EFFECT OF BIOCHAR ON THE FATE AND BEHAVIOR OF ALLELOCHEMICALS IN SOIL

Biochar

- Carbon-rich byproduct of biomass pyrolysis
- Use in carbon sequestration and as a soil amendment
- Benefits
  - Increased crop yield, plant growth, nutrient retention, water holding capacity, enhanced biological activity
- Neutral and negative effects
  - Plant growth suppression, decreased arbuscular mycorrhizal fungi
Biochar - diversity

- Remarkable variety in the chemical and physical properties of biochars
- Due to variation in:
  - Feedstock materials
  - Pyrolysis conditions
  - Post-production factors
- Mixing feedstock materials in different ratios prior to pyrolysis further enhances the diversity
Biochar - diversity

- Biochars from feedstock mixtures offer potential customization of properties → “designer biochars”
  - Rebalance soil P concentrations
  - Improve soil moisture retention

- Combination biochars have chemistries non-predictable from their individual components

- Range of heterogeneous materials with non-uniform properties effects and behaviors
Biochar - sorption

- Variability in surface properties affects sorption
  - specific surface area (SSA)
  - aromaticity
  - microporosity

- Research heavily focused on pesticides and environmental contaminants

- Naturally occurring aromatic acids (i.e. phenolic acids) from root exudates and vegetative materials may also be immobilized
Phenolic acids

Influence:
- Nutrient uptake
- Protein synthesis
- Humus formation
- Plant signaling
- Development of mutualistic relationships
- Allelopathy

- Allelopathic effects ➔ potential use in weed management in agroecosystems
Phenolic acids - phytotoxicity

- Phytotoxicity of phenolic acids is affected by their bioavailability, persistence, and fate in soil
- Only effective in their free form (unbound)
- Sorption studies necessary to determine efficacy
  - Sorption to soil research available
    - Cecchi et al., 2004
    - Tharayil et al., 2006
  - Sorption to biochar research is lacking
    - Ni et al., 2011
Biochar and allelochemicals

- Plant growth studies
- Biochars greatly differ in their ability to disrupt the function of allopathic chemicals
- Reduce inhibitory effect of allelochemicals on corn seedling growth
- Asparagus- phenolic acid allelochemicals suppress seedling growth
Biochar and allelochemicals

- Allelochemicals negatively affect AM root colonization in asparagus (Elmer & Pignatello, 2011)
- Biochar can impact on mycorrhizal abundance/functioning
- One proposed mechanism: detox of allelochemicals or alteration of plant-fungus signaling
Objectives

- Characterize the influence variation in biochar feedstock has on the sorption of 2 phenolic acids, ferulic acid and syringic acid, and dichlorocatechol
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- Characterize the influence variation in biochar feedstock has on the sorption of 2 phenolic acids, ferulic acid and syringic acid, and dichlorocatechol.

- Determine how sorption by biochars prepared from mixtures of feedstock materials differs from those prepared from the pure feedstocks.
Biochar feedstock materials

- Switchgrass (SG)
- Swine solids (SS)
- Poultry litter (PL)
- Pine chips (PC)
Biochars

- Switchgrass (SG)
- Swine solids (SS)
- Pine chips (PC)
- Poultry litter (PL)

- SG:SS (80:20)
- PC:PL (90:10)
- PC:PL (80:20)
- PC:PL (50:50)

- Pyrolysis: 350°C, 2 hrs
- Waukegan silt loam soil (Rosemount, MN) included for comparison
## Biochar properties

<table>
<thead>
<tr>
<th>Feedstock mixtures (w:w ratios)</th>
<th>pH</th>
<th>% ash</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
<th>SSA (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG:SS (80:20)</td>
<td>6.5</td>
<td>7.3</td>
<td>75.9</td>
<td>4.6</td>
<td>10.8</td>
<td>1.35</td>
</tr>
<tr>
<td>PC:PL (90:10)</td>
<td>6.4</td>
<td>4.4</td>
<td>78.1</td>
<td>4.8</td>
<td>11.7</td>
<td>1.11</td>
</tr>
<tr>
<td>PC:PL (80:20)</td>
<td>7.5</td>
<td>7.3</td>
<td>75.8</td>
<td>4.6</td>
<td>10.8</td>
<td>1.09</td>
</tr>
<tr>
<td>PC:PL (50:50)</td>
<td>7.4</td>
<td>18.5</td>
<td>63.7</td>
<td>3.8</td>
<td>10.3</td>
<td>1.14</td>
</tr>
</tbody>
</table>

