Matching Biochar Characteristics with Metals-Contaminated Soil to Effectively Reduce Metal Bioavailability at Mining Sites

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Outline of Presentation

- What is biochar?
  - How is biochar made?
- Biochar properties
- Biochar and metal sorption
- Why EPA and biochar?
- Biochar as an amendment for metal contaminated spoil soils
- Tuning biochar properties to address spoil soil limitations
  - Insuring a good match between site conditions and soil amendments
- Field Studies
  - Target soils
  - Monitoring site conditions
- Summary
- Outlook for the future

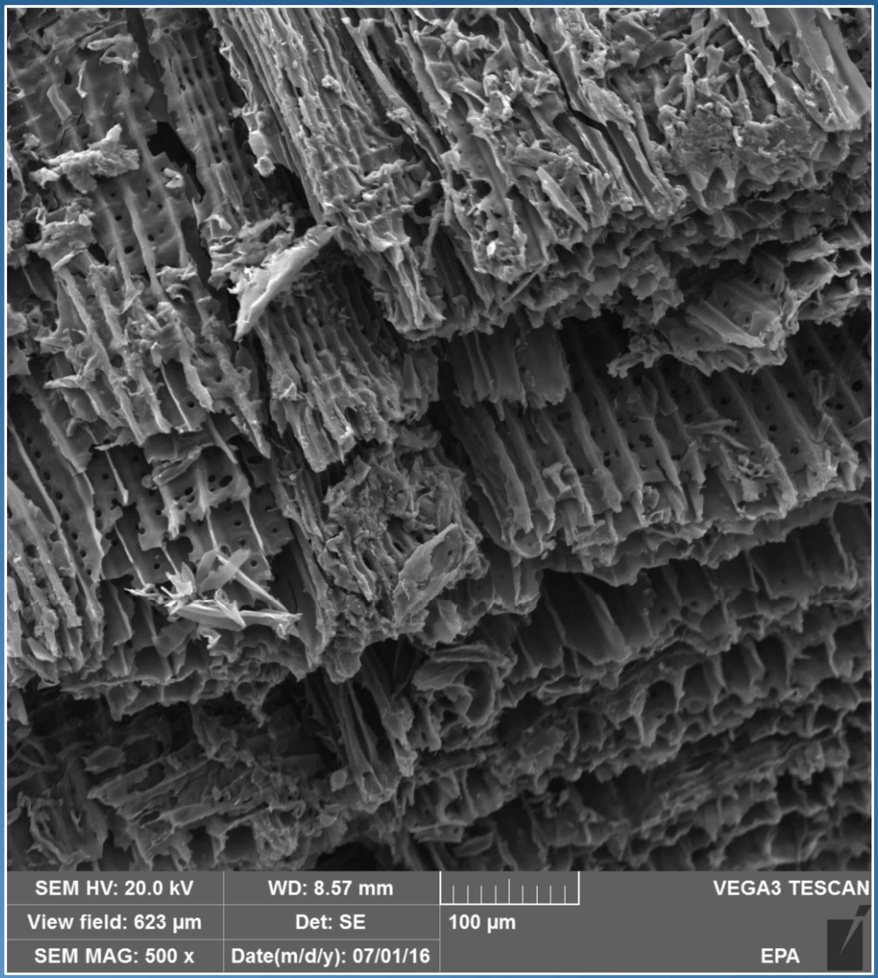
What is Biochar?

- Carbon-rich solid produced by heating biomass in the absence of oxygen (pyrolysis)
- Residual product of bio-energy production
- Porous solid with a number of beneficial properties
- Properties depend upon feedstock, pyrolysis conditions and possibly other modifications

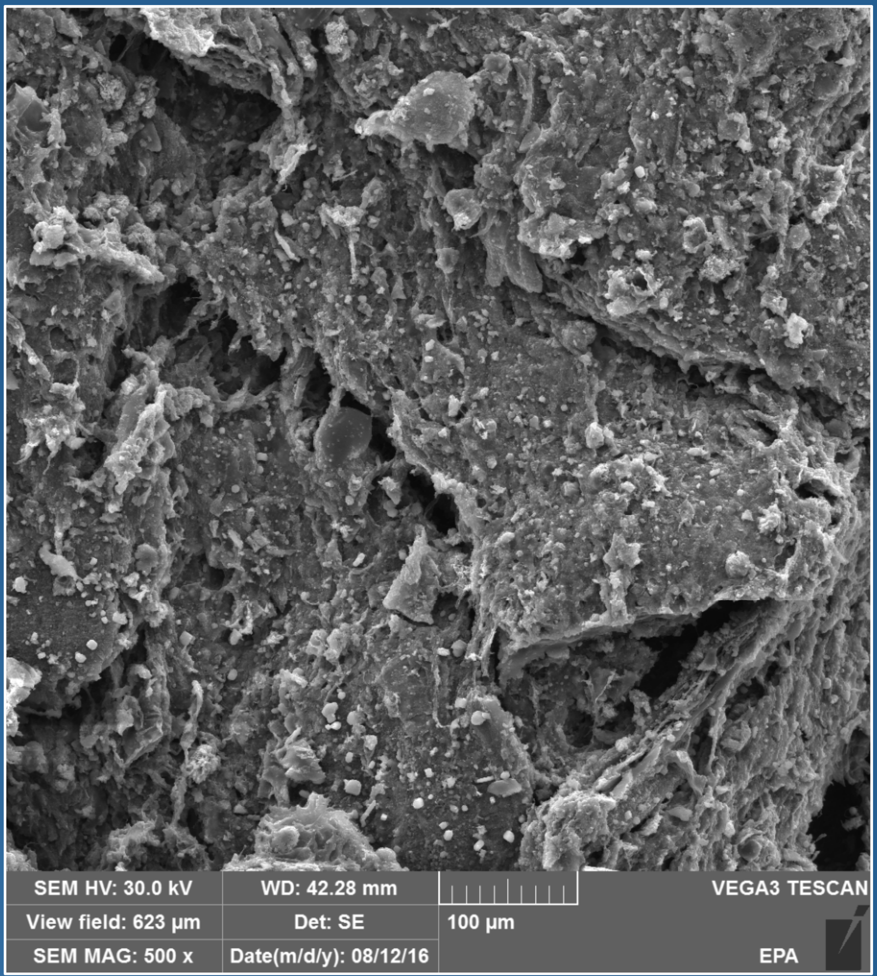
Biochar from Wood Chips

Biochar from Wood Pellets

What is Biochar?



Ponderosa Pine Biochar

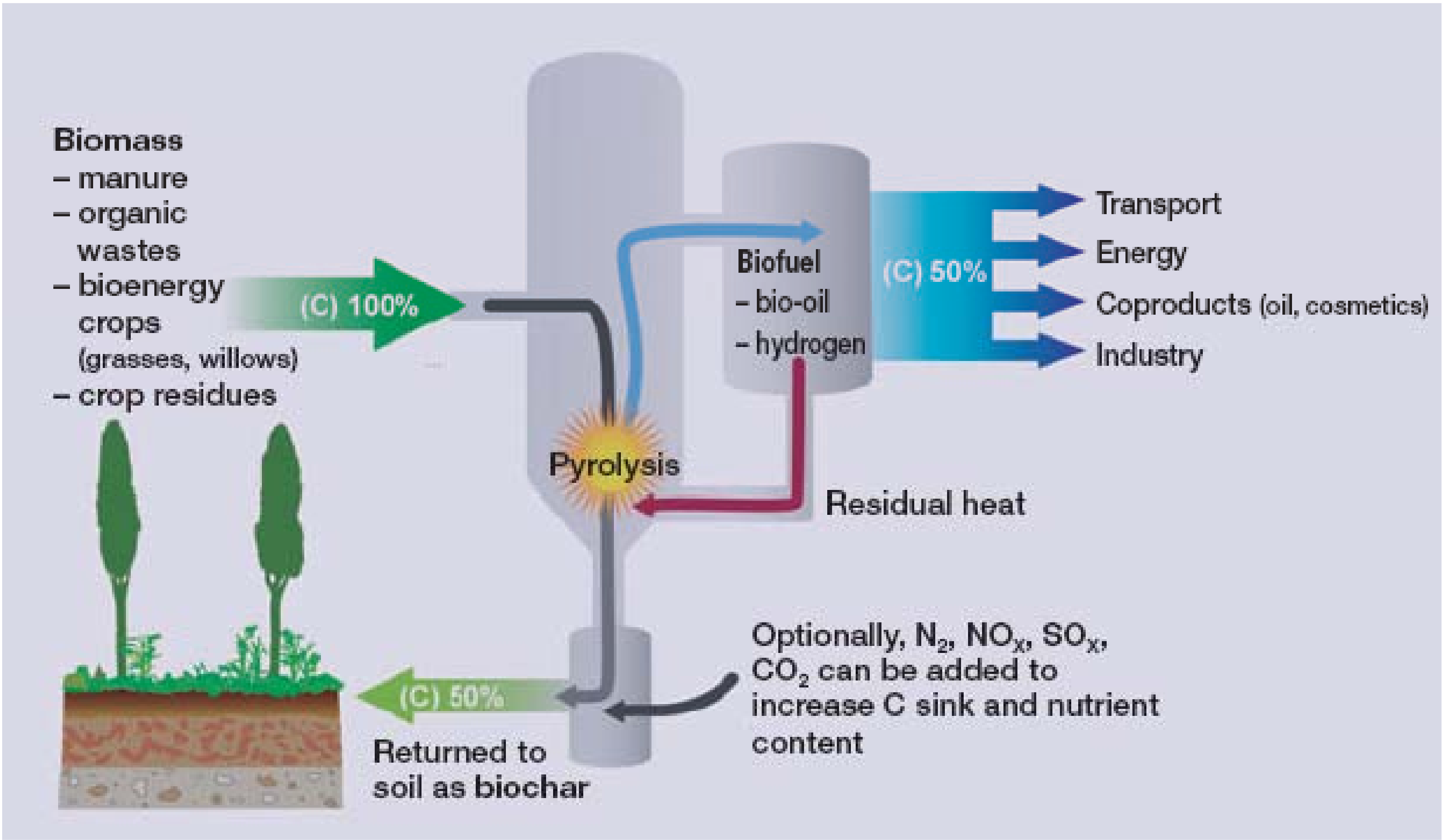


Poultry Litter Biochar

How Nature Makes Charcoal

Charcoal being added to Willamette Valley soil following a grass field fire

Making Biochar via Pyrolysis: Energy Extraction from Biomass



Concept diagram of low-temperature (350 to 500 °C) pyrolysis based bio-energy production with biochar storage in soil. Typically, between 20 and 50% of the initial biomass carbon is converted into biochar and can be returned to soil (Lehmann, 2007).

