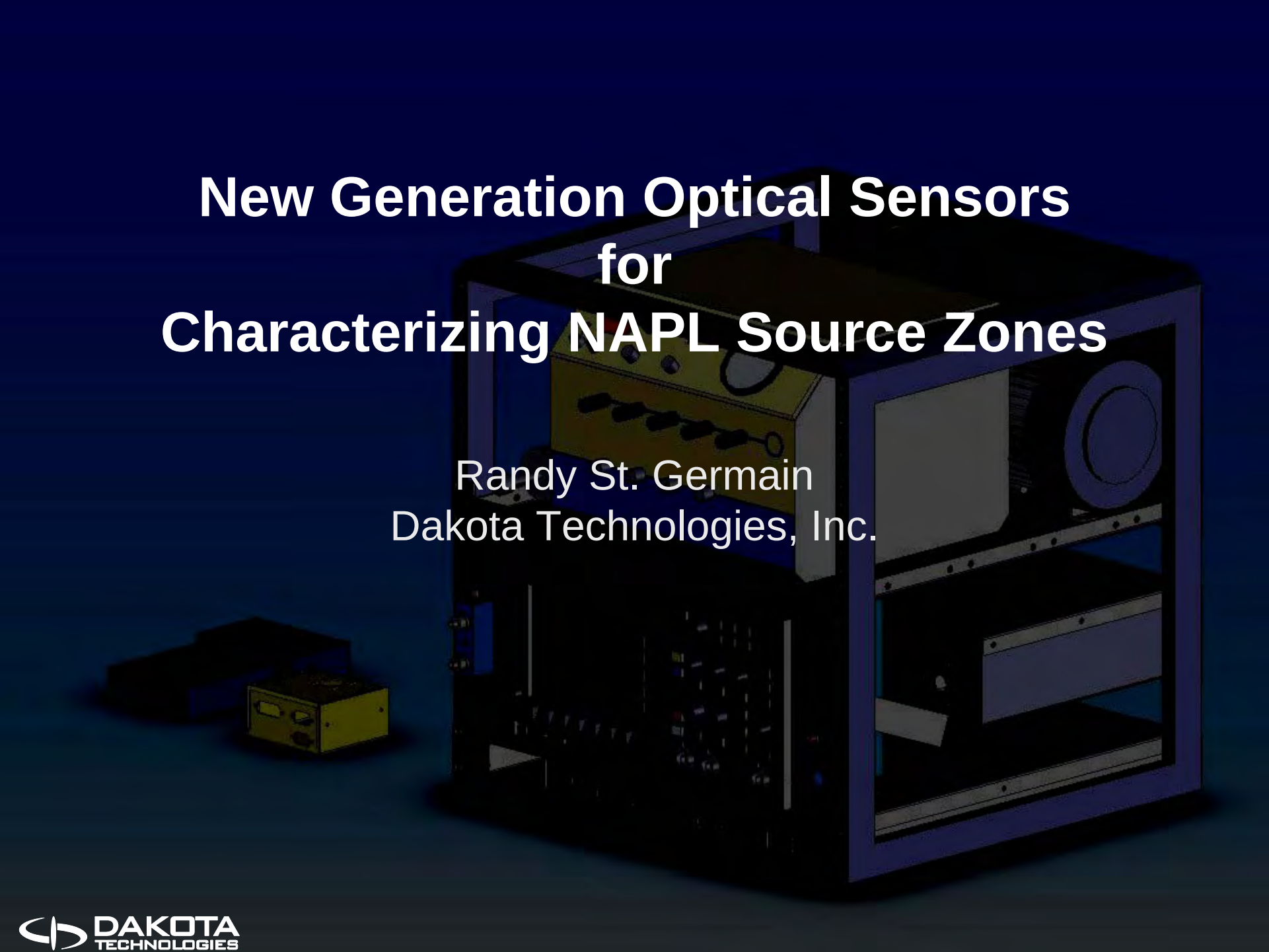
New Generation Optical Sensors for Characterizing NAPL Source Zones

Randy St. Germain
Dakota Technologies, Inc.



DAKOTA TECHNOLOGIES

Optical Screening Tools

- Technology description
- Past/Present OSTs
- Deployment methods
- Advantages/Limitations
- Field data samples

What are Optical Screening Tools?

- spectroscopic (light-based)
- all employ a sapphire-windowed probe (patented by U.S. Army Corps of Engineers)
- require “direct push” delivery - dynamic (Geoprobe®/AMS) and static (CPT)
- typically employ lasers for excitation (but not always)
- log a light-based phenomenon vs. depth (usually fluorescence of PAHs)
- sometimes referred to collectively as “LIF” (laser-induced fluorescence) – but inaccurately so since one uses Hg-lamp (or possibly modified with LED)
- often employ fiber optics – some don’t – pros/cons for each

windowed probe - percussion

windowed probe – submerged derrick

windowed CPT “sub” above CPT

Dakota Technologies' LIF History

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

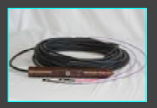
1992

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

1993

1994

Dakota Technologies Incorporates



Dakota Develops Percussion-Capable Probe (SPOC)

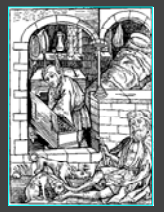
1996

Lockheed Martin sells ROST Fleet to Fugro Geosciences

1997

Dakota Technologies First Provides Regional "ROST" Service

1998



"Dark Ages"

2003

Dakota Technologies Introduces TarGOST Service

2006

Dakota Technologies Introduces UVOST

2007

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

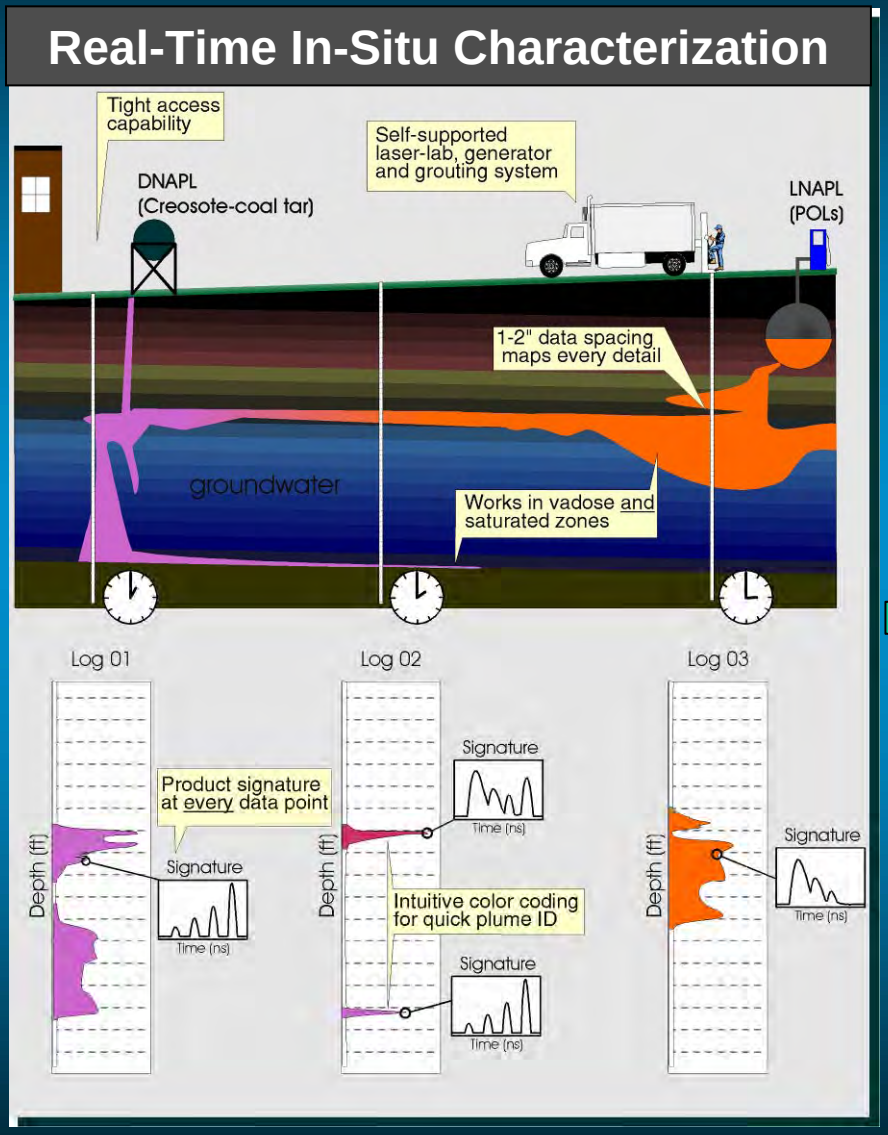
Today's Optical Screening Tools

Model	Manufacturer / Providers	Technology / Deployment	Target
NA	SCAPS (Army/Navy/AF) gov't use	nitrogen laser-337 nm OMA detector CPT only	fuels/oils (poor jet fuel response)
FFD – Fuel Fluorescence Detector	Vertek mfct'd offered by numerous field service providers	CW Hg Lamp - 254.7 nm PMT CPT only	fuels/oils containing low to moderate PAH
ROST - Rapid Optical Screening Tool	Dakota Fugro exclusively	dye laser - 290nm spectral/temporal hybrid CPT only	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 (late stage development)	Dakota mfct'd to be offered by field service providers	broadband white light reflectance Percussion & CPT	Munsell soil color, soil class, ???

Optical Screening Tools – Spring 2008

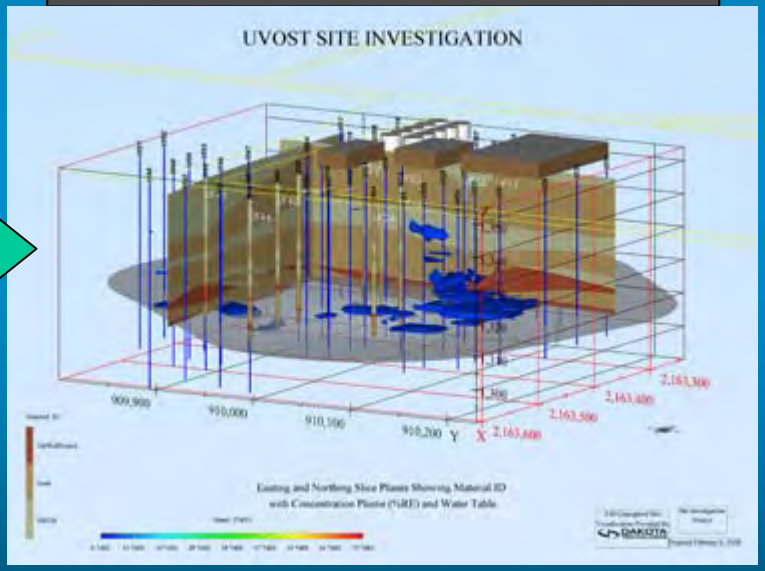
optical screening tools - high production rates and high data density = “big picture”

real time “NAPL hunt”



