



Focus on Total Petroleum Hydrocarbon

Latest Trends & Impacts on Remediation



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Overview



Why do we care about TPH?



What is TPH?



Trends



Implications in site investigation and remediation

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Why Do We Care About TPH?



Approaches to petroleum cleanup inconsistent



Historically focused on target constituents

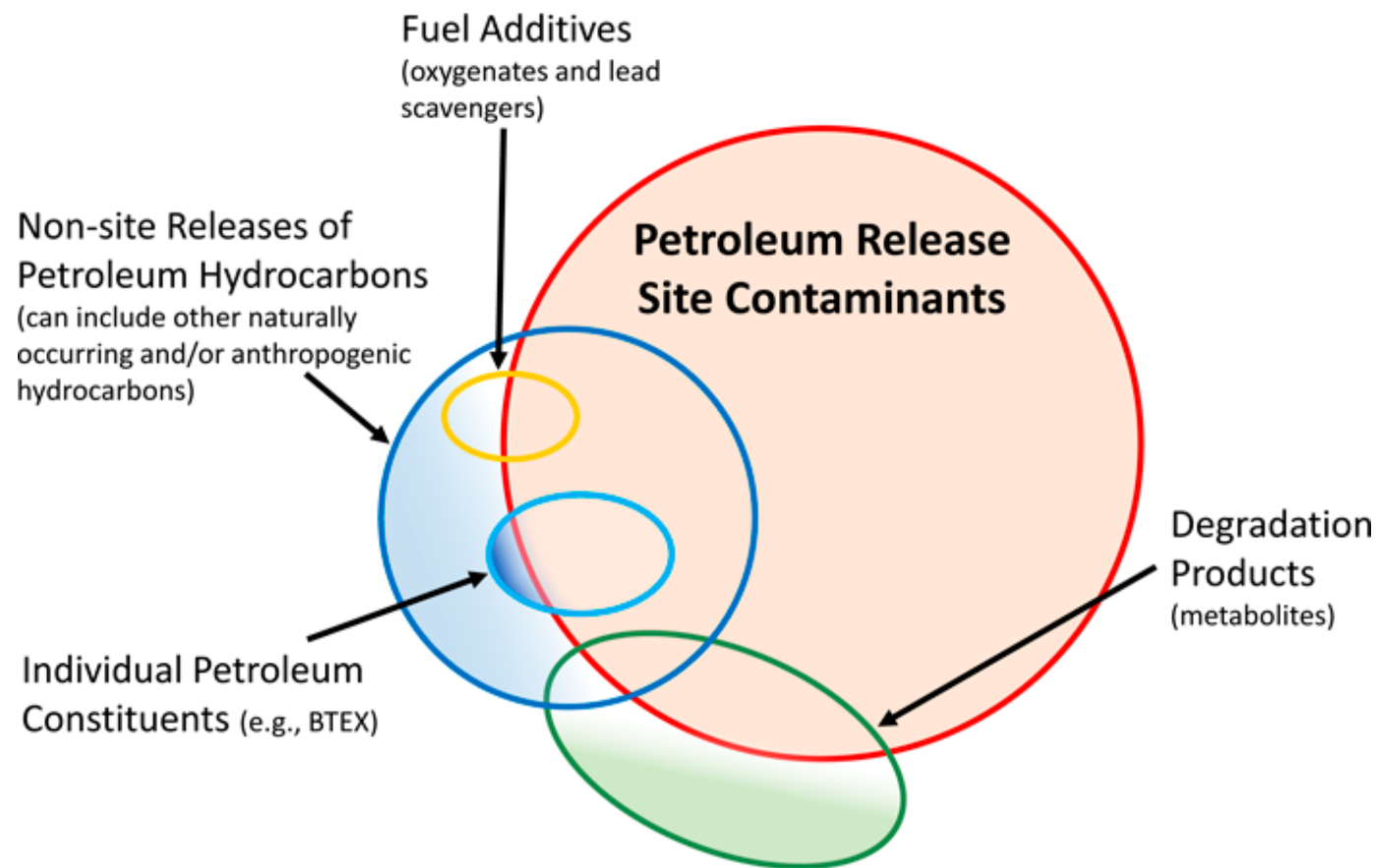
BTEX
PAHs
Fuel additives?



