

Forensic Fingerprinting Petroleum Contaminants using UVF Field Screening Technology

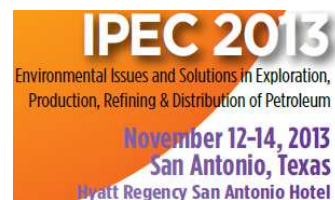


Steve Greason, Speaker
Sitelab Corporation

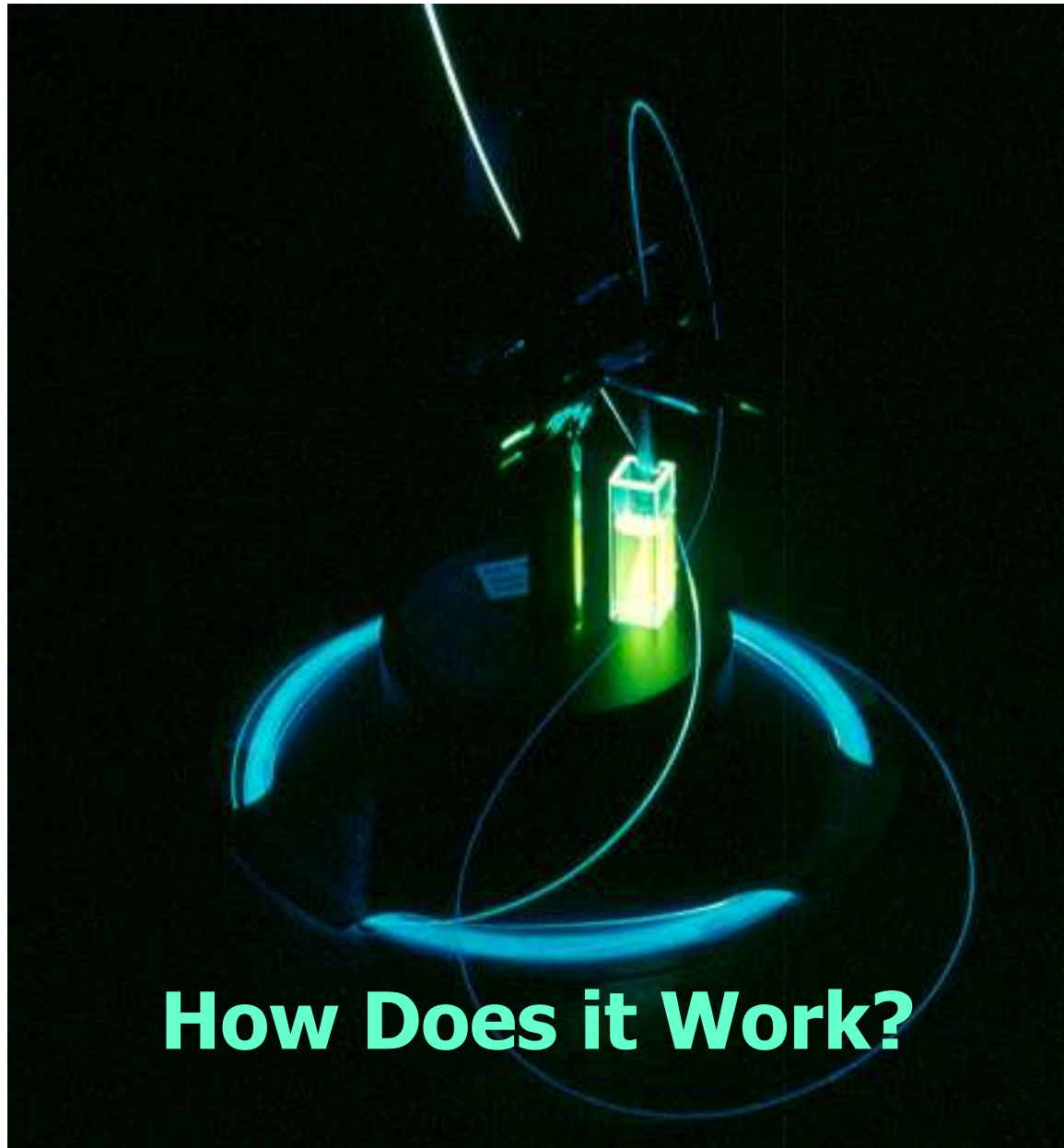


**Technical Session (Frio): Environmental
Forensics for Petroleum Hydrocarbons**

Thursday, November 14th 8:50AM – 9:15AM



What is Ultraviolet Fluorescence?



