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Starting Soon: TPH Risk Evaluation at Petroleum-Contaminated Sites

COUNCIL INTERSTATE TECHNOLOGY
ITRC
ANGLIA 112726

Poll Question

- ▶ TPH Risk Evaluation at Petroleum-Contaminated Sites (TPHRisk-1, 2018)
- ▶ Download PowerPoint file
 - CLU-IN training page at <https://clu-in.org/conf/itrc/TPHrisk/> Under “Download Training Materials”
- ▶ Using Adobe Connect
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 - Select name of link
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Poll Question:

How have you typically evaluated TPH risk? (multiple responses)

Have not evaluated TPH – have based risk assessments on indicator chemicals (BTEX/PAHs) only

Compared bulk TPH data to published screening levels

Compared fractionated TPH data to published screening levels

Conducted risk assessment on TPH fraction data

Use as a semi-quantitative delineation tool

Used to identify fuel type

Welcome – Thanks for joining this ITRC Training Class



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)



Training Course Overview:

Remediation at petroleum release sites is often infeasible for technical or cost reasons. Many of these sites could be depleted in typical indicator compounds, such as BTEXN, but still heavily contaminated in terms of Total Petroleum Hydrocarbons (TPH). The traditional indicator compound approach for managing petroleum contaminants may not fully identify short- and long-term potential environmental concerns, can create delays in project schedules and cost overages for sub-surface utility work or redevelopment. It is important to consider a comprehensive cumulative risk-based approach to more effectively incorporate TPH data in addition to traditional BTEXN data for cleanup and long-term management decisions.

The basis for this training course is the ITRC guidance: TPH Risk Evaluation at Petroleum-Contaminated Sites (TPHRisk-1, 2018). The guidance builds on long-standing and current research and experience, and presents the current science for evaluating TPH risk at petroleum-contaminated sites. The methods and procedures to evaluate human and ecological risk and establish cleanup requirements in the various media at petroleum release sites will assist decision makers in developing and implementing a technically defensible approach. In addition, the guidance provides information and supplemental references to assist practitioners and project managers in the assessment of fate, transport, exposure, and toxicity of TPH. The guidance users will also gain information that may be used in conjunction with classic tiered approaches for risk-based decision making (ASTM 2015b, ITRC Risk 3 2015), including modifications in the assessment and remedial-decision and regulatory framework for TPH impacts through direct comparison to screening levels, site-specific modification of screening levels, and complete site-specific risk assessment for sources, receptors, and pathways, where appropriate.

The target audience for this guidance and training course include:

- Regulators and Program Managers interested in knowing how site management decisions can influence the TPH risk evaluation process.
- Risk assessors new to TPH data or those who want additional knowledge and training in the current methods and common practices for collecting and using TPH data in assessments to more accurately determine human health and/or ecological risks at petroleum-contaminated sites.
- Stakeholders who are either engaged in redevelopment at former petroleum release sites or folks who are involved in community engagement and revitalization activities.

As a participant in this training you will learn to:

- Recognize the ITRC document as a go-to resource for evaluating TPH risk at petroleum-contaminated sites
- Recognize how TPH -impacted media interacts with the environment and changes over time
- Select appropriate analytic method(s) to match site objectives
- Apply the decision framework to determine when a site-specific target level may be more appropriate than a generic screening level for TPH

Training participants are encouraged to view the associated ITRC guidance, TPH Risk Evaluation at Petroleum-Contaminated Sites (TPHRisk-1, 2018) prior to attending the class.

ITRC (Interstate Technology and Regulatory Council) www.itrcweb.org

Training Co-Sponsored by: US EPA Technology Innovation and Field Services Division (TIFSD) (www.clu-in.org)

ITRC Training Program: training@itrcweb.org; Phone: 402-201-2419

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Jennifer Strauss is an Environmental Protection Specialist for the Colorado Division of Oil & Public Safety (OPS) in Denver, Colorado. Jennifer has worked with the Remediation Section since 2012. She reviews and analyzes Site Characterization Reports, Corrective Action Plans, State Lead and Petroleum Brownfields Work plans, and Monitoring & Remediation Reports to support the cleanup of contamination from petroleum storage tanks. Jennifer was involved in the creation of the web-based OPS Petroleum Program Guidance Document and is a member of the Application Review Group for the Recognized Environmental Professional Program. Prior to working with OPS, Jennifer spent eight years at the Pennsylvania Department of Environmental Protection working on stormwater planning and permitting, the Act 2 Voluntary Cleanup Program, and the Corrective Action Program. Jennifer has contributed to ITRC as a team member since 2016 for the Total Petroleum Hydrocarbon Risk Evaluation team. She earned a bachelor's degree in geology from Temple University, Philadelphia, Pennsylvania in 2002.

Manivannan (Mani) Nagaiah is a Project Engineer with Langan Engineering and Environmental Services in Phoenix, Arizona. Mani's career has been focused on the management of small to large-scale, complex NAPL sites as well as petroleum release sites with TPH impacts. Since joining Langan in 2006, he has spearheaded several petroleum release investigations, designed and optimized LNAPL recovery systems and corrective actions, and established technically feasible and practical road maps for site closure. Mani has worked on NAPL/petroleum release investigative and remediation projects in the north-east corridor, Georgia and Florida. More recently, he has moved to Phoenix and the Southwest market. He has authored peer reviewed publications and presented on a wide-range of LNAPL topics in several national conferences. Since 2016, Mani has been an active participant with the ITRC TPH team and is new to the ITRC training team. He is also the co-author of the accompanying HDOH case studies document for the TPH guidance. Mani holds a bachelor's degree in Civil Engineering from ACCET, Madurai Kamaraj University in Tamil Nadu, India (2000) and a master's degree in environmental engineering from Oklahoma State University in Stillwater, Oklahoma (2003). Mani is a registered professional engineer and maintains active licensure in several states.

Rachel Mohler is the Gas Chromatography Technical Team Leader for the Chevron Energy Technology Company in Richmond, California. Since joining Chevron in 2007, her interests have lied in advanced analytical characterization of organic compounds in a variety of matrices. Over the past eight years, she has collaborated with researchers from various disciplines (e.g., biochemistry, toxicology, environmental science, and hydrogeology) to better understand the composition of and the risk posed by organics in the groundwater at historic petroleum release sites. In addition to frequently presenting her research results to audiences at technical conferences, she is also passionate about describing her work to elementary, middle and high school students to promote STEM (science, technology, engineering, and math). Rachel has over twenty publications in peer-reviewed journals, two patents, and serves as a reviewer for multiple technical publications including Environmental Science and Technology (an ACS journal), and Journal of Chromatography A. She has been a contributor and active member of the ITRC TPH Risk Evaluation at Petroleum Contaminated Sites team. Rachel earned a Bachelor's degree in Chemistry from the University of California, Riverside in 2002 and a Doctor of Philosophy in Chemistry from the University of Washington in 2007.

Ross Steenson is a senior specialist geologist with the San Francisco Bay Regional Water Quality Control Board and has worked for the agency since 2008. He has over 29 years of regulatory and professional experience in the investigation and cleanup of a wide variety of contaminated sites. In his current role, he provides technical support to staff, oversees cases, and develops and maintains agency guidance. His technical expertise includes vapor intrusion, contaminated groundwater discharges to surface water, contaminated sediment, and risk assessment. Since 2012, in a team of two, he maintains and updates the agency's Environmental Screening Levels, and is the lead for Total Petroleum Hydrocarbon screening levels. He was the lead author for preparing the agency's 2016 Petroleum Metabolites technical document. He earned a bachelor's degree in science degree in geology from The College of William and Mary in 1986 and a master's of science degree in geology from Miami University in 1991. He has been a certified California hydrogeologist since 1997.

Diana Marquez is an Associate Toxicologist with Burns & McDonnell in Kansas City, MO and has worked for the company since June 1995. She serves as the company's National Practice Leader for Risk Assessment Services. She has over twenty years of risk assessment experience and has worked with a wide variety of sites under CERCLA, RCRA, and state-led programs. She has successfully completed work nationwide for both human health risk assessments and the determination of site-specific cleanup levels. She has direct experience working with large PRP groups on complex sites that require careful negotiations with regulators. Through this experience, she has gained in-depth knowledge of state and federal regulations. She authored 15+ publications on risk assessment, risk-based corrective actions, and vapor intrusion. Diana earned a bachelor's degree in biology from Villanova University in Villanova, PA in 1991 and a master's degree in toxicology from University of New Mexico in Albuquerque, NM in 1992.

Usha Vedagiri is a Principal Risk Assessor and Manager of the Northern California Risk Practice with AECOM located in Oakland, California. Since 1998, Usha has worked at AECOM (formerly URS) specializing in human health risk assessment, ecological risk assessment, risk-based remediation goals, chemical-specific exposure and toxicity assessments and risk management plans. In support of remediation, permitting and exploration/extraction projects, she is responsible for management, scoping and execution of risk assessments, strategy development for risk-based remediation and redevelopment at contaminated sites, and risk identification and mitigation planning for resource development, in the United States and abroad. She has designed sampling and analysis plans and toxicity testing programs for environmental and biological media and evaluated risks related to a variety of chemicals including petroleum hydrocarbons, PAHs, PFAS, PCBs, dioxins, metals, and pesticides in terrestrial, freshwater and estuarine environments. For petroleum hydrocarbons, she has evaluated human health risks using a variety of USEPA and individual state-level guidance and ecological risks using technical methods ranging from screening-level assessments to complex modeling and testing-based approaches. Prior to AECOM, she worked for 8 years in the environmental consulting field with EA Engineering and IT Corporation. Since 2013, Usha has contributed to ITRC as a team member for ITRC's Risk Assessment, Bioavailability in Contaminated Soils, TPH Risk Evaluation at Petroleum-Contaminated Sites and PFAS teams. Usha earned a bachelor's degree in biology from Ethiraj College in India and a master's and Ph.D., in Environmental Science from Rutgers University in New Brunswick, New Jersey.

Jeffrey A. Kuhn is a hydrogeologist and was a program manager for the Montana Department of Environmental Quality (DEQ). Throughout his career Jeff has overseen remediation programs including the Montana Leaking Underground Storage Tank (LUST) Program, Federal LUST Trust Program, Brownfields Program, and DSMOA/FUDS Programs. He also directed research efforts at several complex petroleum projects throughout the state. He had led numerous technical task forces, forums, and work groups, worked as an expert witness on petroleum cases, and served as the LUST Task Force Chair for the Association of State and Territorial Solid Waste Management Officials (ASTSWMO). Jeff also served on ITRC's Board as the State-Member-at-Large. He has participated on many ITRC Teams, such as the Management of Complex Sites Team, LNAPL Team, Petroleum Vapor Intrusion Team, and MBE Team. Jeff currently writes a column for "LUSTline" on site assessment approaches, the use of innovative petroleum remediation technologies, and fuel additives. Jeff teaches geology and natural history in Glacier National Park and leads interpretive hikes for the Glacier Institute and Granite Park Chalet. Jeff has a B.S. degree in Geology and German Language from Juniata College, and an M.S. degree in Geology from the University of Montana, Missoula, MT.

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



TPH Risk Evaluation at Petroleum-Contaminated Sites
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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).

TPH Risk Evaluation at Petroleum-Contaminated Sites (TPHRisk-1, 2018)
<https://tphrisk-1.itrcweb.org/>

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



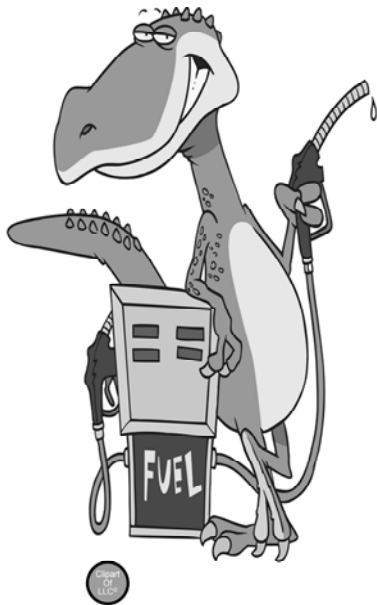
Learning Objectives



- ▶ 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



- ▶ 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

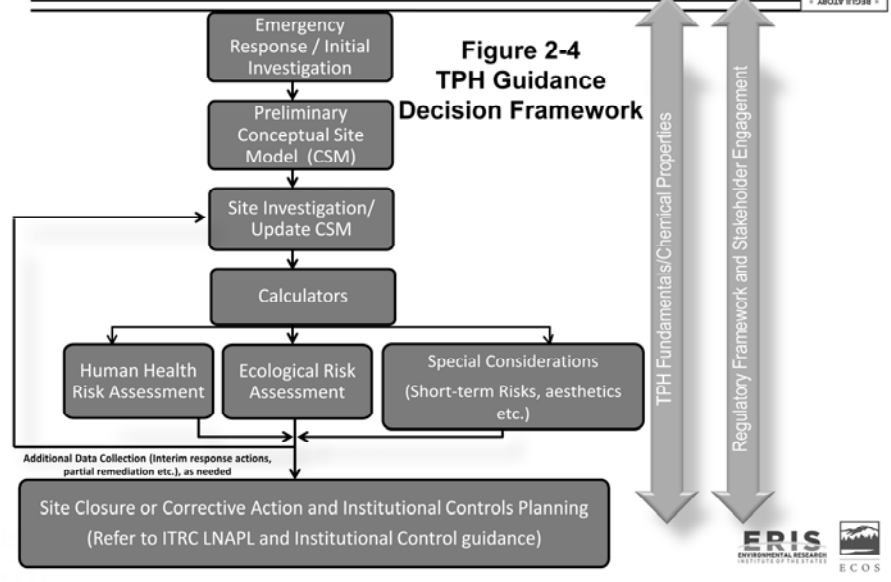


- ▶ Provides practical, applicable guidance on evaluating TPH for risk assessors
 - Regulators
 - Consultants
 - Industry
 - Stakeholders

How to Use This Document



**Figure 2-4
TPH Guidance
Decision Framework**



Case Study: Tank Farm



Case Study



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

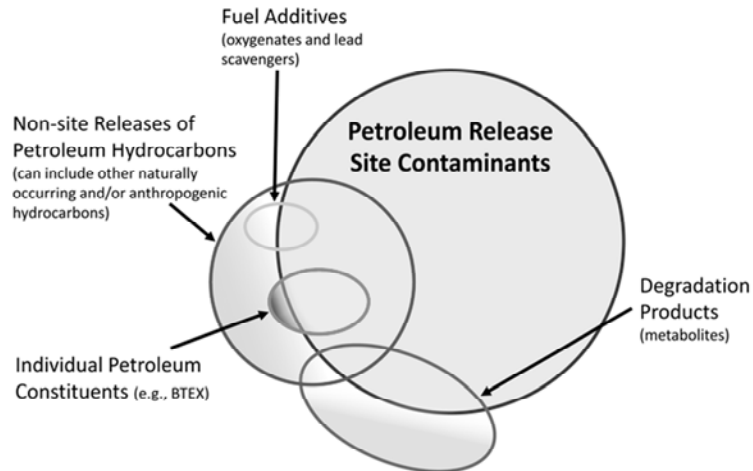
HIDOH Case Study #1 (HIDOH 2018)



How will YOU treat TPH Differently?



