PBC-9: Cultivation-induced alterations recognized in the structural characteristics of resilient humic acids from a sequence of Southern African Soils with different maturity degree

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Extreme aromatisation found in the humic acids from some Southern African virgin soils is an unusual feature when humic substances are not affected by geological dia- and catagenetic processes. Apart from the depletion of aliphatic structures ascribed to intense soil biogeochemical activity, a series of $^{13}$C-NMR spectral patterns such as the low carboxyl/aryl ratio and the weak signals for O- and N-substituted aromatic structures could be pointing to deep abiotic processes as sunlight irradiation, periodic dehydration of the soil matrix, or accumulation of black-carbon related structures ascribed to the effect of soil-affecting fires in the past.

In order to establish the effect of clearing and continuous cultivation on soil organic matter characteristics, six surface soil samples (0–15 cm) from South Africa (Hertzog and Guquka), Zimbabwe (Chikwaka and Domboshawa) and Tanzania (Mafiga and Mkindo) were studied by Curie-point analytical pyrolysis and the corresponding extracted, purified humic acid fractions were analysed by $^{13}$C NMR under quantitative acquisition conditions.

On the whole, cultivation has led to considerable declining of total organic matter levels, although a relative increase in the percentage of colloidal fractions tightly bonded to the mineral fraction (i.e., humic acid and insolubilized humin) was observed at expenses of the percentage of the other fractions, of which fulvic acids behaved as most responsive for the effect of cultivation.

The results obtained by analytical pyrolysis of the whole soils suggested intense lignin alteration in the sites studied, hence methoxyphenolic patterns had a limited value in illustrating the stages through which lignin is transformed into humic acid-like macromolecules. Alkyl pyrolysis compounds (except fatty acids) suggested different biogeochemical trends in the sites studied. Mainly alkadienes and alkanes revealed microbial metabolism and selective preservation of alkyl biomacromolecules (cutans, suberans).

For instance, in Chikwaka and Domboshawa soils (Zimbabwe) a cultivation-induced “alkyl depletion” was observed after pyrolysis of the whole soils. In Guquka, Hertzog (South Africa) and Mafiga (Tanzania) there were less significant changes; whereas in Mkindo...
an intense cultivation-induced “alkyl enhancement” was observed. These differences are being interpreted as regards the extent to which pre-existent organic matter is degraded and substituted by microbial products and compounds from crop residues.

$^{13}$C NMR was used to obtain an insight on the quantitative changes in the different C types of the humic acids (Fig. 1). In general, most of the South African soils studied displayed intense peaks in the 110–160 ppm range suggesting dominant aromatic character. In the case of temperate soils, the $^{13}$C NMR spectra often proved lignin as the major macromolecule contributing to aromatic structures (marked peaks occurring at 153 ppm and 58 ppm for metoxy/amino structures). In the tropical soils studied, however, this situation occurred only in Domboshawa and to a lesser extent in Guquka and Hertzog soils whereas in the other soils a extremely high maturity, aromatisation and demethoxylation of the soil organic matter suggested the above-indicated intense diagenetic transformations and/or accumulation of black carbon type C-forms.

With regard to the effect of cultivation, a progressive pattern between two extreme situations was observed: some soils, Domboshawa and less Hertzog and Guquka, showed comparatively raw organic matter composed of altered lignocellulose from fresh plant biomass. After cultivation, a small aliphatic depletion could be observed, mainly in the $O$-alkyl domain, which is frequent in soils from temperate countries.

Conversely, humic acids from Mafiga uncultivated soil showed extreme aromatisation, demethoxylation and dealkylation. The major effects of cultivation were oxidation and accumulation of aliphatic structures. In particular, before cultivation Mkindo showed the lowest signal intensity for aliphatic structures and the lowest concentration of carboxyl groups. In this soil, cultivation caused the most dramatic aliphatic enhancement in the humic acid fraction.

Guquka uncultivated soil showed similar characteristics to Hertzog: the important aromatic domain coexisted with major aliphatic structures, but the shape of the aromatic region indicated that typical lignin units were not present in high proportions. The humic acids displayed intermediate NMR profiles in terms of the above conditions, and the organic matter characteristics were not significantly affected by cultivation. This situation is similar to that in humic acids from Chikwaka, which behaved resilient with regard to cultivation effects: the prevailing aromatic domain coexisted with aliphatic structures including carbohydrate and alkyl compounds.

In summary, the results suggested contrasting conditions for humic acid formation and also a differential response to clearing and cultivation. The cultivation induced “aliphatic
enhancement" was observed to concur in exceptionally aromatic humic acids, whereas aromatisation after cultivation was noted in humic acids where structural modifications as regards biomacromolecules was less pronounced. From the agronomical viewpoint it is interesting to point out that several soils in the wide area studied show some virtual resilience attributable either to presence of matured organic matter in biogeochemically active scenarios (e.g. Chikwaka soil) or to selective preservation of lignocelluloses biomass (e.g. Domboshawa soil), where cultivation had some effect more similar to those soils in temperate countries with a preferential degradation of aliphatic structures in soil organic matter.

![Fig.1. $^{13}$C NMR spectra of humic acids from some selected Southern Africa soils](image-url)