

Nitrogen-rich higher-molecular soil organic compounds patterned by lignin degradation products: Considerations on the nature of soil organic nitrogen

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The pathways leading to accumulation of covalently bonded nitrogen in higher-molecular soil organic matter (SOM) are still a controversial issue in soil science and geochemistry. Similarly, structural elucidation of the variety of the types of nitrogenous moieties present in SOM is still in its infancy even though recent NMR studies suggest amide-type nitrogen to form the majority of organically bonded nitrogen which is, however, frequently not in accordance with the results of wet-chemical analyses.

Following the modified polyphenol theory of Flaig and Kononova but fully aware of the imperfection of a semi-abiotic simulation approach, this work communicates the results of a study that investigated some potential nitrogen accumulation pathways occurring in the re-condensation branch of the theory following the reactions between well-known low-molecular lignin and carbohydrate degradation products with nitrogenous nucleophiles occurring in soils under aerobic conditions.

Different low-molecular degradation products of lignin, cellulose, and hemicellulose, such as hydroquinone, methoxyhydroquinone, p-benzoquinone, 2,5-dihydroxy-[1,4]benzoquinone, glucose, xylose, and the respective polysaccharides, i.e. cellulose, xylan as well as various types of lignin were subjected to a joint treatment with oxygen and low-molecular N-nucleophiles, such as ammonia, amines, and amino acids in aqueous conditions, partly using respective ¹⁵N labeled compounds for further ¹⁵N CPMAS NMR studies. Product mixtures derived from mono- and polysaccharides have been comprehensively fractionated and analyzed by GC/MS after derivatization. Some of ammoxidized polyphenols and quinones have been analyzed by X-ray photoelectron spectroscopy. Some products, such as those obtained from ammoxidation of methoxy hydroquinone using ¹⁵N labeled ammonia were fractionated following the IHSS protocol. Individual humin (H), humic acid (HA), and fulvic acid (FA) fractions were subjected to elemental analyses and NMR spectroscopy (¹H, ¹³C, ¹⁵N), respectively. The reactions of hydroquinone, methyl hydroquinone and p-benzoquinone with ammonia and dimethyl-ammonium dimethylcarbamate – a source of dimethyl amine - affording the respective (substituted) 2,5-diamino-[1,4]benzoquinones under aerobic conditions have been studied by EPR spectroscopy for both oxygen-free and oxygen-rich conditions.

¹⁵N CPMAS NMR and XPS spectra of ammoxidized technical lignins and of ammoxidized low-molecular polyphenolic and quinoid products of the aerobic, microbial lignin degradation using ¹⁵N labeled aqueous ammonium hydroxide share many similarities, highly indicative for reaction sequences proceeding via common key intermediates. It has been demonstrated that 2,5-dihydroxy-[1,4]benzoquinone which can be surprisingly formed from both lignin and cellulose reacts with N nucleophiles to the respective 2,5-amino derivatives. The latter are semi-stable and react further to nitrogenous compounds of higher molecular weight. Hydroquinone and methoxy hydroquinone react even faster affording the respective 2,5-diamino-[1,4]benzoquinones. EPR experiments revealed that the reaction of hydroquinone with dimethyl amine proceed via radical intermediates. The results of this study strongly support the polyphenol theory and is hoped to contribute to a better understanding of nitrogen accumulation in soil organic matter.

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