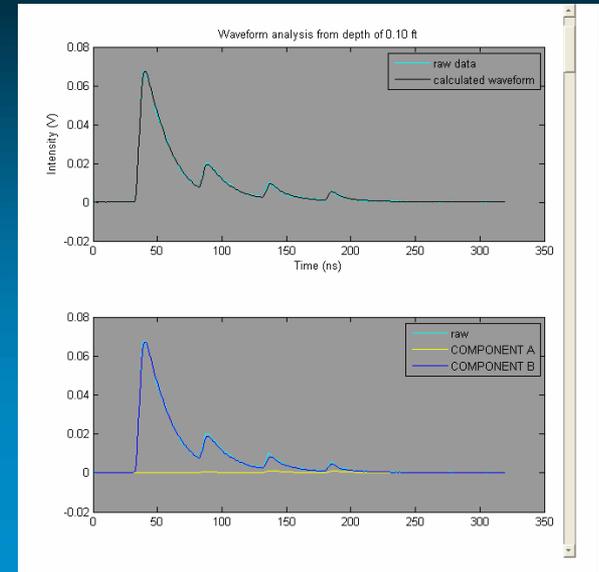
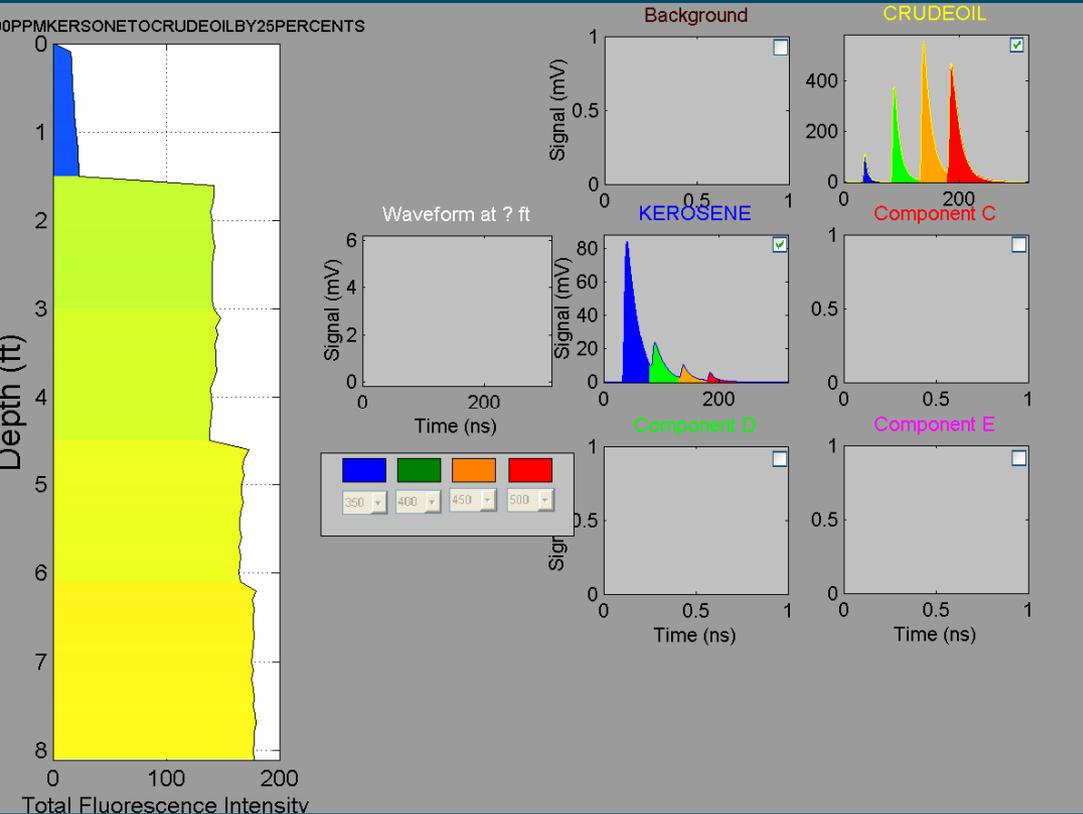


We can harvest “Basis Set” waveforms from areas we know to represent pure products.

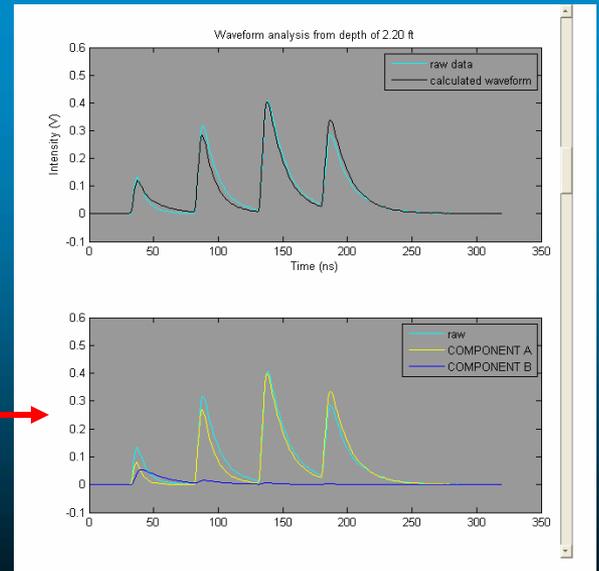
Then do a non-negative least squares analysis on each raw waveform in the log... searching for best combination of the Basis Set waveforms to match raw waveforms – end result are logs that represent contribution of each Basis Set member.

# Advanced Waveform Analysis

100% kerosene – 0% crude



75% kerosene – 25% crude

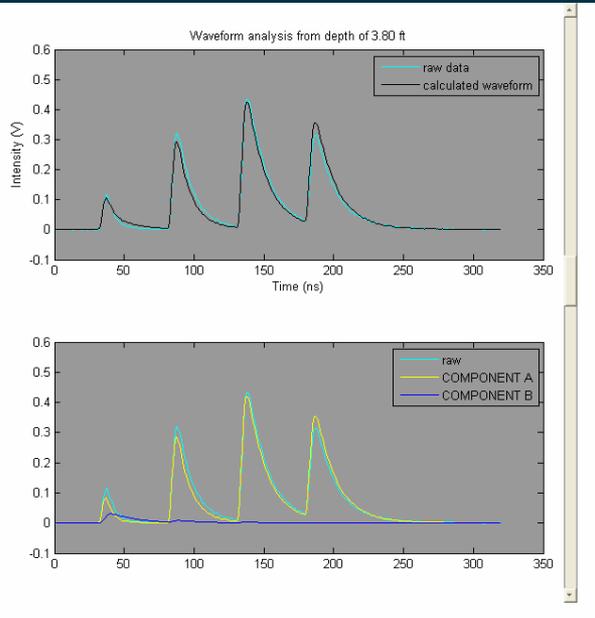


crude is much brighter than kerosene so it is dominating waveforms  
 10,000 ppm crude is “morphed” – so a bit different  
 from 2,500 ppm crude here and you can see match isn't perfect

