Report of the HPTA Science Committee
July 21, 2015

Biochar and humic substances: a comparison

This Science Committee report is in reply to a request by the President of the Humic Products Trade Association (HPTA) for a comparison of biochar to natural humic substances and their related manufactured humic products.

Summary of Science Committee Response

The HPTA Science Committee responded by stating that there seems to be substantial variability in seed germination, crop nutrient uptake, and crop yield on soils treated with biochars. The committee further stated that there are conflicting reports regarding the effectiveness of biochars, which may be due to variable plant nutrient uptake under different soil conditions, the source of the raw materials used to manufacture the 'char' product, and perhaps the duration and temperature of pyrolysis.

Negative responses could result from the presence of toxins in the biochar and perhaps tie-up of cationic soil micronutrients by carboxyl groups, similar to the actions of activated charcoal. There are reports that the presence of certain polycyclic aromatic hydrocarbons (PAH) in some biochars[15] is responsible for inhibition of crop production. As the concentration of PAH in char products is dependent on the time and temperature conditions during manufacture, their concentration can be controlled.

The committee pointed out that humic substances (HS) demonstrate a much higher degree of oxidation compared to biochars. Additionally, the chemistry of freshly made chars compared to chars that have been buried for long periods of time in soils (e.g. *Terra Pretas de Índios* of the Amazon) is different, and both materials are not as complex as HS. Positive crop responses to biochars could be due to favorable nutrients (e.g. calcium, magnesium, potassium and/or phosphorus) or to improved soil aeration via better soil aggregation or better soil retention of water.

Based on the relatively large application rates, the main benefit of biochar would seem to be as a soil amendment, whether for carbon sequestration or improving water and nutrient holding capacity or improving soil physical properties. In contrast, humic product application rates are too low (usually pounds per acre) to constitute a substantive carbon addition compared to the amounts of stable carbon already in the soil or even the amount of carbon incorporated annually as crop residues.

Biochar is primarily promoted as a way to sequester carbon, improve soil water holding capacity, amend acid soils, and increase crop yields when used as a soil amendment. The main benefit of humic products would seem to be as a crop amendment, not as soil amendments. Humic products may increase soil carbon sequestration through promoting bigger root systems and possibly more root exudates.

Biochar Description

For the purpose of this document, the term *biochar(s)* means charcoal materials intended to be used for agronomic purposes that are produced in such a way as to sequester carbon. Biochar is a stable carbon-rich product of oxygen-limited combustion (pyrolysis) of carbonaceous biomass, such as crop residues, cull timber and sawmill wastes.[17]

Background

Interest in biochar materials in the last 20 years seems to have been sparked by the numerous published studies, and sometimes romantic stories, regarding the rediscovery of *terra preta*, the very dark high fertility soils found in the Amazon region that appear to be anthropogenic (intentionally made by humans), and possibly formed through addition of charred plant materials approximately 600 to 1,000 years ago. The stable high fertility of *terra preta* soils is attributed to char residues[1] that have carboxyl functional groups (-COOH) and phenolic groups (-OH) associated with aromatic carbon rings.

Fresh biochar, in contrast to ancient residues, is a less consistent material, whose properties vary[2] depending on the raw materials used (feedstock), pyrolysis conditions, and post-production treatments. Soil pH and differences among the various feedstocks, heating duration and temperatures may contribute to the inconsistent effects on crop production.

Terra preta, char, and humic substances

It is generally accepted that the stability of carbon in fresh biochar is attributed to the fused ring structures that form during pyrolysis, similar to the ring structures of coal. In contrast, the chemistry of char residues found in the *terra preta* sites indicates a more oxidized condition. The structure of terra preta char residues consist of groups of fused aromatic rings with substituted negatively charged COO^- groups[3] (Fig.1) that are responsible for the high cation exchange capacity (CEC) of the *terra preta*. These oxidized fused ring groups are similar to the char residues found in Mollisols: high fertility soils that have a history of grassland fires before European settlement.

