Soil organic matter characterization by modified Rock Eval pyrolysis in a Calcic Chernozem profile

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1. Introduction

Soil organic matter is not homogenous but is a mixture of many organic matters with different chemical compositions and physical qualities. This chemically and kinetically heterogeneous material comprises a mixture of plant and microbial residues of various compositions and with different decomposition rates, as well as their transformation products, in addition to refractory, long-residence-time macromolecular organic substances (kerogen, black carbon). Humification of biopolymers is determined by those environmental parameters (relief, climatic conditions), which define soil types too.

Rock Eval pyrolysis was designed for petroleum exploration to determine the type and quality of organic matter in rock samples. Nevertheless, this technique can be used for bulk characterization of the immature organic matter in soil samples [1] and recent sediments [2]. Deconvolution of Rock Eval pyrograms gives information about organic matter fractions with different thermal stability [3; 4].

Aim of our work was to examine soil organic matter conditions of a Calcic Chernozem profile and to certify Rock Eval pyrolysis is usable method for determination soil horizons, supplements the routinish classical measurement techniques.

2. Materials and Methods

Samples were collected from a Calcic Chernozem profile (Józsefmajor Demonstration Farm, Szent István University, North-Plain, Hungary). Diagnostic horizons are Mollic, Calcic and Cambic. Chemical parameters show classical Chernozem horizons (Table 1).

The Rock Eval data of the soil samples were determined with Delsi Oil Show Analyzer: heating at 180^{o}C for 3 min, programmed pyrolysis at 25^{o}C/min up to 600^{o}C under helium flow and oxidation at 600^{o}C for 7 min under an air flow [4]. The following parameters can be obtained from one single measurement: **S2** the current potential of a rock sample, represents the total amount of oil and gas a source rock can still produce during subsequent complete thermal maturation in an open system (expressed in mg HC/g of rock). **TOC** (total organic carbon) content (expressed in weight %) is defined as the sum of the pyrolysed organic carbon content and organic carbon residue content. **HI** (hydrogen index) is defined as carbon normalized S2 and expressed in mg HC/gTOC.

Table 1 Chemical parameters of examined soil profile [5]

Soil genetic horizon	**Depth**	**pH**	**Organic carbon**	**$CaCO_3$**	**CEC**	**Base saturation**	**Silt %**	**Clay %**	**Volume weight**
szint	**(cm)**	**H_2O**	**(%)**	**(%)**	**cmol/kg**	**%**	**2-0.05 mm**	**<0.002 mm**	**g/ cm^3**
Asz	0-40	6.1	2.2	0.0	30	55	37	36	1.4
A	40-60	6.9	1.6	0.0	29	60	36	37	1.3
B	60-90	7.1	0.5	0.0	19	92	37	33	1.3
Ck	90-130	8.1	0.4	26.0	14	100	41	34	1.2

The experimental conditions of Rock-Eval pyrolysis were chosen that all of the hydrocarbonaceous compounds yielded by soil organic matter are recorded as one single peak. In an immature organic matter, like soil, a wide range of components may be present simultaneously and each of them is represented by a Gaussian curve on the pyrogram (S2 peak) with characteristic mean (M) and standard deviation (σ) values. Each pyrogram is a complicated overlap of several normal distributions curves. In order to define discrete components of the multicomponent mixture, the pyrogram has to be decomposed mathematically. Pyrograms of our samples can be described by a combination of four elementary Gaussian components: F1, F2, F3 and F4 (Figure 1). These four components are related to major classes of organic constituents differing in origin and their resistance to pyrolysis: labile biological constituents (F1), resistant biological constituents (F2), immature non-biotic constituents (F3) and a mature refractory fraction (F4). F1/F2 ratio (R) illustrate the relative evolution of the two ’”bio-macromolecule” classes. The log[(F1+F2)/F3] index (I) quantify the degradation of immature organic matter [4]. T_{max} values of approximated Gauss curves belong three category: original biopolymers (180-340°C), partially docomposed biopolymers (340-420°C), humic substances (420-600°C) [4].