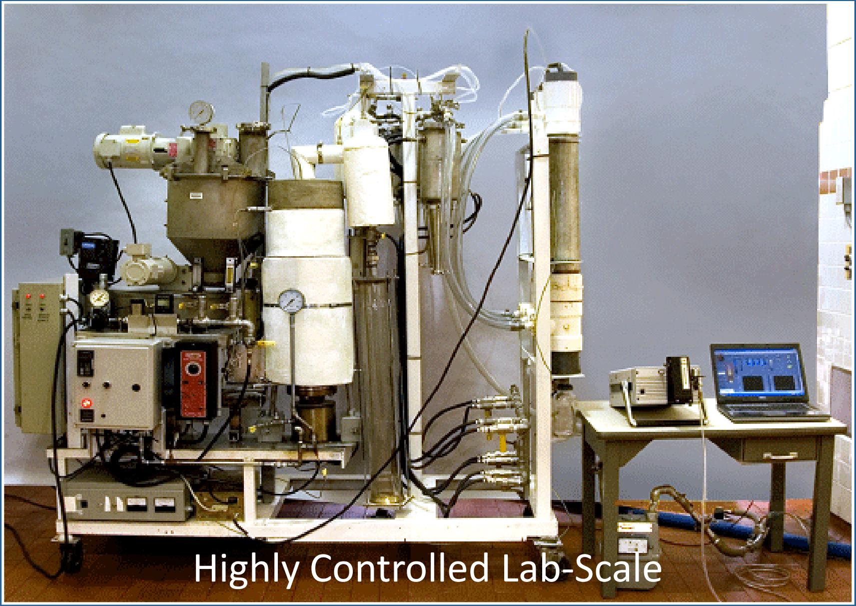
Comparison of Pyrolysis Processes for Syngas (Energy) and Biochar Production

Table 1. Fate of initial feedstock mass between products of pyrolysis processes (IEA, 2007)

Process	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)
FAST PYROLYSIS Moderate temperature (~500 °C) Short hot vapour residence time (<2s)	75% (25% water)	12%	13%
INTERMEDIATE PYROLYSIS Low-moderate temperature, Moderate hot vapour residence time	50% (50% water)	25%	25%
SLOW PYROLYSIS Low-moderate temperature, Long residence time	30% (70% water)	35%	35%
GASIFICATION high temperature (>800 °C) Long vapour residence time	5% tar 5% water	10%	85%

http://www.csiro.au/files/files/poei.pdf

Pyrolyzers: Heating Biomass Without Oxygen



Slide - D. Crowley

Modern Slow Pyrolysis Unit: Prineville, OR


Feedstock Hopper
Biochar
Product
Pyrolysis Retort
LIFTER

Examples of Biochar Feedstocks

Switchgrass

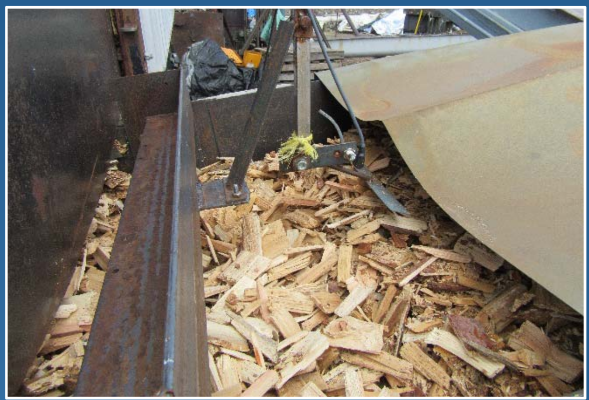
Pine Chips

Swine Solids

Poultry Litter

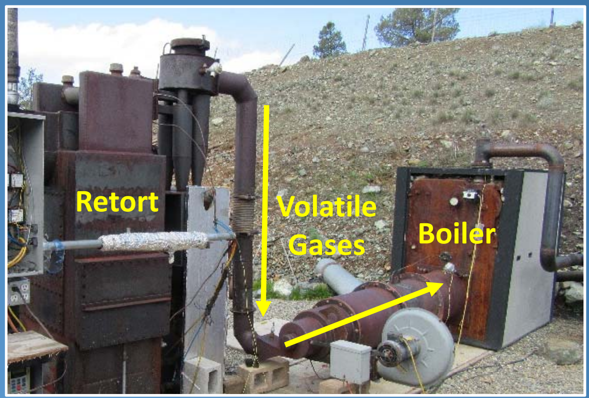
Energy Extraction and Biochar Production

Saw Mill Waste

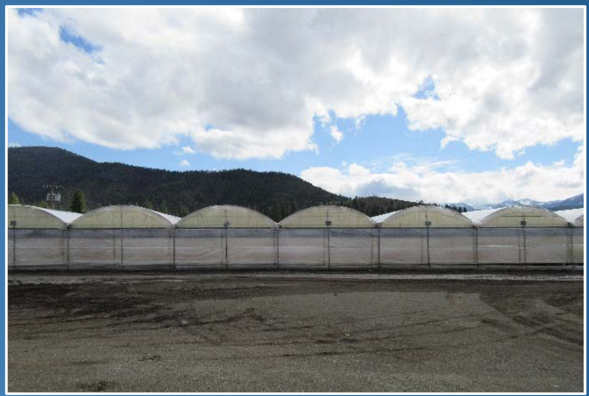


Coarse Wood Chips

Wood Chips Feed Into Gasification Retort



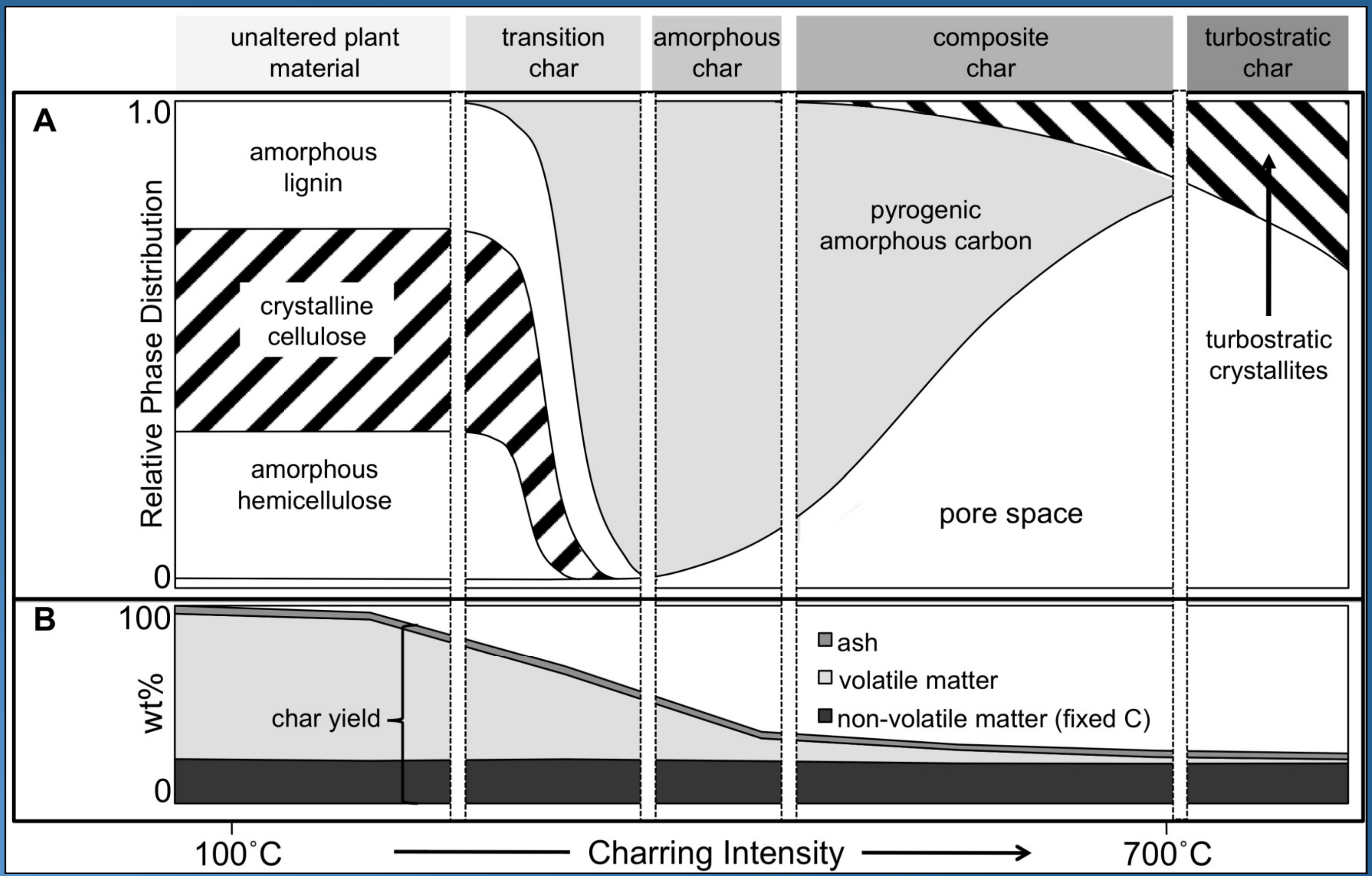
Volatile Gases From Retort Feed Into Boiler



