

Starting Soon: TPH Risk Evaluation at Petroleum-Contaminated Sites

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TPH Risk Evaluation at Petroleum- Contaminated Sites



Prepared by
The Interstate Technology & Regulatory Council
TPH Risk Evaluation Team

Sponsored by: Interstate Technology and Regulatory Council (www.itrcweb.org)

Hosted by: US EPA Clean Up Information Network (www.cluin.org)

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ECOS

▶ Network

- State regulators
 - All 50 states, PR, DC
- Federal partners



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- ITRC Industry Affiliates Program



- Academia
- Community stakeholders

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Read trainer bios at
<https://clu-in.org/conf/itrc/TPHrisk/>

TPH Risk Evaluation at Petroleum-Contaminated Sites (TPHRisk-1, 2018)



Search this website ...

Navigating this Website

1 Overview

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TPH Risk Evaluation at Petroleum-Contaminated Sites

HOME



Welcome

TPH Risk Evaluation at Petroleum-Contaminated Sites (TPHRisk-1)

1 Overview

The Interstate Technology and Regulatory Council (ITRC) **Total Petroleum Hydrocarbons (TPH)** Risk Evaluation team has developed this guidance to assist state regulators and practitioners with evaluating risk and establishing cleanup requirements at **petroleum** release sites. This guidance focuses on factors that are unique to petroleum hydrocarbon releases and builds on other available documents published by the TPH Criteria Working Group (TPHCWG) ([1997a](#), [1997b](#), [1997c](#), [1998a](#), [1998b](#), [1999](#)), ITRC Risk-3 ([2015](#)), Massachusetts Department of Environmental Protection (MADEP) ([2014](#)), California State Water Board–San Francisco Bay Region (CASWB-SFBR) ([2016a](#)), and Texas Commission on Environmental Quality (TCEQ) ([2017b](#)).

Road Map



- ▶ Why the Guidance?
- ▶ Learn What TPH is
- ▶ Learn TPH Analytical Methods
- ▶ Questions and Answers
- ▶ Environmental Fate of TPH
- ▶ Assessing Human and Ecological Risk from TPH
- ▶ Stakeholders Considerations
- ▶ Closing
- ▶ Questions and Answers

Why This Guidance?



► Purpose

- Facilitate better-informed decisions relating to the evaluation of TPH risk at petroleum-contaminated sites, help regulators and project managers, who may not be skilled in risk assessment, interpret results

► Goal

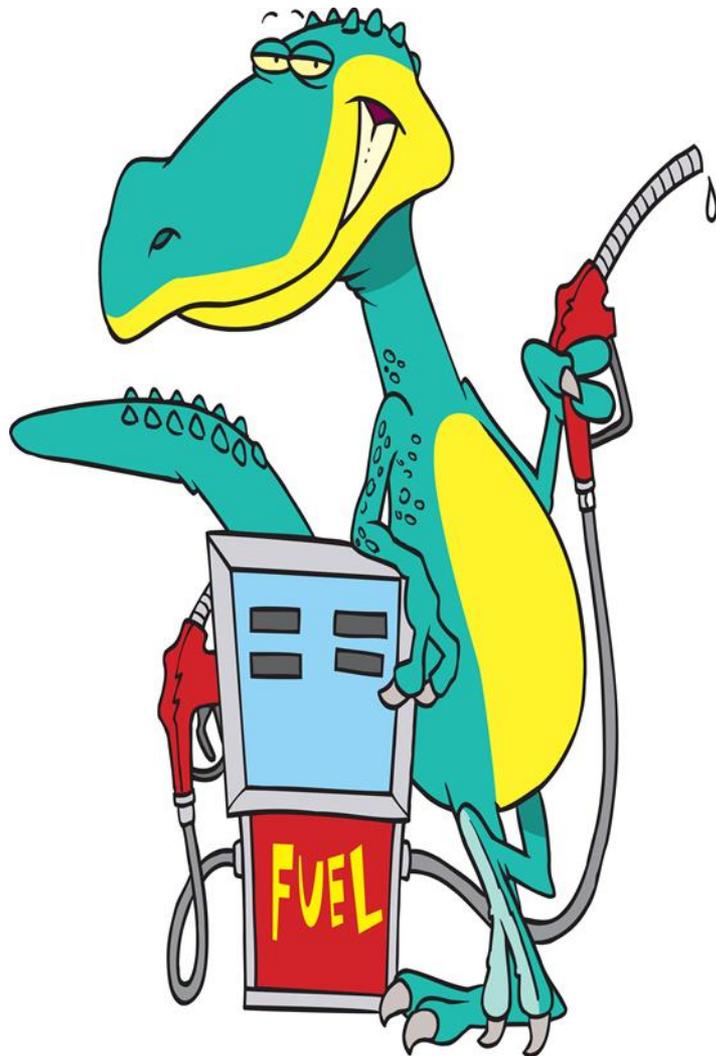
- Create better TPH guidance to help states develop consistent methodology for establishing risk-based cleanup levels and for establishing methods for risk-based corrective actions

Learning Objectives



- ▶ After participating in this ITRC training course you will:
 - Recognize the ITRC document as a go-to resource for evaluating TPH risk at petroleum-contaminated sites
 - Recognize how TPH can change over time
 - Select appropriate analytical method(s) to match site objectives
 - Apply the decision process to determine when a site-specific target level may be more appropriate than a generic screening level for TPH

Regulatory Framework for TPH



Clipart
Of
LLC®

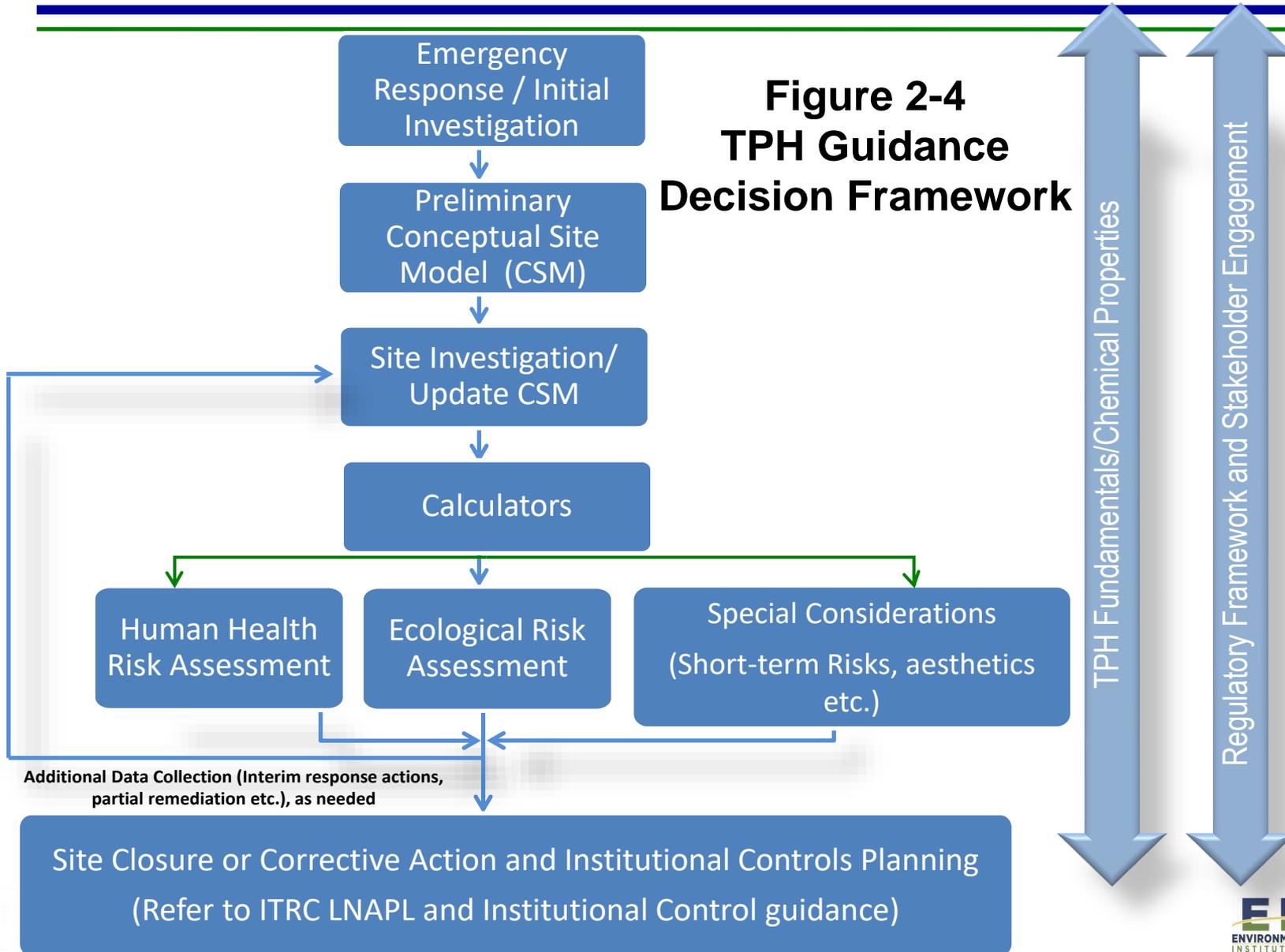
- ▶ Remedial Approaches & Risk Management
 - are not consistent;
 - may not address long- and short-term concerns with petroleum contaminant mass;
 - petroleum cleanups were based on laboratory concentrations to non-detect; and
 - the States Survey (Appendix C) shows a trend to a risk-based approach.
- ▶ Federal & State TPH Regulations
 - challenges
- ▶ State Underground Storage Tank Program Contacts:
 - <https://www.epa.gov/ust/underground-storage-tank-ust-contacts#states>

Benefits to the Audience



- ▶ Provides practical, applicable guidance on evaluating TPH for risk assessors
 - Regulators
 - Consultants
 - Industry
 - Stakeholders

How to Use This Document



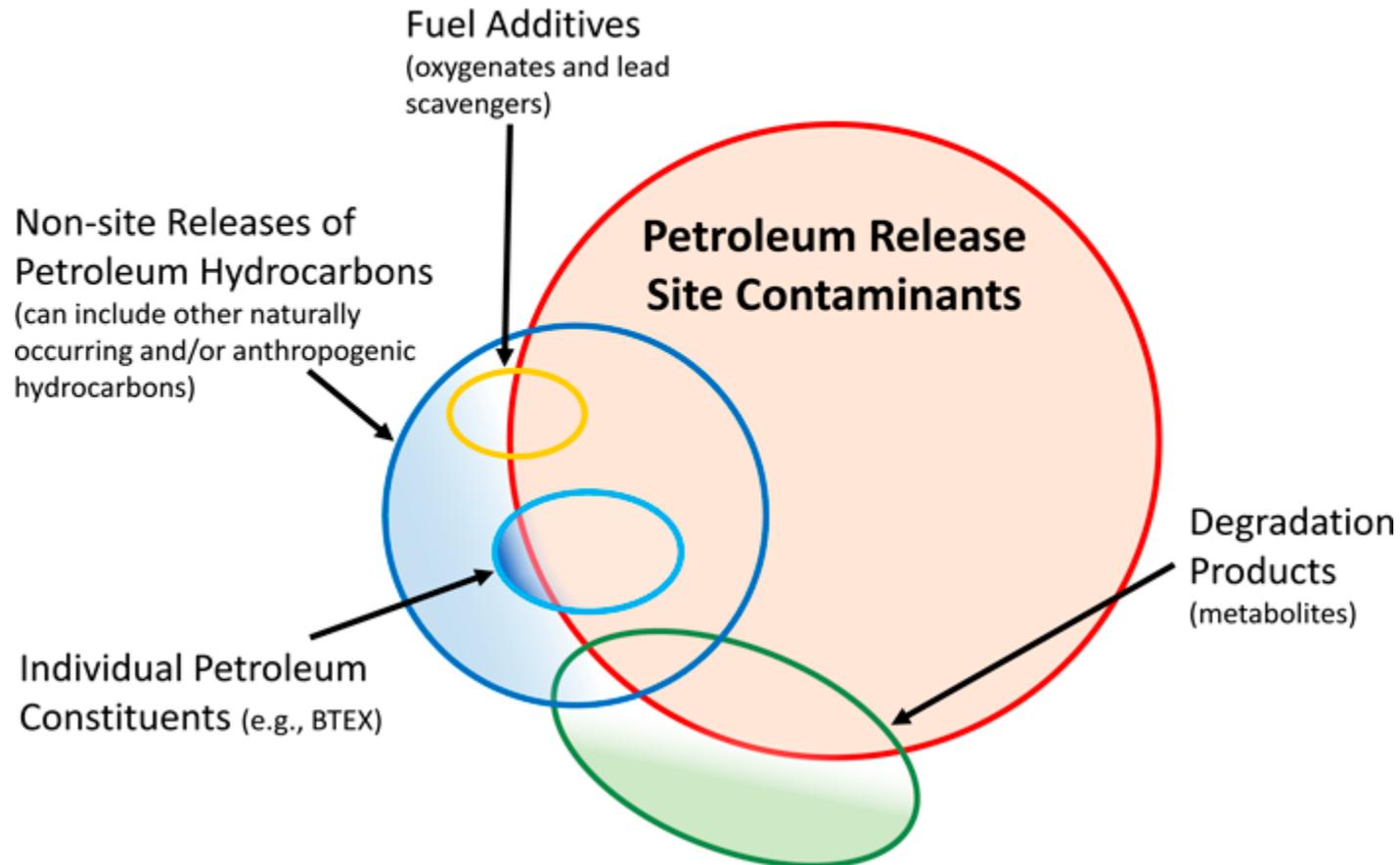
Case Study: Tank Farm



- ▶ **Site Status:** Inactive, Commercial Redevelopment
- ▶ **Petroleum Release Type:** Gasoline & Diesel
- ▶ **Impacted Media:** Soil, Soil Vapor, & Groundwater

How will YOU treat TPH Differently?

Contaminants at Petroleum Release Sites



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Learn What TPH is

GRO DRO EPH PRO
ETPH PVOC Gx STARS
VPH Dx NWTPH
Ran out of Space!

