Assessing PAHs in the Real World

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PAH are Ubiquitous

• Astronomers: ~20% of the carbon in the universe is in the form of PAHs
  – NASA’s web site: “Polycyclic aromatic hydrocarbons… are among the building blocks of life… are pervasive in galaxies like our own Milky Way, and play a significant role in star and planet formation.”

• On Earth, there is no exposure to any one PAH, but the real world is full of PAH-containing mixtures
  – Of which there are uncounted thousands
  – PAH-containing mixtures also contain a variety of heterocyclic PAH compounds and non-PAH compounds
  – Industrial and natural processes produce and use complex mixtures which contain PAHs and hundreds of related and unrelated compounds.
    – In regulatory-speak, Class 2 chemicals: “Unknown or Variable composition, Complex reaction products or Biological materials” (UVCBs)
The PAH Literature is Vast

• PAH-containing mixtures are arguably the most studied materials in the environment
  – and there are human exposure data including occupational, clinical and ambient data

• One deliberately isolated PAH - benzo(a)pyrene - is arguably the most studied substance in toxicology
  – but there are no human exposure data to individual PAHs with 3 or more rings
Everyone is Exposed

“The majority of exposure (>95%), to high molecular weight PAHs in nonsmokers, is through the diet in a variety of foods including breads and cereal grains, vegetables, and smoke-cured or barbequed meats.” Madeen et al. Chem. Res. Toxicol., 2015, 28 (1), pp 126–134 DOI: 10.1021/tx5003996

### Summary of Estimated Daily Intakes of Benzo(a)pyrene Toxic Equivalents (BaP-TE)

<table>
<thead>
<tr>
<th>Source of Exposure</th>
<th>Average Daily Intake (ug/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient air and indoor air</td>
<td>0.006 to 0.02</td>
</tr>
<tr>
<td>Diet</td>
<td>0.2 to 0.6</td>
</tr>
<tr>
<td>Smoking</td>
<td>0.2 to 1</td>
</tr>
<tr>
<td>Second hand smoke</td>
<td>0.005 to 0.26</td>
</tr>
<tr>
<td>Coal tar pharmaceuticals</td>
<td>33</td>
</tr>
<tr>
<td>Coal tar shampoo</td>
<td>0.017</td>
</tr>
</tbody>
</table>
The Regulation and Science of PAHs

• Some Regulations and Regulatory Tools Need Updating
  – Human Health Risk Assessment Methods
  – Hazard Assessment

• Ecological Assessments Should be More Focused on Risk
Assessment Methods: Human Health Toxicity Values Need to be Updated

• “Relative Potency Factor” (RPF) approach
  – Additive toxicity
  – Add B(a)P equivalency factors of EPA-16 Priority Pollutant PAHs or an expanded PAH list [EPA 2010 proposal, California list, etc.]
  – Use of expanded list may exacerbate overestimation of risk
  – 1993 EPA Guidance is provisional, not promulgated

• EPA’s Science Advisory Board
  – RPF approach is scientifically problematic
  – Antagonism, bioavailability/bioaccessibility important mediators of PAH risk
  – Recommended conducting toxicity testing on a variety of PAH-containing mixtures with a view to replacing RPFs
  – Currently promulgated IRIS assessment for B(a)P is out-of-date
Assessment Methods: Hazard Characterization of Mixtures Should be Re-evaluated

• National Academy Recommendation: EPA/IRIS assessment of chemicals adopt methods developed for use in pharmaceutical approvals
  – Systematic Review & Risk of Bias analysis of existing studies, meta-analysis
  – NTP & EPA have been developing guidance

• 5 recent Systematic Reviews (including risk of bias evaluations) including dozens of studies of occupational exposures in PAH-using industries
  – Industries: iron & steel foundries, aluminum plants, cokeries, carbon electrode manufacturing, asphalt pavers & roofers, creosote, tar distilleries

• Little to no association between occupation entailing high PAH exposure and cancer risk
  – Endpoints considered: cancers of the skin, larynx, lung, respiratory tract, bladder, kidney, Hodgkin lymphoma, non- Hodgkin lymphoma, leukemia, multiple myeloma
One Recent Systematic Review

“It cannot be ruled out whether such excesses are due, at least in part, to possible bias or residual confounding.”
Rota et al., Arch. Toxicol., 2014, 88(8), DOI: 10.1007/s00204-014-1296-5
5 Recent Systematic Reviews of Occupational Exposure Literature ....

... Does not include data from clinical literature
Assessment Methods: Ecological Risk

• Often, comparisons are made using “consensus standards”
  – Is that meaningful?

• In Superfund site evaluations, EPA found that sediment toxicity rarely correlates with sediment PAH concentrations
  – Development of Equilibrium Partitioning Benchmarks
  – PAH concentrations in sediment pore water is often a better predictor of bioaccessible PAHs

• Bioavailability found to vary with PAH sources

“…PAH source materials have a dominating influence on partitioning, highlighting the importance of using native field soils in bioavailability and risk assessments.” Xia et al., ES&T, 2016, DOI: 10.1021/acs.est.5b06164
Sediment PAH Concentration vs. *H. Azteca* Survival

There is No Relationship Between [PAH] and Toxicity

EPA *Hyalella azteca* 28-day test – 4 Sites

- Percent Survival (%)
- Sediment Total PAH Concentration (mg/kg)

- Nontoxic Sediment
- Toxic Sediment

4 ppm 20 ppm


Another example – Anacostia River sediment:


https://www.serdp-estcp.org/
Anemones, which are related to jellyfish, became increasingly abundant on the pilings in deeper water (left). Food is collected on the tentacles of these animals using stinging cells called nematocysts, which are triggered by contact with prey. These tiny spears are tipped with poison that quickly subdues copepods, amphipods and other living organisms. In Puget Sound, mussels are generally found high in the intertidal, or on pilings in the Pacific Northwest because the bottom is home to a host of species of starfish who are voracious predators on these and other bivalves. The Sooke Basin crosscut treated pilings were no exception and armies of starfish, like the ochre star (Pisaster ochraceus) seen at right were frequently found grazing on the barnacles and mussels that had settled on the pilings.

The pilings became home to a community of animals that any aquarium would be proud of.
Assessing PAHs in the Real World

• It’s not as easy as adding up B(a)P-equivalencies or comparing to consensus standards

• Must work towards understanding….
  – Source(s) of the PAHs
  – Sinks…
    – What is the behavior of PAH-containing particles once away from their sources, in soil, sediment, air?
  – Bioavailability (& Bioaccessibility)
  – A Mixture approach to toxicity
We will hear progress on all these fronts in the platform presentations & posters (18) today

Questions?