Hot Water From Boiler Heats 5 Acres of Greenhouses

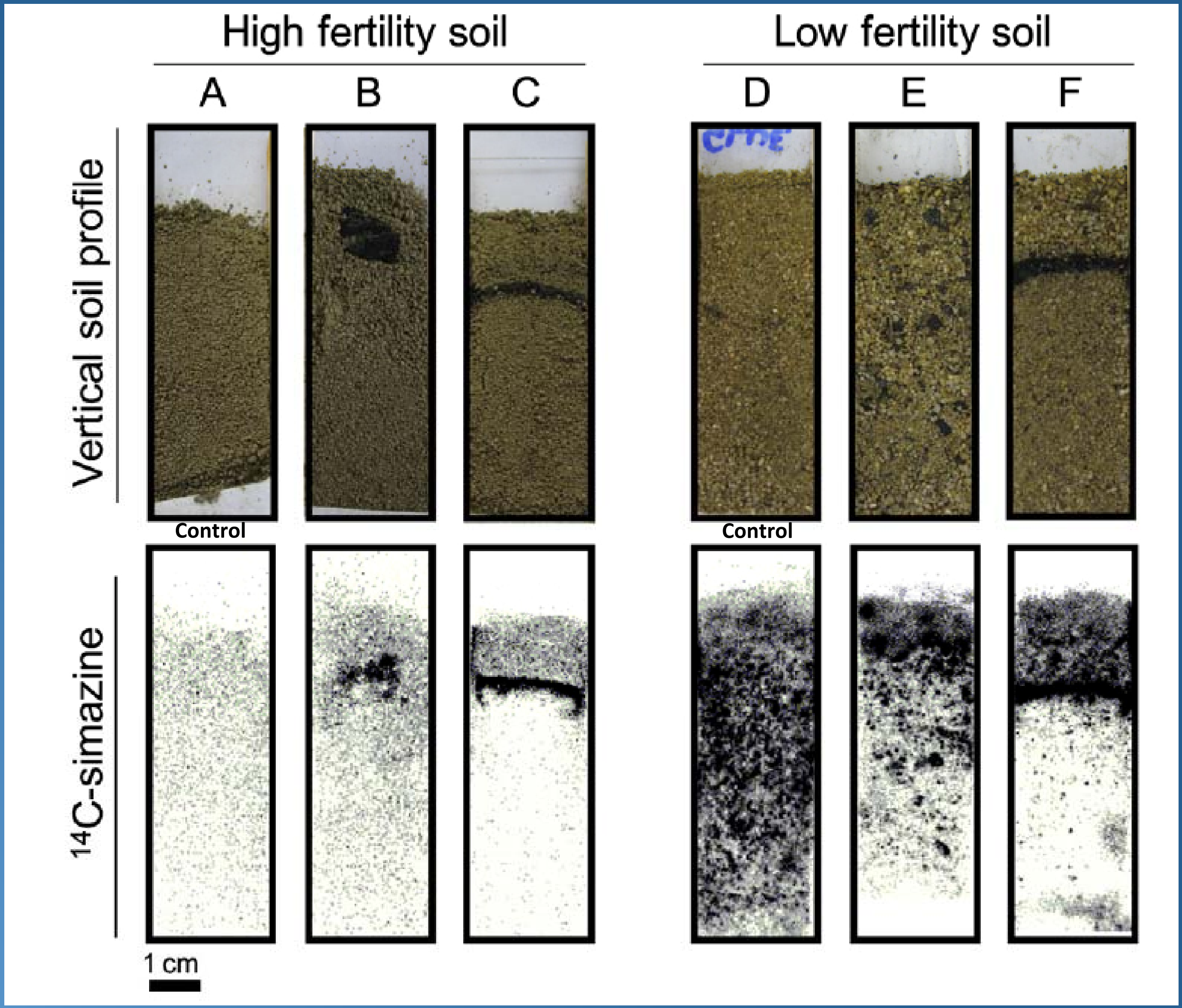
"Waste Product" = High Quality Biochar

Biochar has a Range of Structural Properties that Depend Upon Pyrolysis Temperature and Conditions



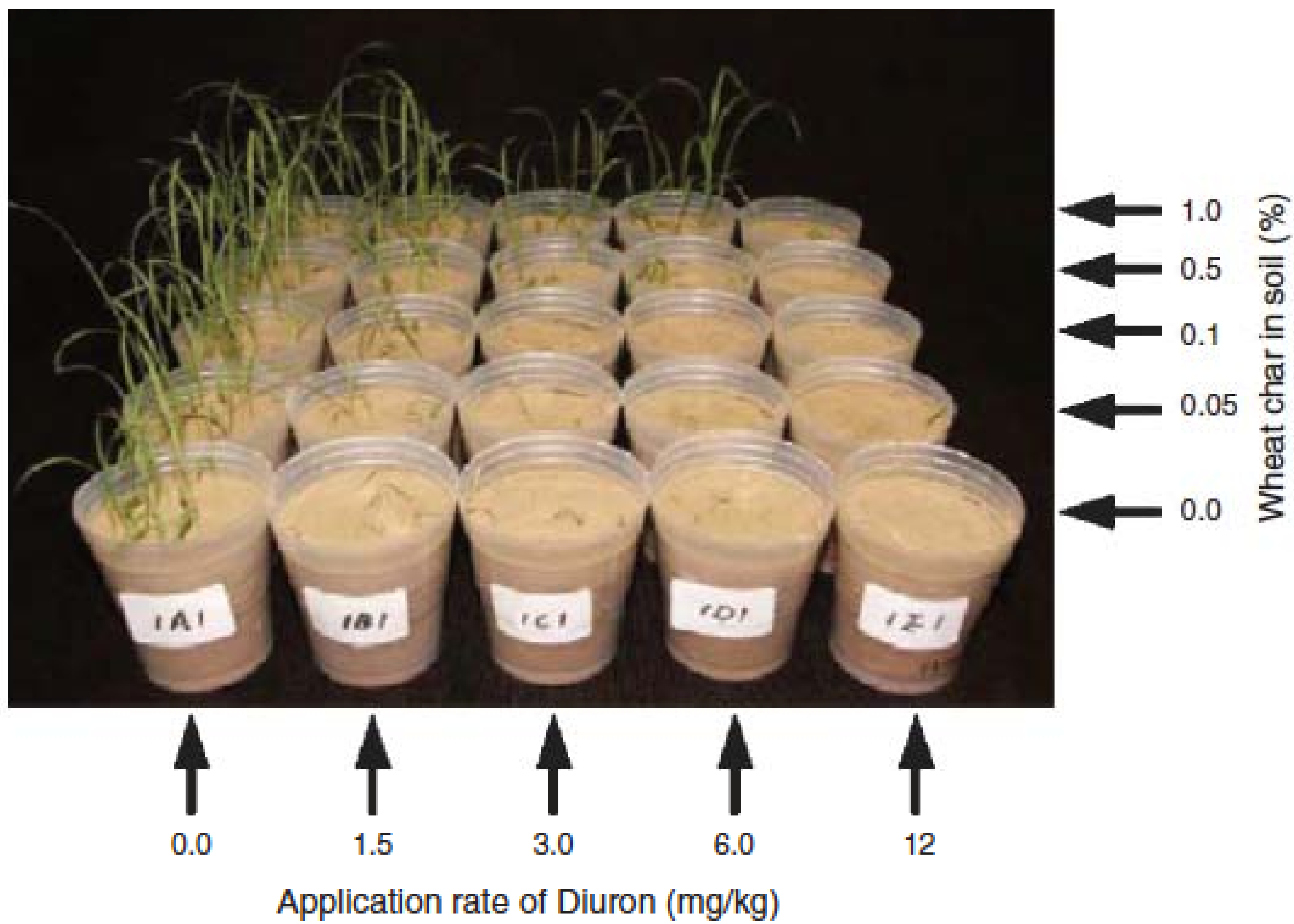
(Keiluweit et al, 2010)

Adsorption, Leaching, and Distribution of Simazine in Soils Amended with Biochar



D.L. Jones et al. / Soil Biology & Biochemistry 43 (2011) 804-813

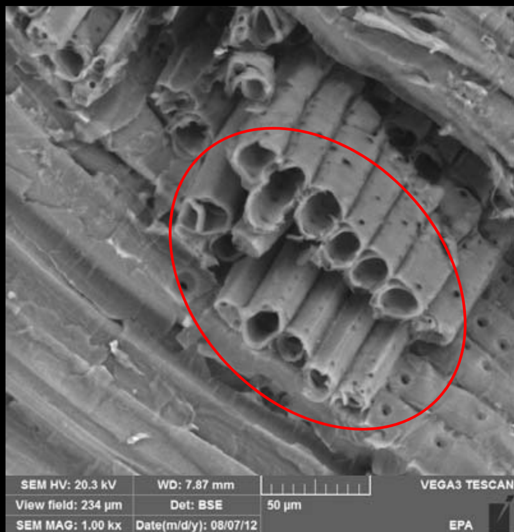
Weed control of barnyard grass with Diuron herbicide applied at different concentrations to soil amended with varying concentrations of wheat straw biochar. (Yang 2006)