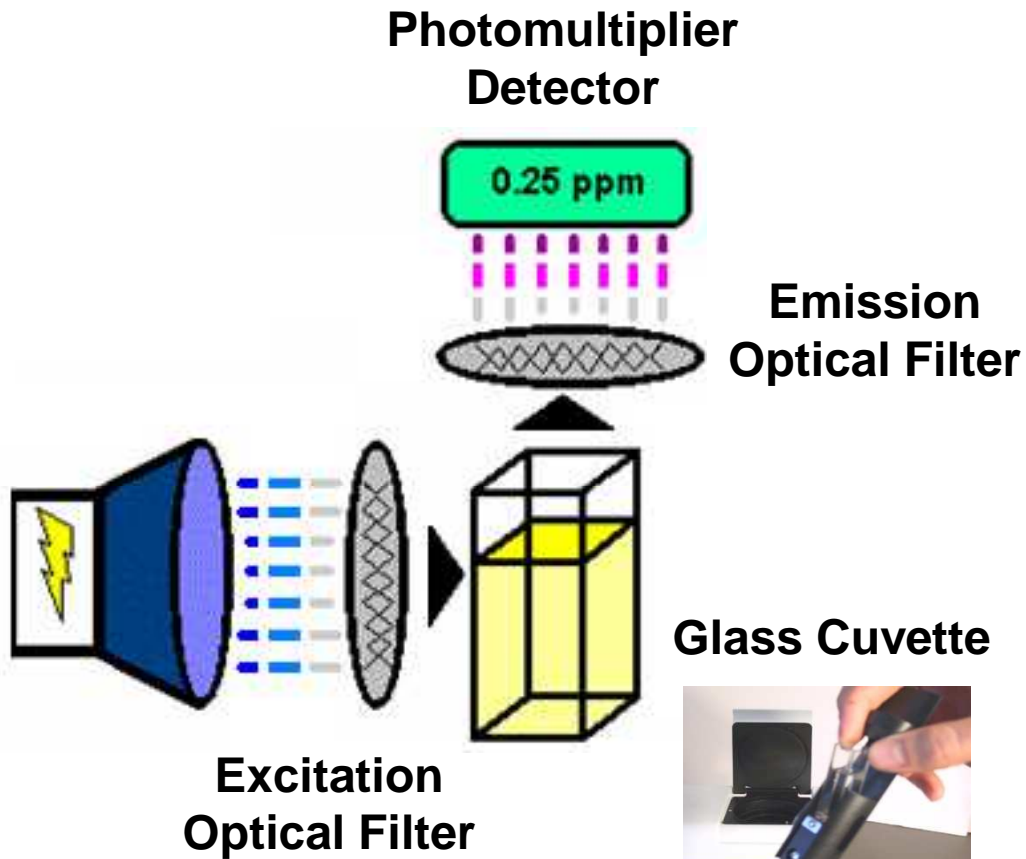
Inside a Fixed Wavelength Fluorometer



UV Lamp



Energizes molecules at 254 nm



Contains sample extract or calibration standard

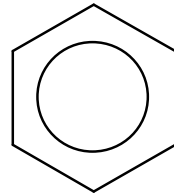
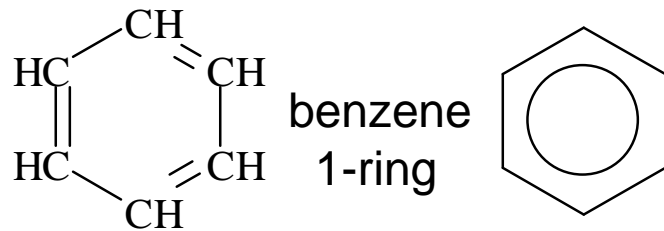


UVF Detects Aromatic Hydrocarbons

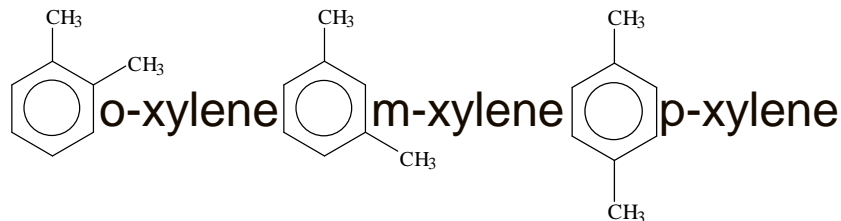
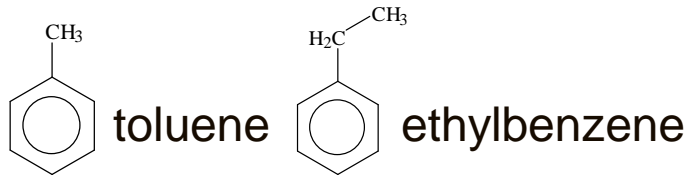
BTEX Compounds:

Benzene, Toluene, Ethylbenzene & Xylenes + other Monoaromatics

C6 to C10 Volatile Petroleum or Gasoline Range Hydrocarbons



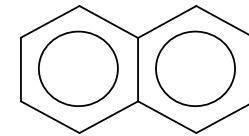
Carbon weight equals the number of C atoms per molecule.



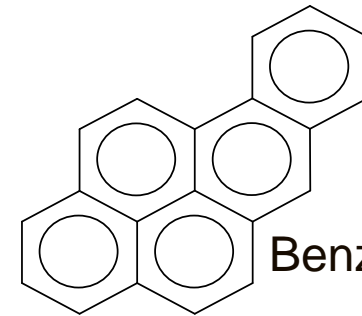
PAH Compounds:

Polycyclic or Polynuclear Aromatic Hydrocarbons

Semi to Non-Volatile Compounds
in the C10 to C40+
Diesel and Oil Hydrocarbon Range



Naphthalene
2-rings



Benzo [a] Pyrene
5 rings

What Fluoresces

- ✓ Gasoline
- ✓ Jet Fuel
- ✓ Kerosene
- ✓ Diesel Fuel
- ✓ Home Heating Oil, No 2. Fuel Oil
- ✓ Heavy Fuel Oil, No. 6 Fuel Oil
- ✓ Motor Oils
- ✓ Waste Oils
- ✓ Lubricating Oils
- ✓ Cutting Oils
- ✓ Transformer Oil
- ✓ Hydraulic Fluid
- ✓ Gas Condensates
- ✓ Drilling Muds & Drilling Fluids
- ✓ Crude Oils
- ✓ Bitumen, Tar Sands
- ✓ Creosote,
- ✓ Coal Tars, Coal Ash

And What Doesn't

Fluorescence does not detect straight chain, aliphatic hydrocarbons:

- ✓ PCE, TCE, dry cleaning solvents
- ✓ Other SVOC chlorinated solvents
- ✓ Methanol or Hexane used with UVF



Popular UVF Applications

- Soil excavation and cleanup
- Site Assessments
- Remediation & Treatment
- UST Fuel Sites
- Oil Refineries, Pipelines
- Power Plants, MGP Sites
- Military Sites, Airports
- Natural Disasters, Oil Spills
- Oil & Gas Production

Portable Analyzers Available:

siteLAB®

Petroleum Hydrocarbon Solutions



INSTRUMENT SPECIFICATIONS

Weight & Dimensions:	13 lbs (5.9 Kg); 11" x 9" x 8" (28 cm x 23 cm x 21 cm).
Power Requirements:	External power supply, 100-120 VAC, Max. 30 watts.
Operating Temperature:	45°F to 95°F; 7°C to 36°C.
Principle of Operation:	Ultraviolet fluorescence spectrophotometer.
Detector:	Factory-installed photomultiplier tube (PMT).
Lamp:	Mercury vapor lamp included with analyzer (approx 10,000 Hr life expectancy). Replacement/spare lamps are available.
Min. Detection Limits:	Varies depending on Sitelab Calibration Kit used; GRO 0.5 ppm, EDRO 0.1 ppm, PAHs 0.05 ppm and TPH-Oil 0.5 ppm.
Display:	16 x 2 character LCD (3.9" x 0.9"; 9.8 cm x 2.2 cm).
Data Output:	100% ASCII format through a 9-pin RS-232 serial cable at 9600 baud. USB adapter available, Part No. 3100-USB, sold separately.
Software:	Menu driven microprocessor-controlled. CD-ROM with software included for computer connection, Microsoft compatible.
Filter Cylinder:	Accommodates up to eight, 25 mm (1-inch) round optical filters (up to 4 excitation and 4 emission filters).
Cuvettes:	Includes cuvette adapter and two glass cuvettes. Replacement/spare cuvettes are available.
Readout:	Direct concentration (in ppm or ppb) or raw fluorescence.
Calibration:	Multi-point calibration for direct concentration measurement.
Blank:	Reads and subtracts blank using methanol or hexane solvents.
Warranty:	One-year warranty, parts and labor.
Approvals:	CE, UL and C-UL. ISO 9001 manufacturing. Made in USA.