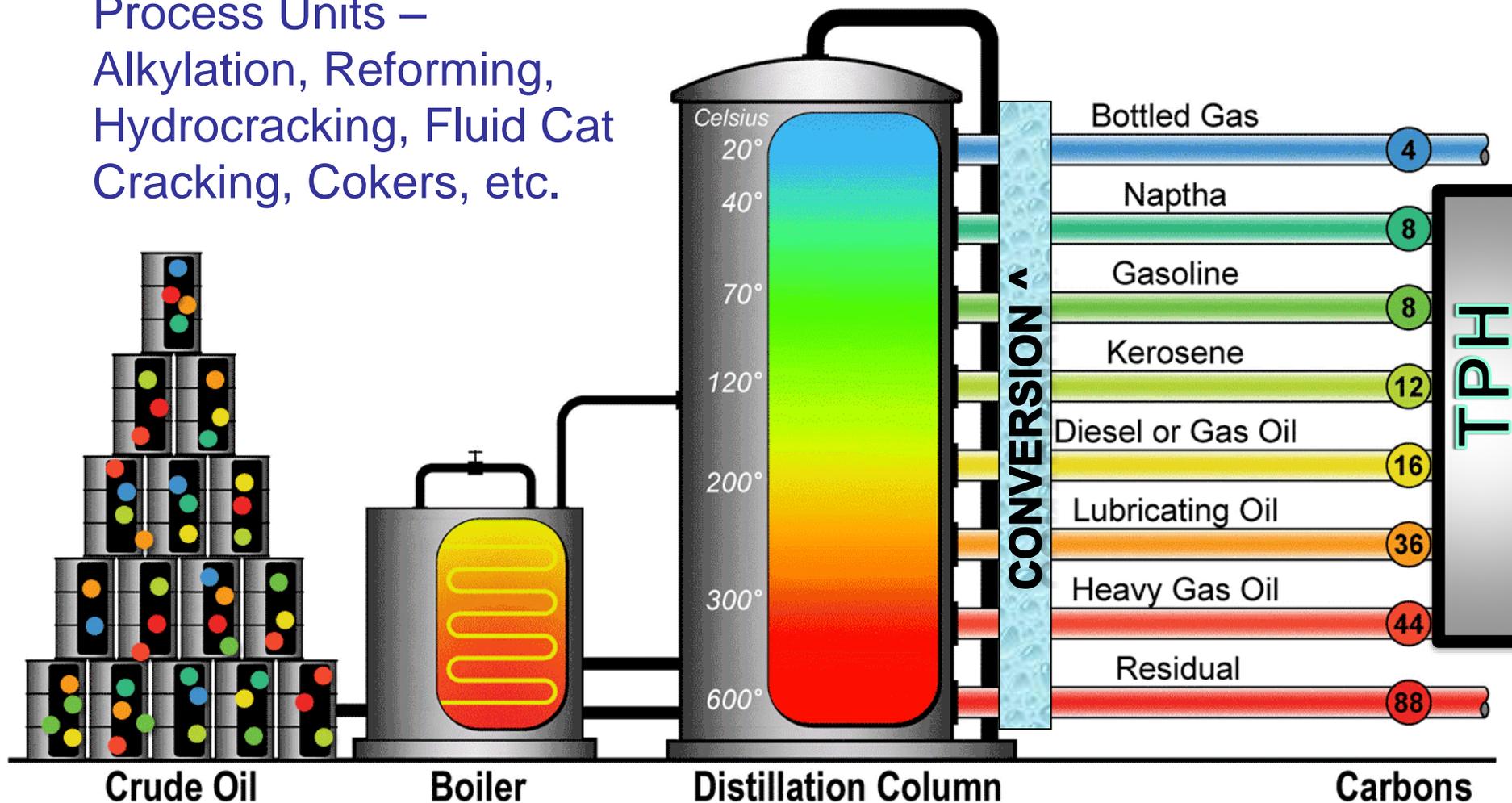
**Let's untangle these
terms!**

Learning Objectives – Learn What TPH is

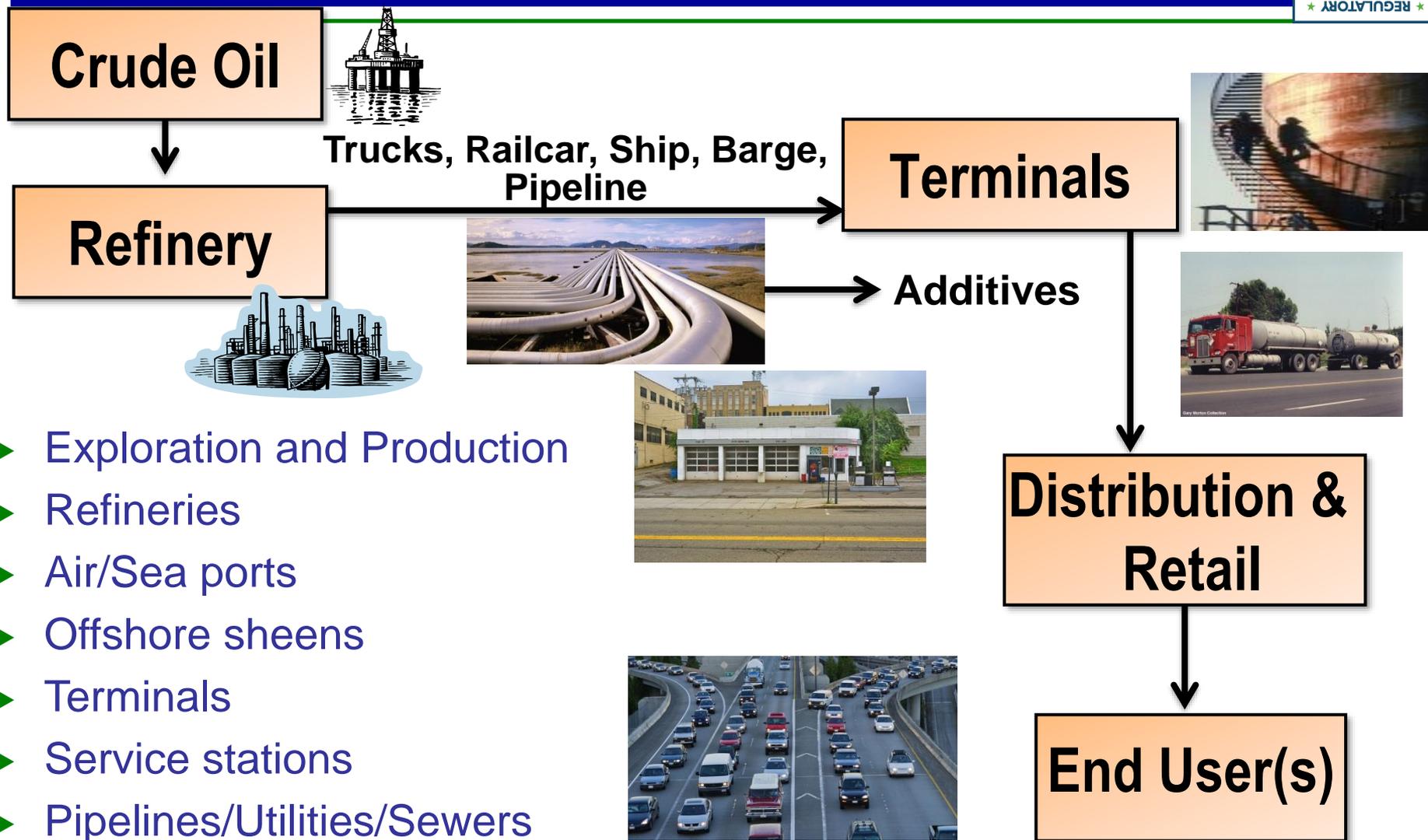
- ▶ Know TPH sources and releases
- ▶ Identify TPH constituents and properties
- ▶ Understand bulk TPH and challenges
- ▶ Provide considerations for TPH - specific CSM using the case study
- ▶ Be familiar with common pitfalls with CSM development

TPH – Where does it come from?

Process Units –
Alkylation, Reforming,
Hydrocracking, Fluid Cat
Cracking, Cokers, etc.



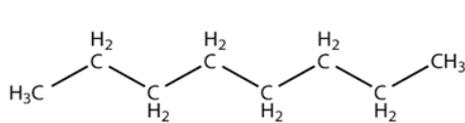
TPH – Where does it come from?



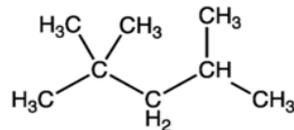
- ▶ Exploration and Production
- ▶ Refineries
- ▶ Air/Sea ports
- ▶ Offshore sheens
- ▶ Terminals
- ▶ Service stations
- ▶ Pipelines/Utilities/Sewers
- ▶ Residential (think heating oil)

TPH Constituents – Key Properties

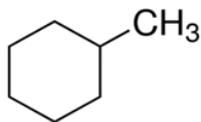
Aliphatic Hydrocarbons



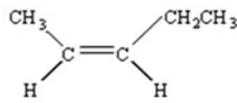
n-paraffins/normal-alkanes



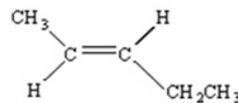
iso-paraffins/i-alkanes



naphthenes/
cycloalkanes



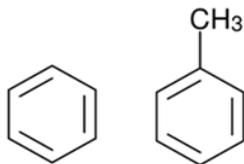
cis-2-pentene



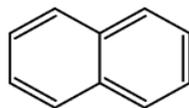
trans-2-pentene

olefins/alkenes
(not in crude)

Aromatic Hydrocarbons



benzenes



polyaromatic hydrocarbons
(PAHs)

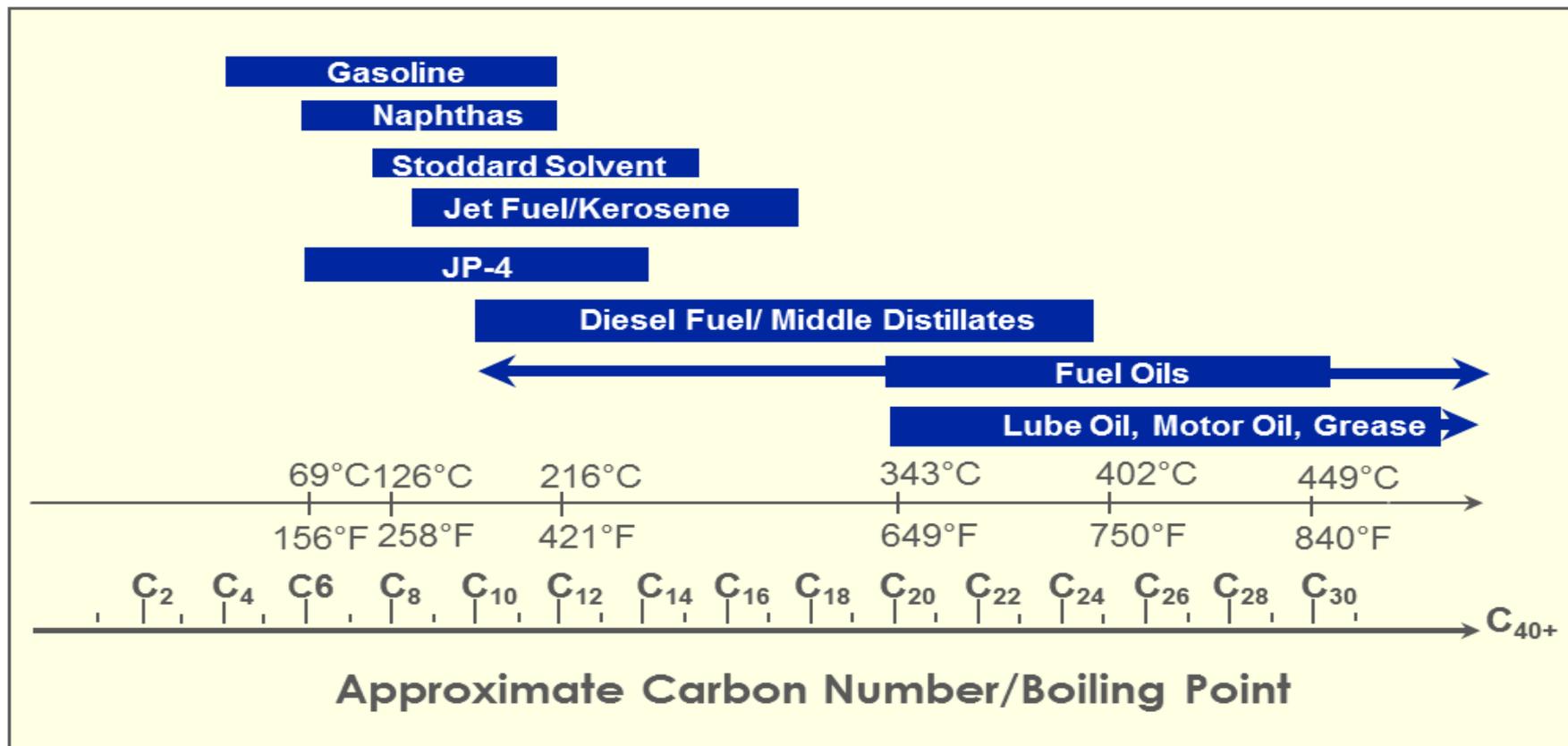
▶ Aliphatic Hydrocarbons:

- Straight, branched and cyclic
- Non-polar
- Low water solubility

▶ Aromatic Hydrocarbons:

- Ring structures
- Some polarity
- Increased solubility in water

What is in that petroleum release?



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

Bulk TPH – What's in that number?

Sample 1

Sample 2

Sample 3

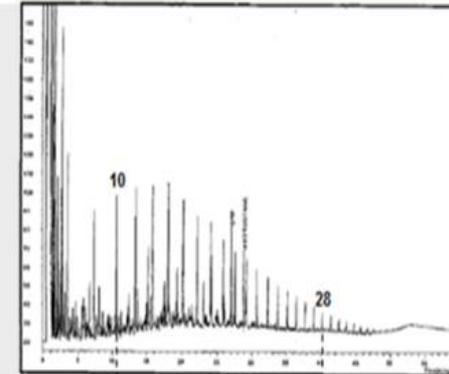
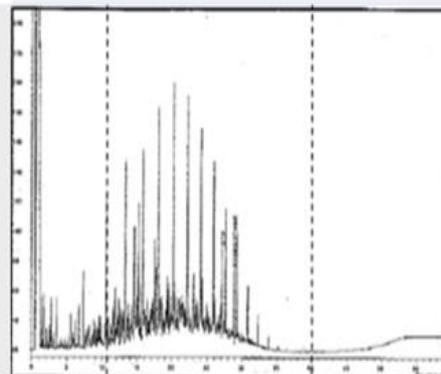
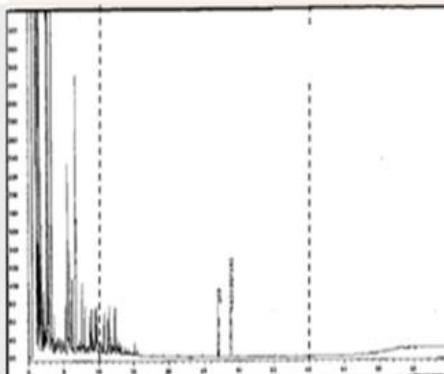
Example Numeric
Result by GC-FID
(8015B) Extractable

15,000 mg/kg

15,000 mg/kg

15,000 mg/kg

Example chromatogram
for same analysis
(Chromatograms courtesy of
Chevron)



Note that the first dotted line on the chromatograms is at C10, the second at C28

Gasoline

Diesel Fuel

South Louisiana
Crude

So 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 hydrocarbons in a complex mixture
 - Provides information about the size and distribution of the hydrocarbons
 - Not necessarily “total”, not necessarily all from petroleum and not necessarily all hydrocarbons

TPH data can only be properly interpreted with a good CSM!

TPH Evaluation - Challenges



- ▶ Composition changes with time and space due to weathering, influenced by site-specific conditions
- ▶ Impractical to analyze for hundreds of individual compounds
- ▶ Limited toxicity data

**Group hydrocarbons with similar characteristics
(e.g., environmental fate, toxicity, etc.)**

Case Study: Tank Farm



Case Study

Common Pitfalls to CSM Development



- ▶ Reliance on BTEX and PAH data for CSM development
- ▶ CSM development allied with human direct exposure only
- ▶ Incorrect consideration for natural degradation data (e.g., consideration for TPH metabolites)
- ▶ Failure to incorporate nature, location and concerns from residual contamination

Poll Question

▶ What is TPH?

1. TPH is defined by the analytical method
2. TPH is an accurate measure of the total hydrocarbons
3. TPH concentration does not include biodegradation products and metabolites
4. None of the above

Road Map



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Learning Objectives – Learn TPH Analytical Methods



- ▶ Select the appropriate TPH Analytical Method based on data quality objectives
- ▶ Properly interpret analytical results
- ▶ Recognize when to question analytical results
- ▶ Recognize uses for field methods

TPH: Method Defined Parameter

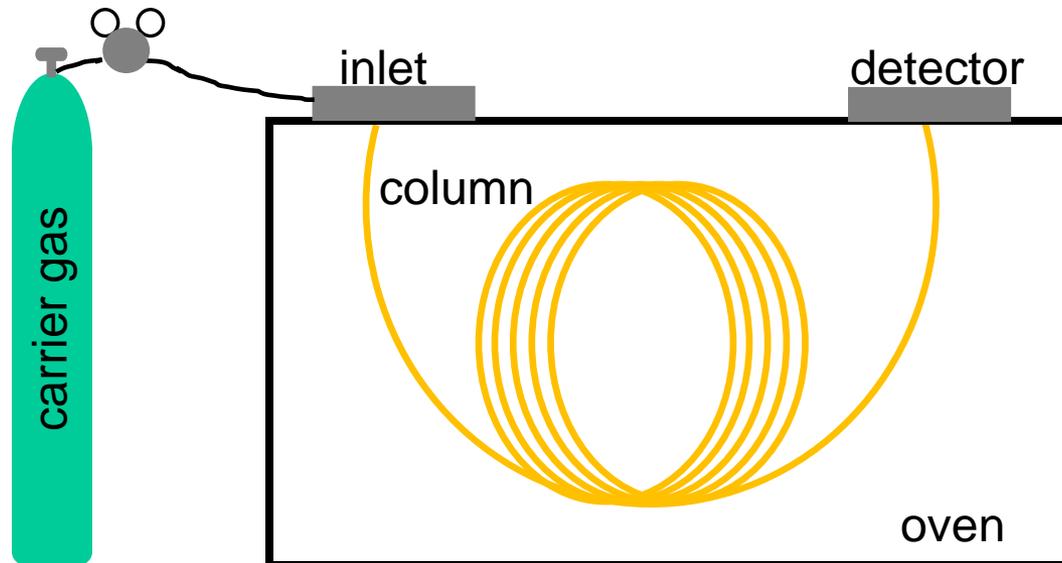


- ▶ Considerations in selecting the analytical method include:
 - Project Objectives
 - Regulatory Requirements
 - Application (detection, delineation, monitoring, risk assessment, etc.)
 - Petroleum type (if known)
 - Media

No method can do everything!

Preferred Laboratory method

- ▶ Laboratory method for TPH analysis: Gas Chromatography
 - For separating mixtures into components
 - Based on volatility of molecules
 - Several options for detectors



Selecting appropriate TPH Lab Methods (Table 5-4)



- ▶ Site Assessment, determination of extent of impacts, total extractable organics
 - EPA Methods 8015 and 8260
 - TX1005
- ▶ Human Health Risk assessment, Ecological Risk assessment, Transport, RSLs, Site Characterization and
 - TCEQ, WA DEP VPH/EPH, WA Dep Ecology
- ▶ Assessment of hydrocarbons only, determination of extent of hydrocarbon impacts
 - EPA Method 3630C with 8015, 8260
 - EPA Method 3630C with TX1005

Talk to the Lab if there are questions!

