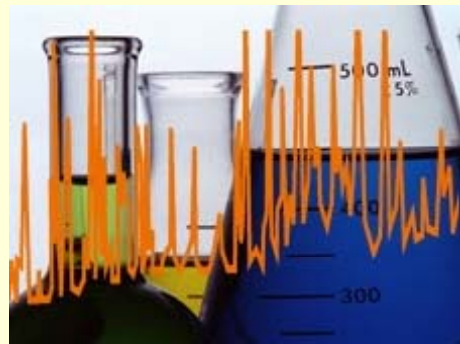
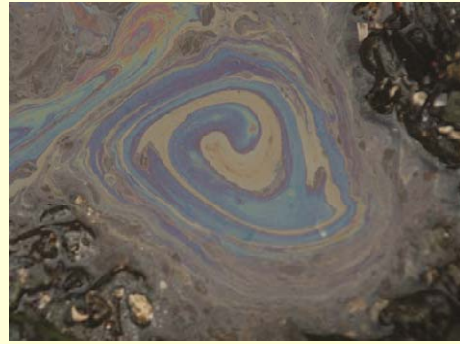
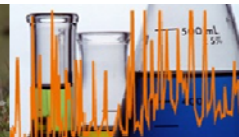


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Field Measurement of Total Petroleum Hydrocarbons in Crude Oil-impacted Soils

Jaana Pietari, Exponent

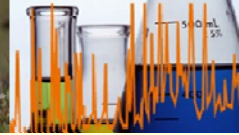
Thomas Hoelen, Chevron

Kirk O'Reilly, Exponent

August 9, 2012

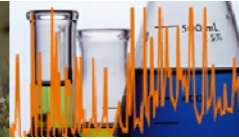
INTRODUCTION





Field Test Kits (FTKs) for Petroleum Hydrocarbons

- Onsite analytical devices can provide near-real time information so that decisions can be made onsite
- (Potentially) lower cost allows more samples to be collected, therefore, less uncertainty for delineation



EPA Sponsored Study

- Innovative field measurement technologies for TPH in soils
 - Seven devices evaluated
 - Summary reports in 2001
 - Focus on soils with weathered gasoline and diesel impacts

United States
Environmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

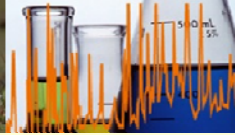
EPA/600/R-01/080
June 2000



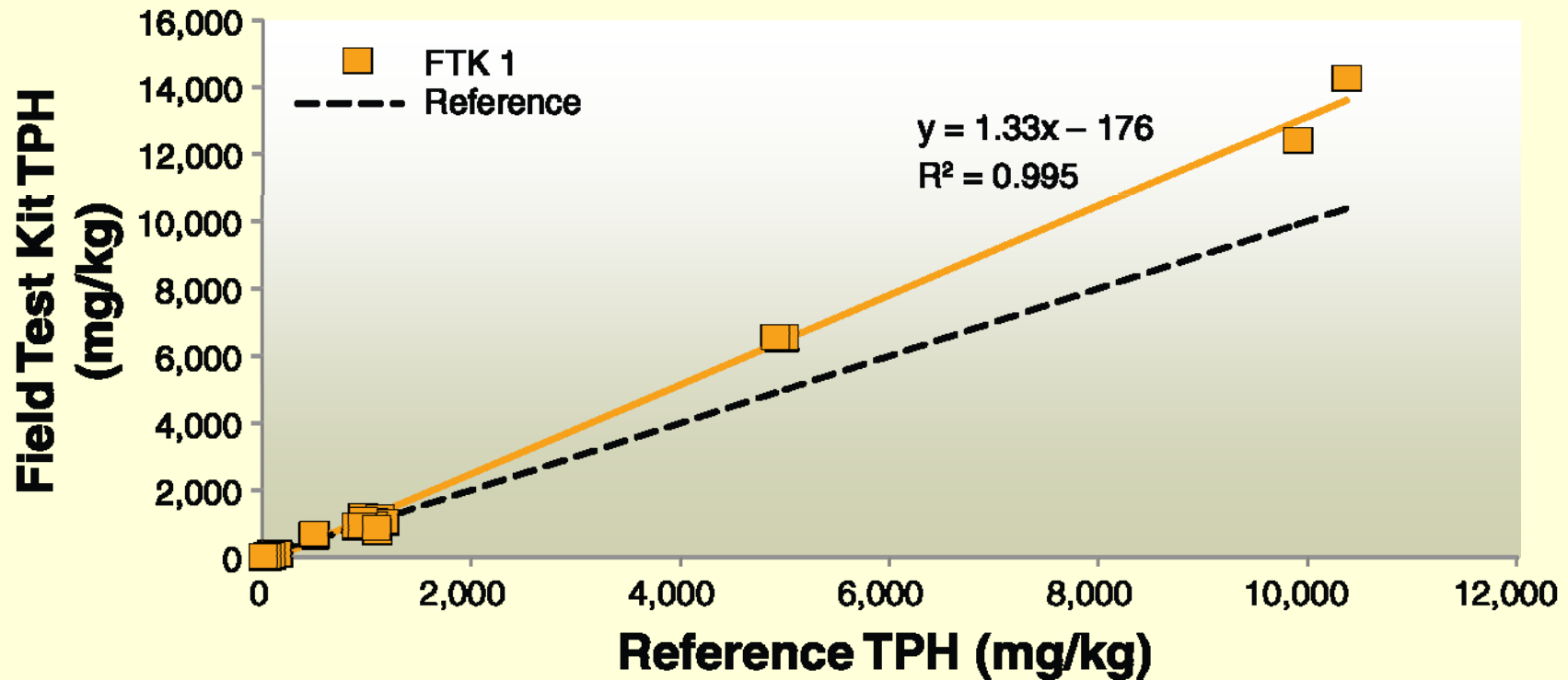
Demonstration Plan

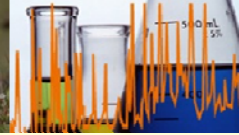
Field Measurement
Technologies for
Total Petroleum Hydrocarbons
in Soil





