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SOIL ORGANIC MATTER CHARACTERISATION BY ROCK-EVAL PYROLYSIS

Theses of doctorate dissertation (Ph.D.)

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Szeged
2009

Introduction

Geological organic matter is present in the atmosphere, natural water, soils, recent sediments and rocks. Organic matter in sedimentary rocks is studied comprehensively, but we have less knowledge about geochemistry of organic matter in soils and recent sediments, although investigation would be important because of its mass and the important role in the global carbon cycle. Soil organic matter (SOM) plays a significant role in controlling the CO_2 content of atmosphere and the global earth temperature. Wearing-away of rocks and pedogenesis processes are influenced by SOM. Adsorption characteristic of organic matter in soils and recent sediments determines the mobility of organic and inorganic pollution thus effects the quality of surface- and groundwater.

The SOM is not homogeneous but is a mixture of 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 with different decomposition rates, as well as their transformation products, and macromolecular organic substances (kerogen, black carbon). Stability of components, speed of degradation, environmental effects are covered a wide range, from some to thousands of years.

Rock-Eval (RE) pyrolysis is considered as a quick and effective tool for evaluating the amount and properties of the organic matter not only in sedimentary rocks, recent sediments and soils. This technique, however, provides information on the total organic matter without recognizing different components of the heterogenous organic mixtures.

The aim of this work was to develop modified RE pyrolysis and to define the proportions of chemically and kinetically heterogeneous organic components with different thermal stabilities. Furthermore, to estimate the humification and biopolimer-geopolimer transformation in soils and recent sediments.

Other aim of this work was to separate the soluble and insoluble (organic and aqueous agent) fractions of organic matter using chemical methods; to develop an isolation protocol; as well as to make a study of the role of climatic conditions and precursor vegetation in soil evolution.

Following the evaluation of the recorded geochemical parameters on initial samples, the method was further checked on loess paleosoil sequences via the analysis of a paleosoil monolith from an archeological examination site. In their case the question was whether or not the method is suitable for the differentiation of minor pedogenetic units, events within the block on the one hand. On the other hand, what new information could be gained compared to the traditional sedimentary, pedologocal approaches.

Materials and methods

The examined soil samples were collected from (1) Chernozems (Cibulka-brook catch basin, West-Hungary); (2) Histosols (Bürgezdi-marshland, Csicsós-marshland and Bivalyfertő, East-Hungary); (3) profiles of Soil Conservational Informational and Monitoring System (TIM): Pécsvárad (TIM132272; TIM161244), Görömböly (TIM 29005) and Kaposvár (TIME6014). We analyzed buried paleosoil samples from an archeological site from North-Eastern Hungary (Polgár-Ferenci-riverback). Sedimentary rock samples were taken from Triassic intra-platform basin (Rezi, Vérhalom) and from Pula oil shale (West-Hungary).

The Rock Eval data of the soil and rock samples were determined with Delsi Oil Show Analyzer and RE6. Seven parameters can be obtained from a single measurement (S1, S2, T_{max}, TOC, HI, PI, CH_{pot}). The RE6 apparatus is capable to determine Oxygen Index too.

In an immature organic matter, like in soils, 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 distribution curves. In order to define discrete components of the multicomponent mixture, the pyrogram has to be decomposed mathematically. Deconvolution of pyrograms were started from low temperature side because thermally labile biomolecules are undergoing pyrolysis first.

The isolation of the organic fractions: After the removal of lipids with chloroform/methanol (3/1, v/v) and fulvic and humic acids by alkaline extraction (0.5 M sodium hydroxide), the residue was submitted to stepwise acid hydrolysis (tri-fluorine acetic acid and hydrochloric acid) to remove proteins and polysaccharides. The resulting insoluble, non-hydrolysable „refractory organic matter" (ROM) was demineralised using 6 N hydrochloric acid and 48% hydrofluoric acid (1/2, v/v). Black carbon was obtained by oxidation of the ROM with dichromate/sulfuric acid (0.1 M/2M) solution. Isolated SOM fractions were investigated by lipid analysis using gas chromatography, elemental and Fourier transform infrared spectroscopic analysis (FTIR), stable isotope analysis and high resolution transmission electron microscopy (HRTEM).