Silica Gel Cleanup (Fact Sheet A.2)

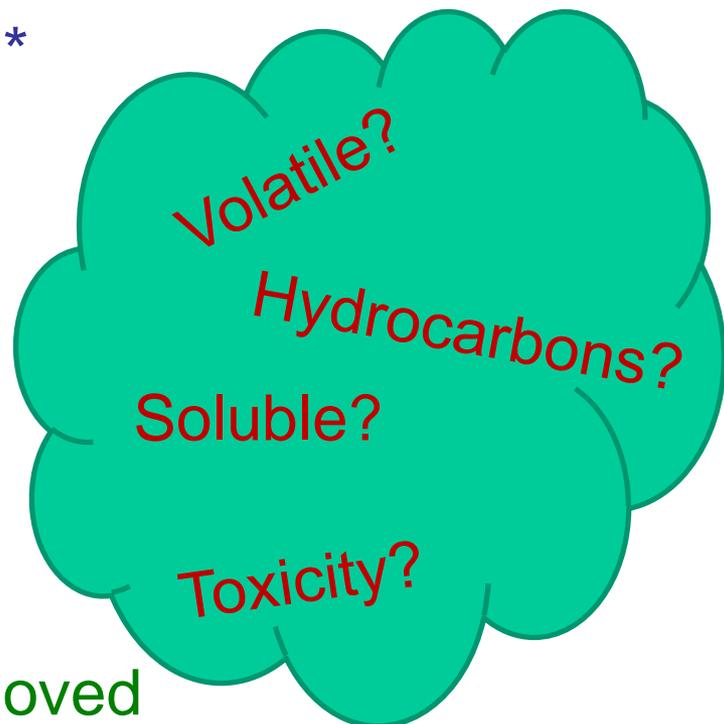
- ▶ USEPA Method 3630C
 - Removes non-hydrocarbons
 - Column cleanup is most effective
 - Should request that lab surrogate be added to ensure efficient cleanup
 - Used with Bulk TPH method
- ▶ Uses include:
 - Determination of extent of hydrocarbon impact
 - Delineation of true hydrocarbons or what could be natural occurring organics in background or metabolites
- ▶ Not to be used for TPHg or Air samples



For additional details see Appendix A of guidance document

Fractionation (Fact Sheet A.7)

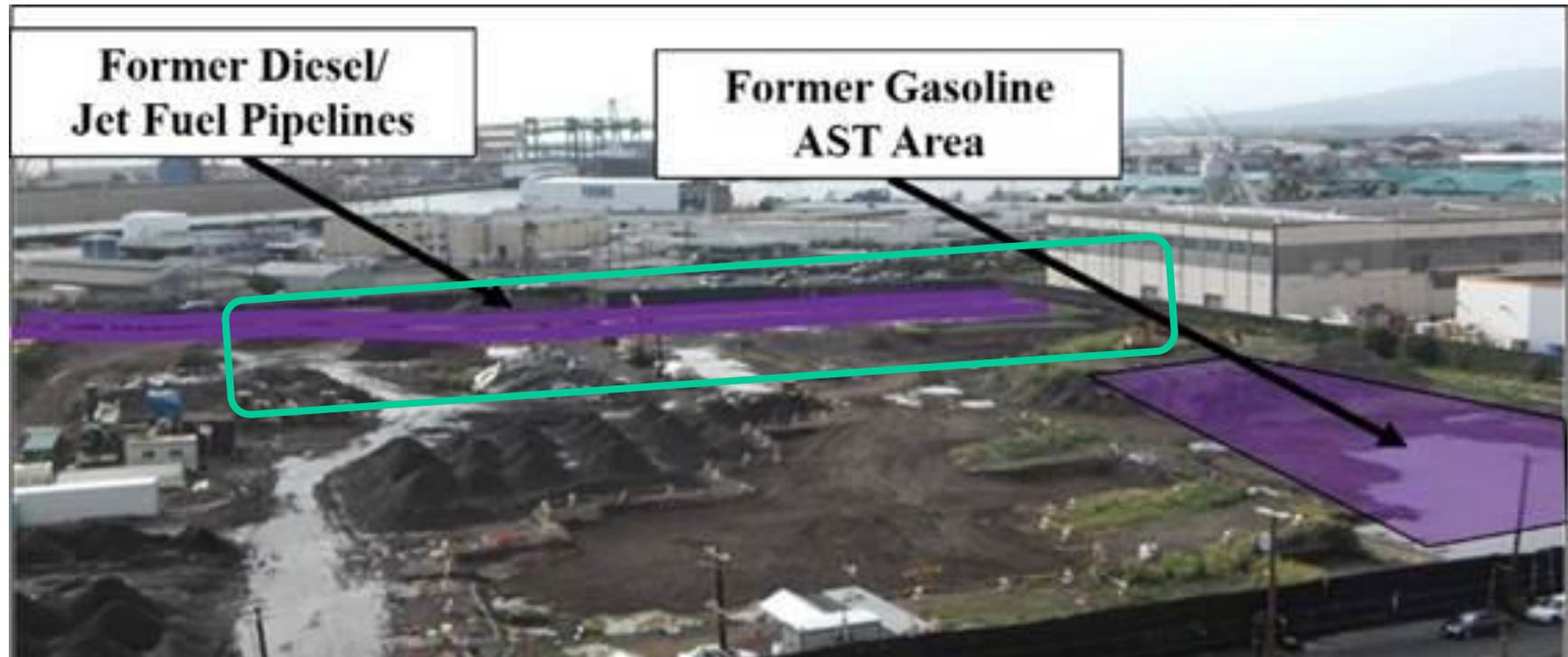
- ▶ Fractionation typically relies on the use of silica gel to separate the sample into aliphatic and aromatic *classes**
- ▶ The fractions are then injected into a GC for separation into *carbon ranges*
- ▶ However, they
 - Cost more than bulk TPH
 - Raise the reporting limits
 - Non-hydrocarbons will be removed from analysis (results)



* Class separation in the volatile range does not rely on use of silica gel

Case Study: Tank Farm

Application of Analytical Methods

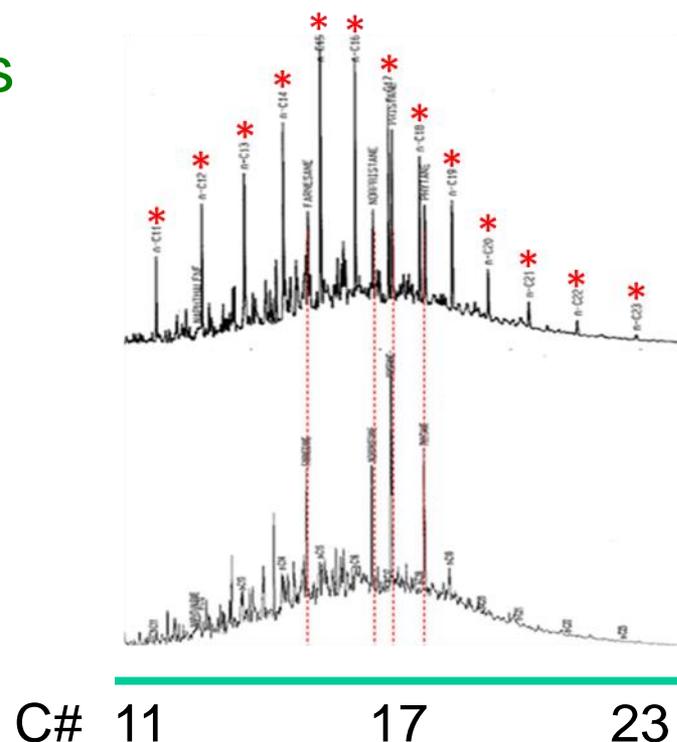


- Soil: Bulk TPH collected across the site
- Soil Vapor: Fractionation data collected at select locations in the diesel plume to determine site specific screening levels
- Groundwater: Bulk TPH with silica gel cleanup collected in select areas along downgradient edges of diesel plume to assess the degradation state and determine locations requiring active remediation

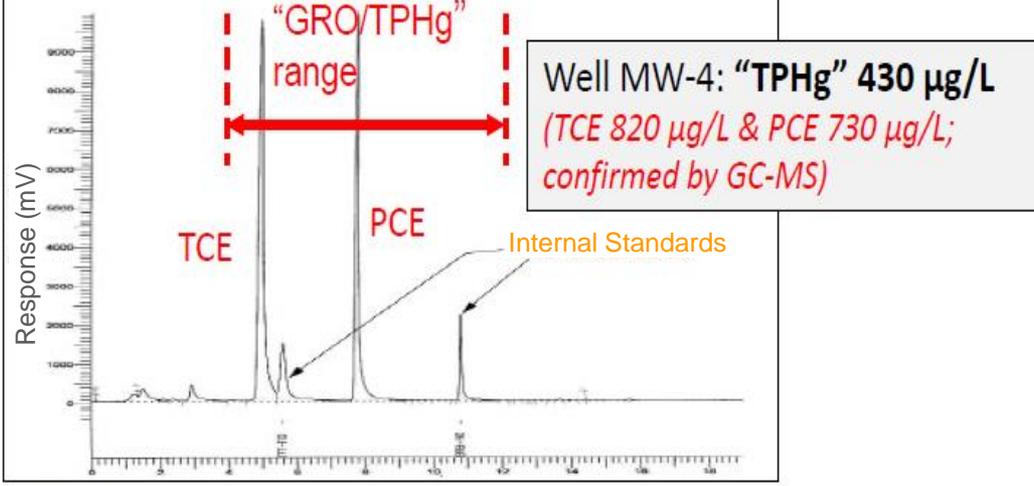
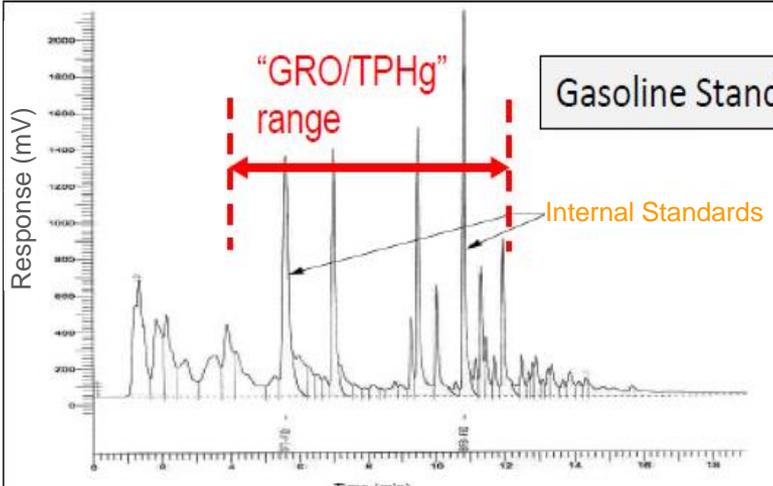
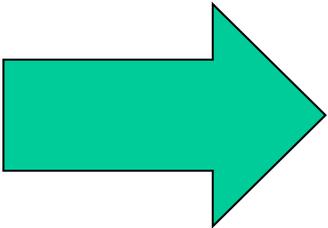
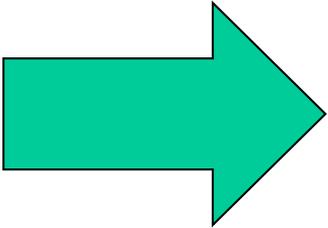
Chromatograms are not just pretty pictures (Fact Sheet A.6)

► Provide information on

- Type of material
- Presence of non-hydrocarbons
- Presence of solvents
- Presence of non-dissolved hydrocarbons
- Poor integration
- Weathering
 - Degree of weathering
 - Type of weathering



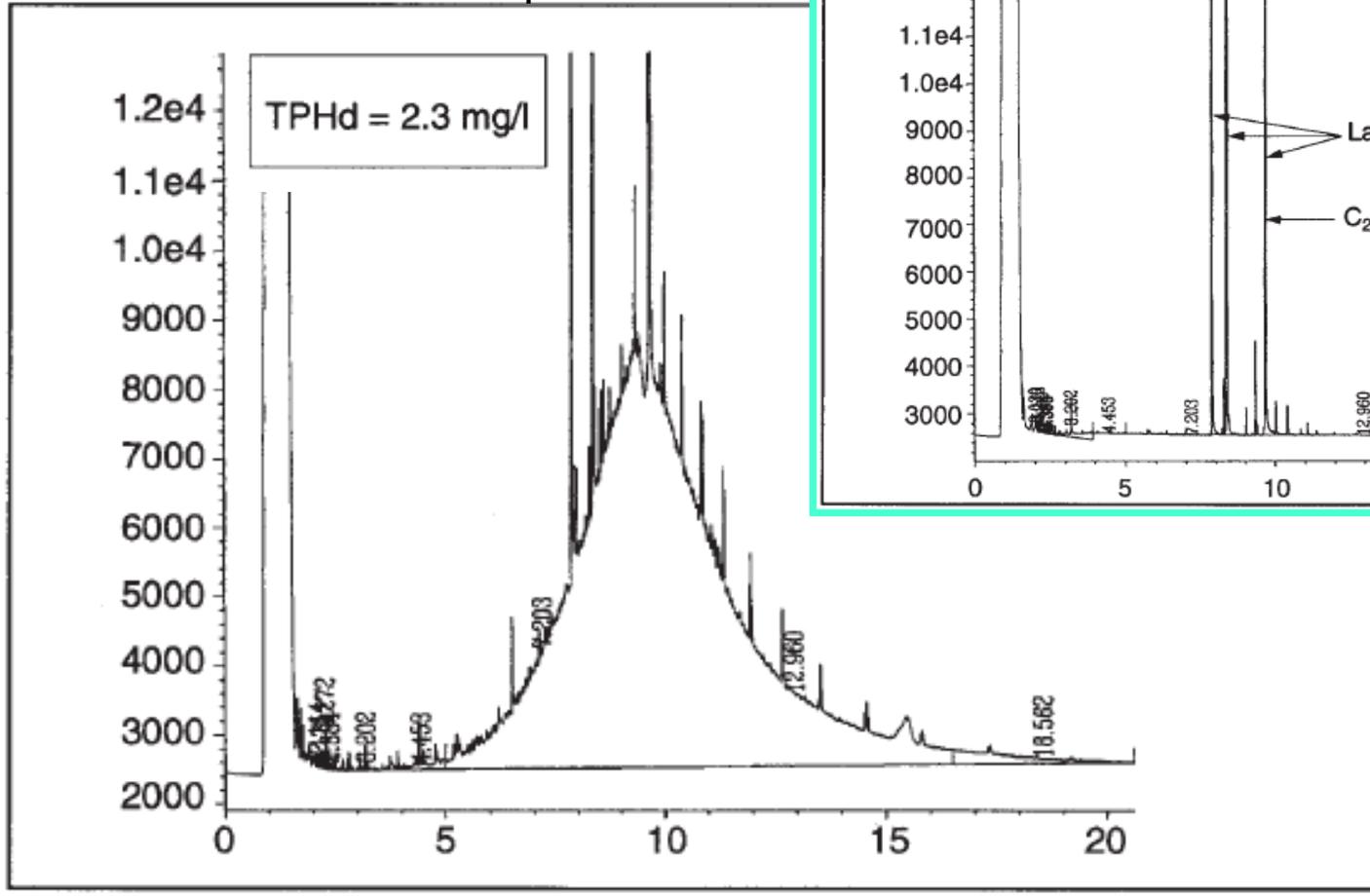
Practical Example #1 of Measurement Interferents (as determined by chromatograms)



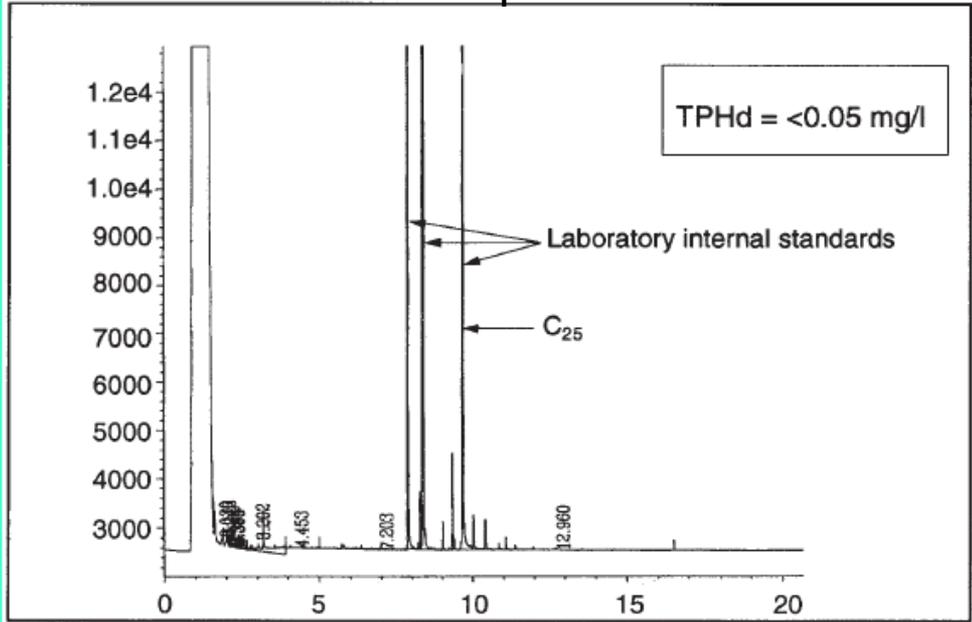
Zemo & Associates, Inc.

