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

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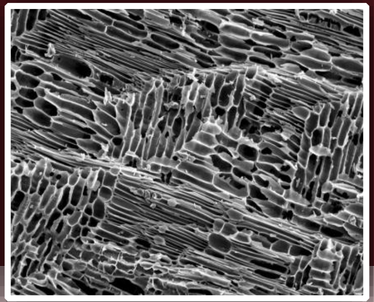
Biochar

- 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

Pyrolysis systems

- 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

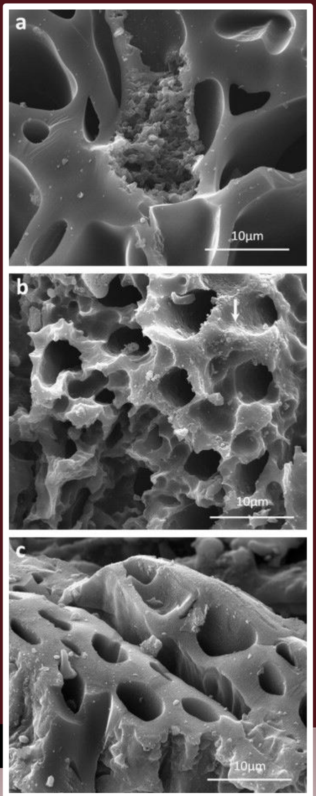
- Biochars from feedstock mixtures offer potential customization of properties→ "designer biochars"
  - Rebalance soil P concentrations
  - Improve soil moisture retention

- 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**

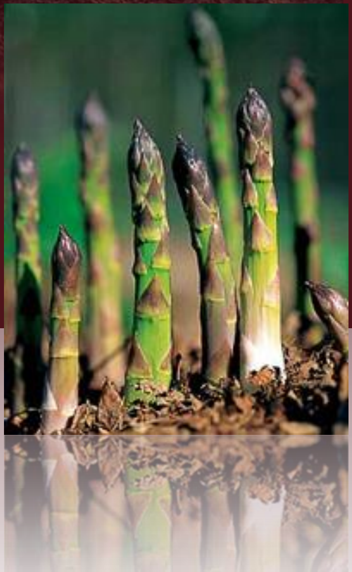
- Allelopathic effects→ potential use in weed management in agroecosystems

