Interpreting Tar Patterns at Former Manufactured Gas Plant Sites

Brian L. Murphy, Ph.D. • INEF, Penn State • June 10, 2013
Why focus on tar?

- Dense, nonaqueous-phase liquid (DNAPL) that can sink into the saturated zone and contaminate groundwater
  - Expensive to remediate

- Insurance coverage litigation
  - How tar got there? (Expected and intended?)
  - When tar got there? (During coverage period?)
  - Is it still moving? (During coverage period?)
Outline

- What is manufactured gas plant (MGP) tar?
- How “tarry” is it?
- How fast does it move?
  - Distance and time scales
- How to interpret boring logs in terms of tar motion
- How can you identify source locations at a site where tar has migrated?
Nomenclature

- “Tar” generally = Density > Water
- “Oil” generally = Density < Water
- “Coal tar” = Tar from different processes
  - Coal gasification
  - Water gas
  - Carbureted water gas
  - Oil gas

Which may not involve the use of coal at all!
Different Processes for Manufacturing Gas

- **Coal gas:** Heat coal in the absence of oxygen

- **Water gas (blue gas):** Steam sprayed on incandescent coke $\text{H}_2\text{O} + C \rightarrow \text{CO} + \text{H}_2$

- **Carbureted water gas:** Petroleum is cracked and added to water gas—most popular Lowe process

- **Oil gas:** Cracked petroleum for low molecular weight gases
Initial Coal Gas Period

- **1812**: First commercial plant chartered, London
- First U.S. gas companies incorporated
  - 1817 Baltimore
  - 1823 New York
  - 1829 Boston
Advent of Water Gas

- **1873**: Lowe Carbureted Water Gas (CWG) Process patented; water gas provided superior illumination
  - 1884: Patents sold to United Gas Improvement Company
  - 1892: Lowe’s patents begin to expire

- **1900**: CWG accounts for 75% of U.S. gas production
  - Coal gas retained at some plants to provide coke for water gas process
Arrival of Natural Gas

- **1943:**
  - Big Inch and Little Big Inch pipelines constructed to carry crude and product from the Southwest to New York Harbor area
  - U-boat concern
  - Converted to carry natural gas at end of Word War II

- **1950s–1960s:**
  - Plants convert to oil gas for natural gas compatibility
  - MGPs dismantled
U.S. Gas Production by Manufacturing Process

Source: Emsbo-Mattingly and Boehm adaption of Harkins et al. (1988)
Most Tar in the Ground is Water Gas

- In addition to greater gas production than coal gas:
  - More tar/cubic foot of gas
  - Can be more difficult to recover chemicals from than coal gas tar
  - Can be “off-spec” due to emulsions
Contemporary Citations Regarding Water Gas and Coal Gas Tar

“In former days it was a common custom to put all these tar tanks, settling tanks, etc. in the ground and to build them of wood. In time these became leaky and the contents would ooze out. Similarly, metal tanks would rust out and leak, and brick tanks would become more or less permeable. The present tendency is toward the use of better tanks, in order to avoid losses of valuable substances and in order to prevent pollution. The wastes from water gas plants are more troublesome in this respect than the waste from the coal-gas plants. …Often the floor of the tanks is built of concrete or brick and there is danger of leakage from such holders, as their area is considerable.” (Whipple 1908)
Contemporary Citations Regarding Water Gas and Coal Gas Tar (continued)

“Experience has shown that a masonry tank will allow very little coal tar to seep through it but water-gas tar frequently escapes. Whenever possible water-gas tar should be stored in steel tanks of 10,000 gal capacity.” (Russell 1917)
Tar Properties: Viscosity, $\mu$

- **Viscosity of tar**
  - Low, light oil water gas/oil gas
  - Medium, heavy oil water gas/oil gas
  - High, coal gas/coke oven gas
## Tar Viscosity at Time of Manufacture

<table>
<thead>
<tr>
<th>Dynamic Viscosity (cP)</th>
<th>Water gas tar #1</th>
<th>Water gas tar #2</th>
<th>Light water gas tar</th>
<th>Low temperature coal tar</th>
<th>Coke oven coal tar</th>
<th>Pacific Coast oil gas tar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.1</td>
<td>9.9</td>
<td>12</td>
<td>60</td>
<td>1,470</td>
<td>119</td>
</tr>
</tbody>
</table>