Contaminants at Petroleum Release Sites



ITRC TPHRisk-1 Figure 2-2

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

Learn What TPH is



GRO DRO EPH PRO
ETPH PVOG 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



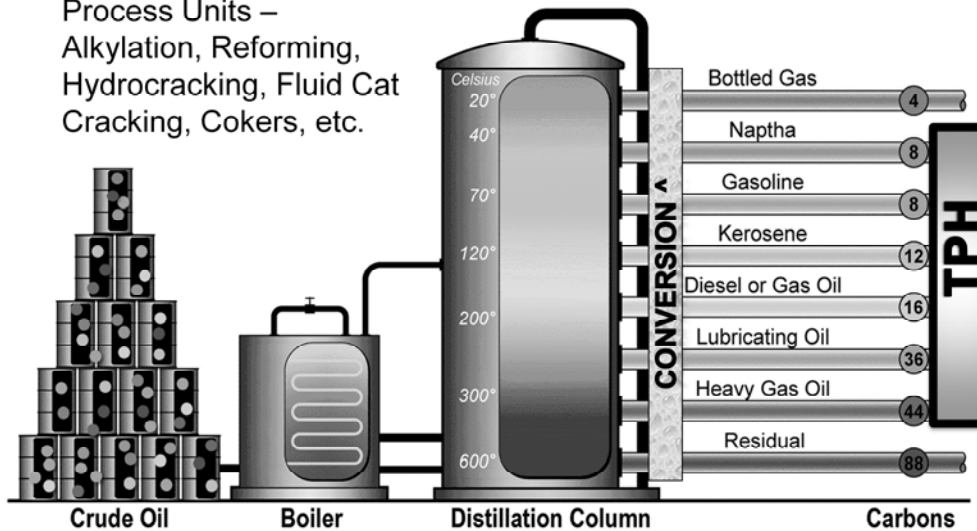
Speaker notes:

In this portion of the presentation, we will understand what TPH is – its sources, constituents, composition and key properties that make it unique. Also, we will use a case study to review the preliminary CSM for a typical TPH release site and work through the interactions with the environment – sources/pathways and receptors. We will also go through an overview of the state of the TPH practice, and pass on to investigative and risk assessment strategies in the subsequent sections.

TPH – Where does it come from?



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



Courtesy of Haley & Aldrich

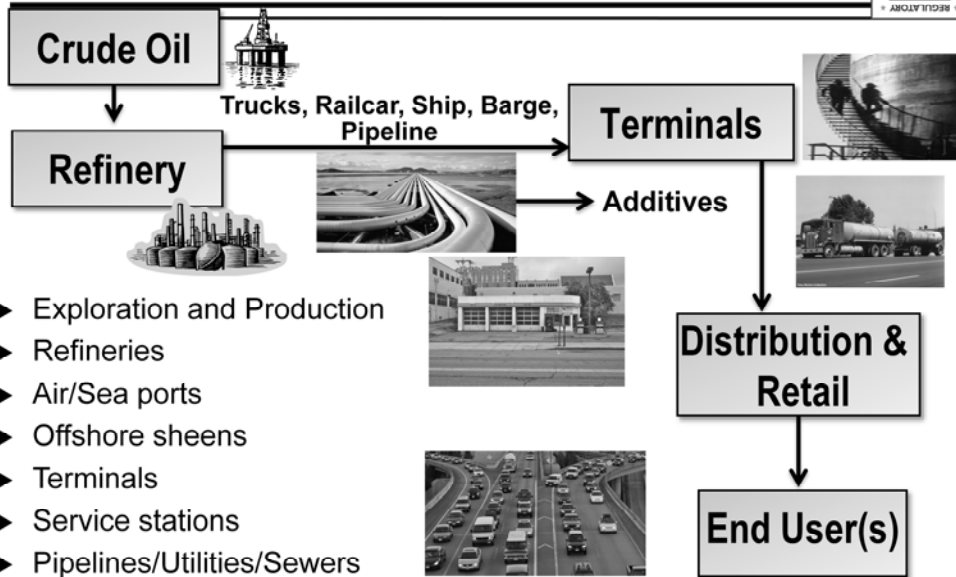
8 Carbon Number



Speaker Notes:

Crude oil and individual refinery products are typically characterized as TPH in environmental media. We are looking at a simple schematic of crude oil processing at a refinery. Crude oil contains hydrocarbons primarily with carbon and hydrogen and includes heteroatoms such as sulfur, nitrogen, or oxygen and inorganic constituents, such as metals. Refining process is essentially distillation and conversion, whereby crude oil is boiled and distillation cuts are taken at different temperatures into various commercial products such as gasoline, kerosene, jet fuel, diesel and so on and do forth. Currently, there are specifications for over 2,000 petroleum products!. In general, TPH includes a carbon range up to C-44.

TPH – Where does it come from?



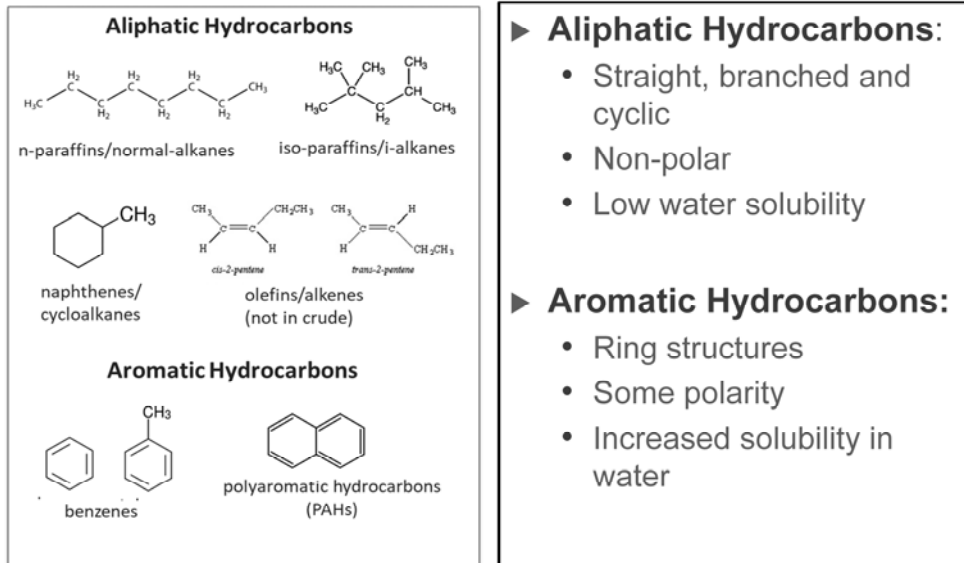
- ▶ Exploration and Production
- ▶ Refineries
- ▶ Air/Sea ports
- ▶ Offshore sheens
- ▶ Terminals
- ▶ Service stations
- ▶ Pipelines/Utilities/Sewers
- ▶ Residential (think heating oil)



Speaker Notes:

What is your typical TPH site?. As you can see, TPH in the environment and human or ecological exposures can occur at any of the stages along the way from the oil wells, through the terminals to the end users. Yes, some of these sites could be your classic LNAPL release site as well. Where petroleum TPH is detected in the environment, there is often petroleum LNAPL not too far way. Participants are encouraged to check out the ITRC documents and training on LNAPL. LNAPL and TPH are often “two sides of the same coin”.

TPH Constituents – Key Properties



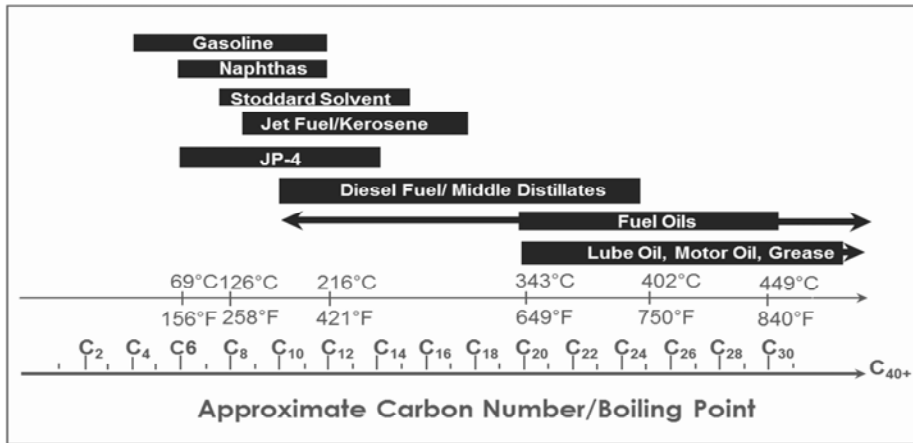
ITRC TPHRisk-1 Figure 4-3

Speaker Notes:

Hydrocarbons can be broadly classified as aliphatics and aromatic. The aliphatics of interest to us are alkanes and alkenes (straight chain, branched and cycloalkanes). Alkenes are less than 5% in fuels. Aromatics are ringed structure hydrocarbons with conjugated bonds – think benzene (the simplest aromatic) and PAHs (like naphthalene, anthracene, phenanthrene etc.)

Key properties that are relevant for a TPH assessment. Aliphatics are non-polar and less water soluble. The aromatics have some polarity and increased solubility in water. Also, in relative terms, the aliphatics have lower boiling point and prone to evaporation than aromatics with the same number of carbons.

What is in that petroleum release?



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

ITRC TPHRisk-1 Figure 4.2 (TPHCWG 1998)

JP – Jet Propellant



Speaker notes:

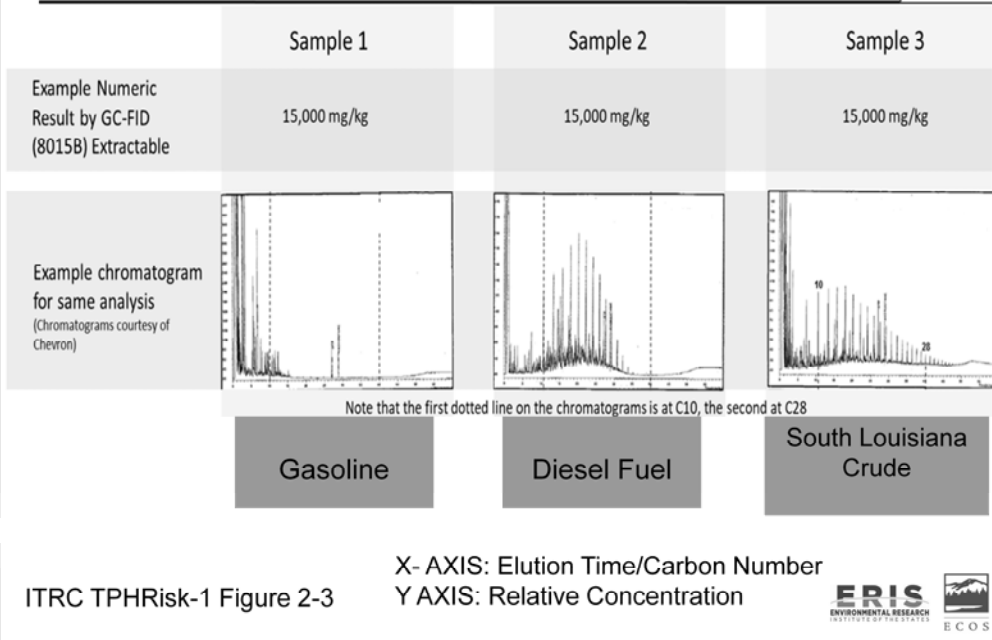
Now we will understand the composition of TPH. Here is a chart showing petroleum constituents and carbon ranges. As noted, products are mixtures of hydrocarbons and the common fuel types overlap in carbon ranges. Those overlapping portions are the same and no method (bulk or speciated) would differentiate them because the components are the same. In terms of risk, if you have hydrocarbon constituents from a certain carbon number range, it does not matter if they are diesel, jet fuel or petroleum.