But does that adequately address all potential risks at a site?

Do Target Compounds Tell the Whole Risk Story?

Contaminants at Petroleum Release Sites



ITRC TPHRisk-1 Figure 2-2

What is TPH?

TPH in environmental media is a measurement that is:

Defined by the analytical method used to measure it

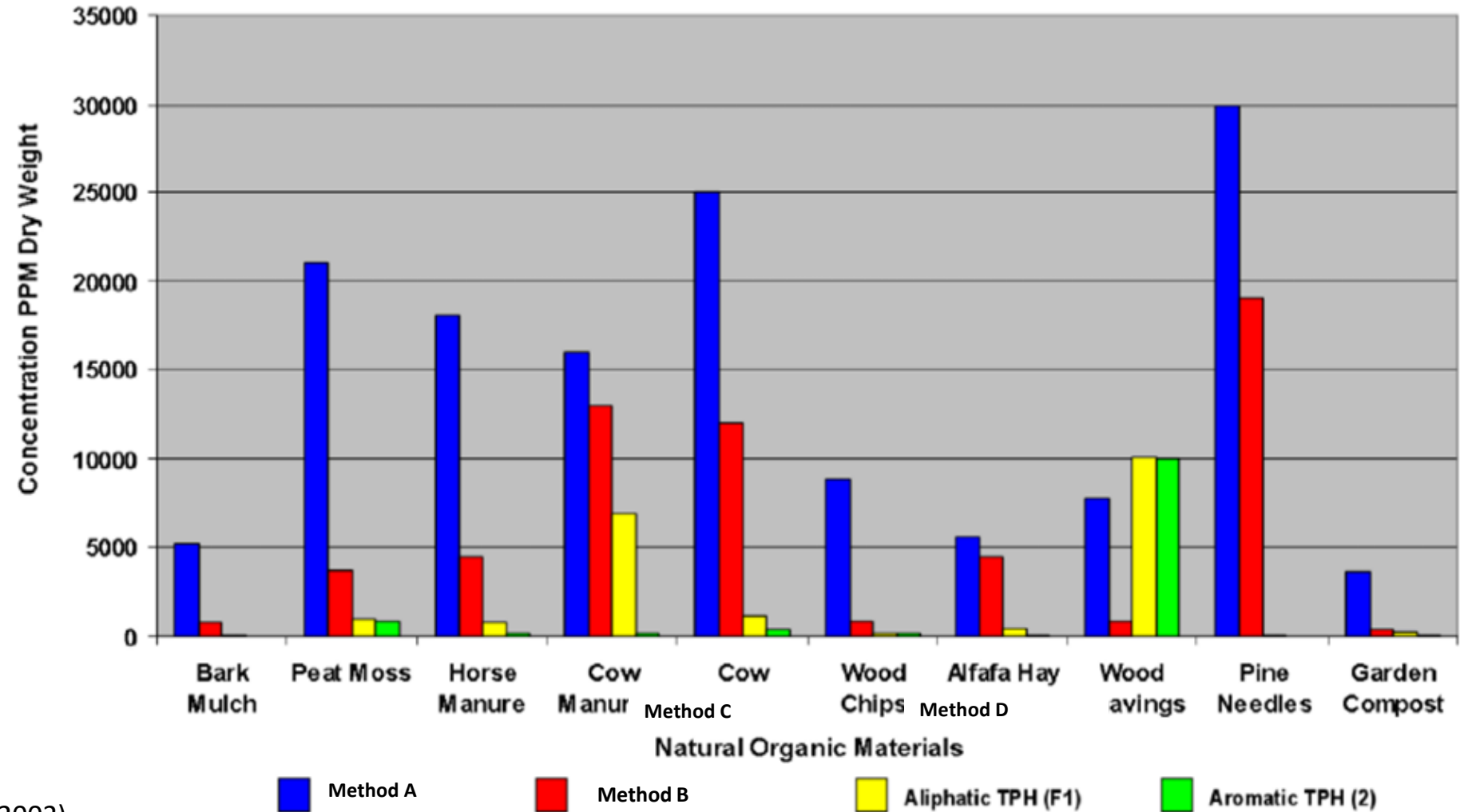
Provides an approximate concentration of the total organic compounds in a complex mixture