Practical Example #2 of Measurement Interferents (as determined by chromatograms)

Before Silica Gel Cleanup



After Silica Gel Cleanup



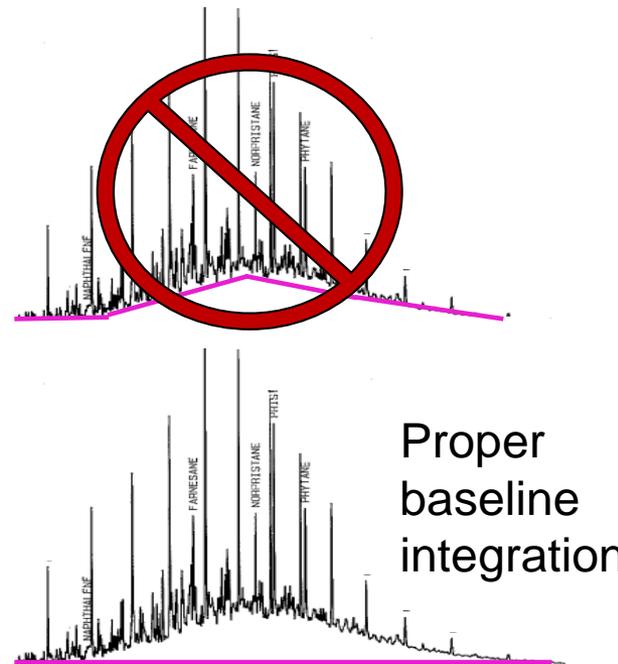
Poll Question



- ▶ All USEPA Method 8015 results are directly comparable, regardless of lab
 1. True
 2. False
 3. Not Sure

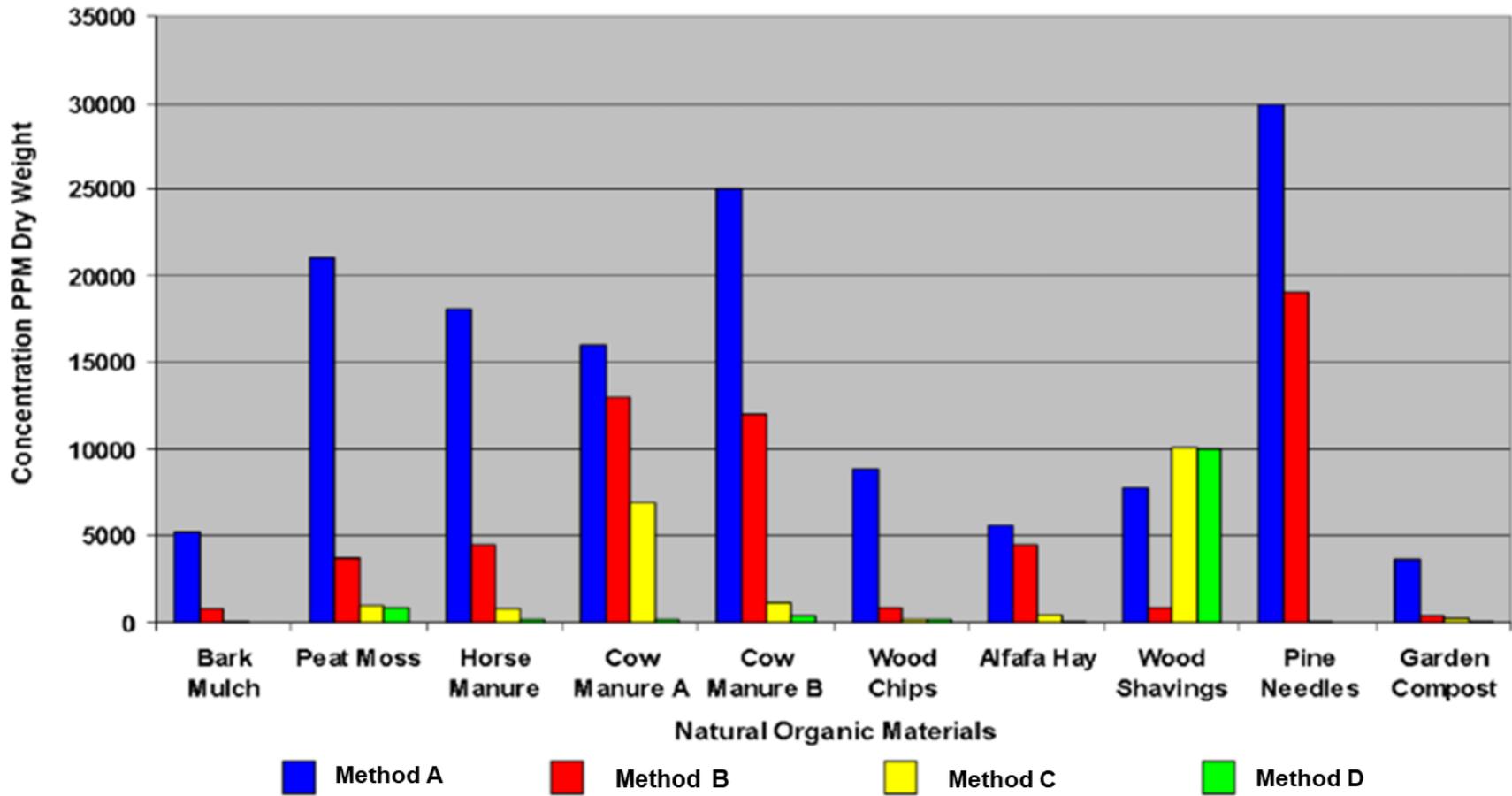
Not all TPHd by EPA method 8015 is Equal

- ▶ Extraction Solvent
 - n-pentane
 - dichloromethane
- ▶ Baseline Correction
- ▶ Carbon Ranges
 - C6-C10 vs. C6-C12
 - C12-C26 vs. C12-C28
- ▶ Calibration Standard



Don't assume a change has occurred at a site if the TPH value suddenly changes!

Four TPH Methods will Yield Four Different Results



And will measure “TPH” for non-petroleum hydrocarbons!



TPH Field Methods

▶ When do field methods make sense

- During initial field screening
- During plume delineation
- While excavation is open

▶ Which field methods make sense

- Is product known
 - Volatiles
 - Semi-volatiles
 - Wet chemistry vs meter

▶ Appendix D

- Pros and Cons



Follow up with laboratory methods to confirm your conclusions!

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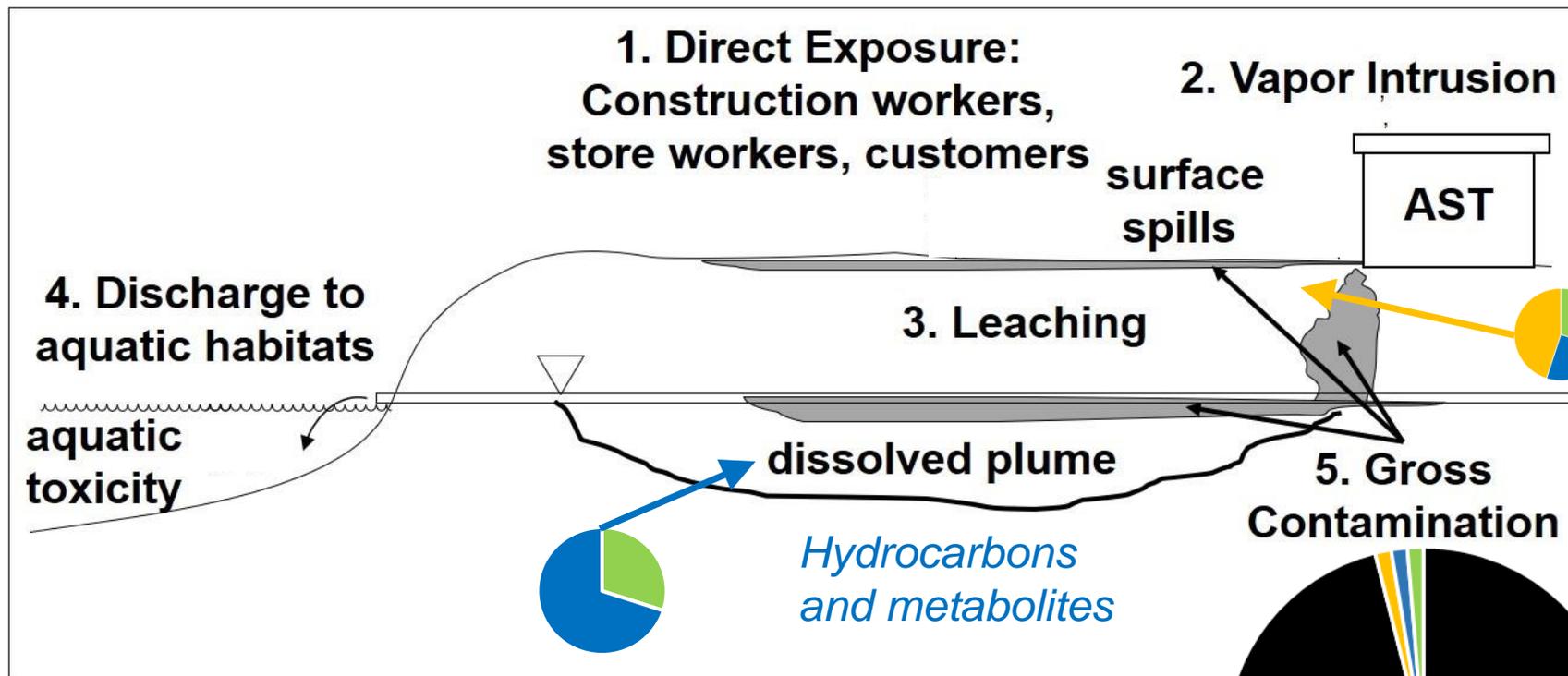
Learning Objectives – Environmental Fate of TPH



- ▶ Key Message: TPH composition changes after release to the environment and composition affects risk.
- ▶ Understand how physical weathering changes TPH composition
- ▶ Understand biological weathering also changes TPH composition and generates petroleum metabolites
- ▶ Anticipate TPH composition changes throughout a site

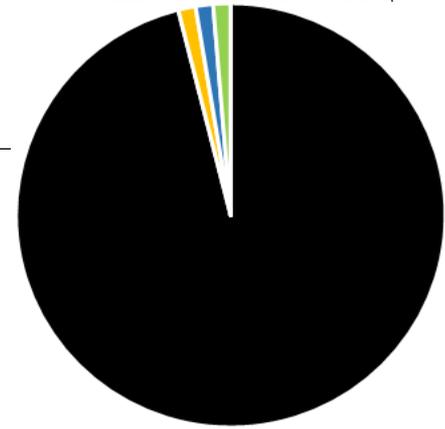
Conceptual Site Model: Source and Migration Pathways

Case Study

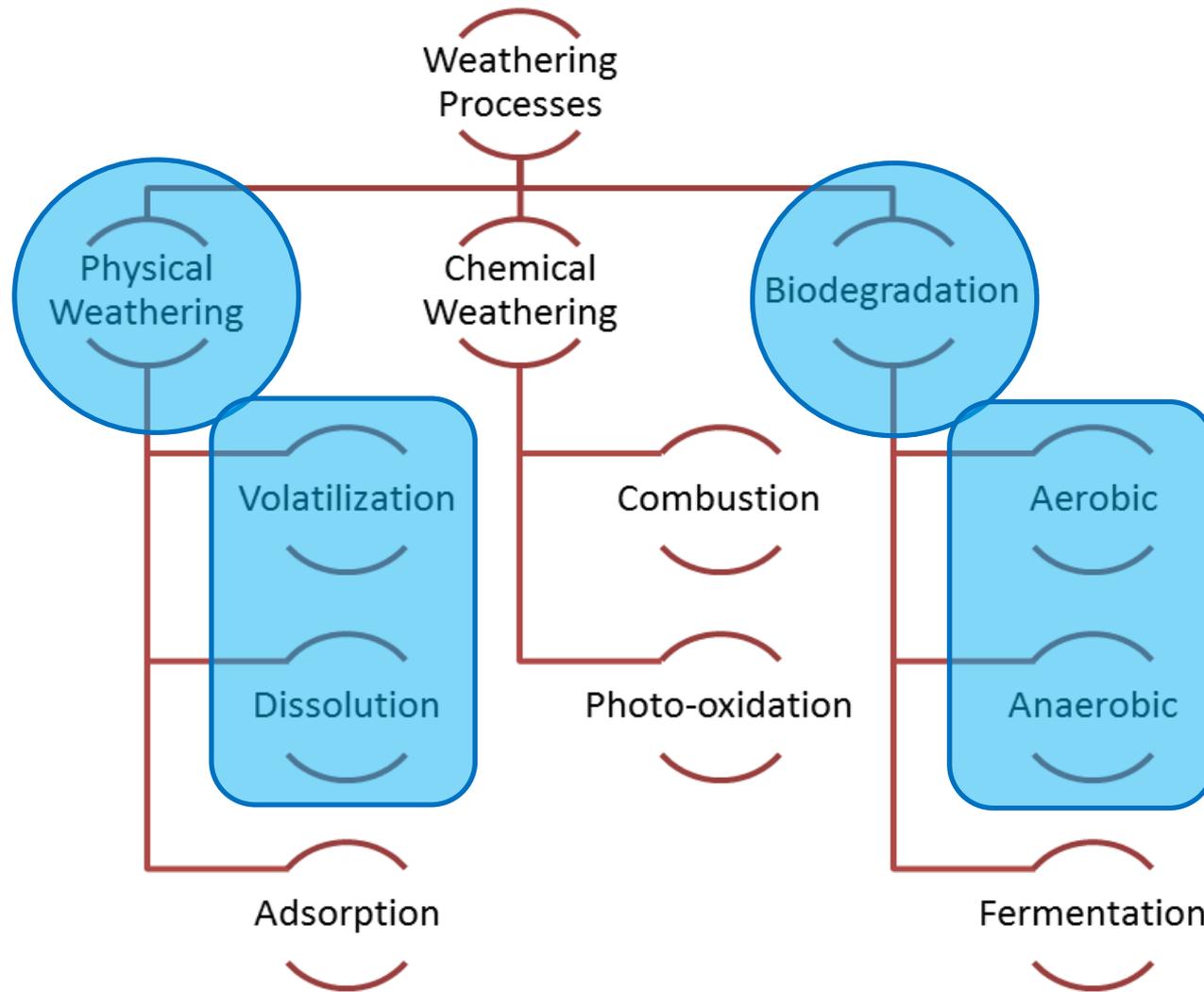


- Phase**
- NAPL (non-aqueous phase liquid)
 - Air/Vapor
 - Water
 - Sorbed

- Releases:**
- Gasoline AST
 - Diesel pipeline
- Contamination extent defined using bulk TPH**



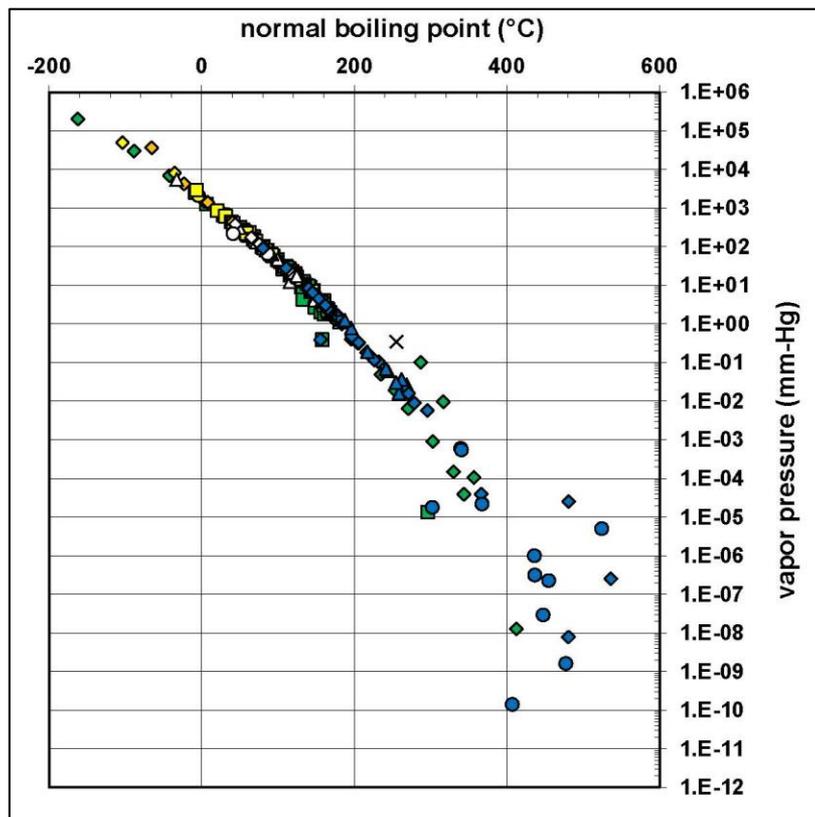
Weathering Processes Overview



ITRC TPHRisk-1 Figure 4-8

Partitioning: Oil to Vapor

Boiling Point vs. Vapor Pressure



■ Aliphatics

■ Aromatics

x Biphenyls

■ Alkynes

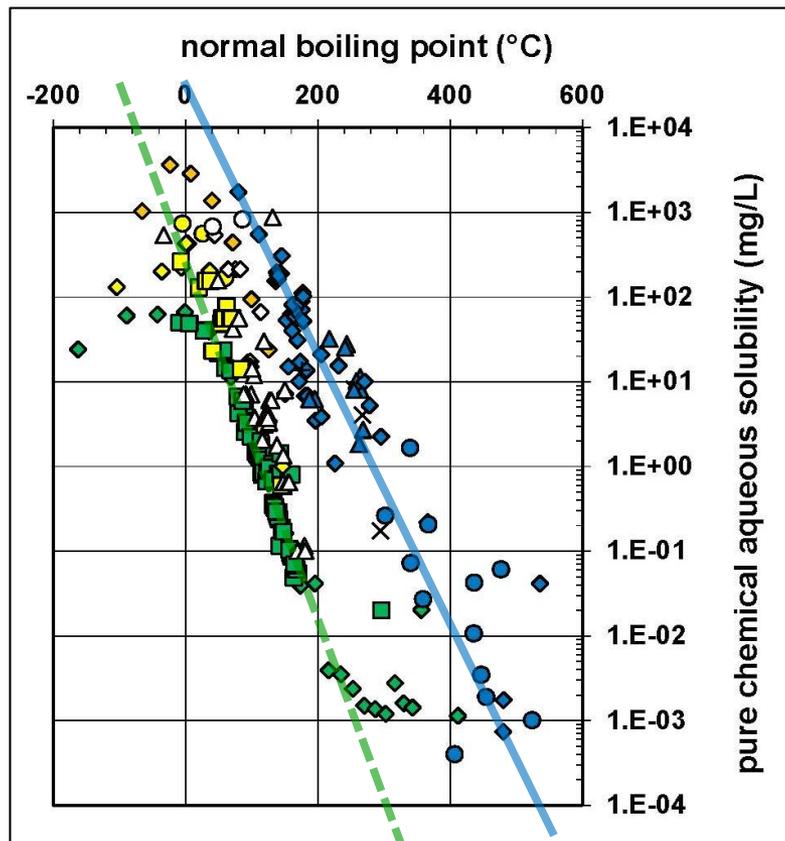
□ Cycloalkenes
and cyclodienes

■ Alkenes (straight and
branched) and Dienes

- ▶ All classes plot along single curve
- ▶ Smaller hydrocarbons have greater volatilization potential and likely dominate TPH vapor composition
- ▶ Note: Scatter at lower vapor pressure is related to measurement difficulty