higher quality information
for higher quality engineering/decisions

Detailed Conceptual Model



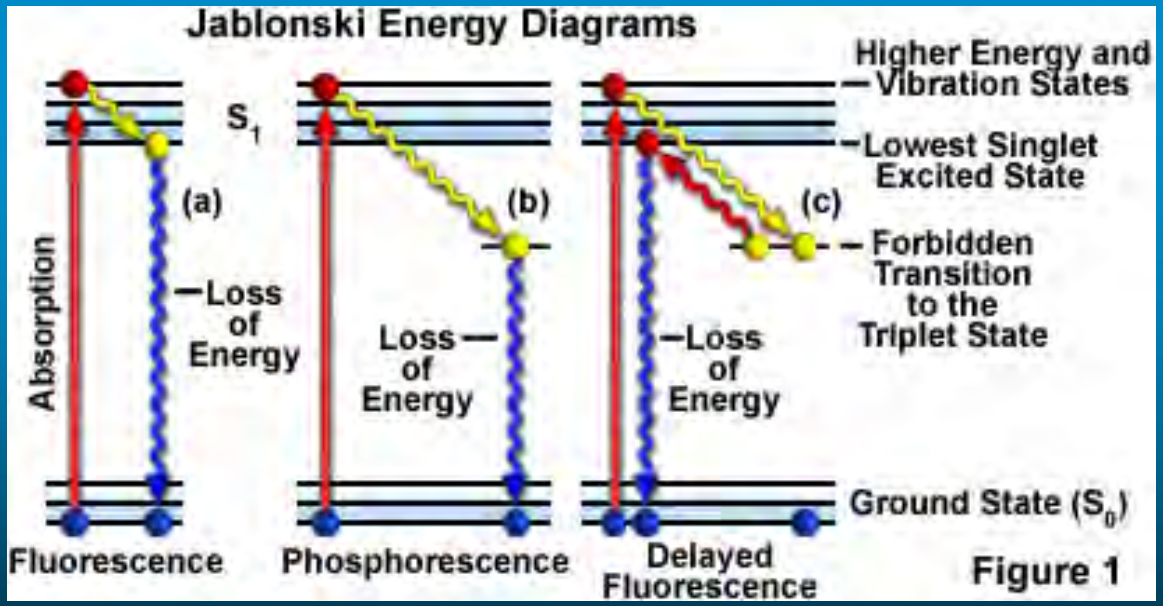
The Technology

most OSTs feature UV fluorescence spectroscopy

(spectroscopy – study of matter by its interaction with light)

vast majority of aromatic (ring-shaped) molecules fluoresce readily

fuels/oils/greases contain mono- & poly-cyclic aromatic hydrocarbons (PAHs)
so they are readily detected via fluorescence



details - see Joseph R. Lakowicz' "**Principles of Fluorescence Spectroscopy**", 3rd Edition

ultra-violet fluorescence OSTs detect…

almost all PAH-containing NAPLs

Reliably

- **Gasoline (highly weathered and/or aviation yield is very low to zero)**
- **Diesel**
- **Jet (Kerosene)**
- **Motor Oils**
- **Cutting Fluids**
- **Hydraulic Fluid**
- **Crude oils**
- **Fuel oils**

Occasionally

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

Never/Rarely

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

OST applications

pretty much any direct-push feasible site where PAH NAPL source term is an issue and requires delineation

- Leaking underground storage tanks

- Pipelines
- Refineries

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

- Surface spills
- Lagoons - waste ponds

OSTs are flexible – suit a variety of delivery platforms and conditions

- •Geoprobe®, PowerProbe, CPT, even drill rigs (in soft materials)
- •on-shore, off-shore, ice, bogs, sediments
- •rain, snow, sleet, sun, wind

UVOST®

Ultra-Violet Optical Screening Tool

world's first commercially available turnkey LIF product – just add direct push

- designed specifically for logging light-midweight fuels/oils
- detects most fuels/oils => 10-100 ppm (basically any "sheen" and higher conc's)
- most useful in cases where NAPL levels dictate either remediation design or major decision making (used as engineering tool)
  - excavation
  - recovery wells
  - ISCO
  - dig/haul
- basically provides
  - location and relative concentration of "source term" PAH NAPL
  - LODs at/near typical state MCLs for PAH NAPL
  - "product type" or class and its heterogeneity/homogeneity
  - precision guidance for physical sampling
  - minimizes sampling LOTS OF "zeros" (in PAH NAPL terms)
  - often provides clues to transport mechanism via location
- does NOT provide
  - dissolved phase conc's used for risk evaluation
  - speciation of PAHs
  - BTEX information
  - chlorinated solvents, metals, or explosives information

calibration

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

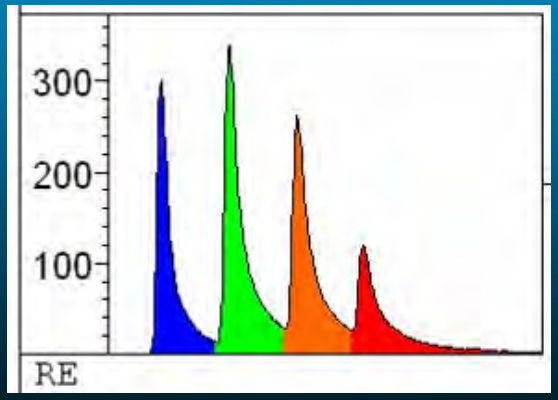
Dakota has used a “reference emitter” (RE) since 1994

RE is placed on window just before each sounding and 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.

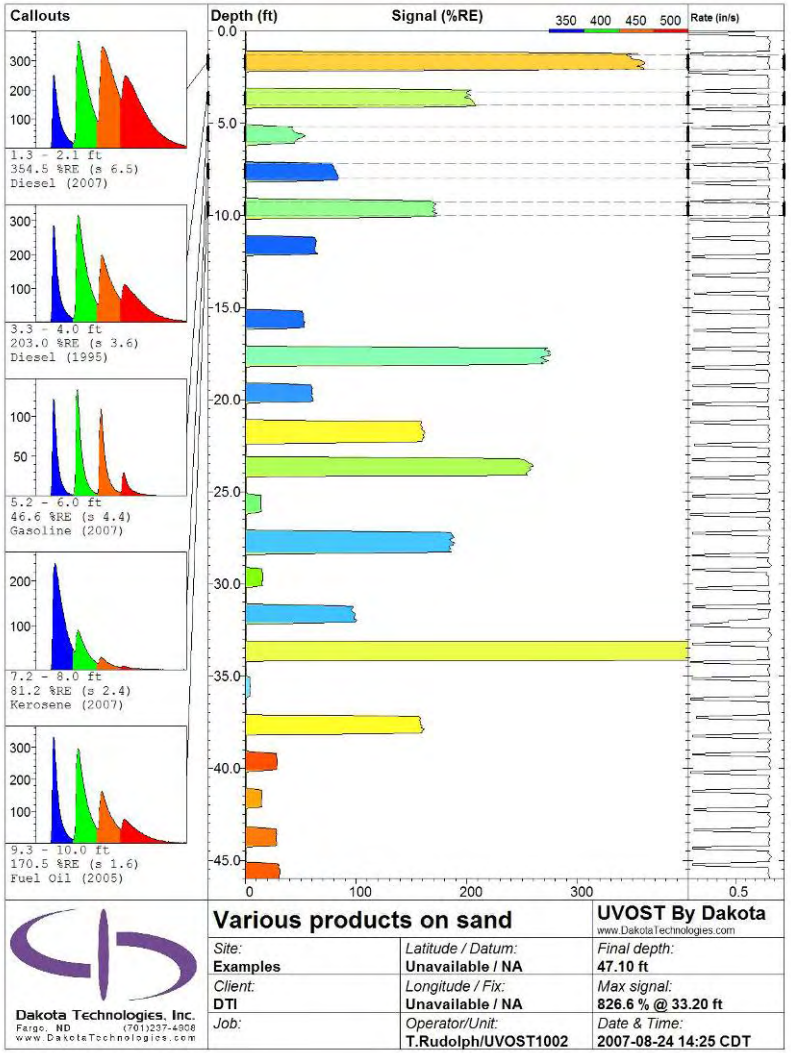
RE approach is used by all ROST and UVOST providers in U.S. and EU

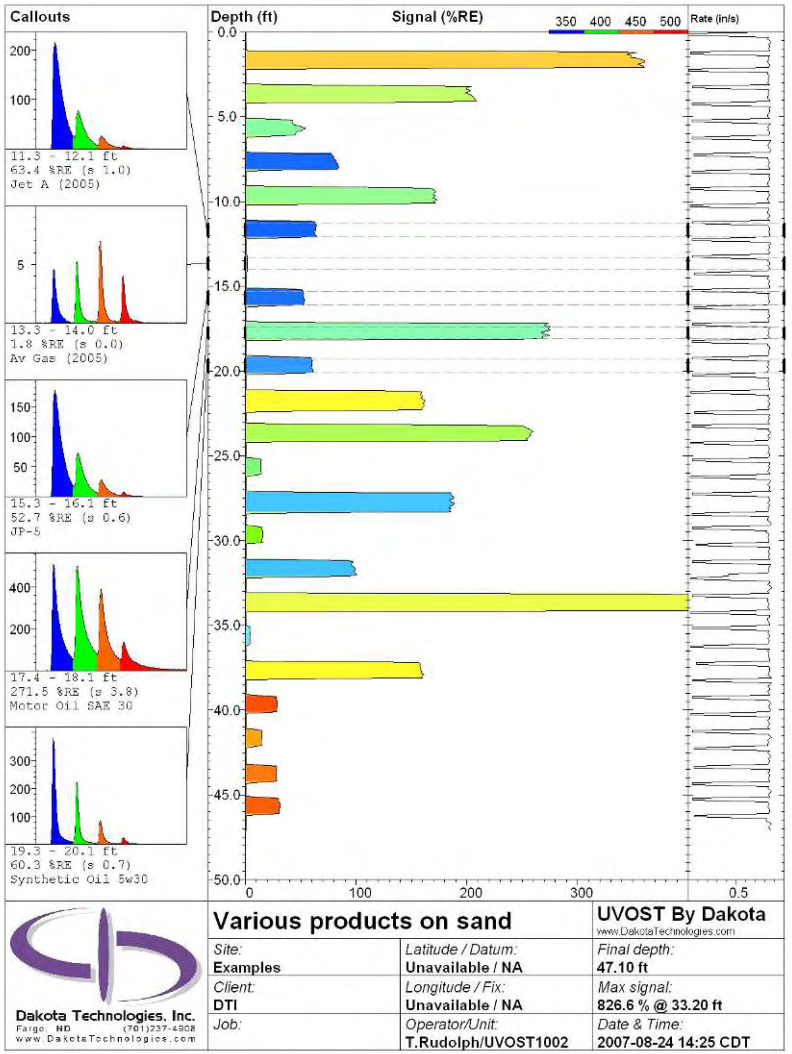
the correct shape of waveform also QA’s the qualitative aspect of the fluorescence



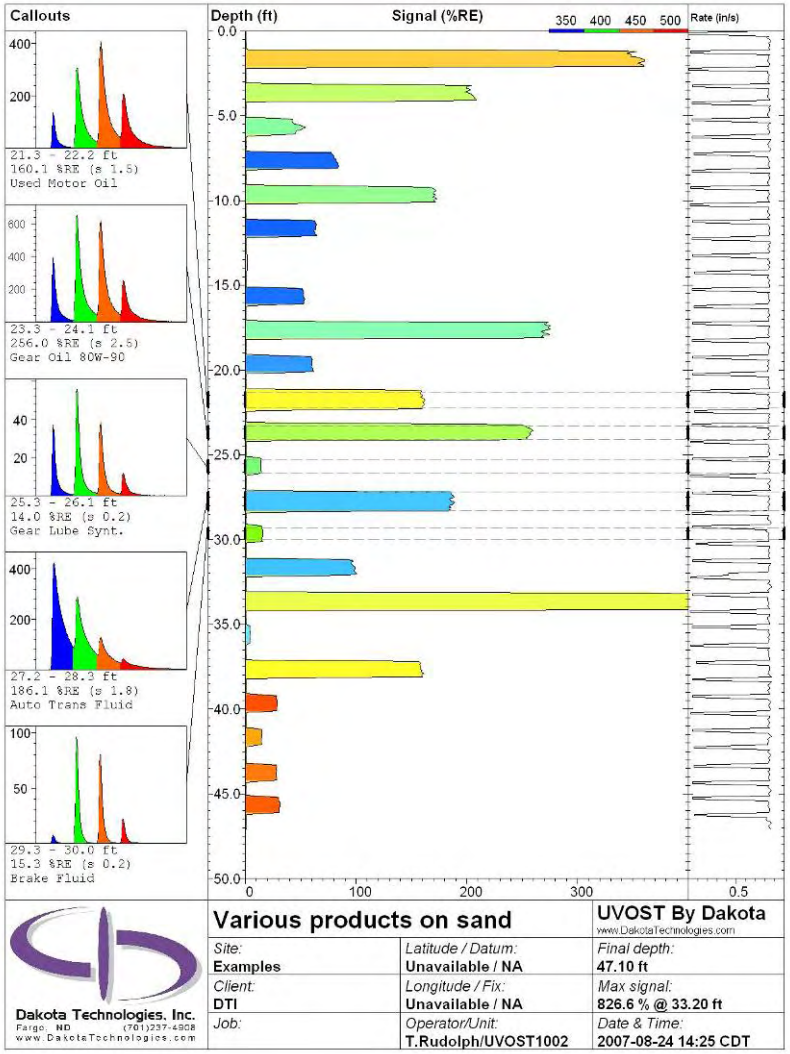
UVOST response to various common PAH-containing NAPLs