Not necessarily “total”, not necessarily all from petroleum and not necessarily all hydrocarbons

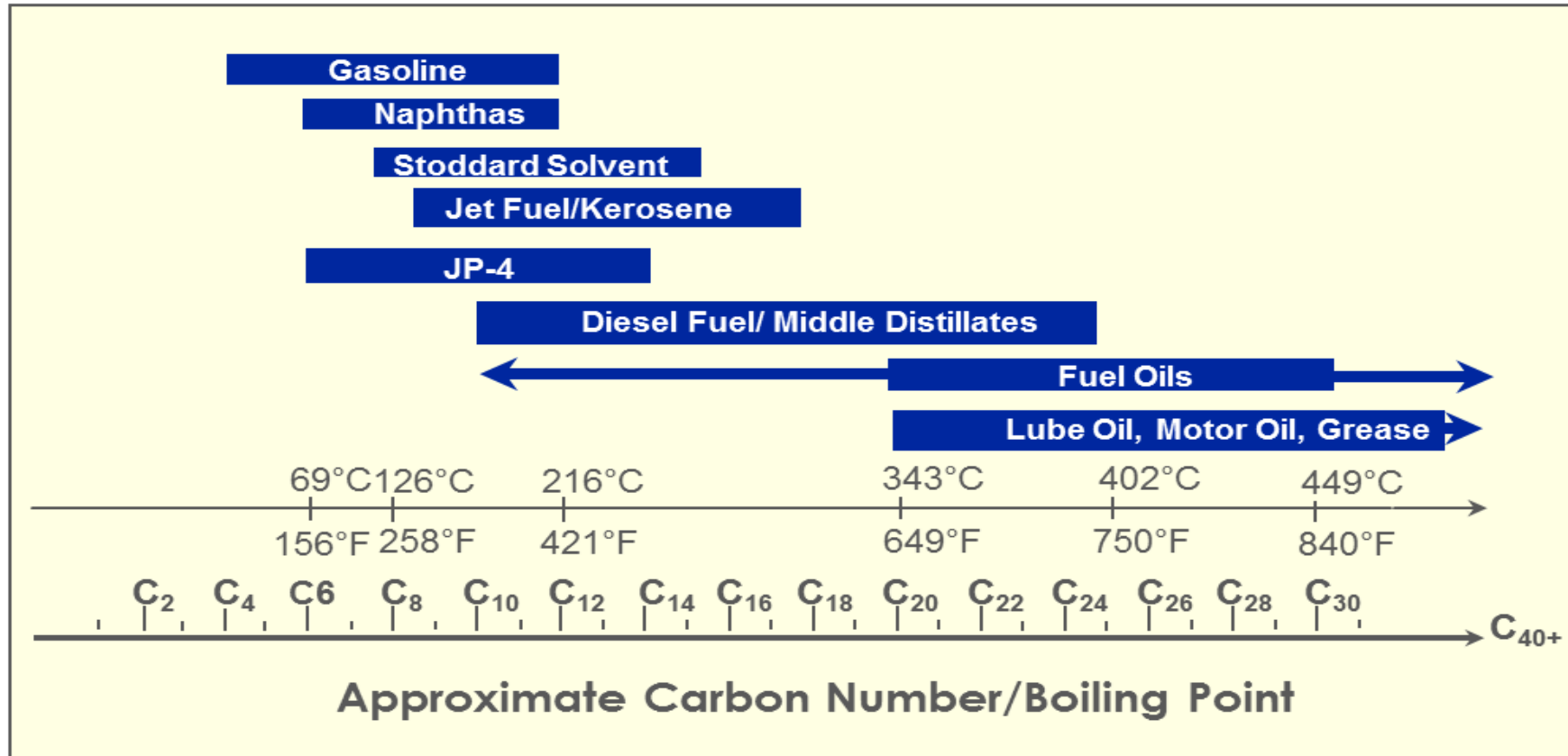
What Does “Defined by the Method” Mean?”

- ▶ Four TPH methods will yield four different results
- ▶ And will measure “TPH” for non-petroleum hydrocarbons!