Partitioning: Oil to Water

Boiling Point vs. Aqueous Solubility



Aliphatics

Aromatics

X Biphenyls

Alkynes

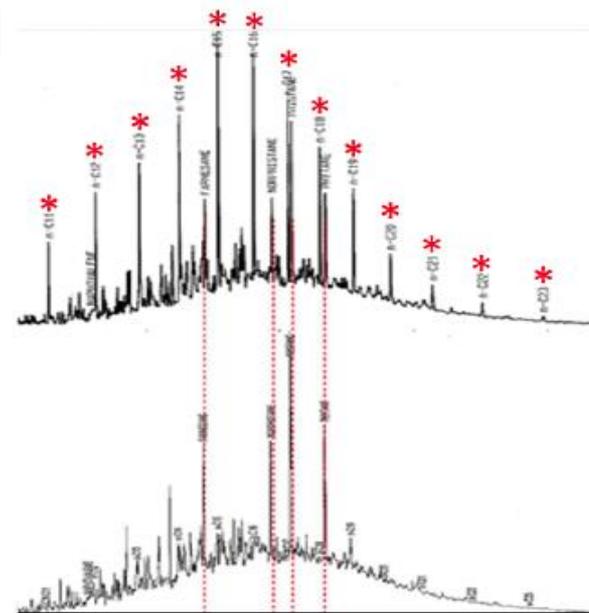
Cycloalkenes
and cyclodienes

Alkenes (straight and
branched) and Dienes

- ▶ Smaller hydrocarbons are more soluble
- ▶ Hydrocarbon structure differences:
 - Aromatics (solid line/right) most soluble
 - Aliphatics (dashed line/left) least soluble
- ▶ TPH water composition likely dominated by aromatics

Biodegradation (Biological Weathering)

- ▶ Biodegradation of hydrocarbons well documented for +100 years
- ▶ Hydrocarbons readily undergo biodegradation under aerobic conditions
 - Some hydrocarbons degrade more readily than others (see figure)
- ▶ Biodegradation is a stepwise process – each step leads to new metabolites
- ▶ Anaerobic biodegradation typically is slower and more prone to buildup of petroleum metabolites



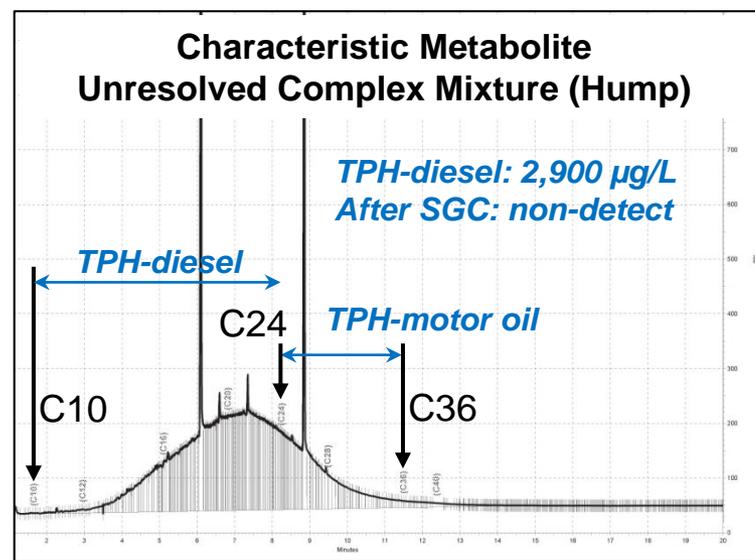
Highly Branched Alkanes Remain After Biodegradation

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
 - Understanding of 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 |



Example TPH Fractions: TPH Criteria Working Group vs. EPA



| | | | | | | | | | |
|---------------------|-----------|--|------------------|------------------|--------|---------|---------|---------|---|
| Molecular Structure | Aliphatic | | EC5-6 | EC6-8 | EC8-10 | EC10-12 | EC12-16 | EC16-21 | EC21-35 (same properties as EC16-21) -- not considered a transport fraction-- |
| | Aromatic | | EC5-7 Benzene | EC7-8 Toluene | EC8-10 | EC10-12 | EC12-16 | EC16-21 | |

Increasing Equivalent Carbon (EC) Number →

**TPH
Criteria
Working
Group
13
Transport
Fractions**

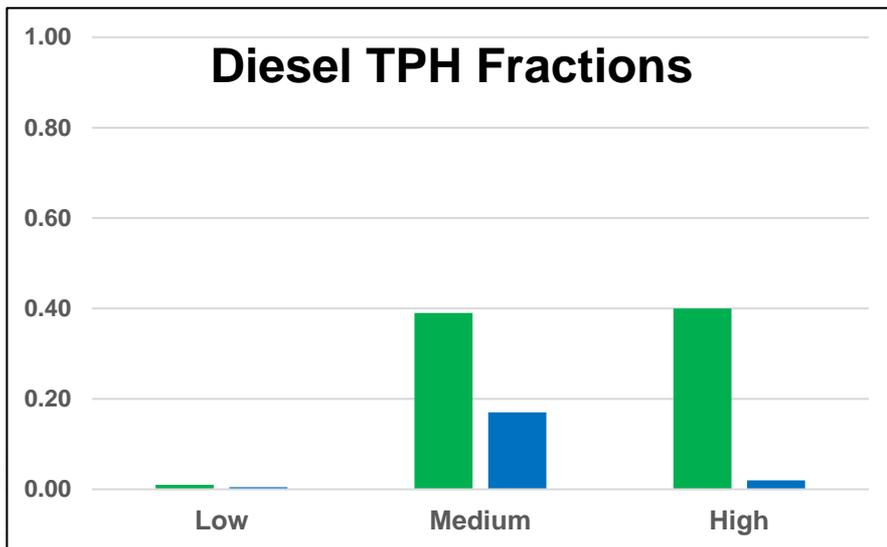
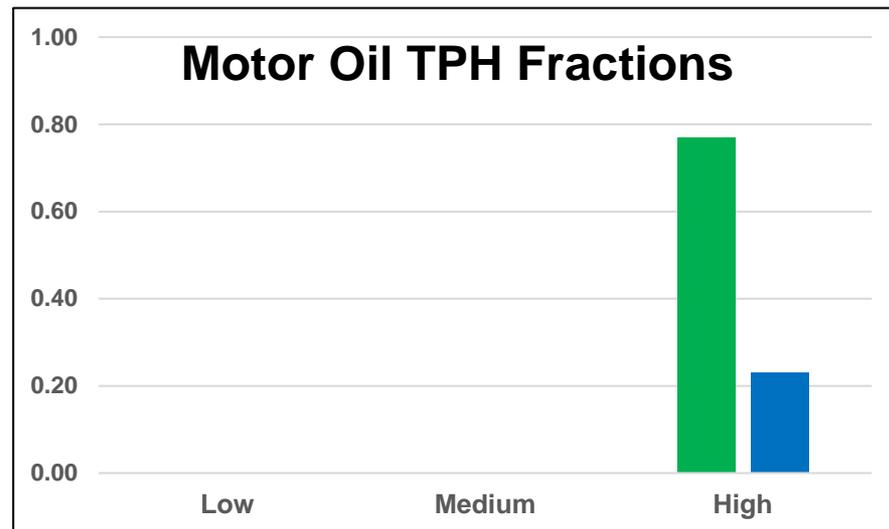
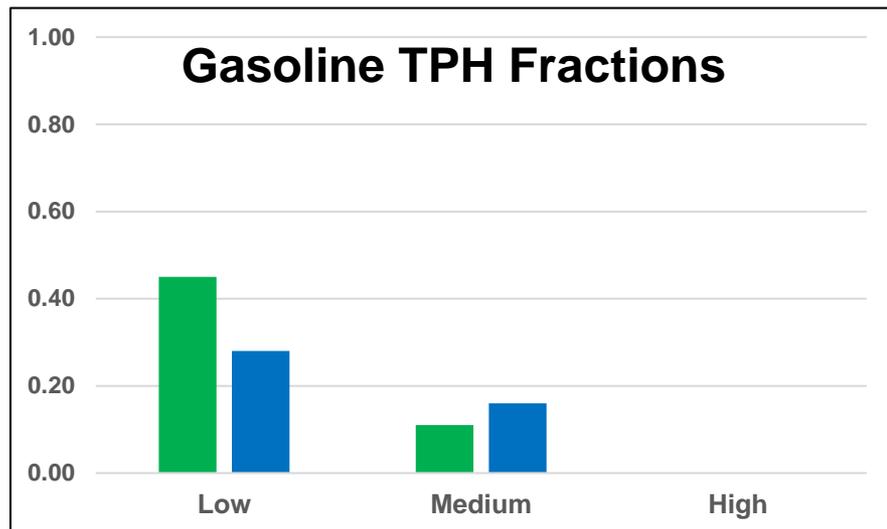
| | | | | | |
|---------------------|-----------|--|-------|--------|---------|
| Molecular Structure | Aliphatic | | EC5-8 | EC8-16 | EC16-35 |
| | Aromatic | | EC6-9 | EC9-22 | EC22-35 |

Increasing Equivalent Carbon (EC) Number →

**EPA
6
Toxicity
Fractions**

TPH Composition in Non-Aqueous Phase Liquid (NAPL)

Example TPH Fraction Proportions in Three Unweathered NAPLs



Aliphatic Aromatic

Y-Axis: Mass fraction (1.00 = 100%)

Using 6 EPA TPH Fractions

Fraction compositions estimated from ATSDR documents

NAPL: TPH Composition Change Due to Weathering



- ▶ Weathering of NAPL is also known as Natural Source Zone Depletion (NSZD) – see ITRC LNAPL-3 (2018)



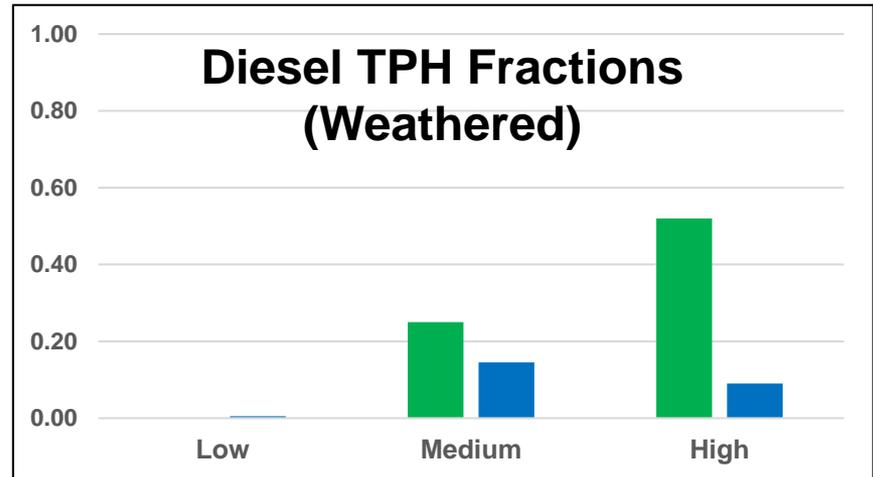
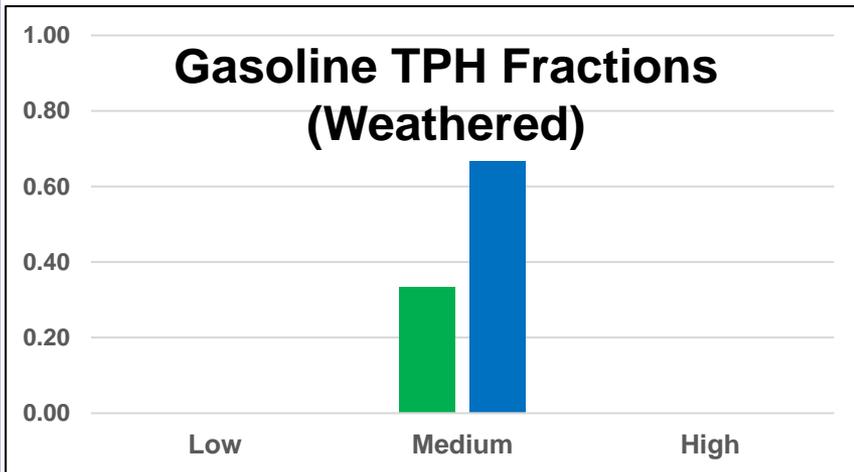
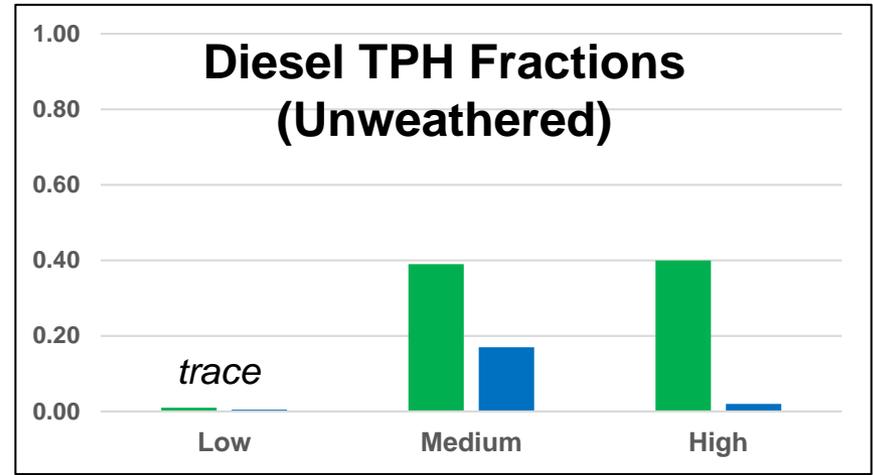
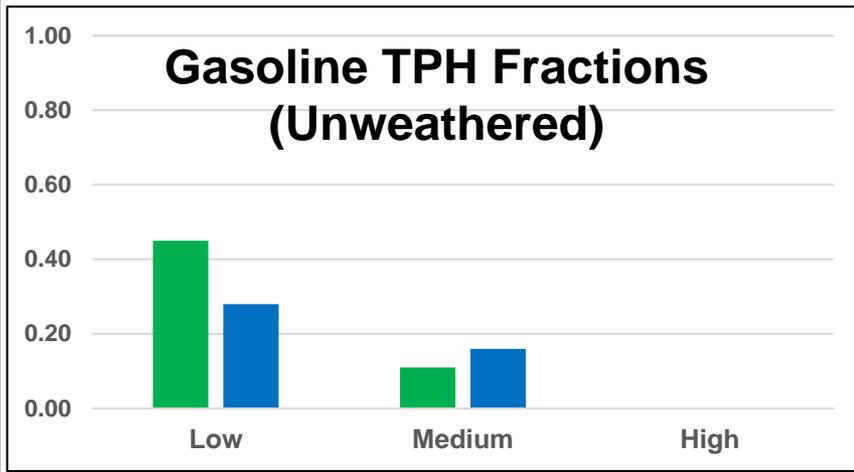
Printed from: Interstate Technology & Regulatory Council (ITRC). 2018. *Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies*. LNAPL-3. Washington, D.C. <https://lnapl-3.itrcweb.org>.

Appendix B-Natural Source Zone Depletion (NSZD) Appendix

- ▶ Over time, weathering changes the remaining NAPL composition (and therefore risk)
 - Mobile hydrocarbons partition out, depleting the remaining NAPL
 - While biodegradation continues, metabolites will be generated

Weathered NAPL: TPH Composition Change Example

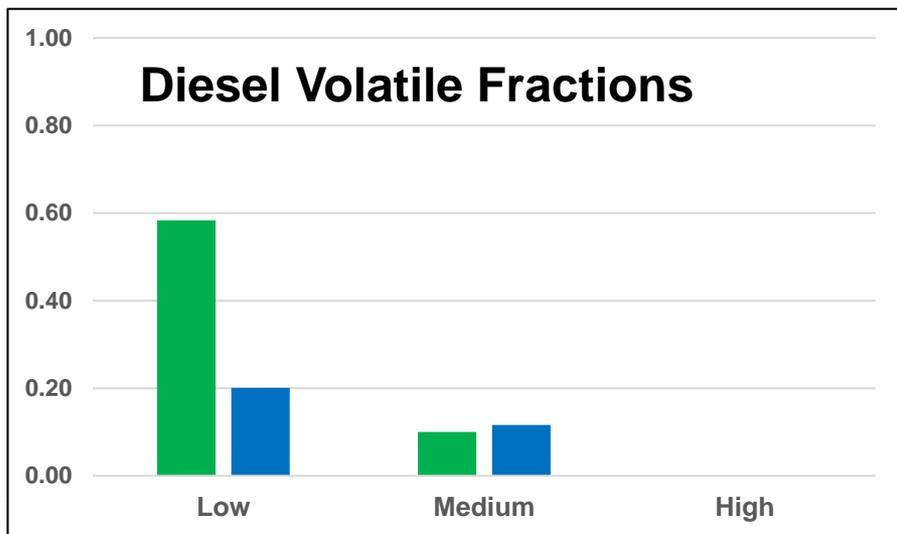
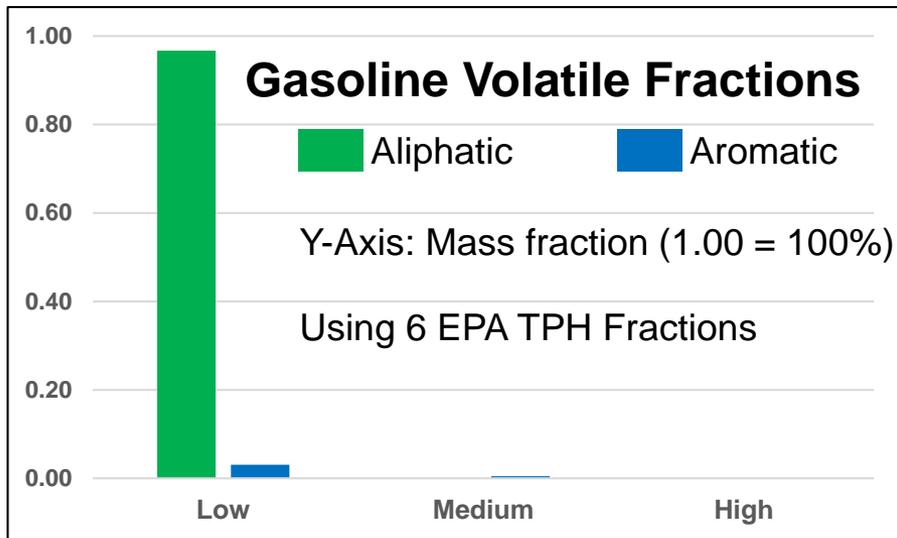
Case Study