UVF 3100

CONTAMINANTS

Ideal for gasoline, jet fuel, diesel fuel, heating oils, lubricating oils, crude oils, gas condensates, creosote, coal tars, coal ash and many other types of petroleum hydrocarbons.

QUICK RESULTS

Test soil, sediment or water samples in just 5 minutes using Sitelab test kits with solvent extraction.

ACCURACY

Correlates well to regulatory lab GC methods performed by certified laboratories. Ranked highest in U.S. EPA's "TPH in Soil" evaluation study. Publication No. EPA/600/R-01/080

FINGERPRINTING

Test BTEX and PAHs for forensic applications to determine the type or age of petroleum on your site.



Sitelab's UVF-3100A and UVF-3100D models include a field case with all the tools needed to perform tests.

The analyzer is fitted with optical filters sensitive to the gasoline range, diesel and oil range and Target PAH ranges. Sitelab's GRO, EDRO and PAH Calibration Kits provide fast, accurate measurement with quality control.

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UVF-3100 Analyzer Brochure

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Petroleum Hydrocarbon Solutions



INSTRUMENT SPECIFICATIONS

Weight & Dimensions:	13.9 oz (0.4 Kg); 1.75" x 3.5" x 7.25" (4.5 cm x 8.9 cm x 18.4 cm).
Power Requirements:	Four AAA batteries. Batteries good for approx. 1,000+ readings.
Operating Temperature:	45°F to 95°F; 7°C to 36°C.
Principle of Operation:	Hand-held ultraviolet fluorescence spectrophotometer.
Detector:	Factory-installed photomultiplier sensor.
Lamp:	Light Emitting Diode (LED).
Min. Detection Limits:	Varies depending on Sitelab Calibration Kit used; TPH-Oil 5 ppm, Heavy PAHs 25 ppb.
Display:	16 x 2 character LCD (2.5" x 0.6"; 6 cm x 1.5 cm); ppm or ppb units.
Data Output:	Not available. Record results manually.
Automatic Power Down:	After 3 minutes of inactivity.
Optical Filters:	Includes two sets of factory-installed excitation and emission filters; use Channel A optics for Sitelab applications.
Cuvettes:	Uses disposable 8 mm round glass cuvettes. Cuvettes are included with Sitelab sample extraction kits and calibration kits.
Calibration:	Single-point and blank.
Blank:	Reads and subtracts blank using methanol or hexane solvents.
Response Time:	5 Seconds.
Diagnostics:	Displays percent fluorescence sensitivity of calibration and blank.
Alarms:	Low battery, circuit failure, high blank.
Warranty:	One-year warranty, parts and labor.
Approvals:	CE, UL and C-UL. ISO 9001 manufacturing. Made in USA.

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TD-500D Analyzer Brochure

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TD 500D

CONTAMINANTS

Test samples for TPH with heavy fuel oils, waste oils or crude oils. Test for PAHs in old, weathered fuel oils, creosotes, coal tars and coal ash.

QUICK RESULTS

Test soil, sediment or water samples in just 5 minutes using Sitelab test kits with solvent extraction.



ACCURACY

When used with Sitelab Calibration Kits, TPH-Oil results correlate well to EPA's 1644 gravimetric method. PAH results correlate well to EPA's 8270 method as sum of PAH compounds.



EASY TO USE

The equipment is simple to operate. Sitelab's TD-500D model includes a field case with all the tools needed to perform tests.



Popular Calibration Kits Available



GRO: Gasoline Range Hydrocarbons (BTEX)
Product No. CAL-025.
Use with Slot B Optics



EDRO: Extended Diesel Range Hydrocarbons
Product No. CAL-042
Use with Slot A Optics



PAHs: Poly Aromatic Hydrocarbons
Product No. CAL-060
Use with Slot A Optics for “Total PAHs”
or Slot D Optics for “Target PAHs”



TD-500D Analyzer: Heavy PAHs
Product No. CAL-061
Contains same PAHs used in
UVF-3100 PAH calibration kit

UVF-3100D is fitted with 3 sets of optical filters which are sensitive to different types of hydrocarbons





Sample Extraction Kits Available...

Test procedure is easy, results in 5 minutes!