Bottom-line:

Bulk TPH analysis is not composition specific. Very good screening method – it is generally not suitable for a solid risk evaluation

Products overlap in carbon ranges

Bulk TPH – What's in that number?



Speaker Notes:

This slide presents bulk TPH data using EPA method 8015 from the same site. Although the visual is poor (I am sorry), the x-axis represents elution time/carbon number and the y-axis represents relative concentration.

The same concentration of TPH in different areas of a site might be composed of dissimilar *products*; which in turn, may represent different risks to human or ecological health and the environment. The TPH concentration (estimated at 15,000 ppm) can represent different sources (in this case gasoline, diesel or crude) and composed of dissimilar fractions, which represents different risk to human and ecological health and the environment.

TPH is a complex mixture, not all hydrocarbons and analytical methods are limited.

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!



Speaker notes:

TPH is a quantitative value representing the amount of petroleum related material in a sample – soil/sediment, water or air. It is defined by the analytical method used to measure it, and the methods used can be variable from state to state and even from lab to lab. TPH is essentially the known or assumed aliphatic and aromatic hydrocarbon mixture that is either originally released into the environment or that remains after weathering. And where it can occur can occur as gross impacts in soil or sediment, dissolved hydrocarbons that have partitioned in groundwater or surface water. Or that partitioned from the mixture to the soil air for the air matrix. Not all TPH is from petroleum, and in some cases what is reported as TPH may be non-petroleum material that simply get detected by the analysis. This could include naturally occurring non-petroleum materials, other organic contaminants, or metabolic products of petroleum biodegradation. For interpreting and reporting TPH properly, make sure you have a good conceptual site model and check the regulatory framework at the state or local level.

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.)**

ITRC TPHRisk-1 Chapters 4 and 6



Speaker notes:

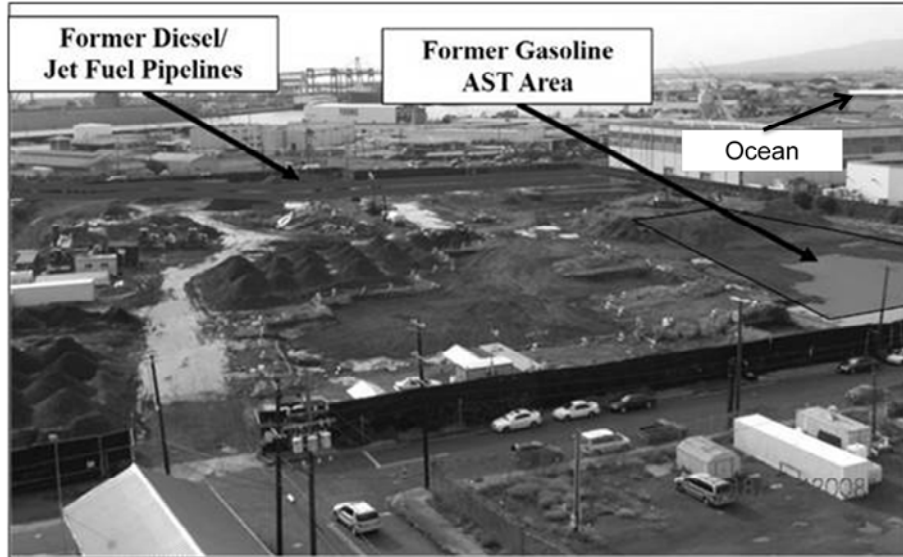
Here is an evolution of the TPH fractionation approach. We have already gone through the challenges of using bulk analysis and the limitation in analyzing hundreds of individual compounds and the limitation of available toxicity data. So what is fractionation?. It is simply the process of differentiating aliphatic and aromatic portion of TPH either instrumentally and chemically. It is an grouping of aliphatic and aromatic compounds (generally about C-44) in which certain carbon ranges having similar properties can be defined and a representative toxicity for the mixture can be assigned for risk assessment purposes. Care must be taken to compare results obtained by methods with different definitions of the carbon ranges. Fraction approach is the key link to relating TPH composition in different media with risk.

Use fractionation analytical methods to quantify fraction concentrations
Assign toxicity values and physical/chemical properties

Case Study: Tank Farm



Case Study



HIDOH Case Study #1 (HIDOH 2018)



Speaker Notes:

Circling back to the case study that we've already mentioned, we're going to talk more about the site features and potential for impacts in nearby areas. The area on the right was the location of the gasoline above ground tanks and the area near the top was the location of the diesel pipeline. All environmental media were impacted, from groundwater to soil gas. The redevelopment company and neighbors were concerned about direct exposure to the soils and groundwater, as well as impacts to the nearby harbor. Care was taken to inform the owners and tenants when sampling was scheduled and that the data generated was sent to the appropriate stakeholders.

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



Speaker notes:

We polled the workgroup early on during the development of the TPH risk evaluation document. Here are some common themes that emerged from the discussion. There can be pitfalls when managing a TPH site. One of the most common is relying on individual constituents (e.g., BTEX) alone when making remedial decisions. Many of them will degrade before the toxic fractions do. Collecting samples for both fractions and individual constituents (e.g., BTEX) is recommended.

Focusing on direct human exposure and leaving out peripheral pathways can underestimate risk. A detailed CSM can help guide risk decisions in the right direction. Also, revising the CSM as the site ages will document changes in the plume and help understand the pockets of residual contamination.

Because petroleum will degrade naturally in the environment, unlike chlorinated compounds, collecting data that takes metabolites into consideration is also recommended.

Another common pitfall is not getting the stakeholders involved in the remedial process early enough. Property owners, neighbors and possible buyers need to be kept informed about progress, setbacks and re-development institutional controls.

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

Answer:

Number 1 – TPH is defined by the analytical method

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 – 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



You've heard from Mani how complicated this TPH mixture can be, so it is very important to have a basic understanding of how the TPH number was calculated, so that these values are not misused to draw erroneous conclusions about a site. TPH is defined by the analytical measurement and after this training each of you should be able to select the best analytical method based on your data quality objectives. You should also be able to properly interpret the analytical results and recognize when the results are questionable. Let's dive in.

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

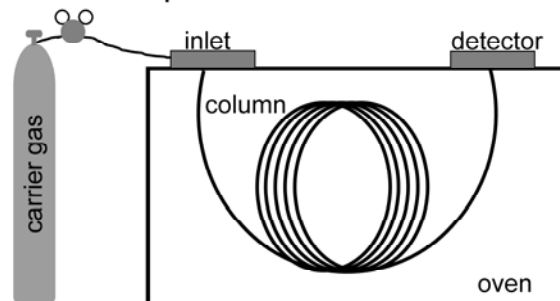
No method can do everything!



TPH is a method defined parameter and since no method can do everything, you should consider the following items in order to select the most appropriate method. What are your data quality objectives and application? Are you looking to delineate the area of contamination or perform a risk assessment? These two objectives could require different analytical methods. Also, certain methods should not be applied to every media. Again, I want to emphasize that TPH is defined by the analytical method used to measure it and results should be reviewed in the context of the underlying characterization and risk evaluation. Methods should be fit for purpose and cost effective

Preferred Laboratory method

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



In order to get some useful information around the what is in the TPH mixture the molecules need to be separated or parsed out. The preferred lab methods use a gas chromatograph also known as GCs. As the name of the technique suggests, this instrument separates molecules in the gas phase to better understand by volatility or carbon number what is present in the complex TPH mixture. There are a variety of TPH analytical methods that are based on analysis by GC.

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, fate and Transport, RSLs, Site Specific Ecological Risk assessment
 - TX1006, MADEP 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

For additional details see Table 5-4 of guidance document, Zemo, 2016 Whitepaper



If you have a choice on what TPH method to use at site, here is a brief summary of TPH methods for water and soil matrices. Bulk TPH methods such as EPA methods 8015, EPA method 8260 or TX1005 are the designed for site assessment, determination of the extent of impacts or quantification of total extractable organics. These methods should be used for every sample collected at a site.

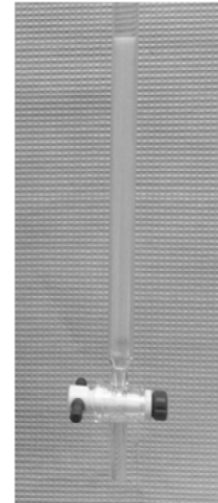
Because it is difficult to evaluate risk for as varied a mixture as TPH, many states have turned to methods that separate the sample into fractions. In order to better understand fate and transport or risk, fractionation methods fractionation methods are frequently applied to a small percentage of the samples to better understand areas hot areas or areas of high uncertainty. Typical methods such as TX1006, MADEP VPH/EPH, or WA Dep of Ecology methods should be used. I'll describe more about what these methods are in subsequent slides.

If you are only interested in hydrocarbons and not total extractable organics or metabolites, EPA method 3630C followed by a bulk TPH method should be used. Additional details on the analytical methods can be found in Table 5-4 of the guidance document or the 2016 Zemo API whitepaper reference in the document. If you are still unsure of what TPH method to use, I encourage you to talk to the chemists at the lab and your risk assessor. If the optimal TPH method has not been used to collected TPH data at a site, Diana will discuss this in the risk section.

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 2 of guidance document



Let's start with a commonly used technique to remove method interferences. EPA method 3630C describes the use of silica gel to remove polar, non-petroleum hydrocarbons and potentially naturally occurring compounds from the analysis. The silica gel cleanup results in a hydrocarbon only sample that can then be analyzed for bulk TPH. The results from this analysis is a TPH number without polar or non-hydrocarbon interferences. This silica gel shown in the column on the right is a fine grain version of the material that is found in various new items such as shoes and suitcases and is used to separate the hydrocarbons from the non-hydrocarbons. There are a variety of cleanup options, but the column cleanup is the most effective at removal of non-hydrocarbons. A lab surrogate should be used to ensure the silica gel efficiently retains the non-hydrocarbons.

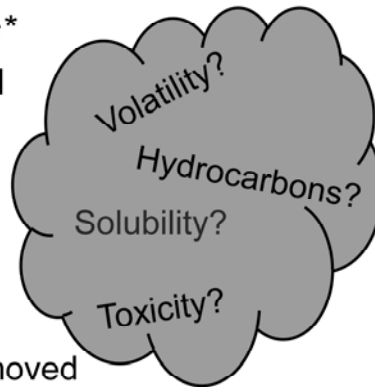
SGC is part of making sure you have your site conceptual model right. Silica gel cleanup is frequently used in the determination of extent of hydrocarbon impact, locations of biodegradation and to better understand where to perform active remediation.

Currently, there is no cleanup method for volatile or air phase samples.

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



Now let's take a look at how silica gel is used for risk assessment or fate and transport purposes. Here silica gel is not used to cleanup the sample but to separate the sample into saturates and aromatics to help answer the questions on the right. Fractionation can be applied to all matrices, NAPL, soil, water, gas, but it is not typically recommended for water because years ago there were a number of studies performed that allowed us to easily predict the hydrocarbons in the water phase. We know that C19 aliphatics or C30 aromatics are not soluble in water. Caution should also be used if fractionating soil gas samples and an alternative fractionation method that does not require the use of silica gel for volatiles should be considered. Please refer to the Fact Sheet in the guidance document for additional information.

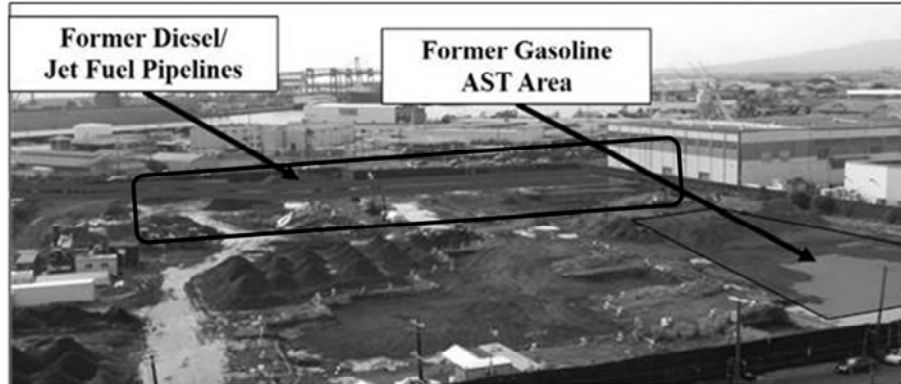
The saturates and aromatics fractions are then injected into a GC to obtain information on equivalent carbon ranges. If you are reviewing fractionation data, be sure to check the carbon ranges, because these will vary depending on where the site is located and the governing agency. Ross and Diana will describe the use of this data in their sections.