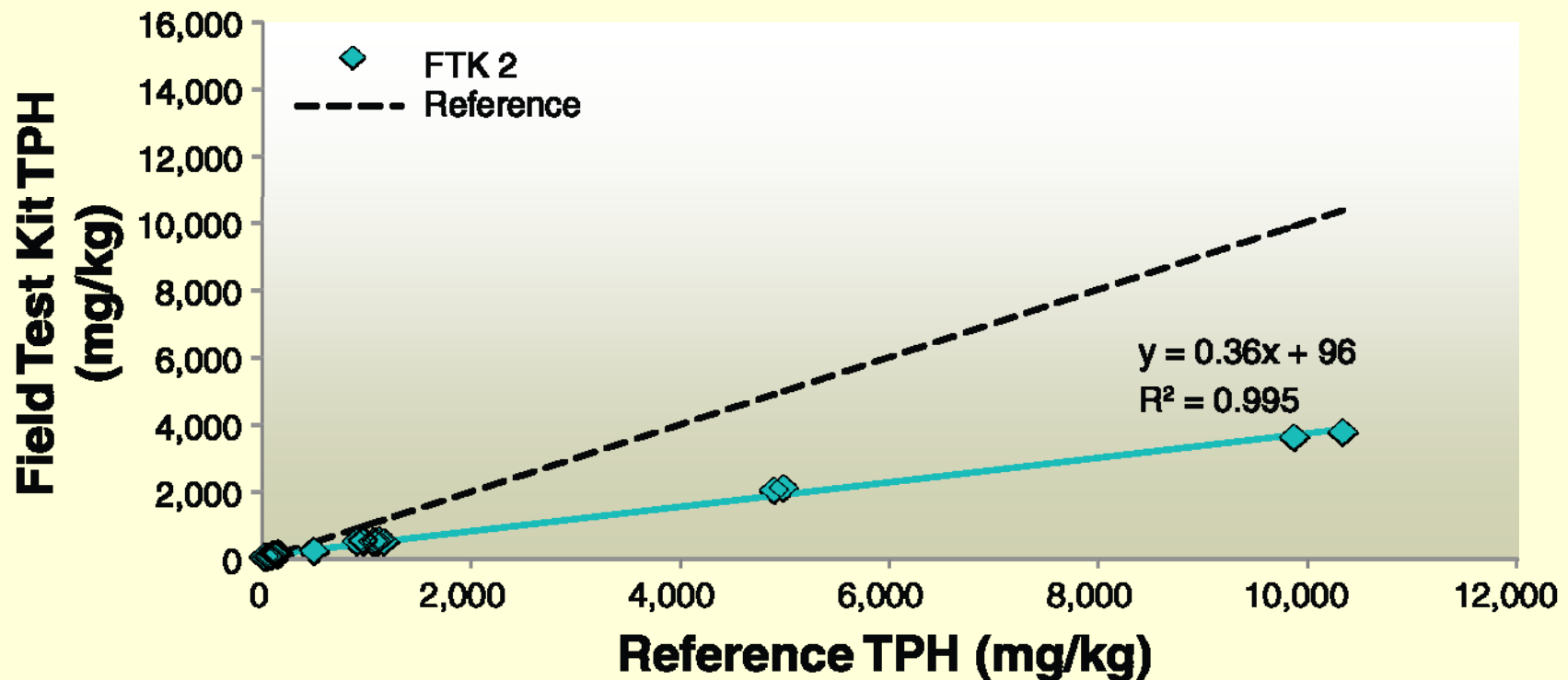
Laboratory Studies with Fresh Diesel and Crude: Some FTK Results are Comparable to Reference...

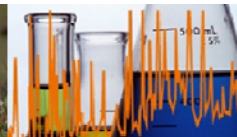




... While Some are Not

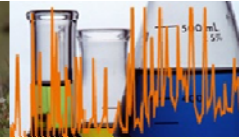
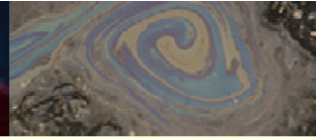
- Because of good correlation, “field calibration” to site-specific conditions allows the use of FTKs that are not accurate relative to the reference





Why FTKs Are Different Than Reference?

- TPH is defined by the method
- Multiple factors influence FTK and reference results
 - Extraction efficiency
 - Limitations in detection
 - Inconsistent correlation between detected compounds (e.g., aromatics) and TPH
 - Non-representative standards
 - Interfering compounds
 - Sample heterogeneity

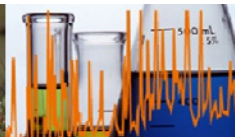


Study Objectives

- Many petroleum sites with heavy weathered crude oil impacts
 - Are FTKs applicable to weathered crude oil-impacted soils?
- Focus on FTK performance for supporting site decisions at two typical cleanup goals of 1,000 ppm and 10,000 ppm
 - Do FTKs support comparable decisions to a reference method?

