Managing tar/creosote contaminated sediments

EPA NARPM meeting
DNAPL session
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Primer on coal tar, creosote, and pitch

- Creosote
- Coal tar
- Pitch
- Weathered pitch
### Characteristics of coal tar

**Table I**

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<tbody>
<tr>
<td></td>
<td>1.207</td>
<td>1.000</td>
<td>1.12</td>
<td>1.18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yorkshire Tar.</th>
<th>Northern Tar.</th>
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<tbody>
<tr>
<td>Ammoniacal liquor.</td>
<td>11.5 per cent.</td>
</tr>
<tr>
<td>Crude naphtha</td>
<td>0.9 „</td>
</tr>
<tr>
<td>Light oil</td>
<td>3.0 „</td>
</tr>
<tr>
<td>Creosote</td>
<td>15.6 „</td>
</tr>
<tr>
<td>Anthracene oil</td>
<td>10.4 „</td>
</tr>
<tr>
<td>Pitch</td>
<td>57.5 „</td>
</tr>
</tbody>
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Coal tar distillation and working up of tar products. Arthur R. Warnes, 1913.
# PAHs in coal tar

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Naphthalene (NPH)</td>
<td>128</td>
<td>31</td>
<td>0.337</td>
<td>0.30</td>
</tr>
<tr>
<td>Acenaphthylene (ACY)</td>
<td>152</td>
<td>3.9</td>
<td>0.02</td>
<td>0.22 (b)</td>
</tr>
<tr>
<td>Acenaphthene (ACE)</td>
<td>154</td>
<td>3.8</td>
<td>0.01</td>
<td>0.20</td>
</tr>
<tr>
<td>Fluorene (FLR)</td>
<td>166</td>
<td>1.9</td>
<td>0.015</td>
<td>0.16</td>
</tr>
<tr>
<td>Phenanthrene (PHN)</td>
<td>178</td>
<td>1.1</td>
<td>0.0447</td>
<td>0.28</td>
</tr>
<tr>
<td>Anthracene (ANTH)</td>
<td>178</td>
<td>0.05</td>
<td>0.0052</td>
<td>0.010</td>
</tr>
<tr>
<td>Fluoranthene (FLN)</td>
<td>202</td>
<td>0.26</td>
<td>0.0018</td>
<td>0.21</td>
</tr>
<tr>
<td>Pyrene (PYR)</td>
<td>202</td>
<td>0.13</td>
<td>0.0027</td>
<td>0.11</td>
</tr>
<tr>
<td>Benz[a]anthracene (BaA)</td>
<td>228</td>
<td>0.011</td>
<td>0.0026</td>
<td>0.04 (b)</td>
</tr>
<tr>
<td>Chrysene (CHR)</td>
<td>228</td>
<td>0.002</td>
<td>0.0019</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

Peters et al. ES&T 1999

Coal tar: 30-40% of total PAHs are parent compounds
Crude oil: only 1% of total PAHs are parent compounds, rest alkylated
Important considerations for tar/creosote dissolution

1) PAH dissolution from tar/creosote can be described by Raoult’s Law

2) Faster depletion of more soluble components changes the composition and PAH dissolution characteristics

3) Dissolution from the surface of tar may cause an interfacial film to develop that reduce mass transfer rate
Raoult’s law describes dissolution from creosote

\[ C^*_i = x_i^c \times S_i \]

- \( C^*_i \) = aqueous phase solubility
- \( x_i^c \) = mole fraction of a PAH in the creosote phase
- \( S_i \) = subcooled liquid solubility

Peters, C.A.; Knights, C.D.; Brown, D.G.

Environmental Science and Technology. 1999, 33, 4499-4507
Sediment dissolution dynamics: aqueous phase concentration and NAPL mole fraction

- Naphthalene is depleted rapidly in the first few years of flushing at typical groundwater velocities.
- Higher molecular weight compounds such as chrysene increases in concentration with time due to the much faster loss of the low molecular weight compounds.
Typical aqueous concentrations in equilibrium with tar

Unweathered tar

Weathered tar
Interfacial films on coal tar can reduce mass transfer

Fresh coal-tar drop in water

coal-tar drop aged in water 3 days

PAH flux from coal tar surface with time

Rapid decline of PAH flux seen with time
Amended caps

Groundwater flow can mobilize PAHs through a sand cap

Caps over creosote contaminated sediment need to account for PAH transport

Carbon amendments can enhance retardation within caps
Sand cap over creosote contaminated sediment
Columns with sediment and capping material

Measuring low PAH concentrations in porewater without disrupting flow is challenging.
SPME measurement of pore water PAHs

Solid phase microextraction (SPME) (Hawthorne et al. ES&T, 2005)

- Equilibration of SPME fiber while stirring for 30 minutes
- Injection to GC/MS inlet for 5 minutes at 320 °C
- Post-clean fiber in helium stream for 15 minutes at 320 °C
Rapid breakthrough of PAHs in sand cap

Initial PAH Profile through Column *without* amendments

PAH Profile after 5 Days (8 Bed Volumes) *without* Amendments

Some contamination of the cap occurs during column construction

Depletion of naphthalene from the sediment source is observed
Comparison of total solid PAH concentration measured in existing field cap vs. laboratory columns

Several PAH measurements in the field cap material are in the range of laboratory column measurements when complete breakthrough is observed in the column pore water.
Strong retardation in AC amended sand cap

Initial PAH Profile through Column with 2% AC (day 0)

PAH Profile in 2% AC column after 18 bed volumes

Some contamination of the cap occurs during column construction

No breakthrough after 18 bed volumes
PAH breakthrough as a function of time

A. Phenanthrene Concentration vs. Bed Volumes
   - Sediment Layer
   - Overlying Water

B. Chrysene Concentration vs. Bed Volumes
   - Sediment
   - Overlying Water

G. Phenanthrene Concentration vs. Bed Volumes
   - Sediment
   - Overlying Water

H. Chrysene Concentration vs. Bed Volumes
   - Sediment
   - Overlying Water

Sand cap

2% AC in sand cap
Long-term predictions of PAH breakthrough

Darcy velocity: 0.015 m/hr
Phenanthrene input concentration = 100 μg/L
Conclusions:

• PAH dissolution from creosote can be described by Raoult’s law.

• PAH breakthrough is rapid in typical sand caps under groundwater advection.

• Amendment of sediment caps with activated carbon greatly reduces PAH transport.

• PAH transport modeled in two phases: 1) time variant dissolution from creosote, 2) retarded transport through the capping material.

• PAH concentration in core solids is a poor indicator of cap performance, especially for sand caps.

• Experiments with sand caps with and without biological activity did not show remarkable difference for the flow conditions tested.
Key publications:


UMBC Graduate Students and post docs:
Phil Gidley; Seokjoon Kwon

Sponsors:
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