Although the fractionation methods can provide detailed information, they do cost more than bulk TPH, they will remove non-hydrocarbons from the analysis and there will be raised reporting limits. The issue around raised reporting limits had a big impact at some sites in Maine where the impacted well was in close proximity to a kerosene tank that spilled. The bulk TPH concentrations were coming back around 200 ug/L however after running the MADEP method, the results were non-detect. This was a problem because there was clearly hydrocarbons present at the site based on odors of hydrocarbons. Be aware that the raised reporting limits can exceed the odor threshold.

Case Study: Tank Farm Application of Analytical Methods



Case Study



- 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

HIDOH Case Study #1 (HIDOH 2018)



Collected groundwater TPH data without and with SGC to determine areas where LNAPL was heavily degraded and likely dominated by TPH-related metabolites

Assess degradation state

Understand what could discharge into a nearby harbor

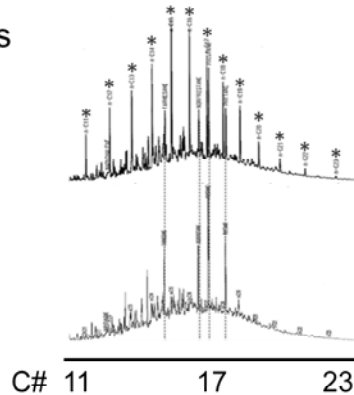
Collected fractionated data to determine carbon range of soil vapors collected around the diesel release

Study recommended considering collecting fractionation data in areas where composition is uncertain or believed to have high variability

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
- ▶ For details ask your chemist



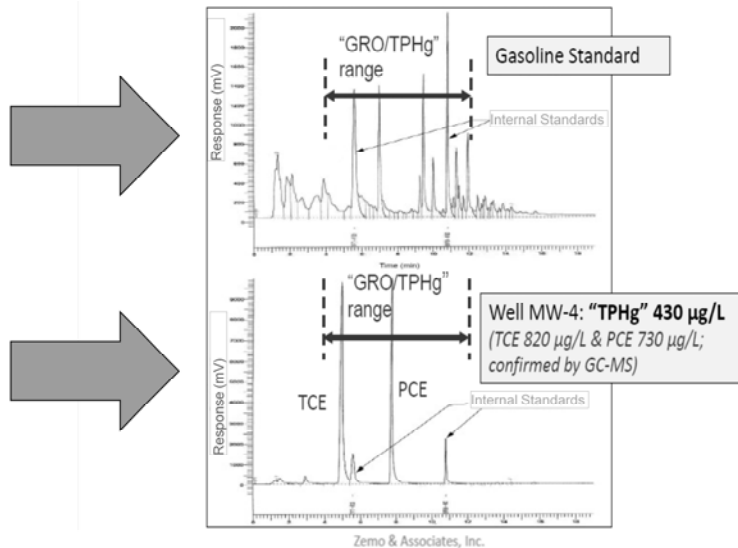
ITRC TPHRisk-1 Figure A5-4



Chromatograms can be provided for the methods mentioned in this section and are more than just pretty pictures. These “pictures” are integrated to yield the TPH values and can provide information on all the items listed here. On the right, I’ve shown two chromatograms collected from the same samples but at different times. As one moves from the left to the right carbon number increases. The samples analyzed here cover carbon numbers 11-23. If the sample is relatively unweathered, a picket fence pattern will stand out as shown by the red asterisks. This pattern is not present in the lower chromatogram and indicates that significant weathering has occurred at the site. On the next couple of slide I would like to demonstrate how chromatograms can be used to interpret what is being quantified as TPH.

PAL: put copy of slide 29 to refer back to Mani’s talk.

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



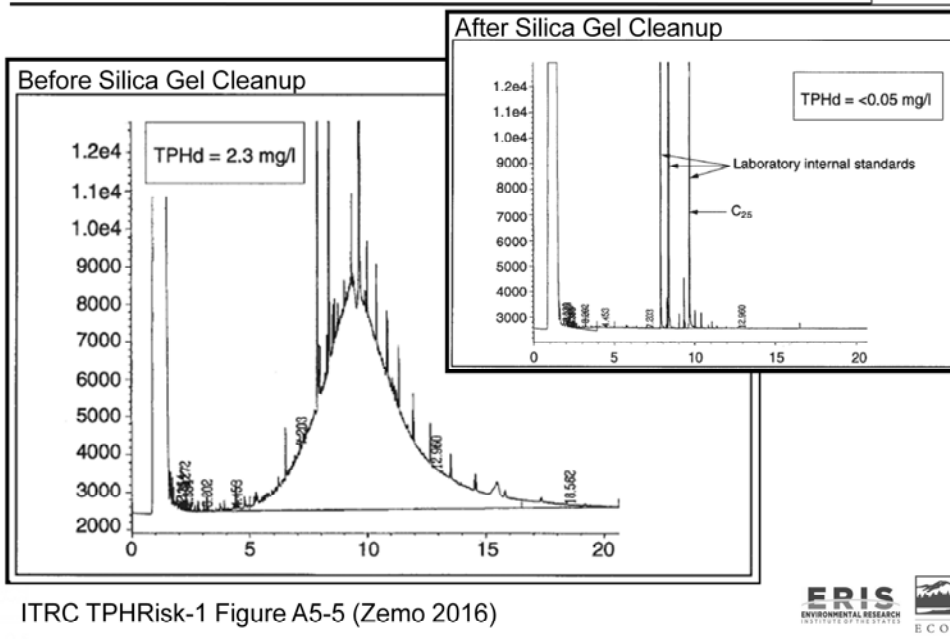
ITRC TPHRisk-1 Figure A5-0

Now I would like to spend a few minutes going through a couple of examples on how chromatograms can be used to quickly identify TPH measurement interferents. The example presented here was a common problem, because historically, at corner strip malls, responsible parties were required to run a TPH by 8015 to analyze for hydrocarbons and 8260 for solvents. Folks ended up chasing phantom gasoline at some sites because solvents will be quantified as TPH. Remember TPH is not always total, not only petroleum and not only hydrocarbons. A review of the chromatograms can be extremely important.

In this example the agency said there was a gasoline plume based on the 8015 TPH results. I would first like to draw your attention to the upper chromatogram showing an expected pattern for gasoline range material. Since gasoline is a complex mixture containing over 300 compounds, one would expect to see a complex chromatogram with lots of peaks. This is exactly what you see in this upper chromatogram showing a gasoline standard.

The chromatogram that was obtained from the well at the site contained essentially four peaks, two of which are internal standards. If there are only a few peaks present in the chromatogram I would be highly skeptical that the GC is actually detecting the presence of hydrocarbons. In this case a GC-MS confirmed that the peaks are chlorinated compounds and not hydrocarbons. Chlorinated compounds can be extracted and quantified as TPH.

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



A site is held open because of TPHd in groundwater. The lab reported a TPHd value of 2.3 mg/L. A review of chromatograms reveals that there are multiple spikes in the chromatogram and a big hump. There are a couple of red flags present in this chromatogram indicating that this sample might not be measuring hydrocarbons. The dead giveaway is the hump and the more subtle indicator is the presence of discreet spikes (or peaks) that are not in a repeating pattern. The hump is centered around the internal standard which is typically a C19 aromatic compound. One would not expect compounds in that carbon range to be very soluble in water. SGC shown in the insert confirmed that these compounds were non-hydrocarbons and the 8015 TPHd concentration lowered to ND.

Poll Question



Poll Question

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

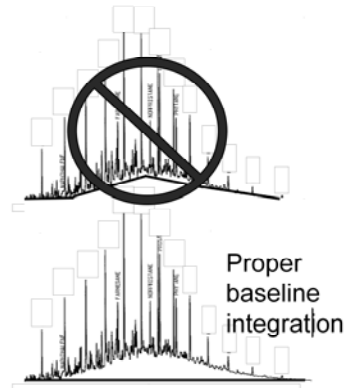


Read the question. The correct answer is False and we are going to describe why on the next slide.

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



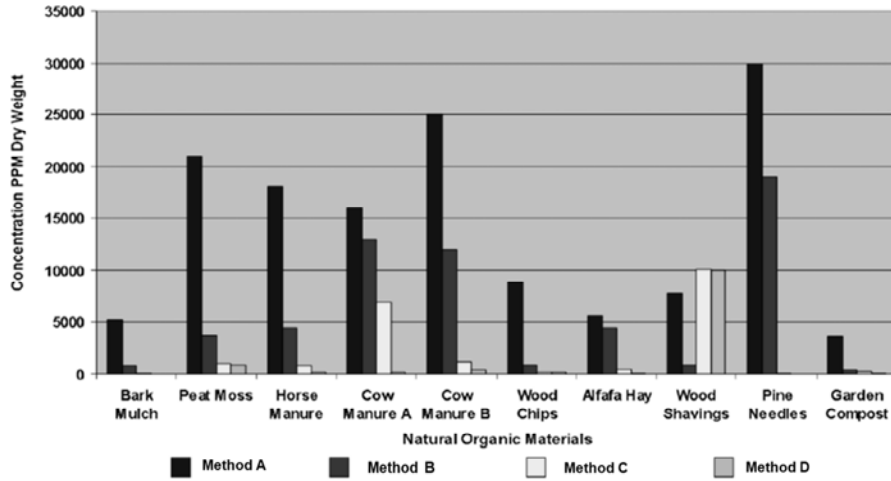
Don't assume a change has occurred at a site if the TPH value suddenly changes!

Modified from ITRC TPHRisk-1 Figure A5-4



When comparing data from different labs and different methods, you need to remember a few things. The first is that you should not assume all data generated by 8015 is the same and comparable. The quantified value depends on the extraction solvent, baseline correction, carbon ranges used for the integration and the calibration standards. Just because the TPH value at a site suddenly increases or decreases, don't assume a change has occurred at a site.

Four TPH Methods will Yield Four Different Results



And will measure "TPH" for non-petroleum hydrocarbons!

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



The second message I want to leave you with is demonstrated by this bar graph. Four methods will yield four different results. Each color bar is a different TPH method and the vertical axis is the TPH concentration. It is readily apparent that there is poor agreement between the methods. Not only will the results be different for the various methods, but non-petroleum hydrocarbons can be quantified as TPH. If your results don't make sense dig into the data a little and review the chromatograms as well as site conditions that could point to naturally occurring compounds

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!

<http://www.buygasmonitors.com/rae-systems-minirae-3000>

Oil-in-soil collected by Maine DEP

<http://www.petrosense.com/PHA-100.html>

www.hach.com/test-kits/immunoassay-test-kits



I would like to conclude by mentioning field methods. These methods can provide valuable information during initial field screening, plume delineation and while excavation is open and ongoing. Examples of field methods include bag headspace using a PID for volatiles and a wet chemistry test like Oil-in-Soil for semi-volatiles. A more in depth description of the pros and cons of these methods can be found in Appendix D of the guidance document. Because the poor precision of these methods, laboratory results should be used to confirm your conclusions.

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

Road Map



- ▶ Why the Guidance?
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- ▶ Questions and Answers

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

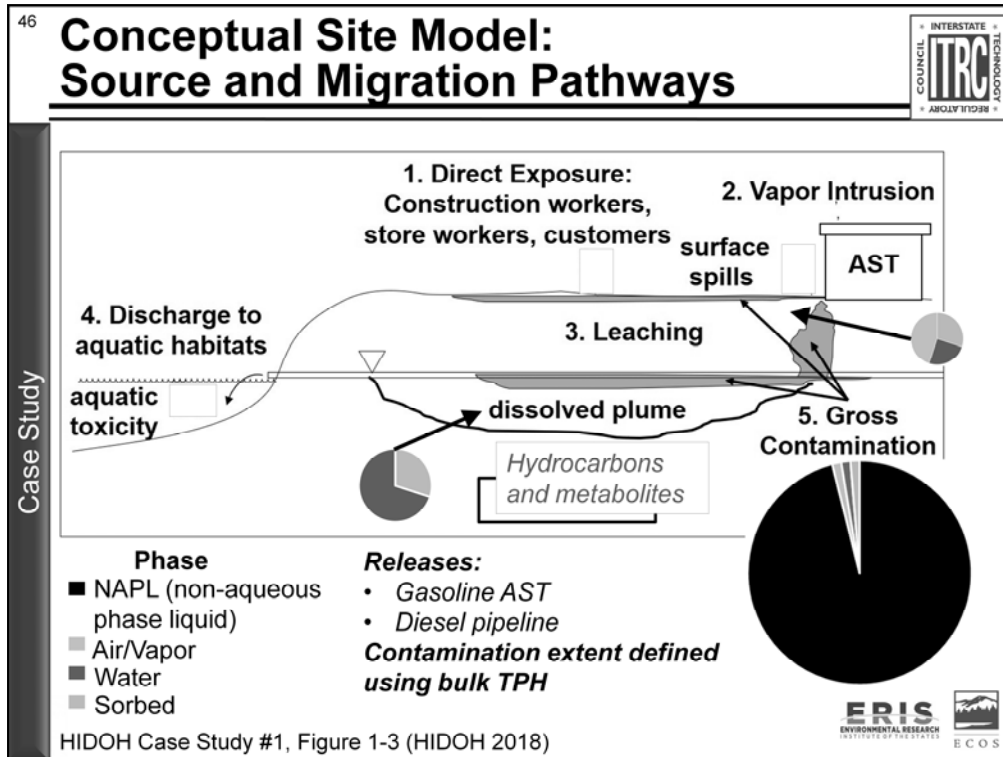


Speaker Notes:

Key Point: TPH composition is important because it impacts risk.

