TPH Methods and Measurements in U.S. EPA's Petroleum Vapor Intrusion (PVI) Database

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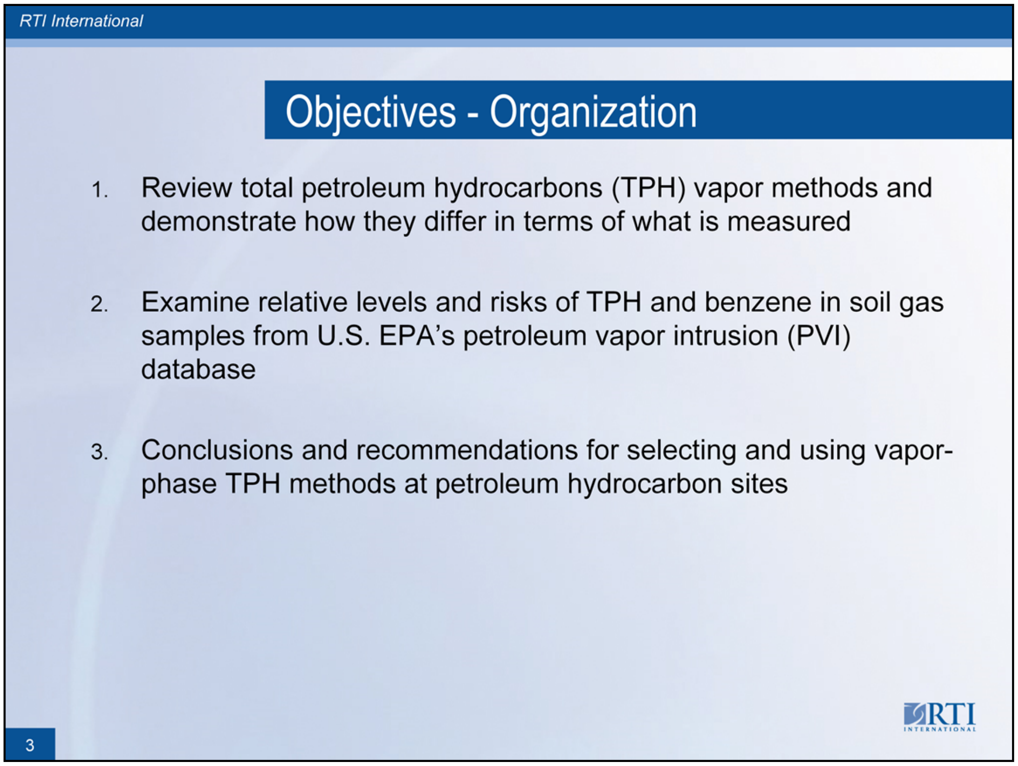
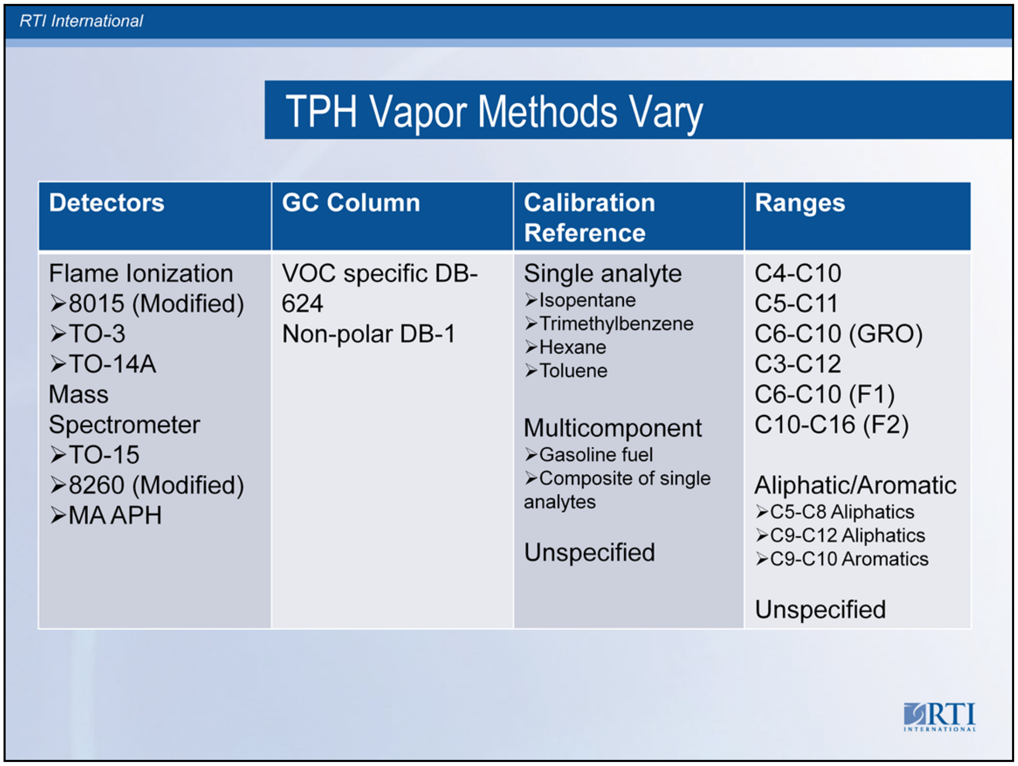
Reason for Presentation (Why?)