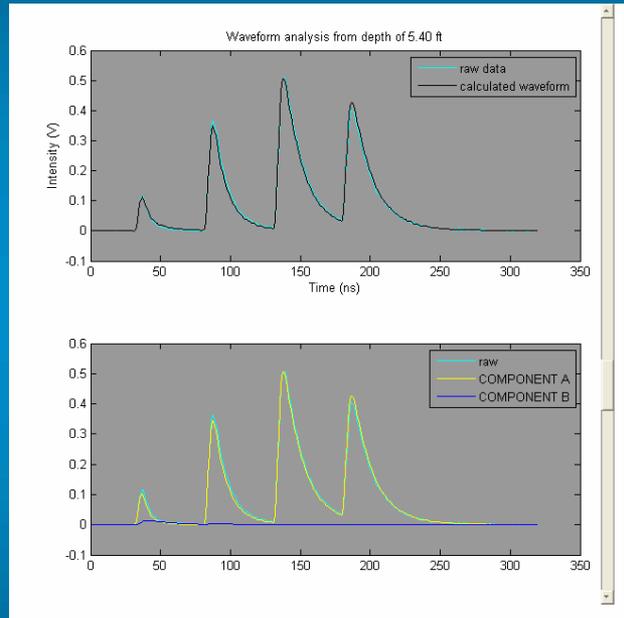


# Advanced Waveform Analysis

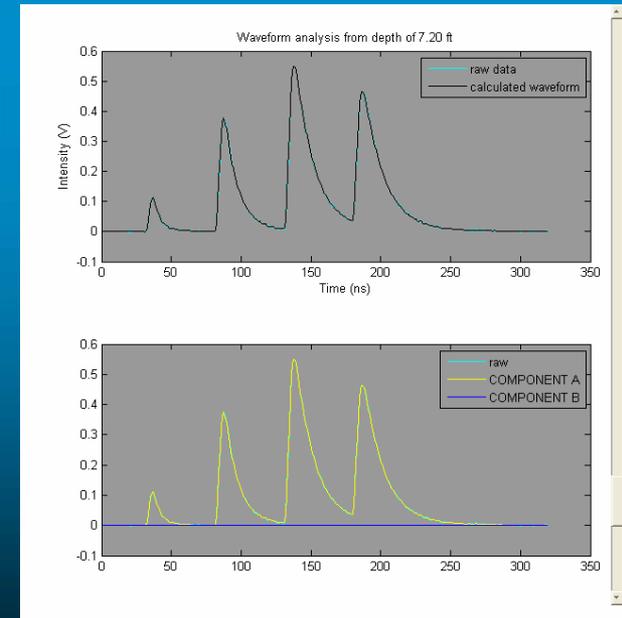
50% kerosene – 50% Crude



25% kerosene – 75% Crude

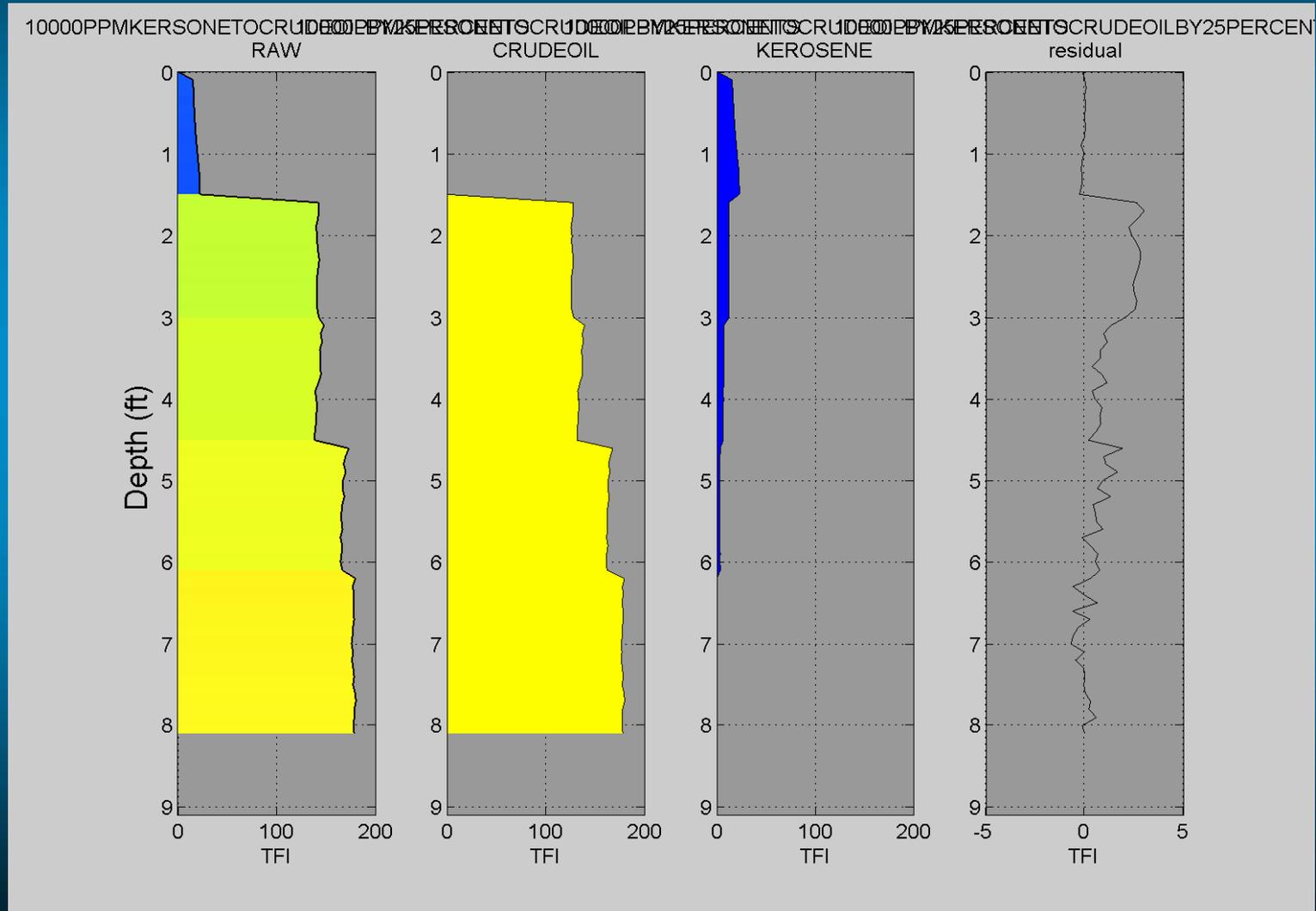


0% kerosene – 100% Crude

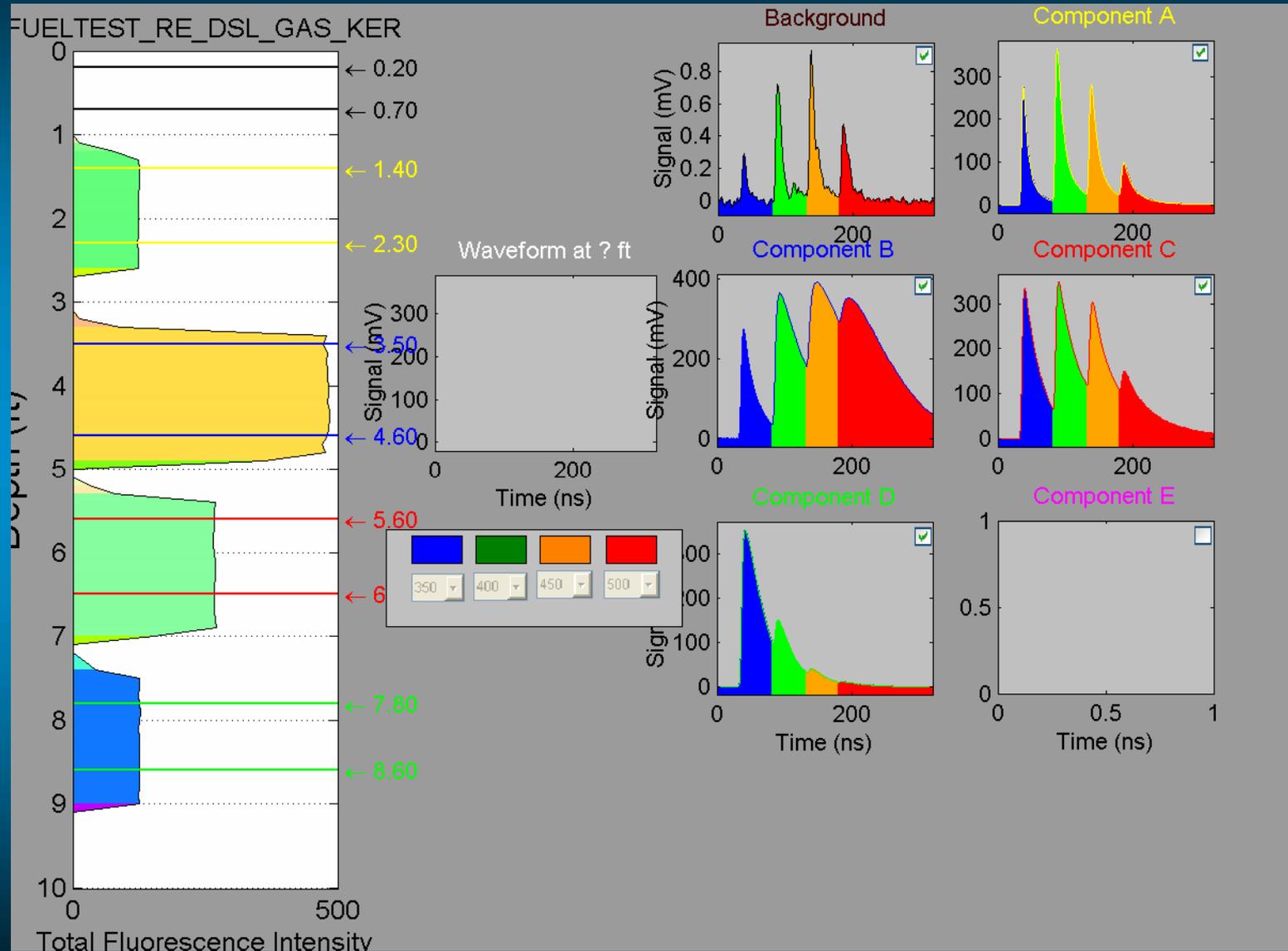


# Advanced Waveform Analysis – Final Result

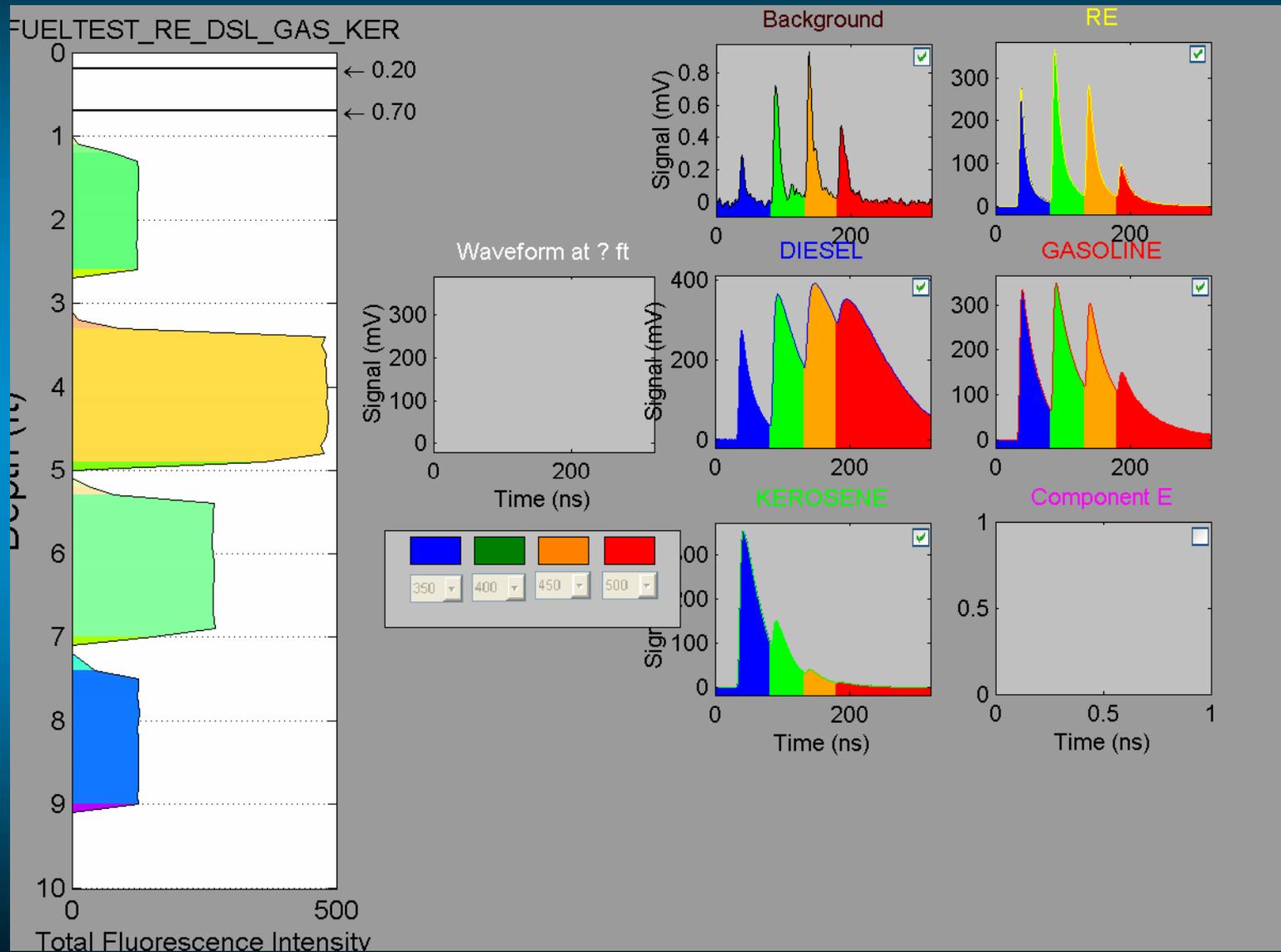
this demonstrates LIF's "additive" behavior under controlled lab conditions – site heterogeneity often limits the ability to parse out tiny amounts of product overwhelmed by other product's fluorescence  
this lab sample example was shown here to demonstrate analytical "power" of LIF under controlled conditions



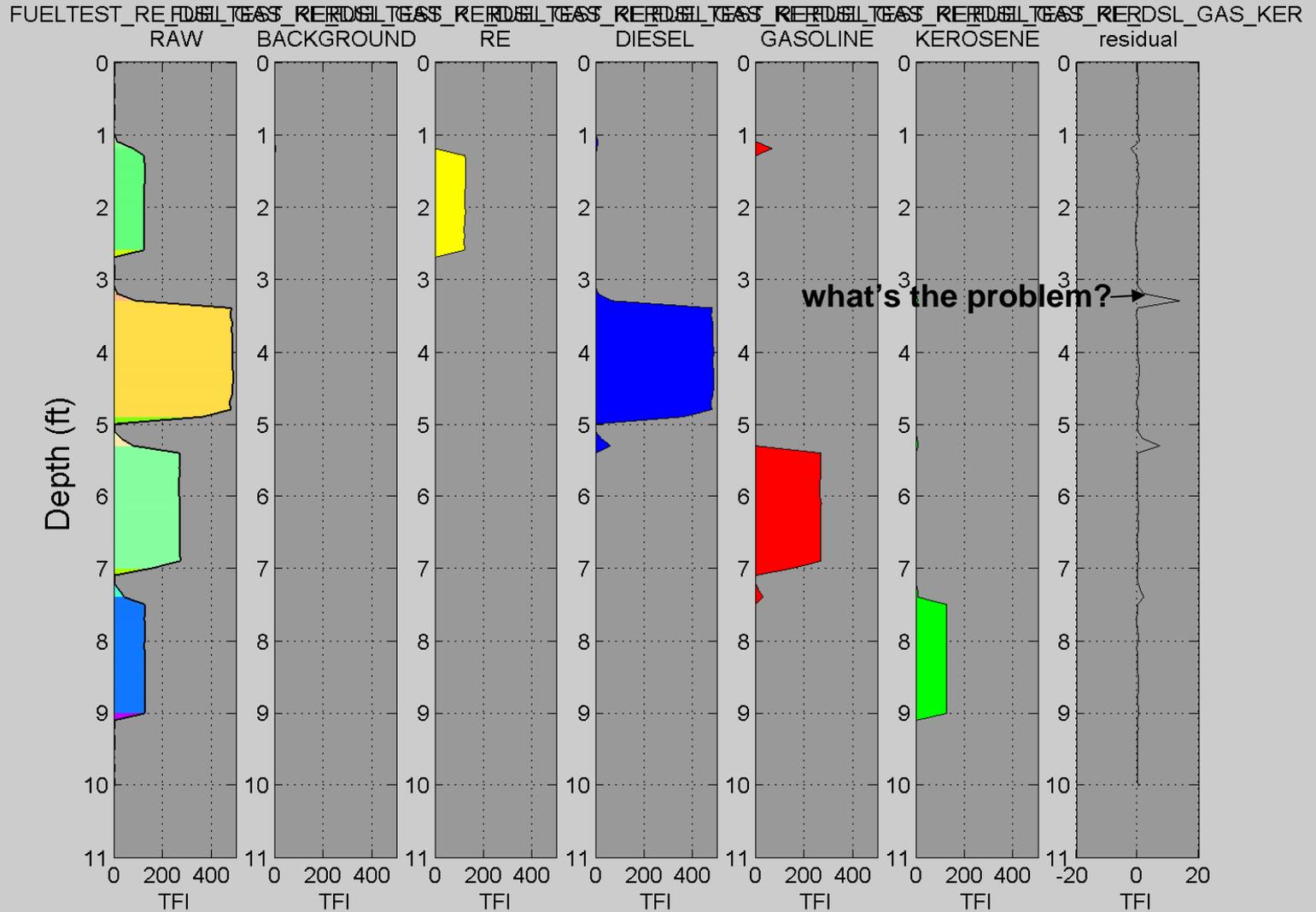
# Various Fuels Log Separation Example



# Various Fuels Log Separation Example



# Various Fuels Log Separation Example

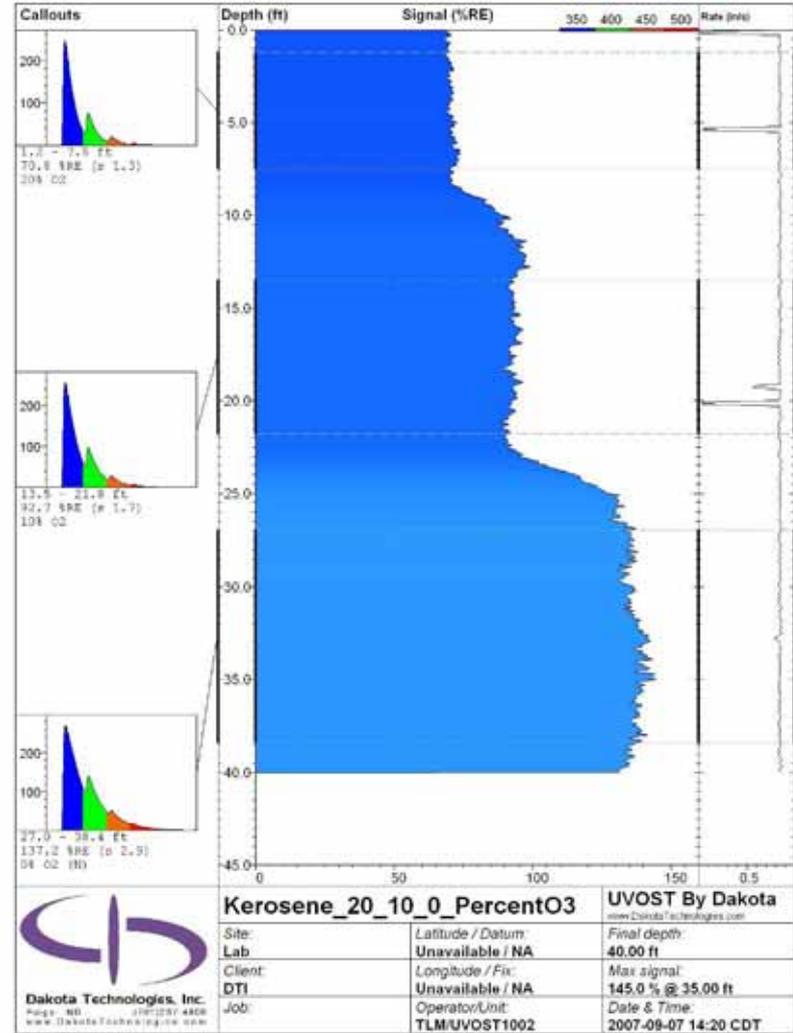
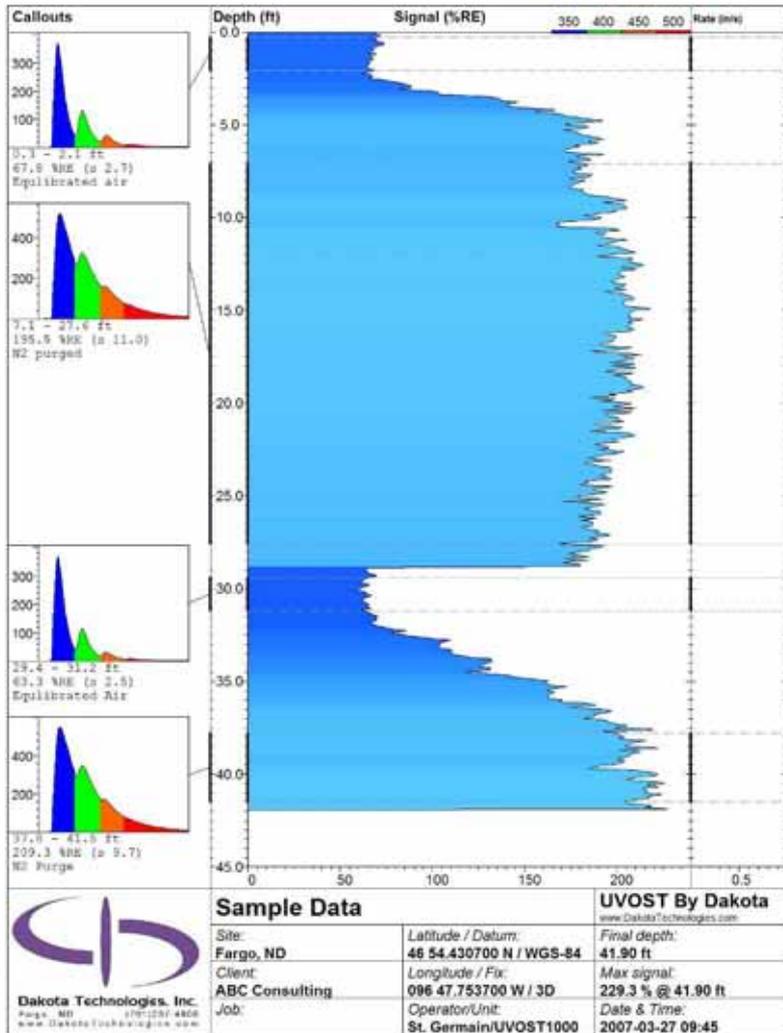