Key Biochar Properties

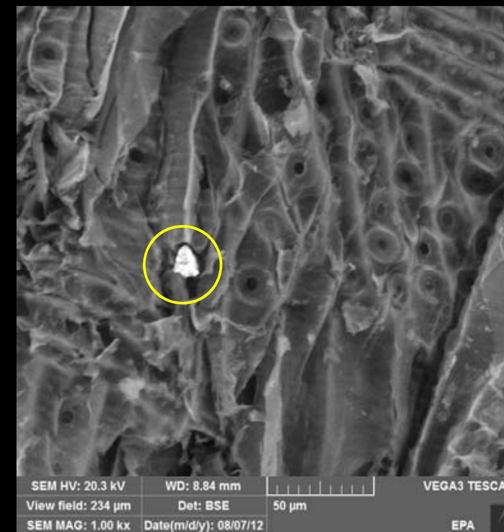
- pH
  - Ash content
- Proximate carbon
  - Volatile matter
  - Fixed carbon
- Surface area
- Porosity
  - Pore size distribution
- Chemistry
  - Total elemental
  - Nutrients
- Cation exchange capacity (CEC)

SEM Images of Douglas-fir Wood Chip Feedstock and Biochar

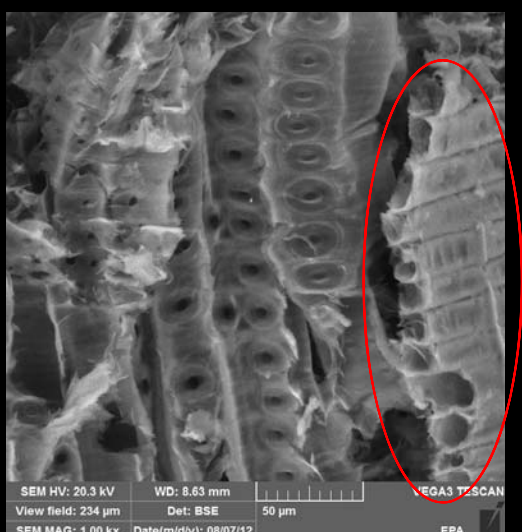


Raw Feedstock

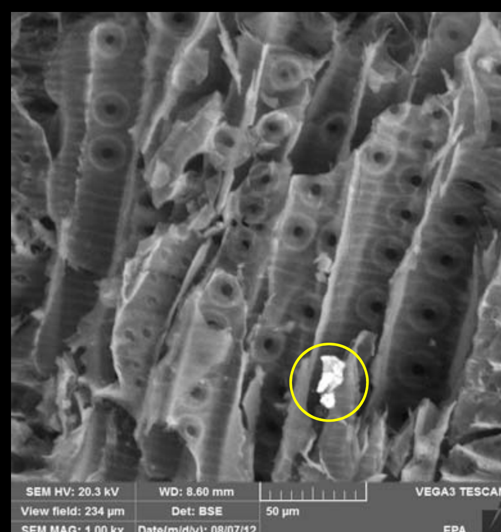
300 °C



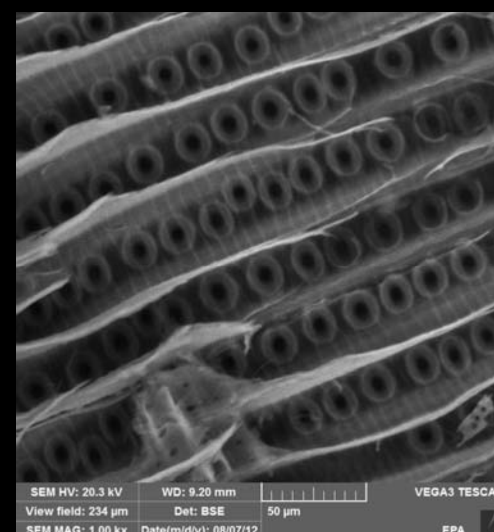
400 °C



500 °C



600 °C



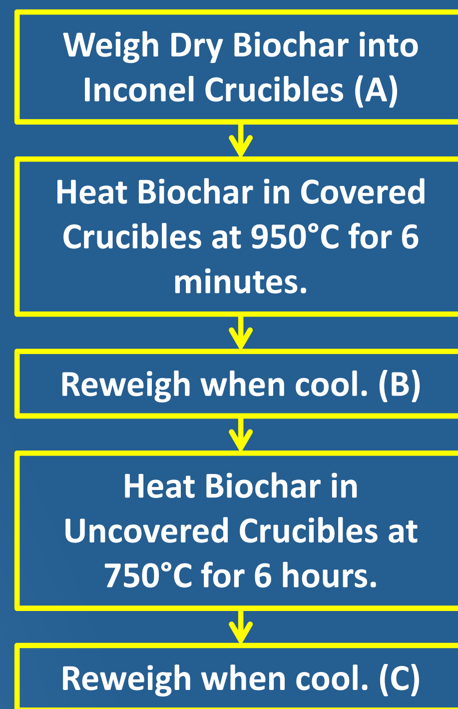
700 °C

Proximate Carbon Analysis

- Quantify three constituents of biochar
  - Volatile matter
    - Low molecular weight carbon
    - Labile carbon fraction
  - Fixed carbon
    - Stable forms of carbon
    - Biopolymer (lignin, cellulose, hemicellulose, etc.)
    - High degree of aromaticity
  - Ash content
    - Residual mineral matter

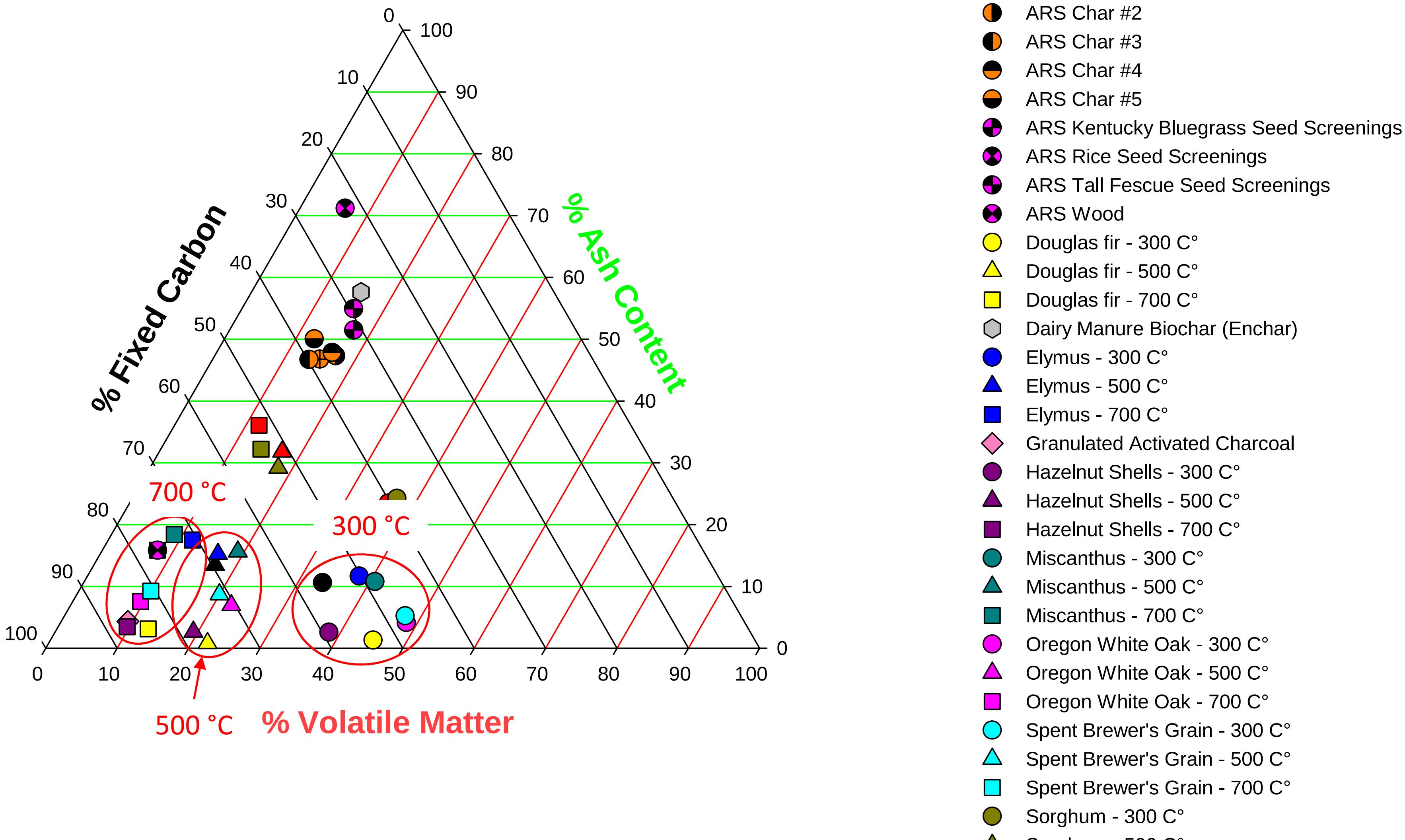
Procedure

Adapted from ASTM Method D1762-84: Chemical Analysis of Wood Charcoal



Volatile matter = B – A; Fixed carbon = B – C; Ash content = C

Ternary Plot of Proximate Carbon Fractions† Formosa Mine Extract Study - Summer 2014