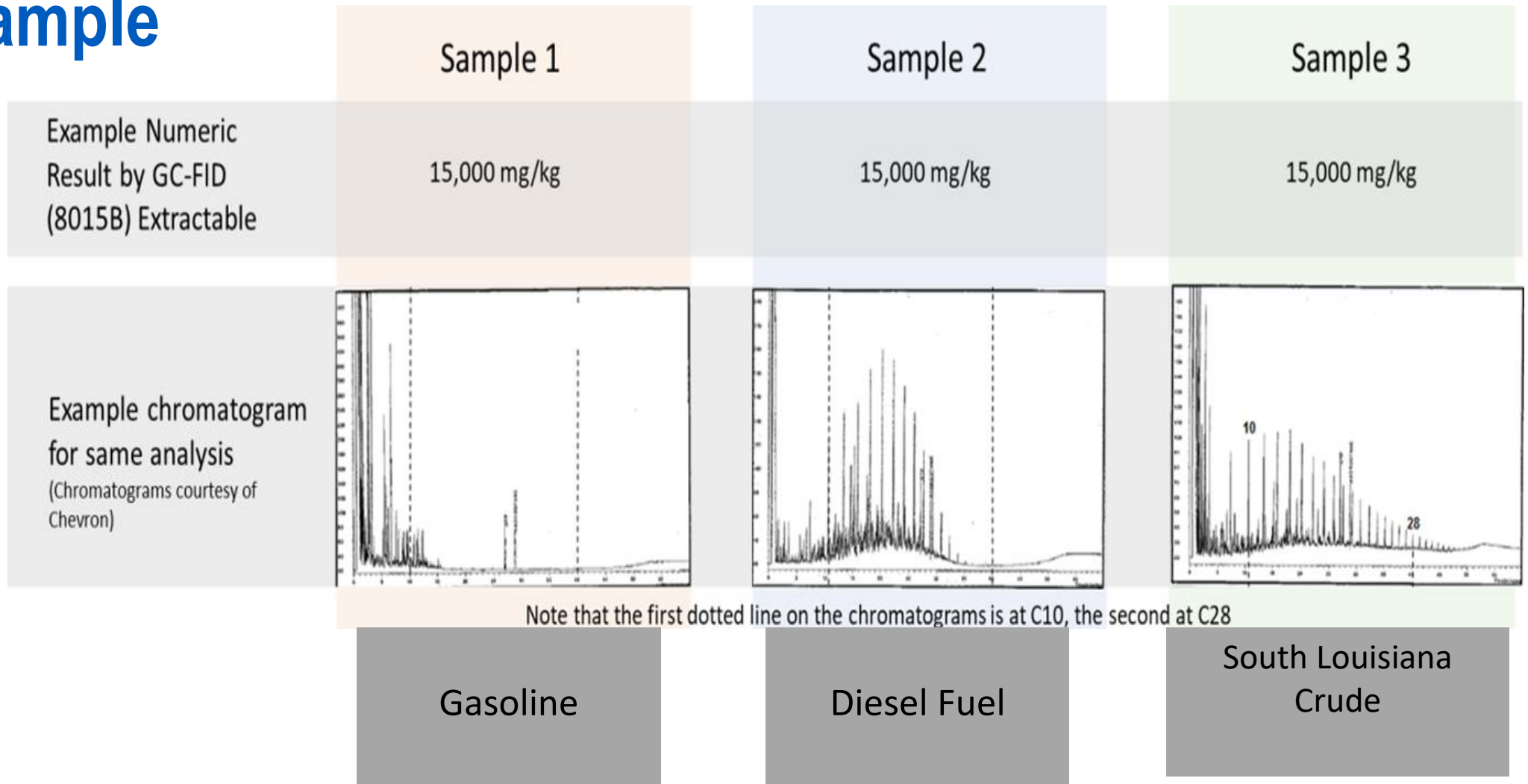
ITRC TPHRisk-1 Figure 5-3 (NewFields. 2002)

Is TPH Analysis Product Specific?



Bulk TPH Analysis is not composition specific.
Products overlap in carbon ranges.

