IOWA STATE UNIVERSITY
Center for Sustainable Environmental Technologies

Biochar Characterization and Engineering

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ISTC Biochar Symposium
September 1, 2010

Outline

- About CSET
- Three Thermochemical Processes
- Biochar Engineering
- Initial Characterization Study
- 17 Char Study
- Bioavailability Study
- Future Plans

Biorenewables Research at ISU

- New Biorenewables Research Laboratory (BRL) Building

BIC
BIOBASED INDUSTRY CENTER

IOWA STATE UNIVERSITY
Bioeconomy Institute

CBiRC
NSF Engineering Research
Center for Biorenewable Chemicals

What CSET Does

- Feedstock handling and pre-processing
- Fast pyrolysis
- Gasification
- Syngas, bio-oil and biochar characterization
- Product upgrading for applications
- Techno-economic evaluations

Reactors

- Three scales of fast pyrolyzers:
  - Frontier® and Pyroprobe® micropyrolyzers (1-100 mg/run)
  - Three bench-scale (100 g-1 kg/hr) reactors with alternative configurations (bubbling fluidized bed, auger, and free-fall)
  - 8 kg/hr bubbling fluidized bed process development unit (PDU) located at ISU’s BioCentury Research Farm (BCRF)

Reactors

Free-fall reactor (operational)

Fluidized bed reactor (undergoing modifications)

Auger reactor (undergoing modifications)

Three Thermochemical Processes

Process	Temperature Range	Primary Product	Atmosphere	Feedstock Particle Size	Char Yield (weight %)
Slow Pyrolysis	400-600°C	Solid: Char	Inert	Not Critical	~33
Fast Pyrolysis	400-550°C	Liquid: Bio-oil	Inert	<2 mm	12-15
Gasification	750-1500°C	Gas: Producer/ Syn Gas	Limited oxygen (~0.15-0.25 equivalence)	<6 mm	<15

Biochar

- Biochar is “a fine-grained charcoal high in organic carbon and largely resistant to decomposition…produced from pyrolysis of plant and waste feedstocks” –IBI Website
- Biochar has history as a soil amendment
  - Black carbon existence in soils after wildfires
  - Japanese horticulture
  - *Terra Preta* sites throughout the Central Amazon
- Energy production can be “carbon negative”
  - Some carbon in feedstock remains as carbon in char
  - Long residence time in soils (100’s to 1000’s of years)

International
Biochar Initiative

Effects of Biochar on Soil

Increase:

Nutrient Availability

Microbial Activity

Soil Organic Matter

Water Retention

Crop Yields

Decrease:

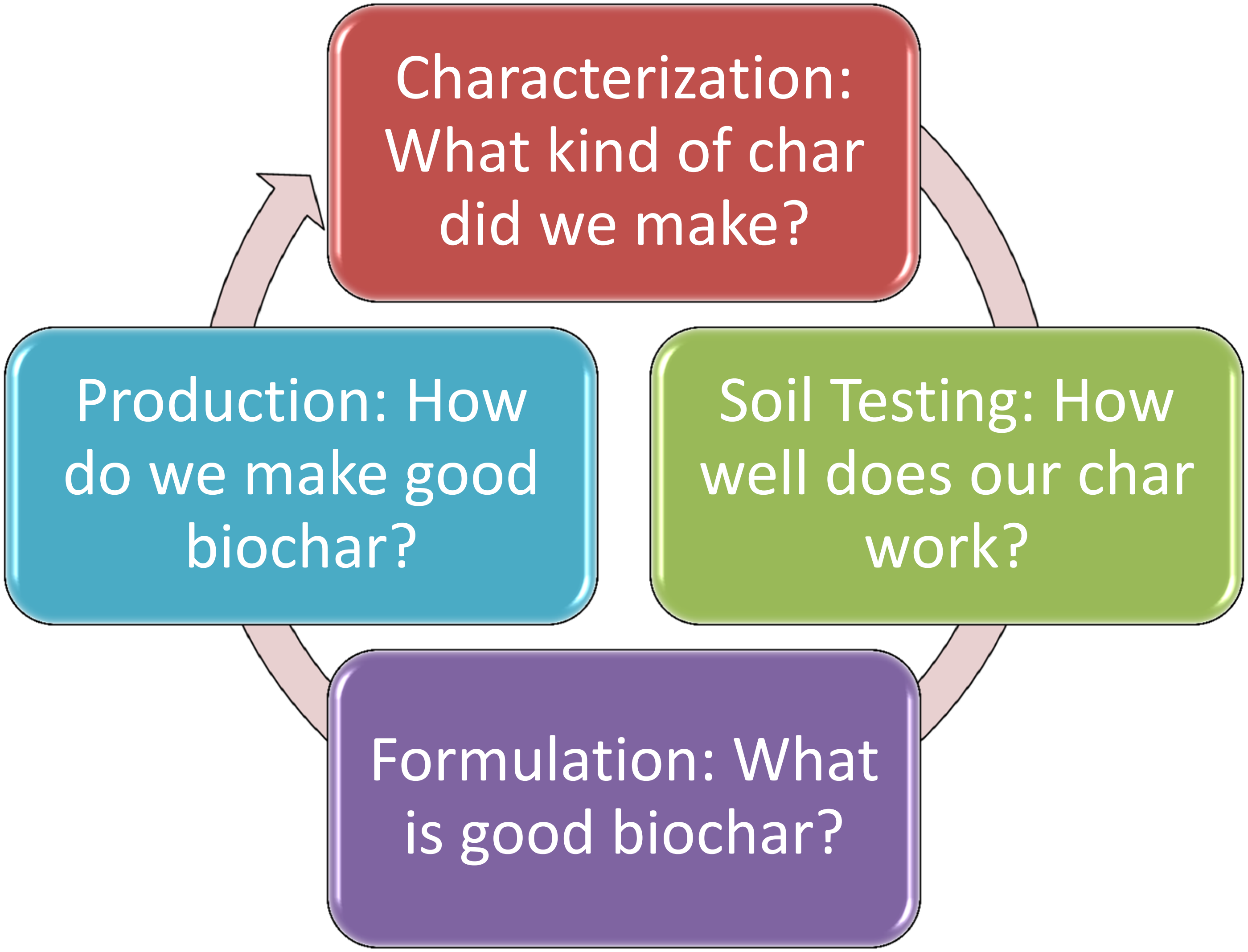
Fertilizer Needs

Greenhouse Gas Emissions

Nutrient Leaching

Erosion

Biochar Engineering



Characterization: What kind of char did we make?

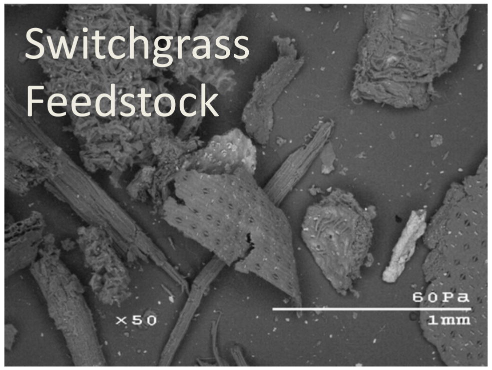
Soil Testing: How well does our char work?

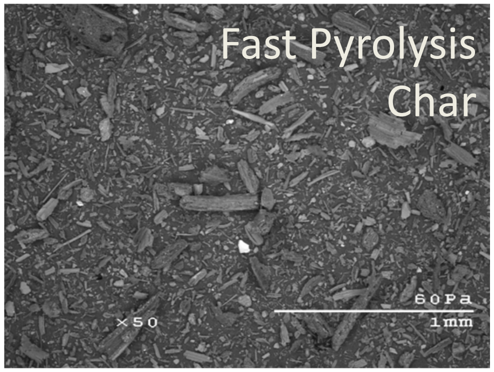
Formulation: What is good biochar?

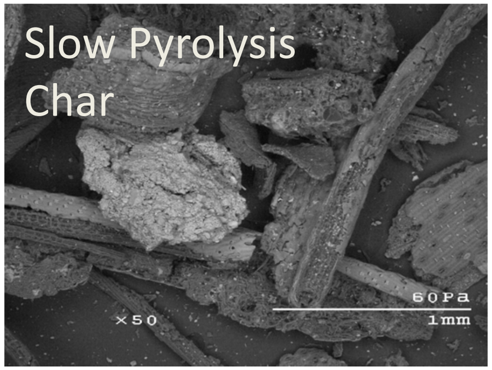
Production: How do we make good biochar?