†ASTM Method D-1762

Physical Properties of Biochar from Different Feedstocks: Grass† vs. Wood‡

Pyrolysis Temperature (°C)	Yield (wt%)	Yield (wt%)	Carbon Content (wt%)	Carbon Content (wt%)	Volatile Matter (wt%)	Volatile Matter (wt%)	Fixed Carbon (wt%)	Fixed Carbon (wt%)	Ash* (wt%)	Ash* (wt%)	Surface Area (m^2g^{-1})	Surface Area (m^2g^{-1})
100	99.9	99.8	48.6	50.6	69.6	77.1	23.5	21.7	6.9	1.2	1.8	1.6
200	96.9	95.9	47.2	50.9	70.7	77.1	23.6	21.4	5.7	1.5	3.3	2.3
300	75.8	62.2	59.7	54.8	54.4	70.3	36.2	28.2	9.4	1.5	4.5	3.0
400	37.2	35.3	77.3	74.1	26.8	36.4	56.9	62.2	16.3	1.4	8.7	28.7
500	31.4	28.4	82.2	81.9	20.3	25.2	64.3	72.7	15.4	2.1	50	196
600	29.8	23.9	89.0	89.0	13.5	11.1	67.6	85.2	18.9	3.7	75	392
700	28.8	22.0	94.2	92.3	9.1	6.3	71.6	92.0	19.3	1.7	139	347

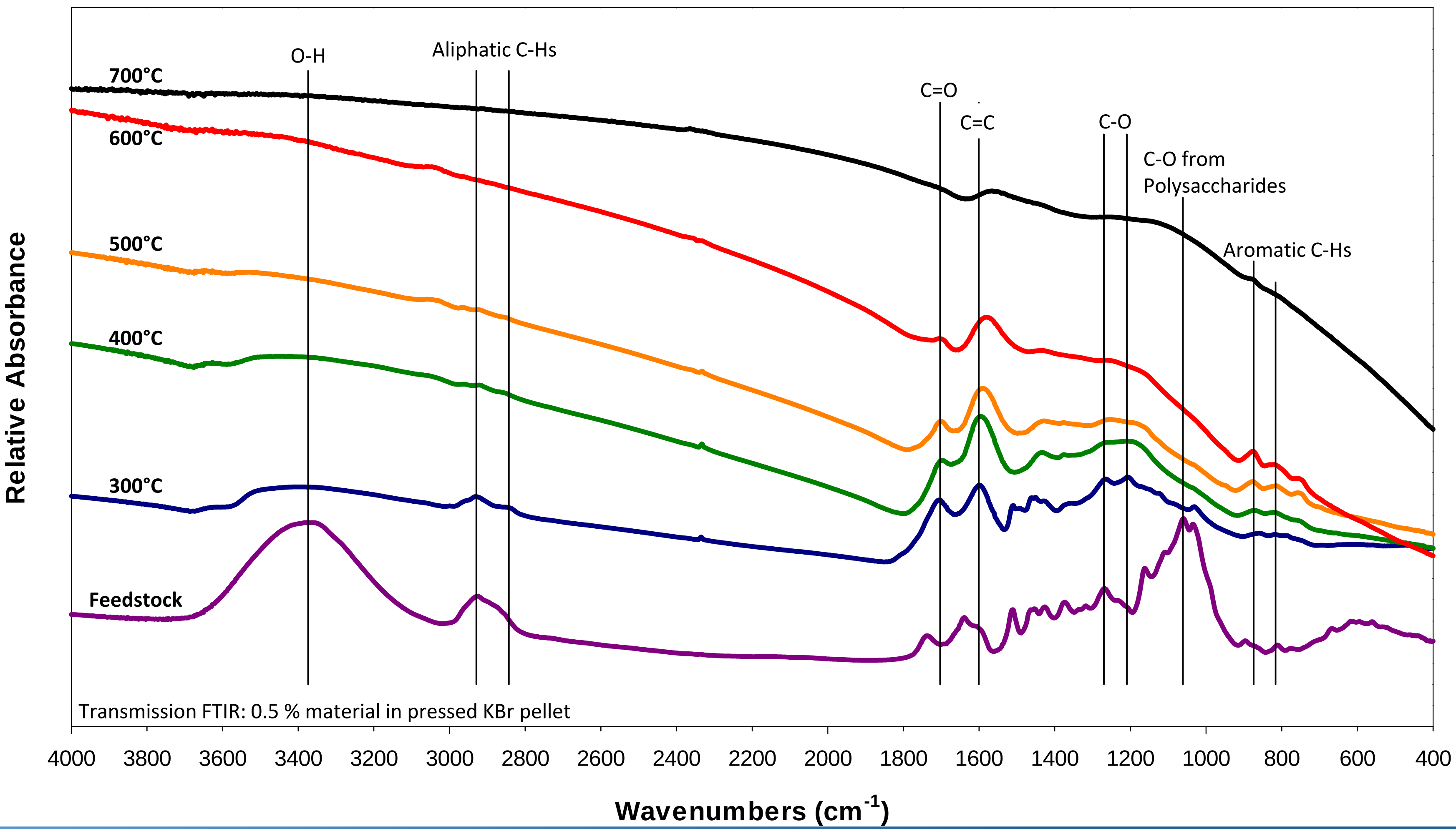
†Tall Fescue, ‡Ponderosa pine

*Ash = Metal and non-metal oxides, chlorides, phosphates, and carbonate residue
(From Keiluweit et al, 2010)

Physical Properties and pH of Douglas-fir Biochar: A Function of Pyrolysis Conditions and Feedstock

Property	300 °C	400 °C	500 °C	600 °C	700 °C
Production Yield (%)	49.9	36.6	31.3	28.8	27.2
Volatile Matter (%)	46.90	32.35	20.54	11.80	7.96
Fixed C (%)	52.70	67.16	78.87	87.51	89.12
Ash Content (%)	0.40	0.48	0.59	0.69	2.93
Surface Area (m^2g^{-1})	3.7	13.7	353.6	391.3	379.9
pH	4.67	5.95	6.68	7.48	8.22

Fourier Transformed Infrared (FTIR) Spectra of Douglas-fir Biochar and Feedstock



Early Research: First Study

Mine spoil “soil” from Leadville, CO

- Simulated Rainwater (SRW) extraction (pH 4.5)
- 25 mls of filtered SRW added to 0.25 g of Douglas-fir biochar
- 24 hour contact time
- Biochar separated from SRW solution
- Characterization of SRW solution with ICP-AES

% Change in Initial Metal Concentration of Simulated Rainwater Extract of Leadville, CO Mine Spoil after 24 Hour Contact with Douglas-fir Biochar

Metal	Initial Metal Concentration (mg kg^{-1} biochar)	300 °C	400°C	500°C	600°C	700°C
Al	247	3.8	21.8	68.2	92.9	98.6
Ca	57922	-0.4	-0.8	-1.0	-2.4	-2.6
Cd	101	3.7	3.9	5.0	5.3	6.4
Cu	204	8.4	17.5	65.1	87.1	97.4
Mg	8441	3.8	3.4	2.8	2.1	5.9
Mn	2364	4.5	4.2	3.7	3.2	7.4
Pb	198	11.2	21.1	54.8	72.5	95.3
Zn	8720	3.6	2.9	3.1	3.6	5.5

