EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN CLAY TARGET FRAGMENTS AND SURFACE SOIL AT SHOT GUN RANGE SITES

Presenter: Glenn Hoeger and Brian Magee
ARCADIS/Malcolm Pirnie
May 11, 2011
Objectives

1. Understand the nature of PAHs in soil containing clay target fragments at shot gun range sites

2. Obtain overview of regulatory risk-based screening levels and the role of bioavailability in site-specific evaluations

3. Become familiarized with the evolving toxicity assessment for PAHs

4. Obtain overview of current approach for site-specific bioavailability study for PAHs in soil

5. Regulatory approval and public acceptance for bioavailability evaluations of PAHs in surface soil at shot gun range sites
Objective 1 - Nature of PAHs in Soil Containing Clay Target Fragments
PAHs in Soil at Range Sites

- Clay target fragments and lead shot are typically distributed in predictable patterns.
- Lead shot found at highest density in a fan between 375 and 600 feet from firing positions.
- Clay target fragments found in highest density in a fan from 65 to 260 feet from firing positions.
Aerial Extent of PAHs

- PAHs in soil generally occur in soils with visible clay target fragments at ranges where no re-development has occurred.

- Aerial extent of soil impacted by PAHs related to number of firing positions at individual range sites.

- Simple range sites with only a single firing positions will have 2 to 5 acres of impacted surface soil.
• Historic shot gun range sites used to train aerial gunners in WWII can have between 10 and 20 firing locations

• Clay target fragment fans overlap among adjacent firing positions

• Large range sites with only a multiple firing positions will have 20 acres or more of impacted surface soil
Source of PAHs

- Clay targets are made of 67 percent dolomitic limestone and 33 percent coal tar pitch or petroleum pitch as a binding agent.
- Coal tar and petroleum pitch are the source of PAHs in targets.
- High molecular weight PAHs are principal chemicals of concern in coal tar and petroleum pitch.
Principal chemicals of concern in soil with clay target include the following 7 High Molecular Weight PAHs (4 to 6 rings):

- Benz [a] anthracene
- Benzo[a] fluoranthene
- Chrysene
- Benzo[a]pyrene
- Indeno[1,2,3-cd]pyrene
- Dibenzo[a,h]anthracene
- Benzo[k] fluoranthene
Chemical & Physical Characteristics

- Low vapor pressures
- Low water solubility
- High octanol:water partition coefficients
- Strongly adhered to particles entrainment in stormwater runoff and wind-blown dust potential transport mechanisms of concern
- Volatilization and migration to groundwater not of concern
- Direct contact principal concern (ingestion, dermal absorption, & inhalation)
### PAH Concentrations and Soil Fractions

<table>
<thead>
<tr>
<th>PAH</th>
<th>Soil Sample w/ Target Fragments</th>
<th>Soil Sample w/o Target Fragments (No. 4 Sieve)</th>
<th>Fine Fraction &lt;250 micron Soil Sample (No. 60 Sieve)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>1,000</td>
<td>160</td>
<td>41</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>790</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>1,400</td>
<td>110</td>
<td>25</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>750</td>
<td>81</td>
<td>21</td>
</tr>
<tr>
<td>Chrysene</td>
<td>960</td>
<td>160</td>
<td>32</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>120</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>770</td>
<td>130</td>
<td>34</td>
</tr>
</tbody>
</table>

Concentrations in mg/kg
Mechanical Weathering

- PAHs associated with clay target fragments
- Mechanical weathering creates smaller particles
- Small particles account for PAHs in fine fraction soil samples
Objective 2 – Regulatory Risk-based Screening Levels and Bioavailability
1. U.S. Environmental Protection Agency uses risk-based soil screening levels prepared by Oak Ridge National Laboratory – Regional Screening Levels (RSLs)

2. Many States have adopted risk-based regulations to manage hazardous waste (e.g.):
   - Illinois – Tiered Approach to Corrective Action Objectives (TACO)
   - Texas – Texas Risk Reduction Program (TRRP)
   - Washington – Model Toxic Control Act (MTCA)