# examples of oxygen's affect on common fuels/NAPL

can cause 2-3 fold increase or decrease in extreme cases

basic technique: bubble N/O2 mix through neat fuel in cuvette

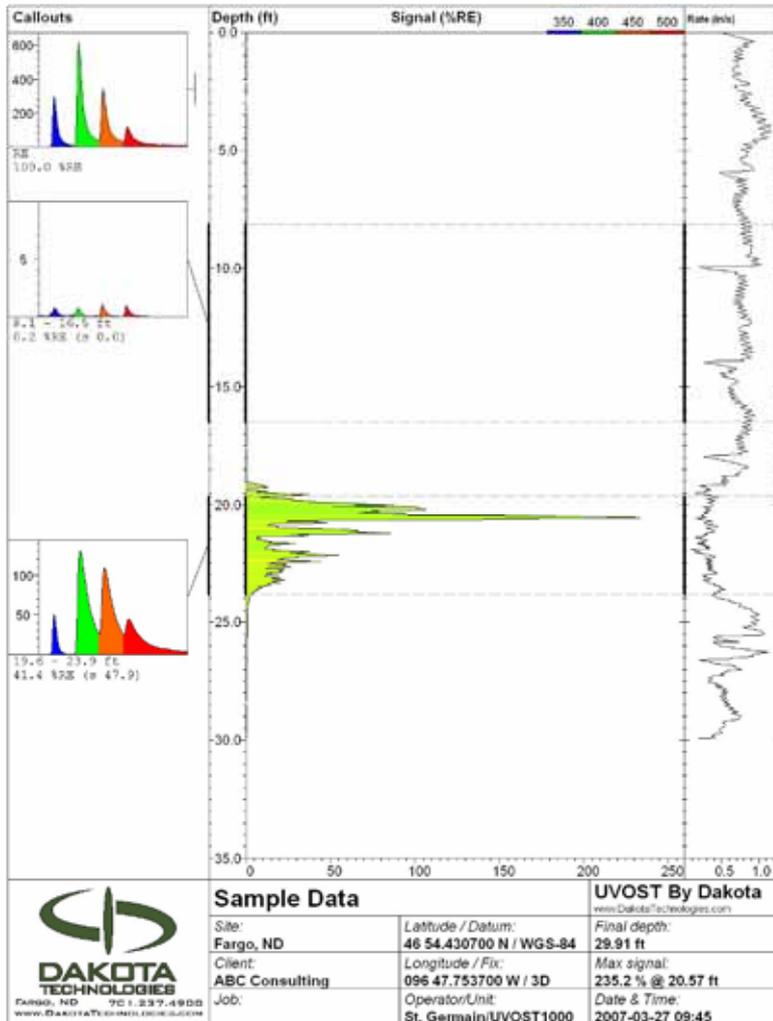
## different product waveform? – no - O2 quenching



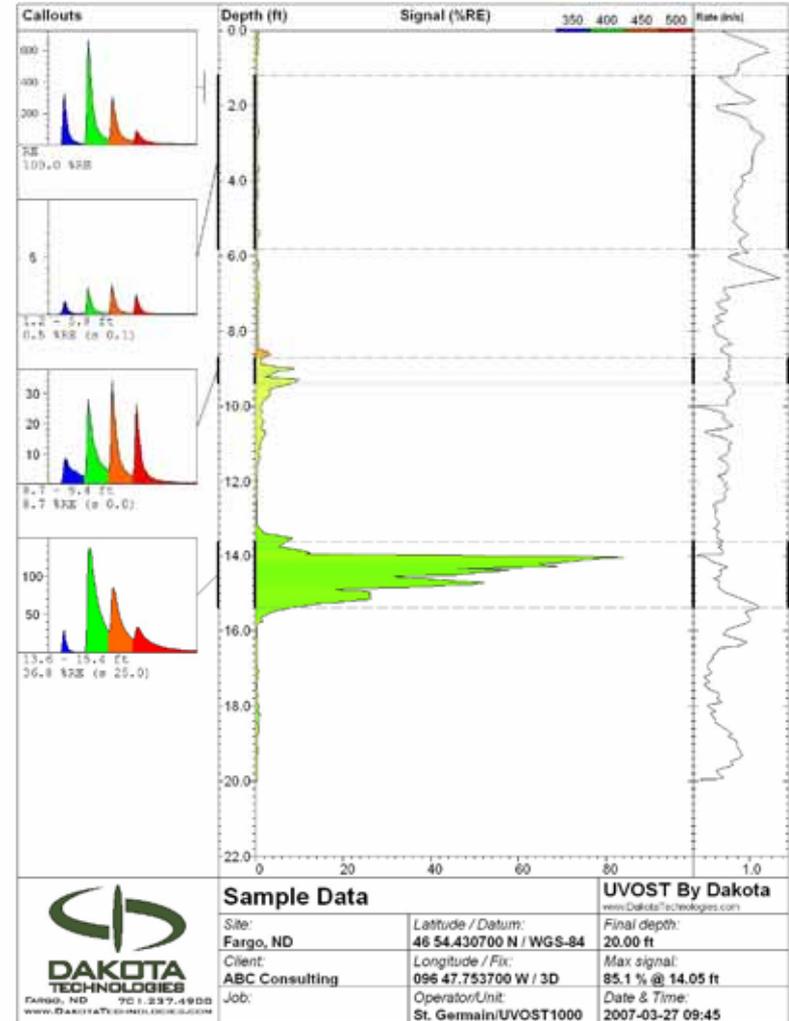
customer's NAPL from a well - 2005

kerosene from pump

# Example Field UVOST Logs

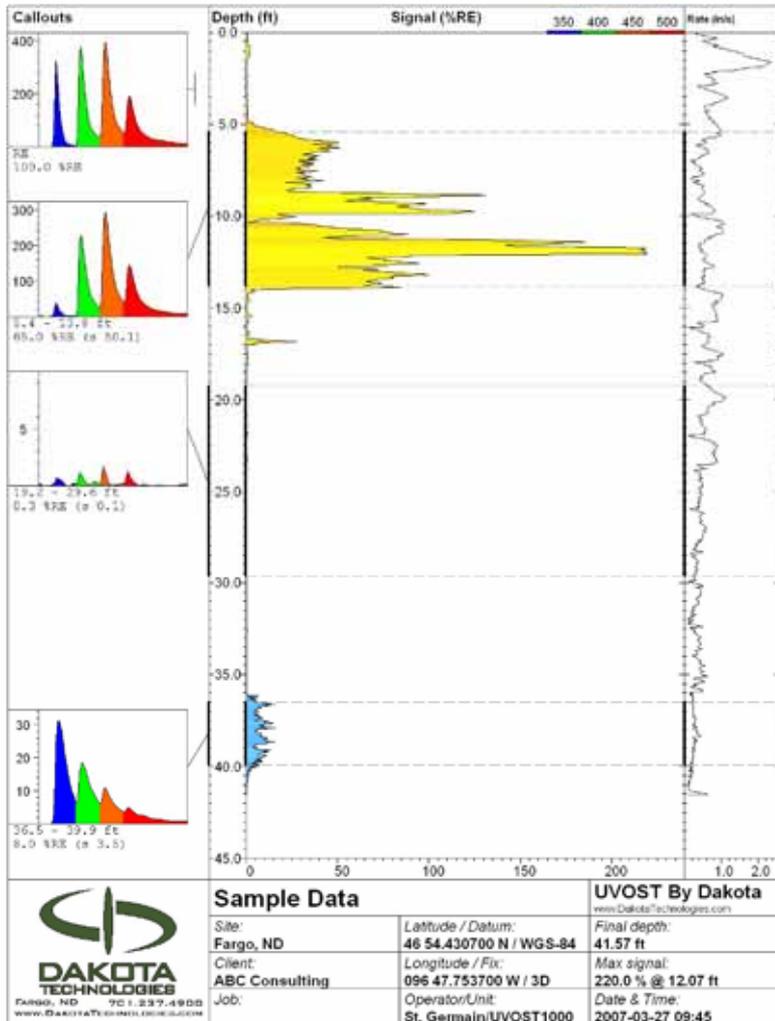


IA – railroad yard diesel

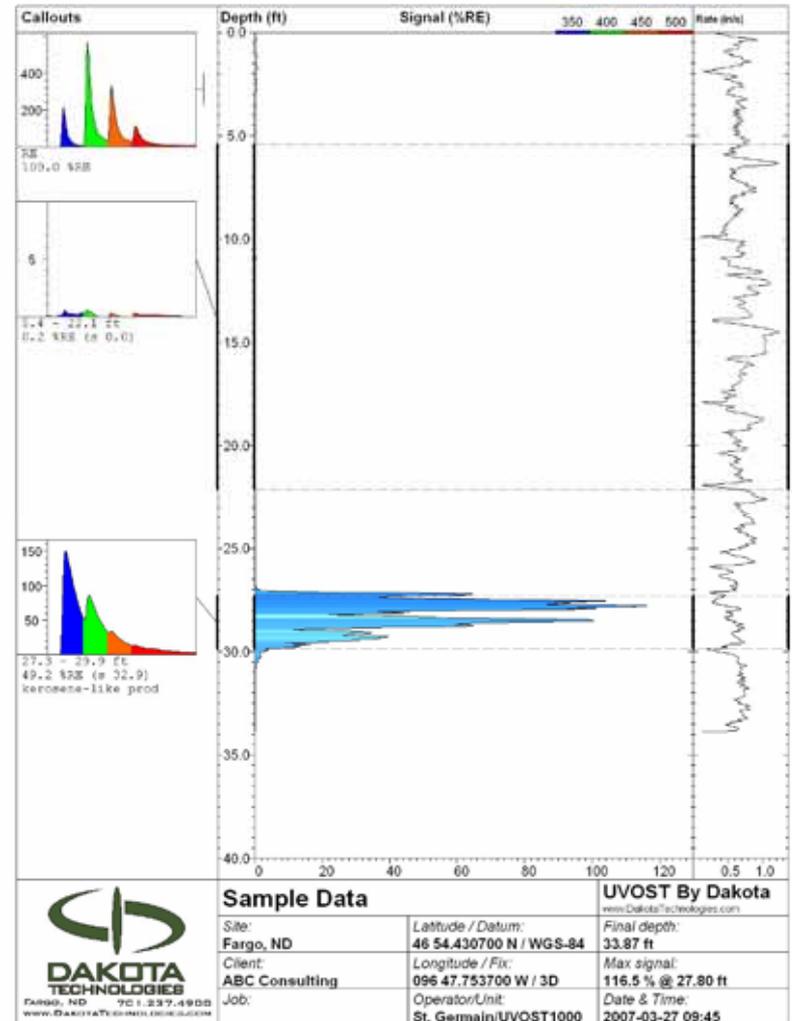


WI – plastic plant - plasticizer cut w/diesel fuel previously “remediated” (dug out) to 10 feet later, free product in a well – LIF shows flawed CSM

# Example Field UVOST Logs

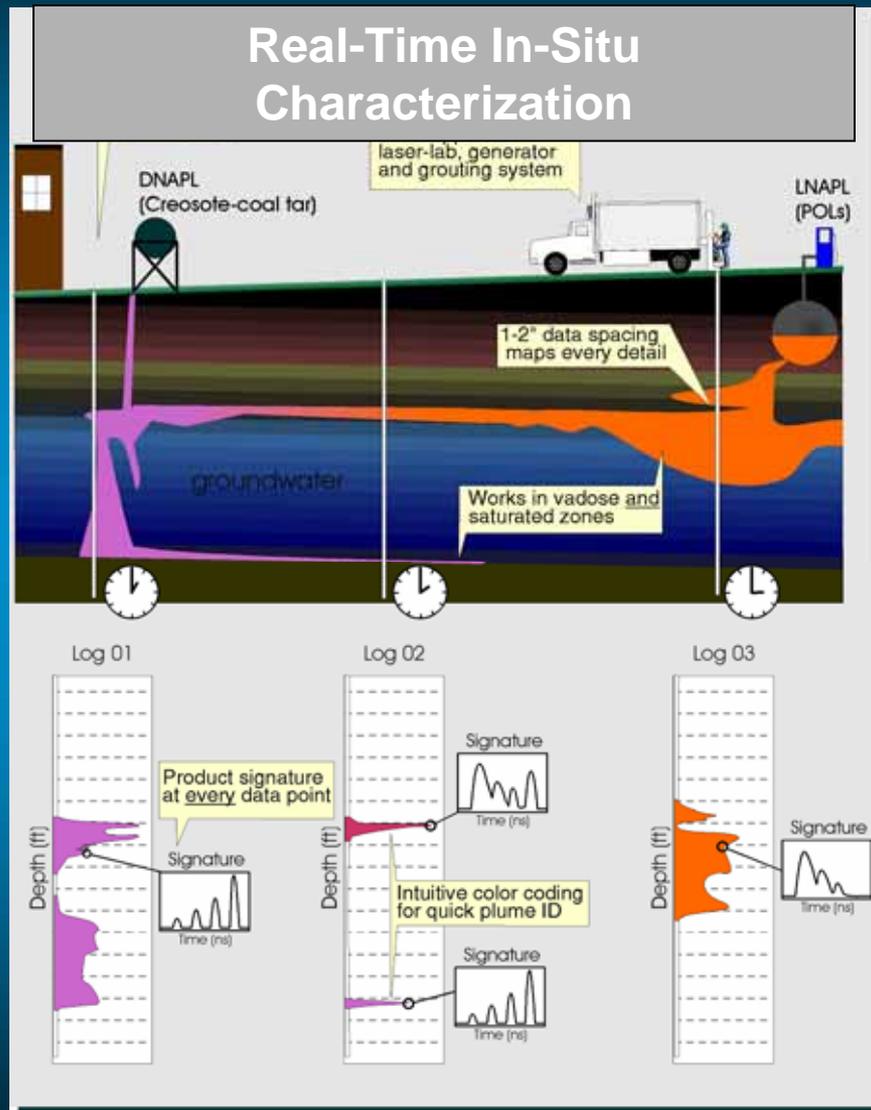


MN – Service Station - 2 NAPLS  
(oil top.... gasoline bottom)