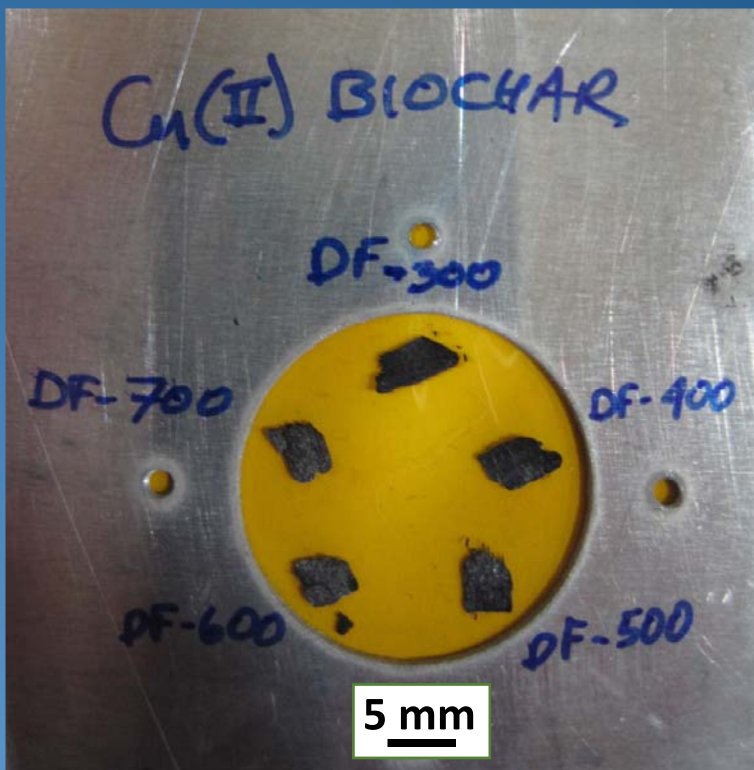
Early Research: Second Study

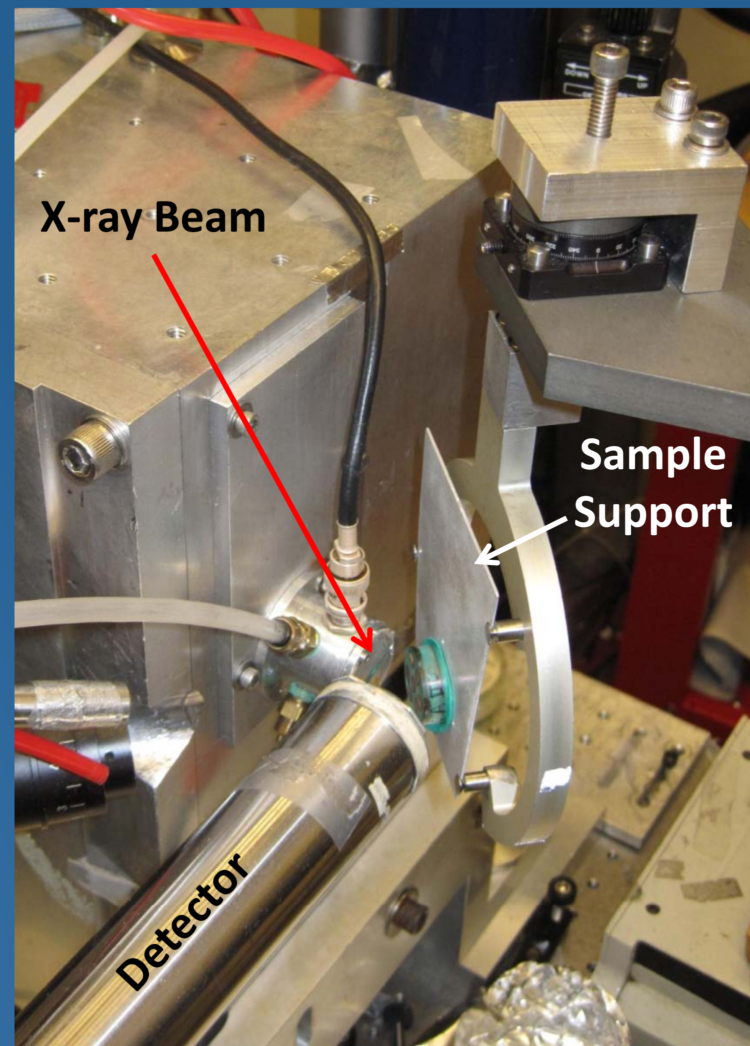
Cu sorption on biochar

- 25 mls of a 5 mM $Cu(NO_3)_2 \cdot 2.5\ H_2O$ solution added to 0.25 g of Douglas-fir biochar
- 24 hour contact time
- Biochar separated from Cu solution, washed with MeQ water and dried
- Cu sorption characterized with X-Ray Absorption Spectroscopy

Micro X-ray Absorption Spectroscopy (µXAS): ALS Beamline 10.3.2

Samples Mounted with Kapton tape

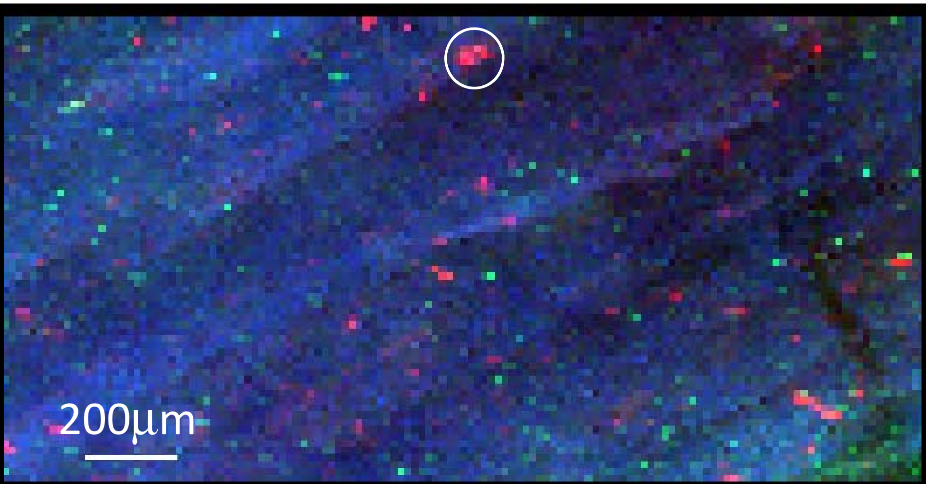




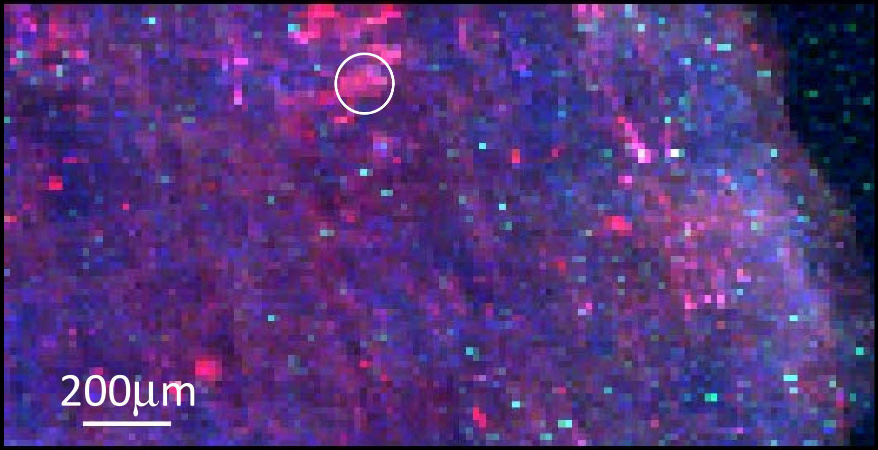
X-ray beam spot size: 3 – 10 µm

Biochar Fluorescence Chemistry Maps

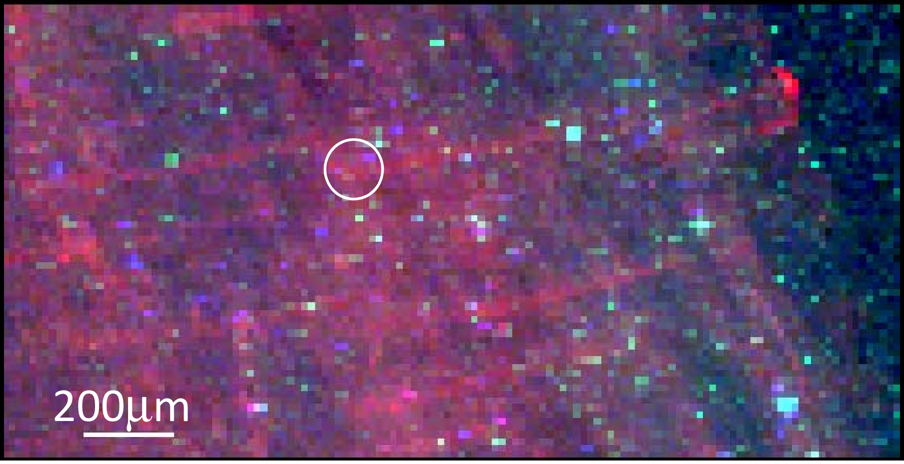
300 °C
Douglas-fir Biochar treated with 5mM Cu
CuCaK