Initial Characterization Study

- Used seven chars to develop characterization methods
  - Switchgrass slow pyrolysis, fast pyrolysis and gasification
  - Corn stover slow pyrolysis, fast pyrolysis and gasification
  - Hardwood slow pyrolysis
- Found switchgrass and corn stover chars have:
  - High ash contents
  - High C:N ratios
  - Low surface areas


Switchgrass Feedstock


Fast Pyrolysis Char


Slow Pyrolysis Char


Gasification Char

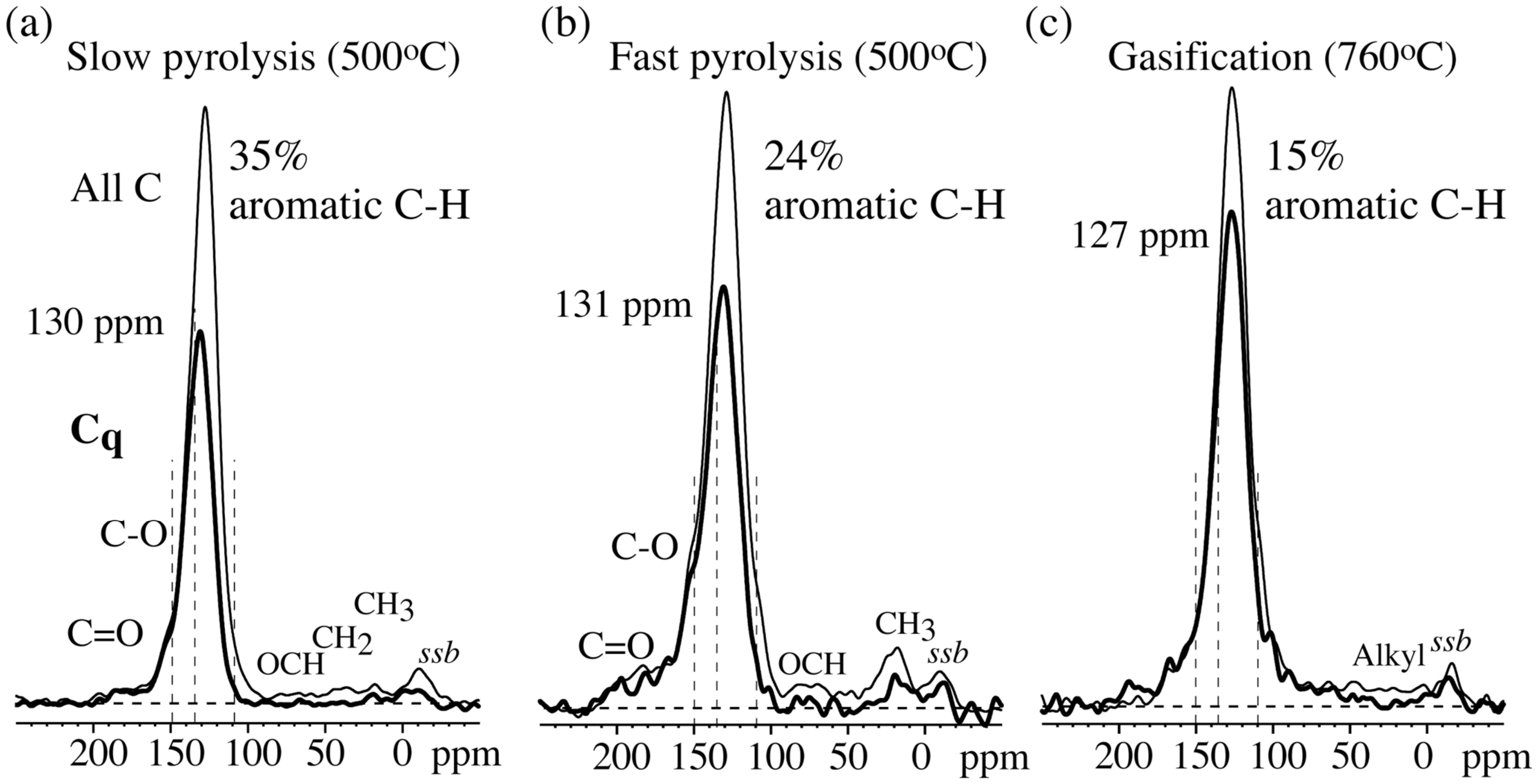
Brewer, C. E.; Schmidt-Rohr, K.; Satrio, J. A.; Brown, R. C. *Environmental Progress & Sustainable Energy* ***2009,*** *28,* 386-396.

Inorganic Composition

Element (wt %)	Switchgrass Fast Pyrolysis Char	Corn Stover Fast Pyrolysis Char	Hardwood Char
Al_2O_3	0.49	2.33	0.60
CaO	3.65	3.80	22.37
Cl	0.47	0.59	0.03
Fe_2O_3	0.76	1.87	2.36
K_2O	6.00	4.03	1.35
MgO	1.55	2.02	0.48
MnO_2	0.15	0.13	0.83
Na_2O	0.07	0.20	0.06
P_2O_5	3.86	1.19	0.20
SiO_2	43.62	29.98	5.67
SO_3	0.99	0.28	0.27
Other	0.25	0.64	0.51

Brewer, et al. *Environ. Prog. Sustainable Energy* ***2009,*** *28,* 386-396.

Quantitative Solid-State ^{13}C NMR



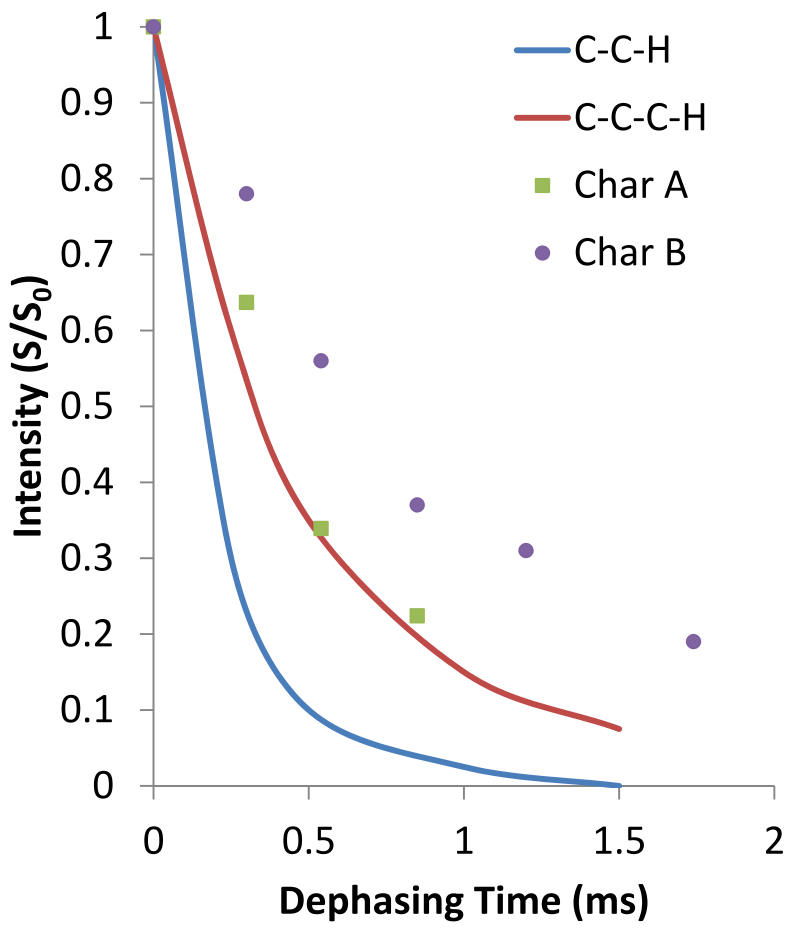
Brewer, et al. *Environ. Prog. Sustainable Energy* ***2009,*** *28,* 386-396.