- TPH methods contained in the EPA PVI database vary, from state to state, from site to site, and from publication to publication.
- This method variation = uncertainty in what each different measurement type represents in terms of TPH.
- This uncertainty led to limited use of TPH in the analysis of the PVI database recently published by EPA.
- Although benzene is usually assumed to drive vapor risk at petroleum sites, recent work by Roger Brewer, State of Hawai'i (Fall 2012), suggests that TPH can drive risk, especially for heavy petroleum hydrocarbons or old, degraded spills.



Objectives - Organization

1. Review total petroleum hydrocarbons (TPH) vapor methods and demonstrate how they differ in terms of what is measured
2. Examine relative levels and risks of TPH and benzene in soil gas samples from U.S. EPA's petroleum vapor intrusion (PVI) database
3. Conclusions and recommendations for selecting and using vapor-phase TPH methods at petroleum hydrocarbon sites



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TPH Vapor Methods Vary

Detectors	GC Column	Calibration Reference	Ranges
Flame Ionization ➢8015 (Modified) ➢TO-3 ➢TO-14A Mass Spectrometer ➢TO-15 ➢8260 (Modified) ➢MA APH	VOC specific DB-624 Non-polar DB-1	Single analyte ➢Isopentane ➢Trimethylbenzene ➢Hexane ➢Toluene Multicomponent ➢Gasoline fuel ➢Composite of single analytes Unspecified	C4-C10 C5-C11 C6-C10 (GRO) C3-C12 C6-C10 (F1) C10-C16 (F2) Aliphatic/Aromatic ➢C5-C8 Aliphatics ➢C9-C12 Aliphatics ➢C9-C10 Aromatics Unspecified

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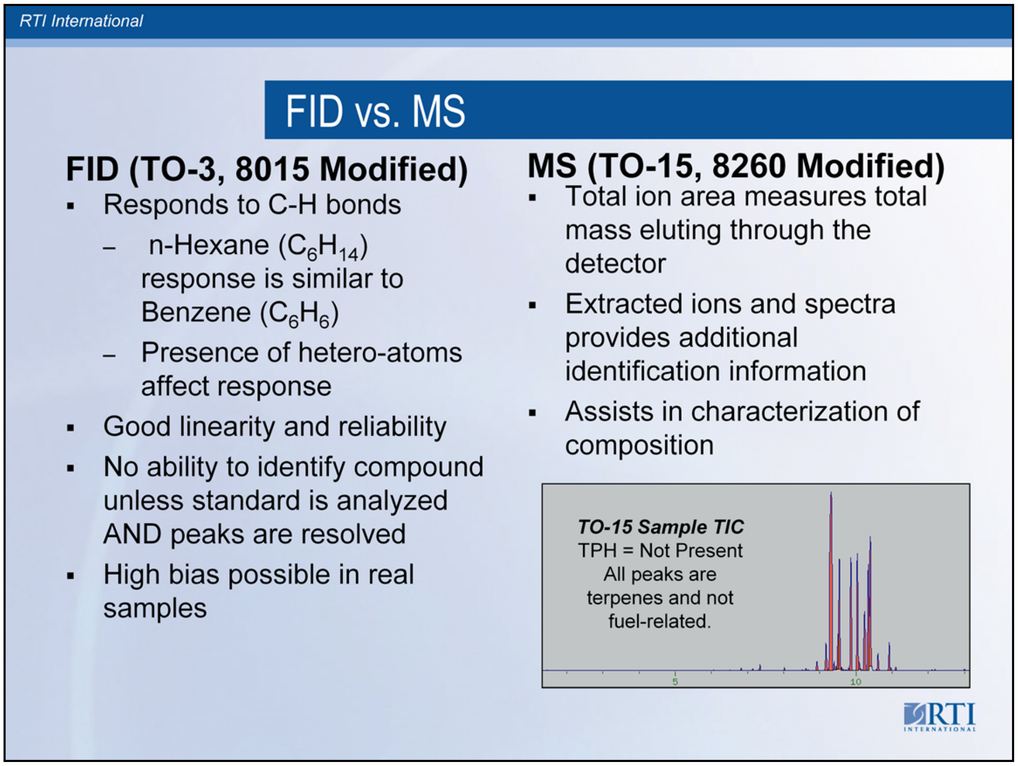
This slide lists some of the more common TPH methods and how they differ in terms of detectors, columns, calibration reference points, and carbon fraction ranges. When it comes to air-phase TPH, none of the traditional air methods such as TO-15 and TO-3, provide any direction on how to measure ‘TPH’. While the MA DEP APH method does provide a prescriptive, defined approach, this method measures aliphatic and aromatic ranges as compared to a total TPH. Due to the expense of this method, MA DEP APH method is not a routine request for most fuel-impacted sites.