1. Weigh Soil



2. Add Solvent



3. Filter Extract



4. Dilute Extract

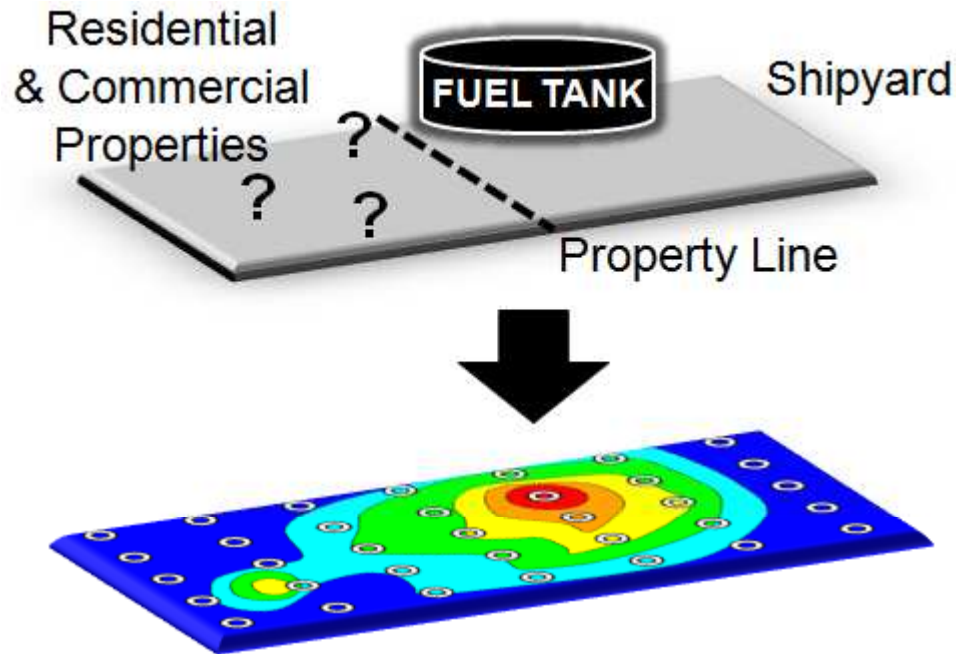


5. Pour into Cuvette



6. Test Sample

Example of a Contaminated Petroleum Site





UVF vs. Photo-Ionization Detectors at Gasoline Site

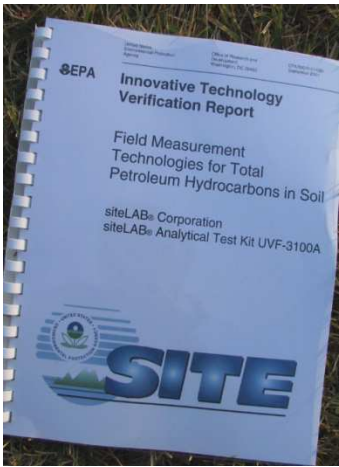


Concentrations in ppm (mg/Kg)

Soil Depth:	UVF-3100 GRO results	Jar Headspace PID Results	PID vs. UVF? Correlation
2'	ND <1	1	Good
3'	1,010	6	Low!
5'	7	320	High!
7'	2,690	10,000	Fair
8'	400	8	Low!
11'	3,037	115	Low!
14'	9	435	High!
15'	4	28	Fair
16'	5	63	High!
18'	175	590	Fair
19'	600	1,010	Good

Certified Lab GC Result → **2,700**

PID was calibrated to isobutylene and performed by an experienced operator



Sitelab Ranked Highest by U.S. EPA for TPH in Soil Evaluation Study

	<u>Accuracy</u> Percentage of Spike Samples within 50% to Lab GC Results	<u>Method Detection Limit</u> Compared to Lab GC Result of 6.3 ppm
Sitelab Corporation UVF-3100 - Fluorescence	72%	3.4 ppm
Horiba Instruments, Inc. OCMA-350 - Infrared (IR)	50%	15.2 ppm
Chemetrics, Inc. RemediAid – Fiedel Crafts Reaction	48%	60 ppm
Wilks Enterprise, Inc. Infracal TOG - Infrared	48%	76 ppm
Dexsil Corporation Petroflag - Emulsion Turbidity	21%	20 ppm
Strategic Diagnostics, Inc. Ensys - Immunoassay	Inconclusive	Inconclusive

Hydrocarbon Fingerprinting





U VF Fingerprinting Applications

The proportions or ratios of GRO and PAHs detected in a sample is used to identify the age or type of petroleum



1. Test for GRO (BTEX)

Calibrate UVF-3100D using Sitelab's GRO Calibration Kit on Slot B optics.



2. Test for Total PAHs

Rotate optical filter cylinder to Slot A. Recalibrate analyzer using Sitelab's PAH calibration kit.



3. Test for Target PAHs

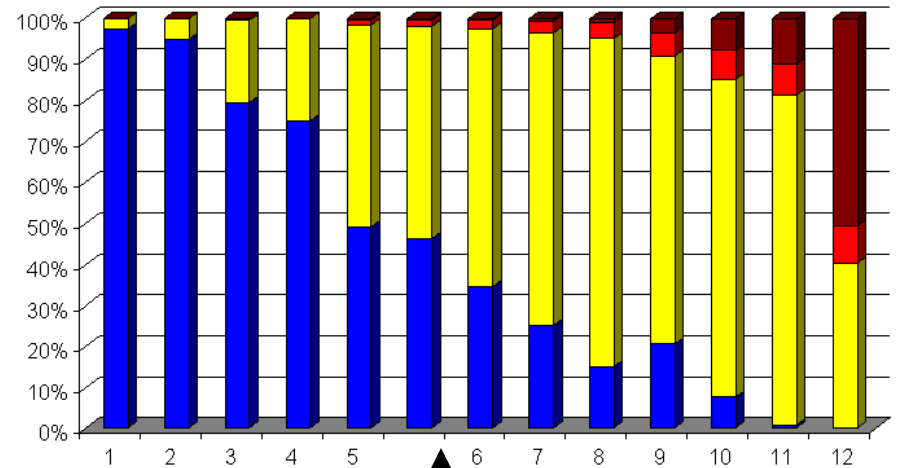
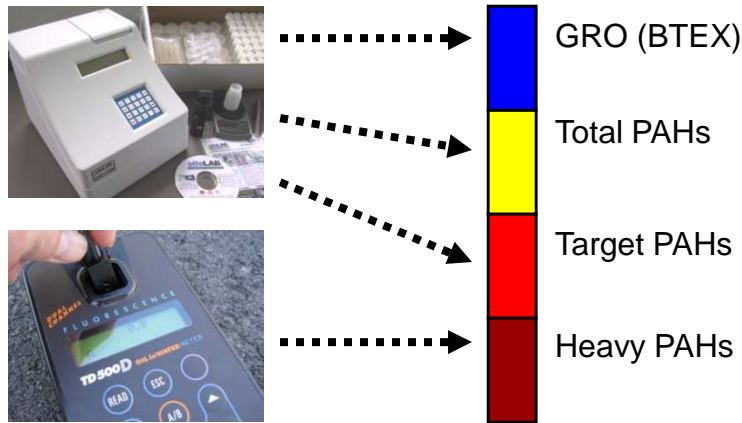
Rotate optics to Slot D and retest sample. PAH calibrators respond the same, new calibration not necessary.



