



NMR studies on the chemical alteration of soil organic matter precursors during controlled charring

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Beside the production of volatiles, vegetation fire transforms various amounts of labile organic components into recalcitrant dark colored and highly aromatic structures. They are incorporated into soils and are assumed to represent an important sink within the global carbon cycle. In order to elucidate the real importance of PyOM as a C-sink, a good understanding of its chemistry is crucial. Although several "Black Carbon" (BC) models are reported, a commonly accepted view of the chemistry involved in its formation is still missing. Its biogeochemical recalcitrance is commonly associated with a highly condensed aromatic structure. However, recent studies indicated that this view may be oversimplified for PyOM derived from vegetation fire. In order to bring some more light on the structural properties of PyOM produced during vegetation fire, charred plant residues and model chars derived from typical plant macromolecules (casein, cellulose, lignin and condensed tannins) were subjected to controlled charring under oxic conditions (350°C and 450°C) and then characterized by nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. Subsequently, the chemical features of the PyOM were related to its chemical recalcitrance as determined by chemical oxidation with acid potassium dichromate.

Charring cellulose (350°C, 8 min) yielded in a low C-recovery (11%). Treating casein in the same way resulted in a survival of 62% of its C and 46% of its N. Comparable high C-recoveries are reported for lignin. After charring *Lolium perenne*, 34% of its N and C were recovered. NMR-spectroscopic studies revealed that for this sample most of the charred N and C occurred in pyrrole-type structures. Our studies further indicate that the aromatic skeleton of char accumulating after a vegetation fire must contain remains of the lignin backbone and considerable contributions of furans and anhydrosugars from thermally altered cellulose.

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. These 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. The atomic H/C ratio, however, remained above 0.5 showing that in average at least every second C is protonated.

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 confirmed that the thermal, chemical and biological recalcitrance of biochars is related to their chemical structures and N-contents, which on the other hand depend on the source and the respective charring conditions. The resulting high chemical variability of biochars is in accordance with the concept of BC as a continuum and explains the high discrepancy among BC quantifications obtained with common approaches assuming BC as a highly condensed polyaromatic network.