### Pure feedstock (100%)  

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>pH</th>
<th>% ash</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
<th>SSA (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG</td>
<td>7.4</td>
<td>3.2</td>
<td>75.5</td>
<td>4.6</td>
<td>16.2</td>
<td>0.50</td>
</tr>
<tr>
<td>SS</td>
<td>6.5</td>
<td>35.0</td>
<td>51.0</td>
<td>3.7</td>
<td>3.2</td>
<td>1.01</td>
</tr>
<tr>
<td>PL</td>
<td>9.4</td>
<td>32.1</td>
<td>51.5</td>
<td>3.6</td>
<td>6.9</td>
<td>1.94</td>
</tr>
<tr>
<td>PC</td>
<td>7.1</td>
<td>1.8</td>
<td>78.7</td>
<td>4.9</td>
<td>14.3</td>
<td>&lt;0.10</td>
</tr>
</tbody>
</table>
14C labeled chemicals provided by Dr. Konrad Haider, Deisenhofen, Germany

Purified by thin-layer chromatography
Sorption experiment

- Performed in duplicate using **batch equilibration method**

Biochar/soil (0.5 g) added to 35 mL glass centrifuge tubes with Teflon lined caps

5 mL of a 1 ug mL\(^{-1}\) phenolic acid (>17 Bq mL\(^{-1}\) \(^{14}\)C) in 0.005 M CaCl\(_2\) solution added

Samples were shaken horizontally approx. 18 h and centrifuged

Supernatant was analyzed for \(^{14}\)C by liquid scintillation counting with a Packard 1500 counter
Sorption calculations

- Sorption distribution coefficient, $K_d$ (L kg$^{-1}$)
  
  $K_d = \frac{C_s}{C_w}$

- Normalization to biochar OC content, $K_{oc}$ (L kg$^{-1}$)
  
  $K_{oc} = \left(\frac{K_d}{\%OC}\right) \cdot 100$
## Pure feedstock biochar sorption

<table>
<thead>
<tr>
<th>Biochar K\textsubscript{d} values (L kg\textsuperscript{-1})</th>
<th>Switchgrass</th>
<th>Swine solids</th>
<th>Poultry litter</th>
<th>Pine chips</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferulic acid</td>
<td>1.4 ± 0.18</td>
<td>1.6 ± 0.15</td>
<td>3.1 ± 0.40</td>
<td>75 ± 8.00</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>0.07 ± 0.10</td>
<td>0.41 ± 0.02</td>
<td>0.43 ± 0.00</td>
<td>6.03 ± 0.06</td>
</tr>
<tr>
<td>Dichlorocatechol</td>
<td>*</td>
<td>*</td>
<td>25 ± 0.25</td>
<td>*</td>
</tr>
</tbody>
</table>

syringic acid $<$ ferulic acid $<$ dichlorocatechol

* Chemical was sorbed completely
Cinnamic acid derivatives (ferulic) sorb more strongly than benzoic acid derivatives (syringic) to soil (Dalton et al., 1989).

At pHs of biochars in this study (pH=6.4-9.4) syringic and ferulic acid are predominantly anionic; dichlorocatechol remains neutral.
Pure feedstock biochar sorption

Sorption strength related to chemistries of compounds

- Syringic acid, $pK_a = 4.34$
- trans-Ferulic acid, $pK_a = 4.58$
- 4,5-Dichlorocatechol, $pK_a \approx 9.48$

- Biochar has negative surface charge → molecular phenolic group more readily sorbed
- Free phenolic groups → greater sorption to soil (Cecchi et al., 2004)
Pure feedstock biochar sorption

- Ferulic and syringic acid may also rapidly react with iron and manganese oxides in biochar.