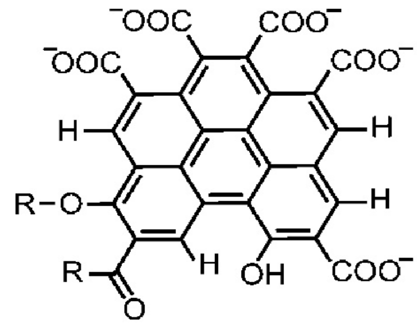

Figure 1. Fused ring structure of char residues. Mao et al., 2012.

Wildfire chars are thought to contribute to the fertility of some soils by undergoing both biotic and abiotic carboxylation of their fused aromatic ring structures, and convert to HS over long periods of time.[4] The surface chemistry of fresh char materials applied to soils changes over long periods of time by undergoing natural oxidation, demonstrated by an increase in carboxyl (-COOH) and phenolic (-OH) functional groups and the concomitant evolution of surface charges from positive to more negative.[5] In addition to the surface oxidation of char particles themselves, it is possible that the relatively high CEC could result from the adsorption of highly oxidized organic matter onto the char surfaces over long time periods.[6] The amount of time required to convert char into more oxidized materials that contribute to soil fertility suggests that simply adding biochar to soils does not necessarily result in *terra preta-like* materials during the relatively short time frames of agronomic production.[7]

Compared to biochar, HS demonstrate higher density of carboxyl (-COOH) and phenolic (-OH) functional groups, along with ketone (-C(O)C-) and aldehyde (-CHO) groups distributed across numerous aromatic, cyclic, and aliphatic chains (Fig. 2). These functional groups are responsible for numerous interactions with soil components through hydrogen bonding, electron donor-acceptor complexation and

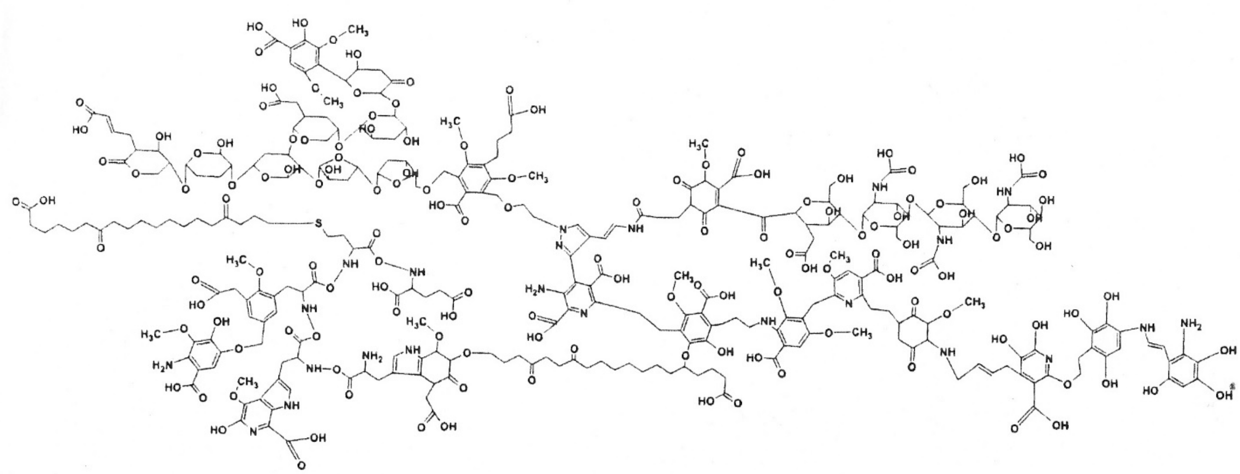

Figure 2. Proposed structure for a portion of soil humic acids.

