Biochar Stability & Carbon Sequestration

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Biochar can be defined as biomass charcoal when used or found in soil. There is great interest in the potential for manufacture and application of biochar to be employed as a means of greenhouse gas emission reduction and carbon sequestration for climate change mitigation. Biochar created from woody biomass, pyrolyzed at temperatures above 500 ^{o}C and using commonly available equipment, has shown to be highly recalcitrant in soil and thus an ideal candidate for carbon sequestration (1). However, certain other types of biomass and/or pyrolysis conditions have resulted in products that do not appear to be ideal candidates for carbon sequestration (2). In order to better understand what is currently understood about this, a review of research was conducted, and is summarized in this paper.

The fate of biochar carbon and its persistence in soils is dependent on numerous factors including the characteristics of feedstocks, production and processing parameters, soil conditions, and environmental influences. The pathways for biochar loss from a given soil include disintegration into smaller particles, translocation out of topsoil, decomposition into smaller molecules and metabolites, and mineralization to carbon dioxide. Studies attempting to calculate Mean Residence Times (MRTs) from experimental data have used different curve-fitting models and extrapolation techniques when studying biochar persistence making it difficult to establish standard MRTs for biochar. In general, biochar carbon contains both labile and recalcitrant fractions necessitating the use of multiple-pool models for predicting exponential decay in order to accurately fit the experimental data (2). An 8.5 year study found that calculated decomposition rates over the course of the study were 2.5 times slower than those calculated during the first 3.5 years leading to the conclusion that short duration studies may present an incomplete picture of carbon loss over time (6).

When comparing mineralization rates for pyrogenic (fire-derived) and non-pyrogenic organic matter, studies show that pyrolyzation (charring) reduces the mineralizable fraction of organic carbon by the condensation of cellulose, hemicellulose, and lignin fibers into complex poly-aromatic carbon structures and graphitic domains. Biomass feedstocks rich in these woody fibers produce biochars with higher degrees of aromaticity and recalcitrance. It is well documented that woody biomass pyrolyzed above 500 ^{o}C for at least ten minutes produces a biochar with H/C_{org} ratio <0.4 and a mean residence time >1000 years (3).

The International Biochar Initiative (IBI) examined a number of assessment methodologies to determine the most accurate and feasible testing method for determining biochar stability over a period of 100 years (BC_{+100}). The method which correlated best with experimental observations and molecular analyses was the measurement of H/C_{org} ratio. Testing of this method revealed that a biochar with H/C_{org} <0.4, relates to >70% biochar carbon remaining after 100 years. An upper limit, where the term biochar no longer formally applies, was established by the IBI at

H/C_{org} >0.7 resulting in BC_{+100} values of potentially less than 50% biochar carbon remaining after 100 years (4).

Biochar manufactured in California from forestry residues and distributed by Pacific Biochar has been analyzed to have an H/C_{org} ratio of 0.21. Using the prediction methods determined most accurate by the IBI and detailed calculations provided in Chapter 10 of Biochar for Environmental Management, and assuming a soil temp of 10 ^{o}C, this biochar material will have a mean residence time of 2,291 years, and a BC_{+100} of 95.7% (2).

Our understanding of biochar stability and persistence in different soil types under varying climatic and management regimes would benefit from further clarification with rigorous research projects. One important thing that has become clear from studies over the past decade is that woody biomass pyrolyzed sufficiently at high temperature (>500 ^{o}C) will remain stable in the soil for time periods measured in centuries and millennia, therefore providing an effective means of stabilizing organic carbon and sequestering it long-term.