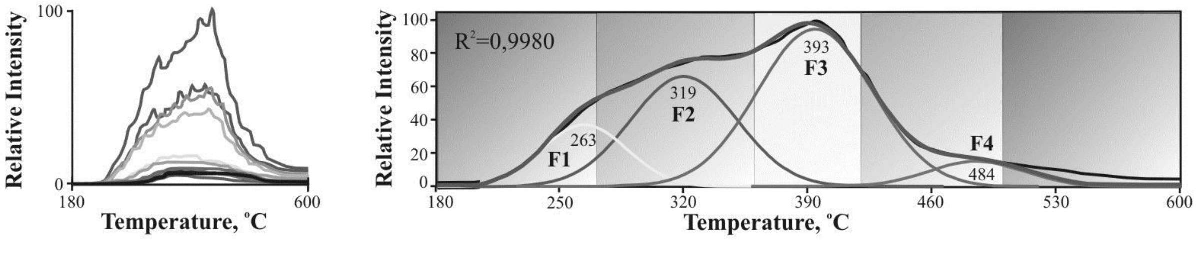

Figure 1 Rock Eval programs (S2 peaks) of soil profile and four elementary Gaussian components are related to major classes of organic constituents

3. Results and Discussion

Changes are shown by vertical profiles of bulk Rock Eval details (TOC, HI), in the relative contribution of the bio- and geo-macromolecules (F1; F2; F3; F4) and by theirs derivable details (C_I; C_I/TOC; R; I) in different fractions of soil organic matter (Figure 2).

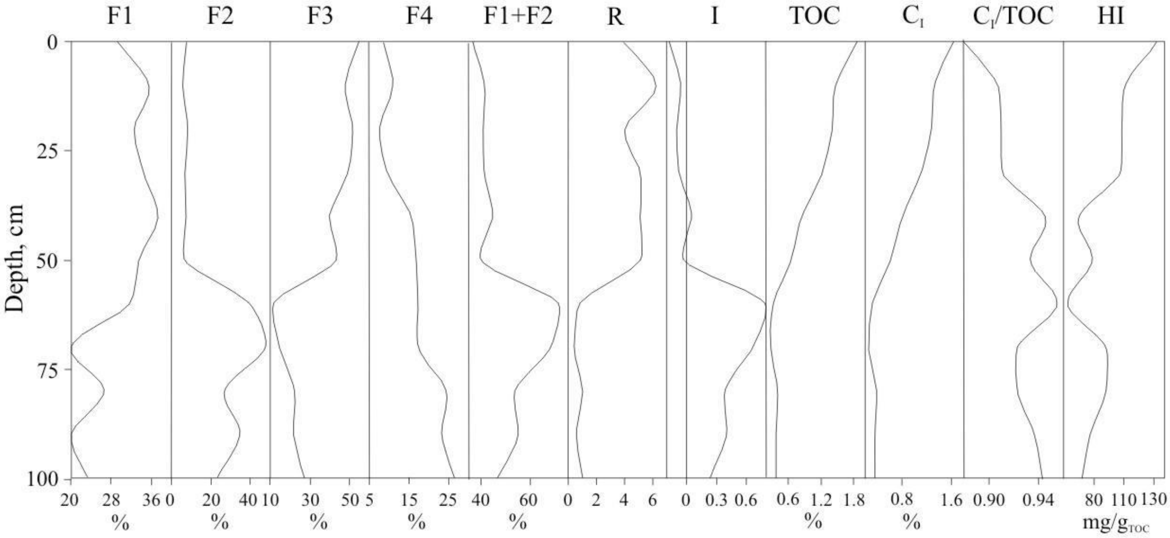

Figure 2 Vertical profile of labile biological constituents (F1), resistant biological constituents (F2), immature non-biotic constituents (F3), mature refractory fraction (F4), relative evolution of the two ”’bio-macromolecule” classes (R ratio), quantify the degradation of immature organic matter (I index), total organic carbon (TOC), inert carbon (C_I), C_I/TOC ratio and Hidrogen Index (HI)