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

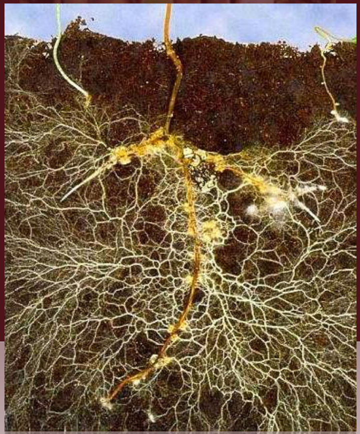
Biochar and allelochemicals

- 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

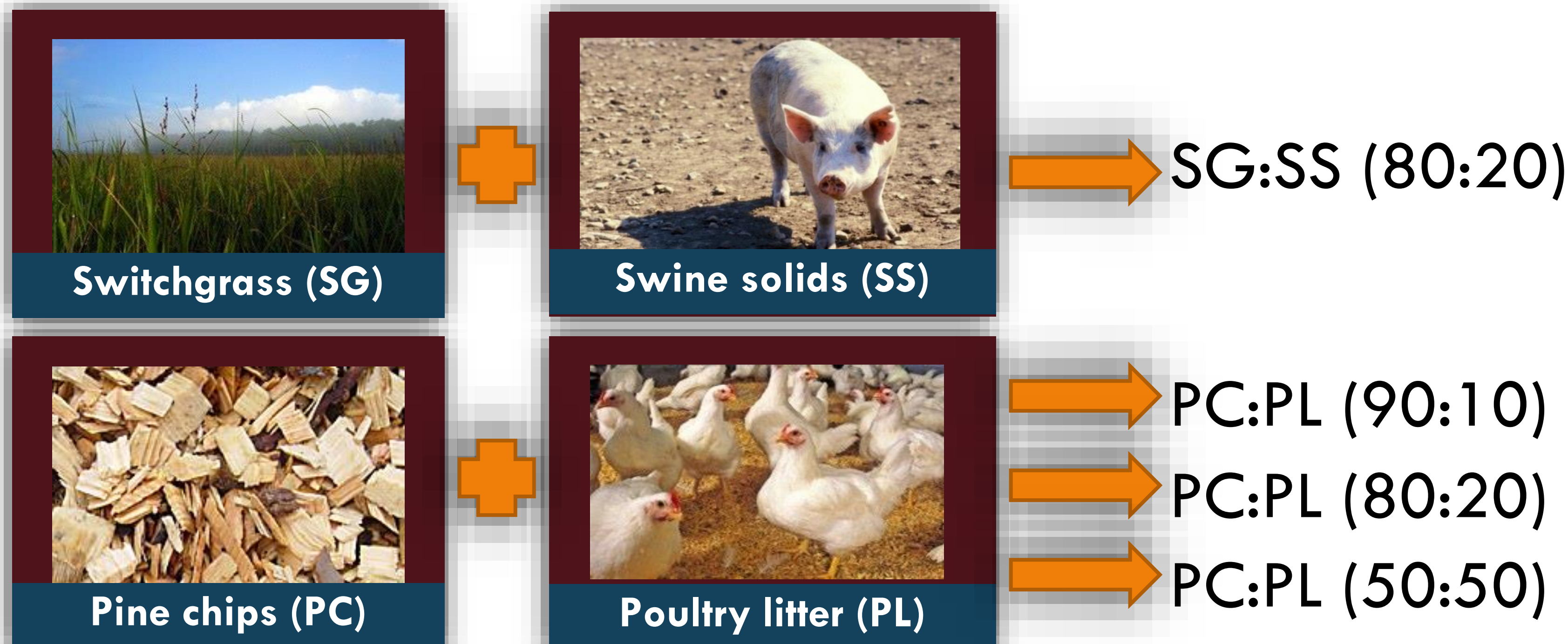
Switchgrass (SG)

Swine solids (SS)

Poultry litter (PL)

Pine chips (PC)

