Structural correlation between soil humins and kerogens as seen by analytical pyrolysis

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INTRODUCTION

The possibility of the accumulation in soils of stable aliphatic materials has been postulated as a non-exclusive alternative to classical models for humus formation, based on the selective preservation of aromatic biomacromolecules. Such a hypothesis represents an actualistic approach to the formation process of fossil organic sediments and conforms to recent findings regarding the humification process in specific compartments in active terrestrial soils. In order to bring some light into this possible connection we investigated the pyrolytic behaviour of humin preparations isolated by two physical methods.

Alkali-insoluble humins represent a considerable part of the stabilized, biologically resistant pool of organic carbon on the Earth's surface, and often makes up more than a third part of the total organic carbon in soils. The small number of conclusive investigations about the origin and chemical structure of humin is largely determined by methodological problems derived from its heterogeneous nature and stable association with the mineral matrix.

The classical concepts considering humin mainly as humic colloids irreversibly associated to soil minerals by physical and chemical linkages have been questioned over the last few years. In fact, most humin can be isolated by physical methods avoiding the use of drastic reagents. These types of humins are considered to consist of microscopic particles (diagenetically altered organic matter) retained in soil microaggregates. These hypotheses somewhat resemble the selective preservation of biomacromolecules recently postulated by different authors (Tegelaar et al., 1989; de Leeuw et al., 1991) as an alternative basis for the formation of kerogens. Such theories have brought about the need to justify the genetic relationship between resistant biomacromolecules in plants and geomacromolecules in their fossil counterpart. This has encouraged the research into insoluble, non-saponifiable highly aliphatic biomacromolecules in extant organisms which, after selective preservation with minor chemical changes upon fossilization, could contribute directly to kerogen formation. This conception is nothing but a geochemical approach to the "inherited fractions" of classical studies on humus chemistry. In this study, the above considerations are discussed on the basis of the results obtained by analytical pyrolysis from humins isolated by contrasting procedures from widely different types of humus in forest soils.

RESULTS AND DISCUSSION

Two independent methods were used to concentrate the humin: i) ultrasonic disruption of soil and further separation by flotation (*inherited humin*; Duchaufour et al., 1975) and ii) recovering the organic fraction in the interlayer formed between two non-miscible liquids with a different partition coefficient (water-methylisobutylketone; *MIBK-humin*; Rice et al., 1989). The former method is based on the comparatively low density of the organic matter particles formerly entrapped in soil microaggregates, whereas the latter takes advantage of the hydrophobic character of the soil organic matter. Special care was taken in removing not-humin organic fractions, *ie*, not-yet decomposed plant particles and humic colloids, which were removed by flotation in a 1.8 g cm^{-3} CHBr$_3$-ethanol mixture and extractions with 0.1 mol dm^{-3} NaOH, respectively.

Both humin preparations were isolated from Segovia soils (Central Spain): i) a Calcic Cambisol (*Quercus rotundifolia* forest) on Miocene limestone [pH 6.6, C/N 21], ii) an Entic Luvisol on metamorphic rocks (*Fagus sylvatica* forest) [pH 4.6, C/N 16] and iii) an Eutric Cambisol on sandy limestone (*Pinus pinea*) forest [pH 6.2, C/N 26]. The litter was removed and the soil samples were taken from the organic horizons (A$_0$+A$_1$), air-dried and homogenized to 2 mm.

Flash pyrolysis was accomplished in a CDS Pyroprobe 190 unit equipped with a Pt-coil heater programmed for 500 °C at a rate of 20 °C s^{-1}; the operation was repeated five times and the volatile products, carried by He flow, were condensed in an "U" tube (2 mm i.d.) submerged in liquid N$_2$. The off-line pyrolysis products were dissolved in methylene chloride and immediately injected in a Hewlett-Packard 5988A GC/MS system.

Fig. 1 shows the main pyrolysis products of the humins from Calcic Cambisol with patterns similar to those in the other soils. Both types of preparations yielded an unexpectedly high proportion of alkyl molecules (alkanes, alkenes and fatty acids) making up more than half of the total pyrolysis products (Table 1). The other products consisted of phenols, catechols, alkylphenanthrenes, fluorenes and some methoxyphenolic compounds, which suggests the contribution of lignified tissues (Martin et al., 1979). The release of condensed products such as alkylnaphthalenes is more typical from coalified materials, but have been reported as minor pyrolysis products of bark tissues in extant plants. The pyrolysis patterns obtained from humins separated by the contrasted isolation procedures were qualitatively similar. This pyrolysis pattern is not compatible with the presence of a dominant fraction of preserved lignocellulosic material in the humins. On the contrary, it suggests an accumulation of polymer structures incorporating a large proportion of polymethylene molecules, also including entrapped long-chain hydrocarbons.
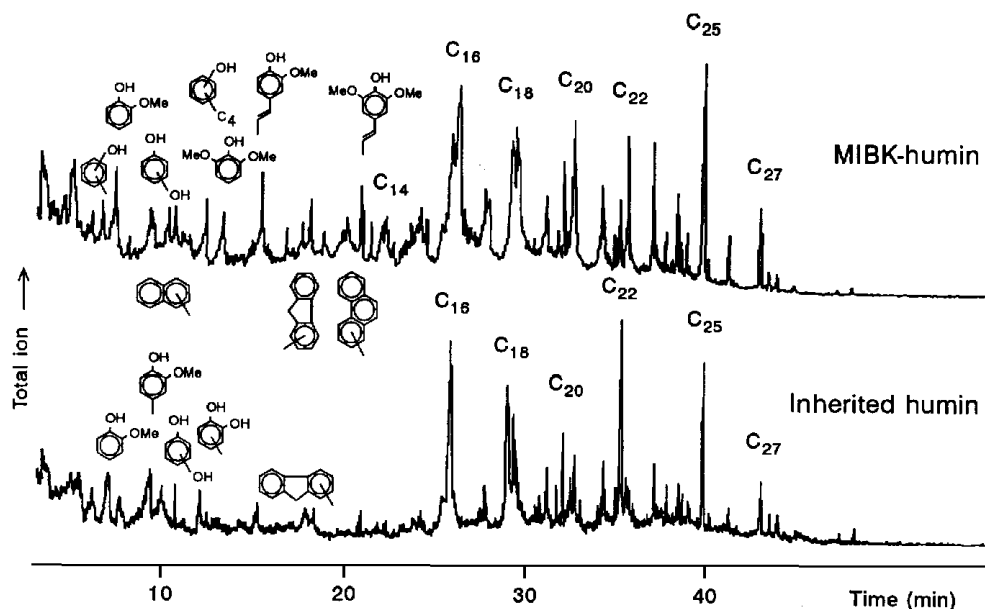

