## ANALYSIS OF NONVOLATILE SOIL LIPIDS BY CURIE-POINT PYROLYSIS. REVISITING THE ENVIRONMENTAL INFORMATION GAINED FROM SOIL BIOMARKER ASSEMBLAGES



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Soil lipids have been for a long time recognized as a first order source of environmental information. In fact, soil lipid molecular assemblages are highly responsive to recent changes in the structure of the trophic system and also represent a valuable agrochemical record of environmental changes in the past.

Conventional analysis of soil lipids can be straightforwardly performed by gas chromatography-mass spectrometry (GC-MS) applied to soil extracts obtained with organic solvents and achieve maximum derivatized to volatility. Nevertheless, several recent experiments have evidenced that the molecular information provided by the soil lipid fraction is far to be completely utilized. In fact, a series of quantitative studies on lipid extracts from forest and cultivated Mediterranean soils has shown that up to 50% of the total lipid "invisible" under "normal" remain chromatographic conditions. It is clear that most of this material has a very low volatility and probably remains in the injector liner or retained in the first centimeters of the capillary column.

Table 1. Lipid markers (as their methyl derivatives) in soil extracts (petroleum other 40-50°C) from soils under pine (Plaus pines, P) oak (Quercus Ser sap. robundfolis, Q) and landow (Austraces Marches & Servets).

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Percentage of total volatile products (acyclic aliqui compounds not included). Components representing less than 0.1% (stahles) were not taken info consideration. Model pyrograms selected for Figs. 2 and 3 correspond to sample JZ.

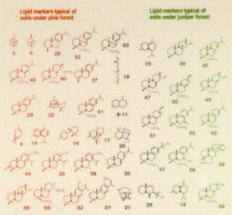


Fig. 1. Chemical structure of major cyclic products identified in Continental Mediterranean soils under commonperm vegetation.

Some progress has been achieved in the last years concerning the above In particular, i) forced limitation. chromatographic conditions with ultrahigh-temperature metallic columns have indicated that some of the non-detected material consists of long-chain alkyl compounds, ii) the alternative use of fast chromatography in very-short (<3 m) columns have evidenced the occurrence of additional soil lipid components, such as wax esters, polyditerpenes and esteryl esters and, iii) the use of highresolution 13C NMR on whole lipid samples showed complex aromatic/ unsaturated signals including isoprenoid compounds such as polyprenols and complex cycloalkane structures.

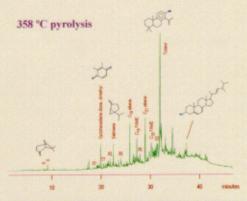


Fig. 2. Currie-point pyrogram (DSPC) of a methylated lipid extract of soil under (uniper forest feat of the compounds previously identified by direct injection occur in the pyrogram the information is local, which however is deminated by biomarker compounds (i.e., not artifacts) not based by direct GC-BS.

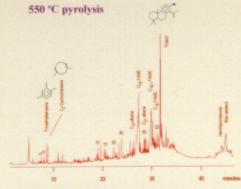


Fig. 1. Curie-point pyrogram (550 °C) of a methylated lipid extract of soil J3 under jumiper forest. Pyralytic patterns are similar at 358° and 550°C. In oak forest samples, major pyralysis products not detected by direct injection GCMS (results not shown) correspond to complex allyobarterne series.

## RESULTS

The analysis of soil lipids by Curiepoint analytical pyrolysis (Py-GC-MS) showed some common features with the results from direct injection indicating that rapid (Table 1) thermoevaporation of a considerable proportion of the lipid material occurs, but also an unexpectedly high amount of new structures not observed in the nonpyrolysed volatile fraction were observed. molecular additional pyrolytic assemblages are interpreted as coming from fragmentation of a macromolecular or oligomeric lipid probably formed from fraction reactive resinification of lipid compounds in addition to products the high-range derived from homologues of alkyl compounds.

Our preliminary results, obtained from a collection of lipid samples from unaltered or disturbed soils from Central Spain, indicate that analytical pyrolysis may provide enhanced biogeochemical information. The results are especially promising in the case of those lipid samples yielding cyclic biomarker structures (i.e., presumably not artifacts) by Curie-point pyrolysis (Figs. 2 and 3).