Grinhut, T., Y Hadar, and Y.Chen, 2007. Degradation and transformation of humic substances by saprotrophic fungi. Fungal Biology Reviews 21:179-189.

hydrophobic interactions. Despite the fact that there is not a generally accepted structure for HS, molecular analysis suggests that HS are highly dynamic, demonstrating conformational flexibility and self-assembly of complex mixture components.[8]

Numerous reports state that a primary purpose of biochar is to improve moisture-holding capacity of soils, which is achieved through the porous physical structure of the char product (Fig. 3). HS are amphiphilic, having diverse chemical groups that impart both hydrophobic and hydrophilic character within their proposed structures, allowing them to interact with many soil processes. HS are known to have high moisture content as well, but they retain moisture both by hydration of polar groups and voids in secondary structures (Fig. 4).

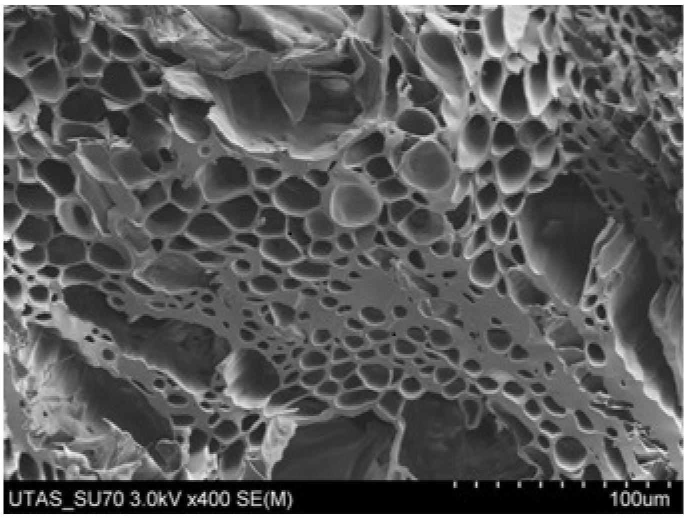

Figure 3. Scanning electron micrograph of a cross section of biochar.

Origin and Properties of Biochar

There are substantial differences in the physical and chemical properties of synthetic biochars depending on the feedstock, time and temperatures used during pyrolysis, and post production practices. Because of the variable properties of the final products, and as there are no standardized materials, comparison of experiments is very difficult. Post production "activation" of chars is accomplished by either cooling rapidly in the atmosphere or with water. Both processes oxidize the surfaces of the materials, altering the character of the surface groups that interact with soil components.[9]

The production of biochars is in stark contrast to the genesis of HS. Biochars are produced from celluloistic materials, such as corn stover, switchgrass, or wood, that are subjected to relatively high temperatures over short periods of time under reducing (oxygen deprived) conditions. Biochars therefore have little or no oxygen content. Although the materials used in humic products typically originated as celluloistic materials also, they formed over much longer time periods. The process typically begins with microbial decay and subsequent chemical and biochemical reactions[10] that form the materials under more aerobic conditions. Because of that, HS have relatively high concentrations of oxygen containing phenolic and carboxylic functional groups that account for the high chemical reactivity of HS.[11]

Zheng et al.[12] reported the content of water-soluble nitrogen (NH_4^+) and water-soluble phosphorous in biochars manufactured at relatively low temperatures (≤300 °C) were significantly higher than chars manufactured at higher temperatures (≥600 °C). In another study,[13] where various feedstocks were pyrolyzed under different time and temperature conditions, biochar from pecan shells heated to 700 °C was effective in sequestering carbon, but low temperature biochars (250 °C) from switchgrass were more effective for retaining soil moisture. The authors suggested that certain feedstocks and pyrolysis conditions could be tailored to make "designer biochars". Sewage sludge biochars obtained at 600-900ºC contained lower concentrations of plant-available nutrients, fulvic-acid-like materials, and humic-acid-like materials, compared to sewage sludge biochars

