TPH Methods and Measurements and Petroleum Vapor Intrusion (PVI) Risks

Robert Truesdale, RTI International
Heidi Hayes, Eurofins Air Toxics
Ian Hers, Golder Associates
How do petroleum & chlorinated hydrocarbons differ in vapor intrusion?

- Actual PVI is very rare
- Why? PHCs biodegrade readily; CHCs do not = a thickness of “clean” (aerobic) soil is all that’s needed to prevent PVI (NAPL or dissolved)
- CHCs can be treated as single chemicals; PHCs are a complex mixture.

http://www.epa.gov/oust/cat/pvi/pvicvi.pdf
Reason for Presentation (Why?)

- Total petroleum hydrocarbon (TPH) definitions and methods vary, from state to state, from site to site, from publication to publication, & within EPA’s PVI database.
- This variation = uncertainties: (e.g., what chemicals does a particular TPH measurement represent?)
- This uncertainty led to limited use of TPH in EPA’s analysis of the PVI database
- Although benzene is usually assumed to drive vapor risk at petroleum sites Brewer et al. (2012) and this presentation suggest that TPH often drives vapor risk, especially with the new EPA inhalation RSLs for TPH fractions.
Objectives - Organization

1. Review 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
TPH is a Complex Mixture

TPH Fractions – GC PID Chromatogram
(MADEP, 2002)
## TPH Vapor Methods Vary

<table>
<thead>
<tr>
<th>Detectors</th>
<th>GC Column</th>
<th>Calibration Reference</th>
<th>Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame Ionization</td>
<td>VOC specific DB-624 Non-polar DB-1</td>
<td>Single analyte - Isopentane, Trimethylbenzene, Hexane, Toluene</td>
<td>C4-C10, C5-C11, C6-C10 (GRO), C3-C12, C6-C10 (F1), C10-C16 (F2)</td>
</tr>
<tr>
<td>8015 (Modified)</td>
<td></td>
<td>Multicomponent - Gasoline fuel, Composite of single analytes</td>
<td>Aliphatic/Aromatic - C5-C8 Aliphatics, C9-C12 Aliphatics, C9-C10 Aromatics</td>
</tr>
<tr>
<td>TO-3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO-14A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Spectrometer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8260 (Modified)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MA APH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8260 (Modified)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.
Gasoline Standard – MS vs. FID

TO-15 GC/MS

TO-3 GC/FID
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
### Sample Comparison

<table>
<thead>
<tr>
<th>Range</th>
<th>TPH Ref Gas</th>
<th>TPH Ref Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3-C12+</td>
<td>55,000 ppbv</td>
<td>67,000 ppbv</td>
</tr>
<tr>
<td>C6-C10 (GRO)</td>
<td>26,000 ppbv</td>
<td>19,000 ppbv</td>
</tr>
<tr>
<td>C3-C12+</td>
<td>49,000 ppbv</td>
<td>36,000 ppbv</td>
</tr>
</tbody>
</table>

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
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

<table>
<thead>
<tr>
<th>Site</th>
<th>TPH Method</th>
<th>Total Samples</th>
<th>Samples w/ TPH/Benzene &gt; 2,000</th>
<th>Percent</th>
<th>TPH/Benzene Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohio Sites</td>
<td>GRO (8015)</td>
<td>20</td>
<td>7</td>
<td>35%</td>
<td>2,125 - 26,923</td>
</tr>
<tr>
<td>Utah Sites</td>
<td>TO-15 GC/MS</td>
<td>13</td>
<td>2</td>
<td>15%</td>
<td>4,426 - 51,852</td>
</tr>
<tr>
<td>Utah Sites</td>
<td>Modified TO3 (GRO)</td>
<td>139</td>
<td>12</td>
<td>9%</td>
<td>2,561 - 44,444</td>
</tr>
<tr>
<td>Maine Sites</td>
<td>MADEP-APH</td>
<td>29</td>
<td>2</td>
<td>7%</td>
<td>3,572 - 4,641</td>
</tr>
<tr>
<td>N. Battleford, SK</td>
<td>CCME F1</td>
<td>7</td>
<td>2</td>
<td>29%</td>
<td>2,007 - 17,909</td>
</tr>
</tbody>
</table>
EPA Inhalation Regional Screening Levels (RSLs) for TPH Fractions