Note: Viscosity converted from degrees Engler, $T = 104^\circ$ F = 40$^\circ$ C

Source: Harkins et al. (1988)
# Present Tar Viscosity

<table>
<thead>
<tr>
<th>Site Number</th>
<th>1B</th>
<th>2B</th>
<th>4</th>
<th>7</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dynamic Viscosity (cP)</strong></td>
<td>63.6</td>
<td>425.3</td>
<td>144.6</td>
<td>32.0</td>
<td>51.0</td>
<td>62.9</td>
<td>34.7</td>
</tr>
</tbody>
</table>

Notes:  
- T = 22° C  
- Samples 1A and 2A were high viscosity but not measured.  
- Samples 1B and 2B are replacement samples.  
- Samples 3, 6, and 8 had large amounts of solids and were not used.  
- Generally small standard deviations not shown.

Source: EPRI, 2004
# How “Tarry” is MGP Tar: Comparison with Common Fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (cps)</th>
<th>Tar</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (65°F)</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milk</td>
<td>3</td>
<td>Water gas tar #1</td>
<td>9.1</td>
</tr>
<tr>
<td>Blood</td>
<td>10</td>
<td>Water gas Tar #2</td>
<td>9.9</td>
</tr>
<tr>
<td>Gasoline</td>
<td>11</td>
<td>Light water gas tar</td>
<td>11</td>
</tr>
<tr>
<td>Beer</td>
<td>18</td>
<td>#7</td>
<td>32.0</td>
</tr>
<tr>
<td>Cream</td>
<td>20</td>
<td>#11</td>
<td>34.7</td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>40</td>
<td>Low temperature coal tar</td>
<td>60</td>
</tr>
<tr>
<td>SAE 10</td>
<td>88–206</td>
<td>#9</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>#1B</td>
<td>63.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>#10</td>
<td>62.9</td>
</tr>
<tr>
<td>Peanut oil</td>
<td>103</td>
<td>Pacific Coast oil gas tar</td>
<td>119</td>
</tr>
<tr>
<td>Tomato juice</td>
<td>180</td>
<td>#4</td>
<td>144.6</td>
</tr>
<tr>
<td>Maple syrup</td>
<td>435</td>
<td>#2B</td>
<td>425.3</td>
</tr>
<tr>
<td>Latex paint</td>
<td>750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Honey</td>
<td>1,500</td>
<td>Coke oven coal tar</td>
<td>1,470</td>
</tr>
<tr>
<td>Chocolate syrup</td>
<td>2,250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Question: How “Tarry” is the Tar?

Answer: Not Very

- What about samples that were not used?
  - 1A, 2A “High viscosity”
  - Could be coal tar or weathered (evaporated) samples from the surface/near surface
How Fast Does Tar Move

- An EPRI program provides site-specific tar and soil properties allowing for the calculation of movement
Schematic
Equations of Motion

- **Tar Motion**: Controlled by three forces
  - Gravity: \( F_g = \Delta \rho gh \pi r^2 \)
  - Capillary: \( F_c = 2 \delta \cos \theta \pi r \)
  - Viscous: \( F_v = \frac{v \mu n L \pi r^2}{k} \)
Equating Gravitational and Viscous Forces Results in D’Arcy’s Law

\[
\nu = \frac{dS}{dt} = \frac{kg \Delta \rho h}{n \mu L}
\]

\(\nu\) = Tar front migration speed (m/s)
\(s\) = Path length (m)
\(t\) = Time (s)
\(k\) = Intrinsic permeability (m²)
\(g\) = 9.81 (m/s²)
\(\Delta \rho\) = \(\rho_{\text{tar}} - \rho_{\text{other fluid}}\) (gm/m³)
\(h\) = Vertical extent of saturated tar column (m)
\(n\) = Effective porosity
\(m\) = Dynamic viscosity (cP, gm/m-s)
\(l\) = Length of saturated tar column (m)
Saturation, $\alpha$

- “Mobile” saturation
  - Fraction of pore volume filled when the tar is moving through
  - Can approach 1 although water is the “wetting” fluid
  - Mobile saturation values can exist when motion has ceased

- “Residual” saturation
  - Left sorbed to soil or trapped by capillary forces after the tar has drained
  - Residual tar does not contribute to hydraulic head
Supplement D’Arcy’s Law with Conservation of Mass to Relate $S$ and $L$

\[ L_0 \alpha_m = L \alpha_m + (S - L) \alpha_r \]

\[ \frac{dL}{dS} = \frac{\alpha_r}{\alpha_r - \alpha_m} \]