TPH Example



X- AXIS: Elution Time/Carbon Number
Y AXIS: Relative Concentration

ITRC TPHRisk-1 Figure 2-3



TPH Evaluation - Challenges

- ▶ Interpreting analytical data
- ▶ Composition changes with time and space due to weathering, influenced by site-specific conditions
- ▶ Different chemicals have different fate and transport characteristics
- ▶ Impractical to analyze for hundreds of individual compounds
- ▶ Limited toxicity data

**These challenges lead to target compound approach...
but we know more now**



Trends

Trend # 1 – Fraction Analysis

- ▶ Not a new approach, but gaining more widespread application
- ▶ Breaks TPH into smaller “pieces” that are grouped by similar fate/transport and toxicity characteristics
 - Aliphatic and aromatic groups
 - Carbon chain lengths (ex., C5-C8, C8-C16, etc)
- ▶ Analytical methods are hydrocarbon-specific
- ▶ Currently most accurate means of assessing TPH risk

Example TPH Fractions: TPH Criteria Working Group vs. EPA

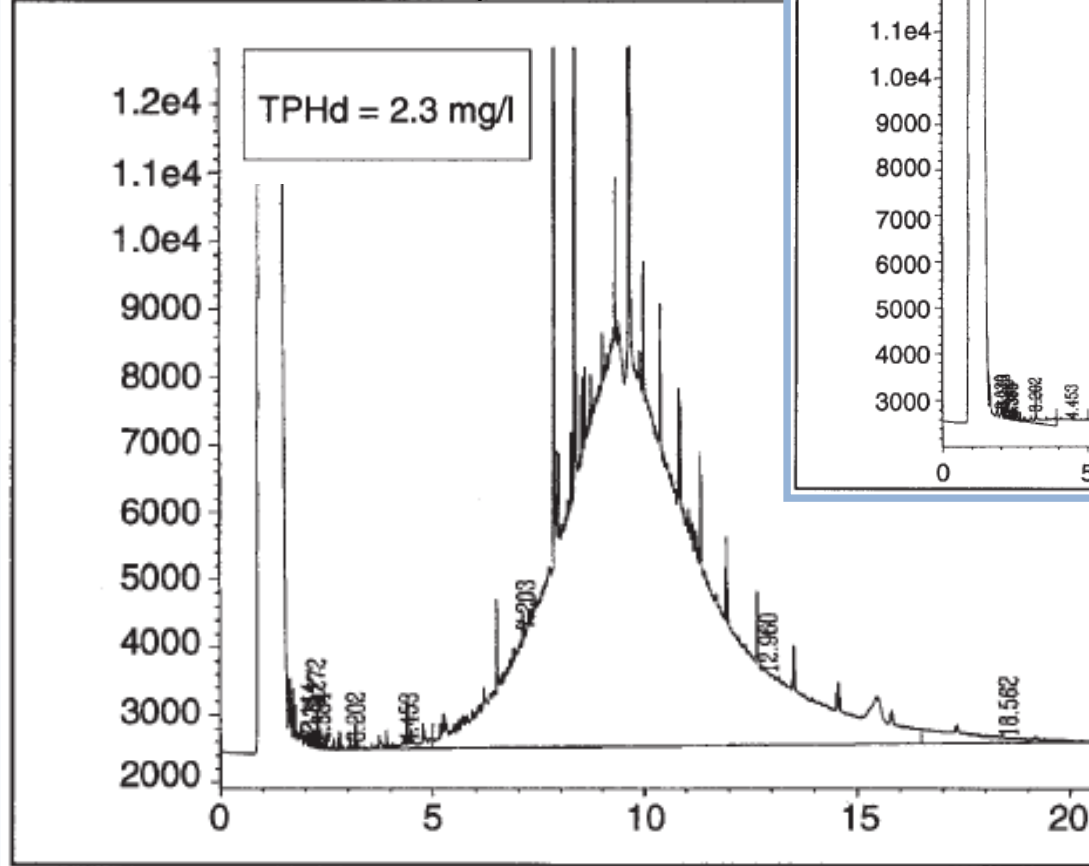
Molecular Structure	Aliphatic		Aromatic				TPH Criteria Working Group 13 Transport Fractions	
	EC5-6	EC6-8	EC8-10	EC10-12	EC12-16	EC16-21		EC21-35 (same properties as EC16-21) -- not considered a transport fraction--
	EC5-7 Benzene	EC7-8 Toluene	EC8-10	EC10-12	EC12-16	EC16-21	EC21-35	
Increasing Equivalent Carbon (EC) Number								