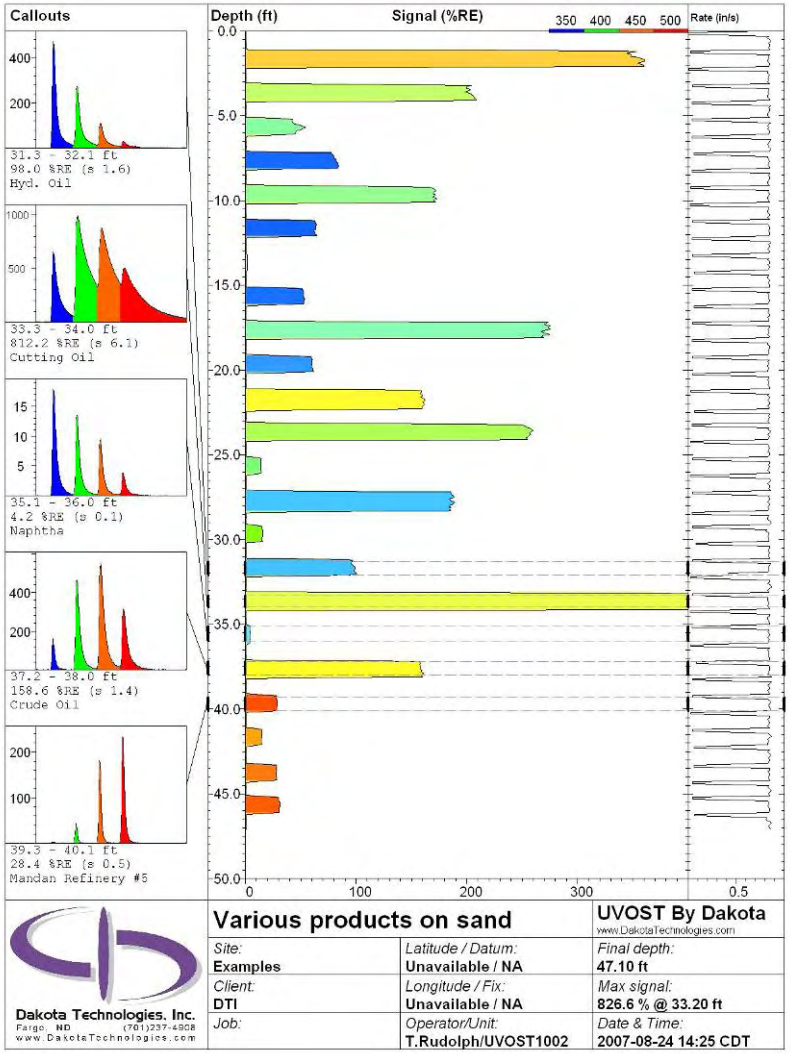
these logs demonstrate quantitative and qualitative response
note the variable waveform shapes and varying intensity (%RE on x-scale)
(similar to how a PID has variable response to VOCs)





UVOST Response of Various NAPLs

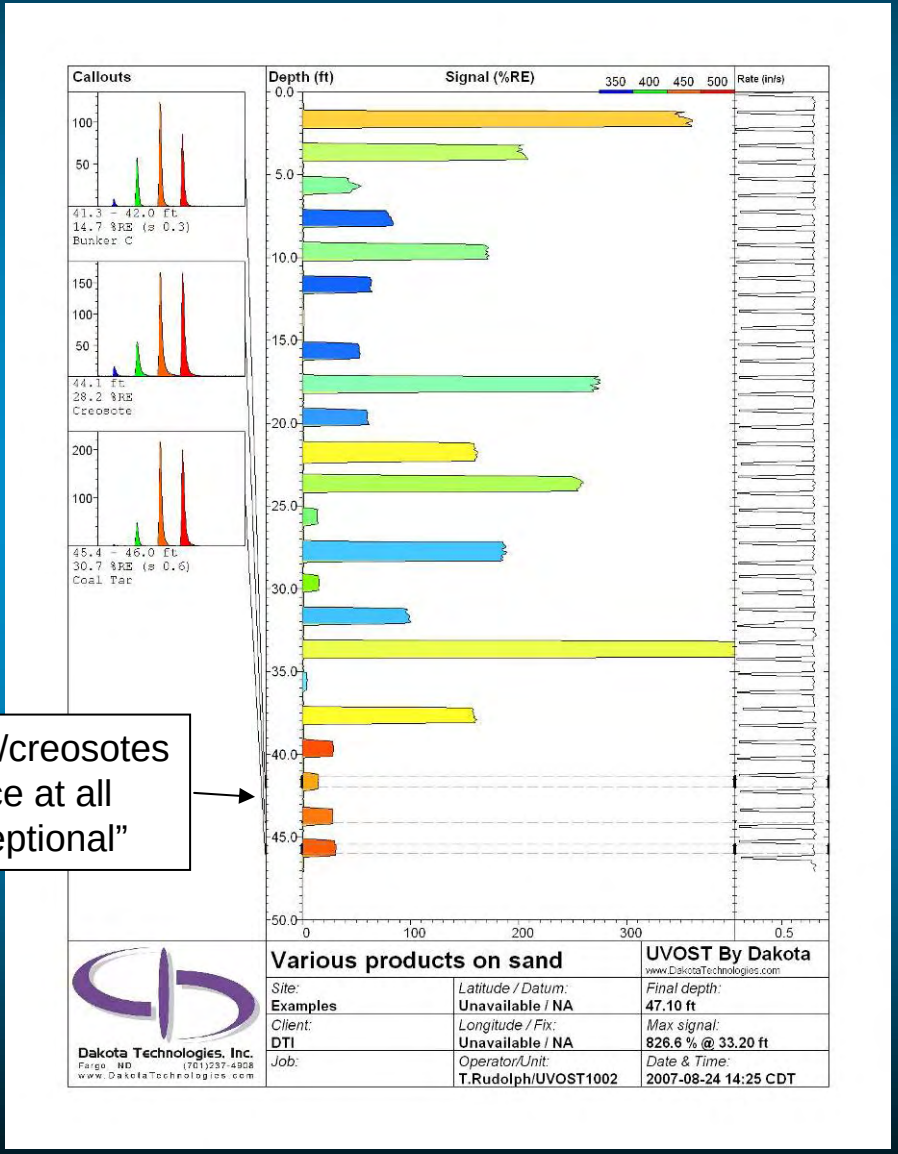




UVOST Response of Various NAPLs

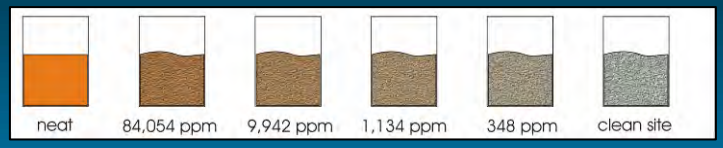
note poor response to coal tar, creosote, bunker (bottom 3) due to energy transfer (**too much** PAH)

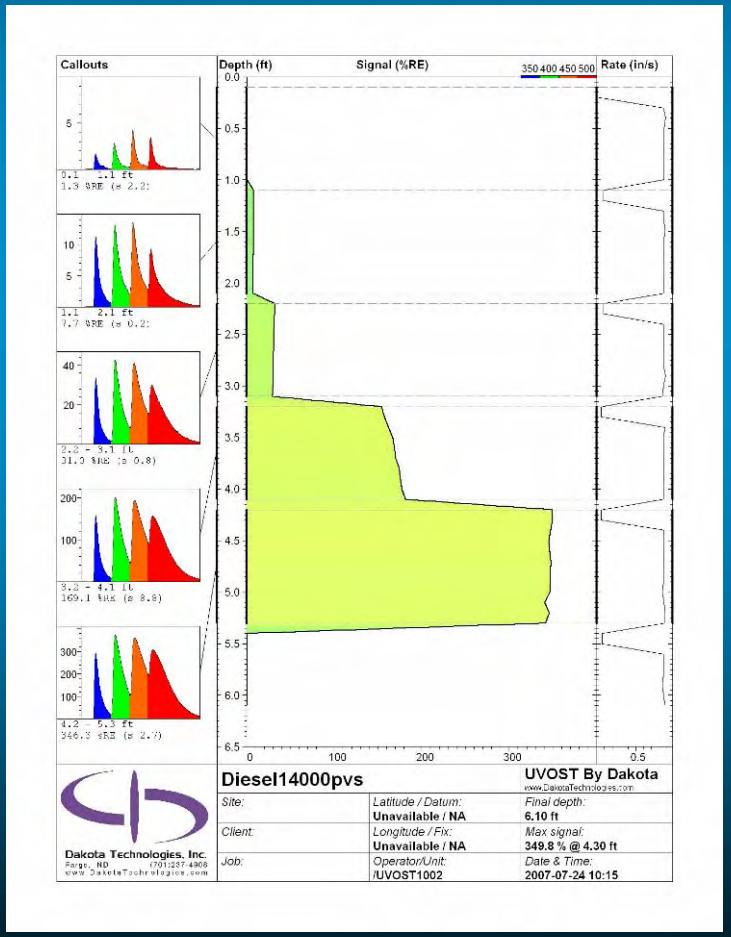
TarGOST (discussed later) provides solution to these problematic compounds

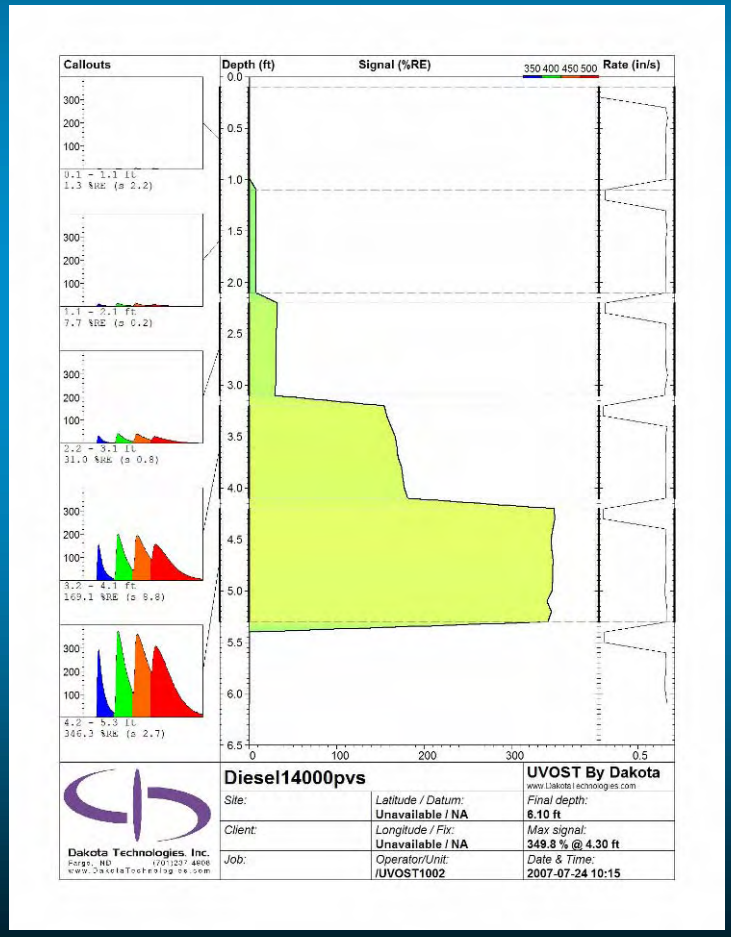


some bunkers/coal tars/creosotes have no fluorescence at all these three are “exceptional”