Fig. 1. Chromatographic separation of pyrolysis products of humins isolated from Calcic Cambisol (evergreen oak forest) by different procedures. The C numbers refer to peaks (alkanes, alkenes and fatty acids) of polymethylene products. The main cyclic products are also indicated.

The humin preparations were observed under scanning electron microscope in order to obtain some clue about the precursor materials, and showed a clearly heterogeneous morphology, where fragments of plant tissues coexist with amorphous microaggregate structures. Higher magnification shows that not only the organic matter aggregates with the fine mineral particles, but, conversely, fine clays are fixed on the surface of altered plant tissues (Almendros et al., 1980). The above morphology, relatively constant in the

Table 1. Percentages (% of the total ion counts) of the main groups of pyrolysis products from humin preparations of different types of forest soils

	Inherited humins			MIBK-humins		
	Calcic Cambisol	Entic Luvisol	Eutric Cambisol	Calcic Cambisol	Entic Luvisol	Eutric Cambisol
Total phenols	5.92	9.23	12.03	11.55	0.70	7.33
Total catechols	4.66	0.00	6.65	2.64	0.94	8.78
Total naphthalenes	2.60	0.00	2.69	1.98	0.73	2.44
Total fluorenes	2.52	0.00	3.25	1.69	0.31	2.38
Total phenanthrenes	0.00	0.00	2.65	3.29	0.24	9.18
Total alkanes	23.40	23.49	19.09	28.46	68.36	24.08
Total alkenes	9.02	29.87	28.26	9.71	5,24	21.07
Total fatty acids	25.02	8.05	16.33	17.66	6.91	30.62
Total aromatics	25.39	13.42	28.36	33.43	3.65	15.34
Total aliphatics	57.44	61.41	63.68	55.83	80.51	75.77

inherited humins as well as in the MIBK-humins (the latter showing greater dominance of the former type of particles, and *vice-versa*), suggests that the discussion of the pyrolysis results should be conducted considering two independent, non-exclusive processes the extreme situations of which are: i) the selective preservation of specific constituents of plant or microbial biomass and ii) the condensation of colloidal or low molecular weight polymethylene molecules resulting in the formation of stable, waterproof microaggregates with a presumable large residence time in soil.

Concerning selective preservation of biomass microparticles, the most straightforward justification of the pyrolysis patterns is considering plant or microbial lipid polymers (cutins and suberins in the most classical studies). Due to their polyester structure, such material is generally judged as not excessively resistant to biodegradation. Despite of the possibile existence of non-hydrolyzable esters in natural macromolecules (Largeau et al., 1986), in recent literature there is a tendency to postulate new types of highly resistant biomacromolecules differing from "classic" biopolymers (de Leeuw et al., 1991). An alternative is to consider the selective preservation of the latter in connection with hyperstructure-dependent features, such as steric hindrances in continuous, non-stoichiometric macromolecular systems in plants. In practice, the variable monomer composition and large possibilities for covalent bonding between different types of structural biopolymers could lead to endless classification of laboratory macromolecular preparations defined from quantitative differences and artificial criteria.

The fact that soil enzymes do not penetrate the inner regions of compact organo-mineral microaggregates, in addition to the physical or chemical immobilization of polymer substrates with non-repeating units, is enough to justify the preservation of regions at subcellular levels of the lignocellulosic biomass (Martínez et al., 1990).

The other alternatives that should be taken into consideration are connected to the possibilities for heteropolymerization in sedimentary media of diffusible aliphatic products, including the abiotic formation of protokerogen-like material, widely described in humus literature. The specific patterns of alkyl molecules obtained from soil humins after wet chemical degradation, in addition to experiments in model systems, are compatible with processes of *in-situ* condensation of fatty acids in the presence of mineral surfaces (Catroux and Schnitzer, 1987; Almendros et al., 1991). In terrestrial ecosystems, typical resinification processes of unsaturated lipids should take advantage of the different levels of compartmentation of the microaggregate structure and the soil reactive matrix.

CONCLUSION

Irrespective of origin, the finding of meaningful processes for selective concentration in soil microcompartments of polyalkyl recalcitrant material derived from higher plant or microbial sources opens interesting perspectives in organic geochemistry studies in terms of increasing the knowledge about early transformations of depositional organic matter, by looking for specific biomarkers disclosing relationships between fossil remains of plants and microorganisms and the insoluble fraction of modern soils.

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