Molecular Structure	Aliphatic		Aromatic				EPA 6 Toxicity Fractions
	EC5-8 <i>Low</i>		EC8-16 <i>Medium</i>			EC16-35 <i>High</i>	
	EC6-9 <i>Low</i>			EC9-22 <i>Medium</i>		EC22-35 <i>High</i>	
Increasing Equivalent Carbon (EC) Number							

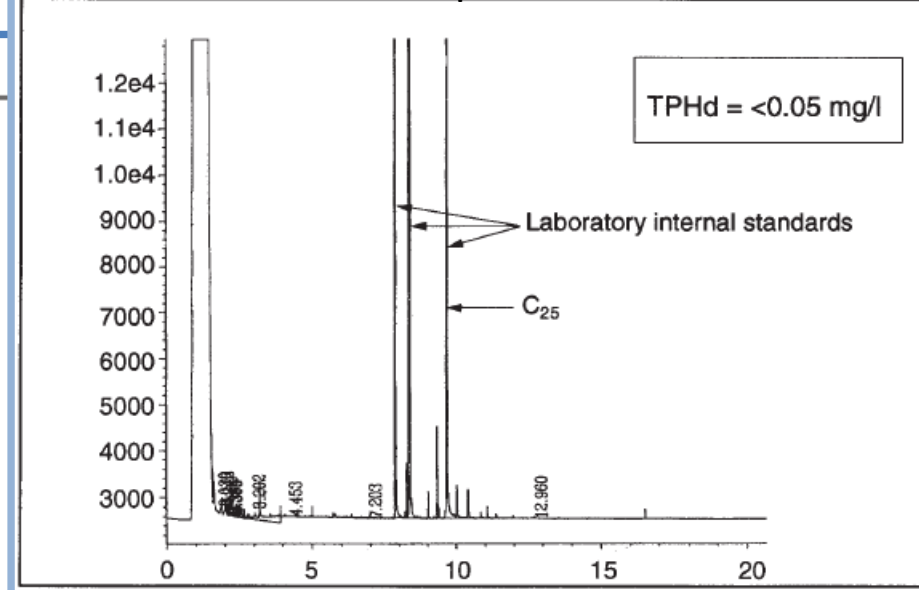
Trend #2 – Silica Gel Cleanup

- ▶ Removes non-hydrocarbons
- ▶ Can be added to bulk TPH methods
- ▶ Integrated into fraction methods
- ▶ Not to be used with volatile/air samples

Before Silica Gel Cleanup



After Silica Gel Cleanup

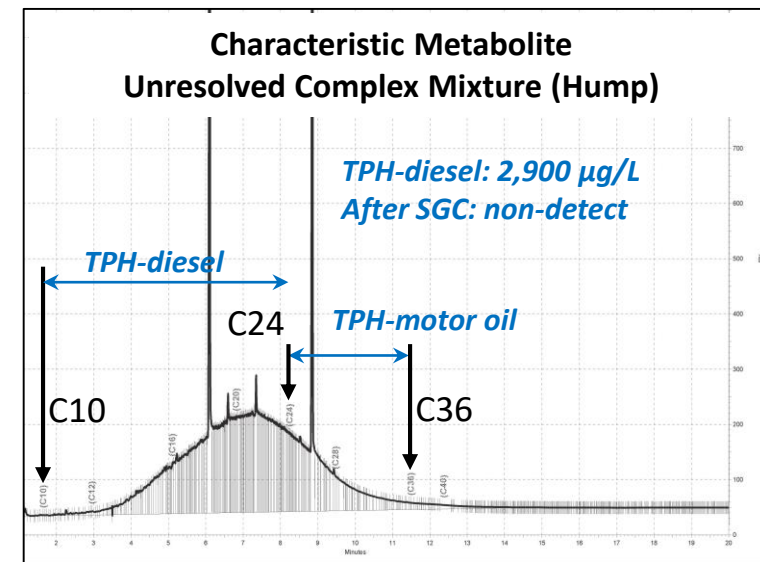


Trend #3 – Petroleum Metabolites

- ▶ Are intermediate biodegradation products
- ▶ Molecules include oxygen and have properties different from hydrocarbons (e.g., polar)
- ▶ Commonly detected as extractable TPH when silica gel cleanup (SGC) not used. Identify using:
 - Chromatogram pattern
 - Analysis with and without SGC
 - Solubility
 - Conceptual site model