The paleosol monolith samples were analysed at the Department of Geology and Paleontology, University of Szeged. First the soil profile was described visually; the pH, and grain-size distribution, the relative proportion of organic matter and carbonate were measured via Dean-type "loss on ignition". The grain-size was analysed by a Micromeritics SediGraph type 5000ET. Statistical analysis was made using SPSS 11.0 programme on every measured parameters (all measured and calculated values from Rock Eval pyrolysis and results of pedological and sedimetological investigations).

New scientific results

1. Results of the modified RE analysis and the mathematical deconvolution of pyrograms are suitable for detailed characterisation of immature organic matter in soils and recent sediments. These methods present limited information about thermal mature organic matter of petroleum source rocks that we can characterise by standard Rock-Eval pirolysis.

2. In order to test the applicability of the modified RE pyrolysis and the deconvolution of pyrograms, series of pyrolysis were carried out. According to our findings by the precision of organic matter determination is affected by heating rate significantly. The main component of SOM the so-called inert total organic carbon. It can be measured reliably at heating rate of 25^{o}C/min.

3. RE pyrolysis and the mathematical evaluation of pyrograms is suitable to separate soils developed in different ecosystems and prove their genetic relations. Results are in conform with reference groups of World Reference Base for Soil Resources (WRB). WRB is a diagnostic system and it makes use of soil horizons and characteristics for soil classification instead of pedogenetic processes**.**

4. From the approaches, developed for the isolation of a single fraction generally known in the literature, a new method was developed which is suitable for: (1) quantitative isolations and (2) complete organic-geochemical analysis of all fraction and (3) the determination of their mass ratio.

5. The amount of black carbon determined by chemical isolation shows a high correlation with the values given by the integration of RE pyrograms. Consequently, RE pyrolysis is suitable for estimating black carbon content eliminating the need for time-consuming traditional chemical isolation.

6. In case of RE pyrolysis is capable to define parameters, which help the determination of unknown genetic types and allow for the identification of minor pedogenetic episodes.

Publications

List of publications concerning the topic of the dissertation:

Journals:

1. Hetényi, M., **Nyilas, T.**, M. Tóth, T. (2005) Stepwise Rock Eval pyrolysis as a tool for typing heterogeneous organic matter in soils. Journal of Analytical and Applied Pyrolysis 74/1-2, 45-54.

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2. Hetényi M., **Nyilas T.**, Sajgó Cs. and Brukner-Wein A. (2006) Heterogeneous organic matter from the surface horizon of a temperate zone marsh. Organic Geochemistry, Volume 37, Issue 12, 1931-1942

IF_{2006}: **2,331**

3. Hetényi M., **Nyilas T.** (2007) Variation of Rock-Eval data as a function of heating rate. Acta Mineralogica-Petrographica, Volume 47, 47-52

4. **Nyilas T.**, M. Tóth T., Hetényi M. (2008) Quantification of soil organic matter degradation by Rock-Eval pyrolysis, Proceedings Paper, Cereal Research Communications Volume 36, 2007-2010, part 3

IF_{2008}: **1,190**
ΣIF: **4,786**

Proceedings Papers:

1. **T. Nyilas** (2005) Soil organic matter characterisation by Rock-Eval pyrolysis. 5th International Conference of Ph.D. Students. Miskolc, Hungary 2005. Proceedings Paper, ISBN 963 661 681 7 Abstract Volume, 355-359.

2. **Nyilas T.** (2005) A talaj szerves anyagának humifikációja. A Környezettudomány Elmélete és Gyakorlata – Környezetgazdálkodás európai keretben. Szeged, CD kiadvány 1-5.

3. **T. Nyilas**, M. Imre (2009) Rock Eval pyrolysis as a tool for characterization of organic matter in environmental and pollutant samples. 10th International Symposium „Interdisclipinary Regional Research" ISIRR, Proceedings Paper, S6-15.