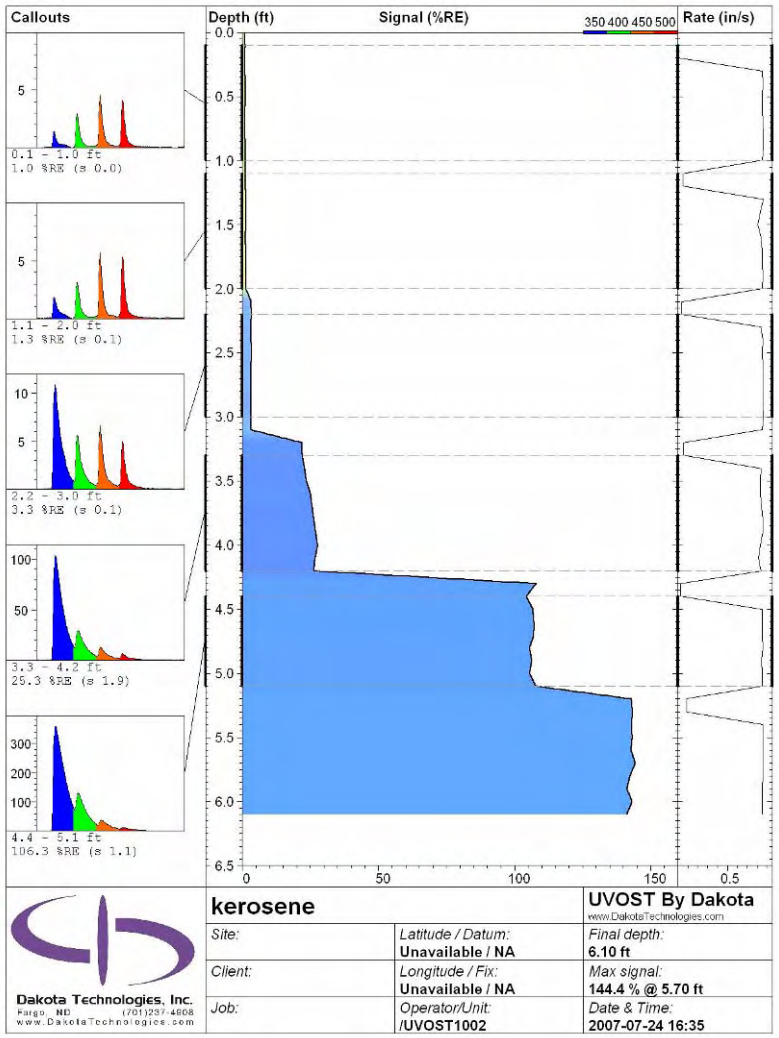
lab study – demonstration of “semi-quantitative” performance of UVOST

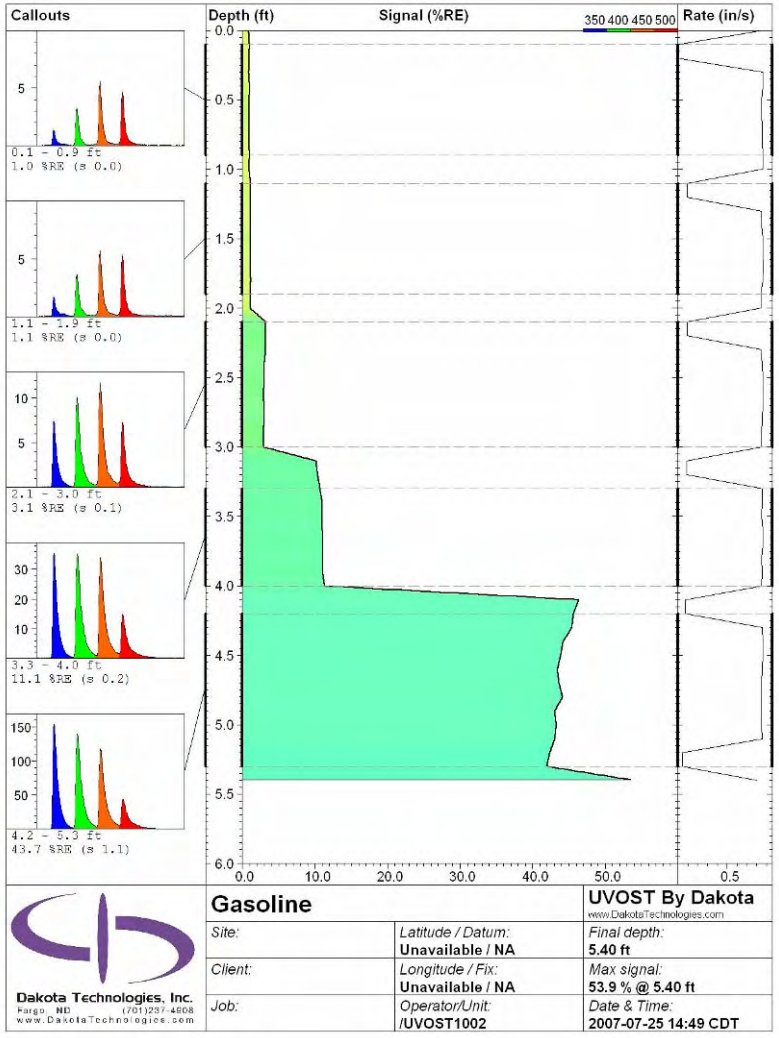






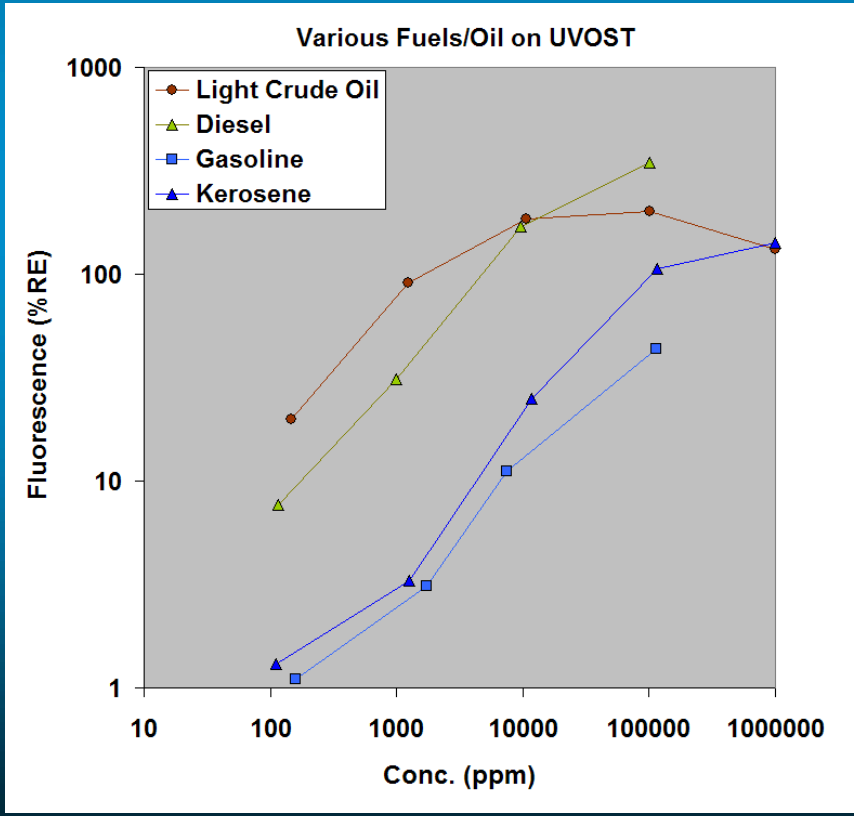
UVOST logs contain both semi-quantitative and qualitative data

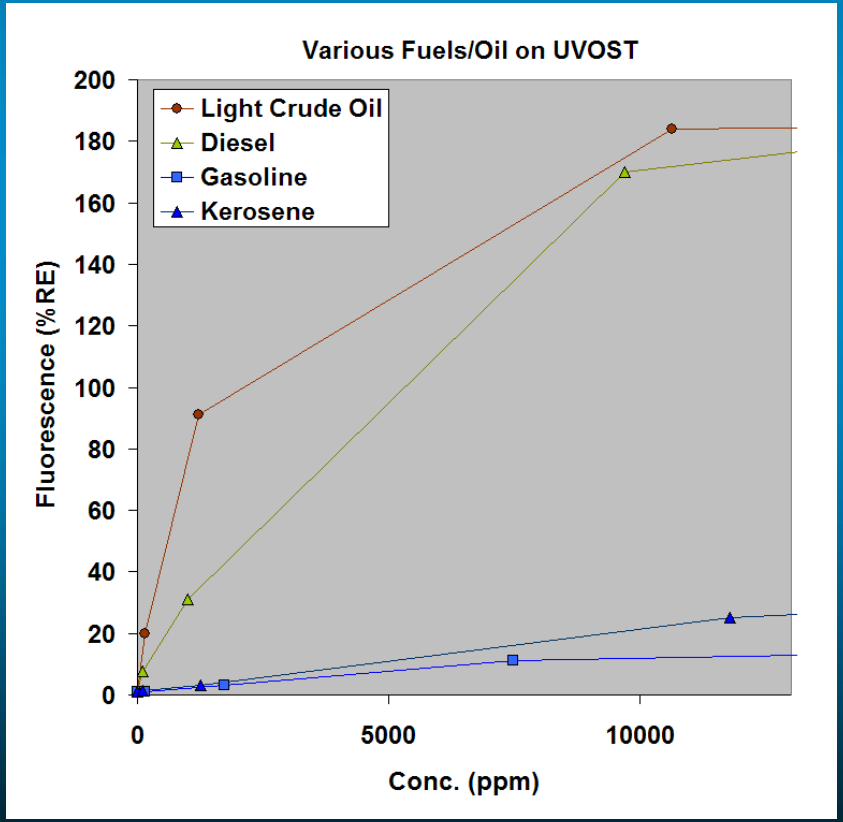




UVOST's "semi-quantitative" performance

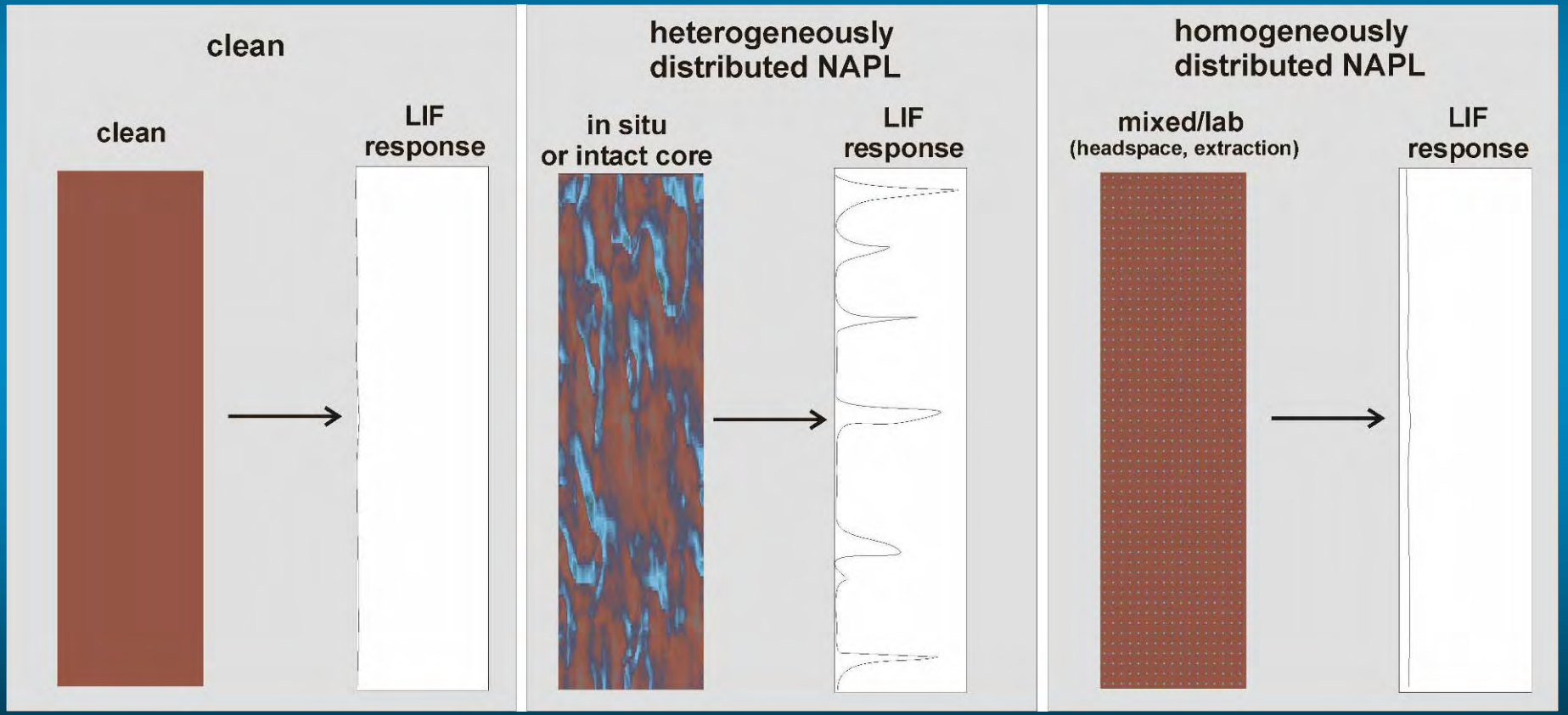
- usually a monotonic response – if "rollover" occurs at high end – no problem
- note the variable response - some fuels/oils simply "glow" better than others
- lab studies like this underestimate in-situ LODs due to homogenization



