

Chemical alterations occurring during biomass charring and their impact on char recalcitrance

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Introduction

The application of biochar to soil is proposed as a novel approach to establish a significant, long-term C sink and to improve soil fertility. Beside the production of volatiles, charring transforms labile organic components into recalcitrant dark colored and highly aromatic structures. Bearing in mind that they are chemically and physically distinct from soil organic matter (SOM) formed during fire-free humification, a good understanding of the chemistry of biochars is crucial to ensure its sustainable use as soil amendment. Therefore, in this presentation, recent and previous [1][2] studies elucidating the chemical alterations during controlled charring of plant residues and their typical biomacromolecules (casein, cellulose, lignin, tannins) are presented. Subsequently, the chemical features of the model chars were related to its chemical recalcitrance as determined by chemical oxidation with acid potassium dichromate [3]. Additionally, the biodegradability [4] as well as the recalcitrance of plant chars in soils are elucidated.

Results and Discussions

After charring at 350°C for 4 min, casein showed a C-loss (34%) that was lower than for cellulose (76%), but in the range determined for condensed tannins (spruce) (33%) and only slightly smaller than for lignin (23%). Although the C-losses increased, this pattern remained comparable after augmentation of the temperature to 450°C. Since no major differences were observed between C and N-losses, it can be assumed that N is an integral part of the BC derived from peptide-like materials. The comparably low organic N losses further demonstrate that during charring N has a tendency to be incorporated into structures, which are highly resistant to heating. Similar C and N losses were also observed after charring of grass residues, although the higher temperature reduced the C- and N-recovery by a factor of two. However, wood sawdust

depicted a lower heat resistance than the grass residues.

NMR-spectroscopic studies revealed high thermal recalcitrance of the lignin backbone and considerable contributions of furans and anhydrosugars from thermally altered cellulose (Figure 1). Black nitrogen (BN) occurs mostly in pyrrole-type structures. Accordingly, it was calculated that in non-woody biochars, such compounds may consume up to 17% and sometimes even up to 60% of their organic C. Bearing in mind the high frequency of vegetation fires and the relative high biological recalcitrance of biochars, those numbers imply a considerable relevance of such structures for pedogenetic and also diagenetic processes leading to organic matter stabilization and maturation.

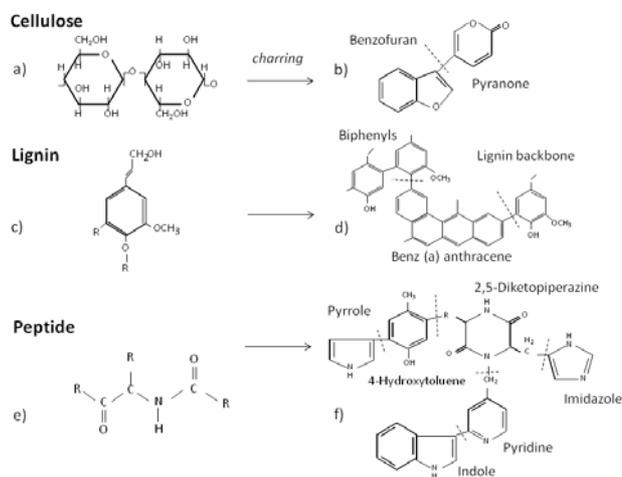


Figure 1. Biopolymers (a,c,e) and their possible charring products (b,d,f) as evidenced by solid-state NMR spectroscopy [1].

Enhancing the temperature during the charring of casein to 450°C decreased the C and N recovery to 30% and 23%, respectively. Comparably the C, O and H recovery were also reduced in the cellulose char, but to a considerably higher extent. The changes went along with a further augmentation of the relative contribution of aromatic C. Increased C, H and O losses were also observed for charring of lignin at higher temperature, although they were

smaller than those observed for casein and cellulose. The higher temperature considerably altered the chemistry of the lignin char.

Subjecting the produced chars to chemical oxidation with acid potassium dichromate clearly demonstrated that the resistance of the casein chars against heat is not necessarily related to chemical recalcitrance. For the char produced at 350°C, only 13% of the C and N remained in the oxidation residues, whereas for that produced at 450°C this value increased to 80%. In contrast, both cellulose chars showed high chemical resistance with a C-survival of more than 80%. Comparatively, the C and N recalcitrance in the grass chars increased with temperature, whereas, the burned wood residues (350°C) suffered an almost complete oxidation. The chars from condensed tannins, on the other hand showed a high chemical resistance independently from the production temperature.

In summary, this study shows that the thermal and chemical recalcitrance of plant chars is highly variable and is related to its chemical structure. The latter depends on the source and the respective charring conditions. Biotic degradation studies of grass chars confirmed such a relationship for biodegradation.

However, one has to consider that recalcitrance of plant chars in soils depends not only upon its chemistry but also on the environment in which it is accumulating. Comparable to the humification of fire-affected SOM, different mechanisms including O₂-deficiency, unfavorable conditions for microorganisms or interaction with the mineral phase, seem to be involved in pyrogenic organic matter (PyOM) stabilization. According to this concept, the efficiency of the single pathway varies with the respective soil conditions, resulting in a specific PyOM pattern which is typical for a certain soil. Such a scenario could explain the varying abundance and recalcitrance of PyOM in fire-affected soils. In turn, the respective PyOM pattern, which can have been generated over decades and millennia, determines typical soil properties and thus PyOM can be seen to be actively involved in the pedogenic process, leading to soil classes such as Terra preta soils in the Amazon region, and possibly also to Chernozems in

Central Europe or other Black soils all over the world.

Conclusions

More and more reports evidence the degradability of PyOM in soils. Its chemical nature which largely depends on its source and forming conditions determines its stability. Some of its structural components certainly delay its biochemical decay relative to microbially easily available plant residues and several of those may even have an exceptionally high biochemical resistance. However, its final survival seems to be determined by comparable mechanisms that are active with respect to the fire-unaffected SOM, allowing some fractions to survive for millennia while others are quickly degraded. From this point of view, the consideration of charcoal addition to soils as a means of C-sequestration needs a reevaluation, bearing in mind the C-loss during its production. On the other hand, comparable to fire-unaffected and humified (stabilized) SOM with residence times of several thousands years, PyOM can also be involved in pedogenic processes. The latter is expressed in the observation that human activity of Neolithic and earlier times contributed to the formation of soils with typical features. Thus, using fire and charcoal application as an agricultural practice, one has to account for the possibility that such an approach has formerly and will in future alter soil environments and properties not only on a short but also on a long term scale.

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