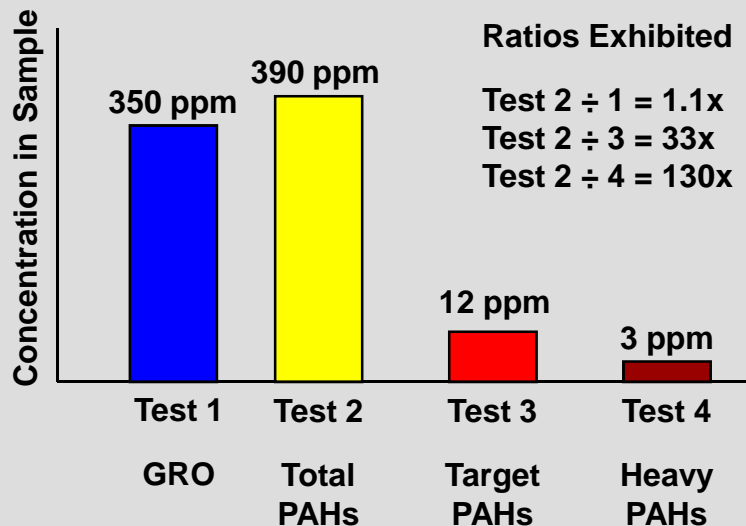
4. Test for Heavy PAHs (Optional)

For additional forensic analysis, test samples a 4th time with TD-500D for PAHs.

Test for GRO and PAHs... Compare "Signatures" to Other Contaminants



Soil collected from UST site:



Examples Tested at 2,000 ppm concentration	Ratios			
	GRO	EPH Total PAH	Target PAHs	TD-500 PAHs
1 Fresh Gasoline	600	15	0.4	0.04
2 Weathered Gasoline	1,500	80	0.6	0.20
3 Weathered Gas + Diesel	950	240	5.0	1.0
4 Weathered Jet Fuel	300	100	0.02	0.012
5 Fresh Diesel Fuel (heating oil)	400	400	10	2.0
Soil collected from Old UST Site	350	390	12	3
6 25% Weathered Diesel	300	540	18	3.5
7 50% Weathered Diesel	250	700	28	7
8 75% Weathered Diesel	160	850	42	10
9 Waste Motor Oil	65	220	18	11
10 MGP Coal Tar	100	1000	90	100
11 No. 6 Fuel Oil	10	1300	120	180
12 Humic Acid (brown coal lignite)	0	80	18	100

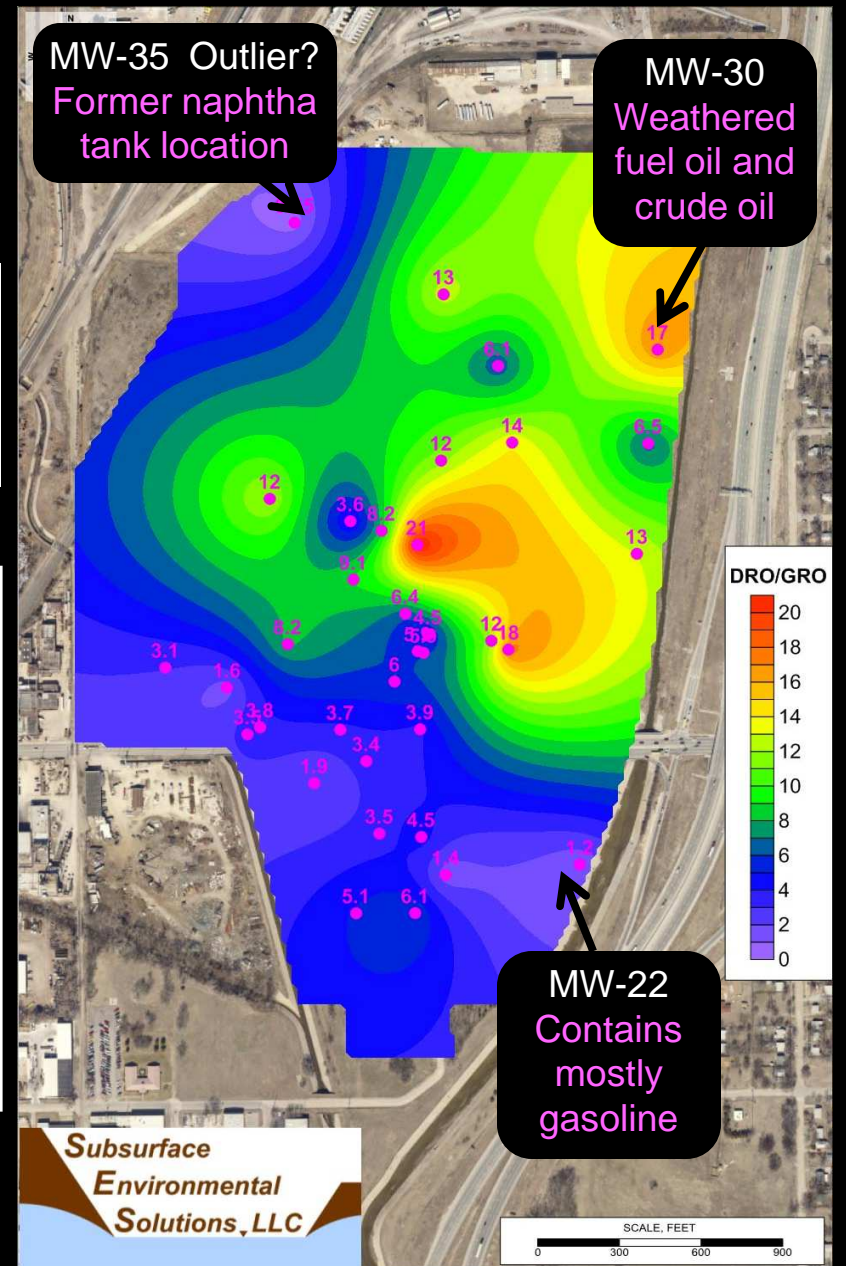
Ratios are similar to fresh diesel fuel!

