

STRUCTURAL DOMAINS IN PEAT AS REVEALED BY PHYSICAL FRACTIONATION, SEQUENTIAL CHEMOLYSIS AND ¹⁵N- AND ¹³C-CPMAS NMR SPECTROSCOPIES

Gonzalo ALMENDROS¹, Francisco-Javier GONZÁLEZ-VILA², Ulrich LANKES³ and Heike KNICKER⁴

1. Centro de Ciencias Medioambientales, CSIC. Serrano 115 dpdo., 28006 Madrid, Spain
2. Instituto de Recursos Naturales y Agrobiología, CSIC. P.O. Box 1052, 41080 Sevilla, Spain
3. Universitaet Karlsruhe (TH) Kaiserstraße 12 76131 Karlsruhe, Germany
4. Lehrstuhl für Bodenkunde, TU München Freising-Weihenstephan, Germany.

A quantitative assessment of the distribution patterns of different C and N forms in peat as seen by solid-state ¹³C and ¹⁵N NMR spectroscopies was carried out. A sapric peat (Buyo basement, Northern Spain) was subjected to a set of physical and chemical fractionations (sequential or parallel), as well as to degradation procedures to obtain the following three series of peat subfractions: **i**) particle-size fractions isolated by wet sieving (particle sizes > 1 mm, 1–0.5 mm, 0.5–0.25 mm, 0.25–0.15 mm, 0.15–0.10 mm, 0.10–0.04 mm, <0.04 mm), **ii**) peat residues after selective extraction with organic solvents and aqueous solutions removing either bitumen-like fractions (ethanol, butanol, dioxane) or humic substances (0.1M NaOH, 0.1M Na₄P₂O₇), and **iii**) peat residues remaining after mild degradation for preferential removal of esters (BF₃-MeOH transesterification), breakdown of ether bonds in *O*-alkyl structures (IH-degradation), or preferential cleavage of carbohydrate, protein and other *O*-containing structures (acid and alkaline hydrolysis, or heating at 350 °C during successive periods). In particular the spectra from series **(i)** would inform on the role of particle size (in peats considered as index for decomposition degree) in the quantitative speciation of C and N forms, whereas series **(ii)** and **(iii)** would yield information on the occurrence of C and N structures in more or less environmentally recalcitrant structural domains (i.e., often considered to be related with resilience, diagenetic transformation and/or biodegradability) such are carbohydrate-derived, nonhydrolyzable alkyl and peptidic structures, residues, thermally-stable ‘cores’, etc.

The ¹³C and to some extent ¹⁵N NMR spectra of the size fractions, which was believed to reflect differences in peat decomposition stages, were very similar. This is interpreted as particle-size distribution being not necessarily surrogate indicator of maturity or diagenetic transformation in selectively-preserved organic matter pools. On the contrary, the fractions isolated or prepared by chemical and thermal treatments showed conspicuous changes as regards the spectrum of the whole peat material. In fact, the progressive thermal treatments removed most *O*-alkyl structures, which was also the case with the hydrolytic treatments, a

behaviour more pronounced after alkaline hydrolysis. Partial degradation with IH led to dramatic changes in the original peat spectrum (removal of the *O*-alkyl domain). In particular drastic chemical degradation methods confirm to us that not only aromatic C-forms, but also alkyl and protein-containing structures represent the recalcitrant core of the peat organic matter. On the other hand, the occurrence of comparatively labile aliphatic structures were recorded mainly in the spectra of the bituminous fractions extracted with ethanol, butanol and even with dioxane. The latter fraction did not show the expected lignin-like spectral profile, which could be interpreted as extensive rearrangement and condensation of residual plant macromolecules in peat.

The parallel use of ^{15}N NMR spectra showed: **i)** the above-indicated very weak trend towards concentration of heterocyclic N-forms in the fractions lower than 100 μm size; **ii)** removal of heterocyclic N forms as direct or indirect effect of transesterification treatments; **iii)** concentration of heterocyclic N in the humic acid fraction, extracted with a chelating reagent ($\text{Na}_4\text{P}_2\text{O}_7$); **iv)** survival of amide N-forms after strong acid hydrolysis indicating that only some the amide N-forms in peat occur in hydrolyzable forms, the remainder being a conspicuous constituent of the stable domains seen in the 'protokerogen-like' ^{13}C NMR profiles obtained after most degradation methods; **v)** significant increase the heterocyclic N moiety after thermal treatment. Quantitative values taking into account C and N balance in extractive fractions and degradation residues revealed that the latter fact was not only necessarily due to the removal of non-heterocyclic N forms but also to endothermic cyclisation reactions. The overall results suggest that distribution of C and N forms in peat structural domains depend more on the global impact of biogeochemical processes on the sedimentary organic matter (e.g., thermal impact, waterlogging, dehydration...) than on a multicompartiment dynamics associated to fractions of different maturity or residence time, which is not reflected in particle-size fractions, and is only fairly defined by patterns of nonpolar extractive fractions and the extent of the nonhydrolyzable aliphatic domain.