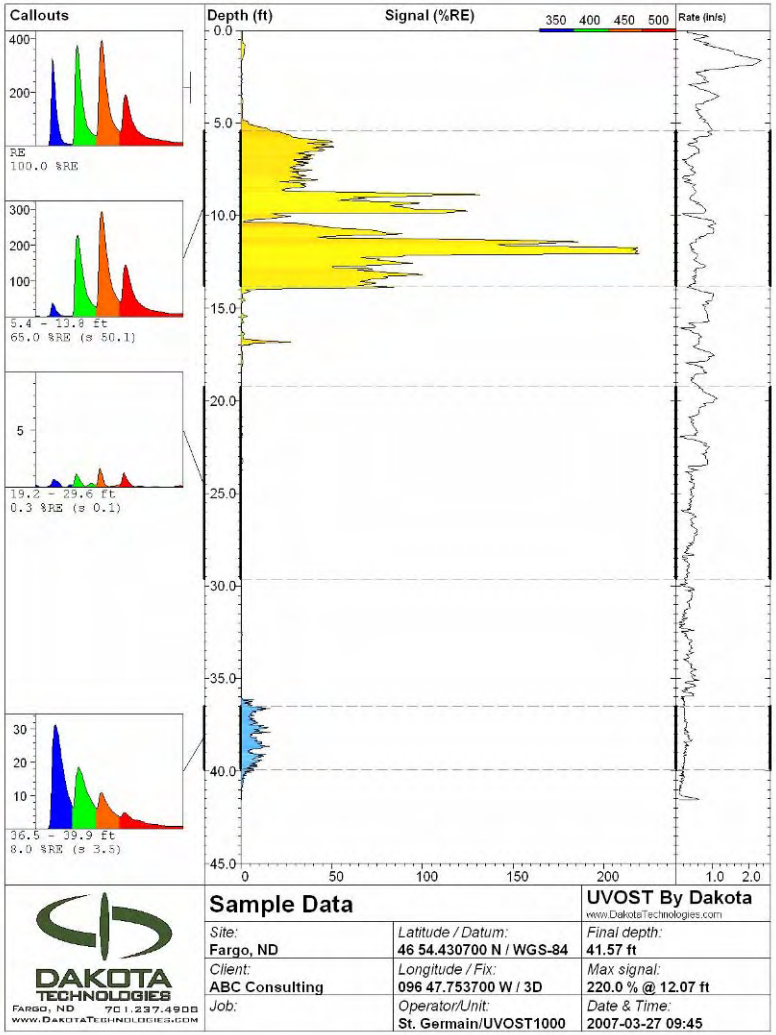


in-situ
vs
lab or “homogenized” samples

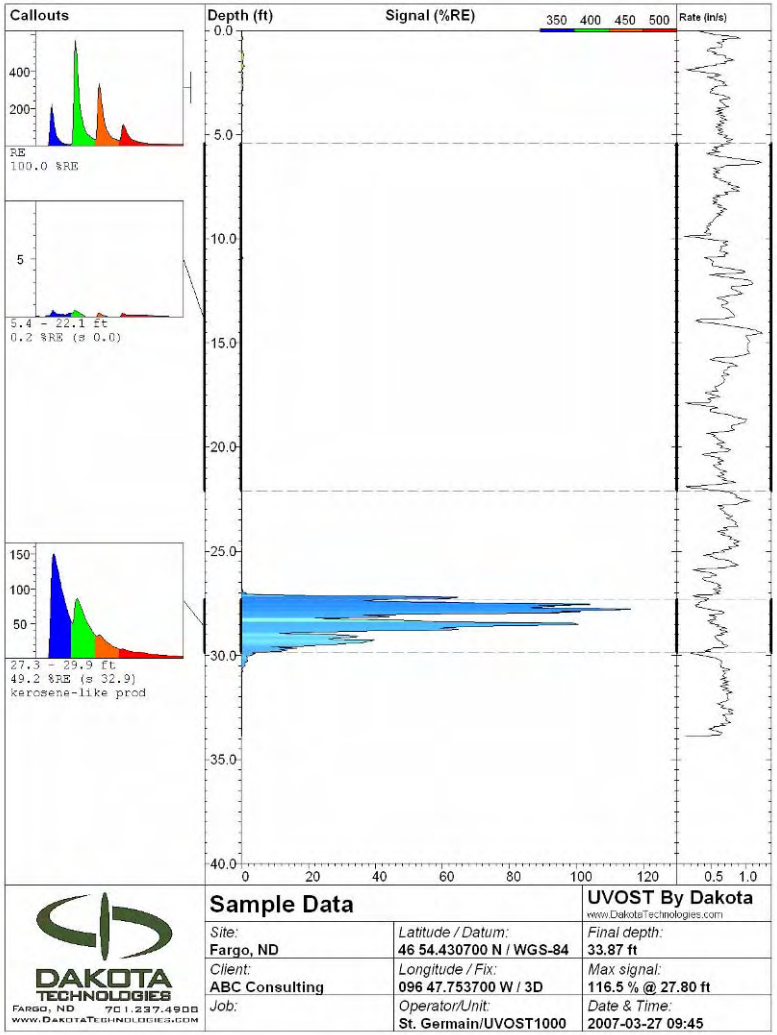
natural heterogeneity often allows “easier” detection of NAPL vs homogenized lab samples
so lab-based LODs are typically conservative



Example Field UVOST Logs

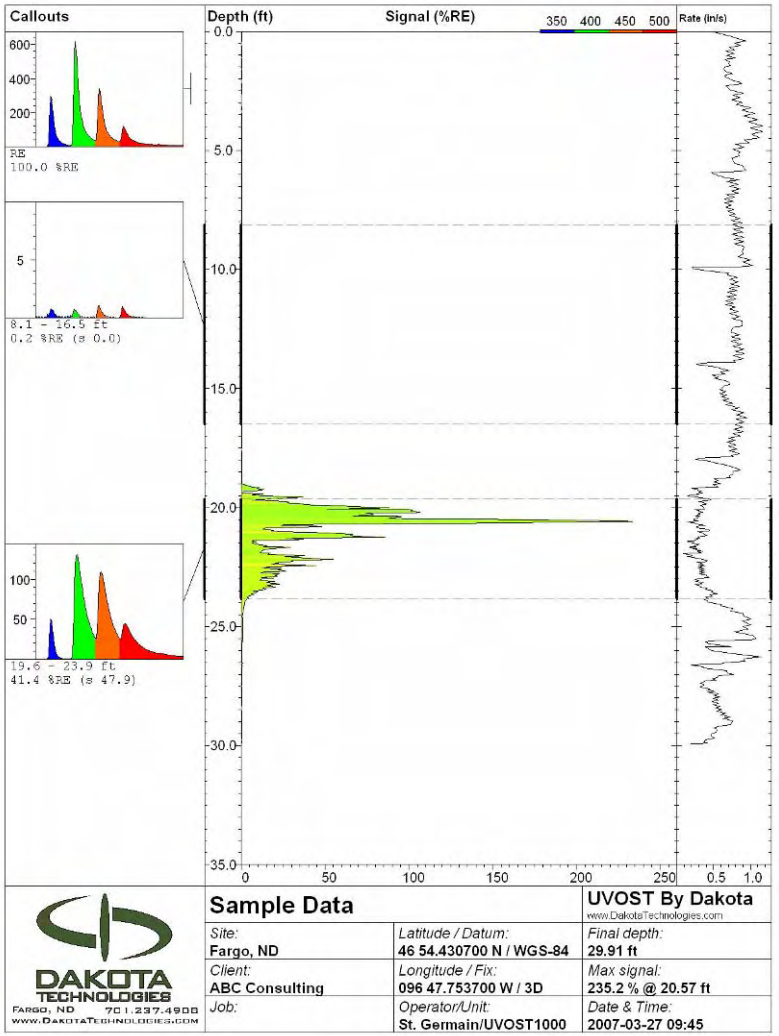


MN – Service Station - 2 NAPLS
(oil top.... gasoline bottom)

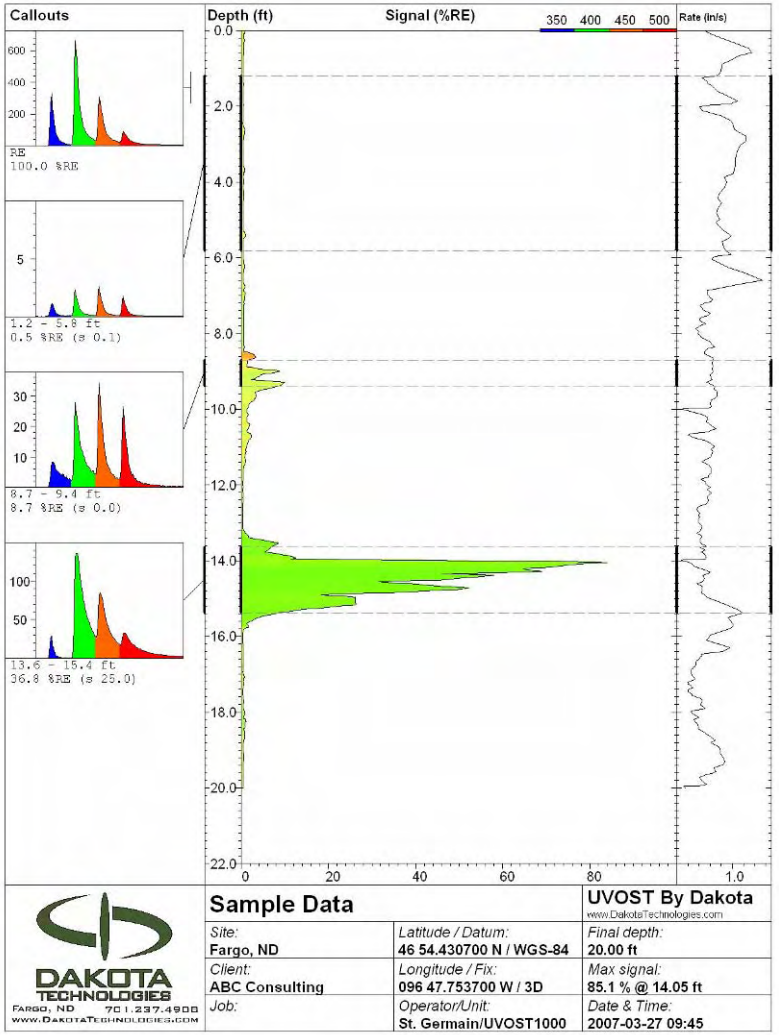


MN - bus garage/terminal
No. 1 Fuel Oil (kerosene)