3. Based on $10^{-6}$ or $10^{-5}$ excess lifetime cancer target risk and mutagenic mode of action (Age-Dependent Adjustment Factors)
Risk-based Assumptions

**Soil Screening Level (mg/kg) =**

\[
\text{Target Cancer Risk} \times \text{Body Weight} \times \text{Averaging Time} \\
\text{CSF} \times \text{RBAF} \times \text{Intake} \times \text{Exposure Assumptions}
\]

1. **Target Cancer Risk** – Typically 10^{-6} or 10^{-5}
2. **Body Weight** – 15 kilograms (kg) for child and 70 kg for adult
3. **Averaging Time** – 365 days per year (d/yr) over 70 years
4. **Exposure Assumptions** – Typically 350 d/yr over 30 years
5. **Intake** – 200 mg/d for child and 100 mg/d for adult
6. **CSF** – Cancer Slope Factor – 7.3 per mg/kg-day for B[a]P & Relative Potency Factors (RPFs) for other PAHs
7. **RBAF** – Relative Bioavailability Factor – Typically assumed to be 1

*Bioavailability is the only input available to apply site-specific data*
### PAH Concentrations in Fine Soil Fractions and Corresponding Regulatory Levels

<table>
<thead>
<tr>
<th>PAH</th>
<th>Maximum Fine Fraction Soil Samples</th>
<th>EPA RSLs</th>
<th>TACO (IL) Residential Ingestion</th>
<th>TRRP (TX) Tier 1 Residential</th>
<th>MTCA (WA) Method A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>41</td>
<td>0.015</td>
<td>0.09</td>
<td>0.56</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>30</td>
<td>0.15</td>
<td>0.9</td>
<td>5.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>25</td>
<td>0.15</td>
<td>0.9</td>
<td>5.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>21</td>
<td>1.5</td>
<td>9</td>
<td>57</td>
<td>10</td>
</tr>
<tr>
<td>Chrysene</td>
<td>32</td>
<td>15</td>
<td>88</td>
<td>570</td>
<td>100</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>5</td>
<td>0.015</td>
<td>0.09</td>
<td>0.55</td>
<td>0.1</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>34</td>
<td>0.15</td>
<td>0.9</td>
<td>5.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Carcinogenic Endpoints</td>
<td>$10^{-6}$</td>
<td>$10^{-6}$</td>
<td>$10^{-5}$</td>
<td>$10^{-6}$</td>
<td></td>
</tr>
</tbody>
</table>

Concentrations in mg/kg
Objective 3 – PAH Toxicity Assessment
1. EPA (1993) developed Relative Potency Factors (RPFs) for 6 carcinogenic PAHs (c-PAHs) based on CSF for benzo(a)pyrene and assessed as Benzo(a)pyrene Toxic Equivalents (BaP-TE)

2. EPRI/GRI/EPA Two-year mouse feeding study for Coal Tar Samples and benzo(a)pyrene (1996), CSF for BaP lower than IRIS value at 1.2 (mg/kg-day)^{-1}

3. CSF for coal tar higher than predicted from BaP-TE

4. EPA (2010) proposed update to RPF approach increasing the list of c-PAHs from 7 to 25 and increased potency of 4 existing c-PAHs

5. Others as high as 60 times more potent than BaP
# Proposed Relative Potency Factors

<table>
<thead>
<tr>
<th>PAH</th>
<th>Current RPF</th>
<th>Proposed RPF</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo(a)pyrene</td>
<td>1</td>
<td>1</td>
<td>1x</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>0.1</td>
<td>0.2</td>
<td>2x</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>0.1</td>
<td>0.8</td>
<td>8x</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>0.01</td>
<td>0.03</td>
<td>3x</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.001</td>
<td>0.1</td>
<td>100x</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>1</td>
<td>10</td>
<td>10x</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>0.1</td>
<td>0.07</td>
<td>0.7x</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>none</td>
<td>0.08</td>
<td>NA</td>
</tr>
</tbody>
</table>
## Additional Proposed PAHs for Evaluation By RPFs