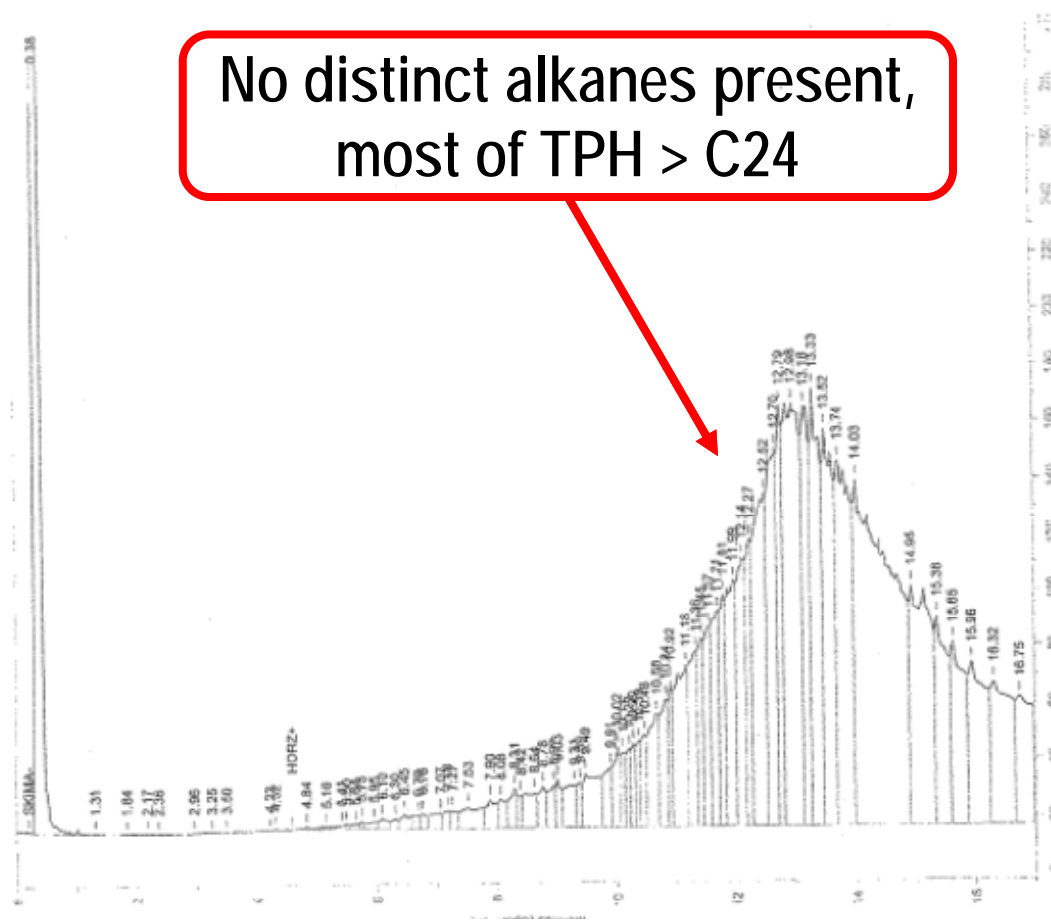
METHODS

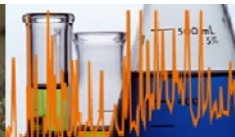




Field Site and Samples

- Site with weathered heavy crude oil-impacted soil in San Joaquin Valley, California
- Soil samples
 - 40 samples collected from two stockpiles and excavation walls
 - Homogenized and split for analyses

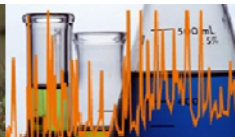




Sample Analysis

- TPH (C10–C32) with GC-FID as a reference (8015 and solvent extraction)
- Five FTKs evaluated





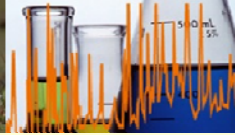
Evaluated FTKs Represent a Range of Available Technologies

Test Kit	Technology	Solvent	Target Analytes
FTK 1	Ultraviolet fluorescence	Methanol (HPLC grade)	Aromatics in gasoline, diesel, or heavier fuels/oils
FTK 2	Ultraviolet fluorescence	Methanol	Aromatics in gasoline, diesel, or heavier fuels/oils
FTK 3	Turbidimetry	Proprietary; contains methanol	Hydrocarbons in diesel and heavier fuels/oils
FTK 4	Infrared spectrophotometry	Hexane, pentane, Vertrel	Alkanes in gasoline, diesel, and heavier oils
FTK 5	Colorimetry	Dichloromethane	Aromatics in petroleum hydrocarbons