$S$ = Path length (m)
$L$ = Saturated tar length (m)
$L_0$ = $L(t=0)$
\(\alpha_r\) = Residual soil concentration ($\text{cm}^3/\text{cm}^3$)
\(\alpha_m\) = Mobile soil concentration ($\text{cm}^3/\text{cm}^3$)
Resulting Solution

- \( S = \frac{\alpha_m}{\alpha_r} L_0 - \left( \frac{\alpha_m}{\alpha_r} - 1 \right) L \)
- \( L = L_0 - ut \)
- \( u = \left( \frac{\alpha_r}{\alpha_m - \alpha_r} \frac{\Delta p}{\mu} \right) \left( \frac{k}{n} \right) g \langle \cos \varphi \rangle \)
- \( \langle \cos \varphi \rangle = \frac{1}{t} \int_0^t \cos \varphi \, dt \approx \frac{1}{t} \int_0^t \frac{h}{L} \, dt \)
- \( \varphi = \text{Time weighted average angle from the vertical} \)
- \( h \approx L \cos \varphi \)
**Elapsed Time**

- \( \frac{dS}{dt} = \left( \frac{\alpha_m}{\alpha_r} - 1 \right) u \)

- \( t = \frac{L - L_0}{u} = \frac{\mu n}{\Delta \rho g k <\cos \phi>} (S - L_0) \)

- \( L_0 \approx \frac{\alpha_r}{\alpha_m} S \)
Parameters Determining Tar Migration

- **Tar properties**
  - Viscosity, $\mu$
  - Density, $\rho$
  - Surface tension, $\sigma$ (ST)
  - Interfacial tension, $\sigma$ (IT)
  - Contact angle, $\theta$
  - Residual saturation, $\alpha_r$

- **Soil properties**
  - Intrinsic permeability, $k$
  - Porosity, $n$
## Tar Properties

<table>
<thead>
<tr>
<th>Site/Sample</th>
<th>1B</th>
<th>2B</th>
<th>4</th>
<th>7</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.066</td>
<td>1.104</td>
<td>1.062</td>
<td>1.076</td>
<td>1.054</td>
<td>1.062</td>
</tr>
<tr>
<td>Dynamic viscosity (cP)</td>
<td>63.6</td>
<td>425.3</td>
<td>144.6</td>
<td>32.0</td>
<td>51.0</td>
<td>62.9</td>
</tr>
<tr>
<td>Surface tension (dynes/cm)</td>
<td>33.75</td>
<td>26.67</td>
<td>34.35</td>
<td>34.17</td>
<td>23.44</td>
<td>33.63</td>
</tr>
<tr>
<td>Interfacial Tension (dynes/cm)</td>
<td>26.70</td>
<td>27.83</td>
<td>22.55</td>
<td>25.79</td>
<td>22.37</td>
<td>24.43</td>
</tr>
<tr>
<td>$\alpha_r$ (cm³/cm³)</td>
<td>0.159</td>
<td>0.226</td>
<td>0.131</td>
<td>0.156</td>
<td>0.192</td>
<td>0.077</td>
</tr>
<tr>
<td>$\theta$ (degrees)</td>
<td>15.8</td>
<td>22.4</td>
<td>26.8</td>
<td>17.4</td>
<td>19.3</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Source: EPRI (2004); Kong (2004). $\theta$ is the average at pH 4.7 and 7.1.
## Soil Properties

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>7</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.420</td>
<td>0.435</td>
<td>0.343</td>
<td>0.451</td>
<td>0.383</td>
<td>0.530</td>
</tr>
<tr>
<td>( k (m^2) \times 10^{-11} )</td>
<td>5.46</td>
<td>4.58</td>
<td>1.93</td>
<td>4.61</td>
<td>1.13</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Source: EPRI (2004). \( k \) calculated based on the method of Kruger using the article size distributions.
Conservative Case

- All motion in the saturated zone
- At an average 60° from the vertical
Time to Migrate 100 m at 60° from the Vertical

<table>
<thead>
<tr>
<th>Site/Sample number</th>
<th>1B</th>
<th>2B</th>
<th>4</th>
<th>7</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Years</td>
<td>4.0</td>
<td>19.4</td>
<td>23.3</td>
<td>2.2</td>
<td>16.7</td>
<td>2.2</td>
</tr>
<tr>
<td>$L_0$ (m)</td>
<td>15.9</td>
<td>22.6</td>
<td>13.1</td>
<td>15.6</td>
<td>19.2</td>
<td>7.7</td>
</tr>
</tbody>
</table>
How long does the tar take to move 100 m in the saturated zone?