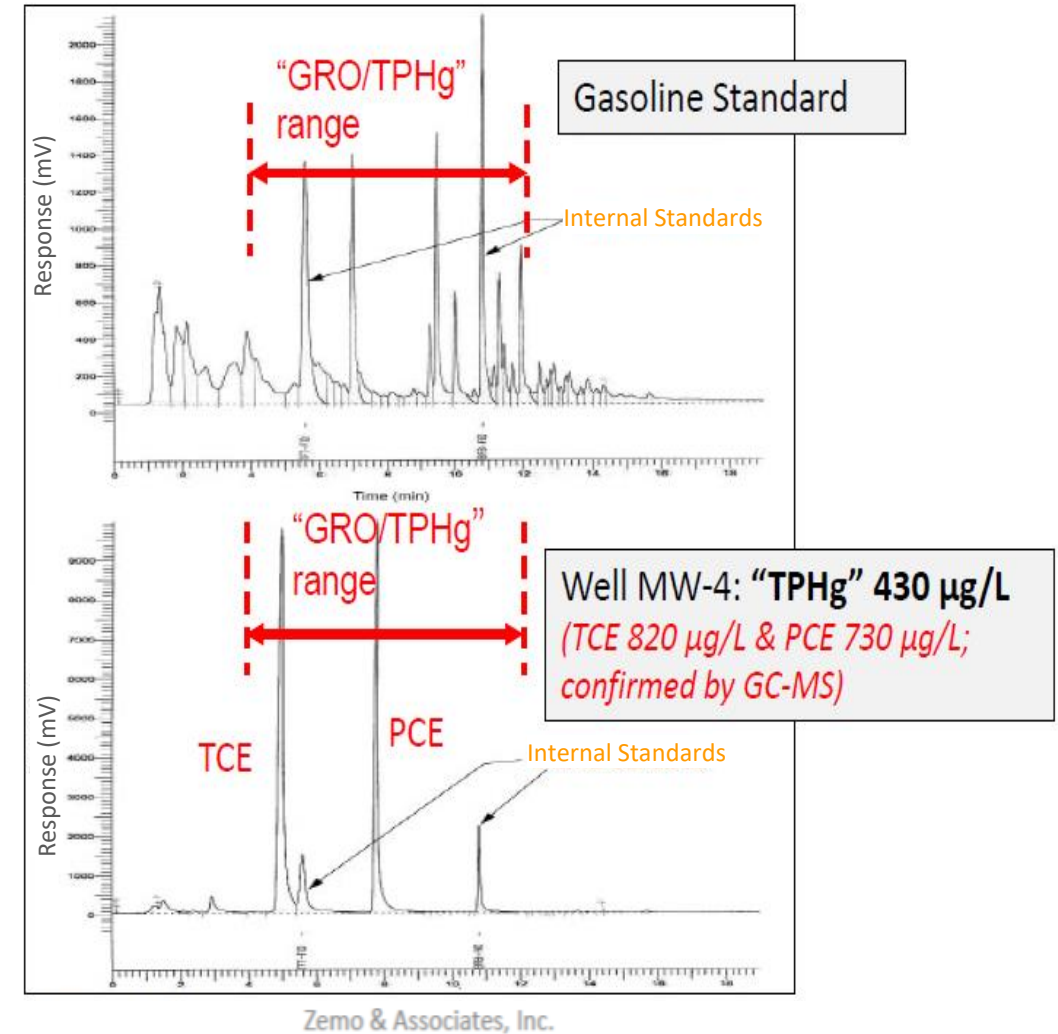
Solubility of n-Hexane vs. Two n-Hexane Metabolites

Chemical	Formula	Boiling Point (°C)	Solubility (µg/L)
n-Hexane	C ₆ H ₁₄	69	9.5E+03
2-Hexanone	C ₆ H ₁₂ O ₁	128	7.7E+06
Hexanoic Acid	C ₆ H ₁₂ O ₂	205	5.8E+06