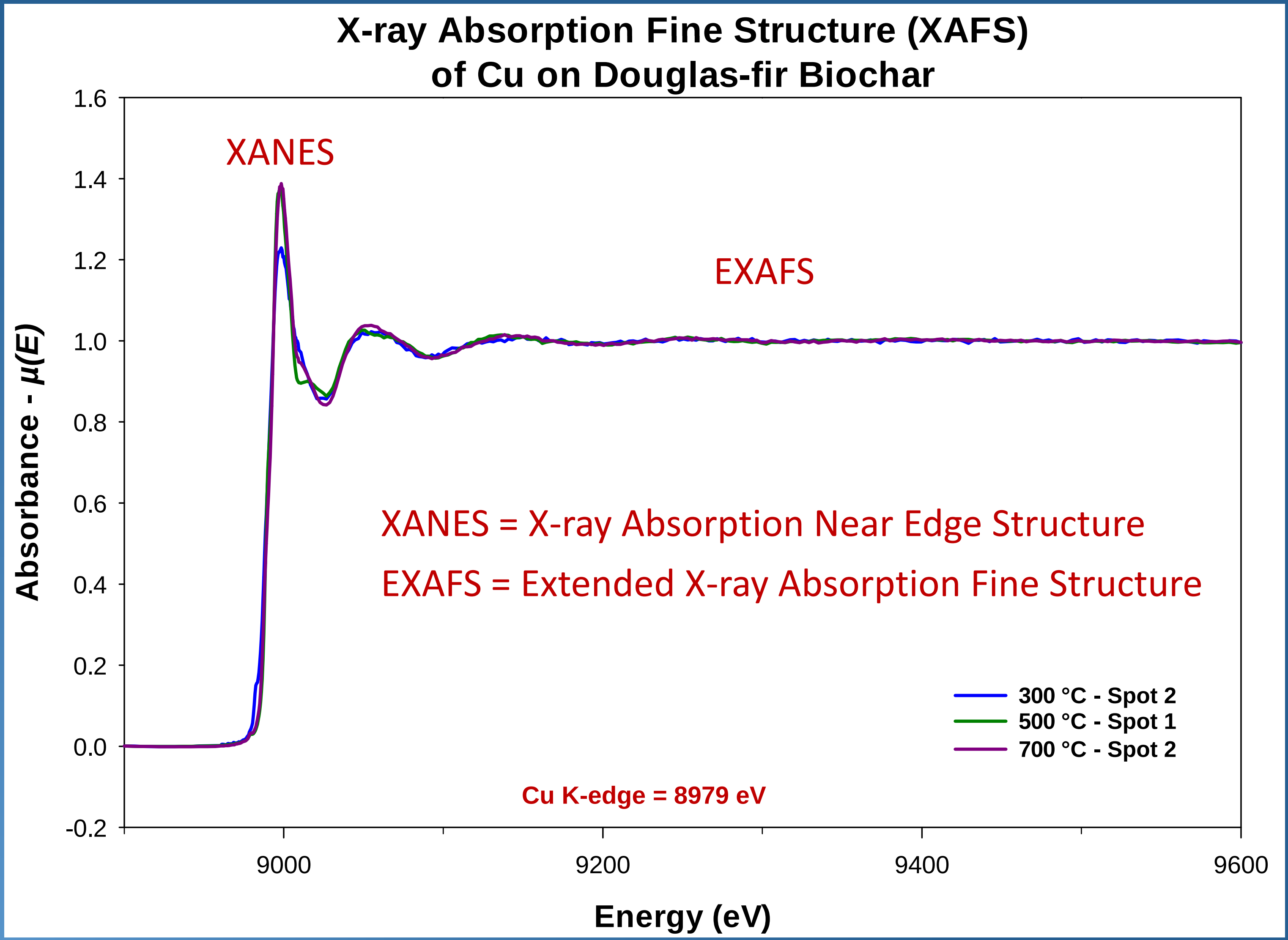


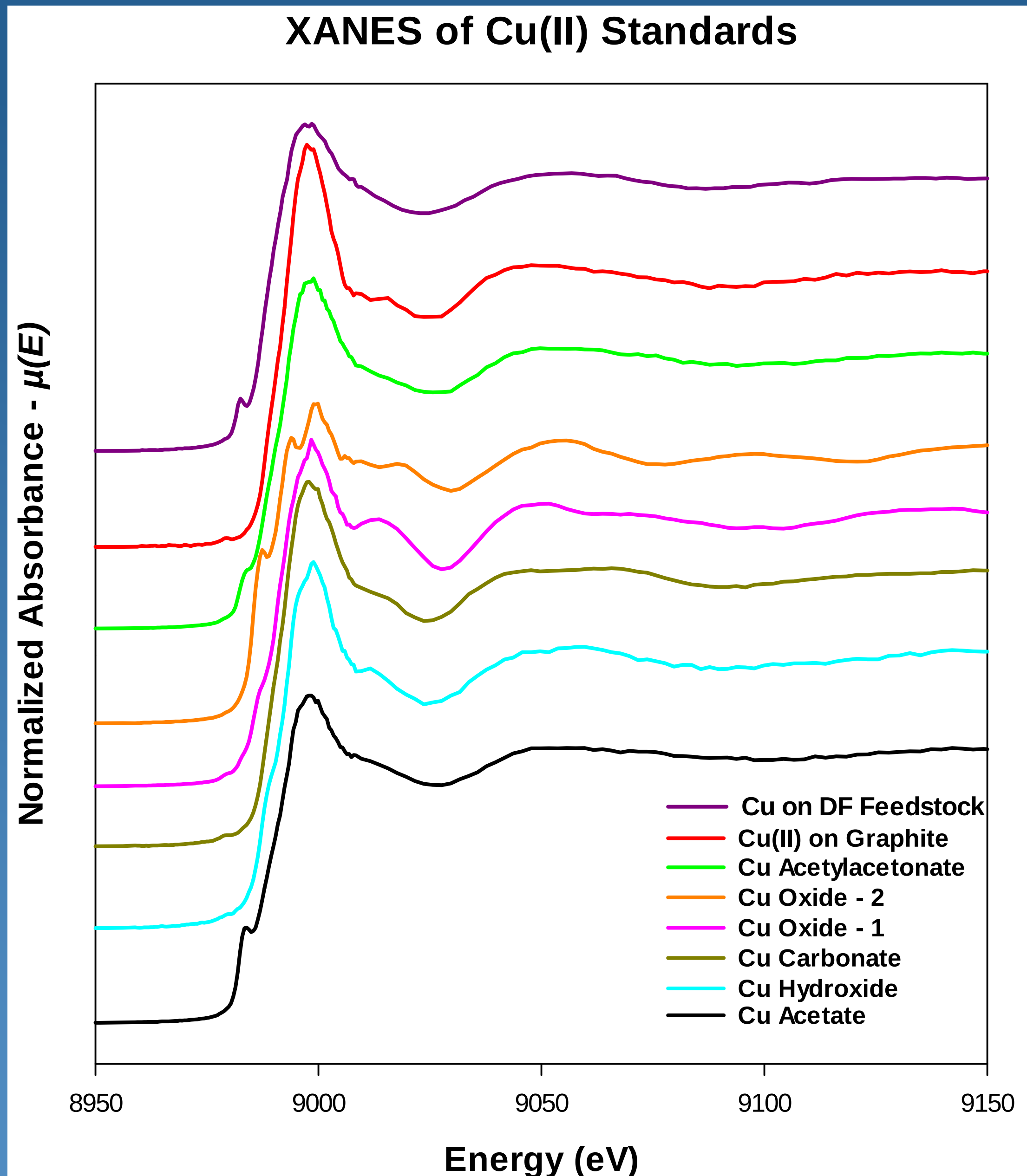
500 °C
Douglas-fir Biochar treated with 5mM Cu
CuCaK



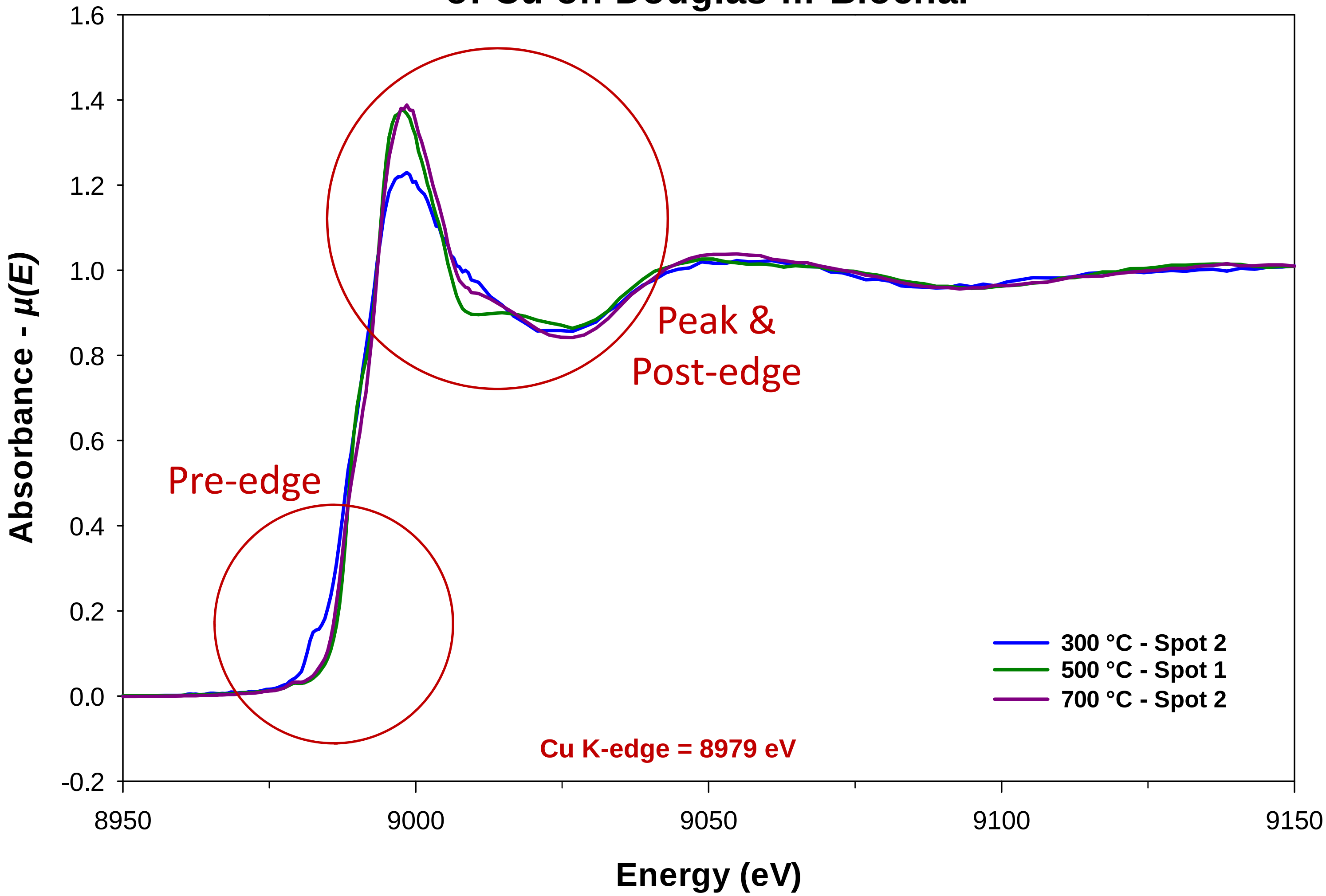
700 °C
Douglas-fir Biochar treated with 5mM Cu
CuCaK