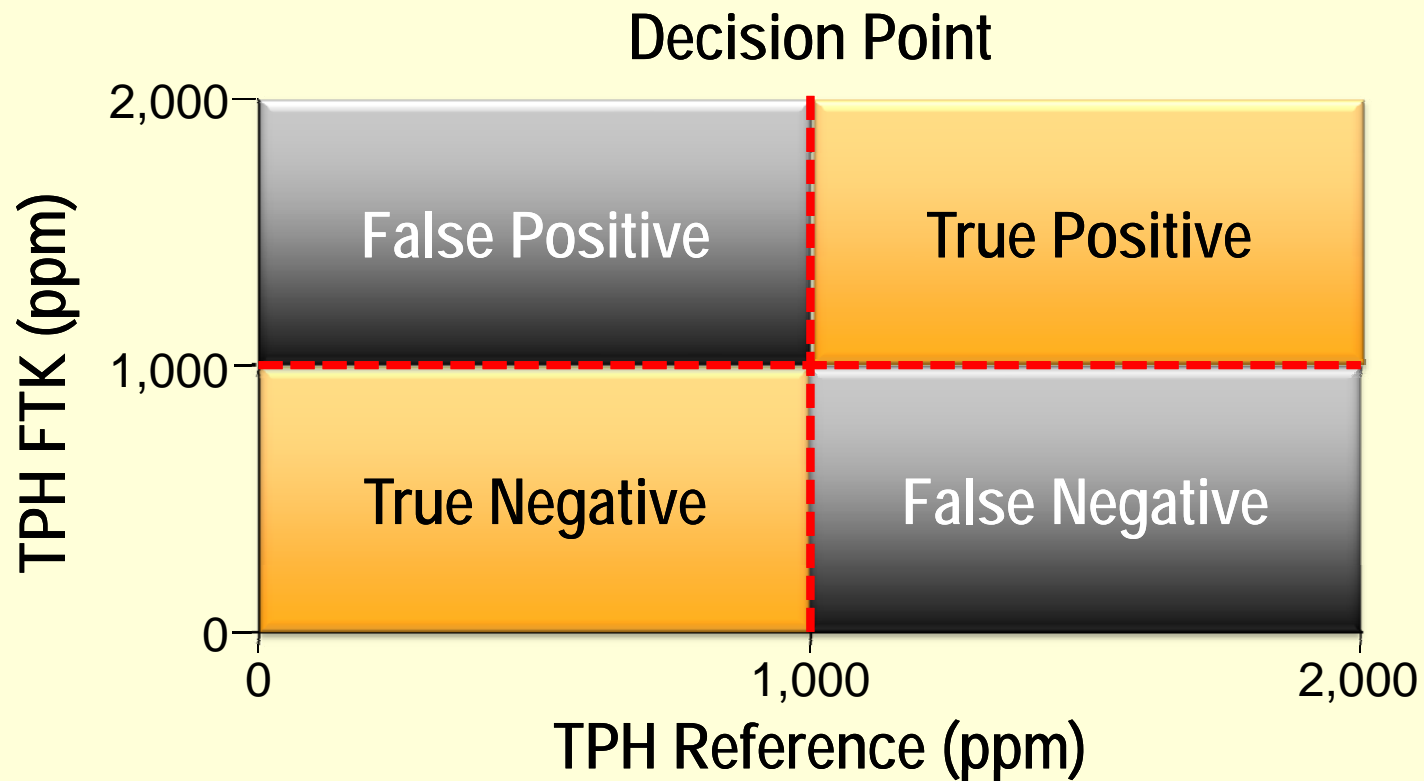


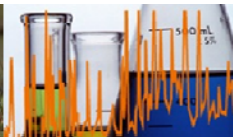
Decision-Oriented FTK Performance Analysis

- Does the FTK result support the same decision as the result with a reference method?
 - Is the decision of “clean” or “dirty” the same based on FTK and the reference result?
 - Is the decision “uncertain”?
- Simulated field operations
 - 15 samples randomly selected for “field calibration”
 - *Demonstration of Method Applicability* (U.S. EPA 2008)
 - Remaining 25 samples were used as validation samples