Fingerprinting NAPL Plume at Refinery Site

Sitelab UVF-3100 response testing oil samples collected from 35 monitoring wells measured at 10 ppm concentrations:

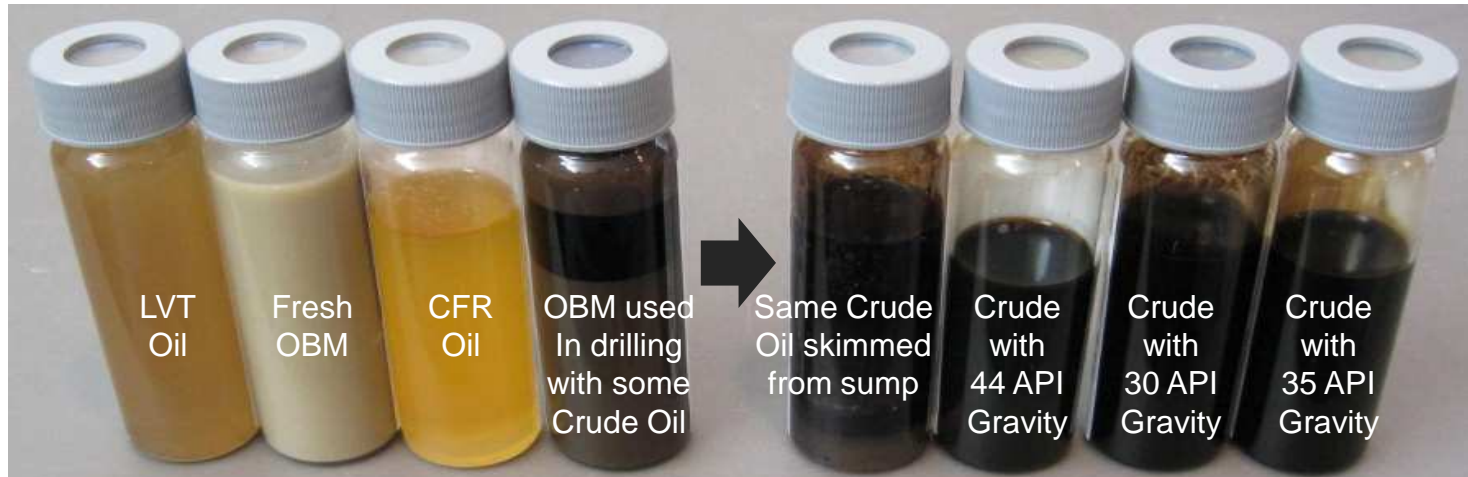


Examples at 10 ppm	GRO Response	DRO Response	DRO/GRO Ratios
MW-22	1.52 ppm	1.80 ppm	1.2
MW-30	0.73 ppm	12.5 ppm	17
MW-35	0.32 ppm	0.18 ppm	0.6

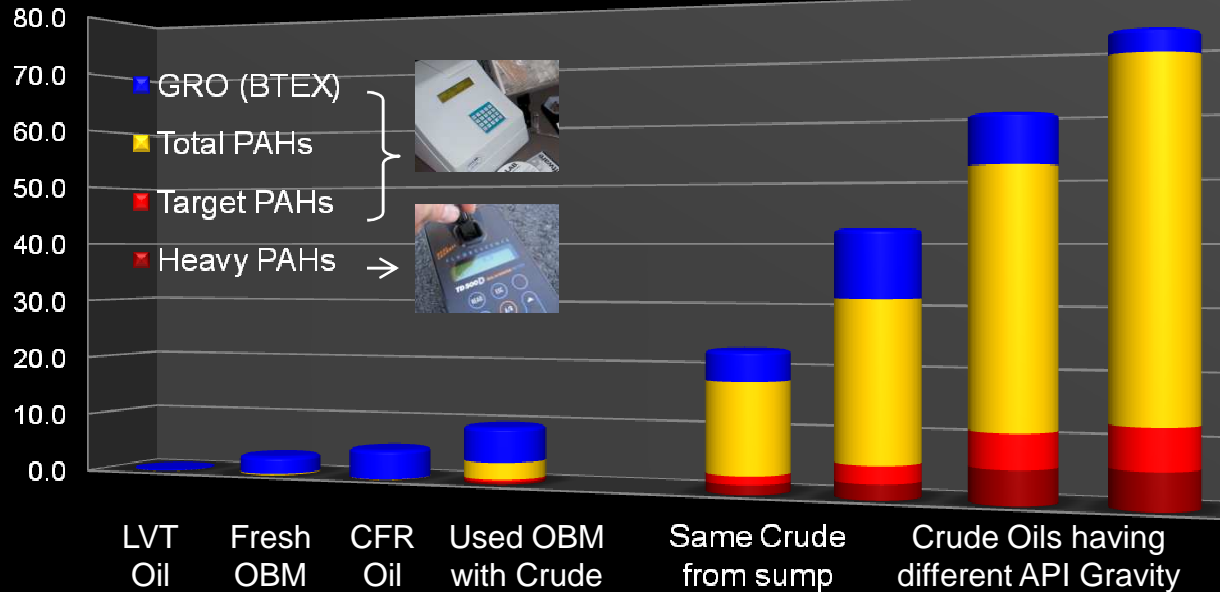




Discrimination Between Crude Oil & Oil-Based Drilling Muds



UVF-3100D and TD-500D Response Comparing Oil Based Drilling Muds vs. Crude Oils at 100 ppm