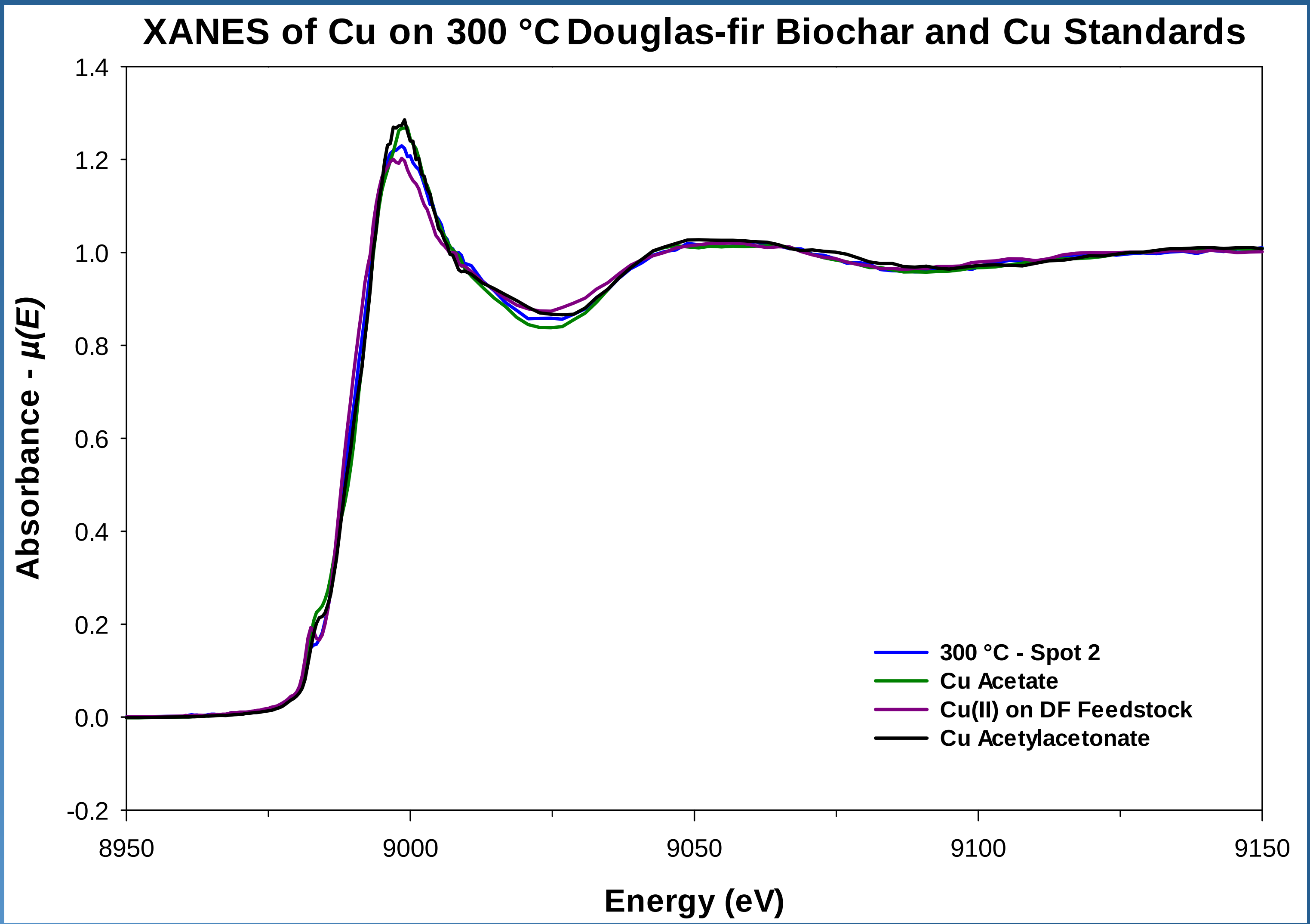


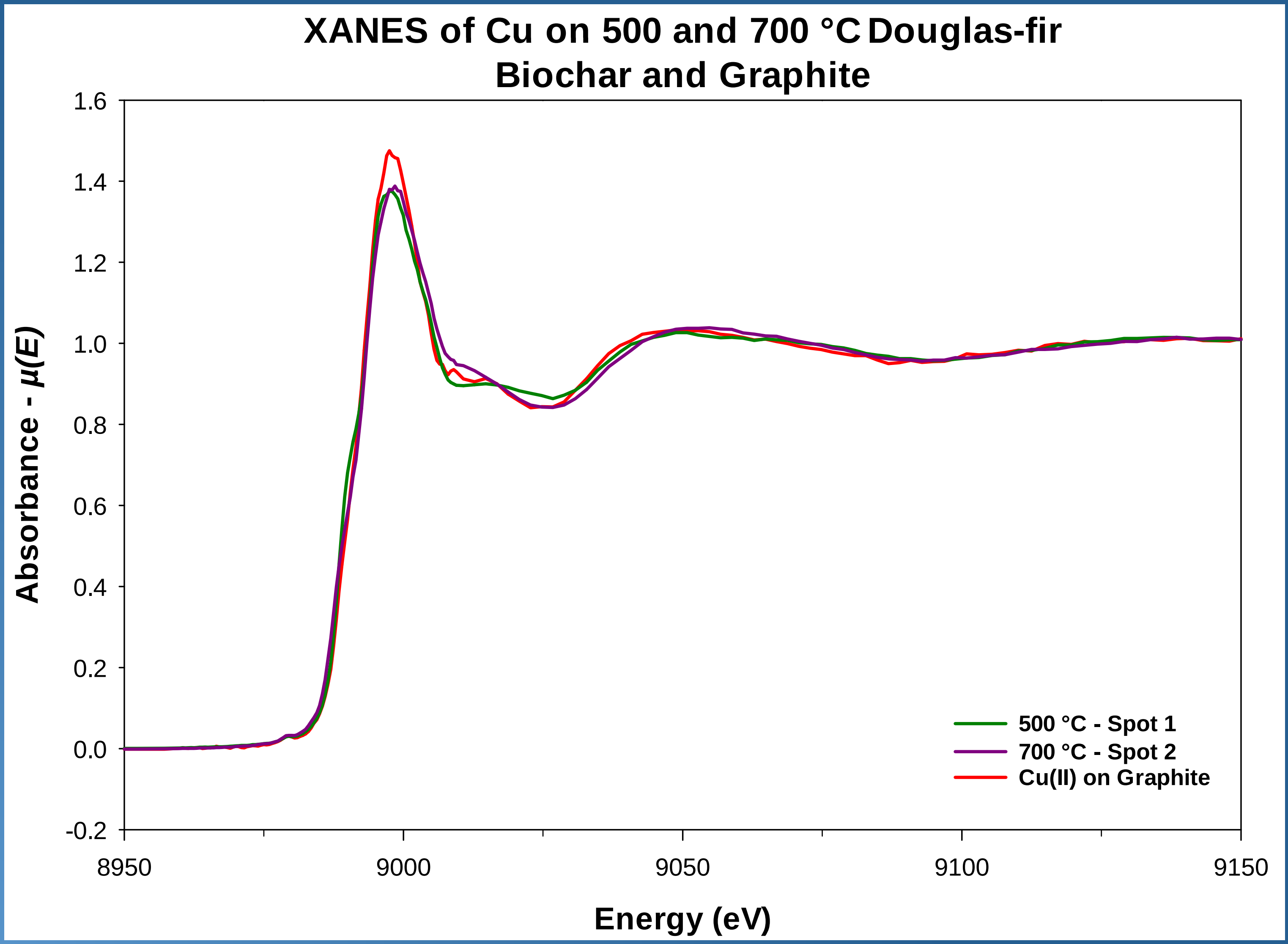

X-ray Absorption Fine Structure (XAFS)
of Cu on Douglas-fir Biochar
XANES
EXAFS
XANES = X-ray Absorption Near Edge Structure
EXAFS = Extended X-ray Absorption Fine Structure
300 °C - Spot 2
500 °C - Spot 1
700 °C - Spot 2
Cu K-edge = 8979 eV
Absorbance - μ(E)
Energy (eV)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
9000
9200
9400
9600


XANES of Cu(II) Standards
Normalized Absorbance - μ(E)
Energy (eV)
8950
9000
9050
9100
9150
Cu on DF Feedstock
Cu(II) on Graphite
Cu Acetylacetonate
Cu Oxide - 2
Cu Oxide - 1
Cu Carbonate
Cu Hydroxide
Cu Acetate

X-ray Absorption Near Edge Structure (XANES) of Cu on Douglas-fir Biochar




XANES of Cu on 300 °C Douglas-fir Biochar and Cu Standards
Absorbance - μ(E)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
8950
9000
9050
9100
9150
Energy (eV)
300 °C - Spot 2
Cu Acetate
Cu(II) on DF Feedstock
Cu Acetylacetonate


XANES of Cu on 500 and 700 °C Douglas-fir Biochar and Graphite
Absorbance - μ(E)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
8950
9000
9050
9100
9150
Energy (eV)
500 °C - Spot 1
700 °C - Spot 2
Cu(II) on Graphite

Observations and Conclusions from Early Studies

- Biochar from Douglas-fir (DF) has the potential for remediating metal contaminated soils and waters for certain metals
- For some metals sorption is a function of the pyrolysis temperature
  - Pyrolysis temperature↑ metal sorption↑
- Metal sorption in low temperature (≤ 400 °C) DF biochar appears to be controlled by oxygen-containing functional groups and appears to be relatively weak association for Cu(II)
- In contrast, metal sorption in higher temperature (> 400 °C) DF biochars does not appear to be controlled by oxygen-containing functional groups
- Possible explanations for sorption in the high temperature biochar include physisorption of metals in micropores and/or pi-bonding with aromatic p systems that form during pyrolysis. The mechanism for this sorption still needs to be resolved.