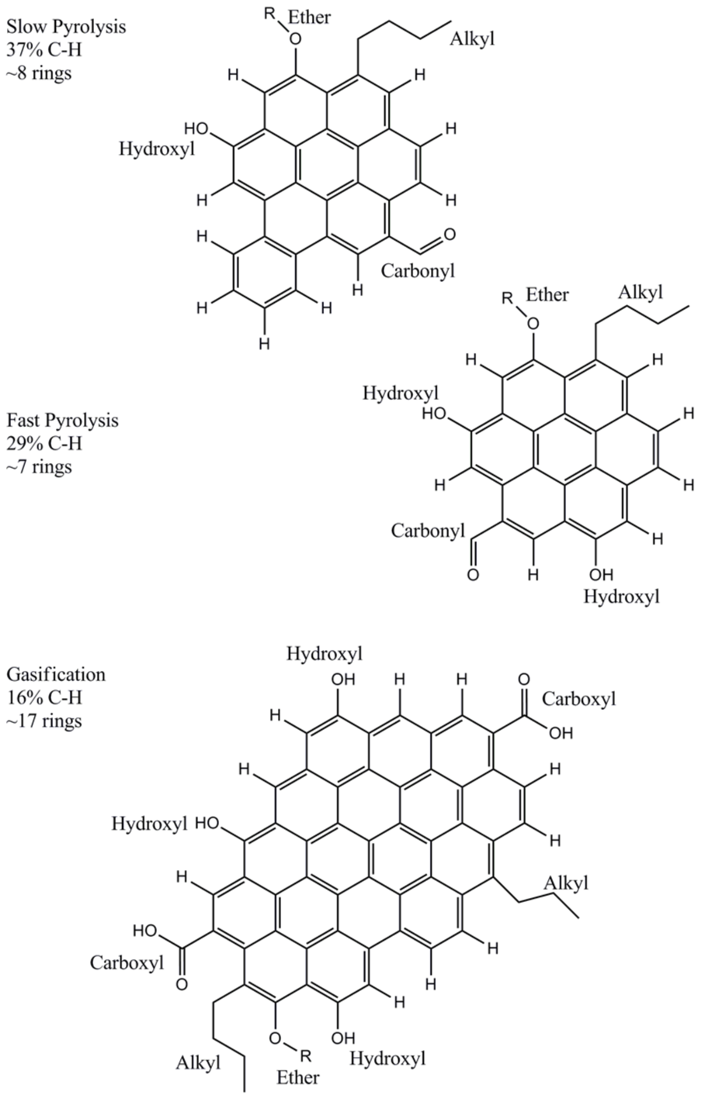
Quantitative Solid-State ^{13}C NMR

	Carbonyls		Aromatics			Alkyls		
Moieties:	**C=O**	**COO**	**$C\text{-}O_{0.75}H_{0.5}$**	**$C_{non\text{-}pro}$**	**C-H**	**$HCO_{0.75}H_{0.5}$**	**$CH_{1.5}$**	**CH_3**
ppm:	**210-183**	**183-165**	**165-145**	**145 - 90**	**145 - 90**	**90-50**	**50-25**	**25-6**
Switchgrass Slow Pyrolysis	0.8.%	1.4%	6.7%	52%	35%	1.4%	1.6%	1.3%
Switchgrass Fast Pyrolysis	3.3%	3.2%	10.3%	49%	24%	3.6%	2.6%	4.0%
Switchgrass Gasification	2.0%	2.2%	6.4%	66%	15%	4.0%	2.0%	2.0%
Corn Stover Fast Pyrolysis	3.5%	4.2%	11.7%	42%	27%	3.3%	3.7%	4.8%
Corn Stover Gasification	2.5%	2.8%	8.2%	61%	18%	3.0%	2.3%	1.3%

Brewer, et al. *Environ. Prog. Sustainable Energy* ***2009,*** *28,* 386-396.

Quantitative Solid-State ^{13}C NMR





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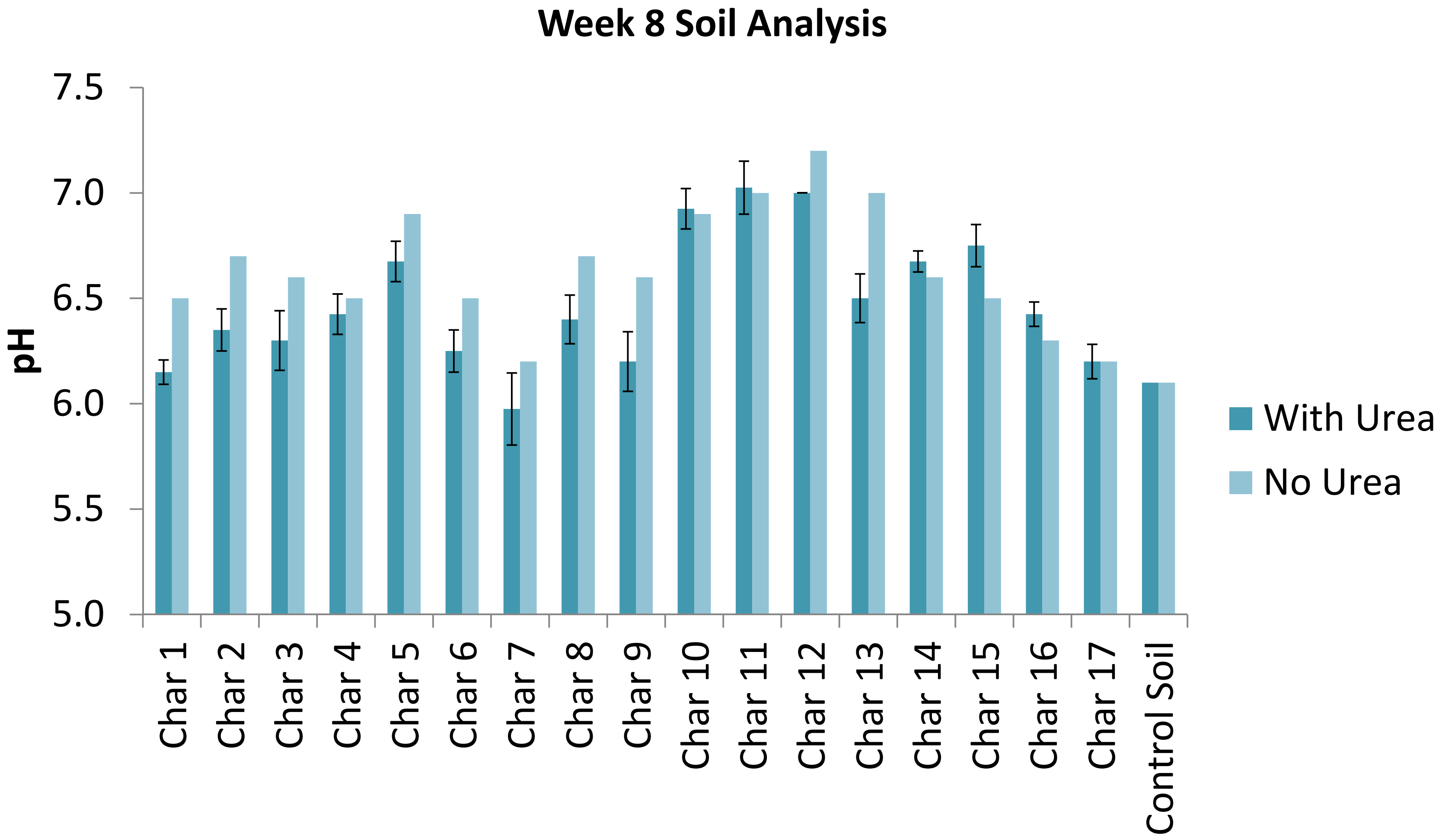
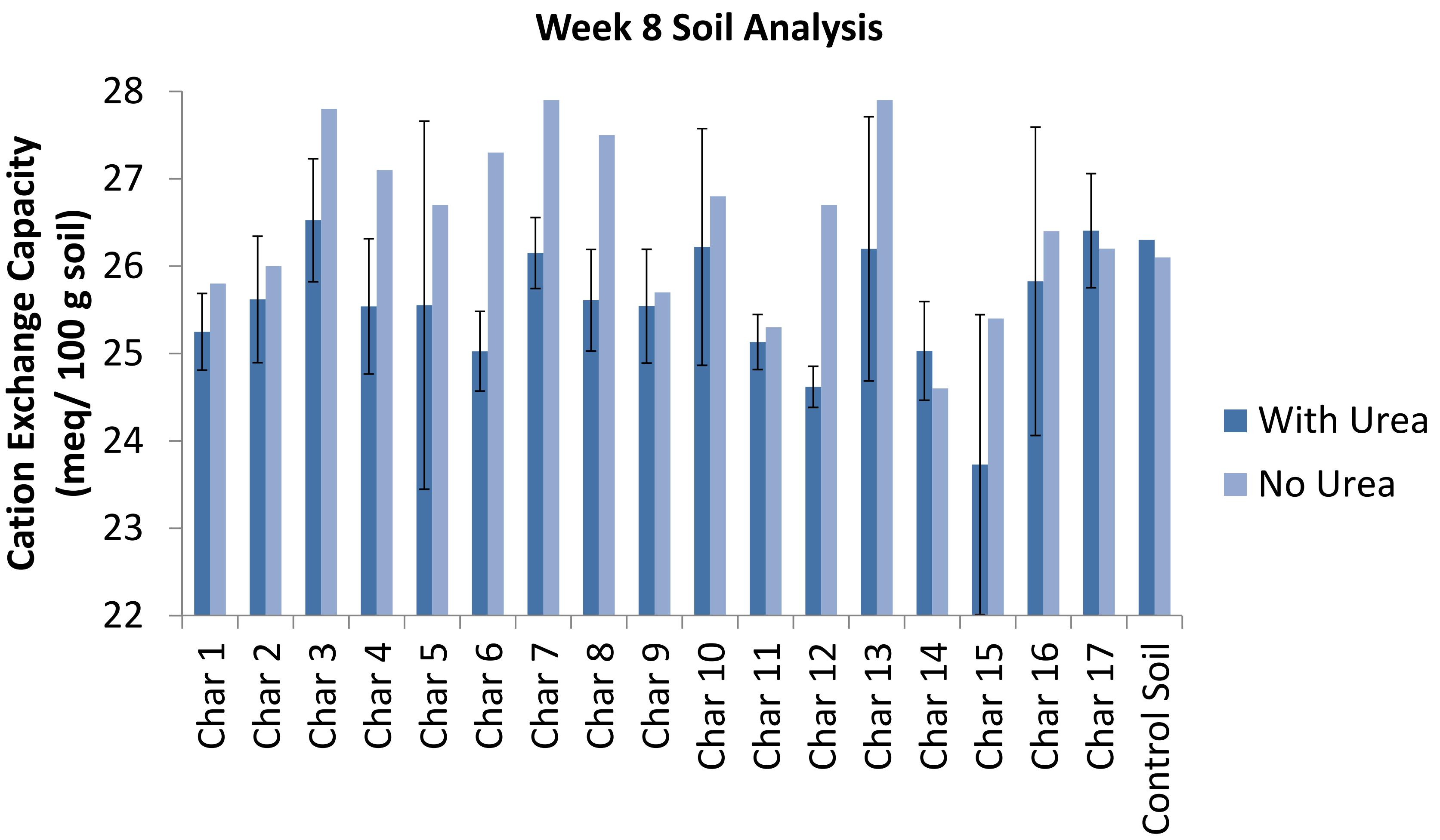
17 Char Study