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

uv fluorescence false positives/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)
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 (or heavily subdued)

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… sometimes contains PAHs making it detectable)

MIP vs UVOST?

should perhaps be written “MIP **and** UVOST… a love story”
they are actually complimentary with little or no overlap

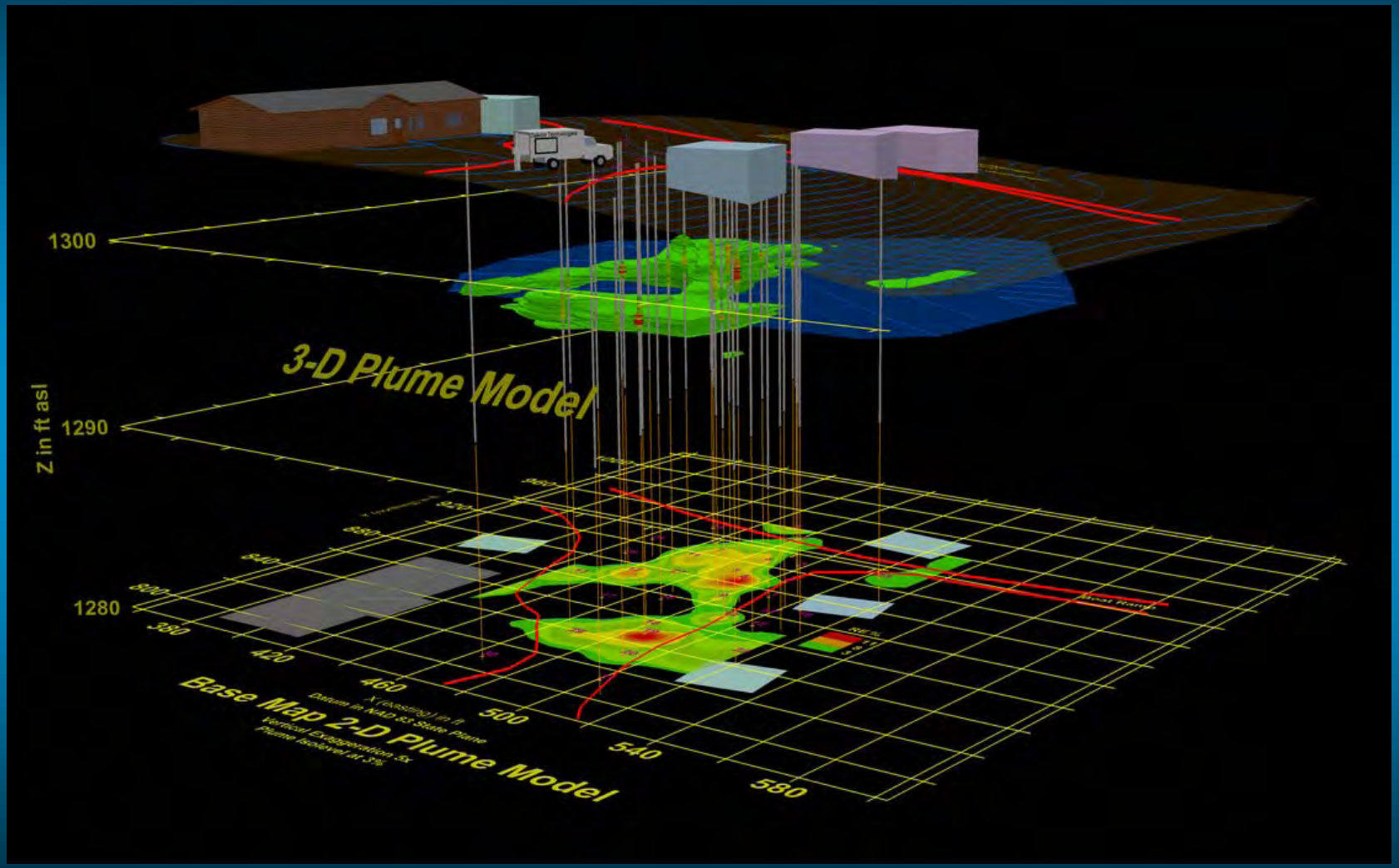
MIP (Geoprobe’s Membrane Interface Probe)

- Designed for dissolved phase VOCs
- “sticky” semi-VOCs known to cause transfer line/carryover problem
- difficult to find “bottom” of NAPL due to carryover and resulting lag time
- logs are often contain strange baseline shifts (compared to LIF) – difficult for a novice to interpret

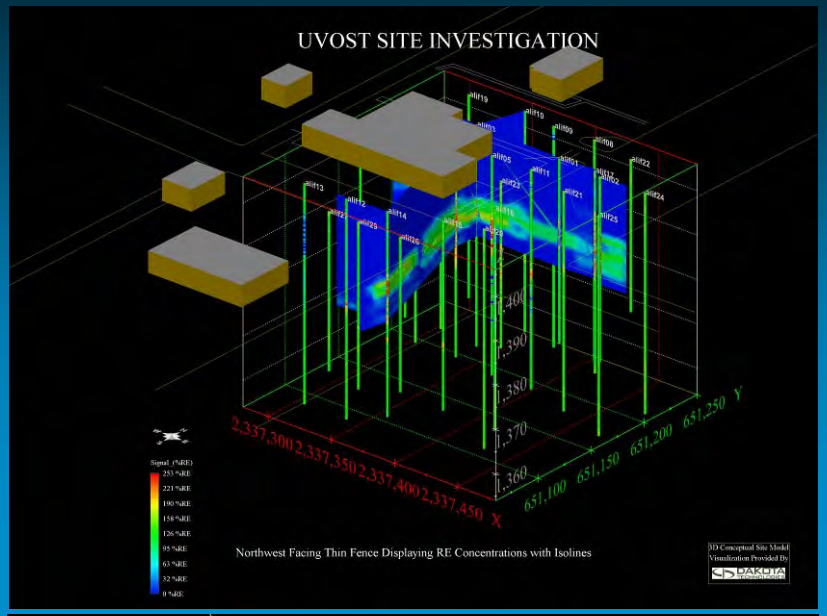
UVOST

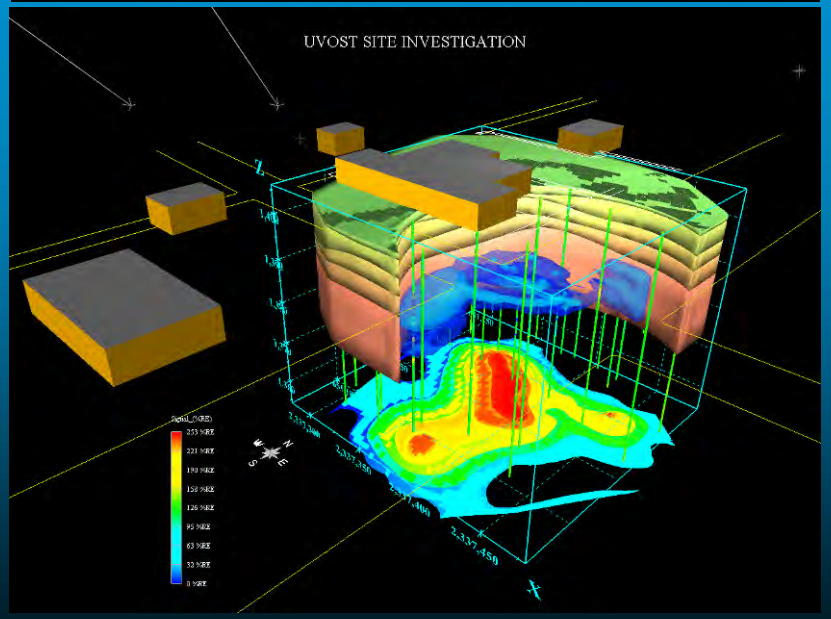
- Designed specifically for PAH-NAPL delineation
- smooth/hard sapphire window is “slick” like Teflon – resists pulldown
- nearly instantaneous rise/fall - and 100% reversible response
- UVOST does NOT see any useful levels of response to dissolved phase
- UVOST shows intimate detail of NAPL distribution (relative to MIP)
- UVOST provides readily interpreted “spectral” information in real time
- UVOST is blind to chlorinateds – even chlorinated DNAPL
- more intuitive - easier for novices to interpret

3D UVOST Field Data CSMs

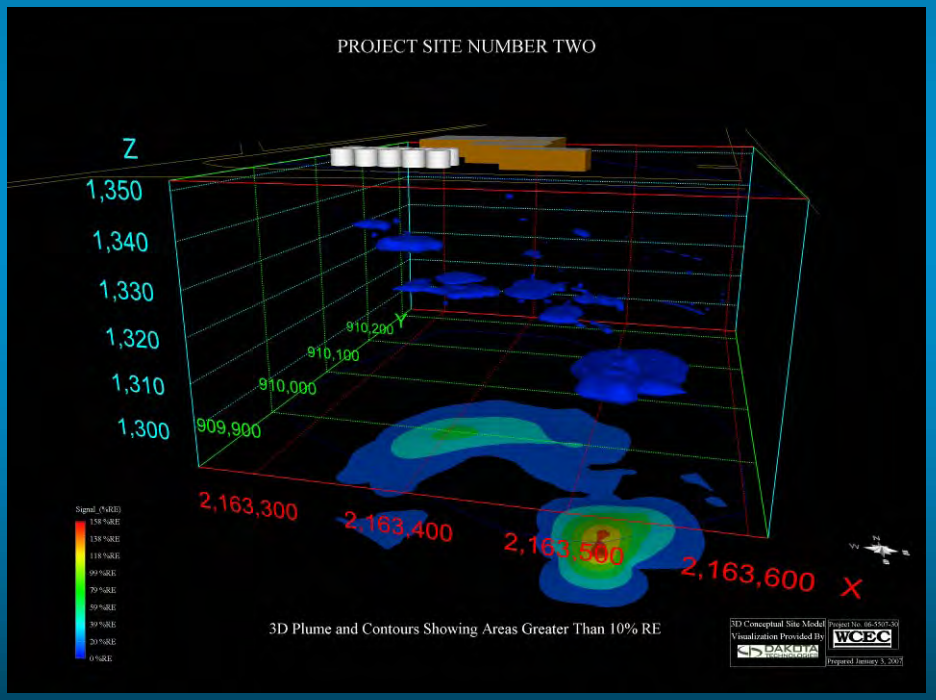


3D UVOST Field Data CSMs





- **OST data is immediately stored in digital format**
- **readily imported into MVS, EVS, Surfer, etc.**
- **can guide field work – but typically used to convey complex data to non-engineer/chemist "decision makers" after the investigation is complete**