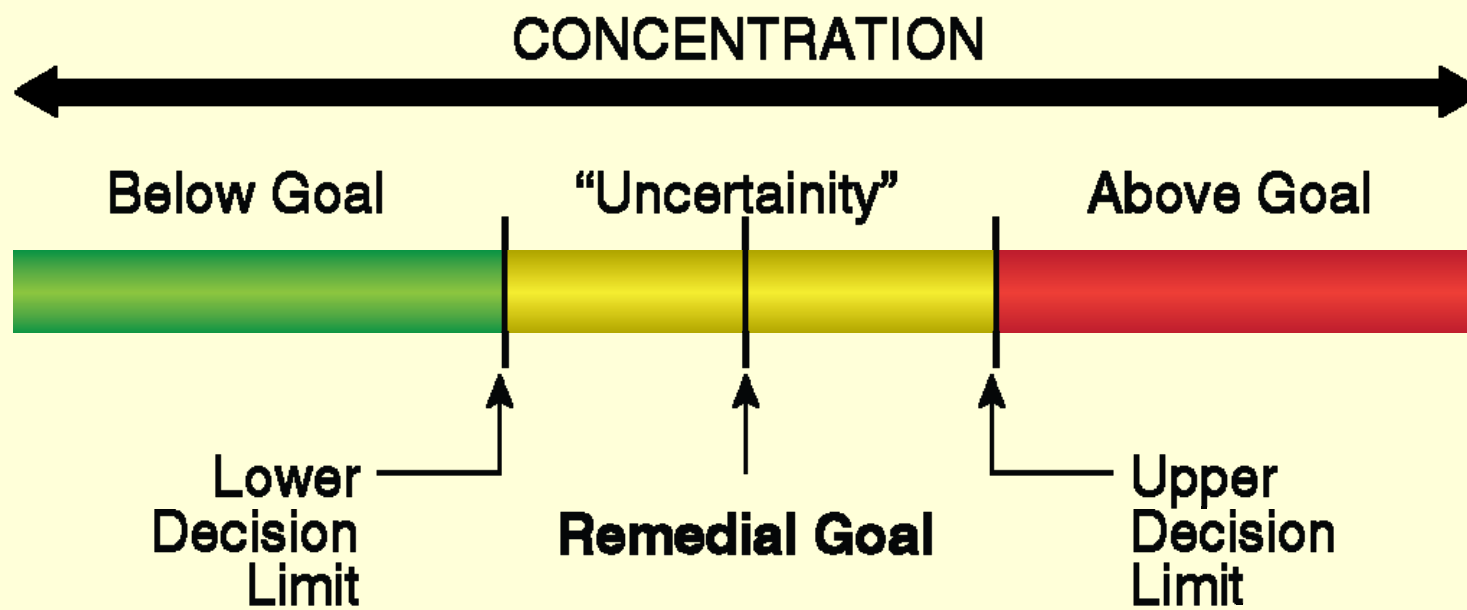


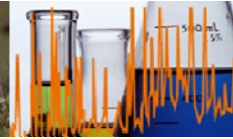
Need to Control for Incorrect Decisions



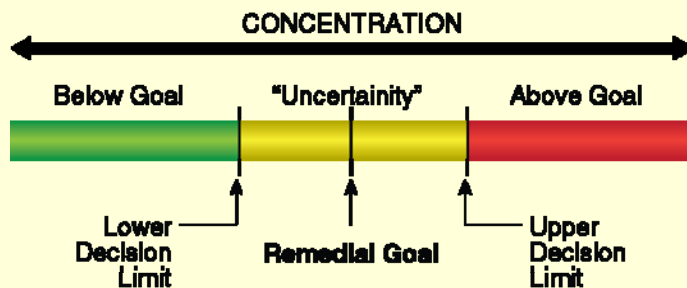


Concept of Uncertainty Interval



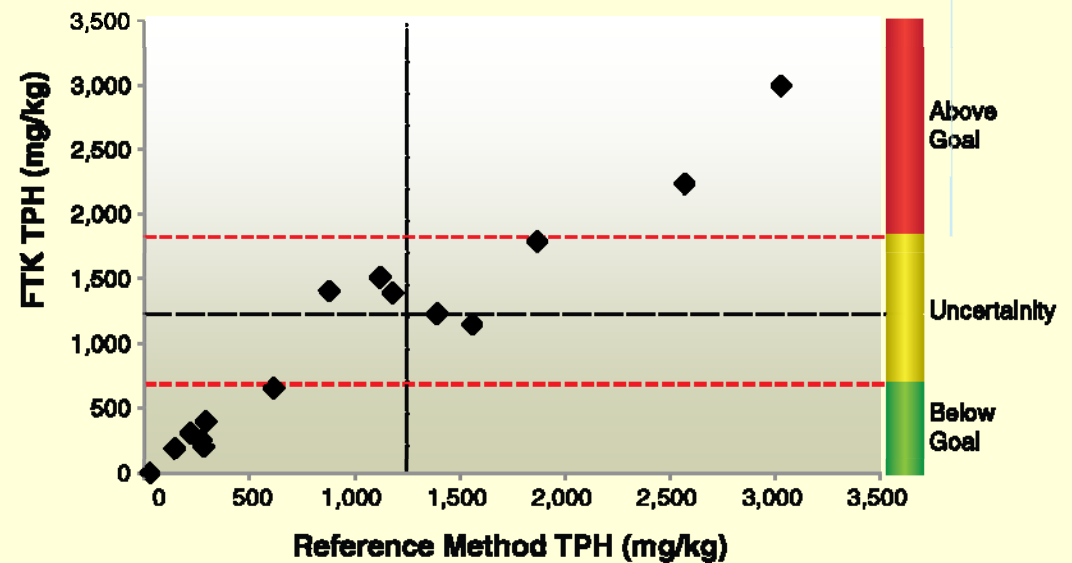


Concept of Uncertainty Interval (continued)



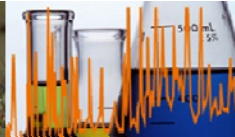
Tradeoff between:

- Increased analytical costs and reduced chance of incorrect decisions
- Lower analytical costs and increased chance of incorrect decisions
- Impact depends on site-specific objectives

