

MOLECULAR PROXIES IN FREE LIPID AND HUMIC ACID PERBORATE DEGRADATION COMPOUNDS FOR THE ASSESSMENT OF THE IMPACT OF CLEARING AND CULTIVATING CENTRAL SPAIN FOREST SOILS



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The quantitative assessment of soil resilience to anthropogenic perturbations requires of sensitive descriptors to the extent to which molecular composition of the soil organic matter reflect permanent changes related to the structure of the trophic system. This early identification is very complicated in semiarid Mediterranean soils where seasonal contrasts and hot summer temperatures lead to humic substances of a relatively high biogeochemical stability. In this work, the information provided by direct extraction with organic solvents (free soil lipid fraction, FSLF) and by oxidative degradation of humic acids (HA) with sodium perborate followed by gas chromatography was used for the quantitative assessment of the impact of clearing forests in the molecular assemblages of soil.

Material and methods

Four sites representative of the original and final situation of forest Mediterranean soils after cereal cultivation or transformation into pastures were selected: C1 (virgin oak forest, Calcaric Cambisol), C2 (cleared oak forest, cereal cultivation, Rendzic Leptosol), C3 (ash forest, Epigleyc Cambisol) and C4 (cleared ash forest, pasture, Ortieutric Cambisol). The FSLF was isolated by Soxhlet's extraction with petroleum ether 40–60°C and perborate degradation method was used for oxidative degradation of HA.

Results and discussion

Perborate degradation yielded up to 92 major compounds (>0.01% chromatographic area) including large amounts of α,ω -alkanedioic and fatty acids with chain lengths suggesting breakdown of hydroxy acid constituents of cutins and suberins. Alkanes were missing and in general aliphatics represented > 33% of the total degradation compounds. The aromatic series included major fractions of phenolic and benzenecarboxylic acids (Table 1).

Table 1. Compounds released by perborate degradation method

Compounds	C1	C2	C3	C4
Total alkanes	0.0	0.0	0.0	0.0
Total <i>n</i> -fatty acids	8.6	12.5	10.1	7.2
Total fatty acids	8.6	12.5	10.2	7.3
Total <i>n</i> -dibasic acids	18.6	12.6	25.2	26.8
Total dibasic acids	21.7	15.0	29.4	30.2
Total phenolic acids	25.9	31.5	24.7	25.2
Total benzenecarboxylic acids	13.1	21.8	13.0	17.0
Total aromatics	45.8	60.3	46.4	49.6
Total aliphatics	36.8	31.4	45.7	44.1
Benzenecarboxylic acids / phenolic acids	0.5	0.7	0.5	0.7
Aliphatics / aromatics	0.8	0.5	1.0	0.9
Aliphatics / phenolics	1.4	1.0	1.8	1.75
Aliphatics / benzenecarboxylics	2.8	1.4	3.5	2.6
Total fatty acids / total dibasic acids	0.4	0.8	0.3	0.2
Syringyl compounds	1.5	2.0	2.9	1.5
Guaiacyl compounds	12.5	9.9	11.4	12.1
Syringyl / guaiacyl	0.1	0.2	0.3	0.1

The amount of the alkyl series changed significantly in the cereal culture (C2): the yield of α,ω -alkanedioic acids decreased and the fatty acid increased. The opposite was observed in the pasture soil (C4), suggesting that the organic matter being formed from underground suberized tissues and associated rhizosphere prevailing in this soil.

References

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A significant increase of the syringyl-to-guaiacyl ratio was observed only in C2 as regards C1, as expected from the accumulation of lignins with a decreased degree of internal cross-linking, whereas in C4 the HA were formed from methoxyphenol-yielding macromolecules with an enhanced condensation. Similarity and biodiversity indices calculated from the total abundances of the molecular descriptors clearly showed that the organic matter changed more in cultivated soil than in pasture soil. Diagnostic changes in FSLF composition were also observed: whereas in C3 there was a series of hydrocarbons and diterpene resin acids probably derived from relict vegetation or aerosol transport from neighbouring forests (dehydroabietin, totarol methylether, dehydroabietal and pimaric acid), in C4 accumulated steroidal compounds from animal origin (cholesterol, ergost-5-en-3 β -ol and β -stigmastenol), as well as a possible root-derived triterpenoid with friedoolean structure (Fig. 1).

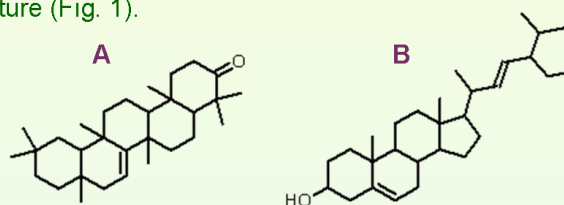


Figure 1. A: Friedoolean-14-en-3-one; B: stigmasta-5, 22-dien-3 β -ol.

Conclusions

Perborate degradation yielded information on the amounts of the different carbon forms accumulated in soils, whereas FSLF included valuable signature compounds suggesting changes in organisms and processes after clearing. Similarity and biodiversity indices calculated from the total abundances of the molecular descriptors showed that the organic matter in cultivated soils changed more than in pasture soil. Qualitative changes in FSLF assemblages were also observed in the cyclic structures: whereas in C3 forest soil there was a series of hydrocarbons and diterpene resin acids inherited from woody plants, the probable origin of most of the organic matter in pasture soil C4 was betrayed by typical biomarkers from animal origin as well as a root-derived triterpenoid with friedelan structure from underground plant biomass.