The lack of method detail has left each lab to define calibration procedures to provide a ‘TPH’ measurement. While the detector is typically defined by the method referenced by the laboratory (TO-15 = MS, TO-3, modified 8015 = FID), the GC column, calibration reference, and carbon ranges for the TPH measurement are not defined.

In reality, it is difficult to determine which selection of parameters from this table is the most ‘valid’ . TPH in the environment is a complex mixture of fuel-related hydrocarbons, the composition dependent on original source, weathering, biodegradation, evaporation, etc. all affecting the composition and carbon ranges present in the environment. One could argue the case for any of these method parameters in designing a TPH method.

Since most of these methods are represented in the PVI database, what is the significance of these different approaches?



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FID vs. MS

FID (TO-3, 8015 Modified)

- Responds to C-H bonds
  - n-Hexane (C_6H_{14}) response is similar to Benzene (C_6H_6)
  - Presence of hetero-atoms affect response
- Good linearity and reliability
- No ability to identify compound unless standard is analyzed AND peaks are resolved
- High bias possible in real samples

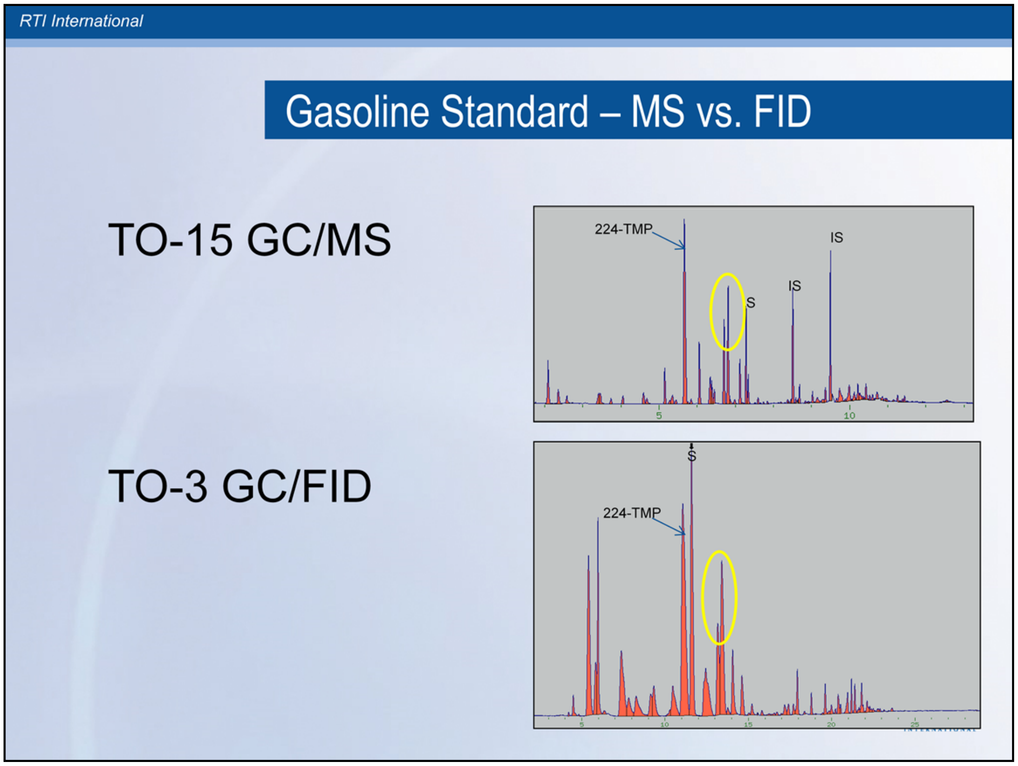
MS (TO-15, 8260 Modified)

- Total ion area measures total mass eluting through the detector
- Extracted ions and spectra provides additional identification information
- Assists in characterization of composition

TO-15 Sample TIC
TPH = Not Present
All peaks are terpenes and not fuel-related.