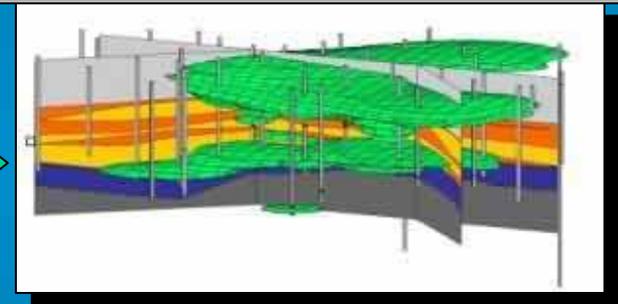
MN - bus garage  
No. 1 Fuel Oil

# LIF Method



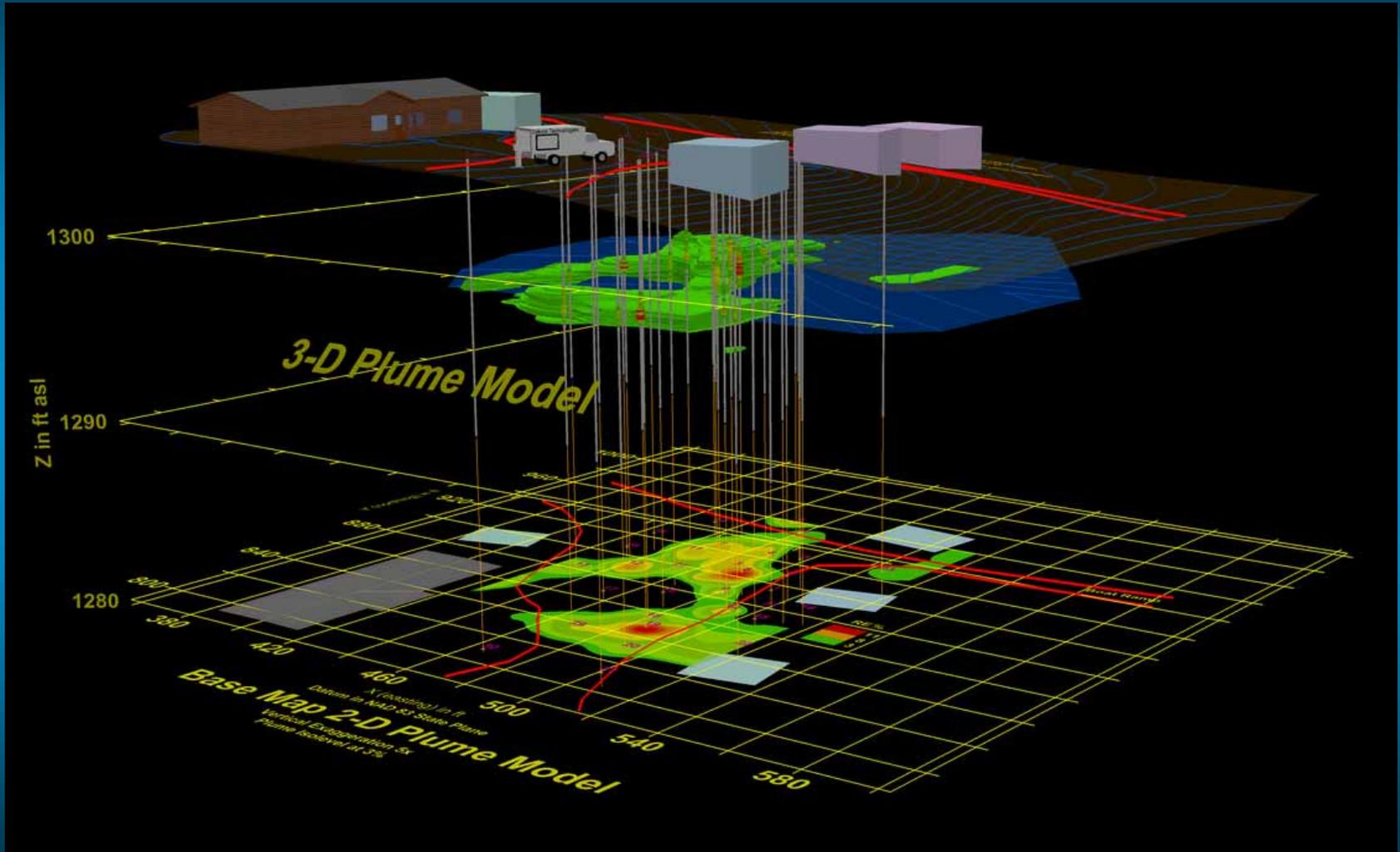
## Desired Result

### Detailed Characterization

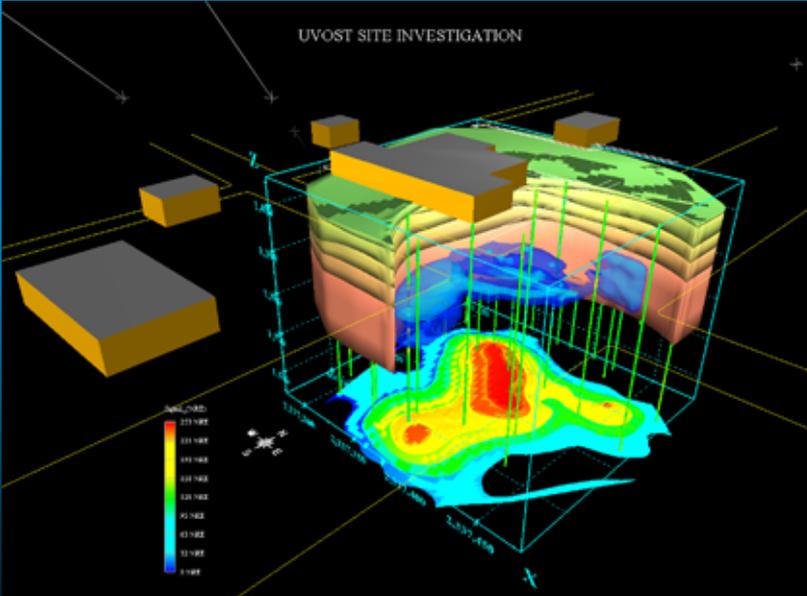
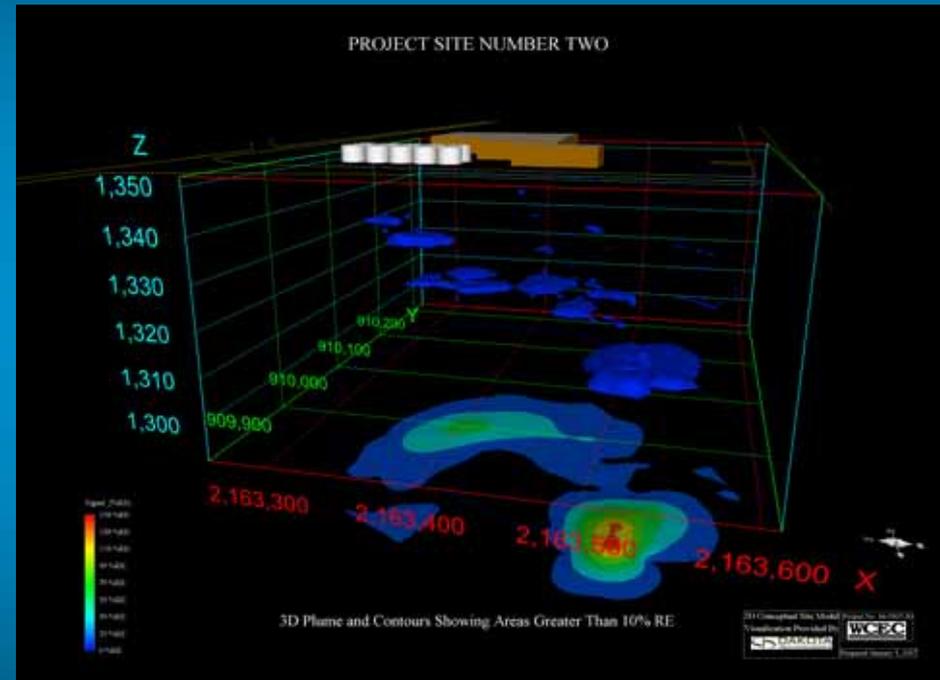
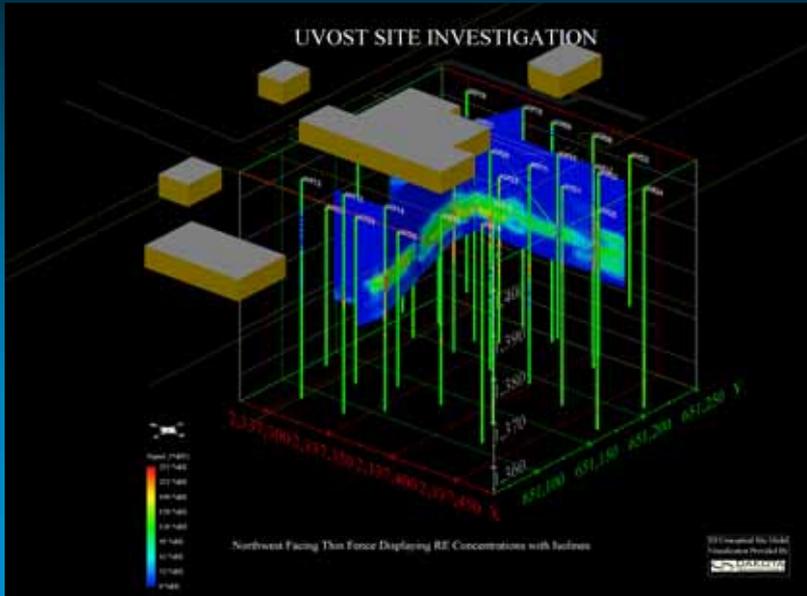


individual logs are certainly useful  
but even more powerful when used in concert  
with other site info to create  
Conceptual Site Model (CSM)

# 3D UVOST Field Data CSMs



# 3D UVOST Field Data CSMs



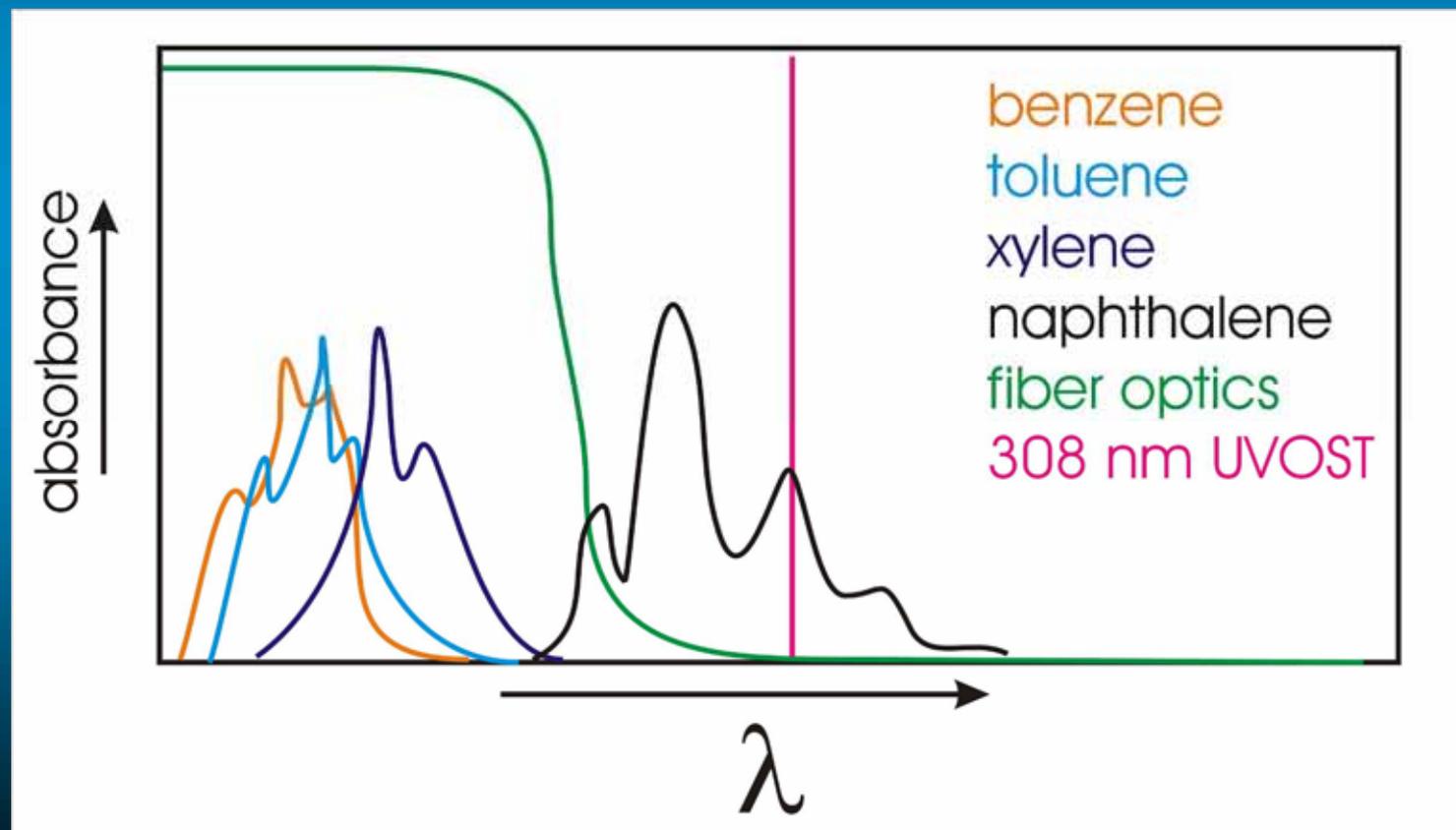
# can UVOST detect BTEX?

no it can't - due to fiber optic absorbance below 280 nm

UVOST would use 266nm if attenuation didn't limit us

bottom line is that BTEX absorbance lies too deep in the UV to reach

in practical sense this doesn't limit LIF much – UVOST “sees” gasoline's PAHs anyway



# MIP or LIF?

## MIP

- Designed for VOCs – including dissolved phase
- “sticky” semi-VOCs cause transfer line/carryover problems
- membrane’s physical form potentially allows NAPL to hang in cracks/crevices
- difficult to find “bottom” of NAPL due to gas line carryover and resulting lag time
- logs are often less intuitive with major baseline shifts (compared to LIF logs)

## LIF

- Designed specifically for NAPL delineation
- smooth/hard sapphire window is “slick” like Teflon – resists carrydown
- nearly instantaneous rise/fall - and 100% reversible response
- UVOST does NOT see any useful levels of response to dissolved phase
- UVOST shows intimate detail of NAPL distribution (relative to MIP)
- UVOST provides readily interpreted “spectral” information in real time
- UVOST is “blind” to halogenated hydrocarbons – even hDNAPL itself
- no transfer lines to contaminate – all signals up/down are light-based

# can UVOST detect dissolved phase PAHs? (naphthalenes, anthracene, etc.)

NO it can't... at least not in useful conc's

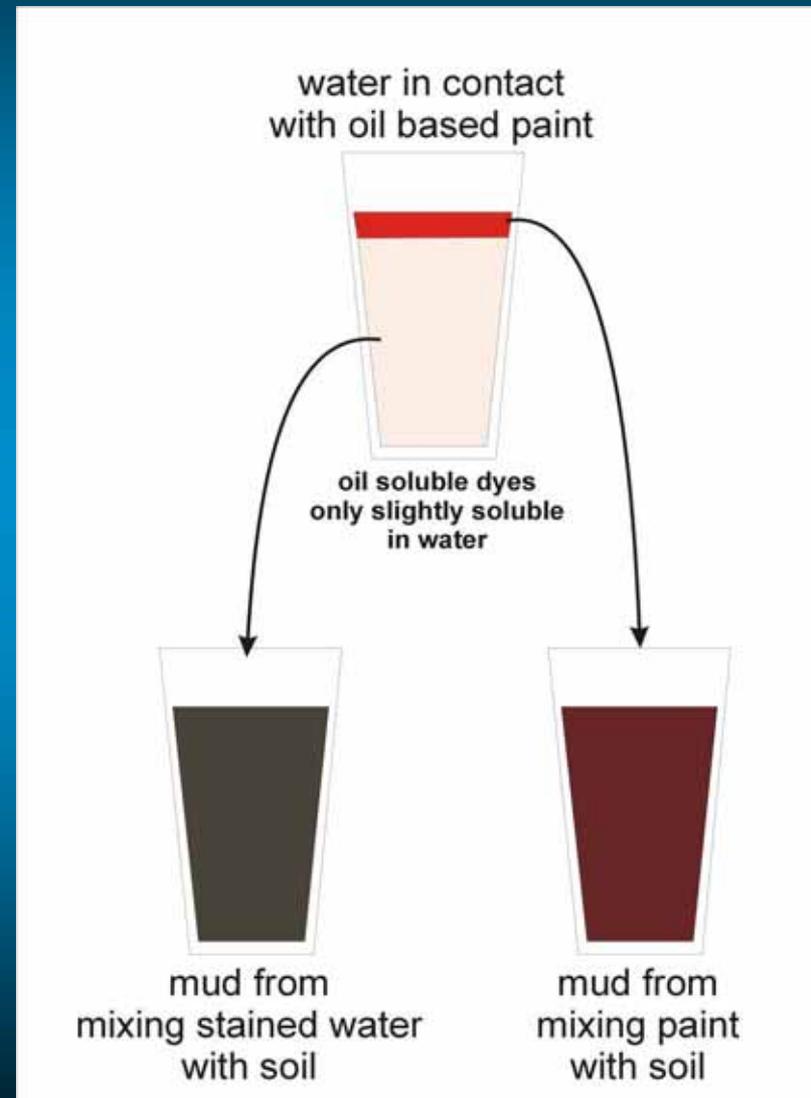
the relative solubility of PAHs in water  
is much less than in NAPL solvent