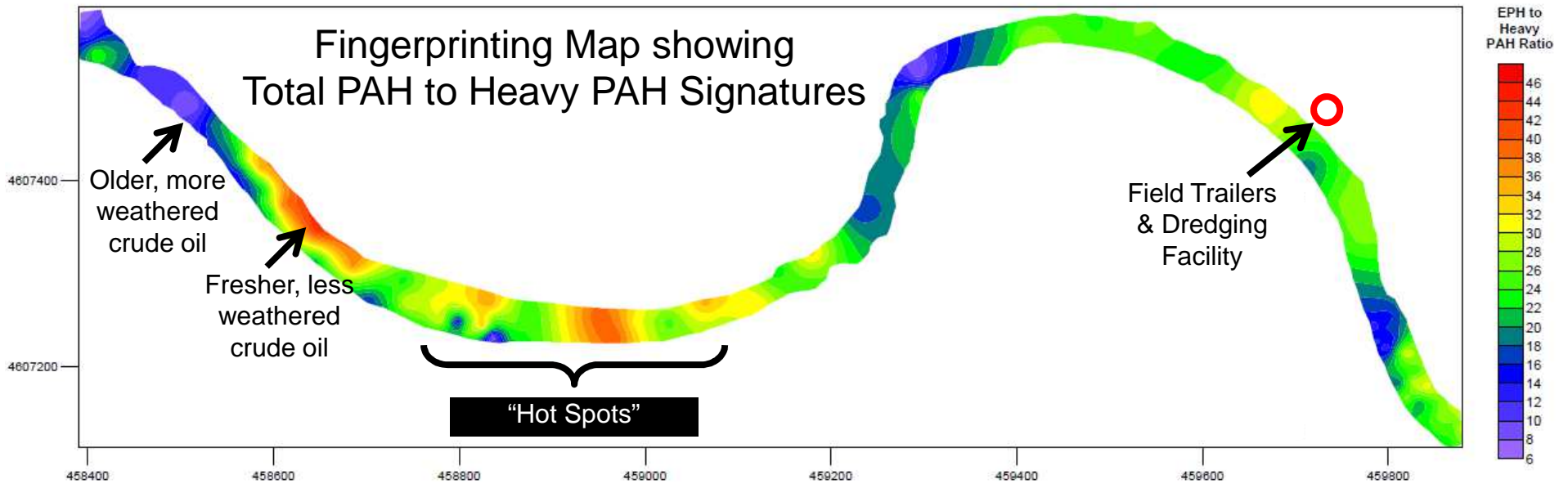
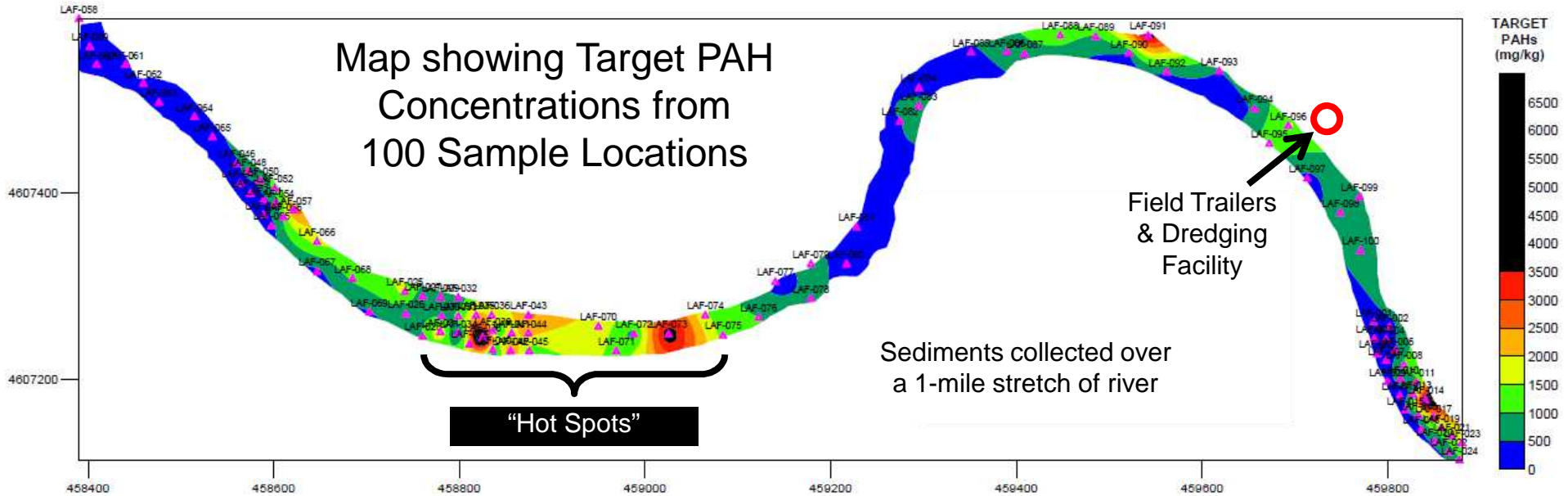


Field Screening PAHs in Sediments: West Branch Grand Calumet River



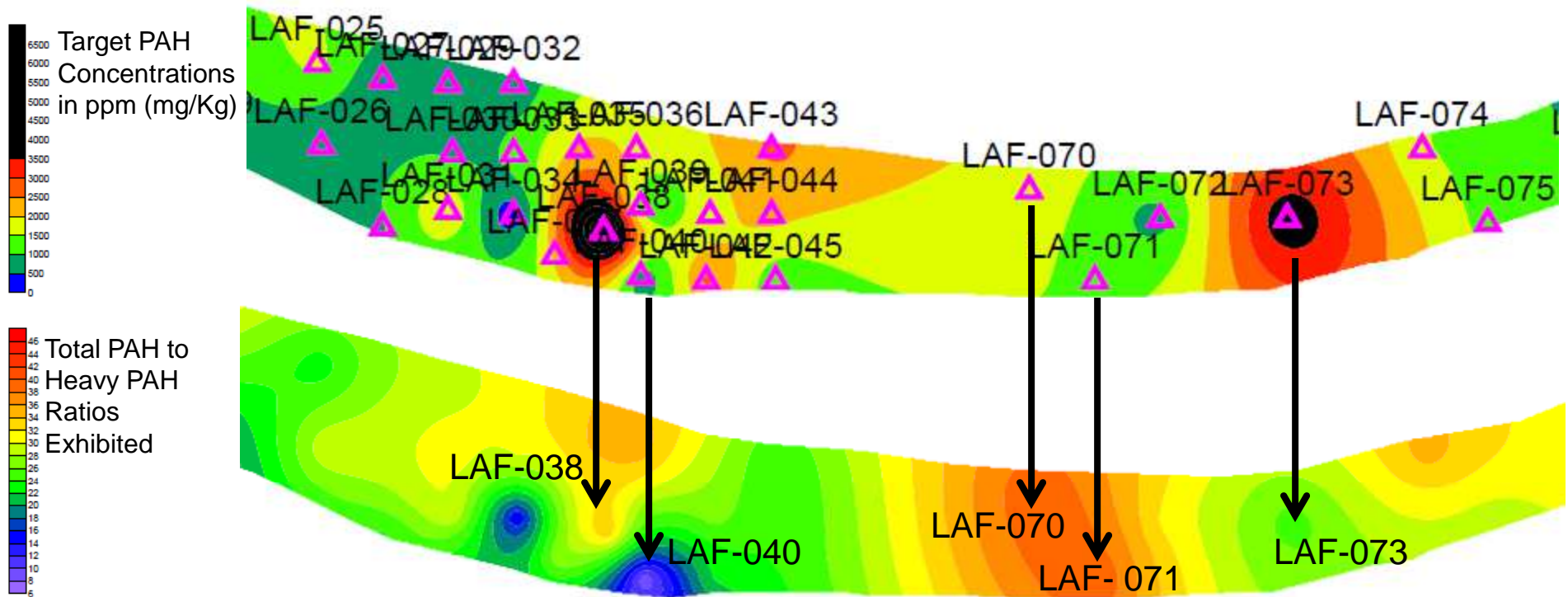
- ✓ Post-Dredge site in Hammond, Indiana, located near Lake Michigan
- ✓ Client: Battelle Memorial Institute
- ✓ Battelle collected 100 sediment samples by boat using push cores
- ✓ Sitelab's test equipment was setup in back of U-Haul truck on-site
- ✓ Sediments were screened for residual contamination. Data used by Battelle & U.S. EPA to determine which locations require further attention as part of cap monitoring plan.

