Evaluation of Sorbed Polycyclic Aromatic Hydrocarbons on Biochar

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Introduction

- Polycyclic Aromatic Hydrocarbons (PAH)
  - Compose a large group of compounds (200+)
  - Characteristic of two or more fused aromatic carbon rings in the structure
  - Composed solely of carbon and hydrogen atoms
  - Simplest PAH is naphthalene
PAH Distribution

- **PAHs are among the most common organic pollutants**
  - Detected on every continent and virtually every location on the globe

- **Universal presence**
  - Universal presence
  - Ease of transport
  - Stability

- **USEPA lists 32 of these PAHs as priority pollutants**
PAH History

• Some PAHs are known human carcinogens

• Sir Percival Pott (1755)
  ▫ Postulated that the high incidence of cancer in chimney sweeps was caused by an agent in chimney soot (later shown to be PAHs on soot)
PAH - Anthropogenic Sources

- Largest stationary point sources
  - Paper mills
  - Factories of consumer wood products
  - Petroleum refining

(ARB, 1997)
PAH Natural Sources

- **Present in Fossil Fuels**
  - Crude oil, coal, shale oils ...

- **Present in gases (smoke) and ashes from**
  - Forest /Prairie fires
  - Volcanoes

- **Biological Routes**
  - Microbial degradation of black carbon
  - Microbial production during humidification (complex SOM)

(HSDB, 1995)
PAH Formation Processes

- **Incomplete combustion**
  - Burning fossil fuels
  - Biomass burning
  - Cooking for meal preparation

- **PAH production also occurs:**
  - Charcoal production
  - Present in bio-oil from biomass pyrolysis (e.g., Ré-Poppi and Santiago-Silva, 2002)
## PAH Presence in Different Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>(\Sigma) USEPA PAH [(\mu g\ g^{-1}) ppm]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soils</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban soil (roadside)</td>
<td>0.04 to 13.5</td>
<td>(Ritschel, 2008)</td>
</tr>
<tr>
<td>Arable soil (farmland)</td>
<td>0.2 to 0.4</td>
<td>(Ritschel, 2008)</td>
</tr>
<tr>
<td>Terrestrial rocks</td>
<td>&lt;0.1 to 45</td>
<td>(Mahajan et al., 2001)</td>
</tr>
<tr>
<td><strong>Other Biomass Materials:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine Needles</td>
<td>0.04 – 1.9</td>
<td>(Ratola et al., 2010; Navarro-Ortega et al., 2011)</td>
</tr>
<tr>
<td>Wood Chips</td>
<td>0.01 to 0.015</td>
<td>(Chinnici et al., 2007)</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>2.2 to 126</td>
<td>(Wild et al., 1990; Ritschel, 2008)</td>
</tr>
<tr>
<td>Composts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood chips/leaves/grass clippings</td>
<td>16.0</td>
<td>(Grossi et al. 2011)</td>
</tr>
<tr>
<td>Fall leaves/twigs</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td>Wood chips/sewage sludge</td>
<td>20.8</td>
<td></td>
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</tbody>
</table>
Biochar is a form of black carbon

- **Biochar**: Name given to the production of black carbon for the purpose of soil carbon sequestration

- Biochar spans the entire spectrum of black carbon

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**Thermo-chemical conversion products**

- **Biochar**: Retains relic forms of parent material
- **Combustion residues**: Complete new structure
- **Combustion condensates**: Combustion residues

Adapted from Hedges et al., 2000; Elmquist et al., 2006; Spokas 2010
## PAH Presence in Black Carbons