- Released summer 2013
- $10^{-6}$ target cancer risk; 0.1 and 1 hazard quotient
- Based on EPA Provisional Peer Reviewed Toxicity Values (PPRTVs)
- Set cancer-based values for C5-C8 and C9-C18 aliphatics and C6-C8 aromatics
- C6-C8 aromatic inhalation RSL = benzene RSL
- Will 2,000 x rule hold?
## Current Resident Indoor Air EPA RSLs

<table>
<thead>
<tr>
<th>Compound/component</th>
<th>Designation</th>
<th>EPA RSL (µg/m³)</th>
<th>10⁻⁶ ECR</th>
<th>HQ = 0.1</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene</strong></td>
<td>C6 aromatic</td>
<td></td>
<td>0.31</td>
<td>3.1</td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>Toluene</strong></td>
<td>C7 aromatic</td>
<td></td>
<td>520</td>
<td></td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>Ethylbenzene</strong></td>
<td>C8 aromatic</td>
<td></td>
<td>0.97</td>
<td>100</td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>Xylenes</strong></td>
<td>C8 aromatic</td>
<td></td>
<td></td>
<td>10</td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>1,3-Butadiene</strong></td>
<td>C4 aliphatic</td>
<td></td>
<td>0.081</td>
<td>0.2</td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>n-Hexane</strong></td>
<td>C6 aliphatic</td>
<td></td>
<td>73</td>
<td></td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>JP-7</strong></td>
<td></td>
<td></td>
<td>31</td>
<td></td>
<td>IRIS</td>
</tr>
<tr>
<td><strong>n-Pentane</strong></td>
<td>C5 aliphatic</td>
<td></td>
<td>100</td>
<td></td>
<td>PPRTV</td>
</tr>
<tr>
<td><strong>Naphthalene</strong></td>
<td>C10 aromatic</td>
<td></td>
<td>0.072</td>
<td>0.31</td>
<td>CalEPA, IRIS</td>
</tr>
<tr>
<td><strong>TPH Aliphatic Low</strong></td>
<td>C5-C8</td>
<td></td>
<td>13</td>
<td>63</td>
<td>PPRTV</td>
</tr>
<tr>
<td><strong>TPH Aliphatic Medium</strong></td>
<td>C9-C18</td>
<td></td>
<td>0.54</td>
<td>10</td>
<td>PPRTV</td>
</tr>
<tr>
<td><strong>TPH Aromatic Low (BTEX)</strong></td>
<td>C6-C8</td>
<td></td>
<td>0.31</td>
<td>3.1</td>
<td>PPRTV</td>
</tr>
<tr>
<td><strong>TPH Aromatic Medium</strong></td>
<td>C9-C16</td>
<td></td>
<td>0.31</td>
<td></td>
<td>PPRTV</td>
</tr>
</tbody>
</table>
Application of RSLs to Maine UST Site Data

- 3 gas station sites from EPA PVI database
- Very coarse (S&G), coarse (S), and fine (silt) soils
- 2 soil gas samples per site
- Sample depths from 2 – 11 feet BGS
- Probes leak-checked
- CH$_4$ BDL; O$_2$ = 14 – 17% (aerobic)
- Detectable BTEX, 1,3-butadiene; naphthalene; MassDEP air phase petroleum hydrocarbon (APH) fractions
- TPH/benzene ratio range: 42 - 359
Petroleum hydrocarbon measurements, Maine soil gas samples - $\mu$g/m$^3$