Sediment Contamination in River



Maps by Subsurface Environmental Solutions, LLC , created with Surfer software using Sitelab data and GPS coordinates

Close up of Sediment "Hot Spots"



Examples showing PAH results and ratios...
 "Signatures" look similar to crude oil!

Sample ID	Total PAHs	Target PAHs	Heavy PAHs
LAF 038	75,900 ppm	6,240 ppm	2,260 ppm
LAF 040	5,940 ppm	590 ppm	696 ppm
LAF 070	19,840 ppm	1,860 ppm	500 ppm
LAF 071	17,000 ppm	1,420 ppm	426 ppm
LAF 073	42,600 ppm	4,000 ppm	1,700 ppm

Total PAH to
Target PAH
Ratios

Total PAH to
Heavy PAH
Ratios

12x

34x

10x

9x

11x

40x

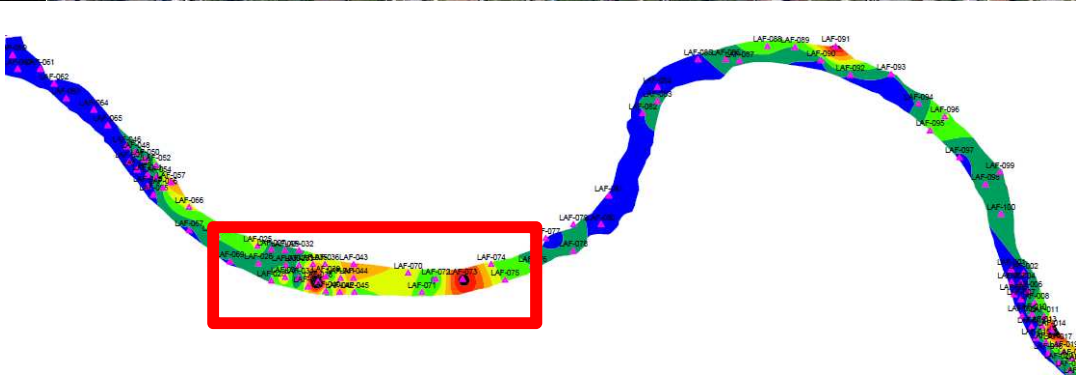
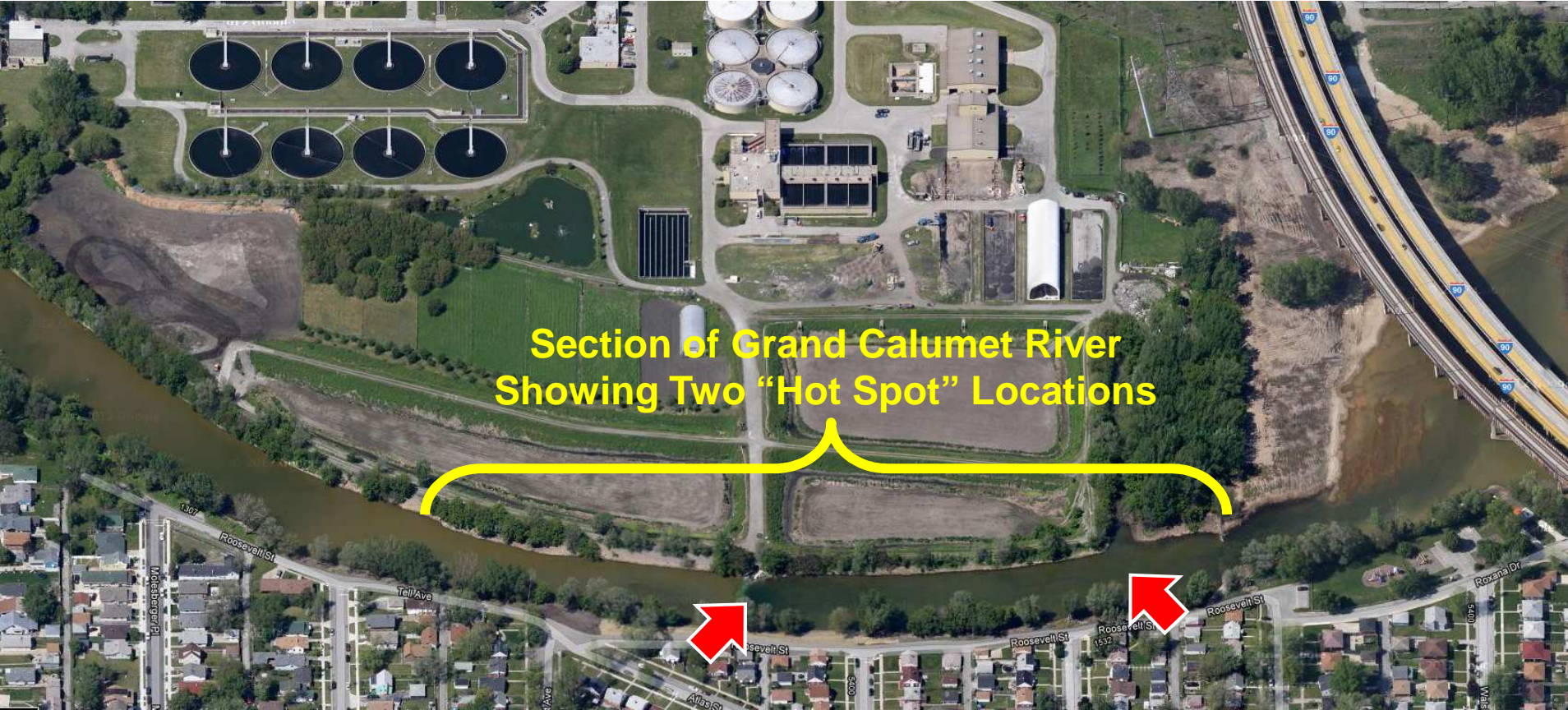
12x

40x

11x

25x

Costs & Benefits using UVF?



- ✓ 400 test results in 4 days for cost of \$9,500.
- ✓ Source of contamination identified as crude oil using fingerprinting data

End of Presentation... Thank You



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