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Molecular-level transformations of lignin during photo-oxidation and biodegradation

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As the second most abundant component of terrestrial plant residues, lignin plays a key role in regulating plant litter decomposition, humic substance formation, and dissolved organic matter (OM) production from terrestrial sources. Biodegradation is the primary decomposition process of lignin on land. However, photo-oxidation of lignin-derived compounds has been reported in aquatic systems and is considered to play a vital role in arid and semiarid regions. With increasing ultraviolet (UV) radiation due to ozone depletion, it is important to understand the biogeochemical fate of lignin exposed to photo-oxidation in terrestrial environments.

This study examines and compares the transformation of lignin in a three-month laboratory simulation of biodegradation and photo-oxidation using molecular-level techniques. Lignin-derived monomers extracted by copper oxidation were analyzed by gas chromatography/mass spectrometry (GC/MS) from the water-soluble and insoluble OM of 13C-labeled corn leaves. Biodegradation increased the solubility of lignin monomers in comparison to the control samples, and the acid-to-aldehyde (Ad/Al) ratios increased in both the water-soluble and insoluble OM, indicating a higher degree of side-chain lignin oxidation. Photo-oxidation did not produce a significant change on the solubility or Ad/Al ratios of lignin from corn leaves. However, the ratios of trans-to-cis isomers of both cinnamyl units (p-coumaric acid and ferulic acid) increased with photo-oxidation and decreased with biodegradation in the insoluble OM.

We also investigated the role of photo-oxidation in lignin transformation in soils cropped with 13C-labeled corn. Interestingly, the organic carbon content increased significantly with time in the water-soluble OM from soil/corn residues under UV radiation. An increase in the concentration of lignin monomers and dimers and the Ad/Al ratios was also observed with photo-oxidation. Iso-branched fatty acids of microbial origin remained in a similar concentration in the water-soluble OM from the UV-radiated and control soils, indicating little microbial contribution to the observed increase in water-soluble carbon. These observations suggest that photo-oxidation may increase the solubility of soil organic matter (SOM) through the oxidation of lignin-derived compounds.

Mechanisms of lignin oxidation (demethylation or side-chain oxidation) and molecular size distribution changes of the water-soluble and NaOH-soluble OM during photo-oxidation and biodegradation will also be examined using solution-state nuclear magnetic resonance (NMR) spectroscopy. Collectively, our experiment demonstrates that while biodegradation predominates in the decomposition of lignin in plant litter, photo-oxidation may play an important part in destabilizing lignin-derived compounds in the soil.