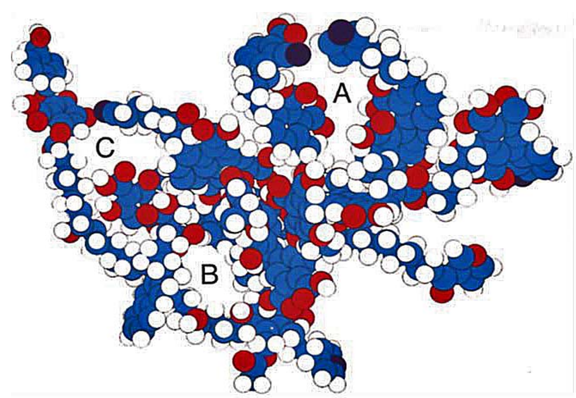

Figure 4. Proposed 3D structure of humic acids by Schulten and Schnitzer (1995). Element colors are: carbon = blue; hydrogen = white; nitrogen = black; and oxygen = red; A, B,

obtained at 300-500ºC.[14] At higher temperatures (600-900ºC), the biochar became increasingly polyaromatic, and its surface area and porosity increased, which increased its adsorption capacity.

Depending on the feedstock and pyrolysis temperatures, biochars may contain toxins or other unwanted materials. Approximately twenty different polycyclic aromatic hydrocarbons (PAH) were reported in one study,[15] 6 of which are known carcinogenic PAH. Their presence was attributed to the "high" gasification temperatures, ranging from 732 to 850 ^{o}C. However, the correlation coefficient (average r = 0.60) between pyrolytic temperatures and PAH concentration in the study suggests additional factors were responsible for PAH formation. Lower temperatures (<500 ^{o}C) produced the lowest concentration of PAH and PAH were further reduced by extending the pyrolysis time to ~30 minutes or washing the char with water. On the other hand, a municipal biowaste biochar applied at 40 t ha^{-1} was found to have a beneficial effect regarding a toxic element, significantly ($p<0.05$) reducing accumulation of cadmium in the root, shoot and grain of wheat.[16]

The International Biochar Initiative (IBI)[17] has established standards of proximate analysis and limits on toxic substances content.[18] Products that meet those standards can be voluntarily certified as compliant with IBI standards.[19] The IBI standards include a *Germination Inhibition Assay*, but the supporting reference for the assay[20] was not a validation study with well defined protocols and sufficient data to enable replication; instead it was a study of agronomic performance and soil fertility as a function of biochar amendments. However, screening for the presence of substances that may inhibit germination and growth can be performed by simple and reproducible germination assays.[21]

Application of biochars

The studies reviewed by the HPTA Science committee and that showed positive responses to biochar were conducted on tropical soils. In one field study, [22] positive effects were seen with application rates in the range of 11 Mg ha^{-1} (~5 tons $acre^{-1}$) and up to 135.2 Mg ha^{-1} (~60 tons $acre^{-1}$) in a greenhouse study.[23] The authors of the field study considered the 11 Mg ha^{-1} application rate to be important for tropical soils because they stated that in their opinion, the 11 Mg ha^{-1} rate is roughly equivalent to the amount of carbon sequestered in some types of tropical vegetation that can be converted to biochar, rather than using what they called slash-and-burn practices. The charcoal content of the current terra preta soils at a depth from 0 to 0.3 meters is estimated to range from 15 to 60 Mg ha^{-1} (~7 to 27 tons $acre^{-1}$).[24]

Biochar is applied to acid soils to raise the pH of acid soils, but the degree to which wood ash in the char contributes to the increase in pH is unknown.[24] Biochar application is more effective on highly weathered acid soils, and hardwood feedstocks can be better at ameliorating acid pH than conifer feedstocks because they are higher in base cations (Ca, Mg, K and Na).[24] In one field study, [25] a hardwood derived biochar applied with manure to an irrigated calcareous soil for silage corn only increased available manganese in the first year after application, but leaf chlorosis of the crop was reported in the second year due to decreases in the bioavailability of nitrogen, magnesium, copper, manganese, and sulfur.