Biochars

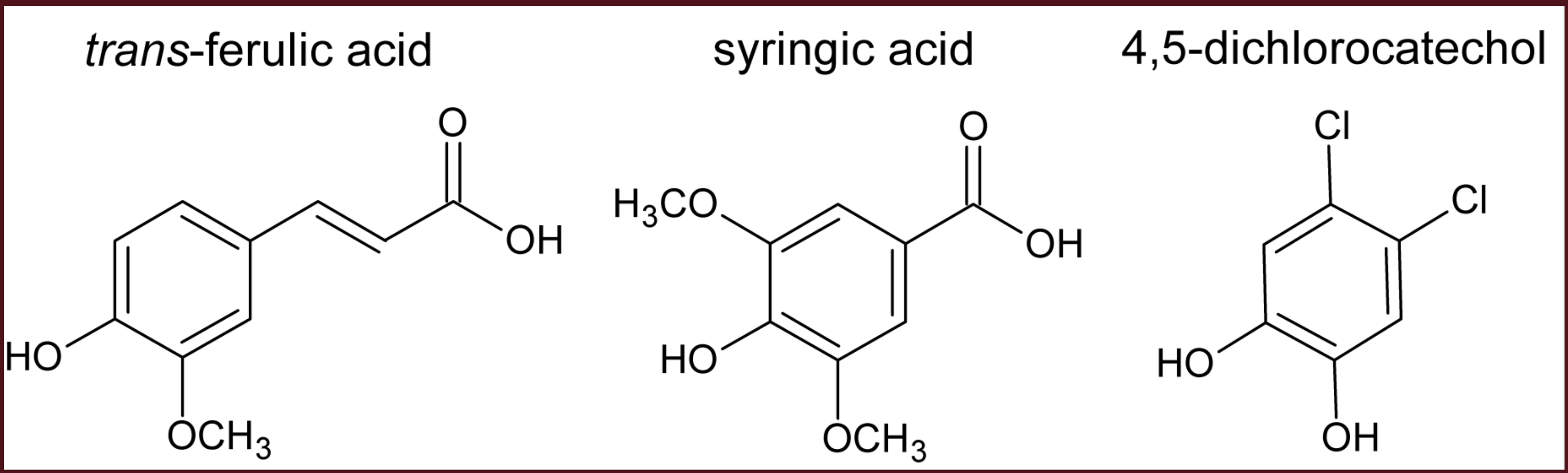


- Pyrolysis: 350°C, 2 hrs
- Waukegan silt loam soil (Rosemount, MN) included for comparison

Biochar properties

Feedstock	pH	% ash	% C	% H	% O	SSA (m^2g^{-1})
Pure feedstock (100%)						
SG	7.4	3.2	75.5	4.6	16.2	0.50
SS	6.5	35.0	51.0	3.7	3.2	1.01
PL	9.4	32.1	51.5	3.6	6.9	1.94
PC	7.1	1.8	78.7	4.9	14.3	<0.10
Feedstock mixtures (w:w ratios)						
SG:SS (80:20)	6.5	7.3	75.9	4.6	10.8	1.35
PC:PL (90:10)	6.4	4.4	78.1	4.8	11.7	1.11
PC:PL (80:20)	7.5	7.3	75.8	4.6	10.8	1.09
PC:PL (50:50)	7.4	18.5	63.7	3.8	10.3	1.14

Chemicals

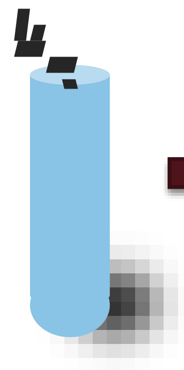


- ^{14}C labeled chemicals provided by Dr. Konrad Haider, Deisenhofen, Germany
- Purified by thin-layer chromatography

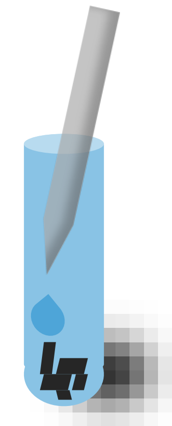
Sorption experiment

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

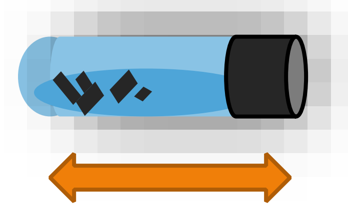
Biochar/soil (0.5 g) added to 35 mL glass centrifuge tubes with Teflon lined caps



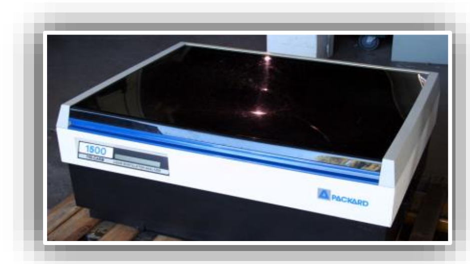
5 mL of a 1 ug mL^{-1} phenolic acid (>17 Bq mL^{-1} ^{14}C) in 0.005 M $CaCl_2$ solution added



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, $\boldsymbol{K_d}$ (L kg^{-1})

$$K_d = C_s/C_w$$

- Normalization to biochar OC content, $\boldsymbol{K_{oc}}$ (L kg^{-1})

$$K_{oc} = (K_d/\%OC) \cdot 100$$

Pure feedstock biochar sorption

Biochar K_d values (L kg^{-1})	 **Switchgrass**	 **Swine solids**	 **Poultry litter**	 **Pine chips**
Ferulic acid	1.4 ± 0.18	1.6 ± 0.15	3.1 ± 0.40	75 ± 8.00
Syringic acid	0.07 ± 0.10	0.41 ± 0.02	0.43 ± 0.00	6.03 ± 0.06
Dichlorocatechol	*	*	25 ± 0.25	*