<table>
<thead>
<tr>
<th>PAH</th>
<th>Average RPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthanthrene</td>
<td>0.4</td>
</tr>
<tr>
<td>Benz[b,c]aceanthrylene, 11H-</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Benzo[c]fluorene</strong></td>
<td><strong>20</strong></td>
</tr>
<tr>
<td>Benz[e]aceanthrylene</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Benz[j]aceanthrylene</strong></td>
<td><strong>60</strong></td>
</tr>
<tr>
<td>Benzo[j]fluoranthene</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Benz[l]aceanthrylene</strong></td>
<td><strong>5</strong></td>
</tr>
<tr>
<td>Cyclopenta[c,d]pyrene</td>
<td>0.4</td>
</tr>
<tr>
<td>Cyclopenta[d,e,f]chrysene, 4H-</td>
<td>0.3</td>
</tr>
<tr>
<td>Dibenzo[a,e]fluoranthene</td>
<td>0.9</td>
</tr>
<tr>
<td>Dibenzo[a,e]pyrene</td>
<td>0.4</td>
</tr>
<tr>
<td>Dibenzo[a,h]pyrene</td>
<td>0.9</td>
</tr>
<tr>
<td>Dibenzo[a,i]pyrene</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Dibenzo[a,l]pyrene</strong></td>
<td><strong>30</strong></td>
</tr>
<tr>
<td>Naphtho[2,3-e]pyrene</td>
<td>0.3</td>
</tr>
<tr>
<td>Dibenzo[a,c]anthracene</td>
<td>4</td>
</tr>
</tbody>
</table>
1. **Absolute Bioavailability (ABA)** – is defined as the fraction of a compound which is ingested, inhaled, or applied to the skin that is actually absorbed and reaches the circulation. Absolute bioavailability can be expressed in the following equation:

\[
ABA = \frac{(\text{Absorbed Dose} \times 100)}{\text{Administered Dose}}
\]

2. **Relative Bioavailability (RBA)** – is defined as the comparative ABA of one compound in two different exposure media via the same route of exposure (ingestion, inhalation, or dermal absorption). Relative bioavailability can be expressed in the following equation:

\[
RBA = \frac{(ABA_{\text{test medium}} \times 100)}{ABA_{\text{reference medium}}}
\]
Why Perform Bioavailability Studies?

• Dose-response studies & toxicological reference values (CSFs) based on *administered* dose, not *absorbed* dose

• Typical studies use protocols with high absorption:
  - Soluble species of metals
  - Dosing media promoting absorption
    - (corn oil)
  - Gavage or drinking water protocols
  - Dermal studies with pure organics or dissolved metals

• Soil/sediment chemical concentrations determined by rigorous extractions (not biologically relevant)
1. EPA has established guidance for performing bioavailability studies for lead in soil (March 2007)

2. No guidance exists concerning bioavailability testing of organic chemicals in soils and sediments

3. Recent EPA review of bioavailability testing for dioxins in soil (November 2010) states that RBA estimates are less than 100% in all soils studied compared to corn oil or diet

4. Site-specific soil characteristics including grain size, organic carbon, and pH have great influence on RBA

5. No regulatory guidance regarding a preferred animal model
PAHs are fat-soluble, organic compounds absorbed in the small intestines via fat globules.

PAHs are metabolized in liver and principally excreted from liver to small intestines in bile.

Excreted PAHs and metabolites can be re-absorbed in small intestines (enterohepatic cycling).

PAH metabolites are also excreted in urine.
Experimental Design

- *In vivo* testing versus *in vitro* testing
- Value of pharmacokinetic testing using $^{14}$C radiolabeled compounds
- Animal model selection (swine/rat/mouse)
- Dosing medium, frequency, and duration
- Measurement endpoints (blood, tissue, urine, and/or feces)
Animal Model Selection

- Literature has principal bioavailability work in mice, rats, and swine
- Juvenile swine recommended for lead bioavailability, because swine are more physiologically relevant to humans than rodents for criteria important for metal absorption
- Lead toxicological criteria are based on human studies, not animal studies
- PAH toxicological criteria are based on effects seen in rodent feeding studies
- Rodents provide the opportunity to increase the number of test subjects
Dosing Media

- Fine fraction of soil (<250 micron) particle size is recommended by EPA for incidental ingestion