Typical TPH methods for measuring TPH rely on either FID or MS for detection. Methods TO-3 and 8015 (modified for air) utilize FID and Methods TO-15 and 8260 (modified for air) rely on MS for TPH measurement. Most labs reporting total TPH are using the total ion area of the mass spectrometer rather than the extracted ion information. The FID is the ‘classic’ TPH detector, as it was born to analyze petroleum hydrocarbons. The FID responds to the C-H bonds and regardless of the mixture of straight chain, branched or aromatic hydrocarbons, the FID responds essentially proportionally to the number of C atoms. Additionally, the FID excels in its linearity and reliability. However, because the FID provides no ability to definitively identify compounds and assist the practitioner in characterizing the fuel composition (aromatic vs. aliphatic) or the laboratory in identifying non-TPH peaks such as TCE and terpenes, many TPH measurements are now relying on MS either to complement the FID measurement or as the standalone method. The example sample in the R-hand corner of the slide is not uncommon for the laboratory to see. A TO-15 TPH measurement was requested for this sample. The sample contained high concentrations of alpha-pinene, limonene and other terpenes, which were not fuel-related. After removal of these peaks, the sample was essentially ‘Not Detected’ for TPH. In contrast, the FID approach would have put the TPH measurement well above the screening level. Bottom-line: FID can get you great sensitivity, but you do not get the positive identifications you do when you measured mass in MS.

If sites, in the PVI database or otherwise, contain a significant concentration of non-fuel related VOCs, the TPH measurement would be expected to exhibit a high bias when using a FID-based method as compared to a MS-based method, and without the positive identification MS provides there is no way to tell, while the MS method can. (Of course, this assumes that the laboratory was diligent in assessing the nature of the MS peaks and did not include inappropriate peaks in the TPH measurement.)



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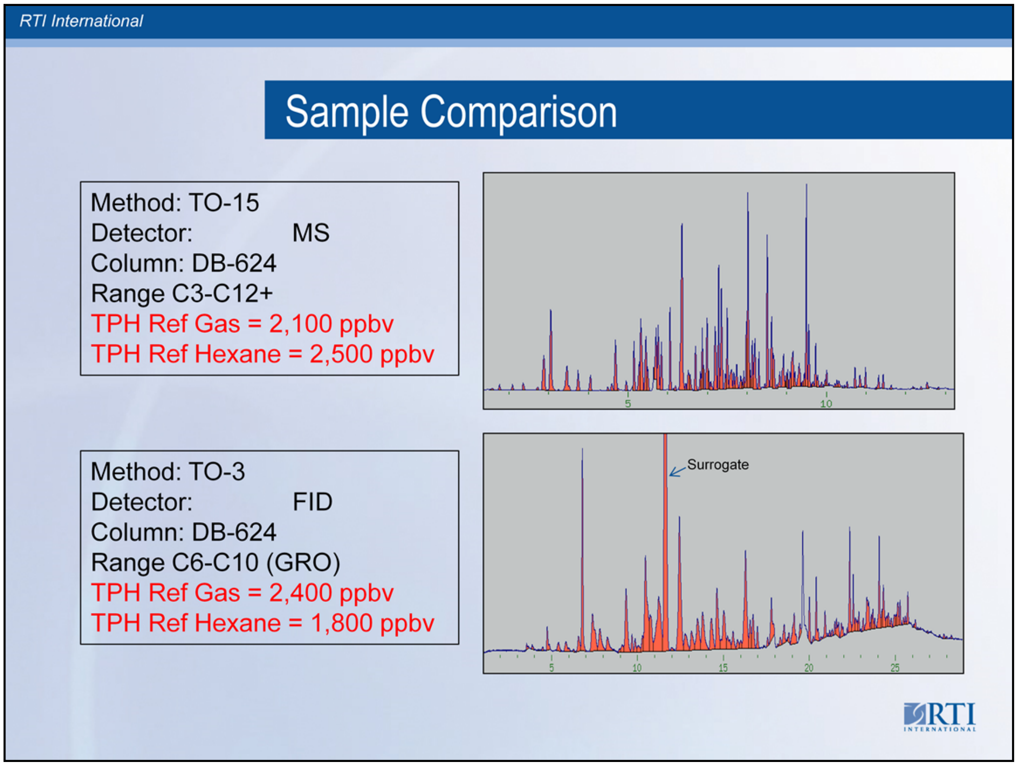
Gasoline Standard – MS vs. FID

TO-15 GC/MS

TO-3 GC/FID

The gasoline standard has a similar chromatographic pattern for both the TO-15 MS run and the TO-3 FID run. The peaks in the MS attributed to surrogate and internal standards are marked with IS or S, and likewise, the peak marked with S on the FID represents a lab-added surrogate. To assist in the comparison, Heidi has marked several common peaks, including the dominant 224-TMP peak and a pair of branched alkanes in the yellow circle.