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Augusta 2'</th>
<th>Augusta 7'</th>
<th>Lewiston 4'</th>
<th>Lewiston 11'</th>
<th>Milo 7.5'</th>
<th>Milo 8'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>5.4</td>
<td>&lt;4.8</td>
<td>14</td>
<td>&lt;30</td>
<td>&lt;2</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Benzene</td>
<td>22</td>
<td>7</td>
<td>480</td>
<td>3,200</td>
<td>34</td>
<td>700</td>
</tr>
<tr>
<td>BTEX</td>
<td>78</td>
<td>51</td>
<td>1,765</td>
<td>12,140</td>
<td>462</td>
<td>2,662</td>
</tr>
<tr>
<td>C9-C10 Aromatics</td>
<td>132</td>
<td>968</td>
<td>1,806</td>
<td>12,581</td>
<td>7,742</td>
<td>38,710</td>
</tr>
<tr>
<td>C5-C8 Aliphatics</td>
<td>46</td>
<td>69</td>
<td>2,615</td>
<td>11,538</td>
<td>231</td>
<td>1,462</td>
</tr>
<tr>
<td>C9-C12 Aliphatics</td>
<td>352</td>
<td>1,389</td>
<td>1,556</td>
<td>17,037</td>
<td>8,148</td>
<td>11,111</td>
</tr>
<tr>
<td>TPH</td>
<td>613</td>
<td>2,477</td>
<td>7,756</td>
<td>53,296</td>
<td>16,583</td>
<td>53,944</td>
</tr>
<tr>
<td>Compound/component</td>
<td>Designation</td>
<td>EPA RSL (µg/m³)</td>
<td>Ref</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>---------------------</td>
<td>-----------------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10⁻⁶ ECR</td>
<td>HQ = 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>C6 aromatic</td>
<td>0.31</td>
<td>6.2</td>
<td>IRIS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>C7 aromatic</td>
<td>1,040</td>
<td>IRIS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C8 aromatic</td>
<td>0.97</td>
<td>200</td>
<td>IRIS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylenes</td>
<td>C8 aromatic</td>
<td>0.97</td>
<td>20</td>
<td>IRIS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>C4 aliphatic</td>
<td>0.081</td>
<td>0.4</td>
<td>IRIS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>C6 aliphatic</td>
<td>146</td>
<td>IRIS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JP-7</td>
<td></td>
<td>62</td>
<td>IRIS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>C5 aliphatic</td>
<td>200</td>
<td>PPRTV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C10 aromatic</td>
<td>0.072</td>
<td>0.62</td>
<td>CalEPA, IRIS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPH Aliphatic Low</td>
<td>C5-C8</td>
<td>13</td>
<td>126</td>
<td>PPRTV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPH Aliphatic Medium</td>
<td>C9-C18</td>
<td>0.54</td>
<td>20</td>
<td>PPRTV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPH Aromatic Low (BTEX)</td>
<td>C6-C8</td>
<td>0.31</td>
<td>6.2</td>
<td>PPRTV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPH Aromatic Medium</td>
<td>C9-C16</td>
<td>0.62</td>
<td>PPRTV</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results: Individual BTEX vs. C6-C8 RSLs (i.e., always break out BTEX)
Risk Exceedence by TPH component: EPA RSLs x 1,000, $10^{-6}$ ECR, HQ = 0.2

Augusta 2' (0.65x)

Augusta 7' (2.3x)

- Napthalene
- BTEX
- 1,3-butadiene
- C5-C8 aliphatic
- C9-C12 aliphatic
- C9-C10 aromatic
Risk Exceedence by TPH component:
EPA RSLs x 1,000; 10^{-6} ECR; HQ = 0.2

Lewiston 4' (7.1x)
- Napthalene
- BTEX
- 1,3-butadiene
- C5-C8 aliphatic
- C9-C12 aliphatic
- C9-C10 aromatic

Lewiston 11' (50x)
- Napthalene
- BTEX
- 1,3-butadiene
- C5-C8 aliphatic
- C9-C12 aliphatic
- C9-C10 aromatic
Risk Exceedence by TPH component: EPA RSLs x 1,000; 10^{-6} ECR; HQ = 0.2

Milo 7.5' (14x)
- Napthalene
- BTEX
- 1,3-butadiene
- C5-C8 aliphatic
- C9-C12 aliphatic
- C9-C10 aromatic

Milo 8' (36x)
Conclusions

1. Although previous studies by Hawaii DOH suggested that benzene concentrations usually drive inhalation risks at PVI sites, the recent EPA TPH-fractions RSLs increase risk levels for non-benzene components so that they are similar or greater than benzene.

2. TPH is an important/driving volatile chemical component at gasoline sites, especially where benzene may be depleted.

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” – for a TPH measurement in gas or other media. Ask the right questions of your analyst and regulator to get the analyses you need for petroleum hydrocarbon decisions.

4. Remember: PHCs readily biodegrade; actual PVI is rare
Recommendations

1. TPH methods do make a difference – be consistent with and knowledgeable of methods and screening levels that 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, but only if applied to the same carbon range AND sample is largely comprised of fuel-related VOCs.
   - 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.
More Information

Robert Truesdale
RTI International
919.541.6152
rst@rti.org

Heidi Hayes
Eurofins Air Toxics
916.605.3341
hhayes@airtoxics.com

Ian Hers
Golder Associates
604.296.4233
email@rti.org