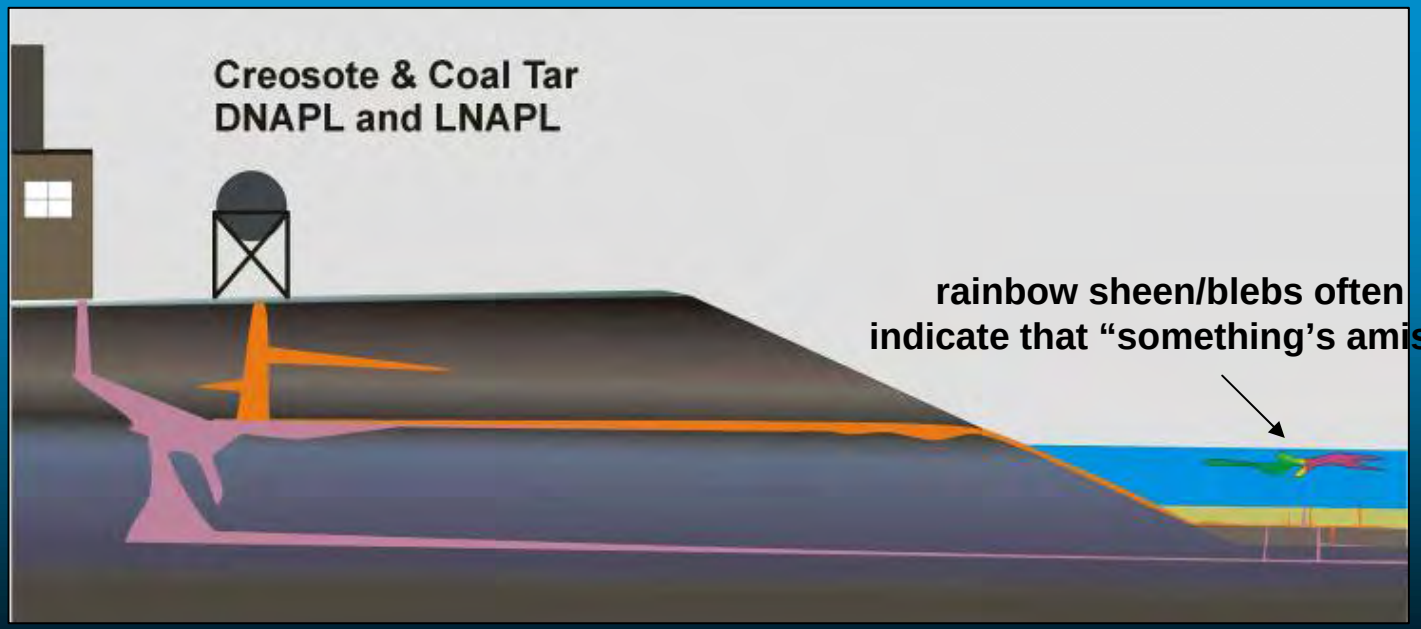
Tar-Specific Green Optical Screening Tool (TarGOST®)

designed specifically for **MGP and Creosote** LNAPL and DNAPL

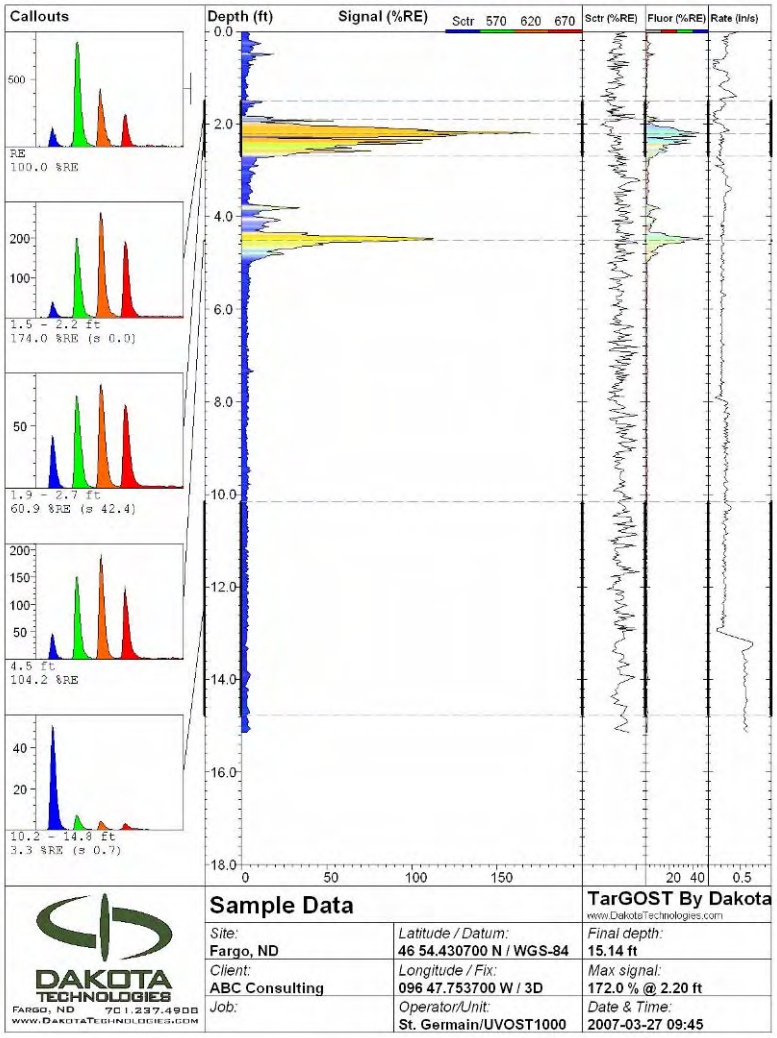
visible excitation defeats the energy transfer trap by "skipping over" the absorbance of the excitation source by the smaller PAHs who "love" to absorb UV but then transfer their energy to larger PAHs… which ultimately "quenches" fluorescence

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 suitable "neighbors" to which they can transfer their absorbed energy instead of fluorescing

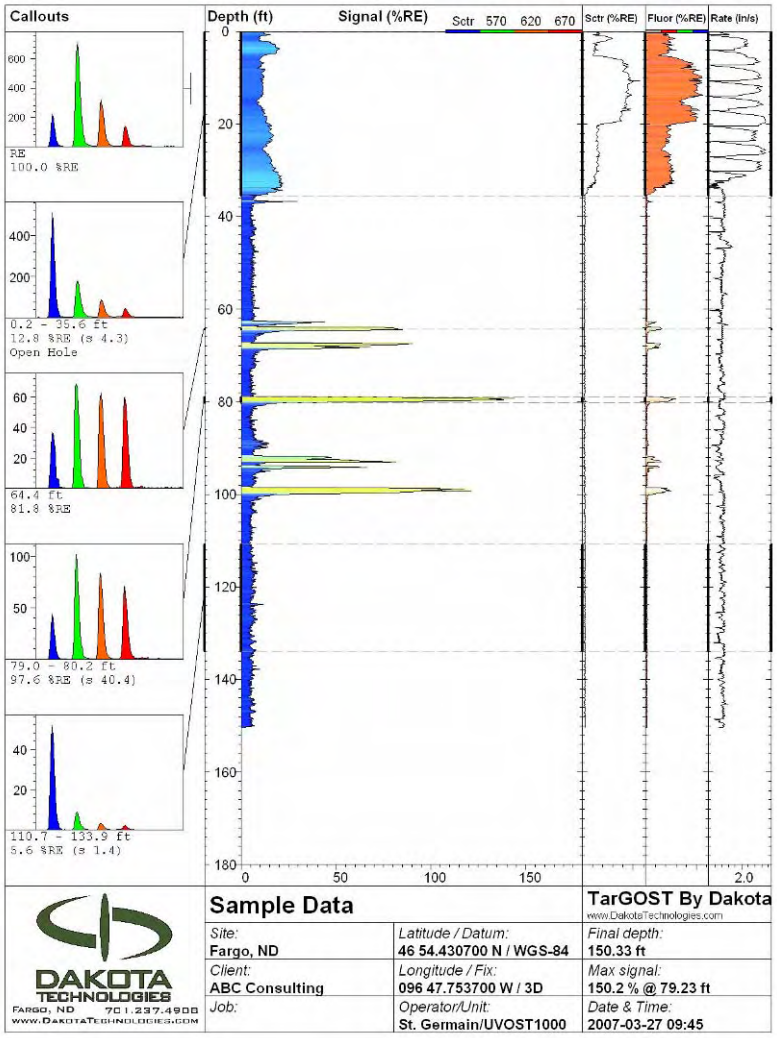
especially effective for "near shore" coal tar in rivers/bays/lake sediments – where drilling is difficult



Example TarGOST Field Logs

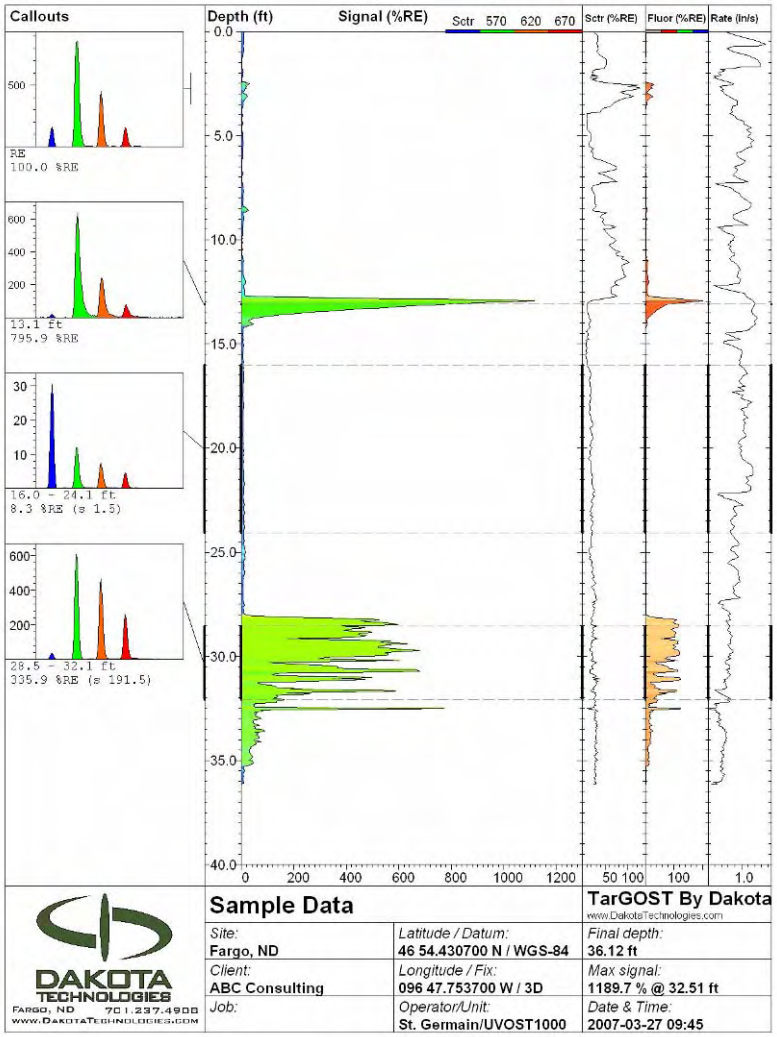


NY – former MGP near river
done from a barge in > 20 ft. of water

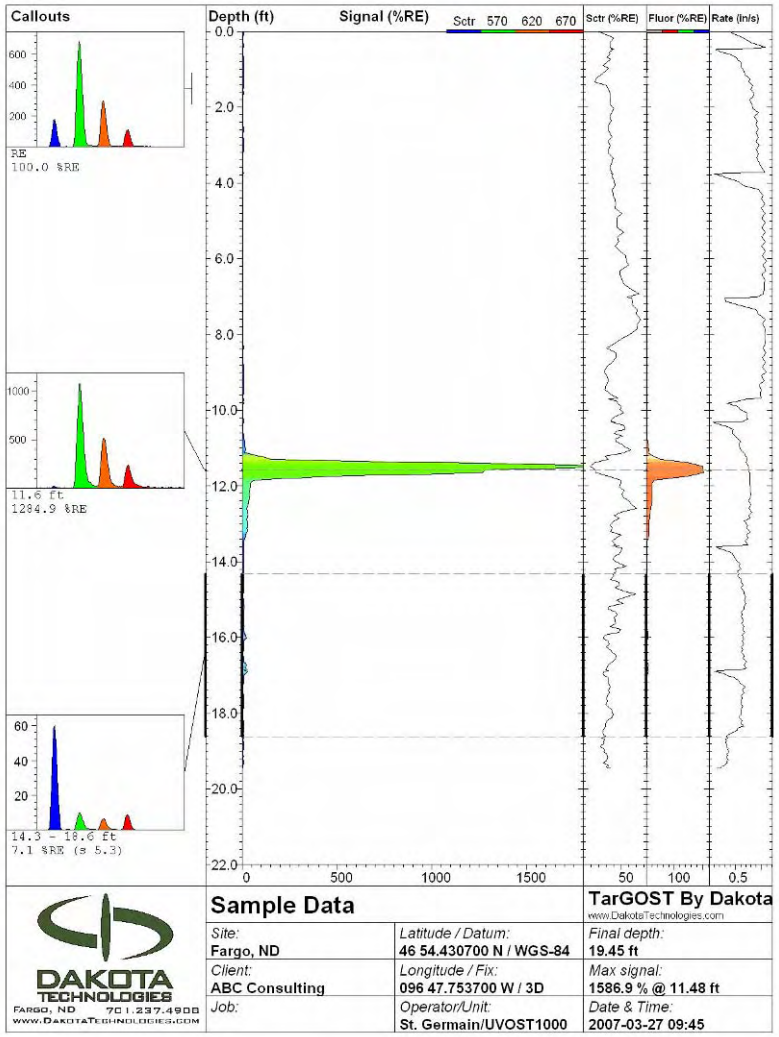


Oregon
150ft – mobile NAPL at 100ft
(first 30 ft were in open hole)