Environmental fate: 1) transport through a compartment (e.g., medium); transfer between compartments (partitioning); and transformation by biological, chemical, or physical processes (weathering).

- Why do we need to understand about TPH in different media?
- How do we collect relevant TPH suitable for a robust CSM and Risk Assessment?
- Effectively evaluate and develop CSMs



Speaker notes: Key Idea: The composition of TPH in a sample from any medium affects risk. It's critical to understand how the composition in the vapor and dissolved plumes differ from the source zone due to partitioning and transformation processes.

Former Fuel Tank Farm CSM from the Hawai'i-hosted case studies for the guidance.

- Releases of gasoline and diesel from an aboveground storage tank (AST) and a diesel pipeline abandoned in place.
- The extent of contamination has been defined using bulk TPH analyses (e.g., TPH-gasoline, TPH-diesel, etc.)
- Areas of gross contamination or presence of NAPL (residual or mobile). NAPL has reached the shallow groundwater table (5-10 feet bgs)

1. Shallow soil - pipeline
2. Subsurface soil/groundwater beneath the AST

Pathways and concerns are listed on the figure: [ONLY POINT OUT ONE OR TWO]

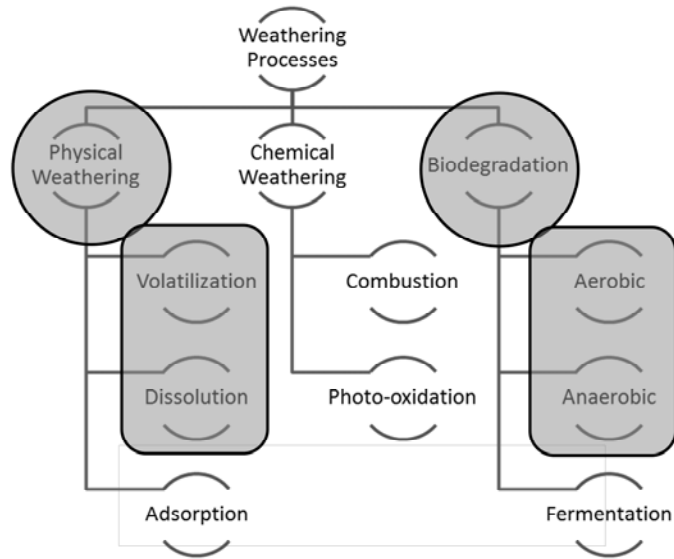
1. Direct exposure risk
2. Vapor intrusion risk (note: impacts are shallow)
3. Leaching to groundwater
4. Contaminated groundwater migration to aquatic habitats
5. Gross contamination (NAPL)

Pie Charts (animation) – These pie charts are intended to convey relative hydrocarbon mass (size of pie) and phase (oil/NAPL, vapor, water, sorbed).

Over 99% of the hydrocarbon mass is in the NAPL.

Figure Source: HIDOH Case Study #1 Figure 1-3 with pie charts created by the Fate team. Relative proportions estimated.

Weathering Processes Overview



ITRC TPHRisk-1 Figure 4-8



Speaker notes: Key Idea: We emphasize the more dominant weathering processes in the coming slides: volatilization, dissolution, adsorption, and biodegradation (both aerobic and anaerobic).

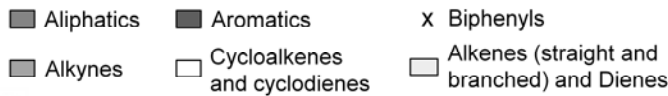
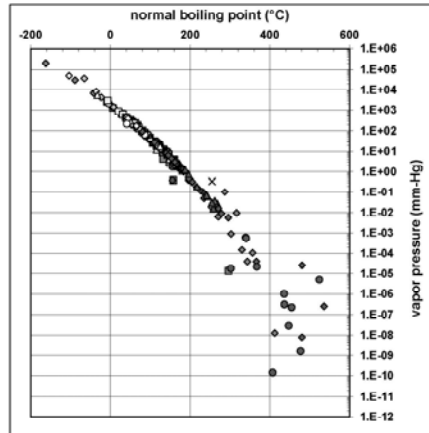
Point to the guidance for further information.

Figure Source: ITRC TPH Risk Assessment Guidance

Partitioning: Oil to Vapor



Boiling Point vs. Vapor Pressure



Graph courtesy of Shell

- ▶ 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



Speaker notes: Key Idea: Smaller hydrocarbons are more volatile than larger hydrocarbons. TPH vapor composition is dominated by these smaller aliphatic and aromatic hydrocarbons.

Explain Graph:

This figure introduces the simplest case, partitioning of hydrocarbons to vapor.

- The x axis is boiling point so this corresponds to retention time in a gas chromatogram.
- The y axis is vapor pressure.
- The colors differentiate the many classes of hydrocarbons such as alkanes, alkenes, alkynes, aromatics and so on. Let's focus on the green (aliphatics) and blue (aromatics). [DON'T ANNOUNCE ALL THE CLASSES]
- Vapor pressure is inversely correlated with boiling point for all hydrocarbons, which is why we call this a simple case. Note the scatter at the bottom of the chart is related to the difficulty in measuring lower vapor pressures.

Additional notes:

Boiling point = temperature at which liquid pressure equals the vapor pressure. Example: propane (C₃H₈) is a gas at normal surface temperatures and pressures so keeping it in storable liquid form requires refrigeration.

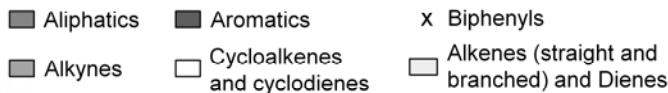
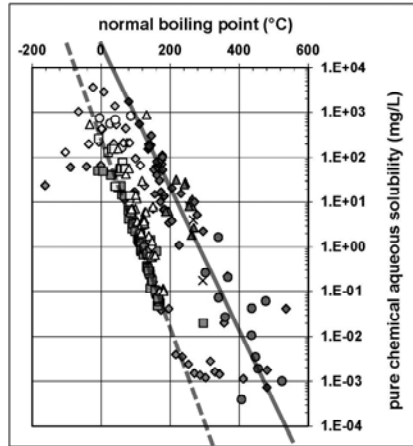
USEPA considers a chemical volatile if VP greater than or equal to 1 mm Hg. This corresponds to the boiling point of n-decane (C₁₀H₂₀).

Figure Source: George DeVaul, Shell, 9/05/18, using TPH Criteria Working Group data (augmented)

Partitioning: Oil to Water



Boiling Point vs. Aqueous Solubility



Graph courtesy of Shell

- ▶ 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



Speaker notes: Key Idea: Smaller hydrocarbons more soluble than larger hydrocarbons, however there are differences based on chemical class/structure. The composition of the TPH water-soluble fraction likely is dominated by aromatics with some other hydrocarbons. The aliphatics generally speaking are not soluble. This is important for characterizing risk related to drinking water exposure and exposure to ecological receptors.

Explain graph:

This figure introduces partitioning of hydrocarbons to water, which is more complex than our previous slides on oil partitioning to vapor.

- The x axis is boiling point.
- The y axis is aqueous solubility.

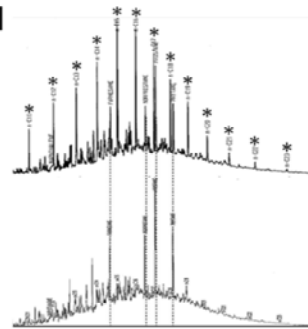
Similar to volatility, smaller compounds have greater solubility than larger compounds, but molecule structure contributes to significant variation. The TPH analysis can capture all of these soluble constituents.

Figure Source: George DeVaul, Shell, 7/17/18, using TPH Criteria Working Group data (augmented)

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

ITRC TPH RISK-1 Figure A5-3



Speaker notes: Key Idea: Biodegradation is well documented as a major contributor to hydrocarbon mass reduction in the environment. The process of biodegradation generates petroleum metabolites that can be further degraded.

Hydrocarbons are susceptible to biodegradation particularly under aerobic conditions, but also under anaerobic conditions. The necessary conditions occur in the majority of soils (e.g., microorganisms capable of utilizing HCs, moisture, oxygen, nutrients).

Most of us are familiar with hydrocarbons tendency to be degraded rapidly and/or over short distances in aerobic conditions. Unless you're new to the industry, you've probably observed this at numerous sites.

Anaerobic biodegradation occurs, but it is much slower. Another way to say this is that it is inefficient, otherwise we wouldn't have oil reservoirs. Notes on metabolites – are susceptible to further biodegradation there just can be a local buildup due to limited availability of electron acceptors (e.g., oxygen).

Diagram: MAY NOT BE NECESSARY TO DESCRIBE THE DIAGRAM IF PREVIOUSLY DESCRIBED IN THE LAB METHODS SECTION

Additional notes:

Occurrence of biodegradation typically assessed using historical trends in contaminant concentration data, water geochemistry data, and measurement of biogases

Rates – Something to keep in mind about rates of biodegradation is that it will depend on the phase. Biodegradation is a stepwise process involving many steps. NAPL tends to take longer to degrade than vapor or water plumes – there is more mass and therefore more electron acceptor demand (e.g., oxygen)

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

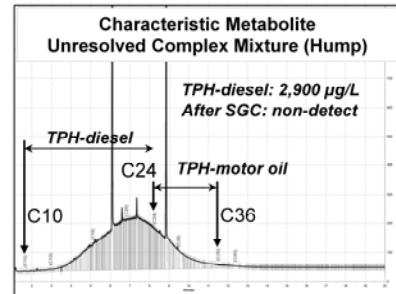


Table values from USEPA Estimation Parameter Interface Suite
Chromatogram from CA site



Speaker notes: Key Ideas listed below:

- Petroleum metabolites are produced during weathering, primarily biodegradation but also photooxidation.
- Metabolites have oxygen in the molecule, are polar (meaning the electrons are not shared equally), and preferentially partition into water.
 - Describe the solubility table: point out differences in solubilities and potentially boiling points
- Metabolites are primarily measured via the extractable TPH analysis when silica gel cleanup is not used. Note that there may be gasoline range metabolites (see 2-hexanone BP in table – that's about C8).
 - Identifying metabolites involves using multiple lines of evidence, several of which are on the slide
 - Chromatogram: Point out the overlap with both the TPH-diesel and TPH-motor oil range
- It has been my observation that at many sites where TPH is tested both with and without SGC, the TPH concentration in groundwater is dominantly metabolites.
- Lastly, the metabolites may pose toxicity different from the parent compounds and would require a different risk evaluation.

Additional notes:

The example chromatogram is one where metabolites were inferred based on multiple lines of evidence: chromatogram matching (e.g., Lang et al. 2009 and Zemo et al. 2003 and 2016), bulk TPH analysis with and without SGC (reminder: using SGC prevents metabolite detection), and CSM (solubility, source location).

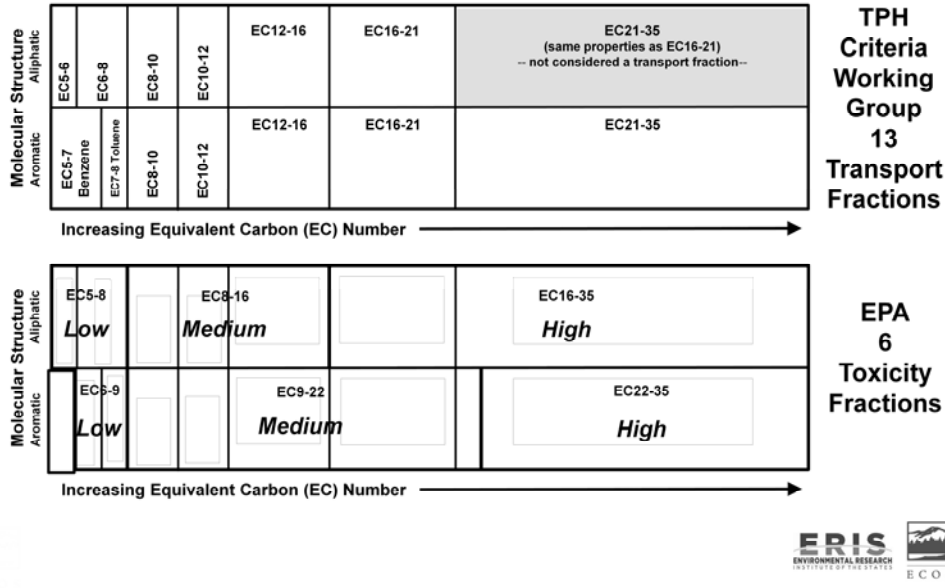
We're using one term "metabolites" to keep things simple. Use of metabolites for photo-oxidation products is not strictly correct. Other terms include polar compounds or polar metabolites. These compounds include alcohols, aldehydes, esters and carboxylic acids. Similar compounds are degradation products of natural organic matter. The source of the oxygen is water or aquifer sediment.

Sources:

Table based on phys/chem properties from USEPA Estimation Parameter Interface (EPI) Suite.

Chromatogram from petroleum site in CA.