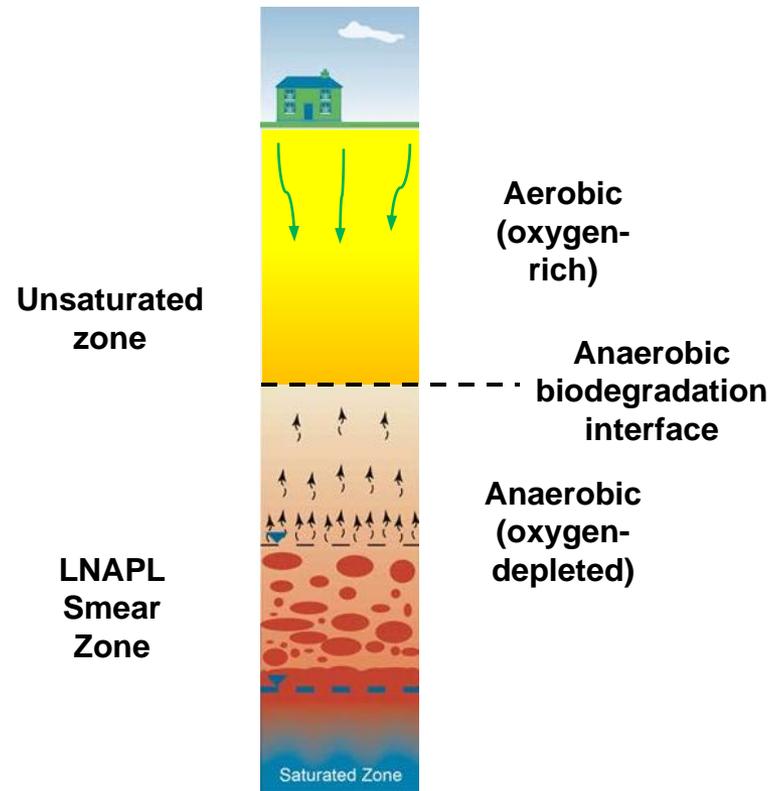
■ Aliphatic
 ■ Aromatic

Composition: weathered gasoline from IRhodes
weathered diesel based on TPHCWG data

Vapor: TPH Fraction Composition Near NAPL and Fate/Exposure



TPH Vapor Attenuation to Surface in Presence of Oxygen

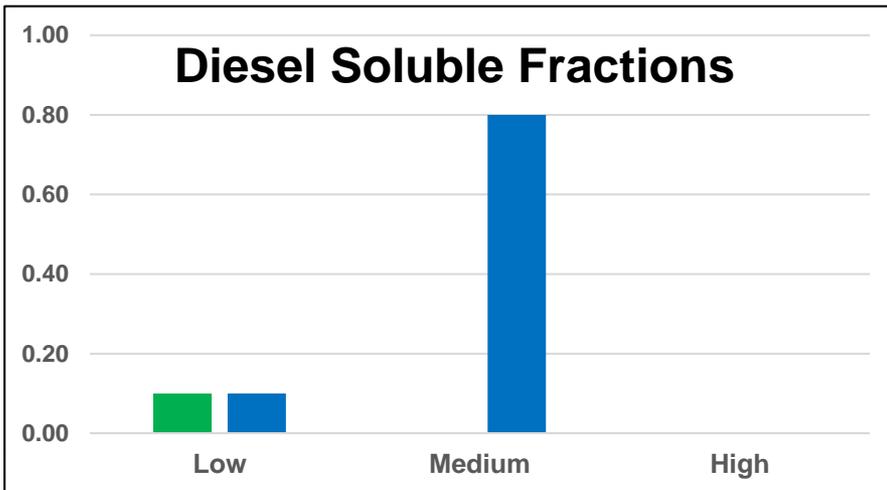
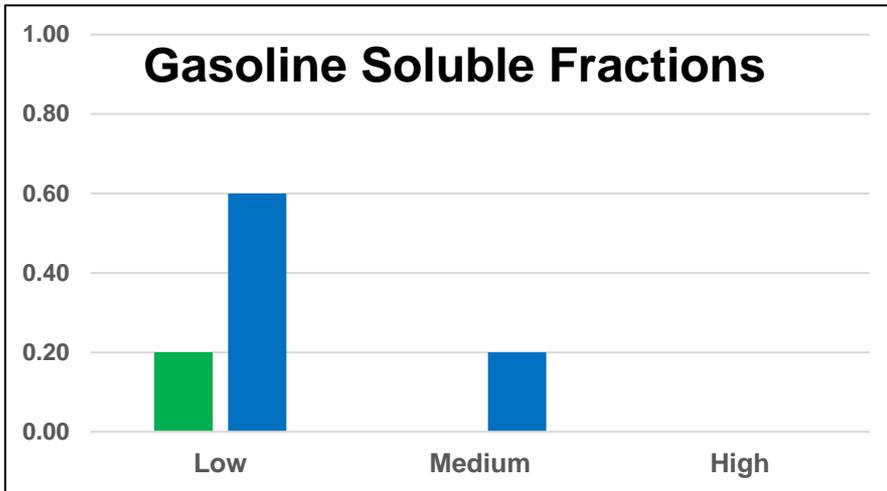


Source: ITRC PVI Guidance 2014



Groundwater: TPH Fraction Composition (Near NAPL)

Example TPH Fraction Proportions in Water from Two NAPLs (Unweathered)



■ Aliphatic ■ Aromatic

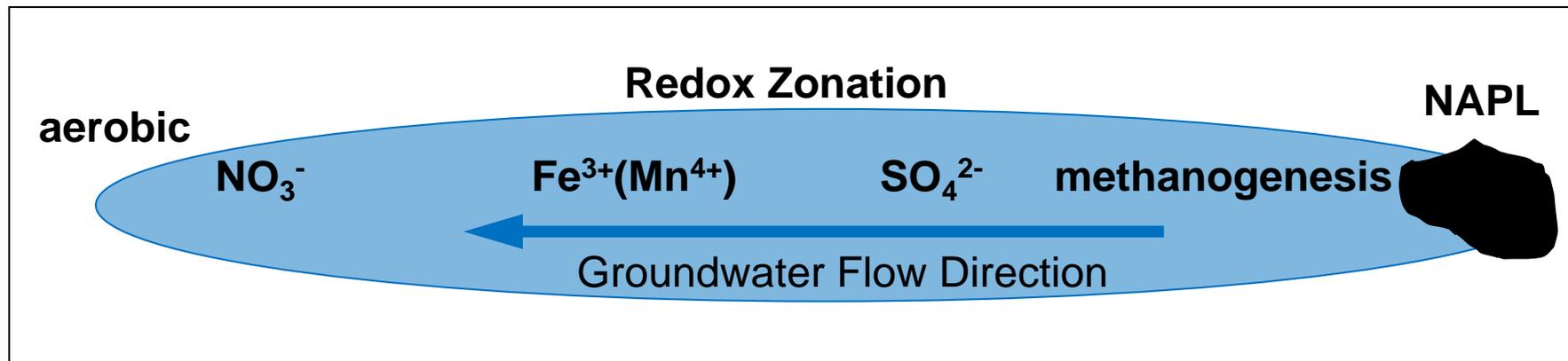
Y-Axis: Mass fraction (1.00 = 100%)

Using 6 EPA TPH Fractions

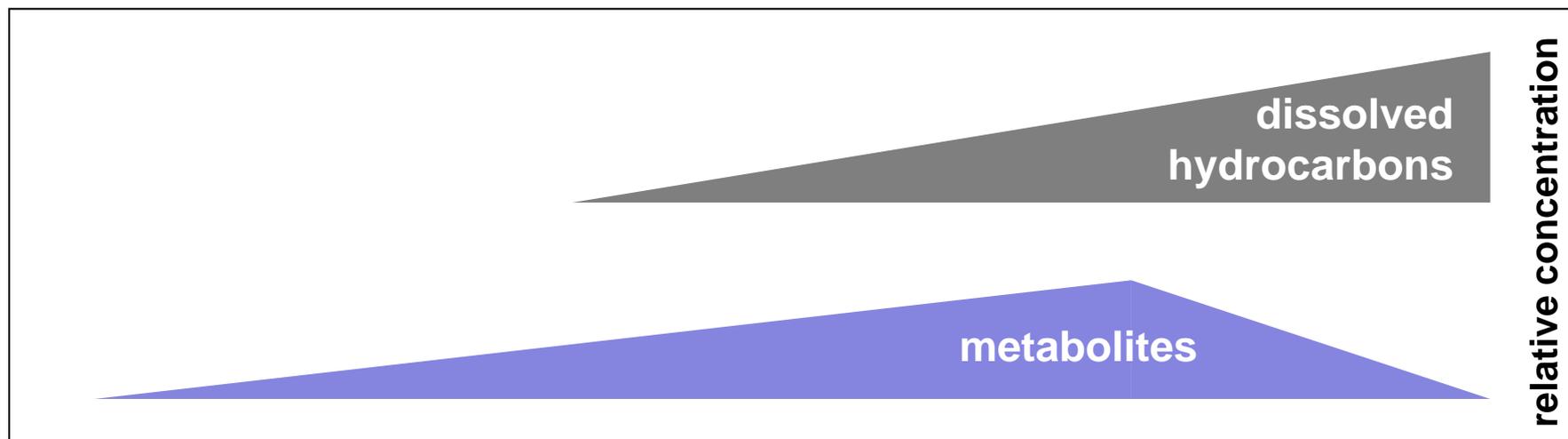
► Fate of TPH Groundwater Plumes

- Dissolved hydrocarbons attenuate with increasing distance from release
- TPH-Gasoline Plume Length (Shih et al. 2004):
 - Median: about 220 feet
 - Max: about 600 feet

Groundwater: Fate and Exposure



← Increasing Distance to the Left →



Information on relative hydrocarbon/metabolite concentrations based on Zemo et al. 2016. Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface (Wiedemeier et al. 1999)

Poll Question



- ▶ CSM: 30-year old, large diesel spill at bulk terminal site, where diesel is about EC8-EC26.
- ▶ What soluble TPH fractions or petroleum-related compounds are more likely present in a groundwater sample downgradient of the source area?
 1. All fractions/chemicals
 2. Low aromatics (EC6-EC9)
 3. High aliphatics (EC16-EC35)
 4. Petroleum metabolites
 5. None of the above

Summary: Environmental Fate of TPH



- ▶ TPH is a complex mixture
- ▶ The mass and composition of TPH change after release in a site-dependent manner depending on:
 - Individual hydrocarbon properties
 - Site conditions
- ▶ Understanding how TPH mass and composition change at a site leads to understanding how TPH risk changes at a site

Road Map



- ▶ Why the Guidance?
- ▶ Learn What TPH is
- ▶ Learn TPH Analytical Methods
- ▶ Questions and Answers
- ▶ Environmental Fate of TPH
- ▶ Assessing Human and Ecological Risk from TPH
- ▶ Stakeholders Considerations
- ▶ Closing
- ▶ Questions and Answers

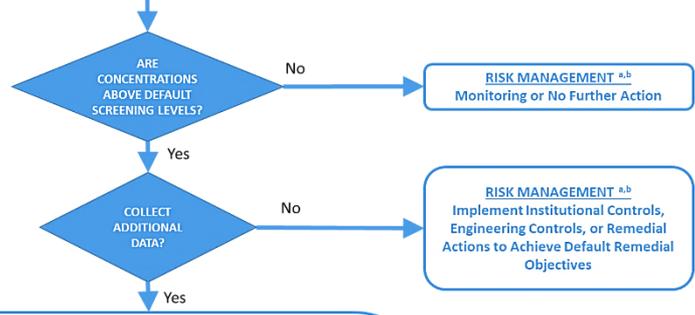
Learning Objectives – Assessing Human and Ecological Risk from TPH



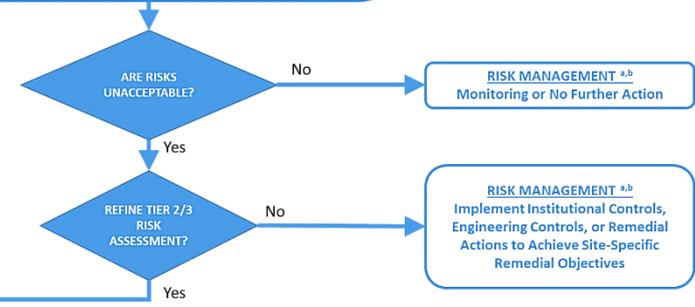
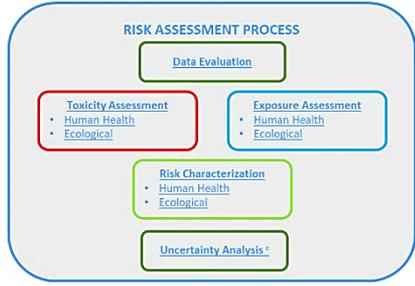
- ▶ Learn how tiered screening-level and site-specific approaches can be applied to human health and ecological TPH risk assessments
- ▶ Recognize how the unique analytical and fate and transport characteristics of TPH as a mixture affect risk assessment
- ▶ Determine whether your existing data is sufficient to estimate TPH risk
- ▶ Gain an appreciation for the uncertainties specific to TPH risk assessment

Tiered TPH Risk Assessment Framework

- TIER 1 – SCREENING-LEVEL RISK ASSESSMENT**
- **PRELIMINARY CSM DEVELOPMENT**
 - Source characterization
 - Initial exposure pathway assessment
 - **INITIAL DATA REVIEW**
 - Evaluate regulatory requirements
 - Review existing TPH data (bulk TPH, individual/indicator compounds, fractions)
 - If no existing TPH data available, collect initial data (bulk TPH and individual/indicator compounds)
 - **SCREENING ASSESSMENT**
 - Compare site data to default screening levels



- ADDITIONAL DATA COLLECTION FOR TIER 2/3 RISK ASSESSMENT**
- **IDENTIFY DATA GAPS**
 - Review existing TPH data, preliminary CSM, and applicable regulatory requirements
 - **COLLECT ADDITIONAL FIELD DATA (AS NEEDED)**
 - Bulk TPH measurement & chromatograms
 - Indicator compounds
 - Fraction
 - **UPDATE CSM**
 - **CONDUCT TIER 2 OR 3 RISK ASSESSMENT**



- ▶ Screening level assessment
- ▶ Site-specific assessment
- ▶ Human health and ecological

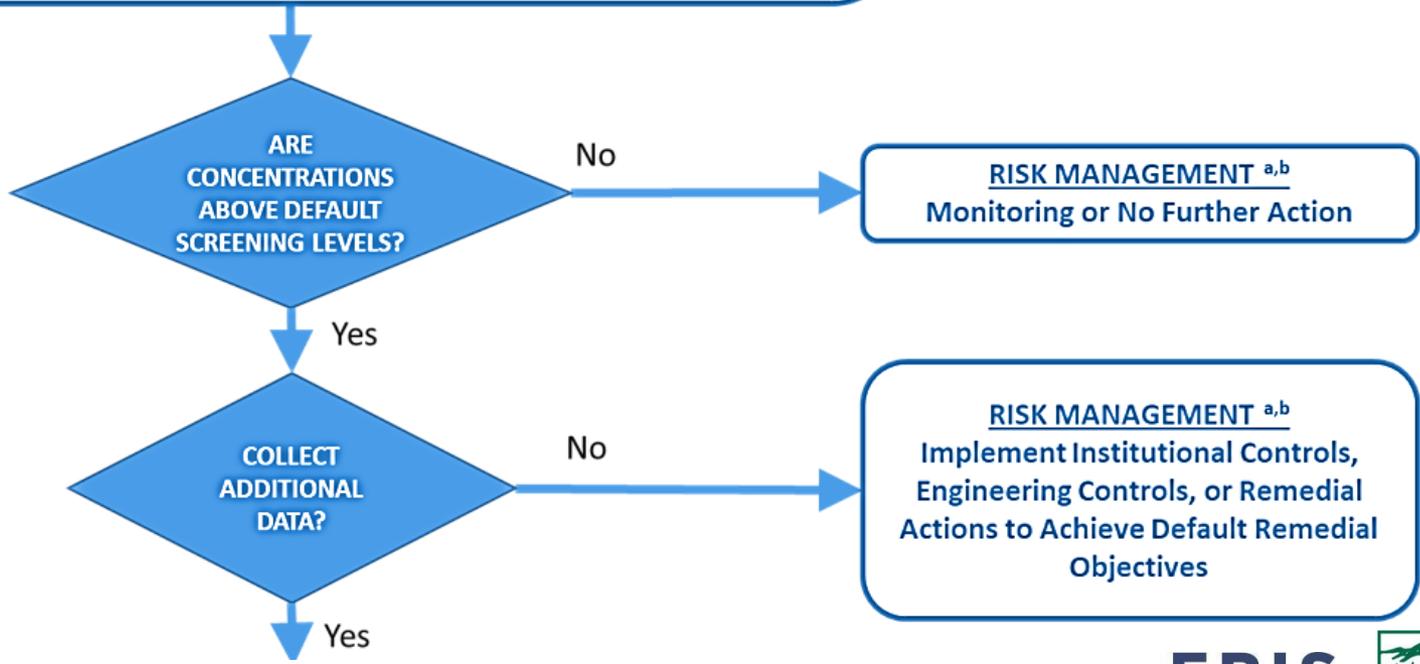
ITRC TPHRisk-1 Figure 1-1

Screening-Level Assessment



TIER 1 – SCREENING-LEVEL RISK ASSESSMENT

- **PRELIMINARY CSM DEVELOPMENT**
 - Source characterization
 - Initial exposure pathway assessment
- **INITIAL DATA REVIEW**
 - Evaluate regulatory requirements
 - Review existing TPH data (bulk TPH, individual/indicator compounds, fractions)
 - If no existing TPH data available, collect initial data (bulk TPH and individual/indicator compounds)
- **SCREENING ASSESSMENT**
 - Compare site data to default screening levels