Recent studies have reported contrary results for improvements in soil quality and crop yields by biochar amendments. Spokas et al.[26] performed a meta data analysis on 46 published studies from 1950 to 2011. Approximately 50% of the studies reported positive yield or growth, 30% reported no significant differences, and 20% reported negative yield or growth impacts. However, due to lack of standardization of the pyrolysis conditions and unclear reporting of all the post production conditions during the studies, it is not possible to draw sound conclusions about which types of biochar are effective on which soils.

Application of Humic Substances

Humic and fulvic acids are sometimes classified as *biostimulants* because they appear to directly affect plant growth and metabolic processes when applied at minute rates relative to typical plant nutrient application rates.[27] Indeed, the *hormone-like* activity of HS has been extensively debated because it is difficult to distinguish between indirect positive growth effects caused by improvement of nutrient uptake[28,29] and the up- and down-regulation of plant genes involved in metabolic and signaling pathways.[30] The definition of *biostimulants* is too broad to address in this review, however, the more complex chemistry and low application rates of humic products sets them apart from biochars.

A recent meta-analysis performed by Rose et al.[31] on 81 published reports of plant growth promotion of applied HS reported an overall 22±4% increase in shoot dry weight and 21±6% increase in root dry weight in response to HS application. Plants were more likely to increase shoot growth under stressful conditions of salinity, metal toxicity, and nutrient deficiency. Plant type was not a significant factor, with the exception of 3 studies that demonstrated woody perennials did not show significant shoot growth response to HS application.

Although HS extracted from composts and soils outperformed HS derived from brown coals and peat, the brown coal-derived HS repeatedly demonstrated positive effects. The data show that HS are effective at relatively low application rates, revealing a non-linear dose-response for shoot dry weight (SDW) as application rates increased beyond an optimal dosage (Fig.5).The authors speculated that non-linear responses may be from different mechanisms that operate at various concentrations, citing Chen et al.[32] as an example of metal complexation decreasing the bioavailability of micronutrients as the concentration of HS in nutrient solution increased.

Approximately half of the shoot dry weight and one third of the root dry weight studies failed to increase growth by more than 5%. Full data sets of experimental conditions, including nutrient availability, pH and temperature conditions were not available. Additionally, not all the data in the meta-analysis were based on materials extracted according to the International Humic Substances Society method.[33] The materials generated by other extraction methods likely included additional substances co-extracted with the HS.

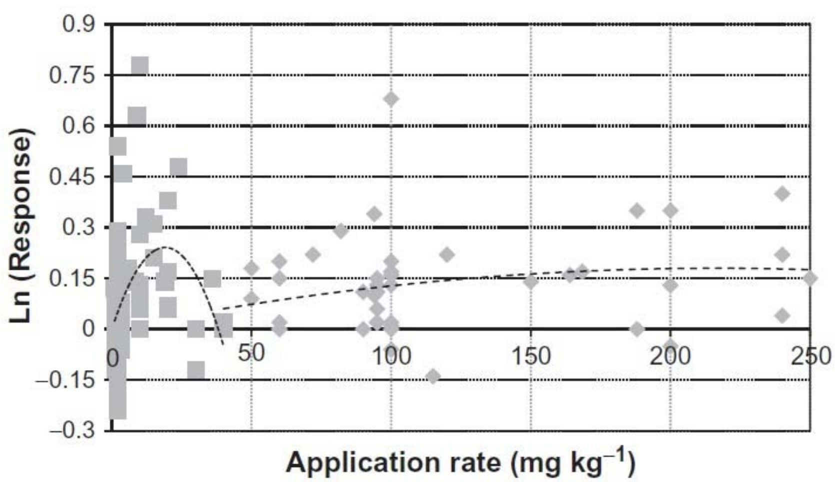

Figure 5. Effect of application rate of brown-coal-derived HS on SDW. Dashed lines show quadratic fits to rates less than 50 mg kg^{-1} (short dash, square points) and rates greater than or equal to 50 mg kg^{-1} (long dash, diamond points).

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