Example TarGOST Field Logs



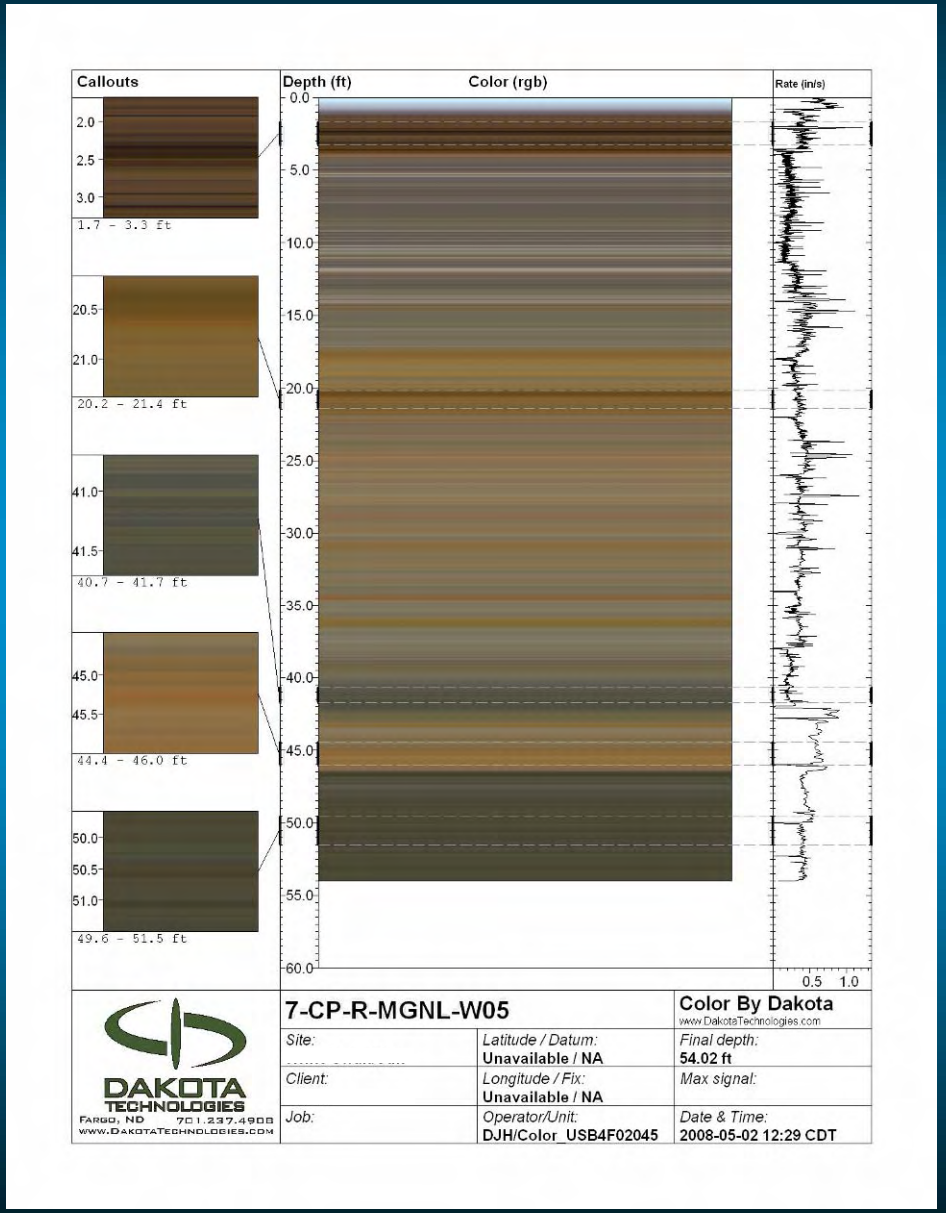
WI - 2 layers of MGP NAPL
separation into LNAPL/DNAPL?



CA crude oil
TarGOST response >>> than UVOST

Munsell Soil Color System

- Compatible with TarGOST and UVOST downhole tooling/fibers
- different “uphole” instrument than TarGOST and UVOST
- currently needs to be done in separate push from LIF
- eventual plan is for simultaneous acquisition along with fluorescence - same window and same fiber optics
- may eventually yield soil class (clay, sand, silt)
- may eventually prove useful for non-fluorescent targets
- to be launched later this year



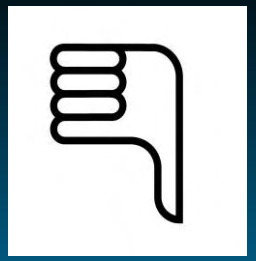
OST advantages

- highly productive (250-500 ft/day)
- 10-12 readings per foot – high definition – no data gaps
- data is “machine vision” and non-subjective – consistent product
- UVOST/TarGOST calibrated/operated same way by all providers
- little to zero investigation derived waste
- fewer mobilizations (often just one)
- real time data and high-res logs encourage adaptive characterization
- minimized exposure risk for personnel
- no carryover, sloughing, mislabeling jars, sample handling – less error
- no waiting for lab sample analysis – not to mention lower lab costs

OST advantages cont'd

- intuitive format – basic content readily interpreted with minimal training
- no "arguing" over results (Minnesota Pollution Control Agency's position)
- yields immense data sets which are key to properly understanding heterogeneously distributed NAPL
- electronic data files readily imported into visualization software for "big picture"
- qualitative response (waveforms) assist in false positive/negative ID
- responds ONLY to the source term – the true target of many remediation designs
- used as a design tool – regardless of regs/rules – tells engineers what they need to know
- sees narrow seams often missed – these seams can fill wells/pits with many feet of NAPL– often LOWERS estimates (m^3) of affected soil for dig/burn or dig/haul
- aids in targeting depths for injection of ISCO, etc.

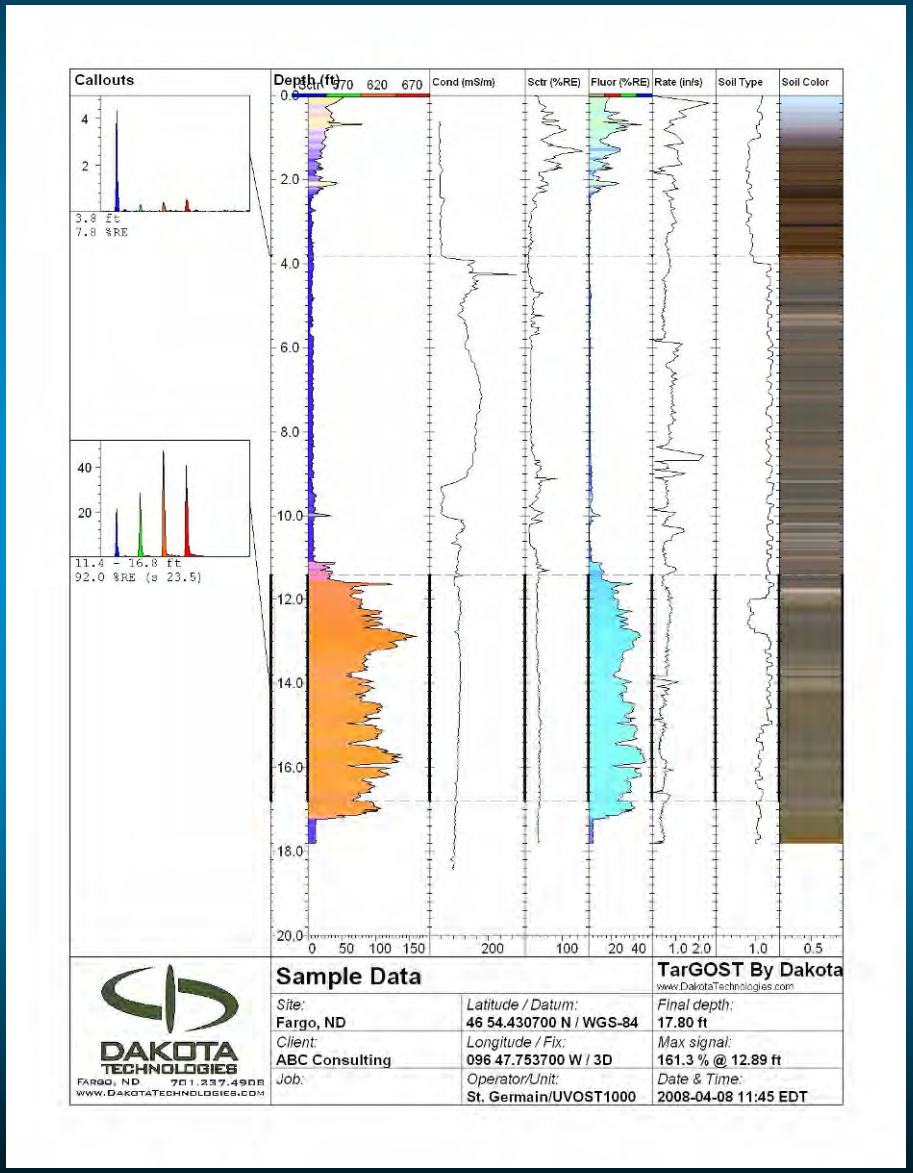
OST disadvantages



- currently not able to detect
  - metals (except for LIBS – not yet commercialized?)
  - trace NAPL (< 10-100 ppm)
  - sorbed PAHs (no NAPL present such as purifier chips, lamp black, etc.)
  - chlorinated solvents – DNAPL or dissolved phase (unless tainted with PAH)
  - explosives
  - poly-chlorinated PCBs/transformer oil
- does not respond to dissolved phase PAHs or BTEX
- no PAH speciation – just “class” of product or fuel type at best
- expensive technology for service providers to invest in – especially if regulators in their market are hesitant or resistant to use
- can require some (ca. 10%) locations be confirmed via sampling (once familiar with OSTs, many regulators accept data without confirmation)
- not “recognized” by many states - no EPA Method, ASTM, etc.
- natural false positives combined with low NAPL conc’s can make interpretation difficult
- operation requires care, skill, and diligence – software/training critical
- so “complex” and seemingly complicated that it “must be snake oil”
- only applicable where direct push can be utilized – no bedrock/boulders

What will OSTs do next?

they **will** advance…



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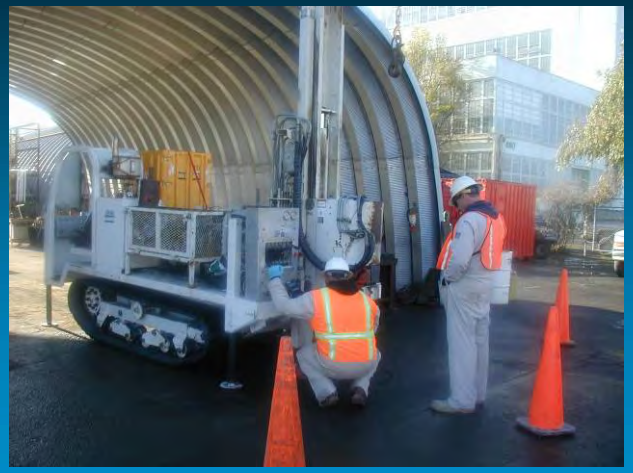

Thank you!

Randy St. Germain, President
Dakota Technologies, Inc.
2201-A 12th St. N.
Fargo, ND 58102
Phone: 701-237-4908
www.dakotatechnologies.com