- Generally a few years
- Worst case about two decades
  - High viscosity
  - Low conductivity
  - Near neutral buoyancy
- Requires a large initial input of tar from 7.7 to 22.6 m thick to go 100 m
- Much faster in the vadose zone
Can “mobile tar” persist longer?

- Bond number $N_b$ is the ratio of gravitational to capillary force
  \[ N_b = \frac{F_g}{F_c} = \frac{\Delta \rho gh r}{2 \sigma \cos \theta} \]

  - As $h$ decreases, capillary pressure overcomes gravitational force ($N_b \approx 1$) and motion ceases
  - $r \sim$ Pore radius, capillary radius, grain radius (m)
  - $\sigma =$ Interfacial tension between tar and other fluid (dynes/cm = gm/s$^2$)
  - $\theta =$ Contact angle
## Value of \( h(r) \) in Meters for \( N_b = 1, \phi = 0 \)

<table>
<thead>
<tr>
<th>( r ) (m) ( \downarrow )</th>
<th>Site/Sample ( \rightarrow )</th>
<th>1B</th>
<th>2B</th>
<th>4</th>
<th>7</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{-4} ) Sand</td>
<td></td>
<td>7.94E-01</td>
<td>5.04E-01</td>
<td>9.36E-01</td>
<td>6.60E-01</td>
<td>7.97E-01</td>
<td>7.47E-01</td>
</tr>
<tr>
<td>( 5 \times 10^{-5} ) Transition</td>
<td></td>
<td>1.59E+00</td>
<td>1.01E+00</td>
<td>1.87E+00</td>
<td>1.32E+00</td>
<td>1.59E+00</td>
<td>1.49E+00</td>
</tr>
<tr>
<td>( 1 \times 10^{-5} ) Silt/clay</td>
<td></td>
<td>7.94E+00</td>
<td>5.04E+00</td>
<td>9.36E+00</td>
<td>6.60E+00</td>
<td>7.97E+00</td>
<td>7.47E+00</td>
</tr>
</tbody>
</table>

Source: USDA Soil classifications
Conclusion “Mobile Tar”

- A column of height $h$ can exist over tight soils

- For silt/clay this column can be from 5 to 9.4 m high below the water table

- Finding saturated tar in soils does not indicate that tar is still moving!
Some Effects Can Produce Local Tar Movement

- Radically falling water table
  - Buoyancy reduced

- Installation of wells

- Test pits
## Interpreting Boring Logs

<table>
<thead>
<tr>
<th>Log</th>
<th>Interpretation</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Weathered saturated tar if mixed with soil, otherwise disposal of 100% tar</td>
<td>( \alpha_m \leq 1 )</td>
</tr>
<tr>
<td>“Saturated”</td>
<td>“Mobile” tar held in place by capillary forces at a lower elevation</td>
<td>( \alpha_m \leq 1^* )</td>
</tr>
<tr>
<td>“Interbedded”</td>
<td>“Mobile” tar held in place in a layered stratigraphy by capillary forces at a lower elevation</td>
<td>50%?</td>
</tr>
<tr>
<td>Blebs, ganglia, lenses</td>
<td>Residual tar with capillary trapping</td>
<td>Upper end of range ( \alpha_r = 7.7–22.6% )</td>
</tr>
<tr>
<td>“Coated soil grains”</td>
<td>Residual tar without capillary trapping</td>
<td>Lower end of range ( \alpha_r = 7.7–22.6% )</td>
</tr>
<tr>
<td>Stains</td>
<td>Tar related if characterized by a naphthalene or “tar” odor. A continuum with “coated grains” or possibly dissolved phase tar components.</td>
<td>Low 3%?</td>
</tr>
</tbody>
</table>
MGP Locations

- Usually located on water bodies
  - Fuel transport
    - Later residuals (coke, tar, ammonia liquor) transport out
  - Steam and cooling water supply
  - Landlocked exceptions on a rail spur with ground water supply
- Often on reclaimed bay, estuary, marsh land
Fill

- Because fill lacks bedding planes it does not facilitate transport over substantial distances

- Determining depth of fill
  - Boring log notation
  - Buried debris
  - Peat layer
  - Shells
Tar in Fill

- Tar in fill only
  - Local source

- Tar in fill and native soil
  - Possibly a regional source

- Tar in native soil only
  - A result of transport
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