Evaluation of Sorbed Polycyclic Aromatic Hydrocarbons on Biochar

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Polycyclic aromatic hydrocarbons

- 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 occurrence

- PAHs are among the most common organic pollutants
  - Ease of atmospheric transport
  - Universal environmental presence
  - US EPA lists 32 of these PAHs as priority pollutants
Primary sources: Anthropogenic

- Largest stationary point source emissions in California:
  - Paper mills
  - Factories of various consumer wood products
  - Petroleum refining

(ARB, 1997)
PAH: Natural Sources

- Present in:
  - Fossil fuels
    - Crude oil
    - Shale oil
    - Coal
  - Coal tars

- Present in gases and ashes from:
  - Forest fires
  - Grassland fires
  - Volcanoes

- Biological Routes
  - Microbial degradation of black carbons
  - Microbial production during complex organic matter formation
    (soil humic substances)

(HSDB, 1995)
Processes to form PAH compounds

- Incomplete combustion
  - Burning of fossil fuels: coal, diesel, gasoline
    - Transportation sector
  - Burning of biomass (e.g. wood, tobacco, brush fires)
  - Cooking for meal preparation

- PAH production has also been confirmed during:
  - Production of charcoal by pyrolysis (e.g., Ré–Poppi and Santiago–Silva, 2002)
  - Present in bio–oil from biomass pyrolysis
# PAH presence in various materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Σ USEPA PAH [µg g⁻¹]</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>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><strong>Composts</strong></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>
</tr>
</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

Adapted from Hedges et al., 2000; Elmquist et al., 2006
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 carbons.

Adapted from Hedges et al., 2000; Elmquist et al., 2006.
## PAH sorbed to black carbons

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<thead>
<tr>
<th>Material</th>
<th>$\Sigma$ USEPA PAH [µg g$^{-1}$]</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td><strong>Black Carbons</strong></td>
<td></td>
<td></td>
</tr>
<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$^{-1}$
## Incinerator/Gasifier Residues

<table>
<thead>
<tr>
<th>Material</th>
<th>( \Sigma ) USEPA PAH [( \mu g , g^{-1} )]</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 \( \mu g \, g^{-1} \))
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
Sorbed PAH on Biochar

- Sum of total PAH range from 0.01 to 83 µg g⁻¹
- Naphthalene was present on all biochars
- Possible influence of production technique
  - Not statistically significant within this sample pool
PAH formation initially linked to higher production temperatures

However, not all data follows this trend

There are some hints on how to reduce PAH content
Analytical Difficulties

- Extraction of PAH from biochar
  - Since each biochar possesses unique properties
  - Also possesses different extraction efficiencies
  - Optimal solvent for one biochar might not be best for another

(Fabbri et al., 2012 – Submitted)
Highest PAH containing biochar

- Producer commented about flames in hardwood chips while producing biochar

- Agrees with data in the literature
  - Flame increase PAH content of the residuals (indication of oxygen presence)
Hale et al. (2012) Biochar Data

Pyrolysis time:
- 30 min
- 1 hour
- 3 hours
- 6 hours
- 3-4 days

Total Hg concentration (g/g)
- 45
- 40
- 35
- 30
- 25
- 20
- 15
- 10
- 5
- 0

Legend:
- HP - Heartland Pine (gasification)
- HW - Mixed hardwood (fast pyrolysis)
- LLP - Lodgepole pine (modern slow pyrolysis)
- DDM - Digested dairy manure (modern slow pyrolysis)
- FW - Food waste (modern slow pyrolysis)
- PIMW - Paper mill waste (modern slow pyrolysis)
- CS - Corn stover (modern slow pyrolysis)
- EFB VESTO - empty fruit bunches (VESTO method)
- EFB NTS - empty fruit bunches (Malaysian traditional stove)
- EFB TLUD - empty fruit bunches (top lit up draft)
- CCGS TLUD - coconut shell (top lit up draft)
- CCGS 3 stone - coconut shell (traditional 3 stone fire)
- WS - Wheat straw (microwave)
- RWSD - Rubber wood sawdust (modern slow pyrolysis)
- O - Oak (modern slow pyrolysis, muffle furnace)
- P - Pine (modern slow pyrolysis, muffle furnace)
- G - Grass (modern slow pyrolysis, muffle furnace)
- OA - Oak aged (modern slow pyrolysis followed by leaching with distilled water)
- PA - Pine aged (modern slow pyrolysis followed by leaching with distilled water)
- GA - Grass aged (modern slow pyrolysis followed by leaching with distilled water)
- PW - Pine wood (modern slow pyrolysis)
- SG - Switchgrass (modern slow pyrolysis)
- Zambia charcoal dust - mixed savannah vegetation (traditional kiln, slow pyrolysis)
- Zambia stover - corn (traditional kiln, slow pyrolysis)
- Indonesia mixed - forest (traditional kiln, slow pyrolysis)
- Indonesia husk - rice (double drum, slow pyrolysis)
- Kenya corn cob, cornstover and sawdust (traditional 3 stone fire)
Factors impacting PAH formation?

- Presence of **oxygen** is necessary to create PAH compounds
  
  (Rey–Salgueiro et al., 2004)

- **Moisture content** of the biomass prior to pyrolysis has been observed to be a vital factor
  - Dryer biomass producing lower levels of PAH
  
  (Bignal et al., 2008)
PAH Impacted by $O_2$ and $H_2O$

- Post–production handling of biochar

- Cooling biochars in oxygen (air) environment
  - Increases sorbed PAH content
  - Lower PAH content in biochars cooled under anaerobic inert ($N_2$) environment

- Moisture differences in the feedstock lead to differences in the PAH content
  - In general, wetter feedstock leads to increased PAH levels

- PAH compounds can undergo abiotic oxidation while sorbed to biochar
  - Time since production important factor; reduces PAH levels
Importance of PAH presence

- Accumulation of PAH compounds by vegetation grown on biochar amended soils
  - Topic will be discussed Wednesday 10:00 am (Cooperage)
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
    - Many sources – air, water, carbohydrates, etc…
    - Biochar cooling – avoid air ($O_2$) contact until cool

- Use of dry feedstocks to avoid PAH formation
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"The nation that destroys its soil destroys itself."
--Franklin D. Roosevelt