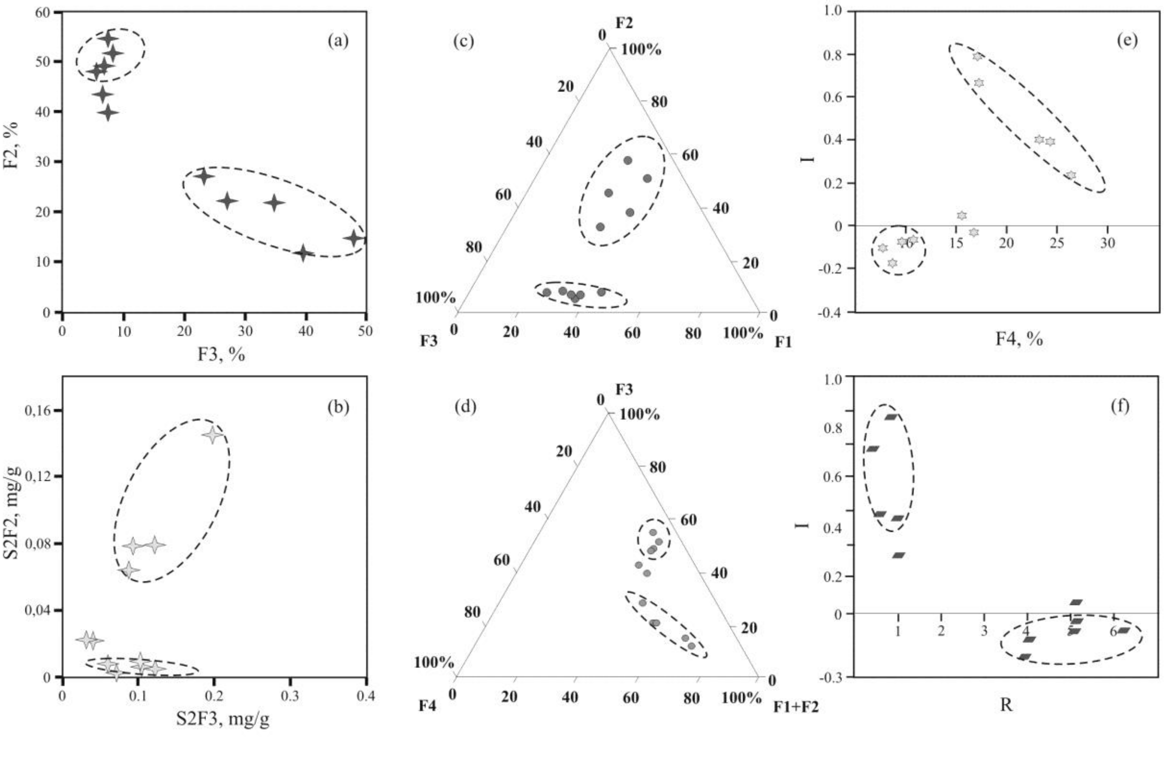

Figure 3 Functionalities of the four constituents

There is a border-line in depth 50-60 cm. We can obtain detailed information about profile with relationship between (a) stabile bio-macromolecules (F2) and immature geo-macromolecules (F3); (b) labile bio-macromolecules (F1) and refractory geo-macromolecules (F4); (c) relationship between components F1, F2, F3 and (d) F1+F2, F3 and F4 components (Figure 3). According to ones three zones can be well separeted. Consequently the horizons prognosticated by pedological description are identifiable from Rock Eval details as well.

4. Conclusions

Rock-Eval pirolysis proved to be suitable for efficient examination of soil organic matter and estimation the measurement of humification. Further advantages, slight sample need to measure (0.1 g), doesn't require preparation, fast measure (25 min.), and we can detect many parameters from one single measurement (e.g. S2, TOC, HI) which we can use perfectly in evaluations. We can escape the lengthy and many chemicals requiring laboratory separates.

Rock-Eval pyrolysis is useable method for determination for determination soil horizons, supplements the routinish classical measurement techniques. The method gives us excess-informations compared to traditional organic matter measure. Accordingly Rock-Eval pyrolysis is capable define parameters, which help determination of unknown paleosoil type and allow identify minor occurences within genetical horizons.

Acknowledgements

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