Investigating Dissolved Organic Carbon Uptake to Biochar



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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.



Proposed Benefits of Biochar

- Reduce greenhouse gas emissions (N₂O and CO₂)
- 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. nonaromatic) preferentially bind to biochar

Materials

- Compost Tea: organic compost shaken in Barnstead Nanopure (BNP) water for 24 hours, centrifuged, then filtered through 0.8um 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











Wood Stock (900° C)

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: $S_2O_8^{2-} \xrightarrow{hv} 2SO_4^{-\bullet}$ $H_2O \xrightarrow{hv} H^+ + OH^{\bullet}$ $SO_4^{-\bullet} + H_2O \longrightarrow SO_4^{2-} + OH^{\bullet} + H^+$ Excitation of organics: $R \xrightarrow{hv} R^*$

Oxidation of organics:

 $R^* + SO_4^{-\bullet} + OH^{\bullet} \longrightarrow nCO_2 + \cdots$

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)



Shimadzu UVmini-1240

$$SUVA = \frac{UVA \ (cm^{-1})}{DOC \ (\frac{mg}{L})} \left(\frac{100 \ cm}{1 \ m}\right)$$
$$UVA = \frac{A}{d}$$

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 bound 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 [Carbon]_{initial}
 - Walnut Shell BC shows increased % Carbon bound with increased [Carbon]_{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: [SUVA]_{final}/[SUVA]_{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



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.

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