To get a direct comparison of several of the methods, we evaluated several samples requiring TPH by both TO-15 and TO-3 to see the magnitude of the differences. This was not intended to be a comprehensive study, but as a limited example of how 2 methods may compare for samples that do have TPH present.

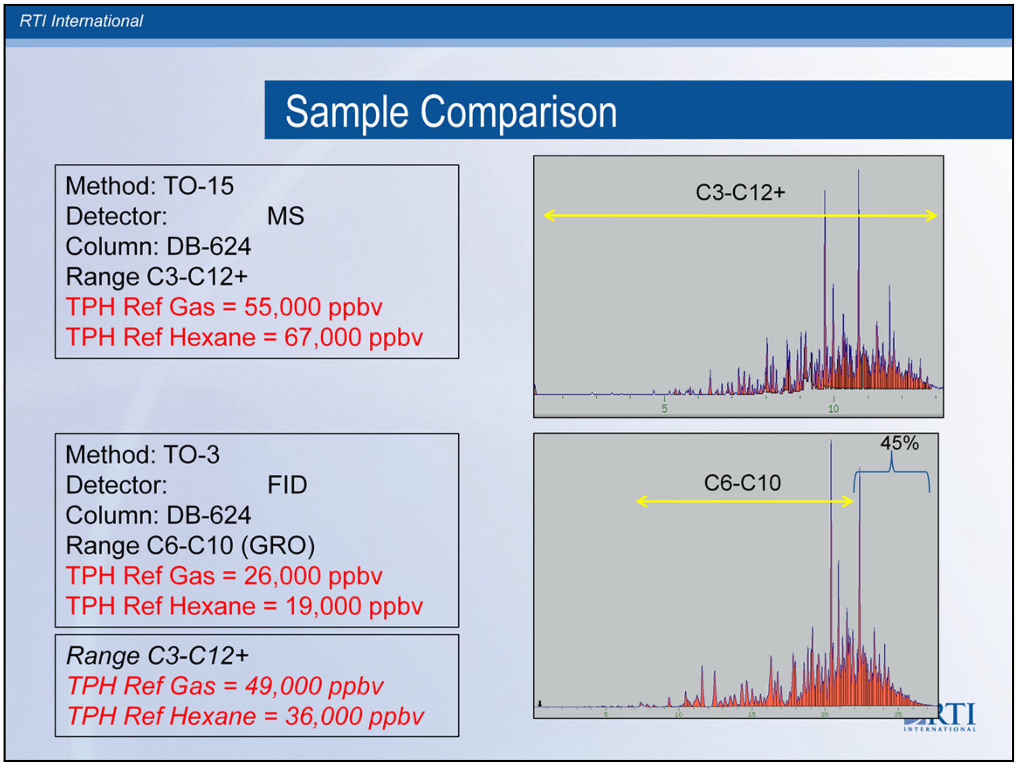


Sample Comparison

Method: TO-15
Detector: MS
Column: DB-624
Range C3-C12+
TPH Ref Gas = 2,100 ppbv
TPH Ref Hexane = 2,500 ppbv

Method: TO-3
Detector: FID
Column: DB-624
Range C6-C10 (GRO)
TPH Ref Gas = 2,400 ppbv
TPH Ref Hexane = 1,800 ppbv

This slide provides a comparison of a TPH measurement generated by TO-15 and by TO-3 on the same vapor sample performed by the laboratory. Even though different detectors, different ranges, different reference compounds are used to generate a response factor, the results are comparable, and these variables have little impact on the reported result.



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Sample Comparison

Method: TO-15
Detector: MS
Column: DB-624
Range C3-C12+
TPH Ref Gas = 55,000 ppbv
TPH Ref Hexane = 67,000 ppbv