- Aged site soils superior to lab-prepared soil mixtures; un-aged chemical-soil mixtures will overestimate site-specific bioavailability

- Soil dosed to animals by incorporation into feed is preferred over suspending soil in corn oil (or similar vehicle) and dosing via gavage

- Extracts of PAHs from fine fraction soil samples serve as reference media for development of RBA assessment
Measurement Endpoints

- Bioavailability studies can include analysis of tissue, blood, urine, or feces
- Biliary excretion, enterohepatic cycling, and further metabolism by intestinal flora make PAH concentrations in feces difficult to interpret
- Tissue, blood, and urine concentrations of PAHs and metabolites represent absorbed compounds
- Tissue and blood volumes limited for smaller test subjects such as mice
- Urine analysis preferred; accounting for administered dose not required when using soil extract of PAHs as a reference medium
Experimental Protocol Schematic
Objective 5 – Regulatory Approval and Public Acceptance
Inert Classification

ITRC cites toxicity testing in aquatic organisms as evidence that clay target fragments are not hazardous waste.

ITRC cites a standard risk assessment on a small arms range as evidence that PAHs in clay target fragments do not pose a significant risk to human health.

These studies do not address Relative Bioavailability, and the scientific basis of the “inert” designation is often rejected by regulators.
Previous risk assessment approach surveyed literature for similar COCs and identified studies with similar characteristics.

No current bioavailability studies for PAHs in the limestone/coal tar matrix of clay targets have been identified from the literature.

Regulators have focused on the importance of bioavailability studies being performed on site-specific soils and are less accepting of generic approaches.
Weight-of-Evidence Evaluations

- Soil samples analyzed using SPLP and TCLP extraction and analysis provide site-specific, anecdotal information on bioaccessibility.
- SPLP and TCLP extraction methodologies have limited or no relationship to gastrointestinal absorption.
- EPA review of Dioxin Bioavailability studies (November 2010) and current literature do not identify a validated in vitro model to accurately predict bioavailability for lipophilic organics; in vitro extraction methodologies are not likely to be accepted in the near future.
- Weight-of-evidence evaluations have been rejected by regulators and will likely continue to be rejected.
Regulatory Approval

Regulators are less willing to accept generic evaluations concerning bioavailability and appear focused on the following issues:

1. Investigation should be site-specific

2. Investigation should be designed to produce scientifically valid Relative Bioavailability factors

3. For chemical groups, such as PAHs, more than one representative chemical should be tested unless sufficient evidence is provided as justification

4. Regulators should be involved in development of the bioavailability protocol
Public Acceptance

- Studies of feral pigs foraging in clay target fall zones were sickened from ingestion of target fragments

- Laboratory studies of clay target toxicity to pigs (Davis and Libke, 1968) reported liver damage consistent with coal tar toxicity

- Results indicate that PAHs are available to some degree at high doses (consuming clay targets)

- This type of information is available to the public on the internet & could spur concern

- Effective risk communication programs are required to educate the public
Summary

1. Soil with clay target fragments can have PAHs 3 to 5 orders of magnitude higher than regulatory risk-based screening levels.

2. PAHs in fine fraction of soil are believed to be within the limestone/coal tar matrix of small weathered particles from larger fragments.

3. Bioavailability is the only parameter in risk-based regulations available for development of alternative exposure assumptions.

4. Site-specific in-vivo bioavailability studies using animal models will be required to gain regulatory acceptance of alternative relative bioavailability factors.

5. Public acceptance will be based on effective outreach and public risk communication programs.
EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN CLAY TARGET FRAGMENTS AND SURFACE SOIL AT SHOT GUN

Glenn Hoeger
ARCADIS/Malcom Pirnie
One South Church Ave, Suite 1120, Tucson, AZ, 85701
Tel: 520-629-8282
Mobile: 520-225-7648
glenn.hoeger@arcadis-us.com

Questions?

Brian Magee, Ph.D.
ARCADIS U.S., Inc.
Two Executive Drive, Suite 303, Chelmsford, MA 01824
Tel: 978.937.9999 x319
Mobile: 978.551.4048
brian.magee@arcadis-us.com