



NMR spectroscopic study of the carbon and nitrogen dynamics of grass-derived pyrogenic organic material during 2.3 years of incubation in soil

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Incomplete combustion of vegetation results in pyrogenic organic material (PyOM) which occurs ubiquitously in soils and sediments. To understand the C sequestration potential of PyOM in environmental systems knowledge is required about the respective degradation and humification mechanisms and the stability of the different chemical PyOM structures. The present study focuses on the microbial recalcitrance of PyOM on molecular scale. Therefore, microcosms incubation experiments were performed using PyOM produced from highly isotopically enriched ^{13}C and ^{15}N rye grass (*Lolium perenne*) at 350°C under oxic conditions for one (1M) and four minutes (4M). Solid-state CPMAS ^{13}C and ^{15}N NMR studies were accomplished to obtain insights into the involved humification mechanisms at different stages the PyOM degradation.

In total up to 38% of the bulk PyOM C was mineralised during the 28 months of incubation. The O/N-alkyl C and alkyl C residues which survived the charring process were effectively decomposed. At the end of the incubation up to 73% and 57% of the initial O/N-alkyl C and alkyl C amount were mineralised or converted to other C groups, respectively. The total aryl C group recovery of the PyOM decreased significantly during the 28 months of incubation ($P \leq 0.001$). After 20 months of incubation between 26% and 40% of the initial aryl C amount was lost. For this group, relative short half time periods in the range of 3.0 and 3.8 years were obtained. The observed loss of aromatic C structures may be attributed to two simultaneous processes, the mineralisation to CO_2 and the conversion to other C groups by partial oxidation. The presence of a readily decomposable co-substrate showed no significant changes in the degradation pattern of the different PyOM, possibly because decomposable sources were already available in the starting PyOM.

Most of the organic bound N of the fresh PyOM was assignable to heterocyclic aromatic compounds such as pyrrole and indole-like structures with contributions of 62% and 72% for PyOM 1M and PyOM 4M, respectively. The other part of the ^{15}N NMR signal intensity was assignable to amide-like structures. No major alteration of the amide and heterocyclic N contribution was detected for the PyOM 1M incubates. For the more charred PyOM 4M, the relative heterocyclic N contribution decreased. After the 28 months of incubation no significant difference in the chemical N composition of PyOM 4M related to the PyOM 1M treatments could be observed ($P=0.472$). Further, we detect a continuous decrease of the total amounts for the amide and heterocyclic N compounds. After 20 months, only 49% to 59% of the heterocyclic N compounds were recovered. The respective amide N recoveries were larger with 59% to 87%.

It can be concluded, that PyOM may not be as highly refractory as it is commonly assumed. During the efficient degradation not only a considerable PyOM amount is mineralised, but also the chemical structure of the remaining PyOM is strongly modified. This includes the formation of O-containing functional groups and the loss of aromatic C and N containing heterocyclic domains by mineralisation and conversion to other C and N groups.