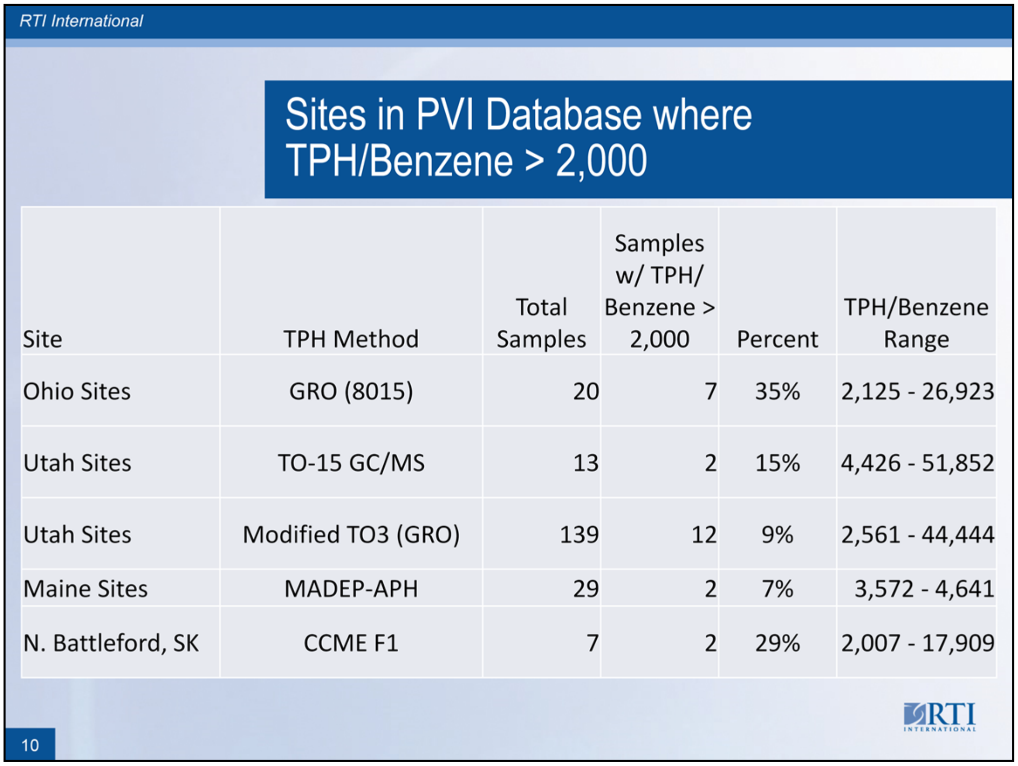
Method: TO-3
Detector: FID
Column: DB-624
Range C6-C10 (GRO)
TPH Ref Gas = 26,000 ppbv
TPH Ref Hexane = 19,000 ppbv

Range C3-C12+
TPH Ref Gas = 49,000 ppbv
TPH Ref Hexane = 36,000 ppbv

In contrast, a sample from the same site shows a significant difference between the 2 results. At first glance, the FID and MS data should be comparable. The TO-15 MS information confirms that the fuel pattern is characterized by aliphatic and aromatic compounds which should respond predictably on the FID. Upon closer inspection, the carbon range applied to the TO-15 was wider and included the heavier fuel fraction which was a significant portion of the TPH. The default carbon range for the TO-3 method was C6-C10 which resulted in the exclusion of about 45% of the total TPH. Clearly the sample fuel pattern did not resemble gasoline and reporting of TPH (GRO) only tells part of the story and may mislead the data user. When the entire carbon range is included, the TO-3 TPH matches the TO-15 result as expected.

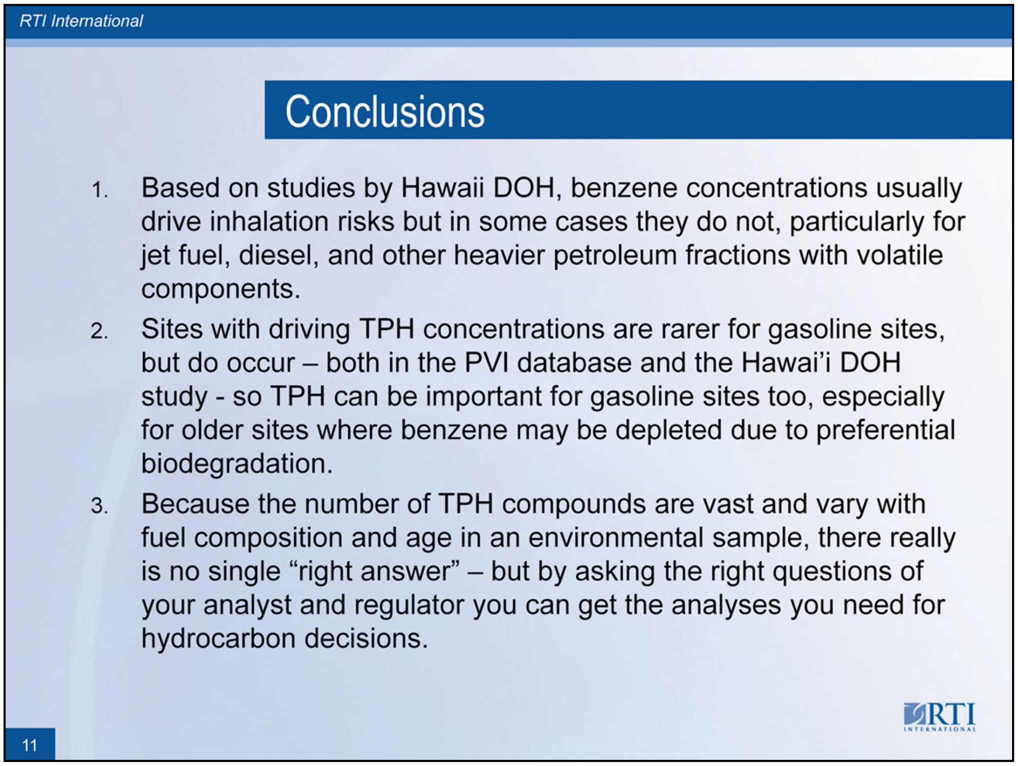
Characterization of TPH vs. Benzene Risk in PVI Database – Problem Identification

