Investigating Dissolved Organic Carbon Uptake to Biochar

Niloufar Ghazal

2010 Kearney Undergraduate Fellowship Report
Department of Land, Air and Water Resources
The University of California, Davis
What is Biochar?

Biochar is charcoal created from biomass, and differs from charcoal only in the sense that its primary use is not for fuel.

- **Biomass** (e.g., crop residue, manure, nut shells, wood chips)

- Biochar may be produced intentionally as a soil amendment or as a waste byproduct in the production of bioenergy.

- Physical and chemical properties vary depending on source of biomass and pyrolysis temperature
Proposed Benefits of Biochar

- Reduce greenhouse gas emissions (N\textsubscript{2}O and CO\textsubscript{2})
- Improve water retention
- Increase soil fertility and crop yields
- Reduce use of synthetic fertilizers and pesticides
- Produce renewable fuels from biomass
- Reduce dependence on fossil fuels
Research Objective

• To determine if biochars source material and pyrolysis conditions have potential to effect carbon and nitrogen cycling for biochar amendments to soil
  – How dissolved organic C and N bind to biochars
  – How carbon fractions (i.e., aromatic vs. non-aromatic) preferentially bind to biochar
Materials

• Compost Tea: organic compost shaken in Barnstead Nanopure (BNP) water for 24 hours, centrifuged, then filtered through 0.8μm filter.

• 5mM NaCl (serves as water)

• 3 types of biochar
  1. Walnut Shell (950° C)
  2. High Temperature Wood Feedstock (900° C)
  3. Low Temperature Wood Feedstock (700° C)

• Other materials for testing
  1. Activated Carbon
  2. Kaolinite
Experimental Design

• Batch experiments were conducted at seven different concentrations of compost tea for each biochar experiment at pH 7
  – 0, 10, 20, 40, 80, 160, and 240 mg C/L

• Each experiment is done in triplicate to give a total of 21 test tubes for each experiment
Methods: Preparation of Samples

- Fill each tube with 0.48g of biochar and 5 mM NaCl and adjust to pH 7 (10 mM HCl)
- Vortex and shake for 48 hours, end over end rotation (8 rpm) to equilibrate biochar
- Add compost tea to reach desired C concentration
- Vortex and shake for 24 hours in the dark, end over end rotation (8 rpm)
- Centrifuge at 8,000 RCF for 8 minutes
- Filter the supernatant through 0.8um filter and store at 4° C for analysis
Methods: Carbon Analysis

- Carbon content analyzed via UV/Chemical (Persulfate) Oxidation (Dohrmann Phoenix 8000)

Free radical oxidants formed:

\[ S_2O_8^{2-} \xrightarrow{hv} 2SO_4^{-} \]
\[ H_2O \xrightarrow{hv} H^+ + OH^- \]
\[ SO_4^{-} + H_2O \xrightarrow{} SO_4^{2-} + OH^- + H^+ \]

Excitation of organics:

\[ R \xrightarrow{hv} R^* \]

Oxidation of organics:

\[ R^* + SO_4^{-} + OH^- \rightarrow nCO_2 + \cdots \]
Methods: Nitrogen Analysis

- Total dissolved nitrogen oxidized via potassium persulfate to nitrate

- Nitrate reduced to nitrite and/or nitric acid (via vanadium (III) in dilute acid) and captured by Griess reagents to produce a red dye

- Solutions analyzed via UV absorbance at 540 nm (Shimadzu UVmini-1240).
Methods: Specific Ultraviolet Absorption (SUVA)

- SUVA (L/mg-m) provides a measure of the aromatic content of dissolved organic carbon (DOC)

\[
SUVA = \frac{UVA \left( \text{cm}^{-1} \right)}{DOC \left( \text{mg} \left( \frac{L}{g} \right) \right)} \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)
\]

\[
UVA = \frac{A}{d}
\]

where:

- \(A\) = UV absorbance at 254 nm
- \(d\) = quartz cell path length (cm)
Results: Carbon Sorption

- Walnut Shell BC and Activated Carbon bind significantly more C than Low Temp BC, High Temp BC, and Kaolinite.

- Note: Low Temp BC was unstable and released C into solution during 48 h pre-equilibration.
Results: Nitrogen Sorption

- Walnut Shell BC and Activated Carbon binds significantly more N than High Temp BC, Low Temp BC, and Kaolinite.

- Note: Low Temp BC was unstable and released some N into solution during 48 h pre-equilibration which increased initial N concentration.
Bound Carbon vs. Bound Nitrogen

- All materials bind significantly more C than N
- Activated Carbon and Walnut Shell bind the most C and the most N – with preferential sorption of C over N
Effect of initial concentration on C and N Sorption

• Nitrogen bound: Materials generally showed increase in Nitrogen bound with increase in concentration of Nitrogen

• Carbon Bound: materials show varying trends
  – Activated carbon decrease % Carbon bound with increased $[\text{Carbon}]_{\text{initial}}$
  – Walnut Shell BC shows increased % Carbon bound with increased $[\text{Carbon}]_{\text{initial}}$

• Results suggest that different and multiple sorption mechanisms are present for compost tea sorption to biochar
Preferential Sorption of the Aromatic Fraction

- All materials preferentially remove aromatic compounds from solution: 
  \[ \frac{[SUVA]_{\text{final}}}{[SUVA]_{\text{initial}}} < 1 \]

- Activated Carbon preferentially binds aromatic fractions at low \([C]\) and decreases with increased \(C\) sorption; however, as bound \(C\) increases further aromatic fractions are again preferred

- Walnut shell binds consistently removes a greater portion of the aromatic fraction of DOC than other materials

- All other materials show general trend of decreased preferential binding of aromatics with increased binding of \(C\)

\[ \text{SUVA}_{\text{compost tea}} = 3.77 \text{ L/mg-m} \]

(highly aromatic)
Conclusions

• The material from which the biochar was made had a significant effect on its ability to bind C and N (ex: Walnut Shell BC vs. High Temp Wood Feedstock)
  – Walnut Shell Biochar and Activated Carbon had significantly greater C and N absorption than the other materials

• The temperature at which the pyrolysis took place had a significant effect on the behavior and properties of the biochar (ex: Walnut Shell BC vs. Low Temp Wood Feedstock)
  – The high temperature biochars (Walnut Shell + High Temp Wood Feedstock) had significantly greater Carbon absorption than their low temperature counterpart

• Due to the hydrophobic nature of biochars they tend to preferentially bind aromatic fractions of DOC. However, as concentrations of DOC increase the sorption of non-aromatic regions of DOC increases. This suggests sorption may occur via multiple mechanisms and exceed monolayer coverage.

• These results demonstrate the need to consider biochar source material and pyrolysis method when amending soil to positively impact C and N cycling in agricultural cultivation.
Acknowledgements

• Fungai Mukome, UC Davis
• T.A. Doane, UC Davis
• Kearney Foundation of Soil Science Undergraduate Research Fellowship
• UC Davis Agricultural Sustainability Institute
• David and Lucille Packard Foundation
• Parikh Soil Chemistry Group, UC Davis