- Two Part Study:
  - Char characterization
  - 8 week soil incubation
- Collaboration between CSET and Agronomy
- 17 chars made under known conditions
- Results to be used to select chars for micro-plot field study

17 Char Study



17 Char Study



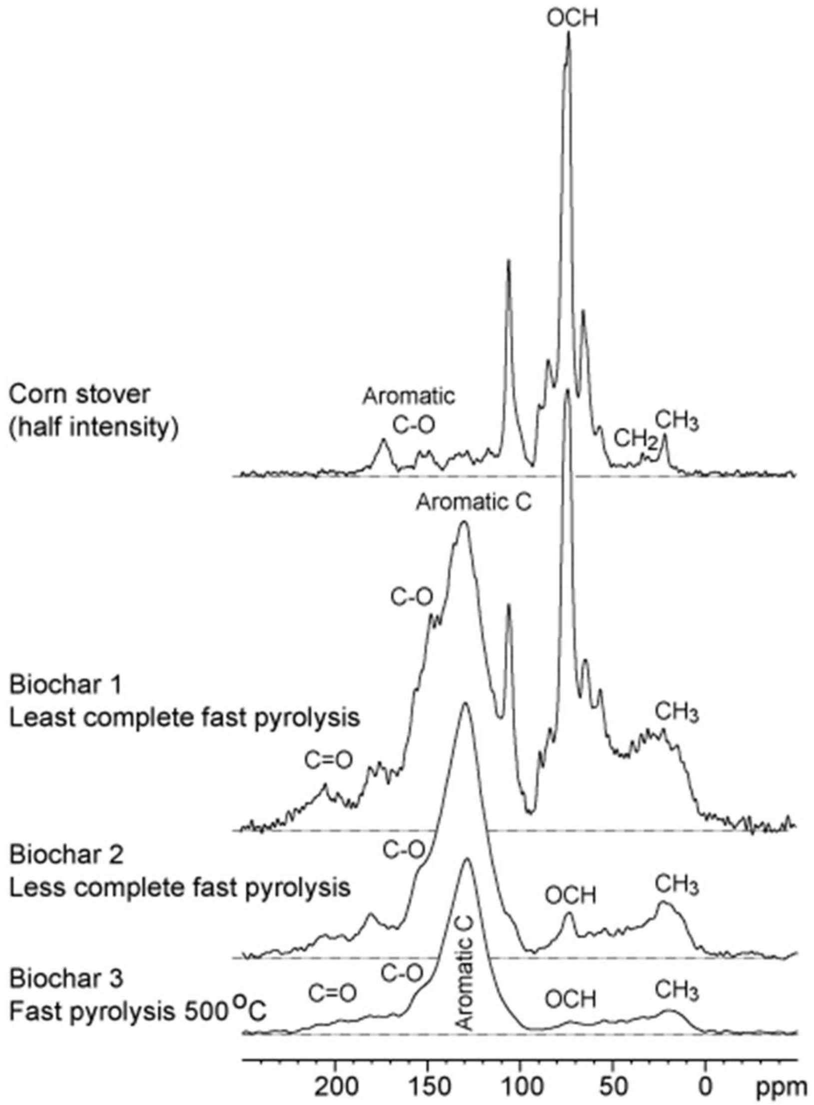
17 Char Study

Char ID #	Feedstock	Reactor	Reaction Conditions
1	Corn Stover	Fluidized Bed Pyrolyzer	Fast Pyrolysis 500°C
2	Corn Stover	Freefall Pyrolyzer	Incomplete Fast Pyrolysis 600°C
3	Corn Stover	Freefall Pyrolyzer	Incomplete Fast Pyrolysis 550°C
4	Corn Stover	Freefall Pyrolyzer	Incomplete Fast Pyrolysis 500°C
5	Corn Stover	Fluidized Bed Gasifier	Air-Blown Gasification732°C
6	Corn Stover	Fixed Bed Pyrolyzer	Slow Pyrolysis 500°C
7	Switchgrass	Fluidized Bed Pyrolyzer	Fast Pyrolysis 450°C
8	Switchgrass	Fluidized Bed Pyrolyzer	Fast Pyrolysis 550°C
9	Switchgrass	Fluidized Bed Pyrolyzer	Fa
10	Switchgrass	Fluidized Bed Gasifier	60
11	Switchgrass	Fluidized Bed Gasifier	50
12	Switchgrass	Fluidized Bed Gasifier	40
13	Switchgrass	Fixed Bed Pyrolyzer	Sl
14	Wood Waste (Chippewa Valley Ethanol Company/Frontline Bioenergy)	Commercial Fluidized Bed Gasifier	Ai ~
15	Mixed Hardwood (Struemph Charcoal Company, Belle, MO)	Commercial Charcoal Kiln	Sl ~
16	Oak flour	Fluidized Bed Pyrolyzer	Fa 50
17	Eastern Hemlock (Advanced BioRefinery Inc., Ottowa, Ontario)	Commercial Auger Pyrolyzer	Fast Pyrolysis 550°C

Feedstock	Reactor	Reaction Conditions
Corn Stover	Fluidized Bed Pyrolyzer	Fast Pyrolysis 500°C
Corn Stover	Freefall Pyrolyzer	Incomplete Fast Pyrolysis “600°C”
Corn Stover	Freefall Pyrolyzer	Incomplete Fast Pyrolysis “500°C”

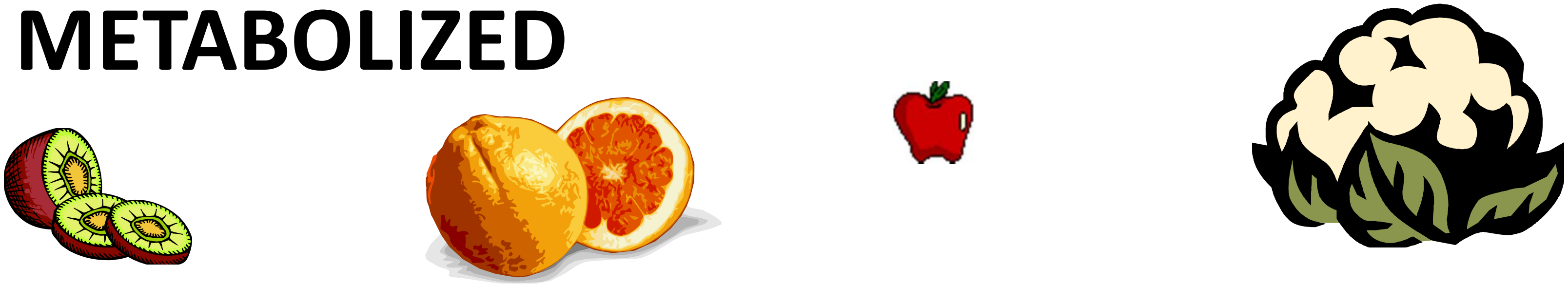
Bioavailability Study

- When characterizing corn stover fast pyrolysis chars by qualitative NMR, a very distinct pattern of pyrolysis completeness between biomass, torrified biomass and biochar was noticed
- Wanted to determine how characteristics related to carbon bioavailability



Metabolized to CO_2, especially by microorganisms.

BIOAVAILABLE = ABLE TO BE METABOLIZED

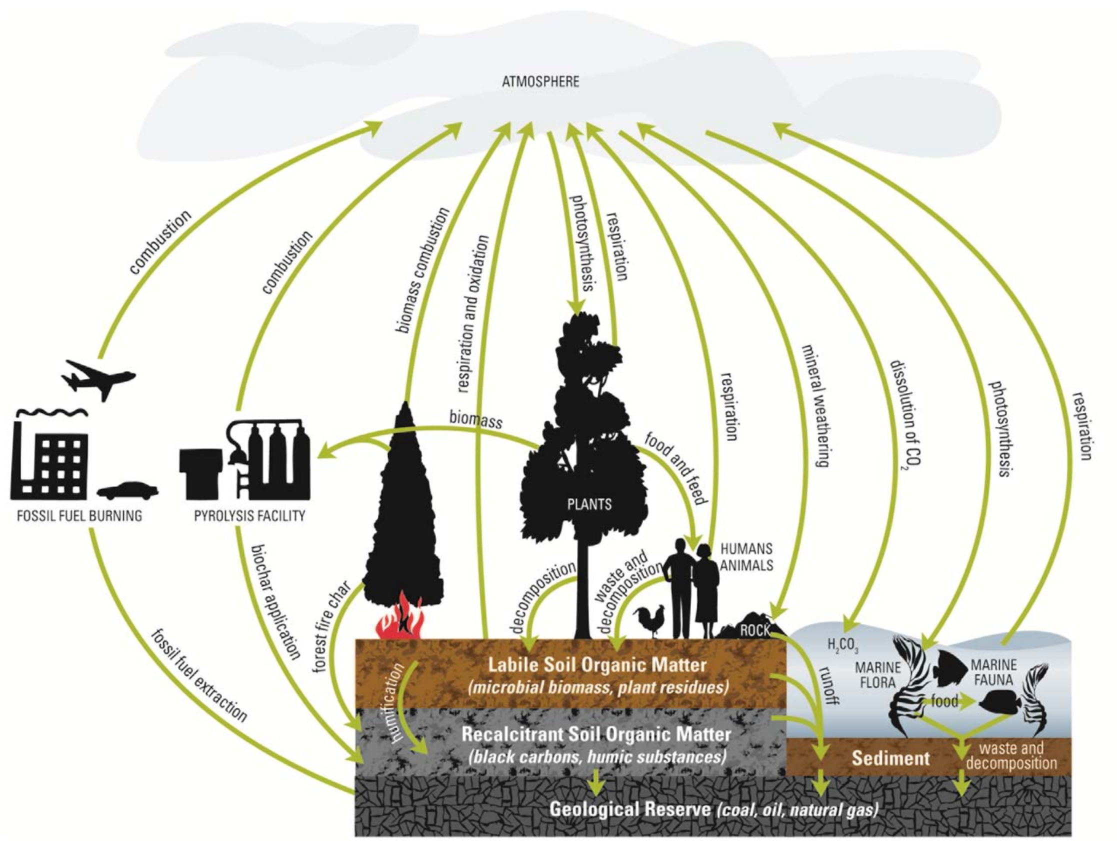


Too Much Bioavailable Carbon

- Soil microorganisms will consume any bioavailable carbon
- Growth requires carbon and nitrogen
- If the C:N ratio is too high, microbes will scavenge the area for nitrogen, leaving too little for plants