Reference section, with personal content notes added:

1. Knicker, Heike. “Pyrogenic Organic Matter in Soil: Its Origin and Occurrence, Its Chemistry and Survival in Soil Environments.” Quaternary International, vol. 243, no. 2, 26 Oct. 2011, pp. 251–263., doi:10.1016/j.quaint.2011.02.037.
    a. Biochar occurs naturally in soils anywhere fires occur and is well documented in the geologic record.
    b. Biochar accumulation in soils due to wildfire, grassland fires, and human induced burning patterns have led to concentrations of black carbon in soils accounting for up to 45% of SOM.
    c. In almost every case, biochar produced from woody materials and at high temperature, >500 ^{o}C, results in increased stability in soils when compared with biochar produced from non-woody vegetation or manures and at low temperatures.
    d. Biochar stability is influenced by interactions with the organic and mineral fractions in soils forming organo-mineral complexes that resist degradation and preserve biochar carbon.
    e. Oxidation and translocation in the soil profile account for the majority of carbon loss from biochars applied to soils.
    f. Where oxidation rates are minimized biochars show increased persistence and where vertical transport is a dominant factor enrichment of lower soil horizons has been observed.

2. “Persistence of biochar in soil” Chapter 10. Biochar for Environmental Management: Science, Technology and Implementation, by Johannes Lehmann, Routledge, 2015, pp. 235–282

a. The fate of biochar carbon and its persistence in soils is dependent on numerous factors including the origin of biochar feedstocks, biochar production and processing parameters, soil type and texture, and environmental or climatic influences.
b. The primary pathways for biochar carbon to leave a given soil include disintegration into smaller particles, translocation out of topsoil (into subsoils or via erosion), decomposition into small molecules and metabolites, and mineralization to carbon dioxide.
c. Experiments studying the persistence of biochar in soils often use an extrapolation of the mineralization rate curve to determine mean residence times in soils depending on the time-scale over which the experiment occurs. Extrapolation from different parts of the curve can lead to dramatically different estimates for mean residence time.
d. Carbonization reactions occuring during pyrolysis create condensed poly-aromatic carbon structures that are difficult for microbes to decompose.
e. Biochar contains extremely recalcitrant graphitic domains that form the stable carbon backbone of biochar particles, a spectrum of aromatic carbon structures with varying sizes and stabilities, and a pool of labile carbon available for microbial decay over much shorter.
f. These carbon fractions or pools influence the mineralization rate over time and it is often necessary to use multiple pool exponential decay curves to accurately fit the rate curve.
g. Charring reduces the mineralizable fraction of organic carbon in biochar by the condensation of cellulose, hemicellulose, and lignin fibers into complex poly-aromatic carbon structures.
h. The O/C_{org} and H/C_{org} ratios in biochar are easily measurable physical properties that reflect the degree of aromatic condensation of biochar carbon directly related to its persistence in soil.

3. Woolf, Dominic, et al. “Biochar for Climate Change Mitigation.” Soil and Climate, 2018, pp. 219–248., doi:10.1201/b21225-8.
    a. When comparing mineralization rates for charred and uncharred organic matter, the charred material often demonstrates an order of magnitude slower.
    b. While mineralization rates will inevitably vary with feedstock material, processing time/temp, application, and environmental conditions it is well documented that woody biomass pyrolyzed above 500 ^{o}C for ten minutes produces a biochar with H/C_{org} ration <0.4 and a mean residence time >1000 years.

4. Budai, Alice & Zimmerman, Andrew & Cowie, Annette & Webber, John & Singh, Bhupinder Pal & Glaser, Bruno & A. Masiello, Carrie & Andersson, David & Shields, Frank & Lehmann, Johannes & Camps Arbestain, Marta & M. Williams, Morgan & Sohi, Saran & Joseph, S. (2013). Biochar Carbon Stability Test Method: An assessment of methods to determine biochar carbon stability.