Example TPH Fractions: TPH Criteria Working Group vs. EPA



Speaker notes: **Transition/Pivot from talking about classes of hydrocarbons to TPH fractions as vehicle/tool for conveying both composition and risk at the same time. Reminder: TPH composition affects risk and something that is unique to TPH risk assessment is the use of fractions.**

The use of a TPH fraction approach with fractionation methods is the considered best for assessing TPH risk because the approach provides accurate hydrocarbon quantitation aligned with toxicity values and physical/chemical parameters. It can be helpful to think in terms of TPH fractions (similar groups of hydrocarbons) for both composition and risk. Here we provide examples of two fraction approaches and in the interest of time will use the simpler one in the coming slides to illustrate TPH composition changes due to weathering. Why? Because TPH composition is critical for understanding risk.

Explain Diagrams:

- Each diagram divides the hydrocarbons into 2 major classes: aliphatics on top in green and aromatics on the bottom in blue
- Each class is sliced into the smaller fractions based on equivalent carbon (EC), increasing from left to right on the x axis.
- TPH Criteria Working Group – The top diagram shows the 13 TPHCWG “transport” fractions (the 14th Fraction, high-boiling aliphatics, is not considered mobile). Starting from the left, each successively larger carbon fraction has transport properties that are about an order of magnitude less. So, by mid-diagram, the fractions are about 4 orders of magnitude less volatile and soluble.
- USEPA – These fractions are based on available toxicity information and are larger simply due to limited availability of toxicity criteria.

Since it is easier to think about TPH composition/risk in the 6 fractions rather than 13 (or 14) fractions, we will use 6 EPA fractions (low, medium, high, aliphatic vs. aromatic) to illustrate TPH composition in following slides.

Additional Notes:

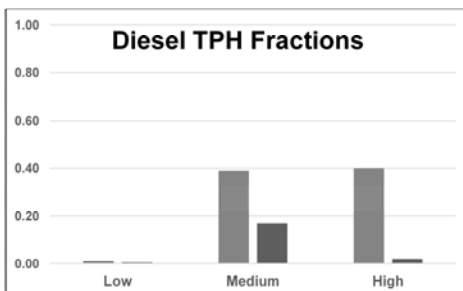
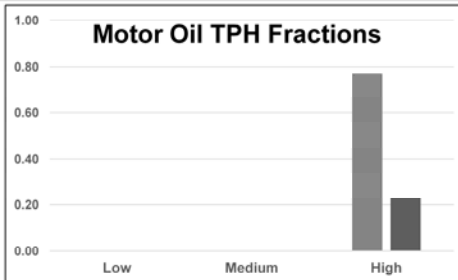
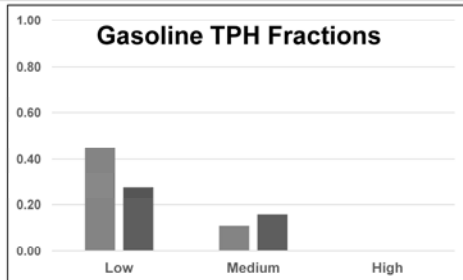
This comparison is for discussion purposes and is not advocating for any particular fraction approach. Other agencies employ a fraction approach but the fractions differ. For example, in Europe, this is referred to as the hydrocarbon block method where the blocks are 3 carbons each (i.e., TPH carpaccio).

Figure Source: Created by the Fate section using the EC and molecular structure from the TPHCWG and USEPA

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



Speaker notes: Key Idea: TPH fraction composition depends first on the oil/fuel (NAPL) composition and then weathering processes. On this slide, we start with the basics: NAPL composition.

Explain how to read the graphs:

- The 3 graphs present the TPH fraction composition for three different TPH mixtures: gasoline, diesel, and motor oil.
- X axis shows the presence of the 6 conceptual fractions in increasing equivalent carbon number: Light, Medium, and High. Colors differentiate the two major hydrocarbon classes: aliphatics (green) and aromatic (blue).
- Y axis is the proportion with a maximum value of 1. For each graph, the total fraction proportions are 1 (100% by weight). For the motor oil, about 76% is heavy aliphatic in this example

Compare two of the mixtures only: gasoline versus motor oil or gasoline versus diesel

Although we are deferring risk discussion to the next section, keep in mind that once you select the fractions and tox values, you can mentally switch back and forth between composition and risk. The fraction composition (e.g., light aliphatic, medium aliphatic, etc.) of different NAPLs are important for risk

Figure Source: Graphs created for training. Fraction composition developed using ATSDR documents and USEPA TPH fractions.

NAPL: TPH Composition Change Due to Weathering



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

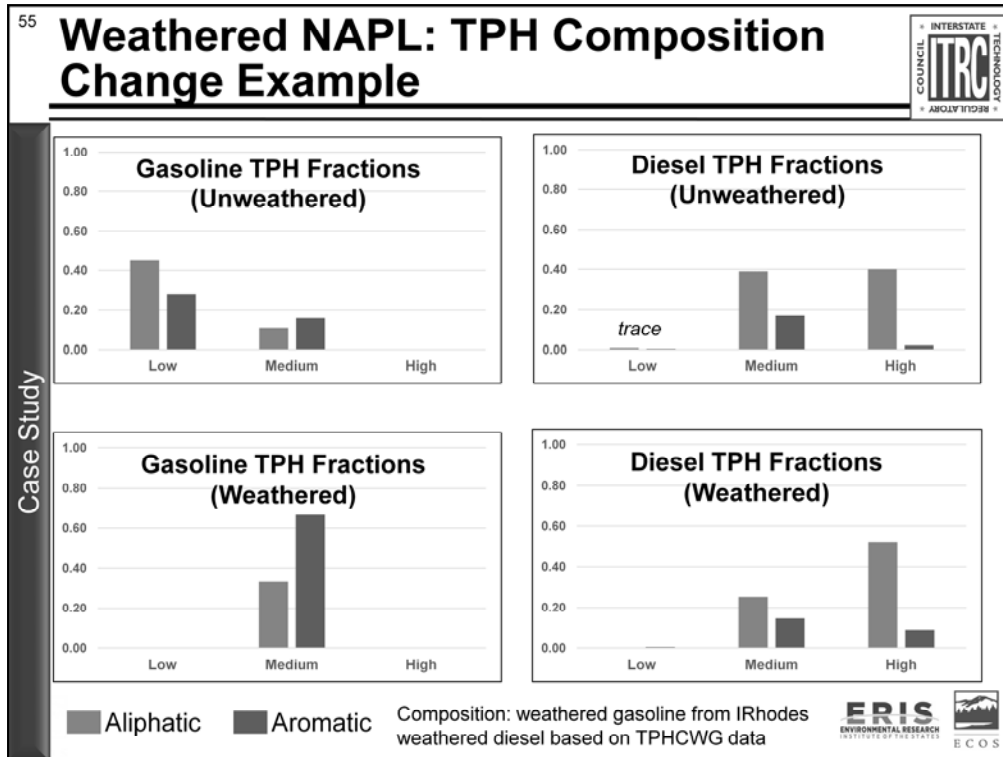


Printed from: Interstate Technology & Regulatory Council (ITRC), 2018. *Light Non-Aqueous Phase Liquid (LNAPL) Site Management: LCSM Evolution, Decision Process, and Remedial Technologies.* LNAPL-3. Washington, D.C. <https://lnapl-3.itrcweb.org>.

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





Speaker notes: Compare these examples of fresh and weathered fuels released at our case study site: gasoline and diesel.

Graphs: Already explained, repeat as needed.

Gasoline:

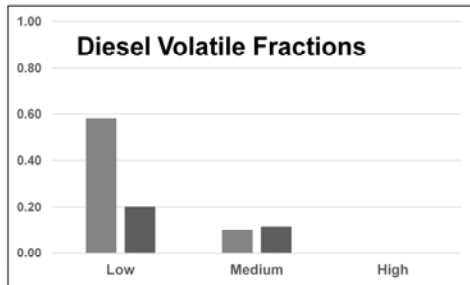
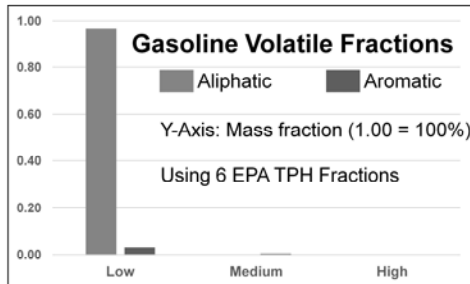
- As you recall from our partitioning graphs, smaller hydrocarbons are the most volatile and soluble constituents
- Compare (unweathered vs weathered gasoline): In this example the low carbon range fractions are completely depleted.
- In the absence of fractionated data, you could infer the fractions by reviewing the sample chromatograms from your bulk TPH analyses.

Diesel:

- Compare overall relative proportional shifts between gasoline and diesel: This weathered diesel example doesn't show quite as much depletion as the preceding weathered gasoline example, but it does illustrate the overall shift to proportionally heavier fractions.
- Compare Medium Aliphatic vs. Aromatic fractions for the unweathered and weathered diesel: There is still a moderate proportion of the medium range aliphatics (probably branched hydrocarbons) while the medium aromatics have been more strongly depleted.
- Again, with knowledge of tox values, you can mentally estimate relative risk.

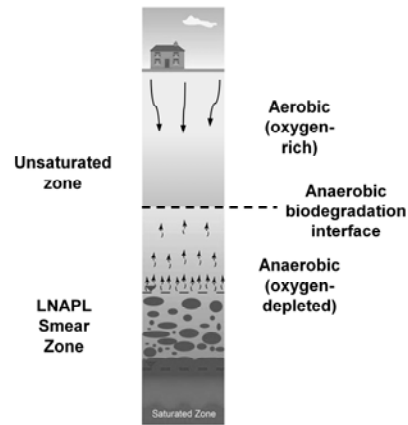
Figure Source: Graphs created by the Fate section. Unweathered NAPL graphs are the same as Slide 74. Weathered composition data from Ileana Rhodes of GSI for weathered gasoline and from TPHCWG for weathered diesel

Vapor: TPH Fraction Composition Near NAPL and Fate/Exposure



Composition based on Uhler et al. 2010

TPH Vapor Attenuation to Surface in Presence of Oxygen



Source: ITRC PVI Guidance 2014



Speaker notes: Key Idea: TPH fraction composition in the vapor phase typically consists of small aliphatics and aromatics, which is important to understand because this relates to vapor intrusion risk. TPH vapors attenuate sharply in the vadose zone over short distances in the presence of oxygen.

Graphs: Already explained, repeat as needed.

Near NAPL TPH Vapor Composition Notes:

These graphs are constructed in the same fashion as the ones for NAPL, with the exception they present vapor compositions.

- The volatile hydrocarbon fractions are light aliphatics and aromatics, and to a much lesser extent medium aliphatics and aromatics
- The vapor phase fraction composition is enriched in these lighter fractions even for middle distillate fuels (e.g., Jet A, diesel)
- Total concentrations of gasoline vapors estimated at 100,000s ug/m³ versus less than 1,000 ug/m³ for diesel

Fate and Transport Effects on TPH Vapor Composition notes:

- Hydrocarbon vapor plumes typically are limited to thin zones around NAPL and heavily impacted media as a result of aerobic biodegradation in unsaturated zone.
- See ITRC Petroleum Vapor Intrusion guidance for further information on hydrocarbon vapor fate and transport

Case Study Notes:

- In our case study, the only area where there is a vapor intrusion concern is in the release area due to significant impacts (gross contamination/NAPL) in shallow soil.

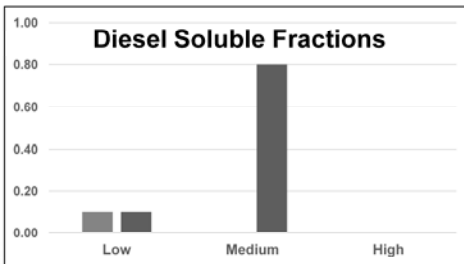
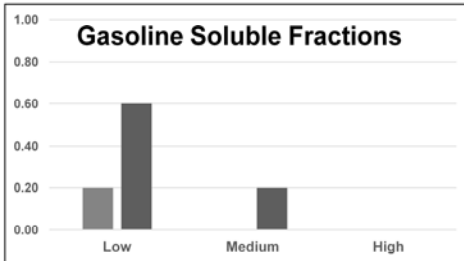
Figure Source: Graphs created for training. Vapor fraction composition estimated based on Uhler et al. 2010. The vapor attenuation diagram is modified from ITRC PVI Guidance Figure 3-1.

Uhler, A.D., K.J. McCarthy, S.D. Emsbo-Mattingly, S.A. Stout, and G.S. Douglas. 2010. Predicting Chemical Fingerprints of Vadose Zone Soil Gas and Indoor Air from Non-Aqueous Phase Liquid Composition. *Environmental Forensics*, 11: 342-354. [cited in Workbook]

Groundwater: TPH Fraction Composition (Near NAPL)



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



Composition based on Zemo and Synowiec (1995)

■ 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



Speaker notes: Key Idea: TPH fraction composition in the water phase typically consists predominantly of small aromatics, with some small aliphatics and some medium aromatics. Such a composition has implications for drinking water exposure to humans and direct contact concerns for ecological receptors.

Graphs: Already explained, repeat as needed.

