Do molecular assemblages released at progressive pyrolysis temperatures reflect different organizational levels in the structure of soil humic acid?

G. Almendros[a,]*, Z. Hernández[b], J.A. González-Pérez[c], L. Cuadra[a], E. Fernández[a]

[a]Centro de Ciencias Medioambientales (CSIC), Serrano 115B, 28006 Madrid, Spain; [b]Dpto Ecología, Univ. Alcalá, 28871 Alcalá de Henares, Madrid, Spain; [c]Instituto de Recursos Naturales y Agrobiología, CSIC. Apdo. 1052, E-41080 Sevilla, Spain
E-mail: humus@ccma.csic.es

Analytical pyrolysis is a classical tool for the structural research of humic substances, invoked as a technique superior to wet chemical degradation because its outstanding potential for the breakdown of the C–C bonds even in the most recalcitrant structural domains. Also, it enables the release of a large variety of products in a wide range of polarity and derived from lipid, carbohydrate, lignin or protein. Nevertheless, the potential of analytical pyrolysis for unbiased structural analysis is the subject of controversy. In extreme cases, it is considered that pyrolysis is only valid for fingerprinting purposes in samples analyzed with the same device under exactly the same analytical conditions.

Due to the above limitations, the structural information inferred from pyrolytical analysis of strongly heterogeneous macromolecular material such as humic substances requires comparison between results from destructive and non-destructive techniques in a set of widely differing, well characterized samples, where pyrolysis under more or less drastic conditions e.g. at different temperatures, is carried out.

Pyrolysis was carried out in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer. The chromatograph had an HP-1 capillary column (30m × 250 μm), and the helium flow was adjusted to 1 ml min^{-1}. Oven temperature was 50 ºC for 1 min, then increased up to 100 ºC at 30 ºC min^{-1}, from 100 to 300 ºC at 10 ºC min^{-1} and isothermal at 320 ºC.

Comparison of the pyrolytic patterns showed dramatic differences in terms of temperatures, the most remarkable being: a) the lack of methoxyphenols in pyrograms at 700 ºC as regards to those at 500 ºC and b) the release of a conspicuous alkyl series mainly in samples at 700 ºC. The latter series consisted of fatty acids (mainly C_{12} to C_{18} with strong even-to-odd C-number preference) and hydrocarbons (alkanes and olefins in the C_7 – C_{21} range and no C number preference).

The preliminary results are interpreted as: a) most of the alkyl products (C_7–C_{17}) are not thermoevaporation products but pyrolytic fragments, b) most of the information concerning lignin and other methoxyphenol-releasing structures are lost after pyrolysis at high (700 ºC) temperature and c) it is postulated that mainly high pyrolysis temperature (700 ºC) provides data on the condensed alkyl domain in humic substances (in some cases referred to as unhydrolyzable residue or protokerogen-like material).