Trend #4 – Chromatograms Aren't Just Pretty Pictures

- Provide information on
 - Type of material
 - Presence of non-hydrocarbons
 - Presence of solvents
 - Presence of non-dissolved hydrocarbons
 - Weathering



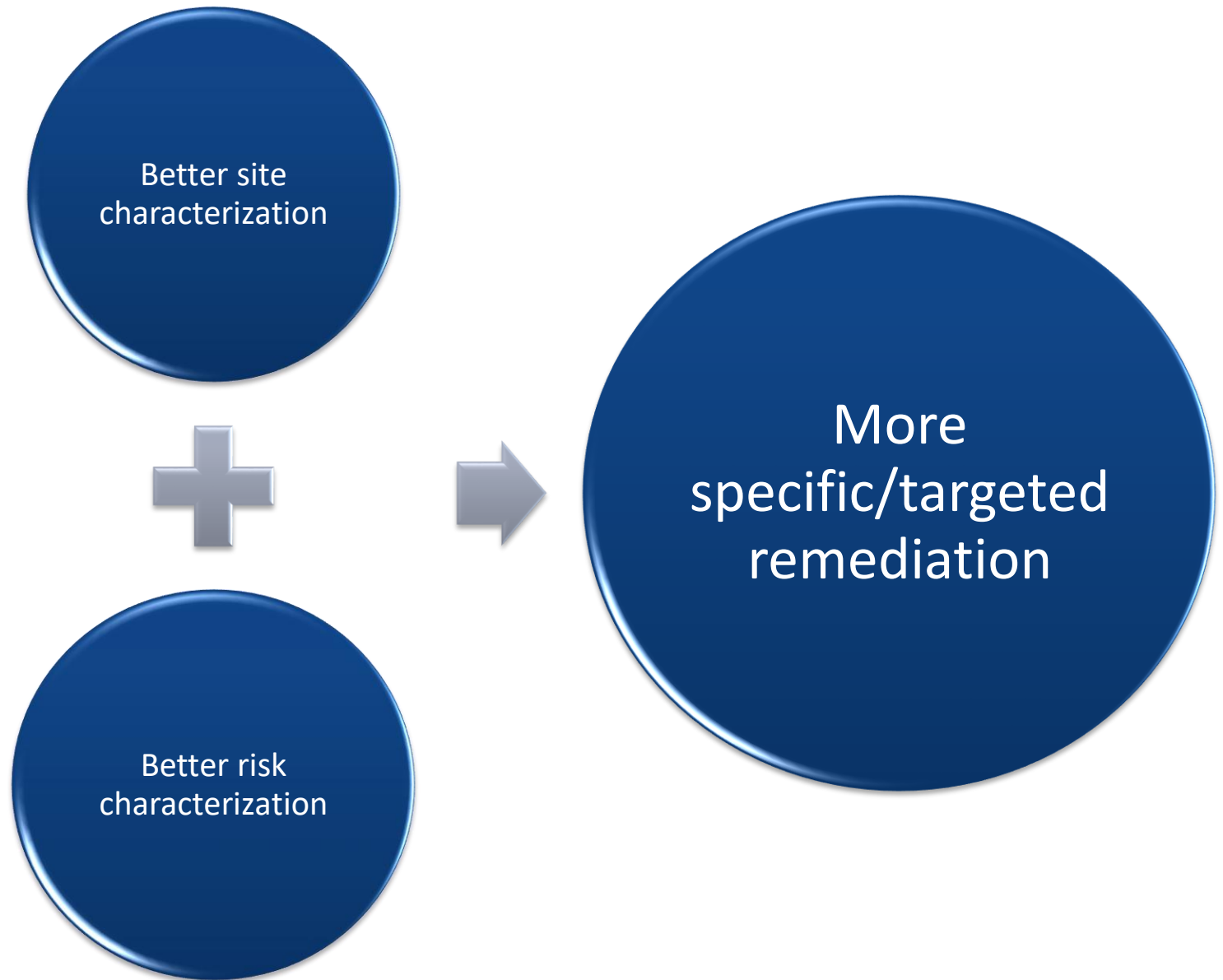
ITRC TPHRisk-1 Figure A5-0

Implications

How Does This Affect Site Investigations?



How Does This Affect Remediation?



Questions?

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CREATE AMAZING.