= corn stover; CCS = carbonized corn stover

to from Steiner, et. al, The Influence of Crop
dues and Carbonized Crop Residues on
ogen Dynamics, North American Biochar

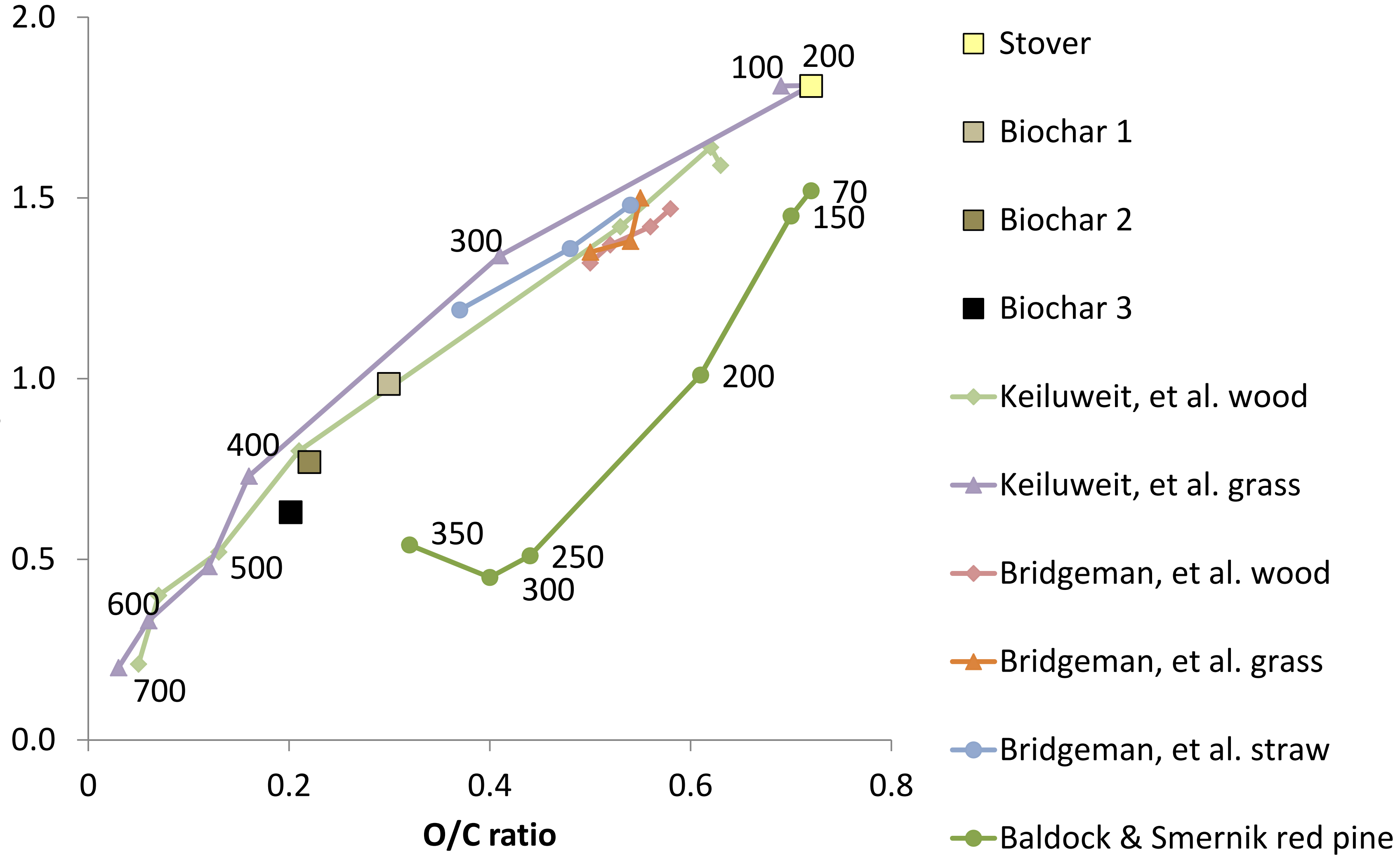


BIOAVAILABLE CARBON IS NOT SEQUESTERED CARBON

Amendment Properties

	Corn stover	Biochar 1	Biochar 2	Biochar 3
Moisture (%)	4	3	2	2
Volatiles (%)	73	26	17	14
Fixed carbon (%)	10	25	25	25
Ash (%)	14	46	56	59
C (%)	41	35	31	30
H (%)	6	3	2	2
N (%)	0.7	0.7	0.6	0.6
S (%)		0.06	0.03	0.02
O (% by difference)	39	14	9	8
BET surface area (m^2/g)		4.5	3.3	8.5
Particle density (g/cm^3)		1.78	1.88	2.06
H/C molar ratio	1.81	0.99	0.77	0.63
O/C molar ratio	0.72	0.30	0.22	0.20
C/N molar ratio	68	51	54	46
Fixed carbon/volatiles	0.14	0.95	1.49	1.83
NMR Aromaticity (% ^{13}C)		62	75	81