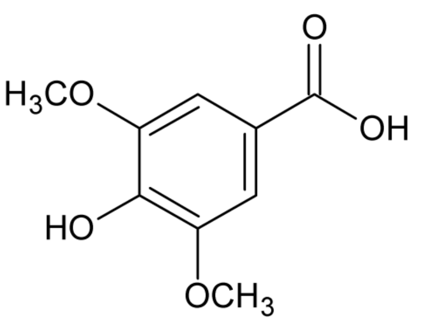
syringic acid < ferulic acid < dichlorocatechol

* Chemical was sorbed completely

Pure feedstock biochar sorption

Sorption strength related to chemistries of compounds

syringic acid



pKa = 4.34

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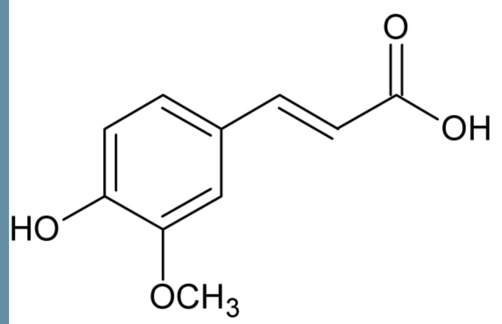
trans-ferulic acid



pKa = 4.58

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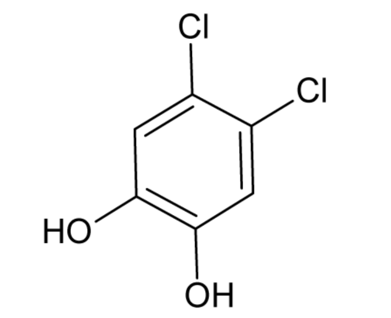
4,5-dichlorocatechol