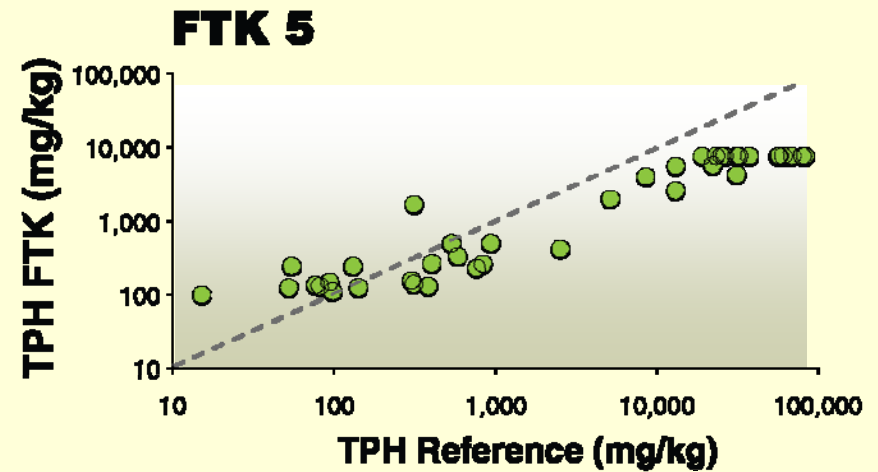
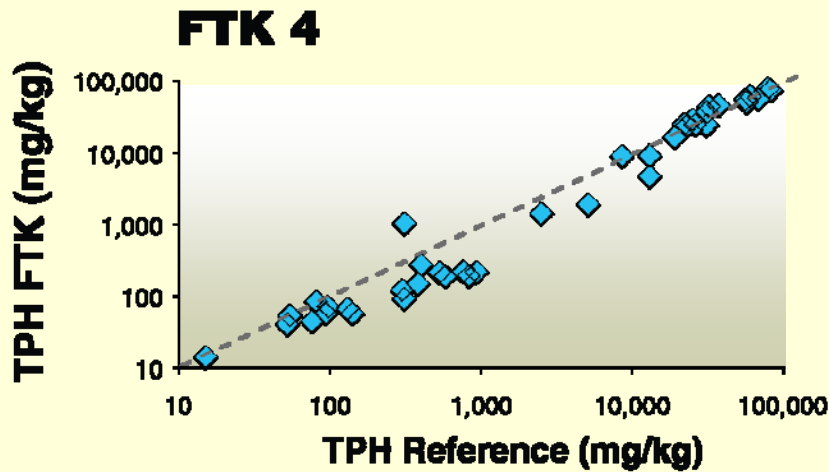
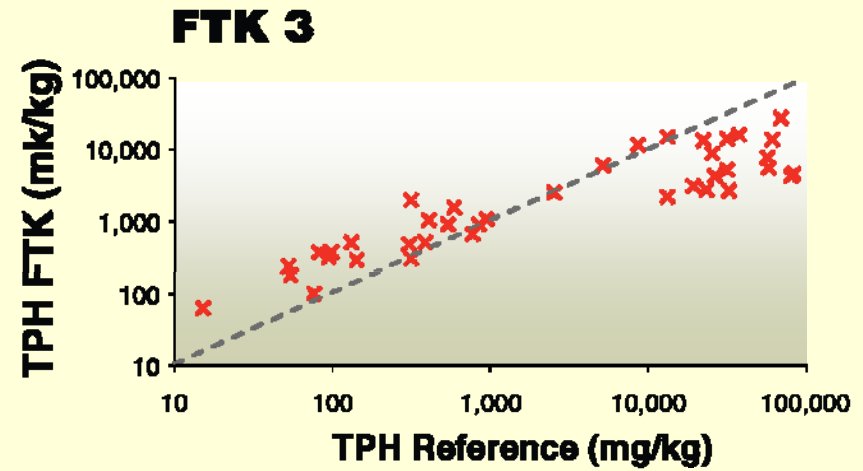
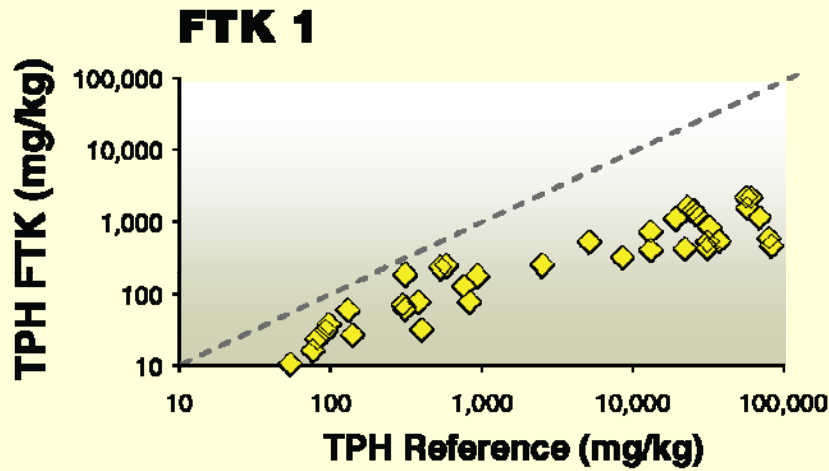