- Calculated TPH/benzene ratios for PVI database samples with detectable benzene and TPH to identify samples where TPH risk may be higher than benzene.
- Simplistic analysis used a TPH/benzene ratio of 2,000 (from Roger Brewer’s work) to roughly approximate point at which TPH risk may be comparable or greater than benzene risk
- Tabulated results by TPH method in PVI database



Sites in PVI Database where TPH/Benzene > 2,000

Site	TPH Method	Total Samples	Samples w/ TPH/ Benzene > 2,000	Percent	TPH/Benzene Range
Ohio Sites	GRO (8015)	20	7	35%	2,125 - 26,923
Utah Sites	TO-15 GC/MS	13	2	15%	4,426 - 51,852
Utah Sites	Modified TO3 (GRO)	139	12	9%	2,561 - 44,444
Maine Sites	MADEP-APH	29	2	7%	3,572 - 4,641
N. Battleford, SK	CCME F1	7	2	29%	2,007 - 17,909



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Conclusions

1. Based on studies by Hawaii DOH, benzene concentrations usually drive inhalation risks but in some cases they do not, particularly for jet fuel, diesel, and other heavier petroleum fractions with volatile components.
2. Sites with driving TPH concentrations are rarer for gasoline sites, but do occur – both in the PVI database and the Hawai'i DOH study - so TPH can be important for gasoline sites too, especially for older sites where benzene may be depleted due to preferential biodegradation.
3. Because the number of TPH compounds are vast and vary with fuel composition and age in an environmental sample, there really is no single "right answer" – but by asking the right questions of your analyst and regulator you can get the analyses you need for hydrocarbon decisions.

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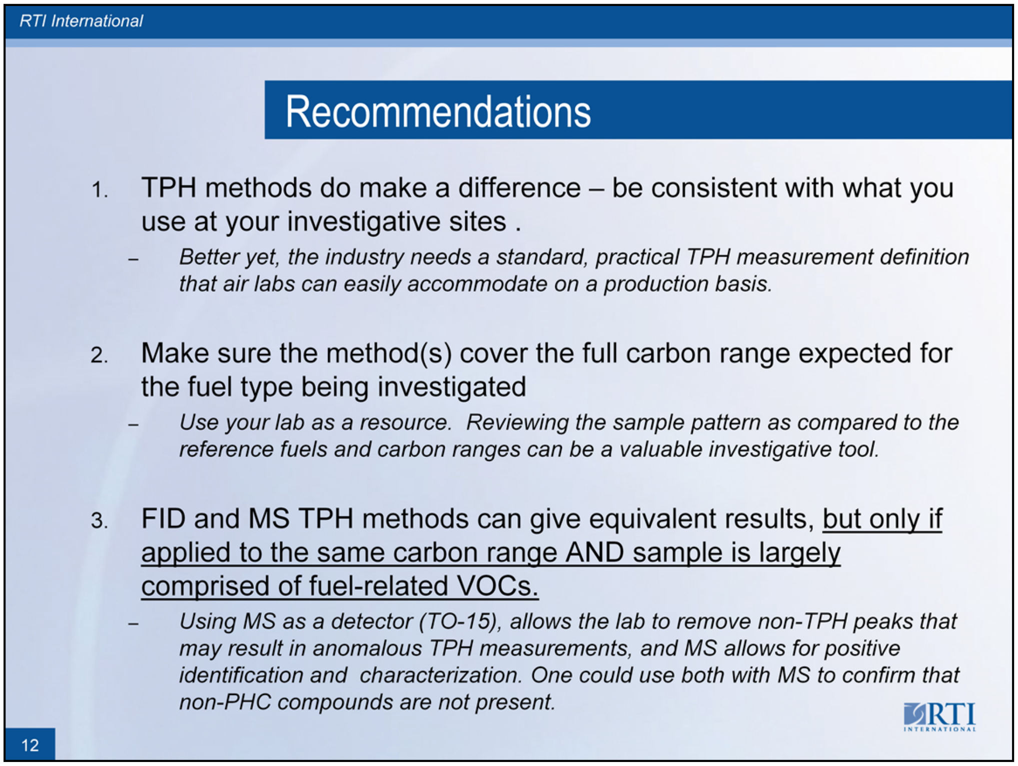
Any analytical approach to generate a TPH sum requires assumptions/estimations. There's not necessarily a 'right' answer. As you can see by the few examples provided, very different TPH air methods (detectors (FID v MS), carbon ranges (C6-C10 v C3-C12), reference compounds (Gas v hexane)) can generate very similar results (example 1) and also very different results (example 2) for samples collected even from the same site. This reinforces the need for a standard definition of TPH that is useful, practical and cost-effective, and allow for consistent comparison and evaluation of TPH values among sites and between labs.