List of other publications:

1. E. Tombácz, **T. Nyilas**, Zs. Libor, Cs. Csanaki (2004) Surface charge heterogenity and aggregation of clay lamellae in aqueous suspensions. Special 8CCC issue of Progress in Colloid & Polymer Science, 125, 206-215

2. M. Fuchs, **T. Nyilas**, T. Szegi, T. Bialkó (2009) Morphological evidences of swelling stress in some high clay content soils of Hungary, Proceedings Paper, Cereal Research Communications (DOI: 10.1556/CRC.37.2009.Suppl.1) (in press)
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3. G. Nagy, **T. Nyilas**, Sz. Ördög, A. Volford (2009) Supporting the reasonable agricultural production with a newly founded environmental laboratory in the South Eastern Region of Hungary. 10th International Symposium „Interdisclipinary Regional Research" ISIRR, Proceedings Paper S6-16.

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1. **Nyilas Tünde**, M. Tóth Tivadar (2007) TEVA Magyarország Zrt. debreceni telephelyéről származó klórozott szénhidrogénekkel szennyezett fúrásmagok vizsgálata p. 1-76
2. **Nyilas Tünde**, M. Tóth Tivadar (2009) TEVA Magyarország Zrt. debreceni telephelyéről származó klórozott szénhidrogénekkel szennyezett fúrásmagok vizsgálata, A kármentesítésre használható anyagok hatása az ásványi mátrixra p. 1-68

Presentations

1. **Nyilas T.**, Heténi M., M. Tóth T. A talaj szervesanyag formáinak szétválasztási lehetőségei. Presented on meeting of Hungarian Academy of Sciences, Scientific Committee of Geochemistry Mineralogy and Petrology, 21st Nov 2006.

2. **Nyilas T.**, Imre M. Paleotalaj jellemzése Rock-Eval pirolízissel: új módszer a paleotalajok vizsgálatában**.** Presented on meeting of Hungarian Academy of Sciences, Scientific Committee of Geochemistry Mineralogy and Petrology, 28th Okt 2008.

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3. Nyilas T. (2003) A montmorillonit felületi töltés heterogenitásának meghatározása. XXVI. OTDK. Magyarország, Budapest, 2003. Abstract kötet 113. oldal

4. Nyilas T. (2004) A montmorillonit felületi töltés heterogenitásának meghatározása. XXXV. Ifjú Szakemberek Ankétja. Magyarország, Sárospatak, 2004. Abstract kötet 63-64. oldal

5. Nyilas T. (2004) A montmorillonit felületi töltés heterogenitásának meghatározása. IX. OFKD. Magyarország, Budapest, 2004. Abstract kötet 59. oldal

6. M. Hetényi, **T. Nyilas** (2004) Organic matter characterization by stepwise Rock Eval pyrolysis. 16th International Symposium on Analytical & Applied Pyrolysis. Alicante, Spain, 2004. Abstract Volume, 132.

7. T. Nyilas (2005) Soil organic matter characterisation by Rock-Eval pyrolysis. 5th International Conference of Ph.D. Students. Miskolc, Hungary 2005. Abstract Volume, 355-359.

8. Nyilas T. (2005) A talaj szervesanyagának humifikációja. A Környezettudomány Elmélete és Gyakorlata – Környezetgazdálkodás európai keretben, Tudományos konferencia. Szeged, Magyarország, 2005.

9. **Nyilas T.** (2005) A szervesanyag humifikációja különböző talajtípusokban. XXXVI. Ifjú Szakemberek Ankétja. Magyarország, Sarlóspuszta, 2005.

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11. T. Nyilas, T. M. Tóth (2005) Recursive deconvolution of soil organic matter pyrograms. IX. Congress of Hungarian Geomathematics. Mórahalom, Hungary 2005.

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13. Nyilas T., Imre M. (2006) Determination of paleosoil type by Rock Eval Pyrolysis. 17th International Symposium on Analytical and Applied Pyrolysis. Budapest, Hungary 2006. Book of Abstracts 102.

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23. G. Nagy, **T. Nyilas**, Sz. Ördög, A. Volford: Supporting the reasonable agricultural production with a newly founded environmental laboratory in the South Eastern Region of Hungary, 10th International Symposium „Interdisclipinary Regional Research" ISIRR 2009, 23-24 April, Hunedoara, Romania, Book of Abstract 30.

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26. G. Bozsó, **T. Nyilas**, M. Hetényi, E. Pál-Molnár: Accumulation and distribution of organic matter in salt-affected lacustrine sediments at the Fehér-lake, (Szeged, Hungary) The 24th International Meeting on Organic Geochemistry, Bremen, Germany, 5th-11th September 2009, Book of Abstract, 508