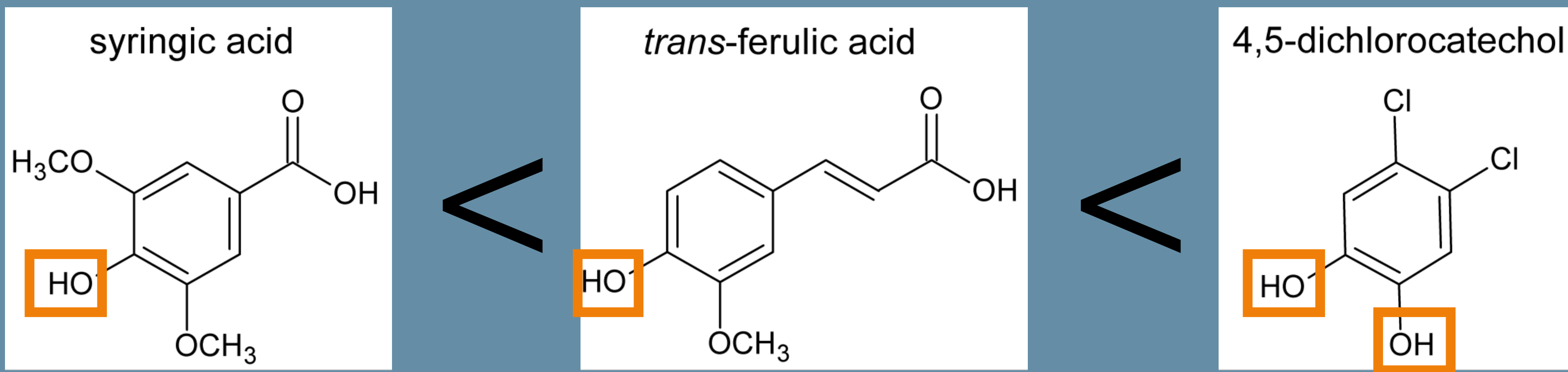


pKa ~ 9.48

- 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

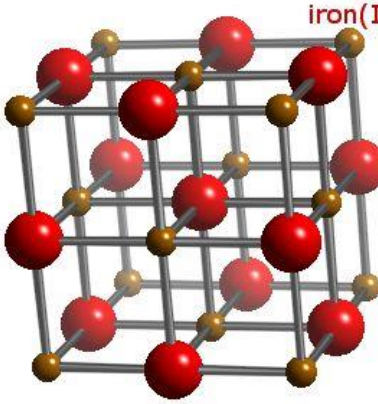


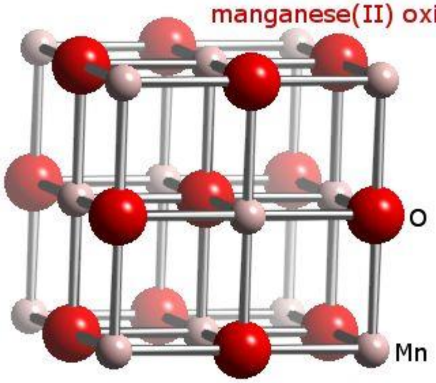
pKa = 4.34 | **pKa = 4.58** | **pKa ~ 9.48**

- 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

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Switchgrass | Swine solids | Poultry litter | Pine chips

- 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

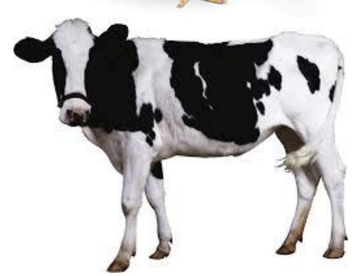
- Biochar characteristics and feedstock material
- Efforts to identify trends
- General grouping of feedstock:

Wood vs Non-wood

Wood has…

PC

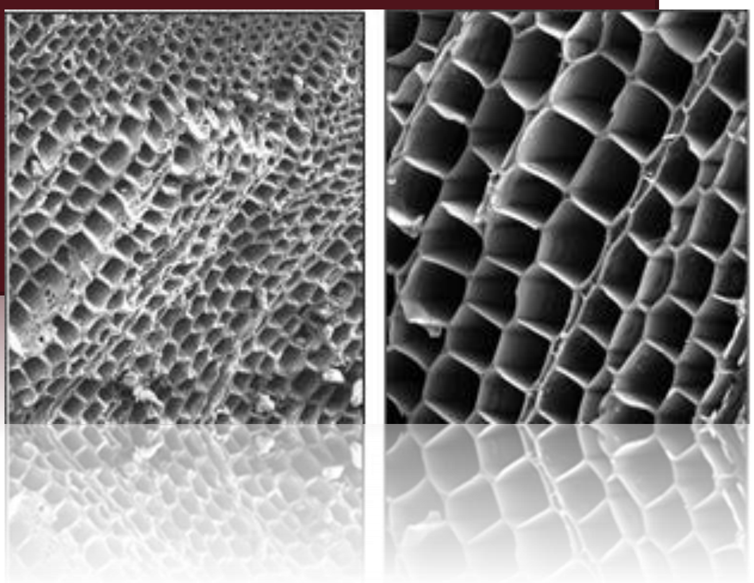
- lower ash content
- lower pH
- higher C/N ratio
- higher SSA