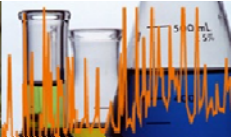
RESULTS



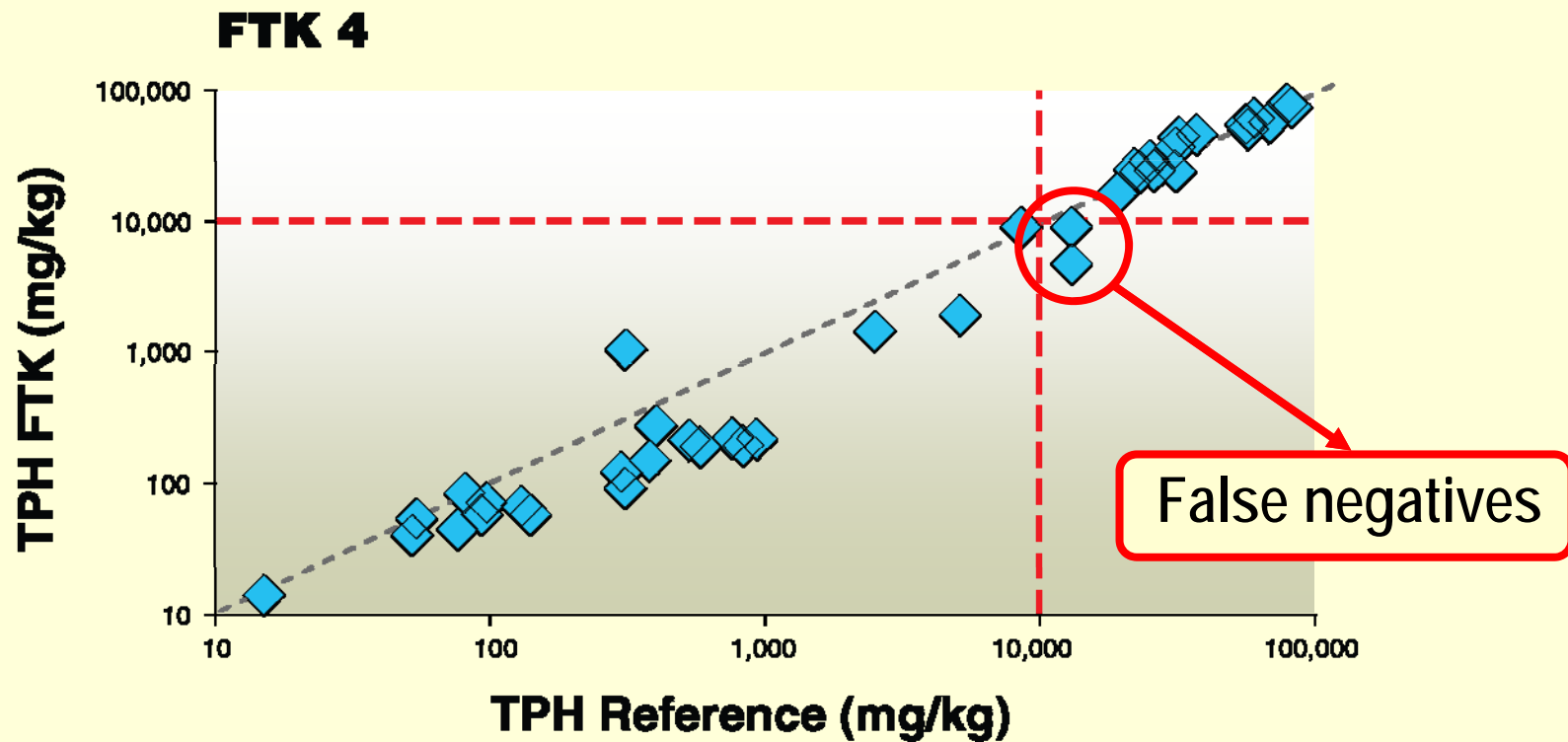


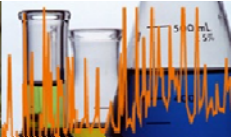
Comparison of FTK Results to Reference



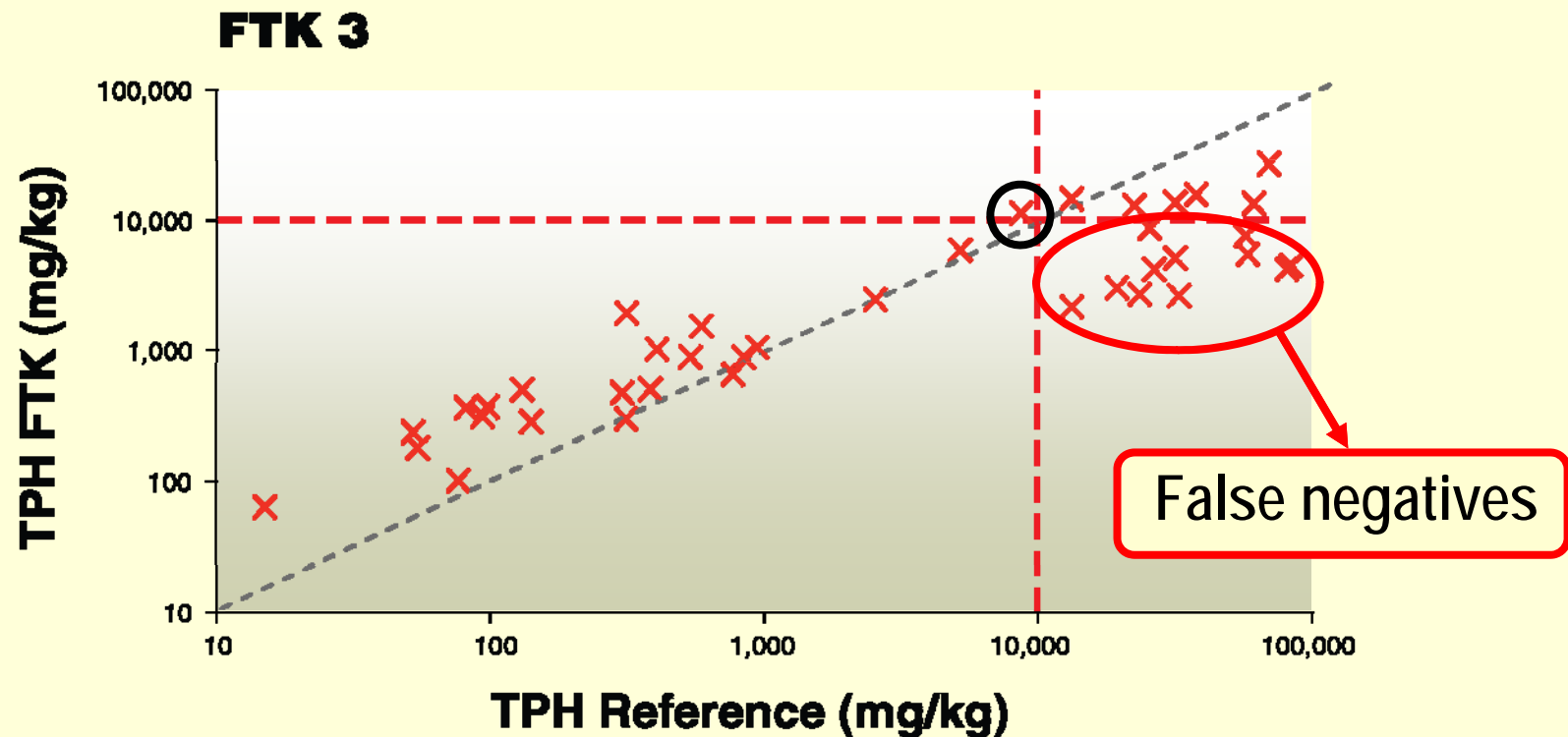


Decisions with FTKs: FTK Data without “Field Calibration”