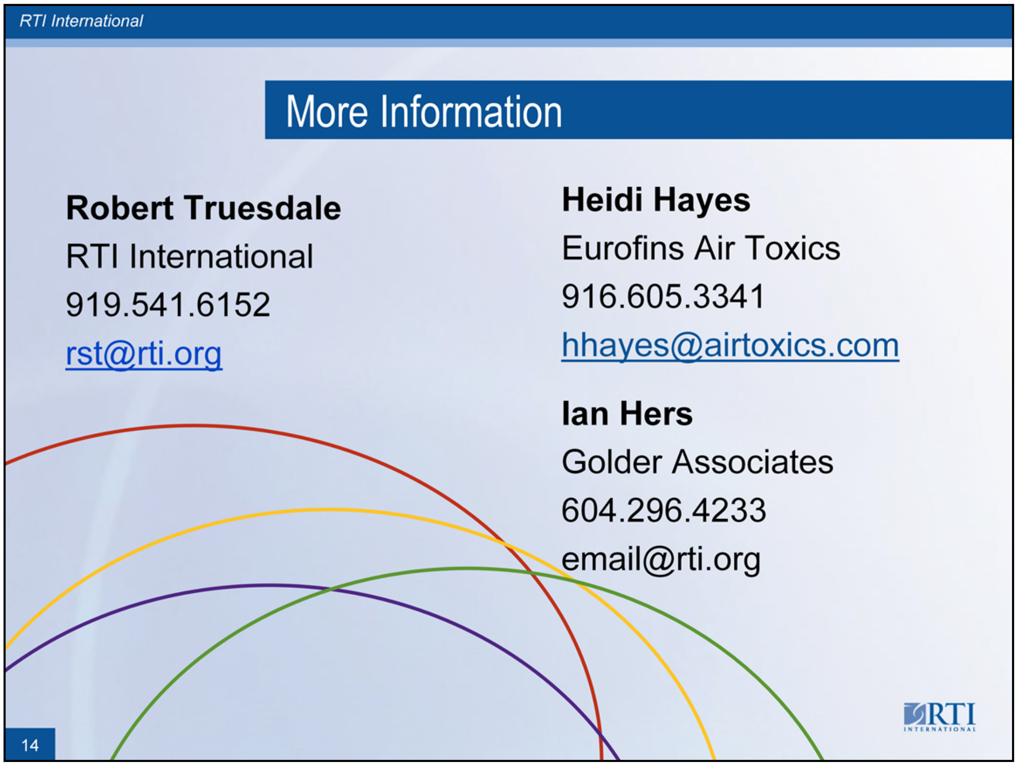


Recommendations

1. TPH methods do make a difference – be consistent with what you use at your investigative sites .
   - *Better yet, the industry needs a standard, practical TPH measurement definition that air labs can easily accommodate on a production basis.*
2. Make sure the method(s) cover the full carbon range expected for the fuel type being investigated
   - *Use your lab as a resource. Reviewing the sample pattern as compared to the reference fuels and carbon ranges can be a valuable investigative tool.*
3. FID and MS TPH methods can give equivalent results, <u>but only if applied to the same carbon range AND sample is largely comprised of fuel-related VOCs.</u>
   - *Using MS as a detector (TO-15), allows the lab to remove non-TPH peaks that may result in anomalous TPH measurements, and MS allows for positive identification and characterization. One could use both with MS to confirm that non-PHC compounds are not present.*

Summary:

There is a need for a standard definition of TPH that is useful, practical, and cost-effective, to enable consistent comparison and evaluation of TPH values among sites and between labs and to allow characterization of vapor phase TPH risk at petroleum hydrocarbon sites.



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