



Occurrence of Stable N-Forms in Chemically- and Physically-Altered Peat Samples as seen by ^{15}N NMR

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It is generally accepted that the exact nature of more than half of the N in soil and sedimentary matter remain practically unknown. The N-containing structures in humic matter have been envisaged through weakly supported hypothetical models including: i) molecular encapsulation of amino-acids or peptides leading to sterically protected bonds within a recalcitrant macromolecular structure, ii) non-biodegradable polyphenol-protein structures stabilized through internal macromolecular cross-linking increasing during humification, iii) microbial melanins formed during the secondary metabolism from free-radical condensation of aromatic reactive precursors, and iv) abiotic Maillard reactions leading to newly-formed melanoidins under certain favourable environmental *conditions*. The present contribution discusses the nature of N forms in a humic acid from a peat material (Buyo peat, Northern Spain) subjected to a set of physical and chemical fractionations, as well as degradation or derivatizing treatments. As revealed from solid-state ^{15}N NMR spectroscopies, only amidation, oximation and nitration of the peat HA resulted in important quantitative changes of organic N, but did not affect the contribution of heteroaromatic N. However, heating of the whole peat at 350°C for up to 120 s produced an increase of signal intensity in the region of pyrrole-type N, which was accompanied by an absolute loss of C and N. This indicates that thermal cyclization is the only effective method to increase the amount of heteroaromatic N. After drastic heating conditions (up to 150 sec in this material) the minor amount of N surviving combustion is mostly of pyrrolic nature, but some intensity in the amide N region remained.

In summary, our study indicated that in the studied sample, exclusively biotic processes do not lead to the formation of heterocyclic N forms, whereas abiotic or high-energy reactions are required to transform proteinaous materials into heteroaromatic

compounds.