  - subgroups: hard-wood, soft-wood, grass, manure

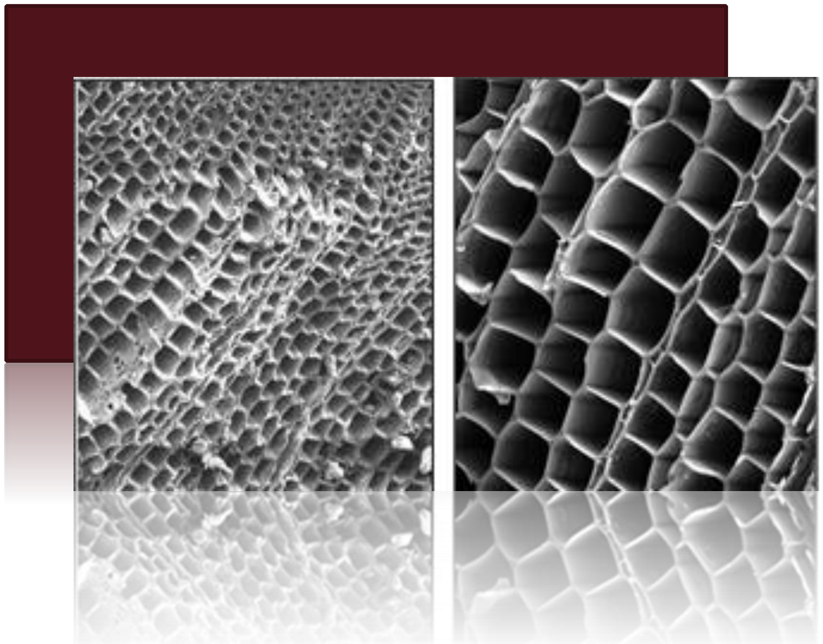
Pure feedstock biochar sorption

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

Pure feedstock biochar sorption

Effects of pyrolysis temperature on biochar properties

Low temp vs High temp

High temperature pyrolysis biochar has…

- Increased SSA
- Increased microporosity
- Decreased H/C ratio

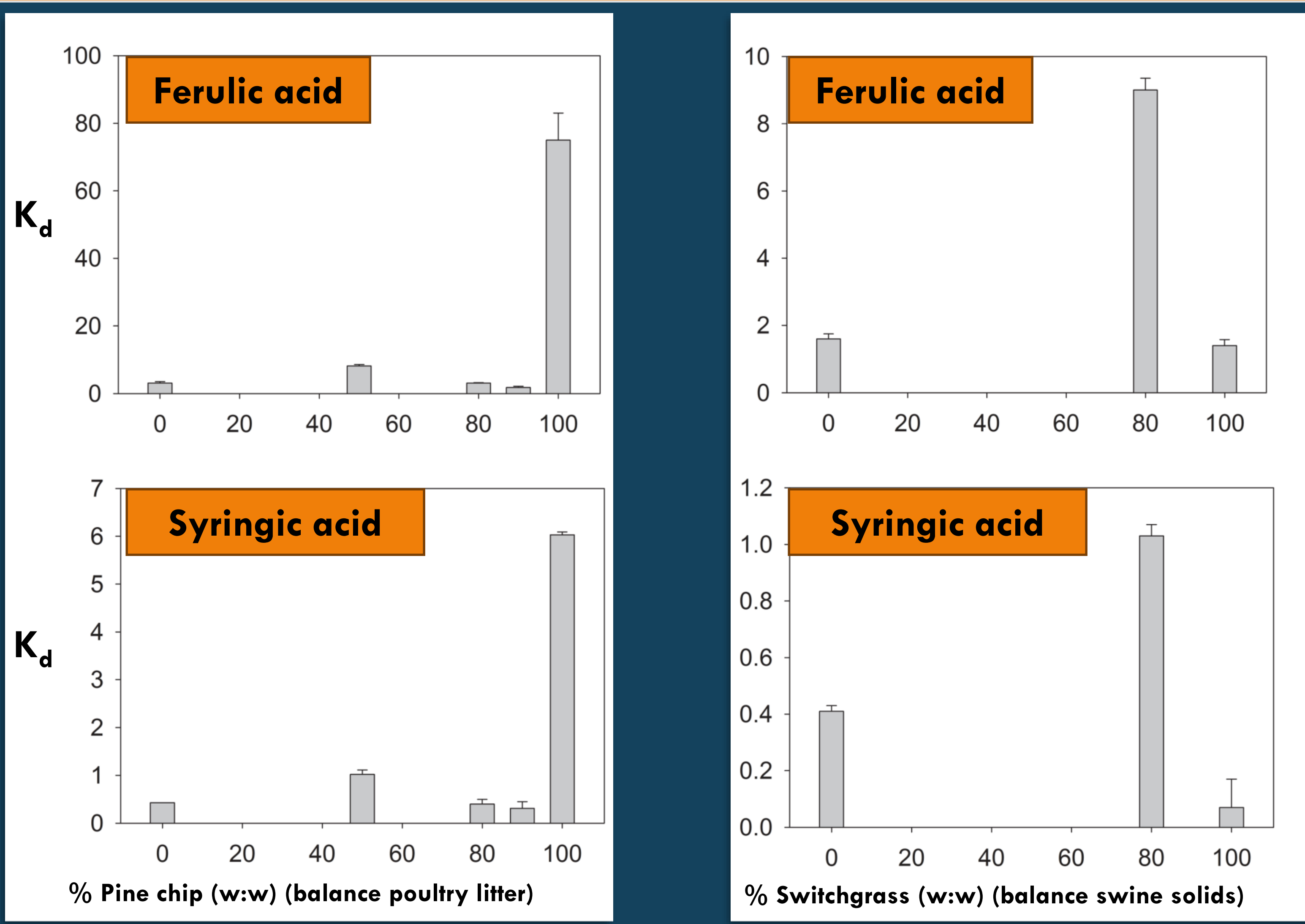
  (i.e. increased aromaticity)
- Decreased cation exchange capacity