a. The International Biochar Initiative examined a number of assessment methodologies to determine the most accurate and feasible testing method for determining biochar stability over a period of 100 years (BC_{+100}).
b. Alpha methods are relatively inexpensive tests used to measure biochar properties related to stability such as H/C_{org} and O/C_{org} ratios or volatile matter content, but do not measure biochar stability directly
c. Beta methods are able to directly measure changes in biochar over time and are used to support and test alpha and gamma methods, these include incubation/field studies and chronosequences.
d. Gamma methods measure molecular properties and are used to relate alpha and beta methods building relationships between observations and easily measured properties. These include NMR spectroscopy, pyrolysis gas chromatography and mass spectroscopy, ring current NMR, and benzene polycarboxylic acid testing.
e. The alpha method which correlated best with beta and gamma methods was measurement of H/C_{org} ratio revealing values of significance at H/C_{org} <0.4, demonstrating a BC_{+100} of more than 70% biochar carbon remaining after 100 years.
f. An upper limit was also established at H/C_{org} >0.7 resulting in BC_{+100} values of less than 50% biochar carbon remaining after 100 years.

5. Wang, J. , Xiong, Z. and Kuzyakov, Y. (2016), Biochar stability in soil: meta-analysis of decomposition and priming effects. GCB Bioenergy, 8: 512-523. doi:10.1111/gcbb.12266
    a. A meta-analysis by Wang et. al. covering 24 studies exploring CO_2 mineralization rates using isotope carbon analyses found that the labile pool of biochar carbon had a mean residence time (MRT) of 106 days and accounted for 3% of biochar carbon, while the recalcitrant carbon accounted for 97% of biochar carbon with a MRT of 556 years.
    b. A meta-analysis covering 21 studies explored positive and negative priming effects on SOM after pyrogenic organic matter (biochar) applications and found that overall biochar addition stimulated a negative priming effect reducing the mineralization rate of non-pyrogenic SOM.
    c. However, in sandy soils a significant increase in SOM mineralization was observed linking the addition of biochar with a stimulation of microbial activity in sandy soils with low fertility and a corresponding increase in soil respiration rates.

6. Kuzyakov, Yakov, et al. “Biochar Stability in Soil: Decomposition during Eight Years and Transformation as Assessed by Compound-Specific ^{14}C Analysis.” Soil Biology and Biochemistry, vol. 70, Mar. 2014, pp. 229–236., doi:10.1016/j.soilbio.2013.12.021.
    a. Decomposition rates calculated over the 8.5 year study were 2.5 times slower than those calculated during the first 3.5 years of the study leading to the conclusion that biochar decomposition rates slow significantly over time.

b. Short duration studies may present an incomplete picture of the extrapolated decomposition rates due to the variable nature of biochar decomposition over time.
c. The study also examined the fate of biochar derived organic carbon incorporated into microbial biomass, which revealed a slower turnover rate when compared with non-biochar organic carbon.
d. Using ^{14}C labeled biochar over an 8.5 year experiment, Kuzyakov et. al. found a decomposition rate of 0.0007% per day, equivalent to a 4000 year lifespan in soil.

7. Cheng C.H., Lehmann J., Thies J.E., and Burton S. 2008. Stability of black carbon in soils across a climatic gradient. Journal of Geophysical Research 113: G02027.
    a. Soils containing historical biochar show concentrations of organic carbon 9 times higher than adjacent soils without biochar.
    b. Organic carbon in biochar containing soils showed reduced levels of labile carbon and a longer half-life for the recalcitrant fraction when exposed to varying mean annual temperature regimes.
    c. The lack of correlation found in the study between biochar mineralization rate and mean annual temperature indicates that biochar stability is minimally related to mean annual temperature
    d. The results indicate that biochar has a stabilizing effect on organic carbon in soils over time leading to increased concentrations of soil carbon and its enhanced persistence across a climatic gradient.

8. Nguyen, Binh Thanh, and Johannes Lehmann. “Black Carbon Decomposition under Varying Water Regimes.” Organic Geochemistry, vol. 40, no. 8, 20 May 2009, pp. 846–853., doi:10.1016/j.orggeochem.2009.05.00
    a. Under varying water regimes, C loss from corn stover biochar was greater than for oak wood biochar and the higher charring temperature at 600 ^{o}C showed reduced C loss than at 350 ^{o}C for both biochar feedstocks.