(hundreds/thousands/millions times higher solubility in NAPL  
than in water)

only in sandy clear pore water conditions  
do PAHs ever get "visible enough" to  
generate a detectable signal (<< 5% RE)

think of NAPL as "paint" for a visual  
intuitive example – the orange stained  
water makes dark mud – the paint itself  
makes orange mud – easy to see the  
painted mud – but impossible to see  
orange water after it's been made into  
mud

PAHs act much the same as orange dye  
in this example



# Potential False Positives and Negatives

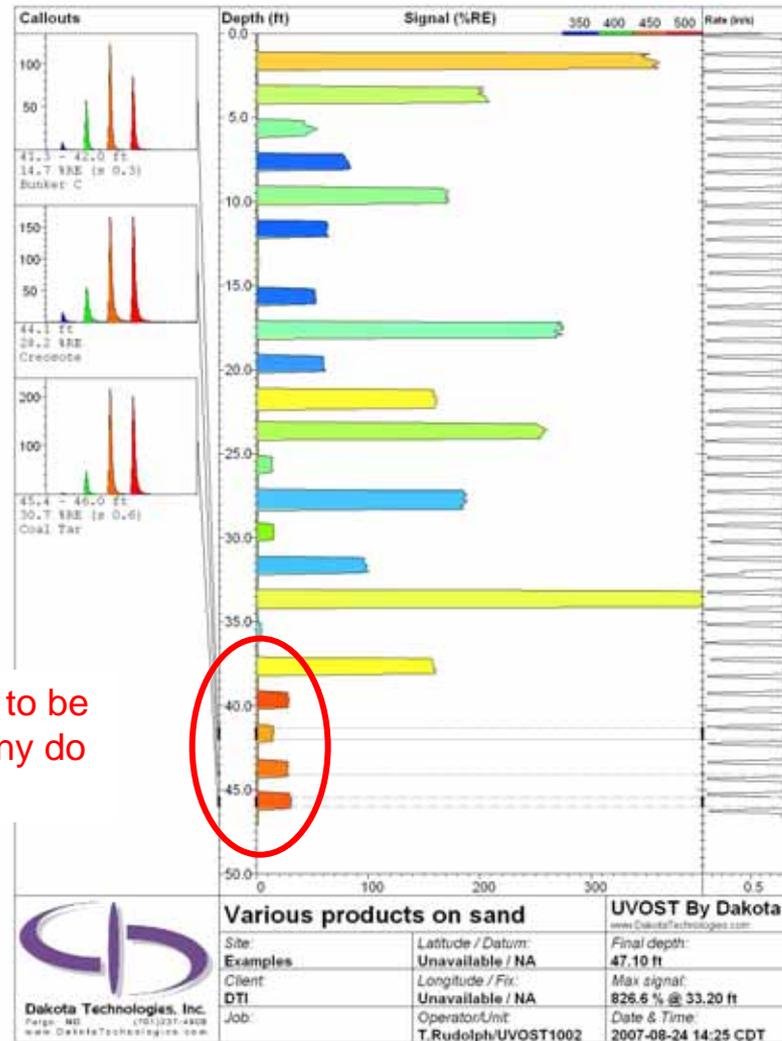
## Previously observed positives [weak 1-3% RE, medium 3-10% RE, strong >10% RE]

sea shells (weak-medium)  
paper (medium-strong)  
peat/meadow mat (weak - medium)  
calcite/calcareous sands (weak-medium)  
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 very weak with UV)  
creosotes (most very weak with UV)  
“dry” PAHs such as aqueous phase, lamp black, purifier chips, “black mayonnaise”  
most chlorinated solvent NAPL (unless containing substantial PAH from degreasing)  
benzene, toluene, xylenes (relatively pure)

# UV LIF DOES NOT see coal tar and creosote reliably! – why?



the tars in this test log happen to be above average in the UV – many do not fluoresce at all!!

# most coal tars and creosotes “roll over” or they simply don’t fluoresce well in UV - why?

a PAH NAPLs’ fluorescence spectra will sometimes “red-shift” with increasing concentration – this is due mainly to electronic energy transfer – the higher the PAH content of the NAPL, the likelier it is to morph with concentration and/or to “roll over” and lose fluorescence with increasing conc. even to the point of being non-fluorescent!

in the UV, excitation light is absorbed by smaller PAHs (they have large bandgap) – in concentrated PAH conditions this absorbed energy is readily transferred to larger molecules (small bandgap) before fluorescence can occur – continued cascading of this absorbed energy up the PAH size chain eventually results in larger PAHs emitting redder light - or “red-shifting”

each “step” along this chain is also fraught with non-radiative energy loss mechanisms – so past a point, the more and more PAHs in a NAPL the likelier it is to be “poorly behaved” in both quantitative and qualitative respects (size and shape of waveforms) – at some point photons just never get produced in appreciable amounts – majority of initially absorbed energy is simply converted to thermal energy without useful amounts of fluorescence

so to summarize - too few PAHs simply cause low signal (av gas for example), just the right amount yields nearly perfect behavior (diesel), very high PAH concentration causes morphing and roll over (crude/bunker), and getting WAY too many PAHs (coal tar) often causes very low signals and extreme rollover to the point where UVOST can be totally unreliable – small conc’s of coal tar actually yield larger signals than pure coal tar – that’s worst case scenario for any screening tool!

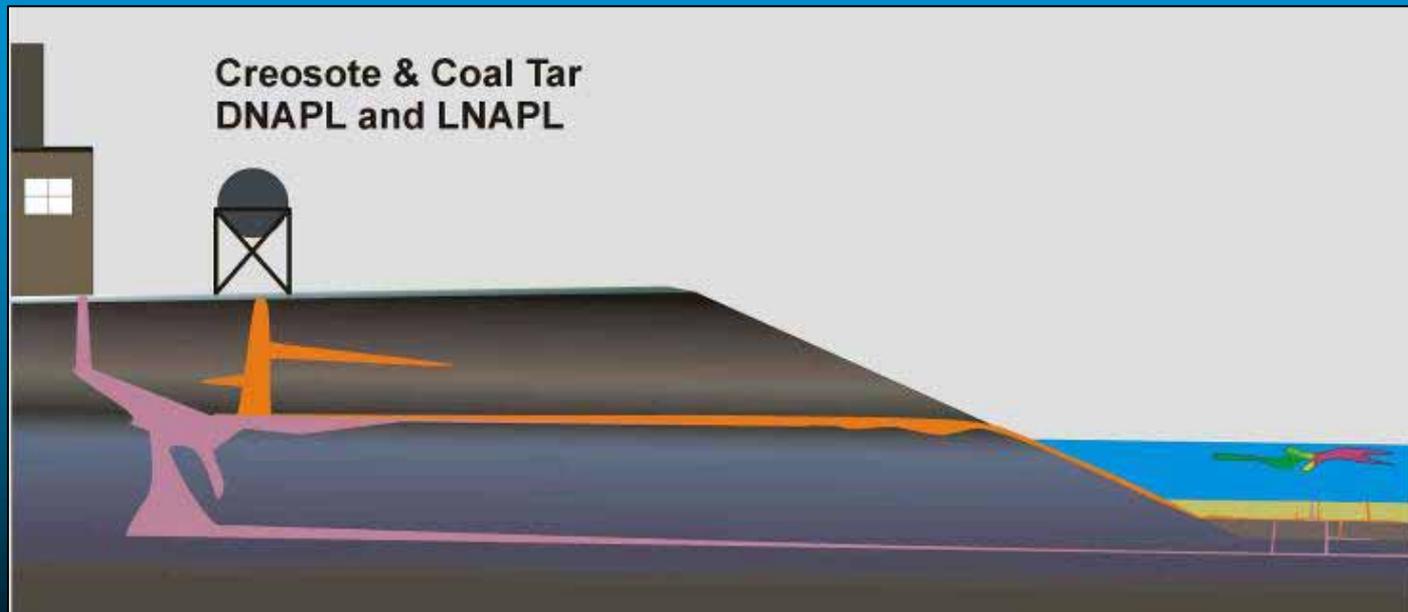
## Visible Wavelength LIF

### Example: Tar-Specific Green Optical Screening Tool (TarGOST®)

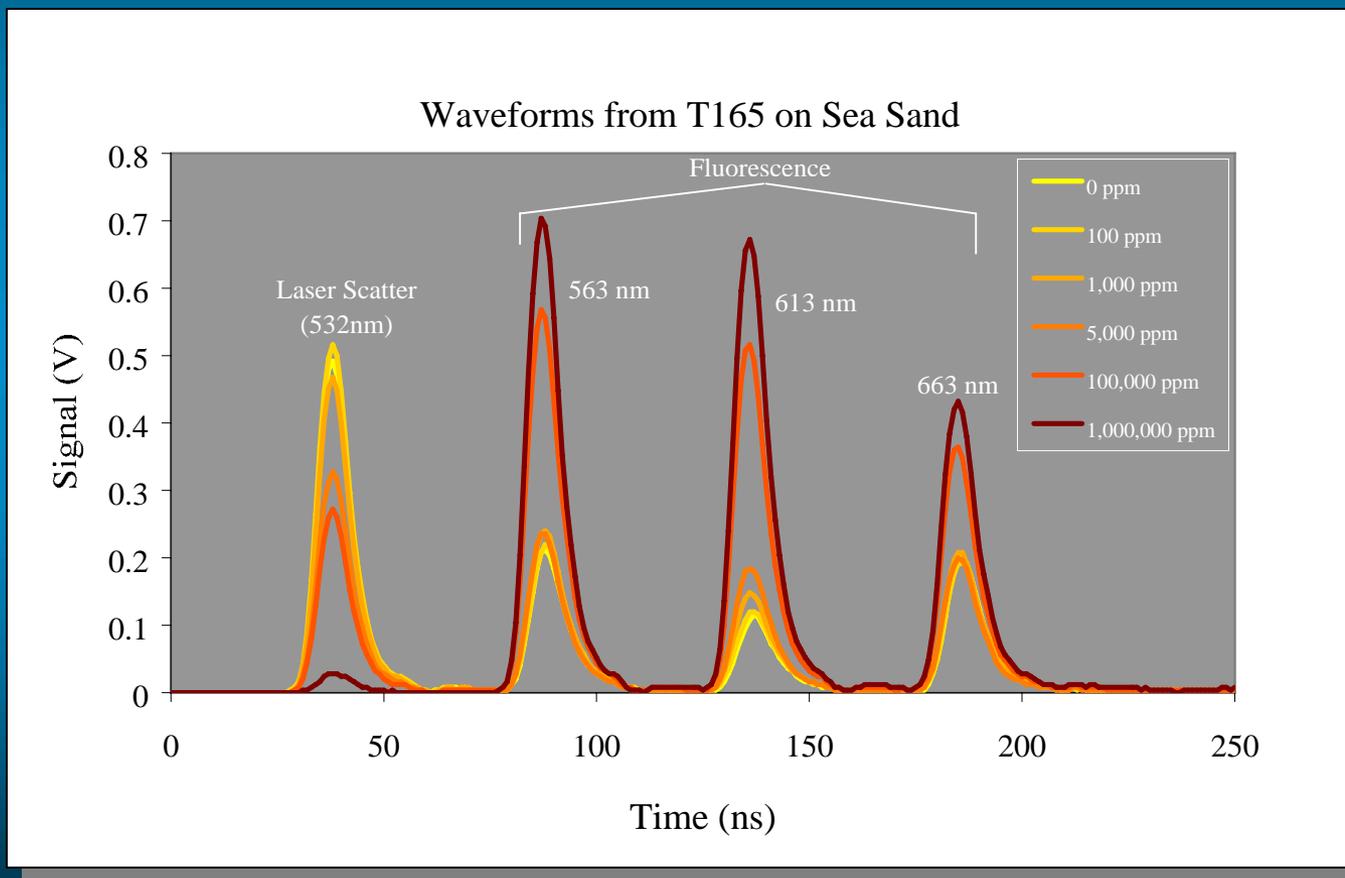
designed specifically for MGP NAPL, creosotes, and pentachlorophenol (typically cut with diesel)

visible excitation defeats the energy transfer trap by “skipping over” the absorbance of the excitation source by the smaller PAHs who “love” to absorb UV

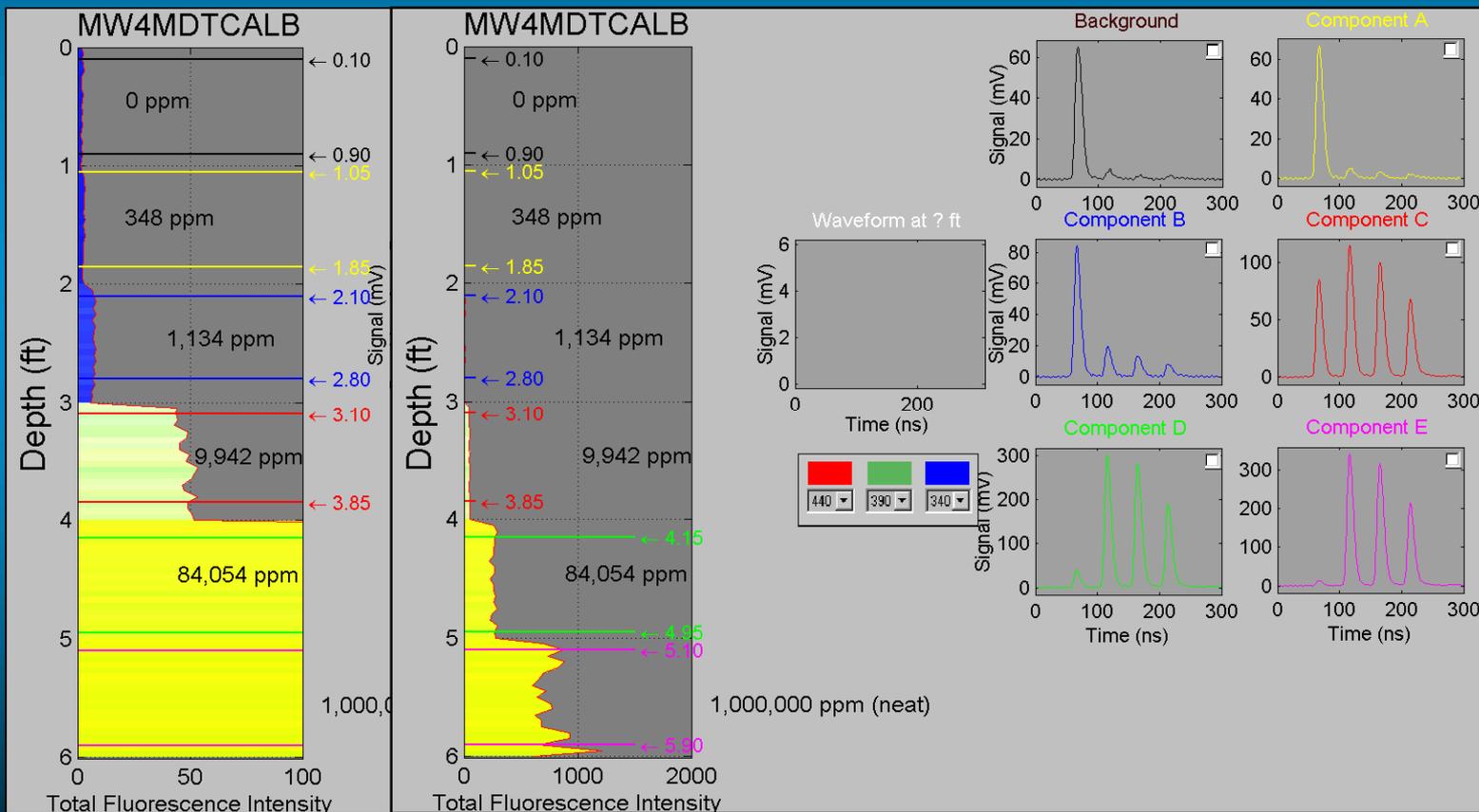
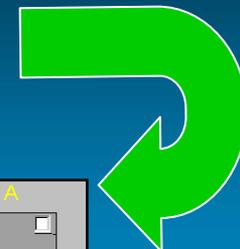
basically the visible light zips through smaller PAHs and is only absorbed by the very large PAHs which are much more likely to fluoresce due to lack of potential “neighbors” to which they can transfer the absorbed energy



