Revisiting Structural Insights Provided by Analytical Pyrolysis About Humic Substances and Related Bio- and Geo-Polymers

J.A. González-Pérez, F.J. González-Vila, G. Almendros, H. Knicker, J.M. de la Rosa, and Z. Hernández

Abstract Progress achieved in the knowledge of the structure and composition of humic substances and related forms of natural organic matter (composted or charred biomass, black carbon, etc.) by the use of analytical pyrolysis and related techniques is reviewed. It is suggested that the fingerprinting potential of pyrolytic techniques, when the results are processed from appropriate 'pyronomic' approaches, may lead to unbiased and operative insights on the functional relationships in recalcitrant C forms as well as to a successful quantitative monitoring of various environmental impacts. On the other hand, classical experimental limitations associated to the low, sample-dependant, yields of pyrolytic compounds and the coexistence of molecular assemblages from different origin (i.e. thermo-evaporation products, thermally altered products and rearrangement products) can be in several cases managed by sequential degradation strategies. In addition, suitable multivariate data treatments can be applied to remove spurious information and to identify compound patterns with improved discriminating potential as regards structural features of humic-type macromolecules and related bio- and geo-polymers.

Keywords Land management • Molecular structure • Compost • Forest fires • Py-GC/MS

J.A. González-Pérez (✉) • F.J. González-Vila • H. Knicker • J.M. de la Rosa
IRNA S-CSIC, Avda. Reina Mercedes, 10, 41012 Seville, Spain
e-mail: jag@irnase.csic.es

G. Almendros • Z. Hernández
MNCN-CSIC, Serrano 115bis, 41080 Madrid, Spain

J. Xu et al. (eds.), *Functions of Natural Organic Matter in Changing Environment*,
DOI 10.1007/978-94-007-5634-2_1,

Introduction

Well-known advantages of pyrolytical techniques (i.e. relatively simple, fast, small sample size requiring) have traditionally encouraged its application in the structural characterization of recalcitrant, heterogeneous macromolecular organic matter, which is the subject of study in a wide number of fields in agricultural and environmental sciences. The classical weaknesses claimed for analytical pyrolysis (for instance, generation of artefacts or of secondary compounds where the original chemical structure is strongly modified) have been overcome to a large extent by taking advantage of advanced pyrolytical devices for controlled, sequential thermal degradation but also by the application of complementary experimental techniques based in thermochemolysis in the presence of e.g. alkylammonium salts. Such methodological improvements can optimize the release of diagnostic volatile compounds informing more accurately about the heterogeneous composition of humic substances and similar (precursor of derived) polycondensed macromolecular materials. In particular, there is a permanent scientific interest in routine monitoring of agricultural and environmental dynamic processes that comprises a variety of biomacromolecules (lignins, polysaccharides, proteins, high molecular weight lipids, etc.) and their partially transformed products, as well as other recalcitrant macromolecular material such as pyrogenic organic matter. The accurate molecular characterization of such materials is in general not amenable to standard spectroscopic and wet chemical degradation techniques.

Experimental

Most of the Py-GC/MS results reviewed in this communication were obtained using a double-shot pyrolyzer PY2020iD (Frontier Lab Ltd., Fukushima, Japan) combined to a GC/MS-system Agilent 6890N/5973N. Standard pyrolysis conditions were as follows: unaltered ground samples (5–20 mg depending on its C content) placed in standard cups were introduced into a micro-furnace set at a pyrolysis temperature between 500 and 600°C. Samples are kept at pyrolysis temperature for 1 min.

The GC is usually equipped with nonpolar fused silica capillary columns, e.g. DB5MS (J&W Scientific); the oven temperature is 50°C for 1 min, then increased up to 100°C to a rate of 30°C min^{-1}, from 100 to 300°C to a rate of 10°C min^{-1} and isothermal at 300°C for 10 min using 20°C min^{-1} heating rate in the scan modus. Helium is used as carrier gas with a flow of 1 mL min^{-1}. The GC is equipped with a mass selective detector (Agilent 5973N), and electron impact mass spectra were acquired with a 70-eV ionizing energy. The identification of individual compounds is usually done by fragmentometry, ion chromatography for different homologous series and comparison with analytical standards, published data and commercial databases (NIST and Wiley).

Review Discussion of the Results

An overview on advances achieved by analytical pyrolysis in the research on humic substances composition and structure, as well as the use of pyrolysis techniques in applied research relevant to agricultural and environmental issues, is reviewed. Relevant results were obtained within the following research lines:

1. Assessment of the impact of land use and changes in soil management on the molecular structure of soil organic matter.
2. Monitoring transformations of crop residues and composted materials applied to agricultural lands. In this case study, special attention is paid to several compound families, i.e. the methoxyphenol pattern obtained by pyrolysis gives information about the progressive transformation of lignin into macromolecules sharing solubility properties with humic substances. Alteration of the pattern of homologous series of alkyl compounds will inform about the extent of microbial reworking of plant wastes. The yields of carbohydrate-derived compounds can be used as an index for soil organic matter and composts maturity.
3. The advantages of thermodesorption and pyrolysis techniques for a direct detection of pollutants, even in complex environmental matrices, in general without the need of preparative chemical treatments.
4. Monitoring the effects of thermal alteration (e.g. wildfires) on the soil organic matter status. In particular, pyrolytic approaches have contributed to demonstrate that charring processes (forest fires or controlled burning of crop residues) do not only lead to selective thermal degradation of the soil organic matter, i.e. the concomitant concentration of heat-resistant organic structures, but fire also induces a series of reactions leading to newly formed condensed heterogeneous structures highly resistant to biological degradation. Molecular complexity of post-fire organic matter enhances to large extent (mainly at expenses of dehydration and further aromatization of carbohydrate- type compounds) but also due to generation of heterocyclic N compounds. Pyrolysis of fire-affected organic matter also evidences accumulation of a polymethylene domain of high molecular weight which survives thermal cracking or thermoevaporation even when thermal weight losses amounted up to 70% of the starting soil organic matter. These structural alterations of humic substances can be considered to contribute to the long-term carbon sequestration on the Earth's surface, which is an important issue regarding global change.
5. Finally, promising current methodological research lines are considered such as (1) critical contrasting of the results from Py techniques as regards those obtained by classical wet chemical degradation methods, (2) the new information gained from pyrolytical approaches applied to complex macromolecular lipids (i.e. not volatile under standard GC conditions), (3) chemotaxonomic assessment of environmental quality, in terms of biodiversity and complexity, based on the multivariate analysis of the pyrolytical compound assemblages and (4) sequential degradation experiments attempting to describe speciation patterns of pyrolysis compounds in different structural domains: in particular,

pyrolysis was found especially suitable for on-line analysis of variable temperature- or chemically assisted pyrolytic cleavage reactions leading to the successive removal of compounds from the heterogeneous structure of soil organic matter.