

Pyrolytic Characterization of Humic Acids in Relation to Carbon Sequestration Mechanisms in Representative Soils from the Basque Country (Northern Spain)

Amaia Ganuza¹, Gonzalo Almendros, María-Cristina Zancada¹,
Oliva Polvillo^{2*}, Francisco J. González-Vila²

¹ Centro de Ciencias Medioambientales, CSIC, 28006-Madrid, Serrano 115, Fax: 34-91-5640800, humus@ccma.csic.es, ² Instituto de Recursos Naturales y Agrobiología, CSIC, 41080-Seville P.O. Box 1052, fjon@irnase.csic.es

Curie-Point analytical pyrolysis was used for the assessment of soil organic matter accumulation processes in representative ecosystems from the Basque Country (Northern Spain).



Fig. 1. Photographs of some of the most representative soil uses and vegetation types studied in the Basque Country

A total of 15 zones representing main soil uses and vegetation types, such as native forests, coniferous plantations, shrubs, pastures and cultures (Fig. 1) were sampled. The pyrolytic behaviour of humic acids (HA), isolated from the sampled soils, was correlated with climatic and geological constraints and with bulk soil parameters such as C content, nutrient availability and distribution of total C in different humic fractions (Fig. 2).

Hundred most abundant pyrolysis compounds from humic acids

No. Compound	MP Compound	No. Compound	No. Compound
1 Pentane	27 C5-Alkylbenzenes	53 Propylpyridinol	76 Diethylstilbenol
2 Hexane	28 Vinylguaiacol	54 Acetylpyridine	80 Indole
3 Toluene	29 Ethylguaiacol	55 Tetralinone	81 Eucetane
4 Phenol	30 Zymol	58 n-Tetralene	82 n-octadecanoic acid
5 Naphthalene	31 Undecane	57 Calixarene	83 n-Eicosane
6 Styrene	32 C2-Alkylmethylphenols	59 Longiphene	84 Octadecanoic acid
7 Ethene	33 n-Undecane	59 Pentadecane	85 Hexadecane
8 Chloro	34 C3-Alkylbenzenes	60 Syringylacetone	86 n-Hexadecane
9 Octane	35 C3-Alkylbenzenes	61 n-Pentadecane	87 Docosane
10 Indane	36 C5-Alkylbenzenes	62 Hexadecane	88 n-Docosane
11 C3-Alkylbenzenes	37 Propylguaiacol	62 n-Hexadecane	89 n-Triacosane
12 Vinylguaiacol	38 Acetylguaiacol	64 Tetradecanoic acid	90 n-Tetradecanol
13 C2-Alkylbenzenes	39 Propylguaiacol	65 Hexane	91 n-Pentacosane
14 Guaiacol	40 Dodecane	66 1,1'-bis(p-ethylphenyl)ethane	92 n-Hexacosane
15 Benzene	41 Methylpyridinol	67 Heptadecane	93 Steroid
16 Naphthalene	42 C3-Alkylmethylphenols	68 n-Heptadecane	94 Steroid
17 n-Heptane	43 n-Dodecane	69 Fatty acid aryliso-C15	95 Steroid
18 Methylbenzenes	44 C2-Alkylmethylphenols	70 Fatty acid aryl-C15	96 Steroid
19 Toluol	45 C3-Toluenes	71 Pentadecanoic acid	97 Steroid
20 C4-Alkylbenzenes	46 Guaiacylacetone	72 Octadecane	98 Steroid
21 C3-Alkylphenols	47 Vinylpyridinol	73 Nonadecane	99 Steroid
22 Methylguaiacol	48 Ethylpyridinol	74 n-Octadecane	100 Steroid
23 Decane	49 Toluene	75 Hexadecanoic acid	
24 C1-Alkylmethylphenols	50 n-Toluene	76 C10-Alkylcyclohexanones	
25 n-Decane	51 C5-Alkylmethylphenols	77 Nonadecane	
26 C2-Alkylbenzenes	52 n-Toluene	78 n-Nonadecane	

