Understanding mechanisms to predict and optimize biochar for sorption of agrichemicals

Kathleen E. Hall, Lucia Cox, Beatriz Gamiz, Kurt A. Spokas
Biochar as a sorbent

Biochar – pesticide interactions have been widely studied.

Applications

Filter material
Water treatment
Soil remediation

Important to understand these interactions, whether intentional or side effect of alternative applications
Biochar diversity

- Available feedstocks and pyrolysis systems
- Differing sorption results limit predictability among biochars
- Limited understanding of the mechanisms driving biochar-pesticide interactions
- There is a need to systematically study chemistry of biochars → greater understanding and optimization
Biochar-pesticide interactions

Sorption depends on both biochar and chemical properties

Proposed mechanisms

- Influenced by biochar surface characteristics
  - Chemical
    - Surface groups
  - Physical
    - Surface area
    - Pore size distribution
- Both can be modified (activation)

(Tan et al., 2015)
Biochar activation

Different techniques include ....

- Heating
- Solvent washing
  - HCl
- Surface oxidation/reduction
  - Steam
  - H$_2$O$_2$
  - CO$_2$
  - H$_2$SO$_4$, HNO$_3$, H$_3$PO$_4$

Goals are to increase sorption by increasing SSA and strategically altering functionality
Objectives

1. Activate biochars by a variety of methods to create “normalized” sorbent materials

2. Evaluate the role of biochar surface characteristics on the sorption of select herbicides with different chemistries
# Materials - Biochars

**Feedstock** = Grape wood

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temp</th>
<th>Moisture</th>
<th>Ash</th>
<th>Volatile</th>
<th>Fixed C</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape wood</td>
<td>350</td>
<td>3.54</td>
<td>10.9</td>
<td>39.5</td>
<td>49.7</td>
<td>66.6</td>
<td>4.0</td>
<td>1.1</td>
<td>17.5</td>
</tr>
<tr>
<td>Grape wood</td>
<td>500</td>
<td>3.99</td>
<td>16.8</td>
<td>19.3</td>
<td>64.0</td>
<td>70.4</td>
<td>2.3</td>
<td>0.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Grape wood</td>
<td>900</td>
<td>1.31</td>
<td>22.2</td>
<td>6.6</td>
<td>71.1</td>
<td>71.6</td>
<td>0.1</td>
<td>1.0</td>
<td>4.9</td>
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Materials - Biochars

Activations

- $\text{H}_2\text{O}_2$
- $\text{CO}_2$
- HCl
- $\text{H}_2\text{SO}_4$
- $\text{H}_3\text{PO}_4$
- HNO$_3$
Materials - Pesticides

Cyhalofop

- post-emergence control of grass weeds in rice crops
- weak acid, pKa = 3.9
- Soil Koc = 186

Clomazone

- control of broad-leaved weeds and grasses in a range of crops
- nonionizable (no dissociation)
- Soil Koc = 300
Methods

Biochar characterization

- ATR - FTIR
- Zeta potential
- Surface area
- pH
- % moisture

Sorption characterization

- Batch equilibration method
- HPLC analysis
- % sorbed
## Results – Pesticide sorption

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Cyhalofop (H₂O)</th>
<th>Clomazone (H₂O)</th>
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<tr>
<td></td>
<td>% sorbed&lt;sup&gt;a&lt;/sup&gt;</td>
<td>pH</td>
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<sup>a</sup> average CV = 0.1

- Greater sorption of clomazone on all biochars
- Lower clomazone sorption at 500°C than 350°C
**Results – $\text{H}_2\text{O}_2$ activation**

Visible changes in surface chemistry with activation
Results – Pesticide sorption

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- Increase with activation more pronounced for cyhalofop
- Greater fraction of cyhalofop in molecular form at low pH
- This emphasizes the influence of pH for weak acid pesticides compared to nonionizable compounds
- pH could be due to added functional groups or alternative alterations
## Results – Pesticide sorption

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- Higher sorption in CaCl<sub>2</sub>
- Sorption increased 6 x and 3 x with activation in H<sub>2</sub>O and CaCl<sub>2</sub>, respectively
- 3 unit pH decrease in both H<sub>2</sub>O and CaCl<sub>2</sub> with activation
Results – CO$_2$ activation

- CO$_2$ activation decreased cyhalofop sorption
- Lost carboxyl groups correspond to decreased sorption
- Supports role of carboxylic group being important to sorption

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<td>7.5</td>
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<tr>
<td>Grape 350 CO$_2$</td>
<td>13.1</td>
<td>7.2</td>
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Conclusions

- Activation can customize biochars for desired sorption properties

- Biochar activation is a useful tool in studying binding mechanisms of organic contaminants

- This information can be used to properly select biochars for intended purposes and environments
Acknowledgements

- University of Minnesota - Thesis Research Travel Grant
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