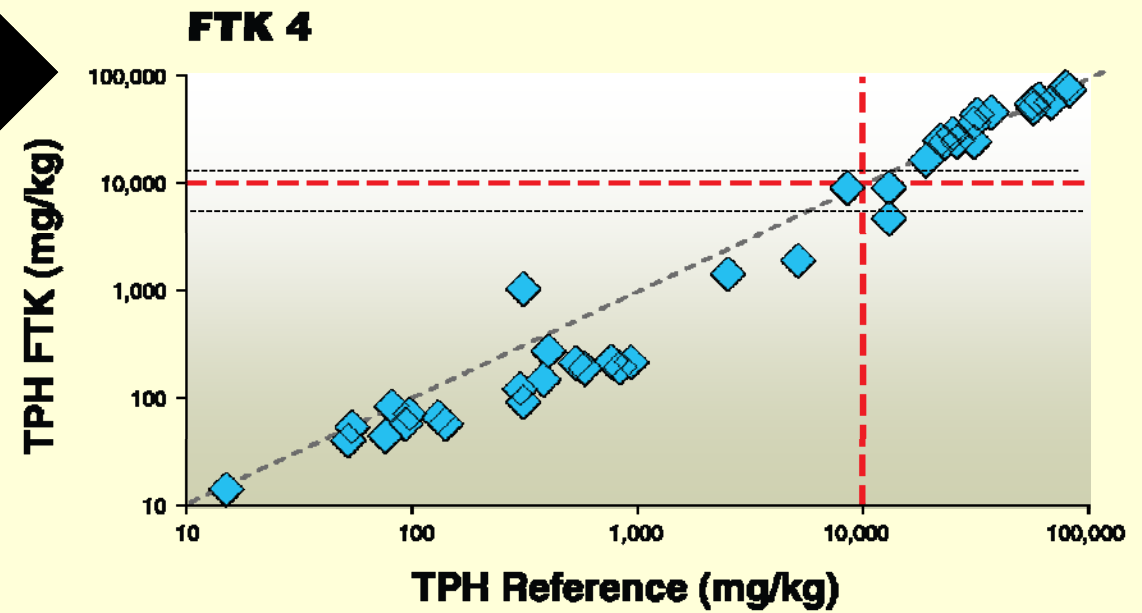
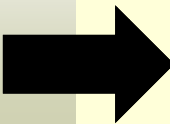
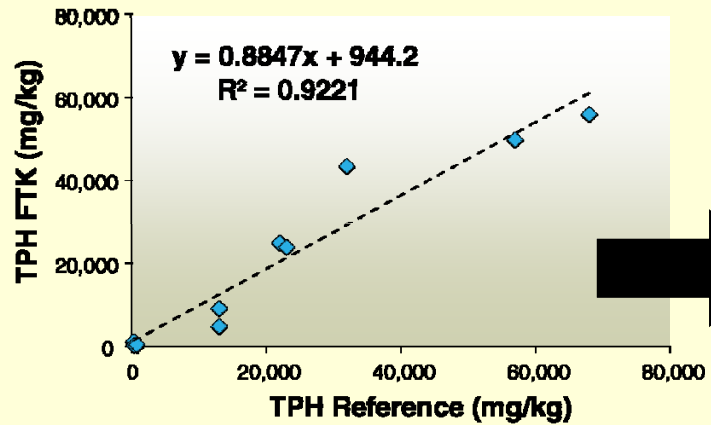


Decisions with FTKs: FTK Data without “Field Calibration” *(continued)*



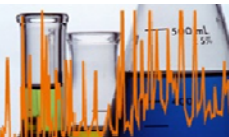


Field Calibration and Uncertainty Interval Around the Remedial Goal



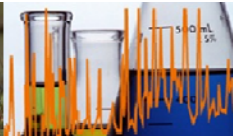
“Field calibration” – Determine the FTK result that corresponds to the cleanup goal using the 15 randomly selected samples

Select uncertainty interval of $\pm 50\%$ of the cleanup goal



Summary of FTK Performance—1,000 mg/kg Cleanup Goal

FTK	Raw FTK Result	Field Calibrated Result	Field Calibrated with Uncertainty Interval	
	False Decisions (%)	False Decisions (%)	False Decisions (%)	Uncertain (%)
FTK 1	30	13	13	5
FTK 2	15	15	13	3
FTK 3	10	8	5	10
FTK 4	3	3	3	0
FTK 5	5	5	5	5



Summary of FTK Performance—10,000 mg/kg Cleanup Goal

FTK	Raw FTK Result	Field Calibrated Result	Field Calibrated with Uncertainty Interval	
	False Decisions (%)	False Decisions (%)	False Decisions (%)	Uncertain (%)
FTK 1	43	13	0	18
FTK 2	35	15	13	8
FTK 3	30	15	13	13
FTK 4	5	5	3	5
FTK 5	43*	5	0	13



Summary of FTK Performance—Uncertainty Interval as a Comparison Tool

FTK	Uncertainty Interval for 5% False Decisions (%)	
	1,000 mg/kg	10,000 mg/kg
FTK 1	250	29
FTK 2	375	150
FTK 3	10	80
FTK 4	0	5
FTK 5	0	10

Results based on the initial field calibration with 15 randomly selected samples.

KEY FINDINGS





Key Findings

- **Results were highly variable; FTK 4 was an exception at this site**
 - Presumably more suitable solvent (hexane) and detection method for weathered crude (IR)
- **Limited FTKs for weathered crude**
 - For most FTKs, response was lower than that of the reference
- **Site-specific conditions and the selected FTK influence the performance**
 - Field calibration or at least a field verification is recommended
- **Use of FTKs tied to Decision Quality Objectives**
 - Users need to determine what is the acceptable rate for false decisions

THANK YOU!

