LIGNIN ALTERATION PATTERNS RESPONSIVE FOR SOIL CARBON SEQUESTRATION MECHANISMS IN UNDISTURBED, REAFFORESTED AND CULTIVATED ECOSYSTEMS (ALMERÍA, SPAIN)


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The Natural Park Sierra María-Los Vélez (Almería, South-eastern Spain) with substrate of limestones, marls and dolomies, is characterized by a Mediterranean-type climate, with strong continental features. The soil types are Mollic-Paric Calcisols, Rendzic Leptosols, Hypocalcic Calcisols, Hypercalcic Calcisols, Luvic Calcisols and Petric Calcisols.

Figure 1. Comparison between spectroscopic patterns of humic acids formed in different biogeochemical scenarios: Left: condensed humic acid with polynuclear chlorophorins and heavily transformed lignin. Right: humic acid with low aromatlicity and structures resembling those in slightly transformed lignins. Top to down: 2nd derivative visible spectra, visible spectra and resolution-enhanced infrared spectra.

The analysis of the soil humic acid fraction by spectroscopic and pyrolytic techniques (2020, Frontier Laboratories device and a GC/MS Agilent 6890 with an HP 5MS column; helium flow of 1 ml min⁻¹; oven temperature at 50 °C for 1 min, increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 300 °C for 10 min using a rate of 20 °C min⁻¹), suggested different features, interpreted extreme situations in a gradient of humification mechanisms reflected in the quantitative balance of soil C sequestration.

From the qualitative viewpoint, a series of humic acids with featureless infrared spectra showed high optical density and polynuclear chlorophorins of fungal origin. The pyrolytic patterns showed major peaks for methoxy-lacking aromatics (alkylbenzenes and alkylphenols) as well as poor yields of alkyl compounds indicative of efficient biodegradation of both microbial and plant-derived aliphatic constituents. This is interpreted as the consequence of biogeochemical mechanisms involving both microbial synthesis and condensation processes.

This pattern contrasts with that in soils with humic acids of marked aliphatic character and low molecular weight: intense 2920 cm⁻¹ infrared band, low optical density and high E₆/E₄ extinction ratio. The infrared spectra displayed typical lignin and amide bands, pointing to preservation of comparatively young organic matter.

This is in agreement with the pyrolysis results, where conspicuous series of methoxyphenols (syringol, guaiacol and their methyl-, ethyl-, vinyl-, propenyl- and acetyl-derivatives) were the major peaks, in some cases accompanied by aromatic compounds of high molecular weight (e.g., biphenyls) and by well-defined alkyl homologues series (alkanes, α-ω-alkanediens and fatty acids), indicating C sequestration mechanisms based on stabilization of plant biomacromolecules and aliphatic structures.


In this latter group of samples, a systematic feature mainly of climatic pine forest is the release of polycyclic aromatic hydrocarbons mainly phenanthrenes and diterpene resin acids (e.g., dehydroabiatic acid) suggesting incorporation of these conifer resin constituents to the soil humic acid. These polyaromatic compounds could represent additional biogeochemical proxies in the Natural Park under study, informing on the intensity of carbon stabilization mechanisms in ecosystems with comparatively low biogeochemical performance.