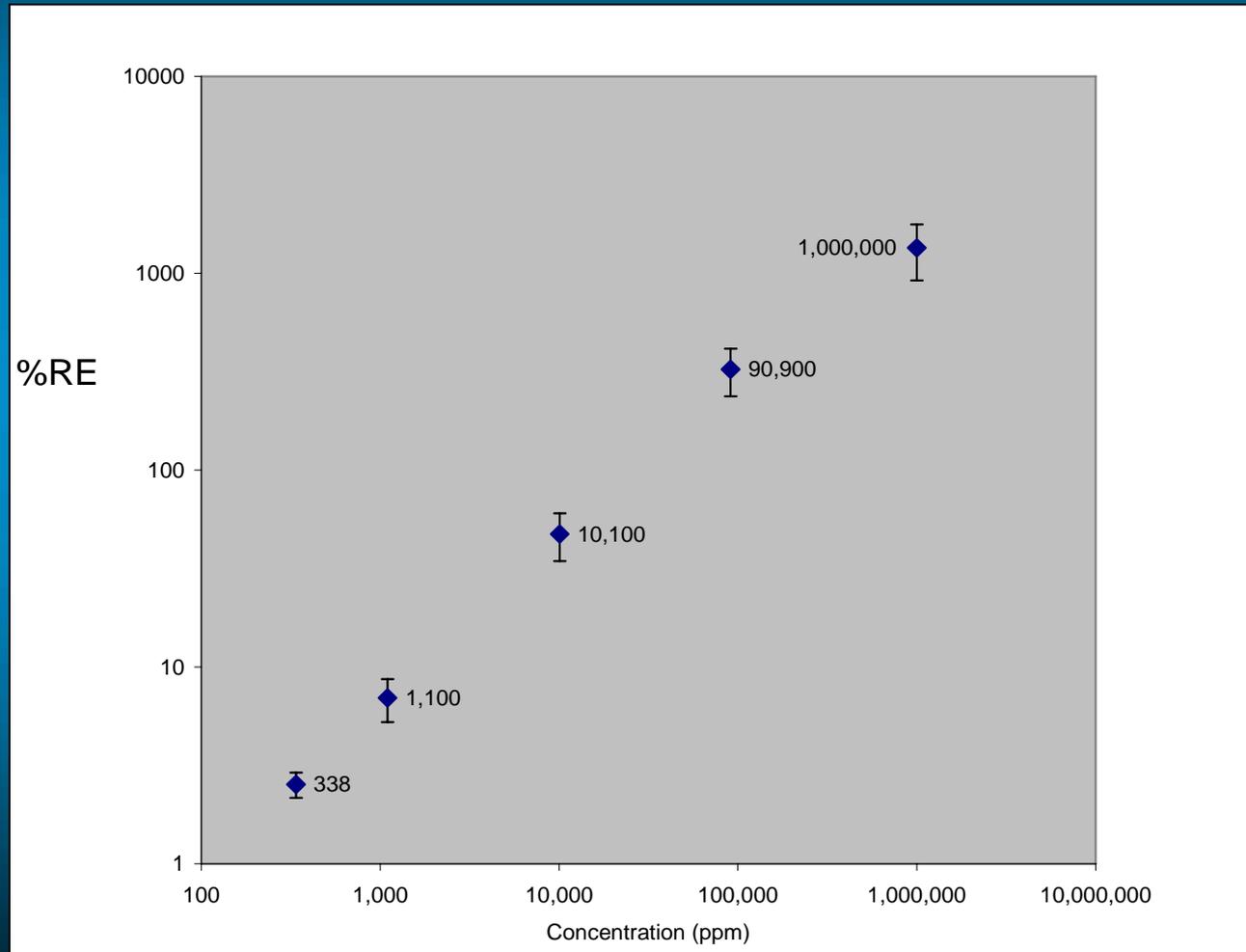
# TarGOST Waveforms vs. Coal Tar Concentration



# Visible LIF (TarGOST)



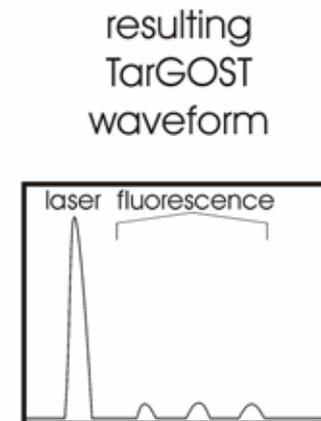
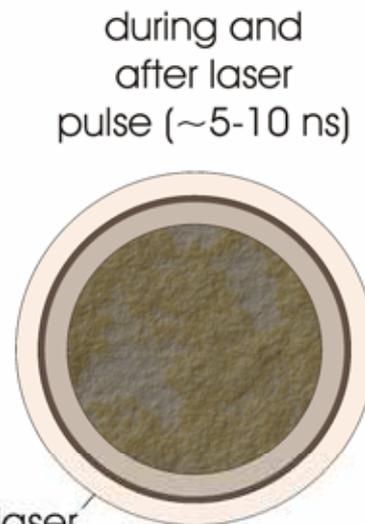
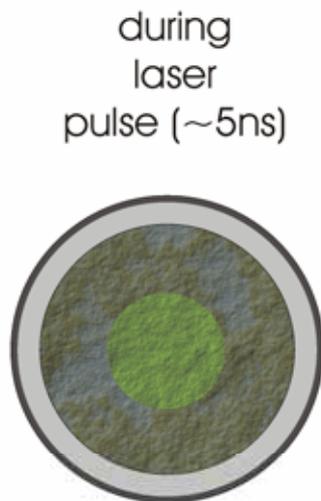
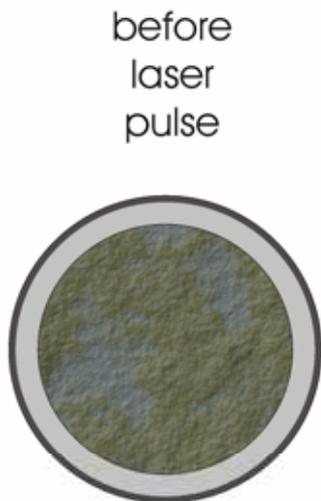
curve resulting from previous slide's coal tar study  
not all tars behave “perfectly” like this – but all are  
monotonic in response to concentration (no rollover)  
when excited with visible laser pulses



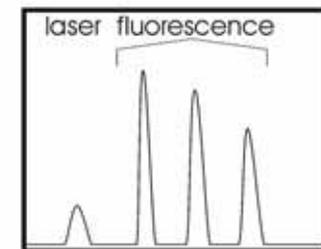
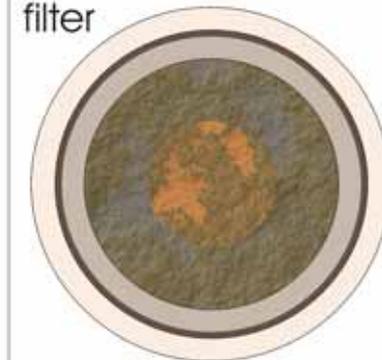
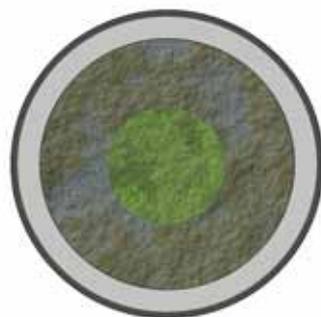
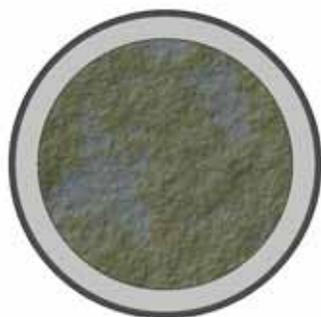
# so how does TarGOST “see” tar?....

here’s a conceptual view of what it looks like outside the window

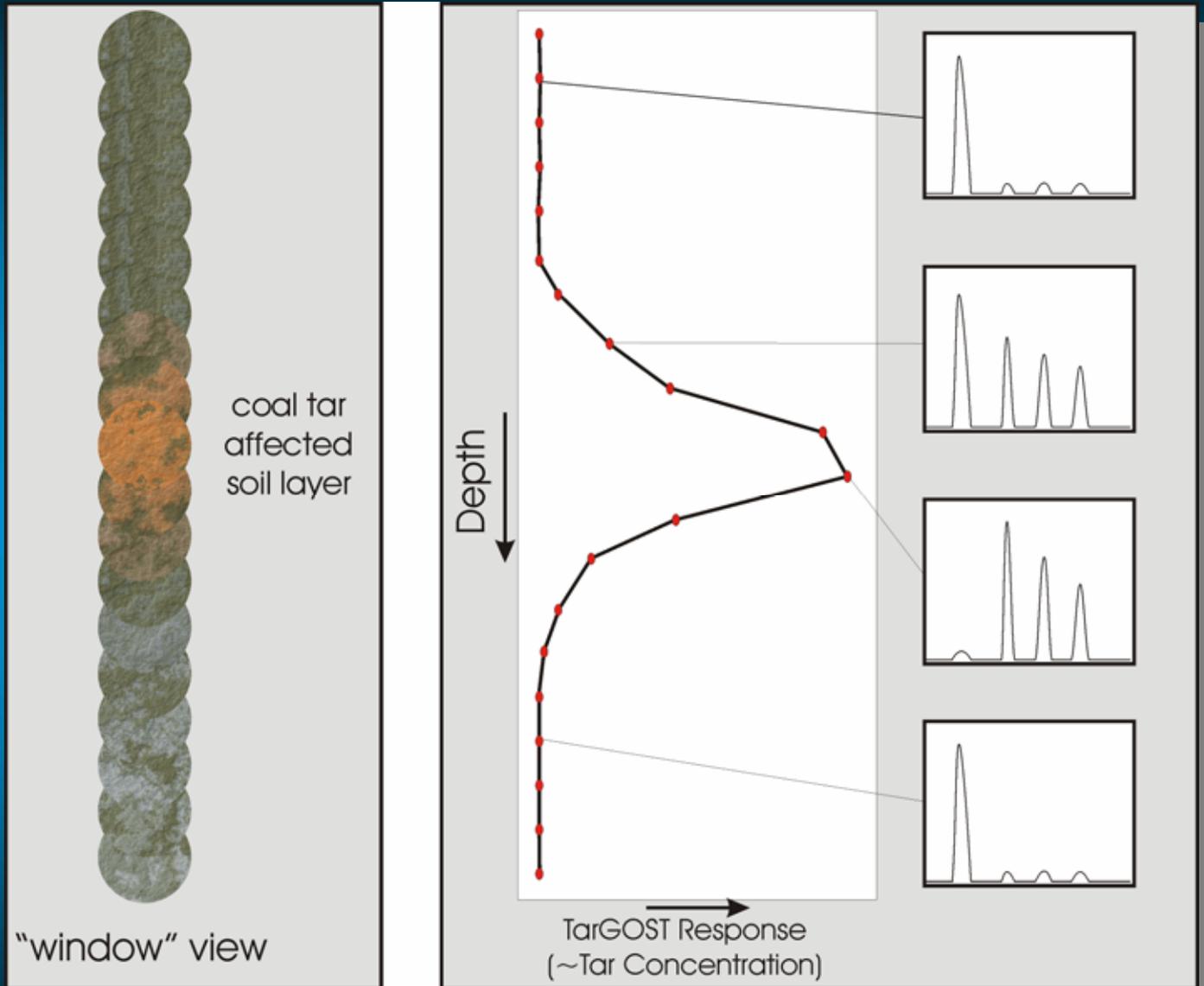
CLEAN



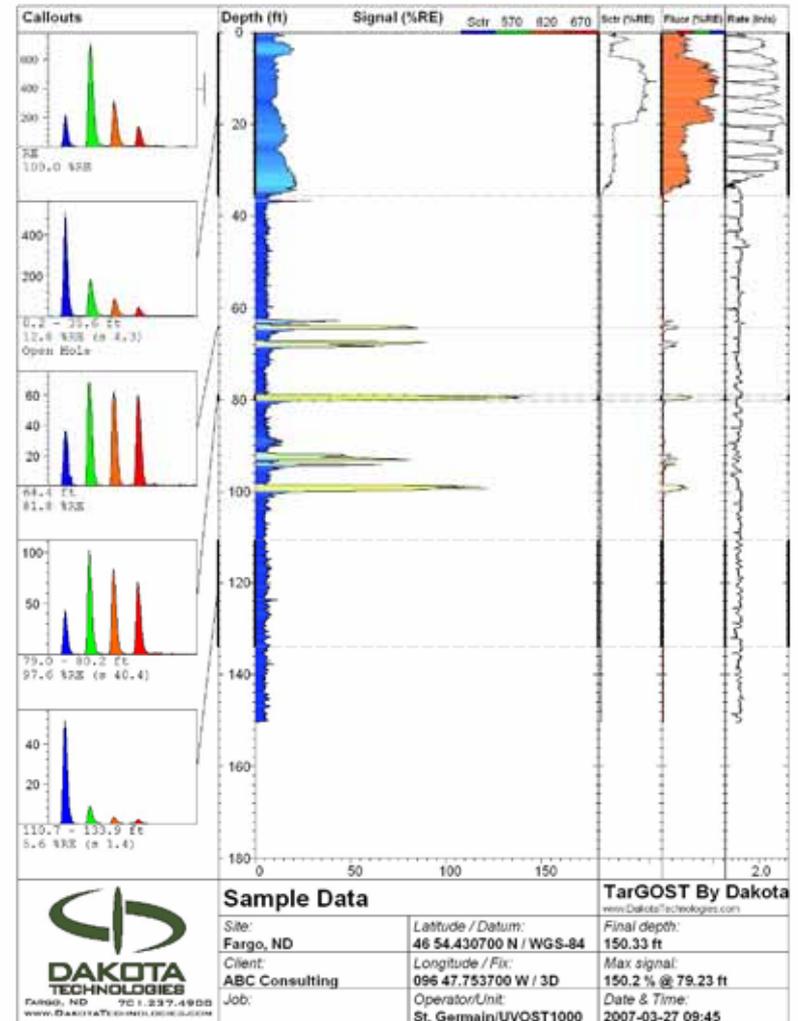
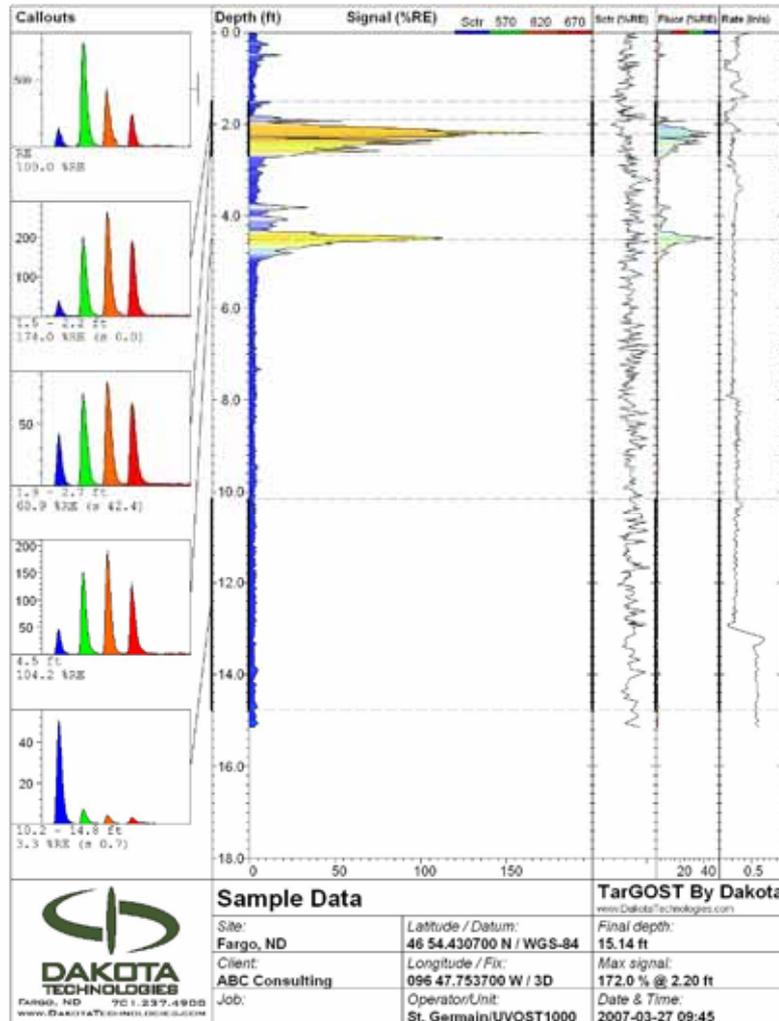
TAR