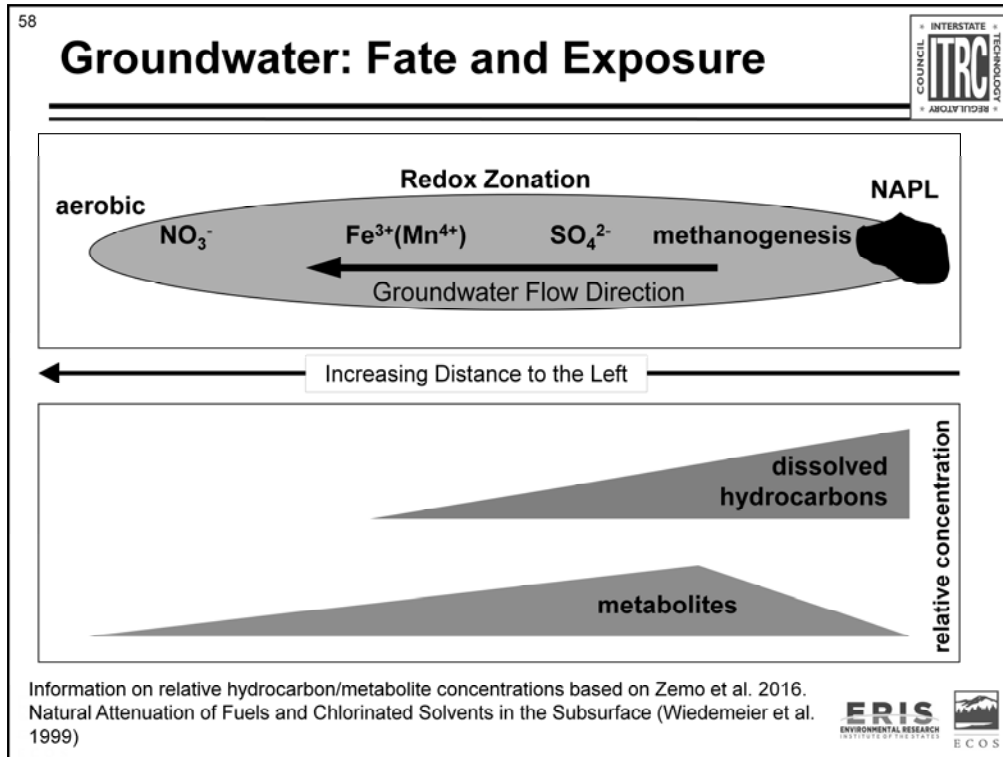
These graphs are constructed in the same fashion as the ones for NAPL, with the exception they present water-soluble TPH compositions.

- The soluble hydrocarbon fractions are light aliphatics and aromatics, and to a much lesser extent medium aromatics
- TPH groundwater plumes can be thin bands around NAPL/heavily impacted media or cigar-shaped plumes

Much of the dissolved mass can consist of metabolites at older, more weathered sites. These typically are mainly detected in the bulk TPH-diesel analysis and as well as the TPH-motor oil analysis.

- Max concentrations of dissolved hydrocarbons for TPH-gasoline are 200 mg/L and about 1-5 mg/L for diesel.
- Both TPH and metabolites attenuate with distance from the source

Figure Source: Graphs created for training. Water soluble fraction composition estimated based on Zemo and Synowiec 1995
 Zemo, D.A. and K.A. Synowiec. 1995. TPH Detections in Groundwater: Identification and Elimination of Positive Interferences. In Proceedings of the 1995 Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, p. 257-271. Westerville, Ohio. National Ground Water Association.



Speaker notes: Key idea: TPH composition changes along the flowpath. This differential in fate affects composition, which in turn affects exposure.

General: Both charts start with the source at the right with groundwater flow to the left [just like the Case Study CSM figure]. Otherwise, the charges are not related.

Top Diagram: TPH composition changes along the flowpath due to:

- differential transport and sorption of individual hydrocarbons
- different susceptibilities of hydrocarbons to biodegradation,
- different redox zones along the flowpath. The chart shows the classic electrochemical sequence from right to left

Bottom Diagram: Looking at bulk TPH composition for the hydrocarbons and metabolites.

- Hydrocarbons: highest concentrations near the source and diminishing downgradient
- Metabolites: the metabolites are generated via biodegradation so concentrations increase downgradient of the source area and highest parts of the dissolved hydrocarbon plume. They also attenuate. Over time, metabolite concentrations may increase near source (the apex of the triangle may shift to the right)

The metabolite extends further than the hydrocarbon plume and has implications for exposure.

The x-axis can be either distance or time

Figure Source: The redox zonation concept is not new. This figure is. The relative concentration figure also is new, partly based on Zemo et al. 2016 and partly team members experience.

Poll Question



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



Multiple answer

General: The potential hydrocarbons present are limited by the composition of the released fuel/oil, partitioning (which compounds dissolve in water or might have been depleted via volatilization) and susceptibility to biodegradation. Since biodegradation is all but certain to occur, petroleum metabolites will be generated.

1-We would not expect all fractions or chemicals considering oil/fuel type and weathering processes

2-Low aromatics are more soluble, however they constitute only a small fraction of diesel and are more likely to have been depleted to physical and biological weathering.

3-High aliphatics have low to trace solubility and are not likely to partition into water to any significant degree.

4-Petroleum metabolites are soluble and more likely to be present than not, given the large release volume and certainty that biodegradation is occurring.

5-It is less likely that no TPH fractions or petroleum-related compounds are present given the large release and age.

Keep in mind that composition can be determined at your site by (1) use of a fractionation analysis and (2) analyzing extractable TPH both with and without silica gel cleanup.

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



Speaker notes: Key Idea: It's important to understand how TPH composition changes because it affects toxicity and the nature of exposure (vapor inhalation, groundwater ingestion and dermal contact, etc.)

After release, hydrocarbons are redistributed from NAPL into the vapor and water phases based on their properties

- Vapor – light aliphatics and aromatics
- Water – primarily light aromatics with some light aliphatics and medium aromatics

The mass and composition of all phases (NAPL, vapor, water, sorbed) are altered over time due to biodegradation, generating metabolites. These mass and compositional changes in turn affects the risk evaluation.

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

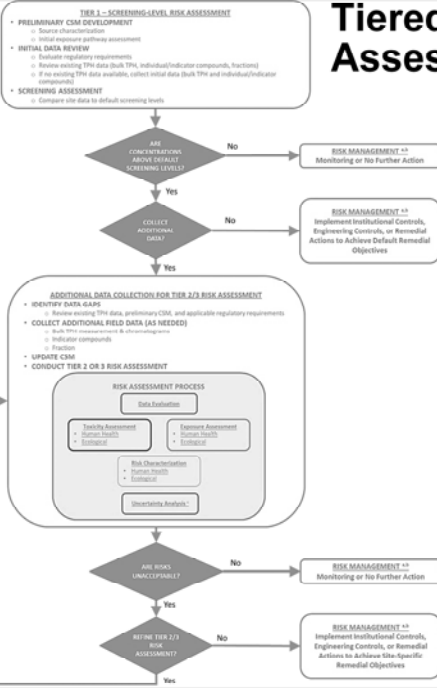


Poll Question

- ▶ 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



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

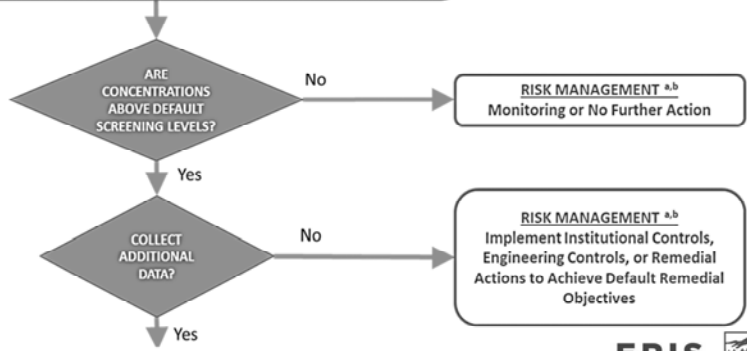
ITRC TPHRisk-1 Figure 1-1



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

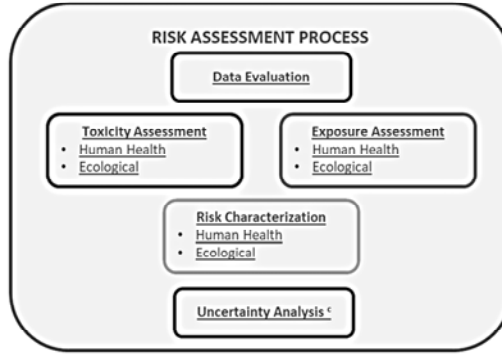


Site-Specific Assessment



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**



ITRC TPHRisk-1 Figure 1-1

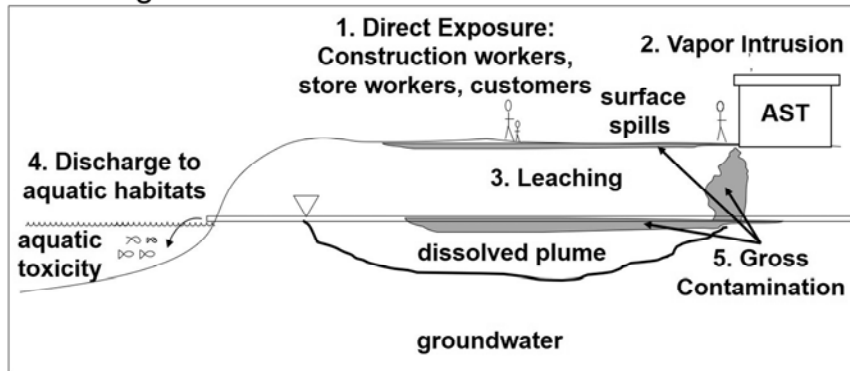


Conceptual Site Model: Exposure Assessment



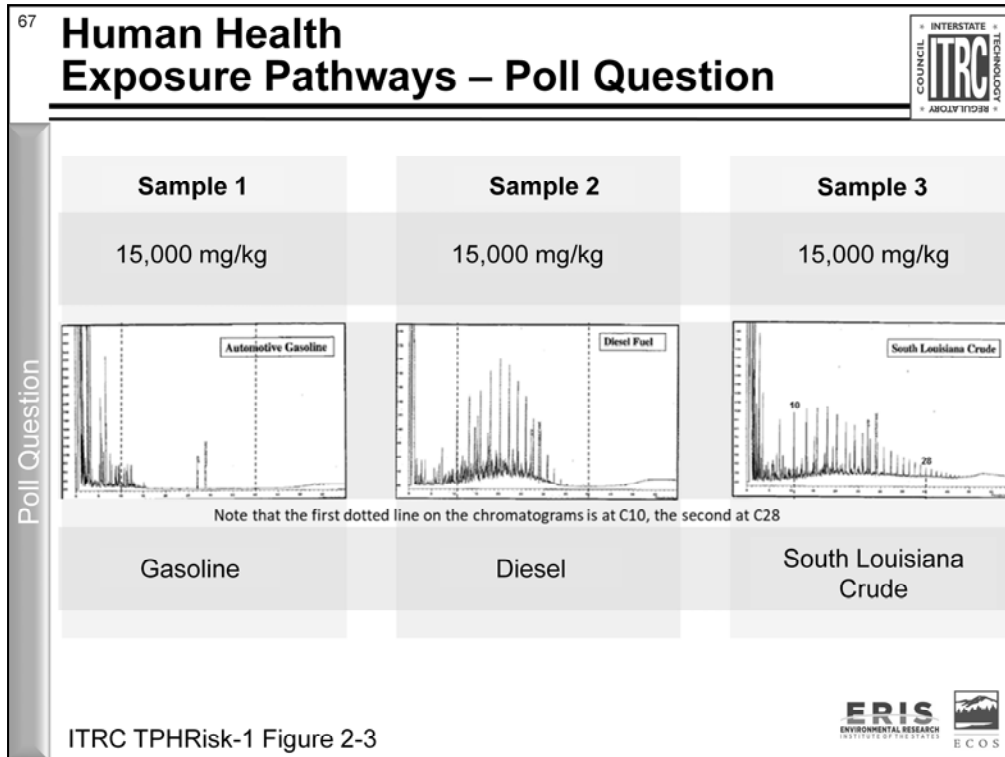
Case Study

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



HIDOH Case Study #1 (October 2018)





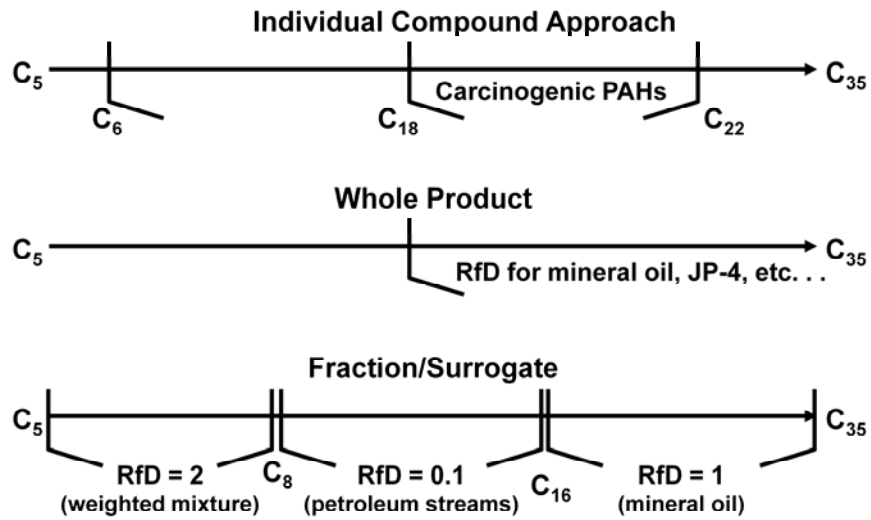
Looking at these three chromatographs and considering what we've learned about fate and transport...