- Biochars and soil can contain these metals—may provide pathways for abiotic interactions with metal oxides.

- Removal of metal oxides from soils largely decreased sorption of phenolic acids.

- Extent not analyzed.
Pure feedstock biochar sorption

- Pure feedstock biochar $K_d$ and $K_{oc}$ values increased in same order for ferulic and syringic acid
- Certain biochar characteristics also influencing sorption
- No correlations between measured biochar properties (pH, OC, ash content) and sorption observed
- Correcting for OC did not reduce sorption variability
Pure feedstock biochar sorption

- Biochar characteristics and feedstock material
- Efforts to identify trends
- General grouping of feedstock:
  - subgroups: hard-wood, soft-wood, grass, manure

**Wood vs Non-wood**

Wood has...
- lower ash content
- lower pH
- higher C/N ratio
- higher SSA

PC
Pure feedstock biochar sorption

Higher SSA typically associated with higher sorption

- PC biochar had the highest sorption, but lowest SSA of all biochars studied.
- Lower SSA may be due to resins, tars, or oils blocking pore space.
- Resins in wood may alter surface properties of pores — alter sorption capacity.
Pure feedstock biochar sorption

- Biochar maintains relic structure of parent material
- Pore distribution can vary
- Feedstock materials with large diameter cells Biochars with more macropores adsorb large molecules
- SSA measurements do not account for size/shape of pores
- Biochar SSA is temperature dependent
High temperature pyrolysis biochar has...

- Increased SSA
- Increased microporosity
- Decreased H/C ratio
  (i.e. increased aromaticity)
- Decreased cation exchange capacity
Pure feedstock biochar sorption

Effects of pyrolysis temperature on biochar properties

- High temperature (550°C) olive mill waste biochar
- Syringic acid $K_d = 14.6$
  - PC (350°C) $K_d = 6.0$
- Ferulic acid $K_d = 236$
  - PC (350°C) $K_d = 75$
- High SSA (9.82 m²g⁻¹)
  - PL (350°C) SSA = 1.94 m²g⁻¹
Combination biochar sorption

Ferulic acid

Syringic acid

% Pine chip (w:w) (balance poultry litter)

% Switchgrass (w:w) (balance swine solids)
Combination biochar sorption

- Unable to predict sorption to combination biochars from amount sorbed to pure feedstock components
- Physicochemical alterations during pyrolysis
  - Trace metal constituents can act as catalysts to alter surface chemistries
Soil sorption

<table>
<thead>
<tr>
<th></th>
<th>$K_d$ (L kg$^{-1}$)</th>
<th>$K_{oc}$ (L kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferulic acid</td>
<td>$29 \pm 0.50$</td>
<td>$1160 \pm 20$</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>$12.0 \pm 0.76$</td>
<td>$482 \pm 30.4$</td>
</tr>
<tr>
<td>Dichlorocatechol</td>
<td>$56 \pm 4.00$</td>
<td>$2240 \pm 160$</td>
</tr>
</tbody>
</table>

- Waukegan silt loam soil (Rosemount, MN)
- 6.0 pH in water
- 2.5% OC
- 15% clay
- 33% sand
Soil sorption

- **Syringic acid**
  Sorption to soil > sorption to all biochars studied

- **Ferulic acid**
  Sorption to soil > sorption to all biochars (except PC)

- Soil $K_{oc}$ much higher than all biochar $K_{oc}$ values

- Higher phenolic acid sorption to soil may also result from mineral interactions
Conclusion

- Biochars in this study (except PC) sorbed ferulic and syringic acid less than the reference soil.

- Incorporation into this soil not likely to alter bioavailability of these phenolic acids to a large degree.

- Biochar may have greater impacts on immobilization if...
  - Incorporated into soil with lower sorptive capacity.
  - Presence of phenolic acids with different chemistries.
Conclusion

- Phenolic acid structure, particularly the hydroxyl group, may impact its sorption to biochar.
- Physicochemical variability among biochars affects their sorptive behavior.
  - No observed correlation between sorption and biochar pH, OC, % ash, or SSA.
- Combining feedstock materials unpredictably affects biochar sorption characteristics.
THANK YOU