# so how does TarGOST “see” tar?....



# Example TarGOST Field Logs

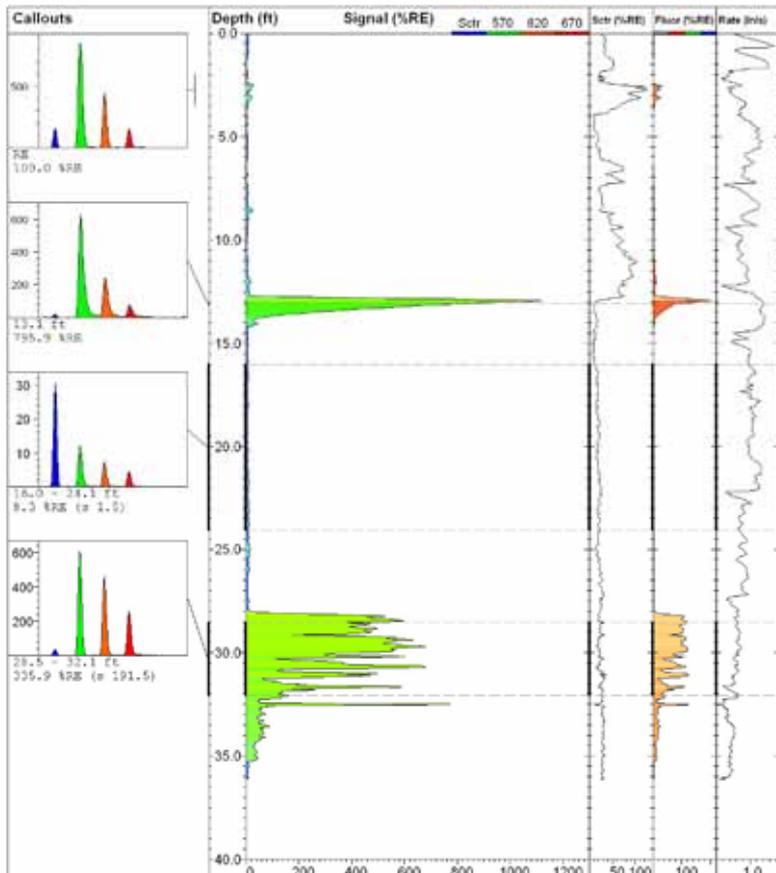


New York - done from a barge in 20+ ft. of water

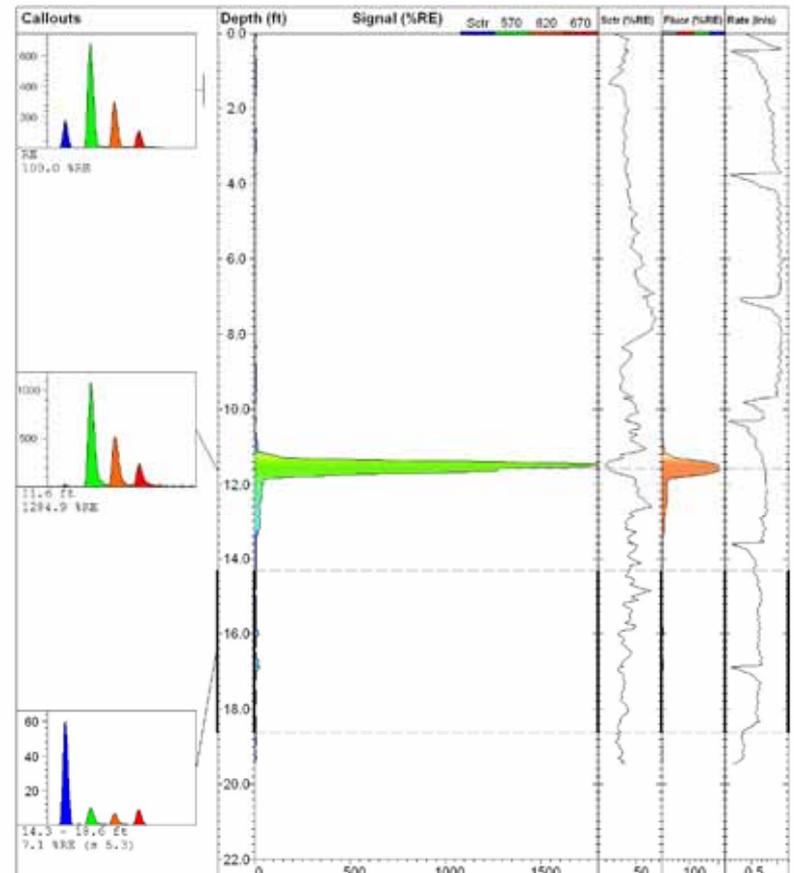
Oregon  
150ft – mobile NAPL at 100ft  
(first 30 ft were in open hole)

LIF Workshop – Jan. 2008

# Example TarGOST Field Logs



 <b>DAKOTA TECHNOLOGIES</b> <small>FARGO, ND 701.237-4900</small> <small>www.DakotaTechnologies.com</small>	<b>Sample Data</b>		<b>TarGOST By Dakota</b> <small>www.DakotaTechnologies.com</small>
	Site:	Latitude / Datum:	Final depth:
	Fargo, ND	46 54.430700 N / WGS-84	36.12 ft
	Client:	Longitude / Fix:	Max signal:
	ABC Consulting	096 47.753700 W / 3D	1189.7 % @ 32.51 ft
Job:	Operator/Unit:	Date & Time:	
	St. Germain/UVOST1000	2007-03-27 09:45	

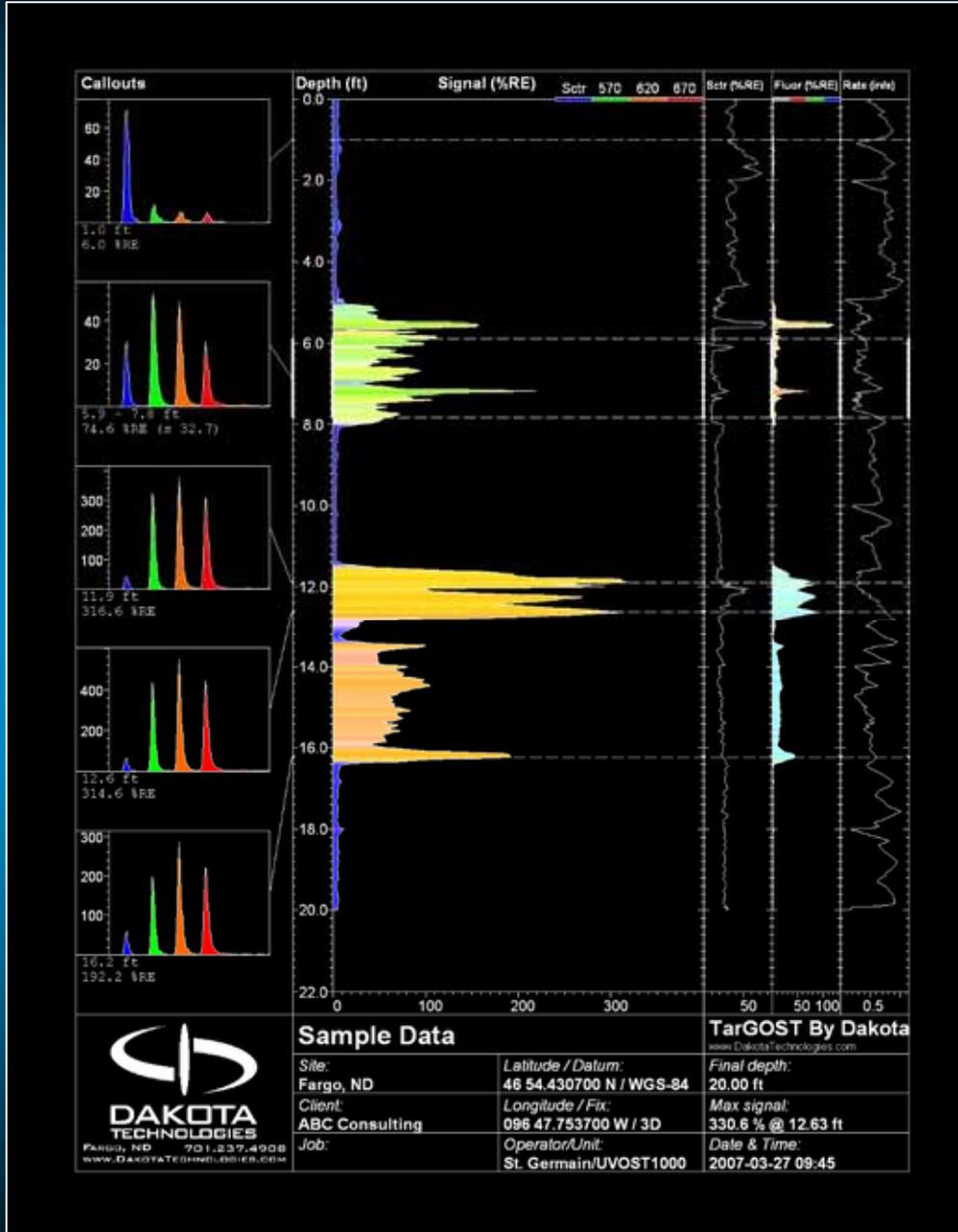


 <b>DAKOTA TECHNOLOGIES</b> <small>FARGO, ND 701.237-4900</small> <small>www.DakotaTechnologies.com</small>	<b>Sample Data</b>		<b>TarGOST By Dakota</b> <small>www.DakotaTechnologies.com</small>
	Site:	Latitude / Datum:	Final depth:
	Fargo, ND	46 54.430700 N / WGS-84	19.45 ft
	Client:	Longitude / Fix:	Max signal:
	ABC Consulting	096 47.753700 W / 3D	1586.9 % @ 11.48 ft
Job:	Operator/Unit:	Date & Time:	
	St. Germain/UVOST1000	2007-03-27 09:45	

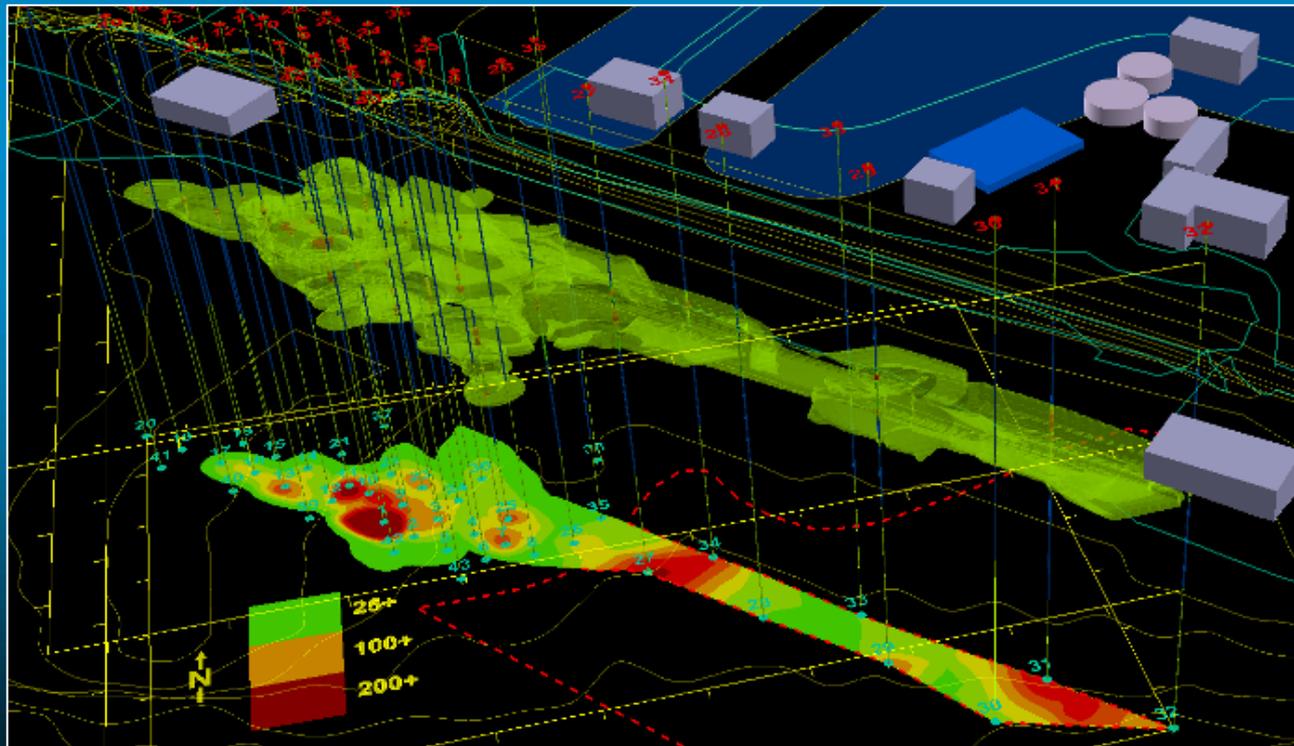
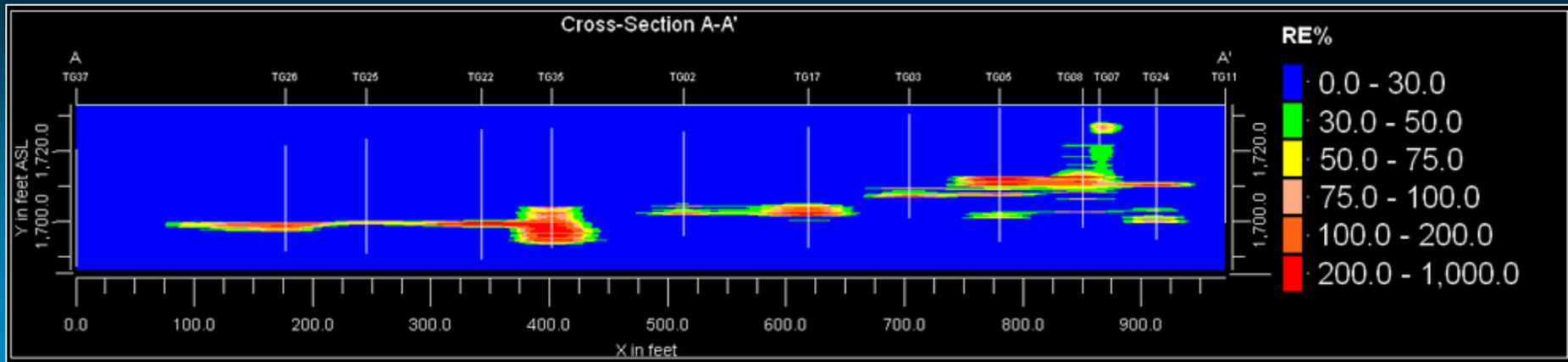
WI - 2 layers of MGP NAPL  
separation into LNAPL/DNAPL?