Poll Questions:

- Looking at Sample 1 – What is the dominant exposure pathway likely to be?
 - Inhalation
 - Dermal contact
 - Ingestion

- Looking at Sample 3 – Are there any exposure pathways that can be readily excluded?
 - Inhalation
 - Migration to surface water
 - Ingestion
 - None of the above

Human Health Toxicity Assessment



ITRC TPHRisk-1 Figure 6-2

Analytical Methods vs Toxicity Values



Group TPH Fractions intervals to be consistent with TPH toxicity values

		Aliphatic																																		Aromatic																																																		
Carbon Chain Length		5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50																																							
USEPA 8015B	TPH-g	TPH-g																																		TPH-g																																																		
	TPH-d	TPH-d																	TPH-d																																																																			
	TPH-mo	TPH-mo																	TPH-mo																																																																			
Fractionation	VPH	VPH																																		VPH																																																		
	EPH	EPH																																		EPH																																																		
Mapping WDOE TPH Fractionation Method Intervals to RBSLs																																																																																						
MA Toxicity Category	Aliphatic C5-C8	Aliphatic C9-C18																	Aliphatic C19-C36																	Aromatic C9-C10																	Aromatic C11-C22																																	
US EPA Toxicity Category	Aliphatic Low	Aliphatic Medium																	Aliphatic High																	Aromatic Low																	Aromatic Medium																	Aromatic High																

from Goldberg Day, AEHS March 2015



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				
			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



ITRC TPHRisk-1 Table 6-1

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)

Case Study

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

HIDOH Case Study #1 (October 2018)



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

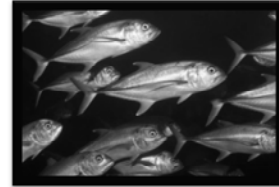
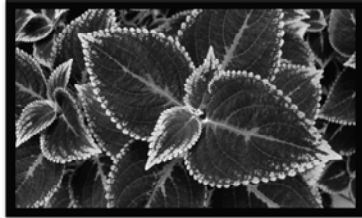


Case Study

- ▶ 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



Poll Questions: You have three different sites with different levels of complexity

1. Which site would be adequately addressed with a screening level ERA?

- A – Site A
- B – Site B
- C – Site C

2. Which site would be best addressed with a site-specific ERA:

- A – Site A
- B – Site B
- C – Site C

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

ITRC TPhRisk-1 Tables 7-12 and 7-13

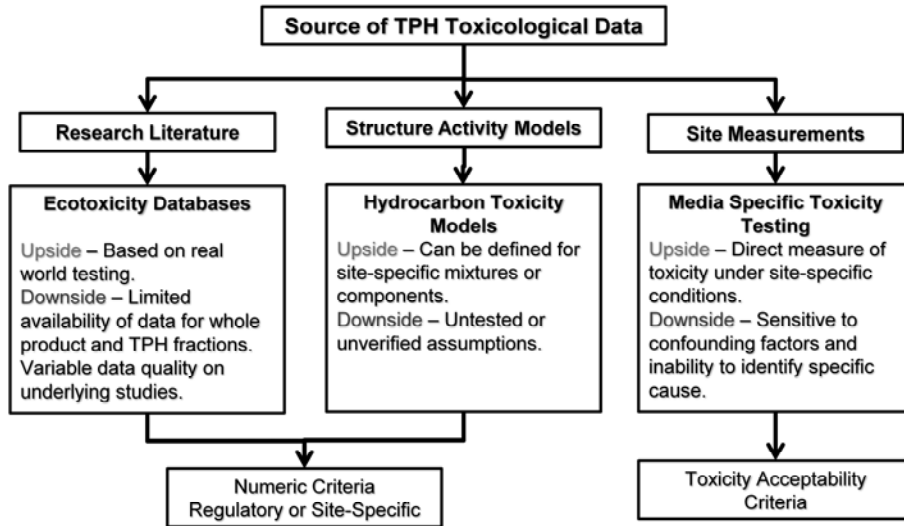


Scoping a Site-Specific ERA



- ▶ 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



ITRC TPHRisk-1 Figure 7-1

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)

ITRC TPHRisk-1 Table 7-15



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



HIDOH Case Study #1 (HIDOH 2018)

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**



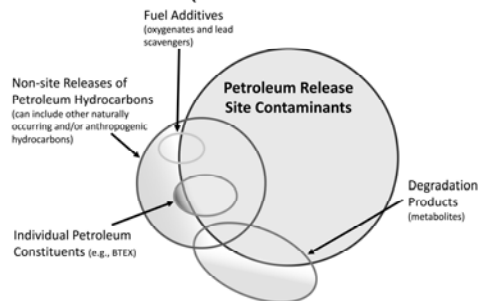
Road Map

- ▶ Why the Guidance?
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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)



ITRC TPHRisk-1 Figure 2-2



Now that you have learned more about TPH, how will YOU evaluate and apply this into your projects in determining what your TPH data truly represents?

As we heard, TPH results depend on the analytical method used and include both aliphatics and aromatic compounds in an identified carbon range. So are you reviewing the chromatograms and determining fractionated compounds in your analyses currently?

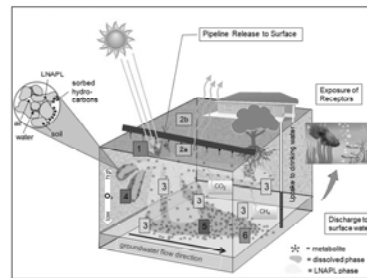
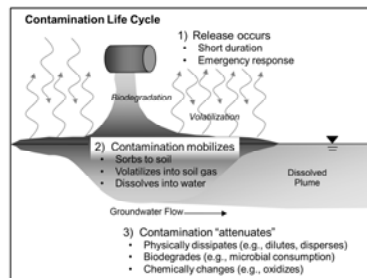
In addition, did you select the appropriate TPH Analytical Methods based on your data quality objectives, including using:

- total methods vs. fractionated methods
- purgeable and extractable methods

Is Your CSM Complete?



- ▶ Are there data gaps or lifecycle considerations?
- ▶ Did you modify the CSM to integrate TPH?
- ▶ How do TPH metabolites affect your CSM?
- ▶ Old bulk TPH data at re-opened sites?
 - Should you resample and update the CSM?



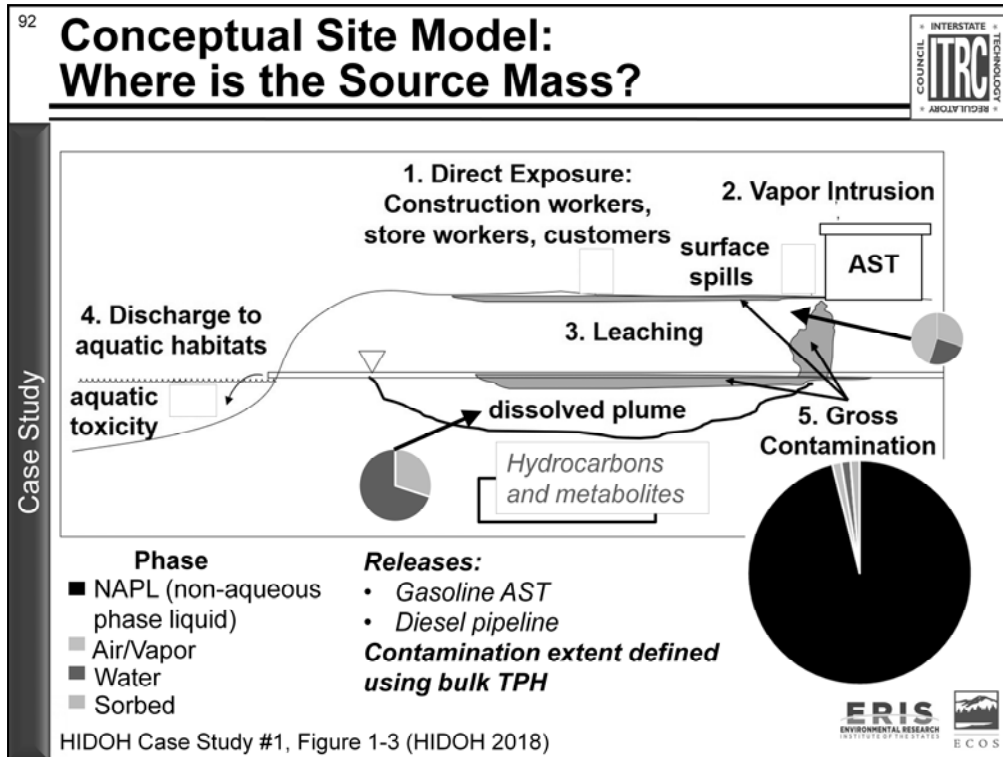
ITRC TPHRisk-1 Figures 6-1 & 4-9



Now the next question you should be asking yourself is "Is my CSM complete?" Your CSM will be used to develop the site investigation strategy and should be updated throughout the risk evaluation, remediation, and closure life-cycle stages.

So there is value at looking through the data again at your sites and reevaluating whether the fate and transport considerations have been thoroughly addressed or have they changed (see picture below).

Is data over 25 yrs old keeping you up at night since they were using previous methods like EPA Method 418.1 or should you be giving the data another "real hard look". Are these sites under institutional control or actually closed? Are they potentially going to reopen based on what we have discussed today?



Speaker notes: Key Idea: The composition of TPH in a sample from any medium affects risk. It's critical to understand how the composition in the vapor and dissolved plumes differ from the source zone due to partitioning and transformation processes.

Former Fuel Tank Farm CSM from the Hawai'i-hosted case studies for the guidance.

- Releases of gasoline and diesel from an aboveground storage tank (AST) and a diesel pipeline abandoned in place.
- The extent of contamination has been defined using bulk TPH analyses (e.g., TPH-gasoline, TPH-diesel, etc.)
- Areas of gross contamination or presence of NAPL (residual or mobile). NAPL has reached the shallow groundwater table (5-10 feet bgs)
 1. Shallow soil - pipeline
 2. Subsurface soil/groundwater beneath the AST

Pathways and concerns are listed on the figure:

1. Direct exposure risk
2. Vapor intrusion risk (note: impacts are shallow)
3. Leaching to groundwater
4. Contaminated groundwater migration to aquatic habitats
5. Gross contamination (NAPL)

Pie Charts (animation) – These pie charts are intended to convey relative hydrocarbon mass (size of pie) and phase (oil/NAPL, vapor, water, sorbed)

Figure Source: HIDOH Case Study #1 Figure 1-3 with pie charts created by the Fate team. Relative proportions estimated.

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



As Usha indicated earlier, stakeholder concerns should be considered and addressed appropriately, especially as they relate to the potential health and ecological impacts associated with these release sites. In order to address these concerns, an assessment of the site conditions such as indoor air and/or sub-slab vapor sampling should be determined to evaluate if there is a potential human health risk to the inhabitants of the associated on-site and/or off-site tenants, if there is a potential explosion hazard, etc.

In addition, are you considering the local State, County, and Cities' nuisance ordinances, especially as it relates to odor and/or visual complaints?

There also may be an associated potential or perceived property devaluation with the subject property or adjacent properties – For example, an adjacent resident to a bulk terminal may be concerned with having the pollution migrate onto their property and is concerned that they cannot sell their property and as such they plan on either taking you or your client to court, etc.

And last but not least is building trust and credibility with the communities. We need to get over the death in the family syndrome, where we are hesitant to share any information with the public. So in order to build trust and credibility, we need to be transparent about the situation and not try to hide it (people can tell when not being truthful). Take time to explain the data in simple terms so that people can understand and state of the science and associated risk involved with it. Be willing to admit on what you don't know if there is an absence of data.

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



So the take home lesson for this presentation is that you should use this guidance!

There are an abundance of useful tools and resources associated within this document such as the on-line calculators, case study examples that may relate to your sites, and seeing what other states are doing currently to evaluate whether your state could benefit from this.

There are numerous benefits that ITRC offers to state regulators and technology developers, vendors, and consultants, which include:

- ✓ Helping you build your knowledge base and raise your confidence about new environmental technologies
- ✓ Helping you save time and money when evaluating environmental technologies
- ✓ Guiding you in the collection of performance data to satisfy the requirements in multiple states
- ✓ Helping you avoid the time and expense of conducting duplicative and costly demonstrations
- ✓ Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

How can you get involved with ITRC:

- ✓ Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches
- ✓ Sponsor ITRC’s technical team and other activities
- ✓ Use ITRC products and attend training courses
- ✓ Submit proposals for new technical teams and projects

Links to additional resources:

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

Your feedback is important – please fill out the form at:

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

Thank You

Follow ITRC:



Poll Question

- ▶ **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>



Need confirmation of your participation today?
 Fill out the feedback form and check box for confirmation email and certificate.



With that we would like to thank you for your time today in participating in the TPH Risk Evaluation at Petroleum-Contaminated Sites presentation and recommend that you look through the additional resources provided in the link below and also give us your feedback on the presentation. Now lets turn the time over to those that have any questions.