Pure feedstock biochar sorption

Effects of pyrolysis temperature on biochar properties

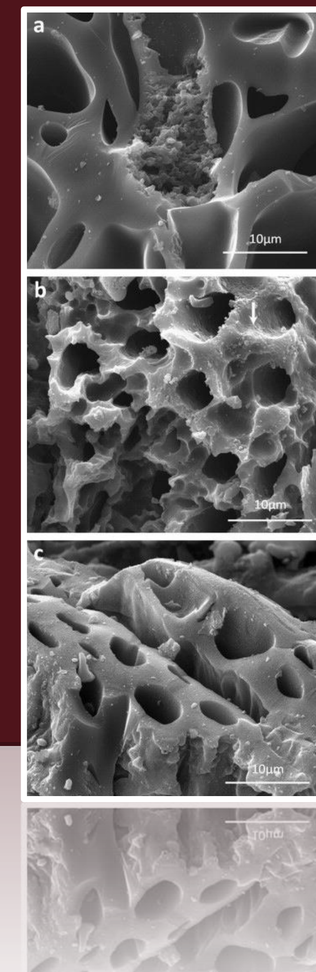
- High temperature (550°C) olive mill waste biochar
- Syringic acid K_d = 14.6
  - PC (350°C) K_d = 6.0
- Ferulic acid K_d = 236
  - PC (350°C) K_d = 75
- High SSA (9.82 m^2g^{-1})
  - PL (350°C) SSA = 1.94 m^2g^{-1}

Combination biochar sorption



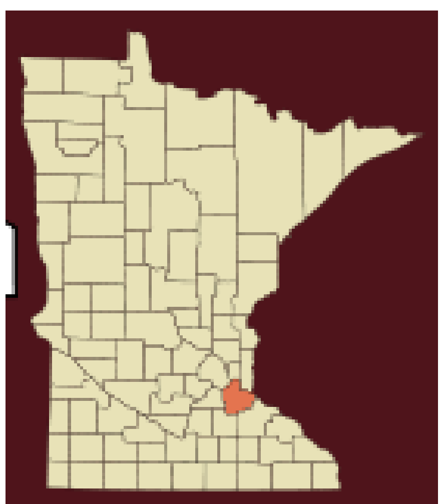
Combination biochar sorption

- 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 alter surface chemistries



Soil sorption

	SOIL	
	K_d (L kg^{-1})	K_{oc} (L kg^{-1})
Ferulic acid	29 ± 0.50	1160 ± 20
Syringic acid	12.0 ± 0.76	482 ± 30.4
Dichlorocatechol	56 ± 4.00	2240 ± 160



- 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 bioavailibility 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