CA crude oil  
showed up better with TarGOST than UVOST

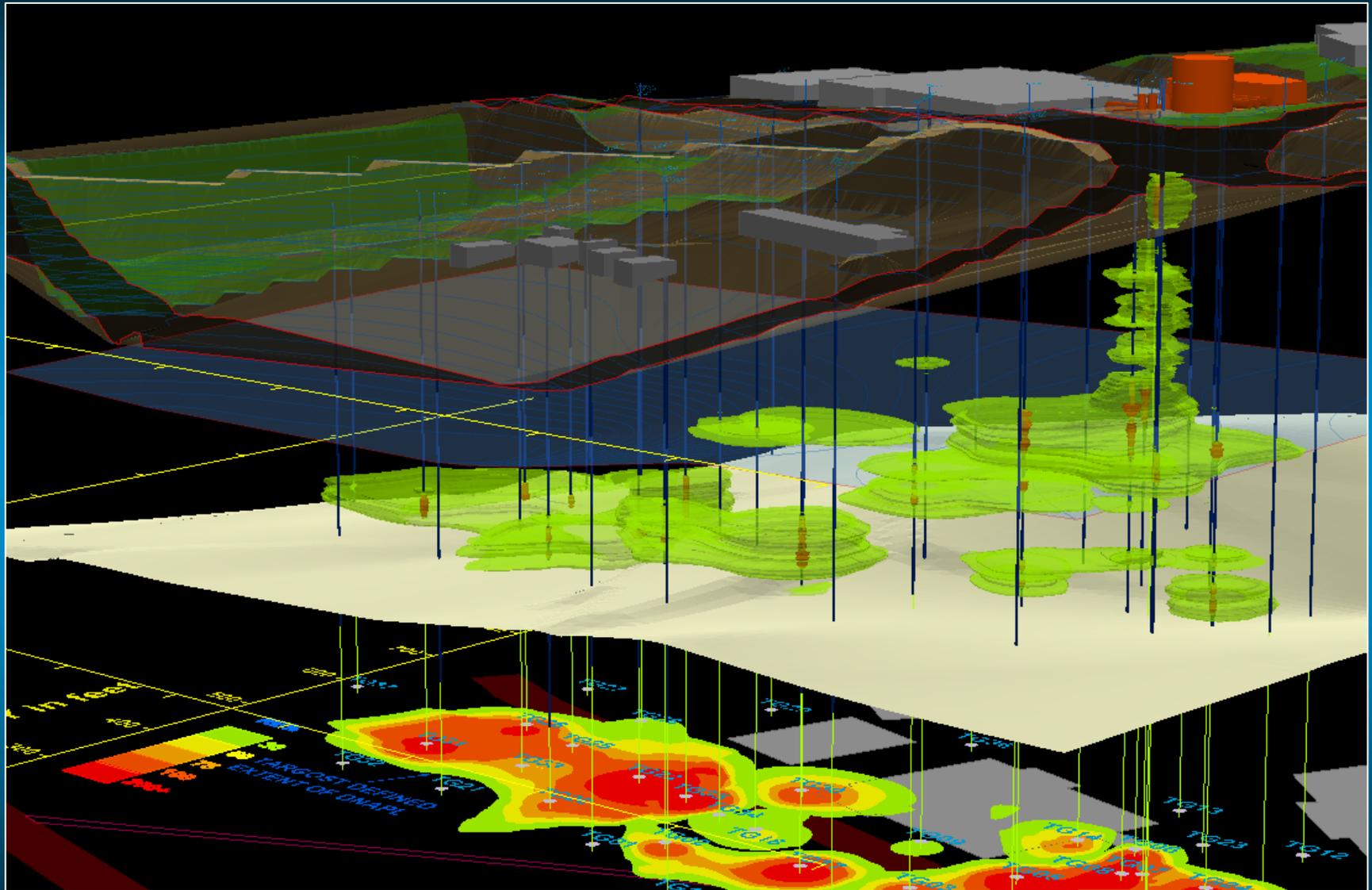
black background – for overlay on CSM software’s typical black background



# 2D and 3D Visualization of TarGOST Data



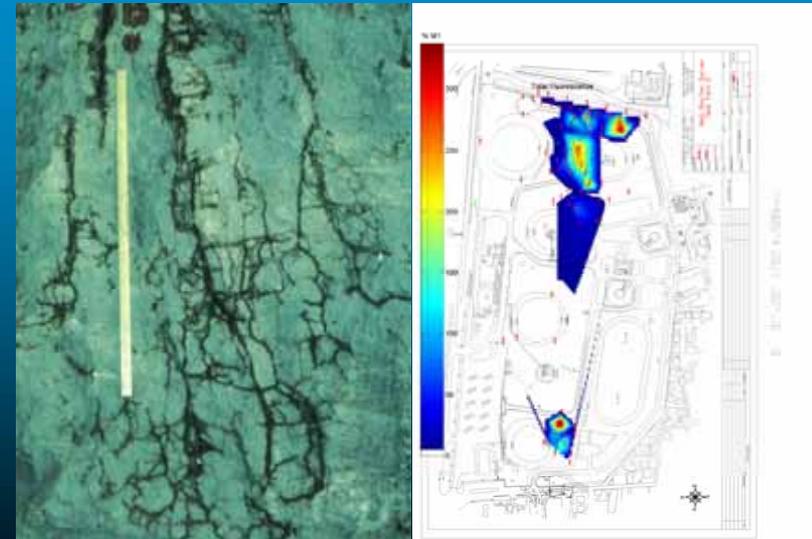
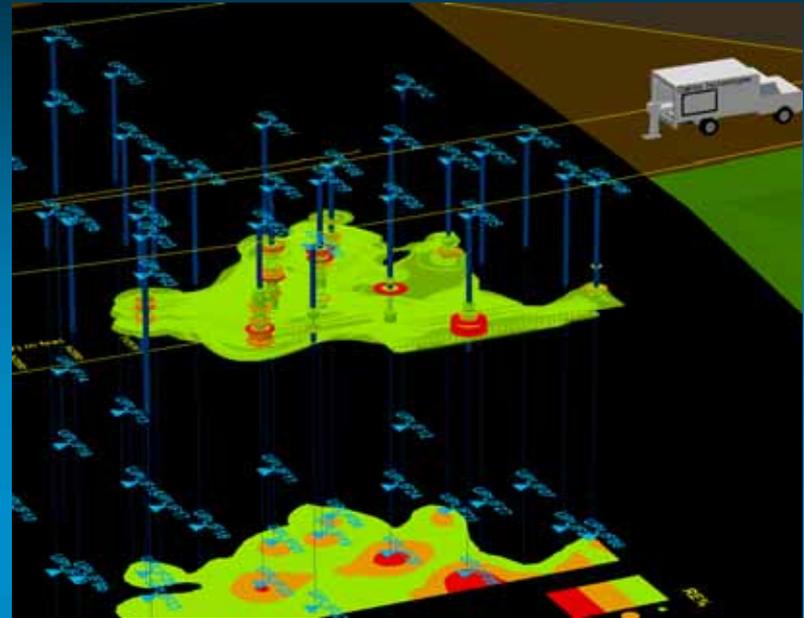
# 3D Visualization of TarGOST Data



MGP NAPL pooling on clay feature (ivory color)

# LIF site investigations

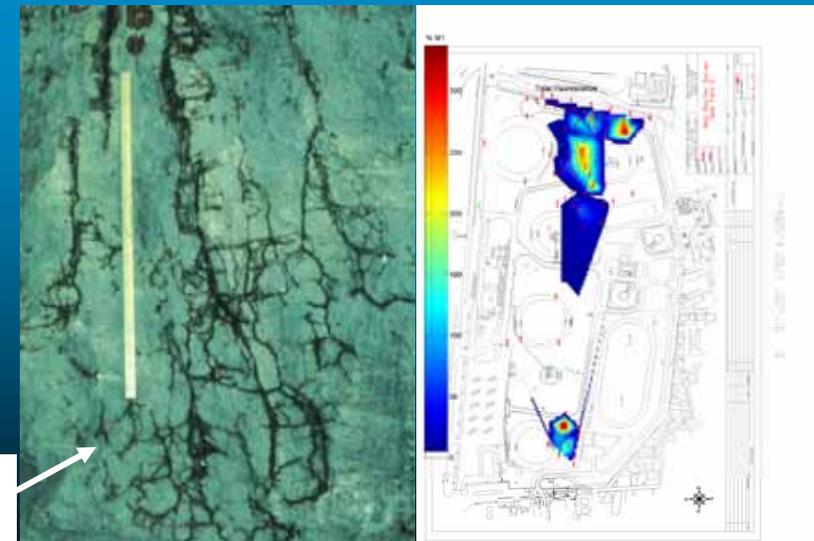
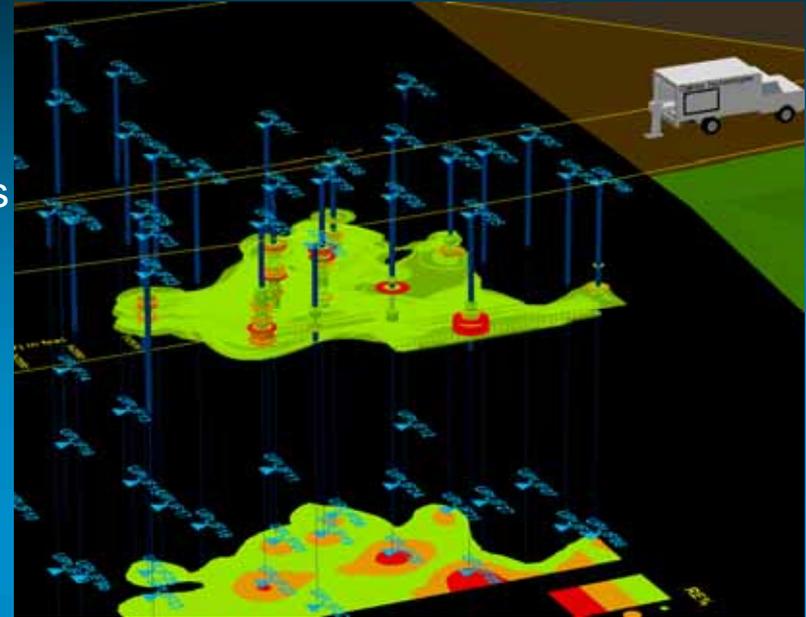
- NAPL can be homogeneous or heterogeneous
  - conduct side by side (“sister” logs) to gauge this
  - remember that LIF scans only a 3-5mm wide swath on the surface of the window/soil interface
  - carryover/carrydown is nearly non-existent
  - spiky log data indicates heterogeneous small scale distribution (running in veins, seams, and fractures)
    - get out of “layer thought”
- start out in the “heart of it”
- bound the NAPL –then move in and define/refine
- you’ll use LIF more than you planned - # holes will generally exceed expectations (due to productivity)
- #1 most common phrase – “it should be clean here”
- 2<sup>nd</sup> most common phrase – “there won’t be any below the water table – NAPL always floats”
- 3<sup>rd</sup> most common phrase – “where have you guys been all my life?”
- 4<sup>th</sup> most common phrase – “what’s your schedule look like?”



# LIF site investigations

general tips and suggestions to conducting the site investigation

- knock out the primary locations first – then fill in the “head-scratchers” and data gaps as time/budget allows
- go well below the primary affected zone - 10 feet is typical – LIF often finds LNAPL well below GWS
- don't get carried away trying to interpret every log – wait until the big picture starts to emerge – doing so early gets you contradicting yourself – but watch for heterogeneity's ability to make it look like “LIF was wrong”
- co-sampling answers the important/tough questions
- in-situ data is nearly always higher than ex-situ
  - O<sub>2</sub> content (subsurface O<sub>2</sub> can be near 0)
  - “wringing out” of NAPL
  - surface film creation (walk on the beach)
- client is in charge of locations and decisions – most LIF service groups are simply data providers – LIF service providers are not able to fully interpret since they aren't privy to all the subsequent supporting data/facts like co-sampling/analysis



**NAPL is sometimes VERY heterogeneous – not in ‘layers’!**

# Data QA/QC

Dakota Technologies have spent several man-decades developing LIF systems. **IF** operated properly, and **IF** LIF's capabilities properly understood, you can be confident of the data produced. **IF** the LIF provider is disciplined they can **AND SHOULD** be consistently achieved. UVOST service providers are taught...

Checklist of key items that lead to quality LIF data:

- Proper RE intensity – RE waveform must be certain intensity and correct shape
- Low Background levels – Background waveform does not exceed 5mV and must be correct shape
- 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 plots
- Elimination/control of fogging – fogging will absolutely corrupt a log – corrupts project data
- Proper depth encoding – a dirty/bad pot or bad wiring can cause misleading depths
- 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 excessive doubt – if operated properly and there is/was fluorescent NAPL in front of the window, LIF **will** see it – heterogeneity simply happens – A LOT – one must not always conclude that LIF was wrong if poor correlation with sampling is observed – it could be heterogeneity – consider LIFing sample splits
- always have LIF provider examine non-typical NAPLs prior to considering LIF for your project

# NAPL in soils - a complicated subject

- Dakota has 15 years of experience with characterizing NAPL with LIF– but publications are not something we’ve focused on
- plenty of anecdotal evidence – but Dakota has not published any comprehensive studies in recent years
- clients WILL try to pin LIF providers down on %RE cutoff levels for “significant” contamination – but co-sampling, previous studies, geology, etc. all have to be factored in when deciding on what’s significant %RE and what’s not – and it’s ultimately the consultant’s job to define/defend that value

## Suggested reading:

- LNAPL in Fine-Grained Soils: Conceptualization of Saturation, Distribution, Recovery, and Their Modeling, Groundwater Monitoring and Remediation 25, no. 1/Winter 2005/pages 100-112
- [http://www.clu-in.org/conf/tio/lnaplsbasics\\_121205/prez/LNAPL-Slides-10-26-05bbw.pdf](http://www.clu-in.org/conf/tio/lnaplsbasics_121205/prez/LNAPL-Slides-10-26-05bbw.pdf)
- API’s LNAPL FAQ – Answers to Frequently Asked Questions About Managing Risk at LNAPL Sites

# UVOST/TarGOST Demo

## UVOST

- the “classic” fuels
  - diesel response vs. concentration
  - various random fuels/oils
  - coal tars
- 
- TarGOST
  - coal tars

