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# CONDENSATION AND POLYMERIZATION EXPLAIN THE HUMIFICATION OF LIGNIN INTO ALIPHATIC AND AROMATIC STRUCTURES IN SOIL

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## Introduction

Soil organic matter (SOM) constitutes a global reservoir of carbon that is more than twice that of either atmospheric carbon or aquatic carbon; however, the manner in which it forms from degraded plant biomass is poorly understood. Some have recently questioned whether plant biomass is involved directly in SOM formation and suggest that it is microbial carbon that constitutes the main source of stable SOM. Such a view implies that above and below ground plant biomass is rapidly decomposed and mineralized. This view contrasts significantly with traditional ones that involve the transformation of plant biomass to recalcitrant humic materials fueled mainly by lignin. One of the main observations for the new viewpoint is that lignin phenols, biomarkers for lignin in plant biomass, become depleted rapidly in SOM and are thought to indicate that lignin, carbohydrates, proteins, and other plant biopolymers are depleted at the same rate.

In the current study we demonstrate that lignin plays a pivotal role in the formation of geologically stable SOM and that the new viewpoint grossly miscalculates the input of microbial biomass. Promoted by the strong oxidation of prevalent reactive oxygen species (ROS) in soil, lignin is not completely mineralized but molecularly transformed to structures not recognizable by lignin phenol biomarker studies. We employ NMR and ultrahigh resolution mass spectrometry on a series of plant biopolymers, synthesized lignin, soil, and peat samples to demonstrate the effect of ROS transformations involving mainly hydroxyl radicals.

## Results

Lignin oxidized by hydroxyl radicals generated by photoirradiation, the Fenton reaction or by fungi (*Phanerochaete chrysosporium*) undergoes an initial oxidation involving OH substitution on the ring as determined by ultrahigh resolution mass spectrometry. This process facilitates abiotic ring-opening reactions to form muconic-acid-like structures. We suggest that these undergo an abiotic Diels-Alder polymerization to form alicyclic structural motifs that participate in radical-driven H scavenging/ H donation reactions to produce both condensed aromatic molecules and aliphatic molecules possessing alicyclic structural motifs as determined by multi-dimensional NMR studies. Thus, two types of molecular motifs are generated and these can be separated from each other by HPLC. These are also highly carboxylated and hydroxylated such that they become readily soluble in dilute alkali and become “humic acids”.

Studies of SOM in soils and peats, dissolved organic matter, and model compounds by the combined use of ultrahigh resolution mass spectrometry and NMR spectroscopy supports the above findings. The results show that molecular entities bearing a strong resemblance to lignin that is molecularly-transformed by the above-mentioned oxidative reorganization exist in natural humic substances. Accordingly, we develop a new model for humification in soil that

involves both biological and abiological transformation of mainly lignin. Other major plant biopolymers such as polysaccharides and proteins undergo microbial mineralization to fuel CO<sub>2</sub> production and microbial biomass to sustain further oxidative decomposition and the production of ROS. Figure 1 is a diagrammatic representation of this model that we call Biological and Abiological Degradation by Reactive Oxygen Species (BAD-ROS).

### Biological and Abiological Degradation with ROS (BAD-ROS)

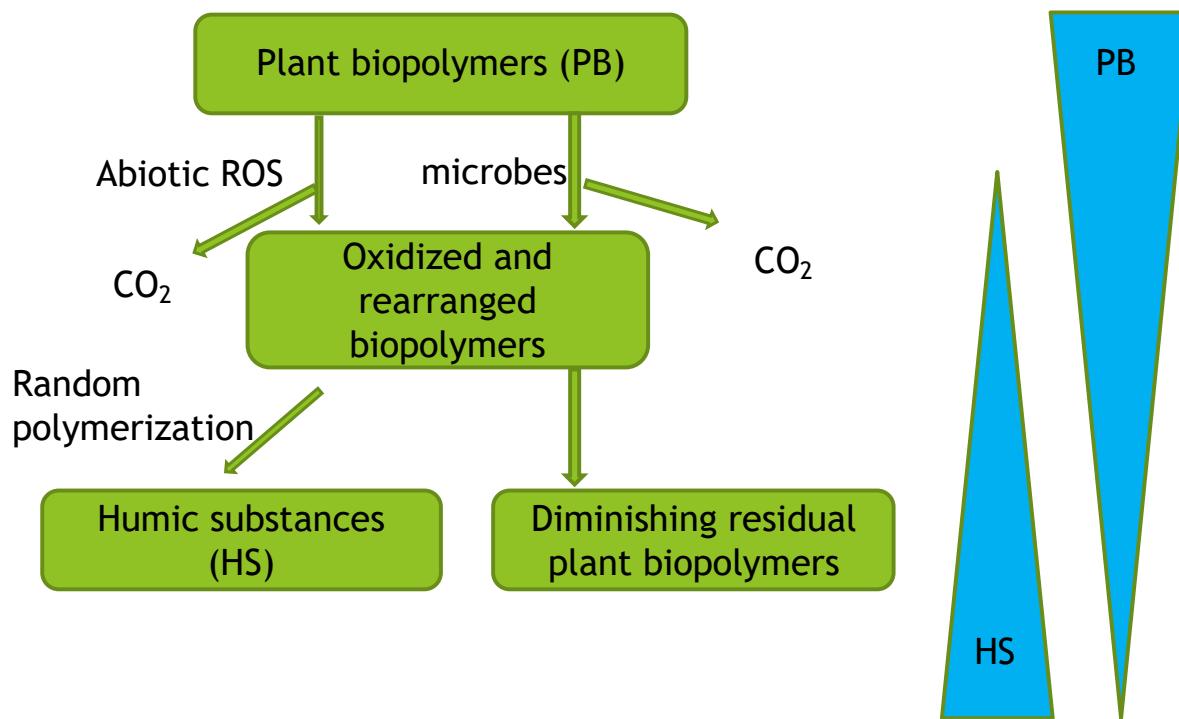


Figure 1. Proposed model for humification in soils, HS= humic substances, PB= plant biopolymers

### Conclusions

Based on modern analyses by ultrahigh resolution mass spectrometry and advanced NMR approaches, we are proposing a new view of the humification process in soil where lignin plays a pivotal role in the production of SOM. Support for this model is founded in the observations from numerous soils, lignin isolates, and synthetic lignin.