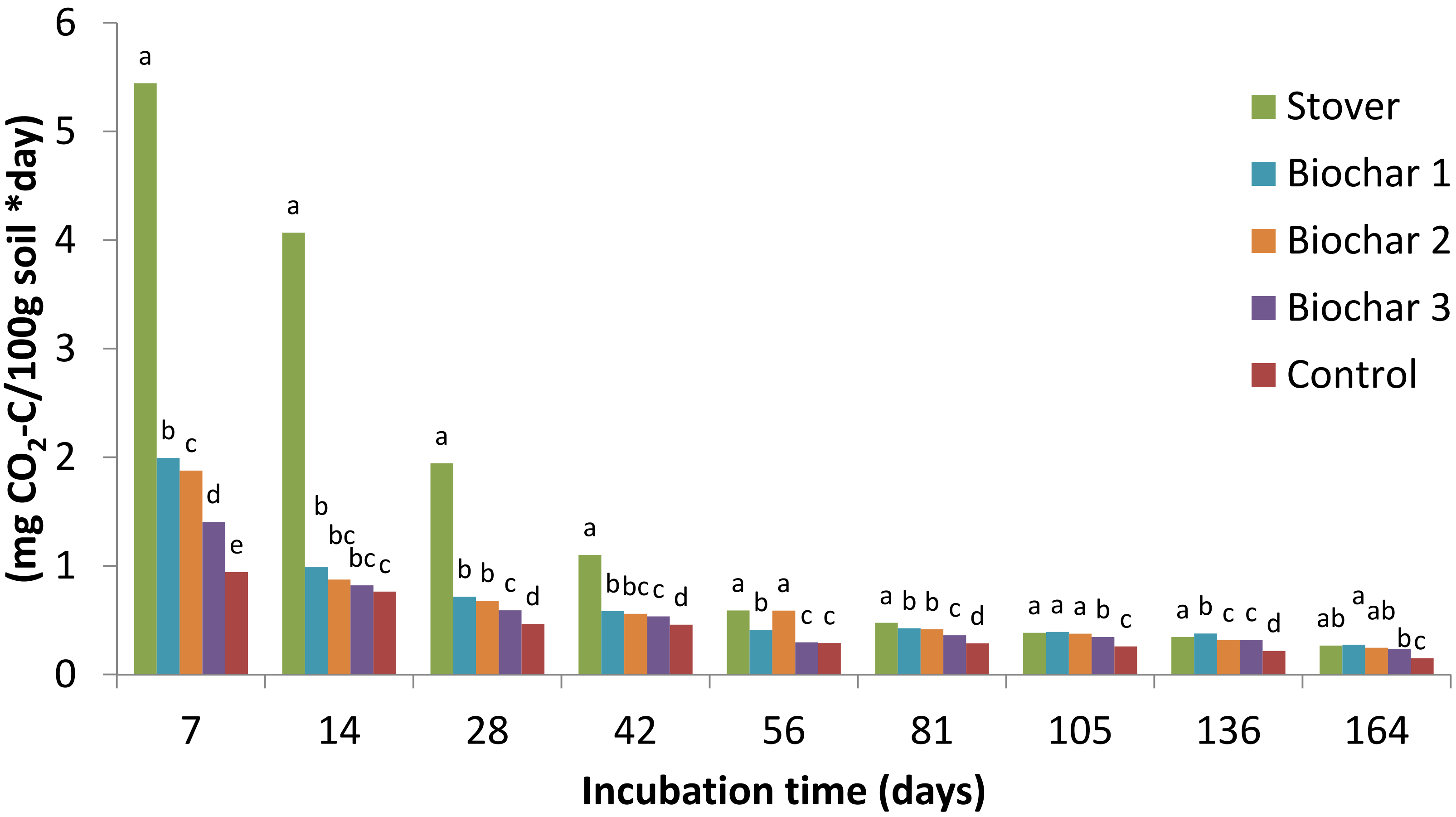
Van Krevelen Plot



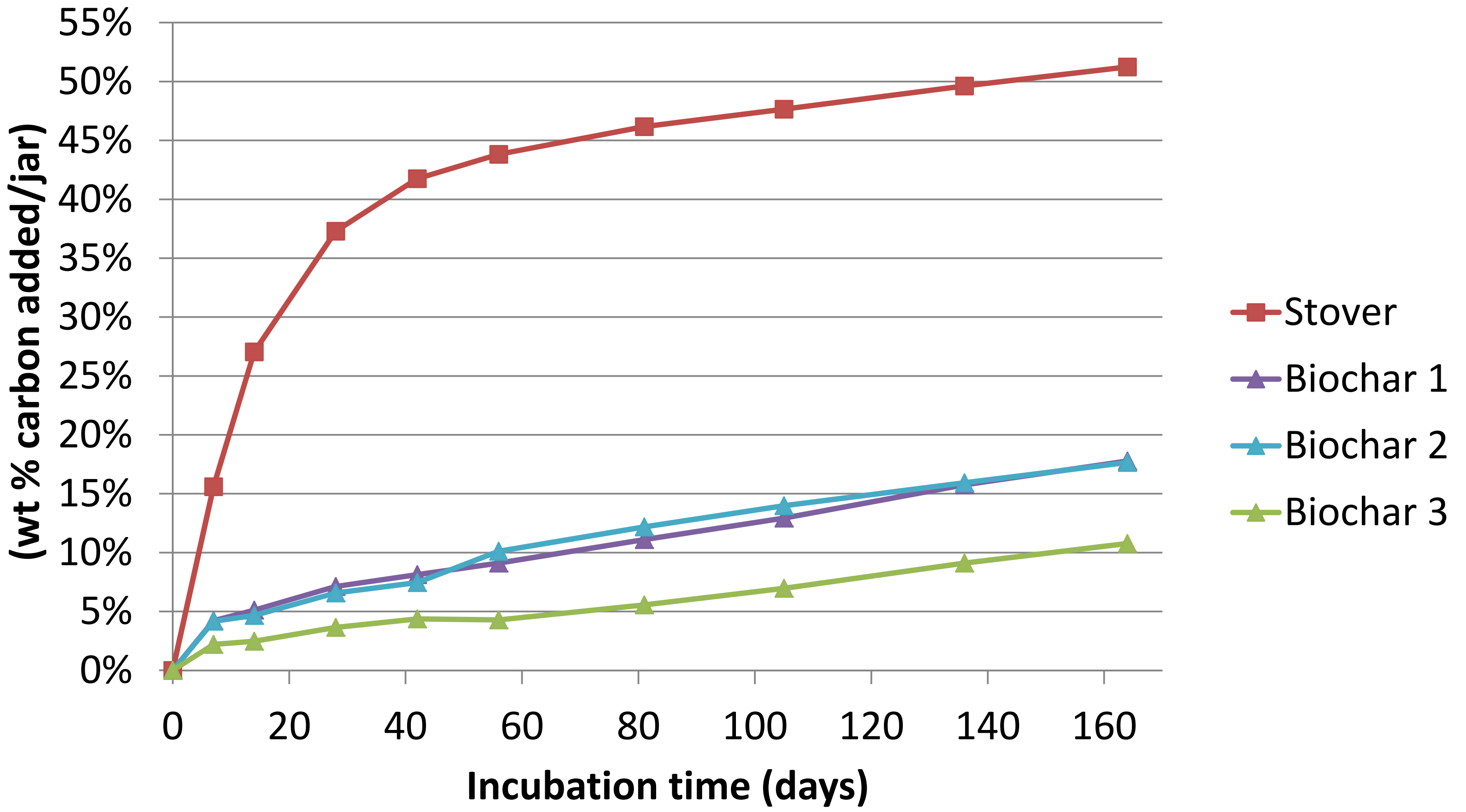
Incubation Study

- Soil: Sparta loamy fine sand
  - (87% sand, 9% silt, 4 % clay)
- 0.5 wt % Amendment
- N, P, S nutrient solution to 10% moisture
- Incubate in the dark at 23°C for 24 weeks
- Soil sampling at week 8
- 9 replicates
- CO_2 evolution measured by alkali trap