<table>
<thead>
<tr>
<th>Black Carbon Form</th>
<th>Σ USEPA PAH [µg g⁻¹] ppm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.3 to 253</td>
<td>(Wang et al., 2010) (Laumann et al., 2011)</td>
</tr>
<tr>
<td>Slow Pyrolysis (wood)</td>
<td>&lt;0.01</td>
<td>(Zhurinsh et al. 2005) (Singh et al., 2010)</td>
</tr>
<tr>
<td>Wood Ash (3.7% C content)</td>
<td>16.8</td>
<td>(Bundt et al., 2001)</td>
</tr>
<tr>
<td>Natural and synthetic charcoal</td>
<td>1.0 to 3.7</td>
<td>(Brown et al., 2006)</td>
</tr>
<tr>
<td>Coconut shell charcoal (CocoNara™)</td>
<td>2.9</td>
<td>(Sepetdjian et al., 2010)</td>
</tr>
<tr>
<td>Hardwood Lump Charcoal</td>
<td>0.5</td>
<td>(Sepetdjian et al., 2010)</td>
</tr>
<tr>
<td>Three Kings™ (waterpipe charcoal)</td>
<td>1.2</td>
<td>(Sepetdjian et al., 2010)</td>
</tr>
<tr>
<td>Biochar (11 biochars/5 feedstocks)</td>
<td>&lt;0.5</td>
<td>(Singh et al., 2010a)</td>
</tr>
<tr>
<td>Biochar (50 biochars) {Majority from same production unit}</td>
<td>0.3 to 45</td>
<td>(Hale et al., 2012)</td>
</tr>
</tbody>
</table>

Current observed biochar range: 0.01 to 45 µg g⁻¹
Biochars Examined

- ≈100 different biochars
- 50+ different pyrolysis units
  - Laboratory scale
  - Entrepreneur scale (homemade units)
  - Pilot scale
  - Small industrial scale units (tons/day)
  - Wood fired boilers (high C wood ash)
- Analyzed by multiple methods
  - Various solvent extraction/clean-up methods examined
Total sorbed PAH on Biochar

- Sum of total PAH range from 0.01 to 83 µg g⁻¹
Total sorbed PAH on Biochar
Total sorbed PAH on Biochar

- Highest sorbed PAH content: Slow Pyrolysis
  - Producer noted: Fire in the reactor that was extinguished with water during production/cooled

![Graph showing total PAH concentration across different methods of production.](image)
Total sorbed PAH on Biochar

- MAP and Hydrothermal produced lower amount of PAH
- Conditions not favorable for the production of PAH (?)
- Some of these used sewage sludge (2 to 126 ppm)
Other studies – Hale et al. (2012)

Fast Pyrolysis and “Traditional” Techniques
PAH formation historically linked to higher production temperatures

Higher production temperatures lead to higher PAH levels

(Morf et al., 2002)
PAH formation historically linked to higher production temperatures.

However, there are exceptions:
- Not all pyrolysis units follow this trend.
Factors in PAH formation

Not solely production temperature

- Original feedstock – PAH levels?

- **Presence of oxygen is necessary to create PAH compounds**
  - Presence of $O_2$ leads to increase PAH production

  (Rey-Salgueiro et al., 2004)

- **Moisture content of the feedstock**
  - Dryer biomass producing lower PAH levels

  (Bignal et al., 2008)
# PAH Presence in Ashes

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Sigma$ USEPA PAH [µg g$^{-1}$] ppm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom/fly ash mixture (wood feedstock)</td>
<td>37 – 77</td>
<td>(Davies et al., 1976; Dugenest et al., 1999; Johansson and van Bavel, 2003a)</td>
</tr>
<tr>
<td>Coal Fly Ash</td>
<td>15 – 185</td>
<td>(Gohda et al., 1993)</td>
</tr>
<tr>
<td>Municipal solid waste incinerator - bottom ash</td>
<td>0.5 to 3.6</td>
<td>(Johansson and van Bavel, 2003b)</td>
</tr>
</tbody>
</table>

- Incineration and gasification residues contain higher amounts of PAH compounds
  
  (0.5 to 185 µg g$^{-1}$)
PAH Formation for Biochar

- **Cooling biochars in oxygen (air) environment**
  - Increases sorbed PAH content

- **Moisture differences in the feedstock**
  - Wetter feedstock leads to increased PAH levels

- **Abiotic oxidation while sorbed to biochar**
  - Time since production = important factor
Conclusions

- Sorbed PAH levels on biochar can be minimized through feedstock, pyrolysis, and storage conditions.

- Production conditions are critical:
  - **Exclusion of oxygen** is the most important, both during production AND cooling.
    - Many sources – air, water, carbohydrates, etc...
    - Biochar cooling – avoid air ($O_2$) contact until cool.
  - Use **dry feedstocks** to minimize PAH formation.
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