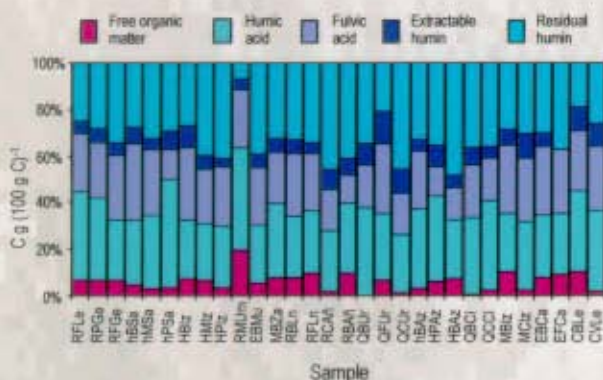


Fig. 2. Concentration of the major organic matter fractions referred to the percentage of total C in the soils studied.

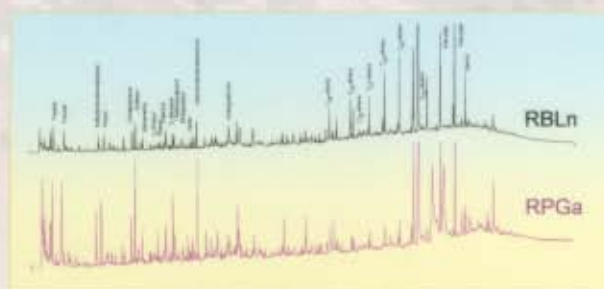


Fig. 3. Pyrograms of HA from soils under *Quercus robur* (RBLn) and pasture (RPGa).

RESULTS AND CONCLUSIONS

Figure 3 shows two representative pyrograms. On the peaks are indicated the nature of the major pyrolysis products. In general terms, it seems that climatic factors, temperature in particular, influence the accumulation of C and also the structural features of the HA fraction.

The main results can be summarized as follows:

Humic acids from soils under typical Mediterranean climate show a poor n-alkane pattern which contrasts with the abundance and diversity of alkanes from HAs in Atlantic soils (C₂₀-C₃₀ with maximum near C₂₅). Alkanes from the HAs in Mesomediterranean sites showed patterns with intermediate characteristics.

The HA fraction generally tends to retain some molecular information about the potential vegetation in the site, which is revealed by the occurrence of signature compounds (alkyl and lignin-derived). The HAs from cleared ecosystems (both pastures and cultivated soils) are dominated by propyl- and keto-substituted phenols, mainly of the syringyl type, typical pyrolysis compounds from lignin in herbaceous plants.

Lignin-derived methoxyphenols were more responsive to vegetation types than to abiotic constraints. The substitution of the spontaneous broad-leaved vegetation by gymnosperms is reflected by the abundance of guaiacyl-type phenols, with local exception in sites recently reforested on calcareous substrate, where the spontaneous oak forest regrows.

Application of multivariate data treatments showed the possibility to discriminate automatically the origin of the soil samples exclusively based on a reduced set of pyrolytic descriptors.

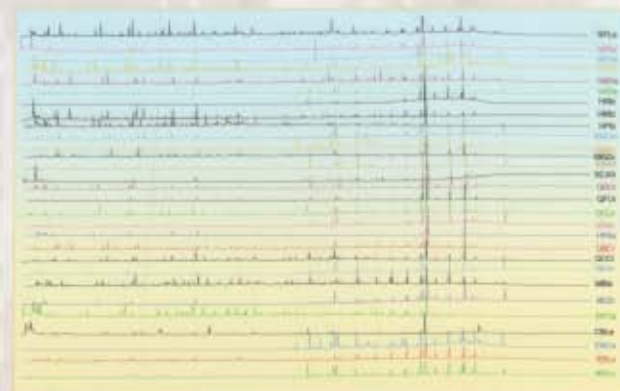


Fig. 4. Total ion pyrogram from the whole set of humic acids.