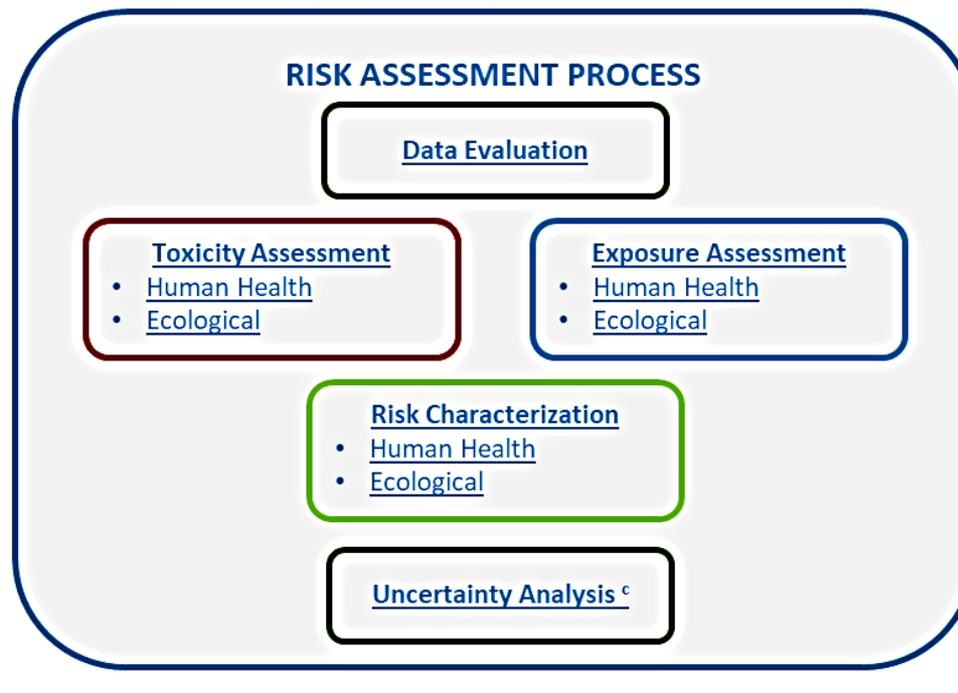
ITRC TPHRisk-1 Figure 1-1



Site-Specific Assessment

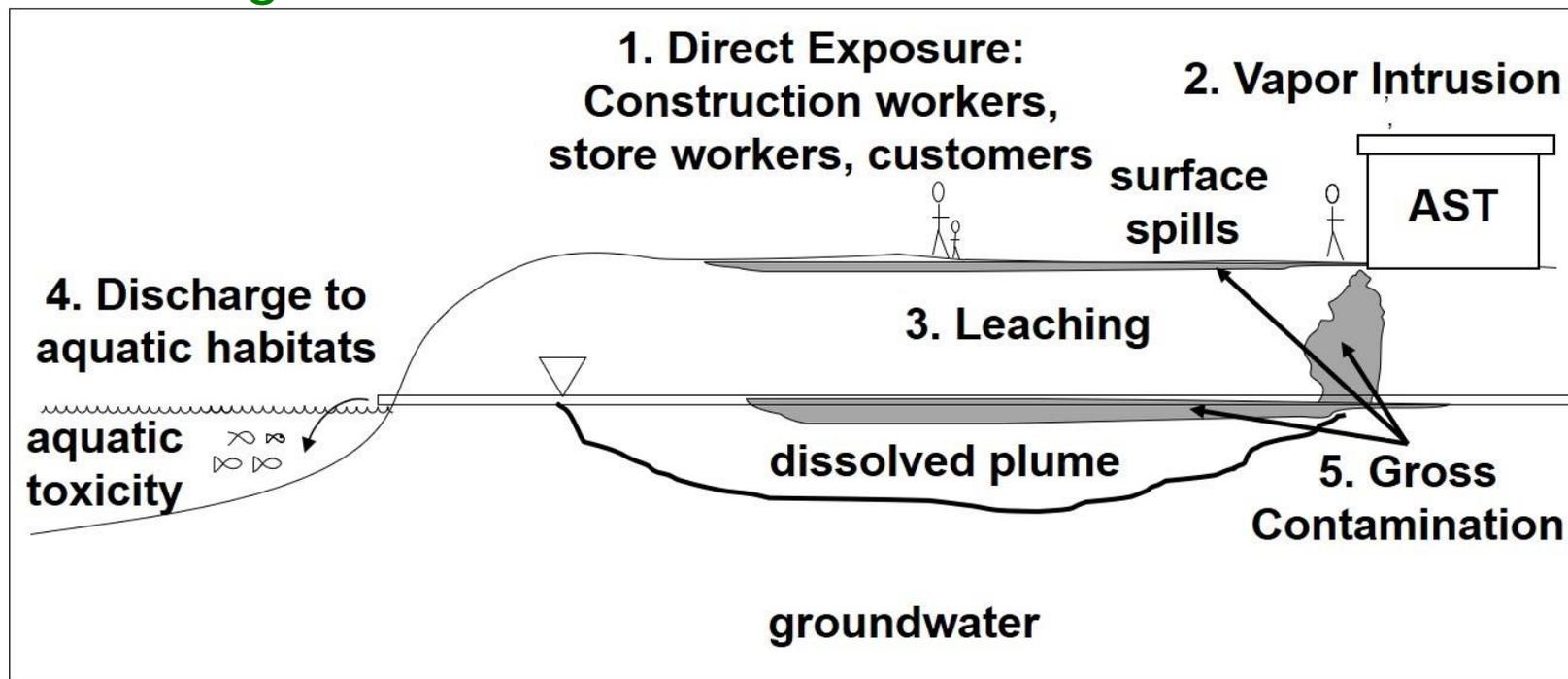
ADDITIONAL DATA COLLECTION FOR TIER 2/3 RISK ASSESSMENT

- **IDENTIFY DATA GAPS**
 - Review existing TPH data, preliminary CSM, and applicable regulatory requirements
- **COLLECT ADDITIONAL FIELD DATA (AS NEEDED)**
 - Bulk TPH measurement & chromatograms
 - Indicator compounds
 - Fraction
- **UPDATE CSM**
- **CONDUCT TIER 2 OR 3 RISK ASSESSMENT**



Conceptual Site Model: Exposure Assessment

- ▶ Unique characteristics of TPH effect exposure assessment
 - Partitioning across media
 - Changes over time



Human Health Exposure Pathways – Poll Question



Sample 1

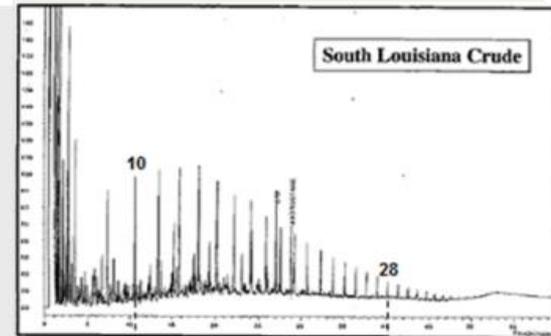
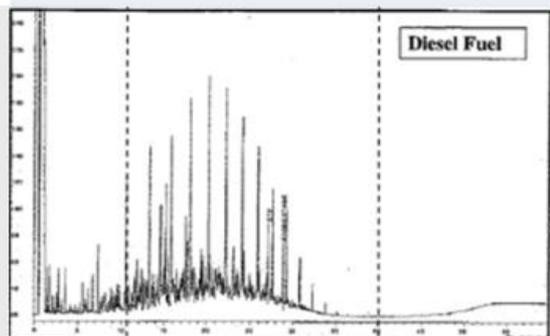
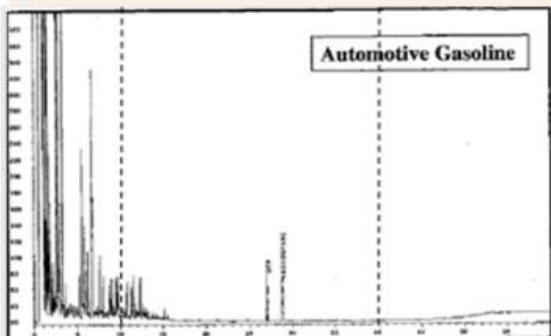
Sample 2

Sample 3

15,000 mg/kg

15,000 mg/kg

15,000 mg/kg



Note that the first dotted line on the chromatograms is at C10, the second at C28

Gasoline

Diesel

South Louisiana Crude

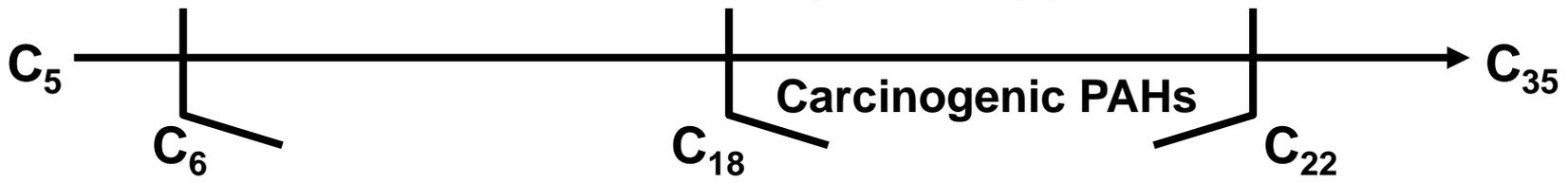
Poll Question



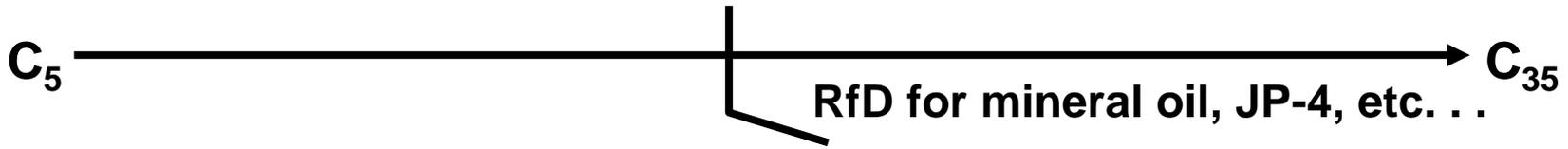
Human Health Toxicity Assessment



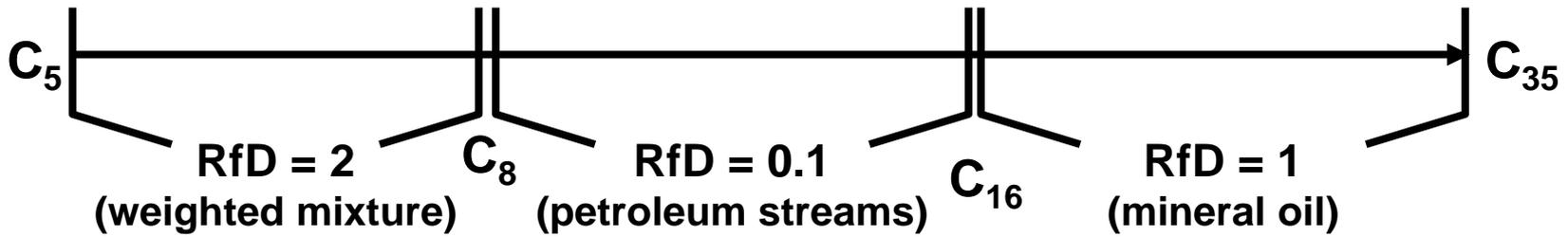
Individual Compound Approach



Whole Product



Fraction/Surrogate



Example Toxicity Values Under TPH Fraction Approach

| Fractions | TPHCWG (1997) | | MA DEP (2003) | | USEPA PPRTV (2009) | | TCEQ (2010) | |
|--|---------------|--|---------------|-------------------|--------------------|-------------------|---------------|-------------------|
| | RfD (mg/kg-d) | Surr (s) Comp (c) | RfD (mg/kg-d) | Surr (s) Comp (c) | RfD (mg/kg-d) | Surr (s) Comp (c) | RfD (mg/kg-d) | Surr (s) Comp (c) |
| Aliphatics Low Carbon Range (C5-C8) (EC5-EC8) | 5 | (s) Commercial hexane where n-hexane is ≤53% | 0.04 | (s) n-hexane | 0.3 | (s) n-hexane | 0.06 | (s) n-hexane |
| Aromatics Low Carbon Range(C6-C8) (EC6-EC<9) | 0.2 | (s) toluene | NA | (c) benzene | 0.004 | (c) benzene | 0.1 | (s) ethylbenzene |
| | | | 0.2 | (c) toluene | 0.08 | (c) toluene | | |
| | | | 0.1 | (c) ethylbenzene | 0.1 | (c) ethylbenzene | | |
| | | | 2 | (c) xylenes | | (c) xylenes | | |
| | | | 0.2 | (c) styrene | 0.2 | (c) xylenes | | |

TPHCWG – Total Petroleum Hydrocarbon Criteria Working Group
 MA DEP – Massachusetts Department of Environmental Protection
 USEPA = United States Environmental Protection Agency
 TCEQ – Texas Commission on Environmental Quality
 PPRTV – Provisional Peer-Reviewed Toxicity Values

Case Study – Toxicity Assessment

Started with bulk TPH data

| COPC | Example Soil Data (mg/kg) | TPH Screening Level | | |
|-------|---------------------------|-------------------------|------------------|-----------------------------|
| | | Direct Exposure (mg/kg) | Leaching (mg/kg) | Gross Contamination (mg/kg) |
| TPHg | 12,000 | 2,400 | 400 | 500 (5,000) |
| TPHmd | 48,000 | 500 | 500 | 500 (5,000) |
| TPHrf | 17,000 | 140,000 | 1000 | 2,500 (5,000) |

Uncertainty in nature of product in diesel range prompted fraction analysis for soil gas

| Carbon Range | Assumed Subslab Vapor Concentration (mg/m ³) | Subslab Vapor Screening Level (mg/m ³) |
|--------------------|--|--|
| C5-C8 aliphatics | 3,200 | 350 |
| C9-C12 aliphatics | 5,500 | 59 |
| C13-C18 aliphatics | 130 | 59 |
| C9-C10 aromatics | 32 | 59 |
| C11-C16 aromatics | ND (<4) | 59 |

Assessment of Metabolites

- ▶ Challenge assessing risk
 - Limited toxicity information for individual metabolites and mixtures
- ▶ Options for evaluating metabolite toxicity
 - Exclude from evaluation
 - Use the RfD from the Rogers et al. (2002) study
 - Adopt the toxicity ranking model from Zemo et al. (2013, 2016)
 - Treat the bulk metabolites and bulk hydrocarbons as having similar toxicity (HIDOH, 2017) and (CSWB-SFBR, 2016)

Case Study – Risk Management



- ▶ Primary pathway of concern was vapor intrusion
- ▶ Acute safety/explosive concern
- ▶ Addressed stakeholder concerns
 - Vapor mitigation systems
 - Asphalt cover to address direct contact
 - Emergency hazard management plans for safety concerns

Now let's move on from humans...



ERA Poll Question

▶ Three different sites:

- Site A – gas station release from a UST, paved site, depth to groundwater at 100 feet below land surface
- Site B – gas station release, paved with channeled groundwater discharge to a creek a half-mile away
- Site C – continuing release from an oil refinery with terrestrial and aquatic habitats nearby

An ERA may not be Necessary When:



- ▶ Absence of viable habitats (e.g., paved sites)
- ▶ Contamination found below the root zone and burrowing zones of ecological receptors
- ▶ No release to nearby, viable (or protected) aquatic and terrestrial habitats
- ▶ Policies and regulations on exclusion criteria (see Table 5-3)

Do a Screening-Level ERA When:



- ▶ State or local regulations require an ERA
- ▶ Screening Level values are available
- ▶ Screening levels are appropriate for site conditions and type of release
- ▶ Data Requirements for Screening ERA
 - Consider data for bulk TPH (TPH-g, TPH-d) and indicators (BTEX, PAHs)
 - TPH fraction data usually not available or necessary
 - See Tables 7-12 and 7-13 for analytical data choices and uses

Example TPH Screening Levels – TPH-g

- ▶ CA Water Board Whole Product Screening Levels for Water (Table 7-1)

| | Fresh (ppb) | Marine (ppb) | Estuarine (ppb) |
|-------|-------------|--------------|-----------------|
| TPH-g | 500 | 3,700 | 500 |

- ▶ Canadian Soil Guidelines for Fraction F1

| | Plants and Invertebrates (ppm) | Wildlife (ppm) |
|-----------------|--------------------------------|----------------|
| TPH F1 (C6-C10) | 210-320 | 11,000 |

- ▶ More details on available screening levels in Section 7.2 and Table 7-1

Do a Site-Specific ERA When:



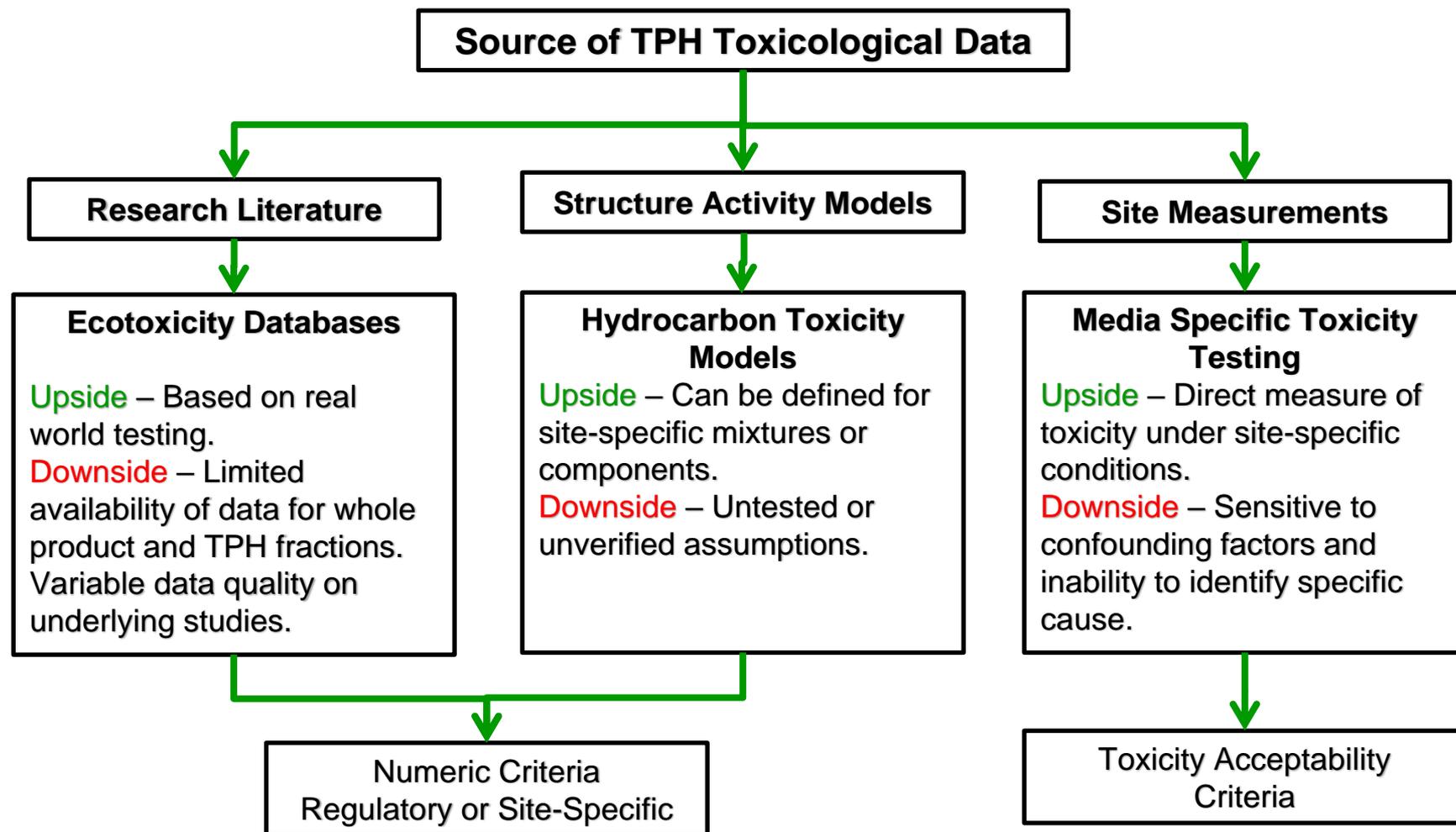
- ▶ When screening levels are lacking or exceeded
- ▶ At complex sites with multiple media, sensitive habitats and receptors
- ▶ Data needs for Site-Specific ERA
 - Consider combination of useful data types
 - Whole product and indicators
 - Water soluble and water accommodated fractions for aquatic habitats
 - Aliphatic/Aromatic fractions primarily available for aquatic assessment
 - See Tables 7-2,7-3 and 7-4 for analytical data choices and uses

Scoping a Site-Specific ERA



- ▶ Exposure Assessment
 - Focus on direct exposure
 - Bioaccumulation
 - Primarily PAHs
- ▶ Toxicity Assessment
 - Aquatic and terrestrial biota
 - Physical toxicity
 - (not included in this guidance)
 - Chemical toxicity
 - Multiple approaches
 - Metabolites
 - Emerging concern under study

Toxicity Assessment - Approaches



Characterizing HH and Eco Risk and Uncertainties

Key Uncertainties

Representativeness of fractions, components and/or surrogates of TPH

Screening levels (representative of TPH mix, risk based source, applicable endpoints)

Non-additivity of TPH risk and TPH component double-counting

Toxicity value/test representativeness to underlying exposure mechanisms, especially when TPH + non-TPH mixtures

Additional direct or indirect impacts from TPH (oiling, direct contact, indirect changes to habitat)

Use of field data

Type of data used (bulk vs fractionated)

Road Map



- ▶ Why the Guidance?
- ▶ Learn What TPH is
- ▶ Learn TPH Analytical Methods
- ▶ Questions and Answers
- ▶ Environmental Fate of TPH
- ▶ Assessing Human and Ecological Risk from TPH
- ▶ Stakeholders Considerations
- ▶ Closing
- ▶ Questions and Answers

Learning Objectives - Stakeholder Considerations



- ▶ Recognize what groups can be potential stakeholders
- ▶ Know what stakeholder engagement tools are available
- ▶ Approach some common sources of confusion and concern about TPH risk assessment and decision-making for stakeholders – e.g., fires, explosions, health, appearance, odor, taste
- ▶ Chapter 10 in the guidance document

WE ALL WANT TO BE HEARD!

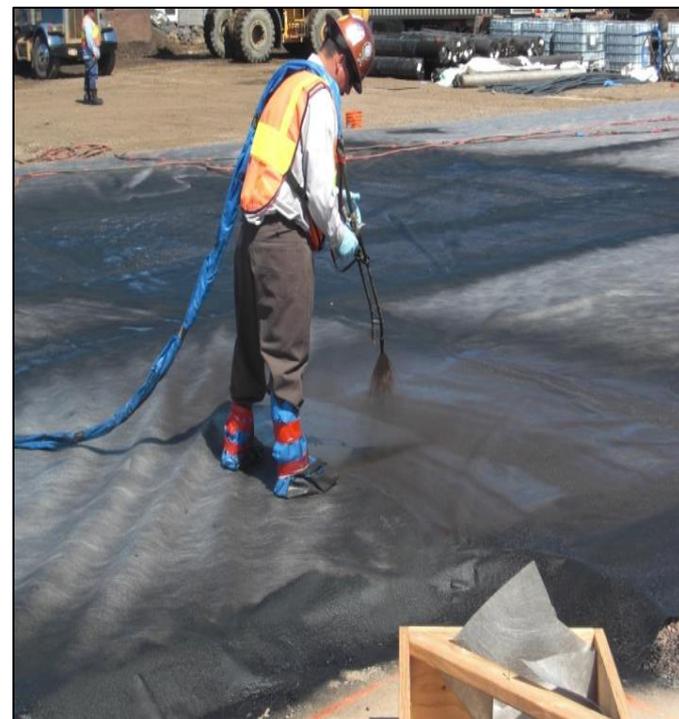
Communication with Stakeholders



- ▶ Who are Stakeholders?
- ▶ Important Components of Risk Communication
 - **Empathy and respect**
 - Understandable facts and conclusions about TPH
- ▶ Required Public Notifications
 - Notify owners and tenants before sampling
 - Provide TPH data with appropriate explanation
- ▶ Appropriate Communication Tools
 - Conveying technical concepts (Table 10-2)
 - Factsheets, posters, outreach meetings
 - Websites and links to TPH information

Tank Farm Redevelopment

- ▶ Community Engagement Plan (CEP)
 - **Town Hall meeting scheduled several years before remediation began**
 - Built credibility and trust through targeted remedial actions, mitigation and monitoring
 - CEPs should be appropriate for the site



Stakeholder Concerns Associated with TPH – Property Values



► Property Devaluation Concerns

- Not unique to TPH
- Devaluation may be real or perceived
- Concern is often related to residual TPH and a Monitored Natural Attenuation (MNA) remedy

► Addressing Property Devaluation Concerns

- Explain why selected remedy is protective and effective, especially for MNA
- Describe how all activities are done with agency oversight
- Address individual property owners concerns too

Stakeholder Concerns Associated with TPH – Technical Issues



- ▶ Household sources of TPH/ "Background" TPH
 - There are many potential sources of TPH
 - Paint thinners, cosmetics, natural oils, urban air (Table 10-3)
 - We can only manage site-related TPH
- ▶ TPH and methane – explosions?
 - Potential degradation product, see ITRC PVI guidance (2014) and ASTM methane standard
- ▶ Understanding what TPH data means – a challenge
- ▶ Nuisance concerns vs health risks?
 - Taste and odor are not health risks but covered in some states
- ▶ **Project Success**
 - **Technical approach + stakeholder engagement**

Road Map



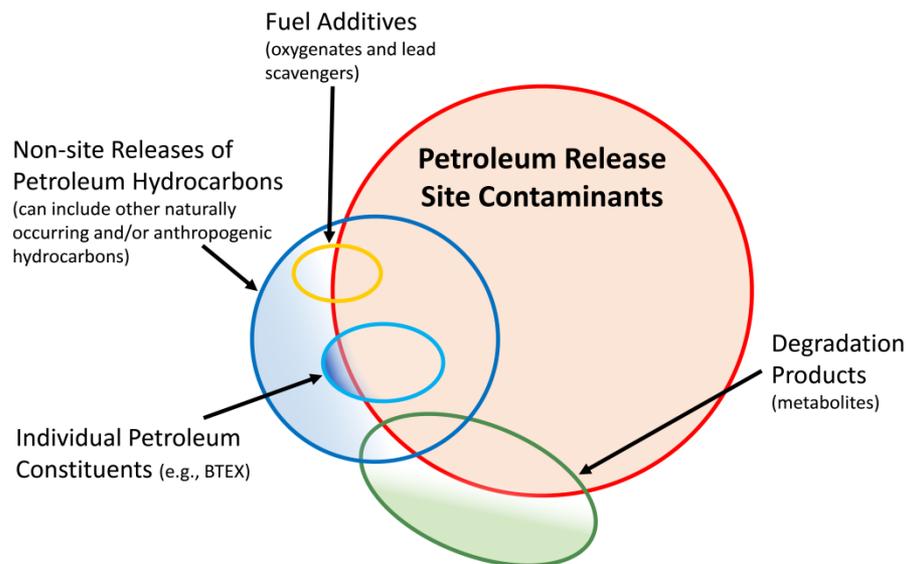
- ▶ Why the Guidance?
- ▶ Learn What TPH is
- ▶ Learn TPH Analytical Methods
- ▶ Questions and Answers
- ▶ Environmental Fate of TPH
- ▶ Assessing Human and Ecological Risk from TPH
- ▶ Stakeholders Considerations
- ▶ Closing
- ▶ Questions and Answers

How will YOU evaluate TPH now?

► What does your TPH site data really represent?

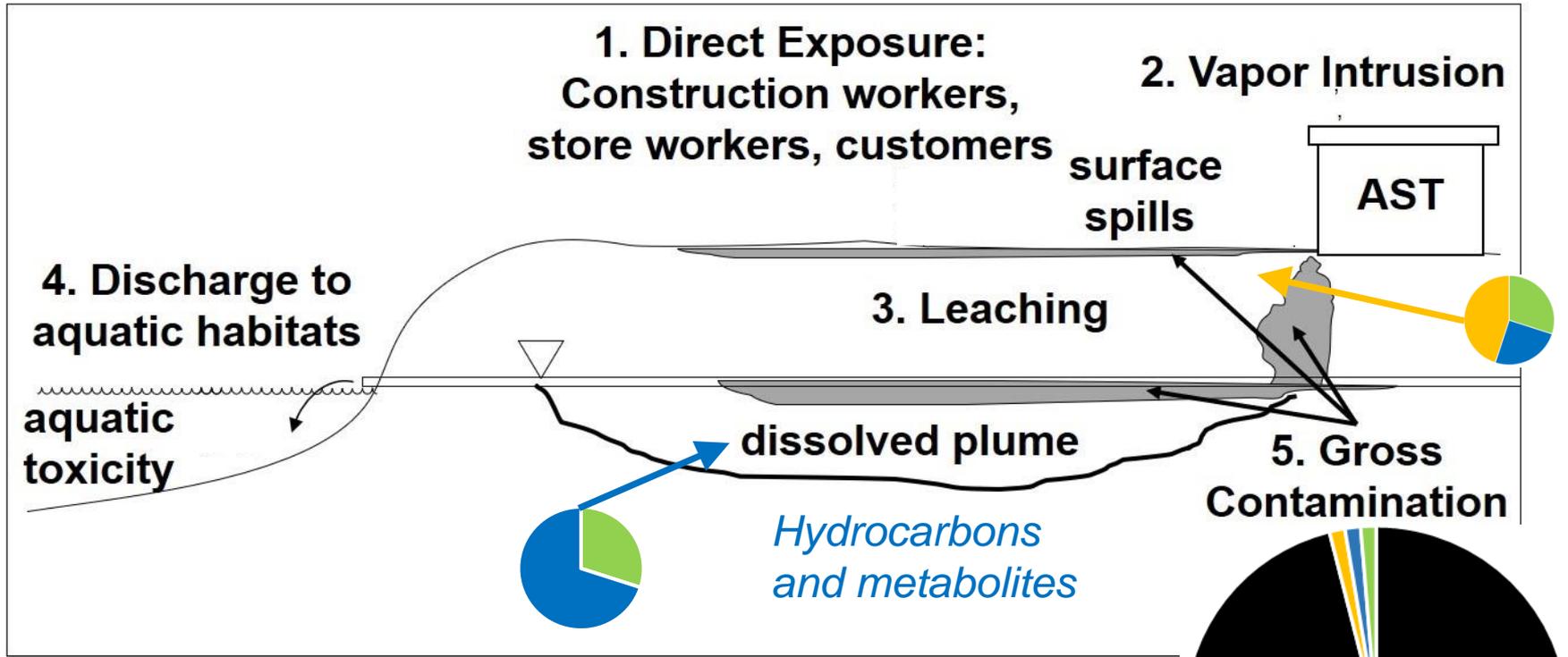
- Have you considered the following:

- Reviewing your chromatograms?
- Fractionating your TPH results?
- Using the silica gel cleanup method to understand the metabolite fraction? (USEPA Method 3630C)



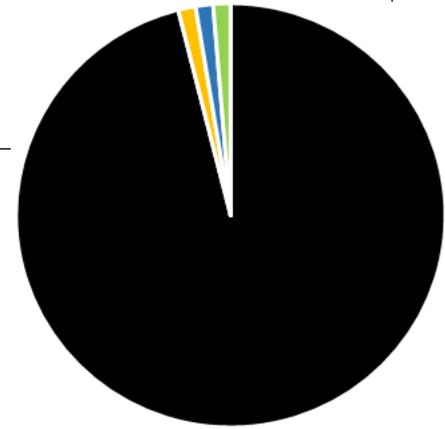
Conceptual Site Model: Where is the Source Mass?

Case Study



- Phase**
- NAPL (non-aqueous phase liquid)
 - Air/Vapor
 - Water
 - Sorbed

- Releases:**
- Gasoline AST
 - Diesel pipeline
- Contamination extent defined using bulk TPH**



Addressing Stakeholder Concerns

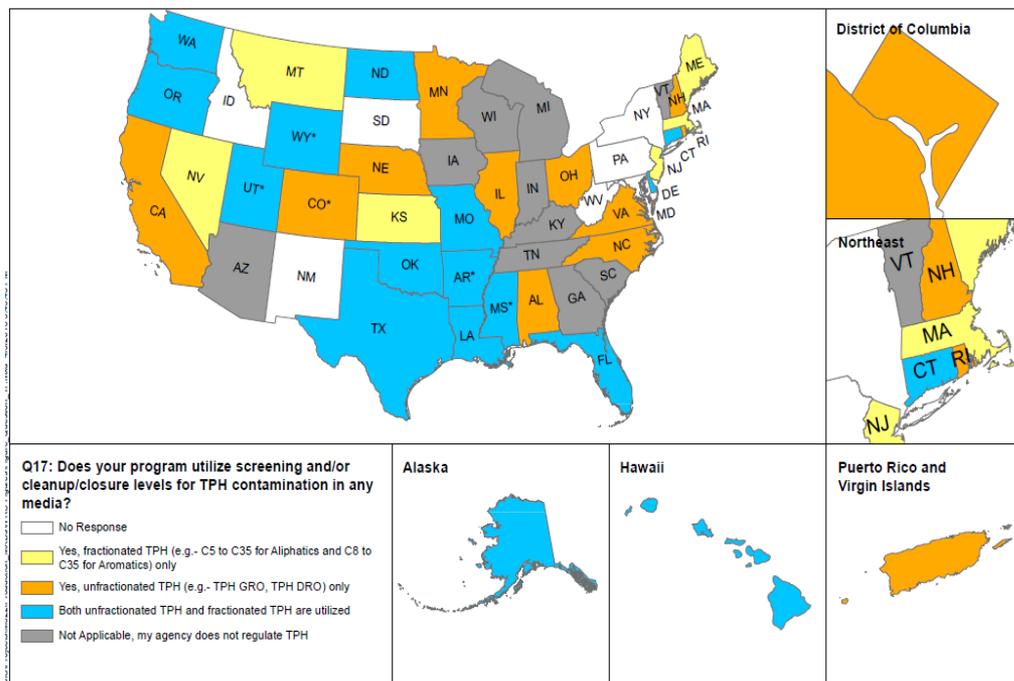


- ▶ Seek to build trust and credibility with communities by addressing real and perceived TPH concerns:
 - Potential Health and Ecological Impacts
 - Assessment of indoor air and sub-slab vapors
 - See ITRC Vapor Intrusion Guidance
 - Aesthetic Criteria
 - State-specific nuisance ordinances
 - Especially odor, visual complaints
 - Potential property devaluation

Use this Guidance!

► Where can I find help?

- On-line calculators (ITRC TPH Risk Chapter 8)
- Examples of Case-Studies using TPH data (HI)
- What are States currently doing with TPH data? (see “TPH State Survey – Screening and/or Cleanup Levels”)



ITRC TPHRisk-1
Figure Q17

Thank You

Follow ITRC:



▶ 2nd question and answer break

▶ Links to additional resources

- <http://www.clu-in.org/conf/itrc/TPHrisk/resource.cfm>

▶ Feedback form – *please complete*

- <http://www.clu-in.org/conf/itrc/TPHrisk/feedback.cfm>

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U.S. EPA Technical Support Project Engineering Forum
Green Remediation: Opening the Door to Field Use Session C (Green Remediation Tools and Examples)
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