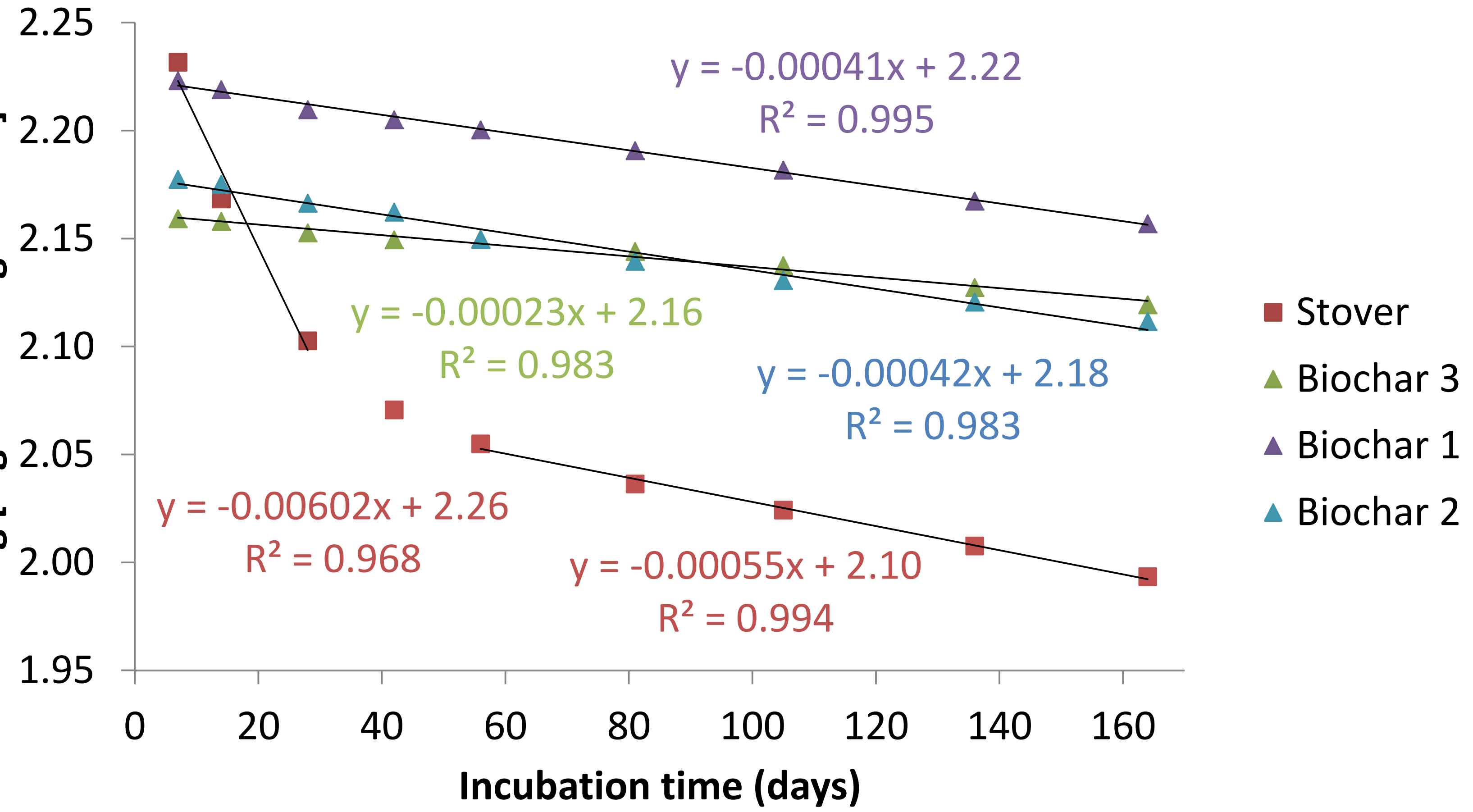
Carbon Mineralization Rates



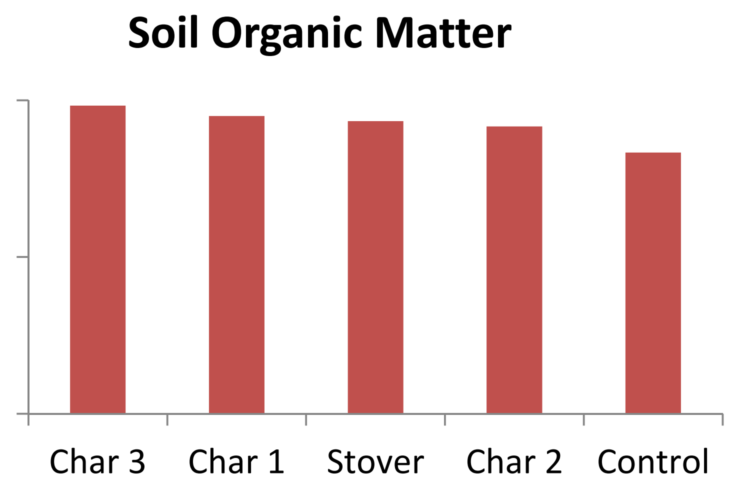
Readily Bioavailable Carbon

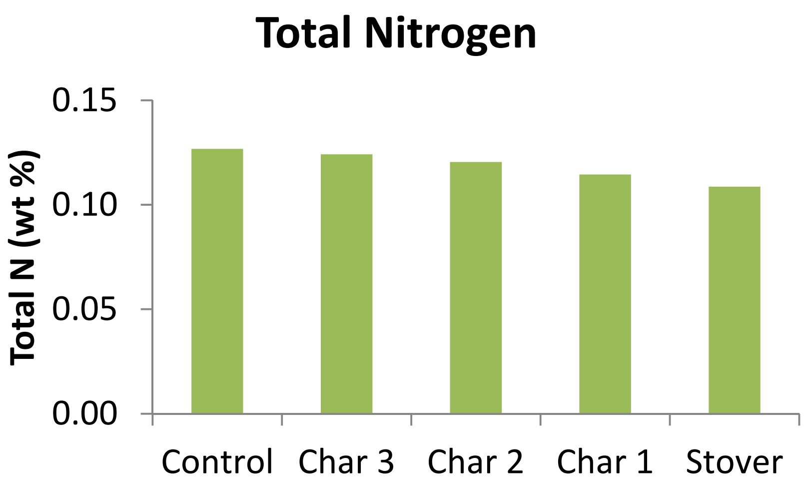


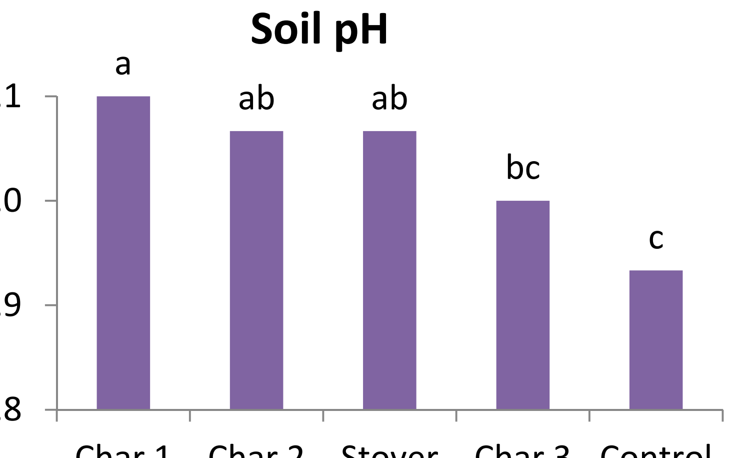
Carbon Mineralization Kinetics

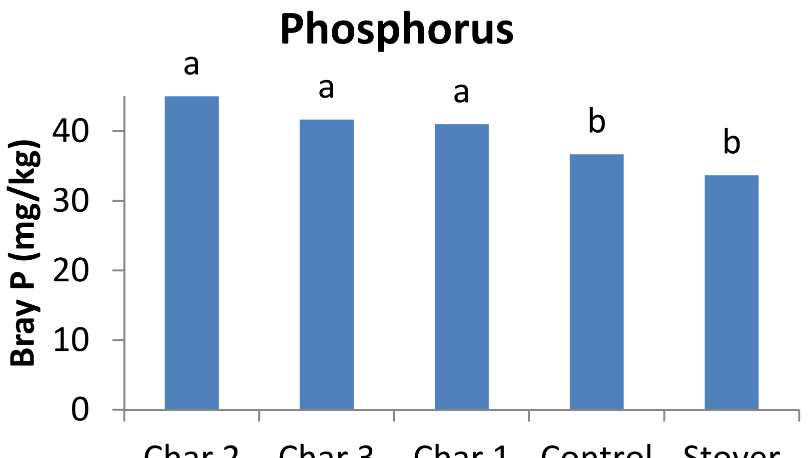


Soil Properties

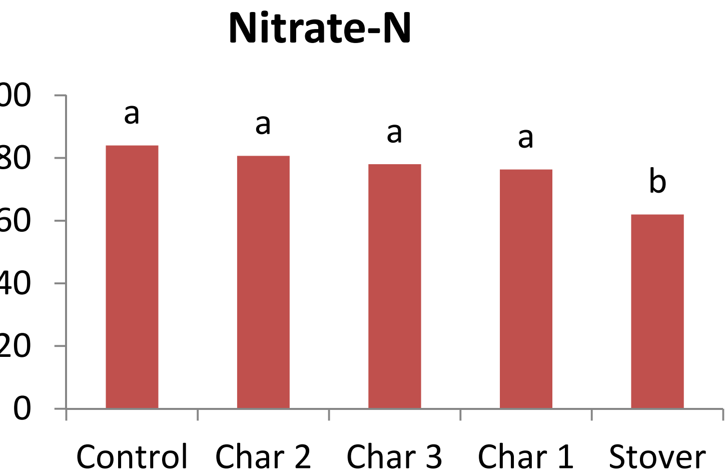


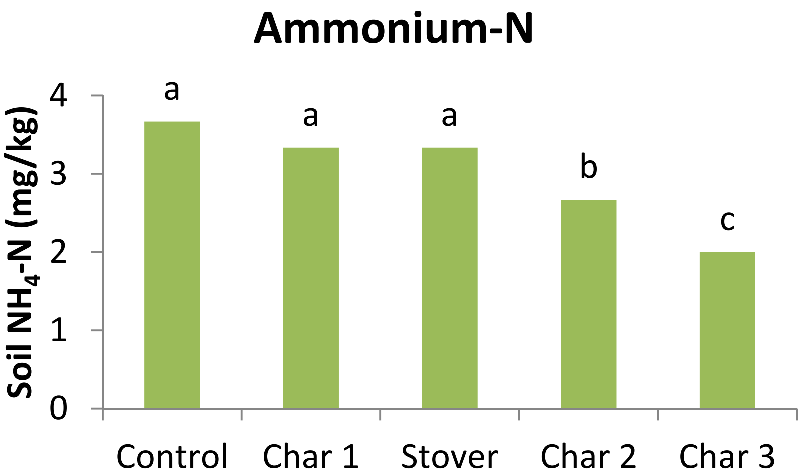


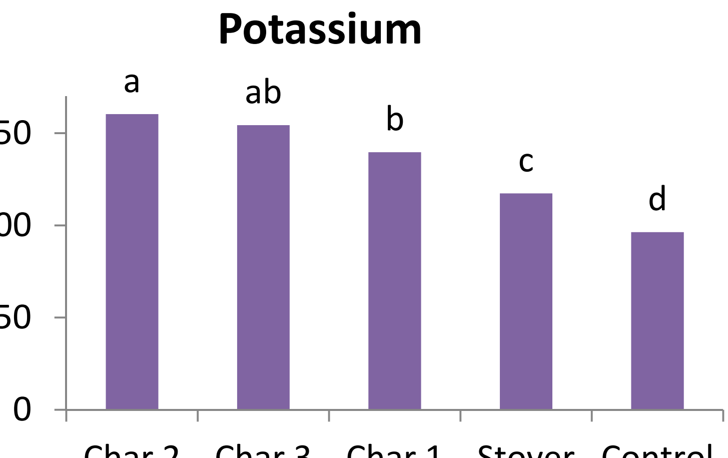


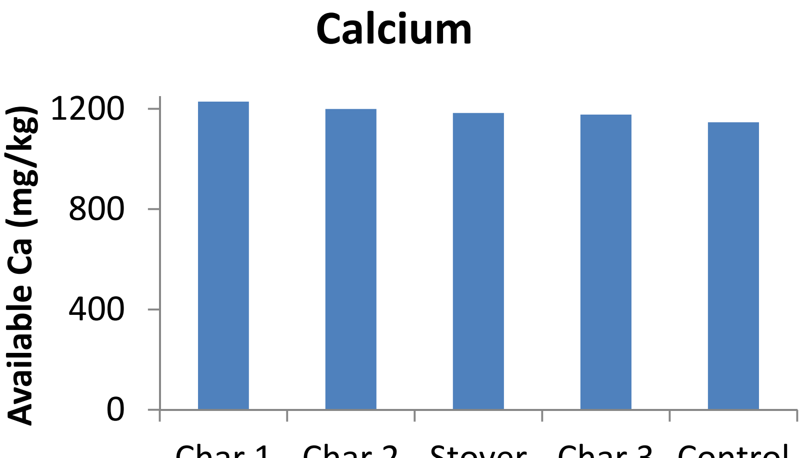


Soil Properties

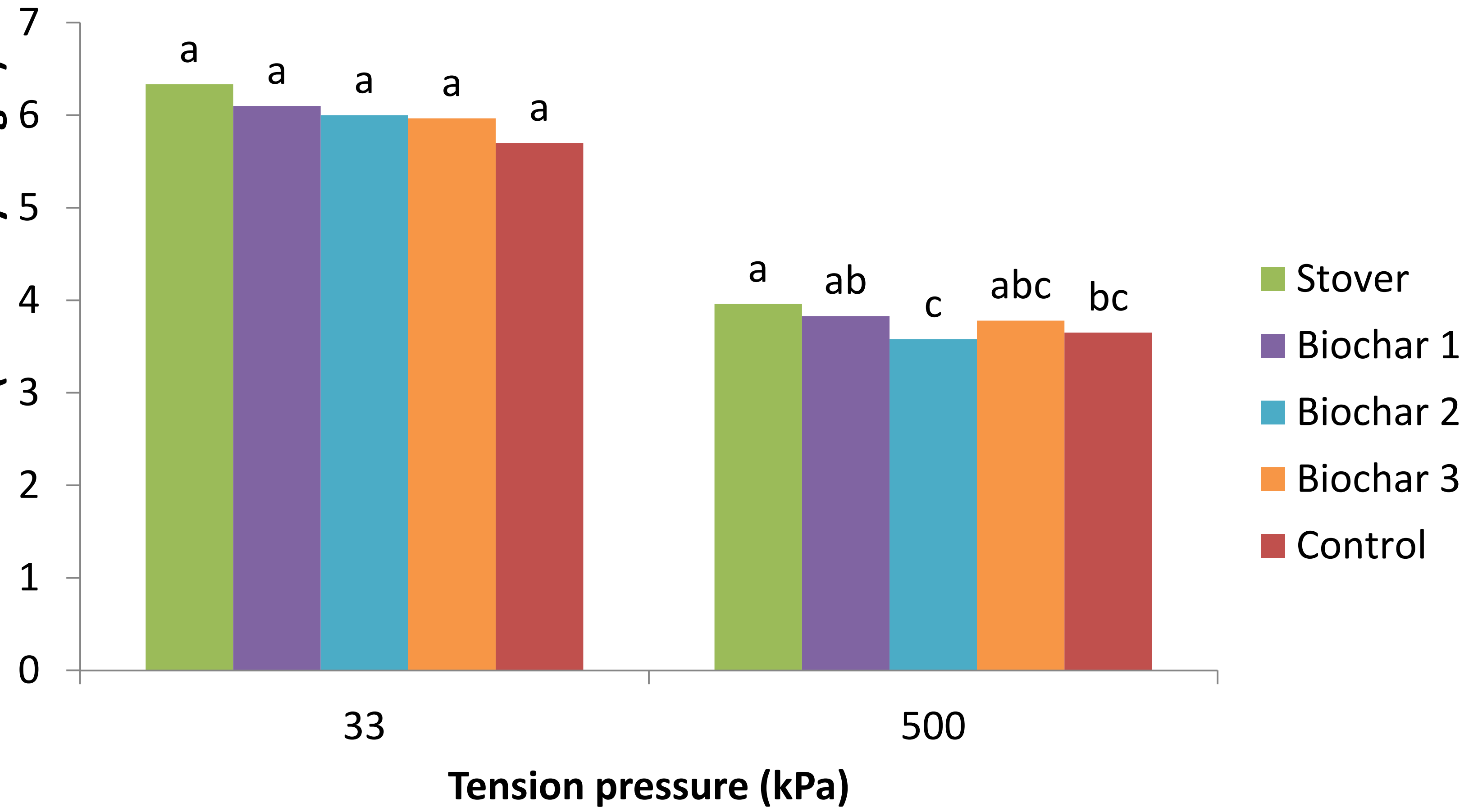




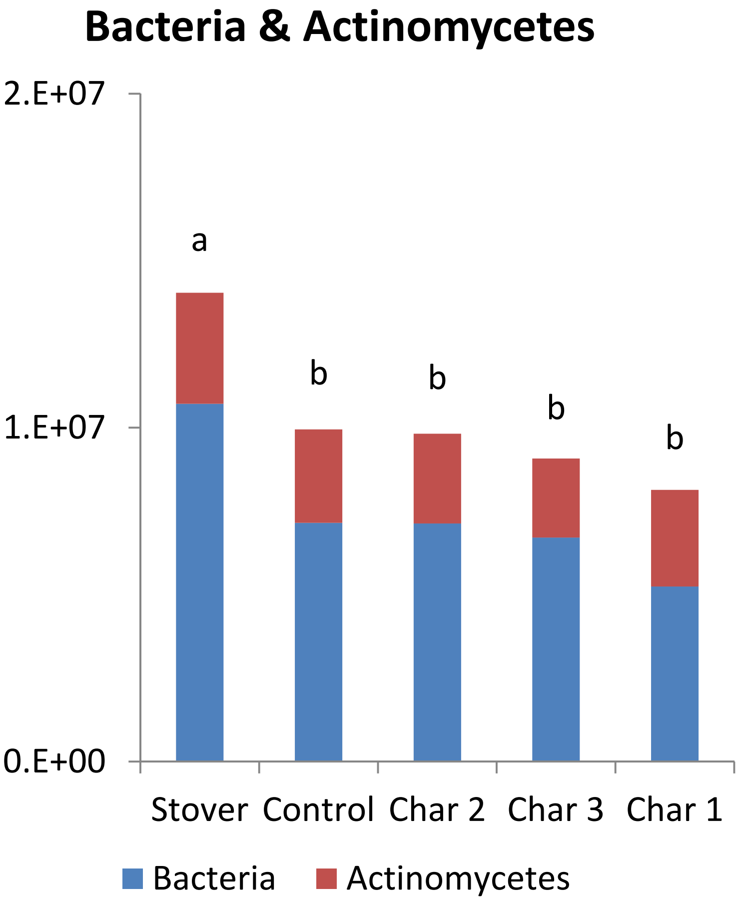


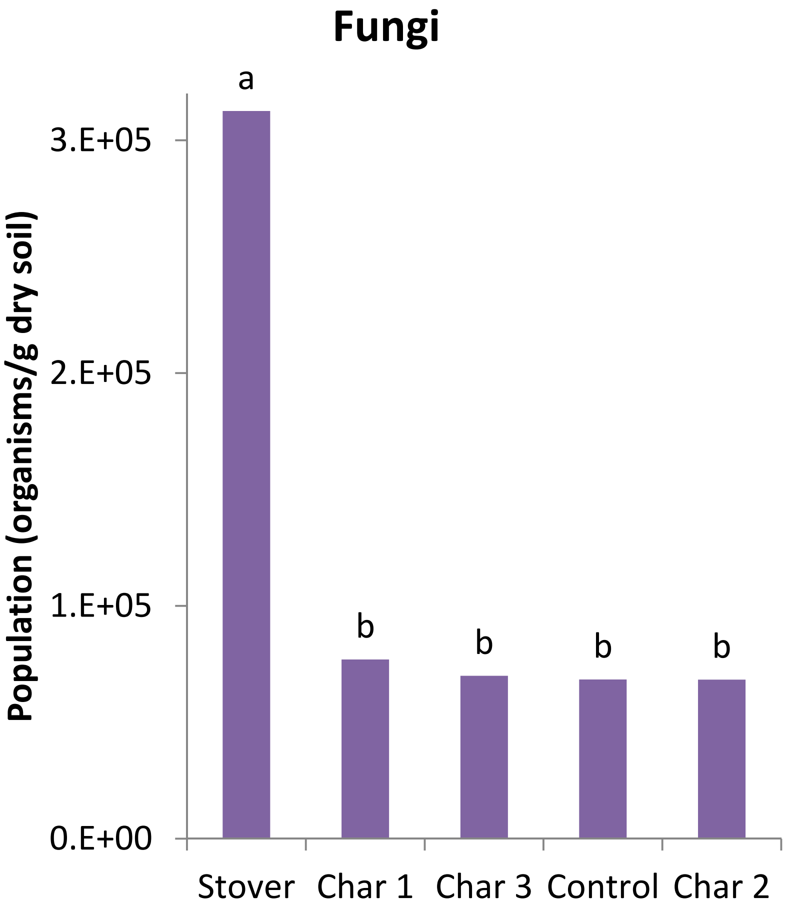


Water Retention Capacity



Microbial Populations





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Conclusions

- Fast pyrolysis and gasification chars are physically and chemically different from traditional slow pyrolysis chars.
- Fast pyrolysis and gasification chars should be included in biochar trials.
- The types of carbon present in chars appear to depend on pyrolysis reaction time and temperature.
- Co-production of biochar and bioenergy may be a more cost-effective and resource-efficient use of biomass crops and crop residues, especially those with high silica ash contents.
- Advanced solid-state ^{13}C NMR techniques can provide quantitative information needed to reliable track changes in carbon structures, which will be meaningful to engineered char production and biochar testing.

Future Work

- Submission of bioavailability study to *Soil Biology & Biochemistry* for publication
- Study of temperature-property relationships in slow and fast pyrolysis chars
- Development of NMR methods to quantitatively track char oxidation
- Safety testing of fast pyrolysis chars

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