Ph.D. dissertation résumé

THE EFFECT OF THE MINERAL PHASE ON THE SOIL ORGANIC CARBON CYCLE

Dóra Zacháry

Geography and Meteorology Ph.D. Program, Doctoral School of Earth Sciences,

Eötvös Loránd University

Supervisors:

Zoltán Szalai, Ph.D. dr. habil.
associate professor
Department of Environmental and Landscape Geography, Faculty of Science
Eötvös Loránd University

Gergely Jakab, Ph.D. dr. habil.
senior research fellow
Geographical Institute
Research Centre for Astronomy and Earth Sciences

Head of Doctoral School: Judit Bartholy, D.Sc., Head of Department

Head of Doctoral Program: Dávid Karátson, D.Sc., Head of Department

The Ph.D. dissertation was prepared at the Eötvös Loránd University, at the SEDILAB of the Geographical Institute, Research Centre for Astronomy and Earth Sciences and at the Isotope Climatology and Environmental Research Centre (ICER) of the Atomki.

Budapest, 2019

1. Introduction and objectives

The reason for the increasing number of researches focusing on the study of the composition and turnover of soil organic matter (SOM) is the key role of soils in carbon sequestration and global carbon cycle. The significant role of soil processes in connection with the global carbon cycle is well known. The global soil carbon pool (2500 Gt) is 3.3 times the size of the atmospheric pool and 4.5 times the size of the biotic pool (Lal, 2004). Therefore, a better understanding of the properties and dynamics of SOM and the identification of the factors that regulate soil respiration in natural and managed ecosystems is critical in predicting ecosystem responses to global change (Ahn et al., 2009).

SOM decomposition depends on many biotic and abiotic factors. The temperature, humidity, air and pH conditions of soils significantly affect the living conditions of the microbial community responsible for the decomposition of SOM. Soil texture is also an important parameter influencing SOM decomposition through factors such as particle surface area and porosity, which affect water-holding capacity, cation exchange capacity and many other factors (Procter et al., 2015). Besides texture, soil mineral phase plays a crucial role in the stabilization of SOM. Soils with higher silt and clay content generally sequester more C than sandier soils, (Barré et al., 2014; Hassink, 1997; Wattel-Koekkoek et al., 2003). However, beyond the determination of the amount of fine fractions, relatively little research studied the mineralogical composition of these fractions and their organic matter stabilizing effects. It is particularly important to study the stabilization of organic matter in temperate soil soils, since these soils contain a mixture of various minerals, layered silicates (in many cases 1: 1 and 2: 1 clay minerals together), crystalline oxides and poorly crystalline materials, which all affect the stabilization of SOM to varying degrees.

Therefore, my aim was to investigate the organic matter stabilizing effect of the mineral phase in a six-month incubation experiment. My objectives were i) to determine the kinetic parameters of the carbon pools of soils under forest vegetation; ii) to investigate the influence of the soil mineral phase composition on the turnover of soil organic carbon and iii) to investigate the effect of the soil properties on the decomposition processes of SOM.

2. Materials and methods

Thirteen topsoil (0-20 cm) samples were collected from six sites in Hungary: four samples from Sopron Mts., three samples from Aggtelek Mts., two samples from Cserhát Mts, two samples from South Nyírség, one sample from Geresdi Hills and one sample from Pilis-Alpár sand ridge. In order to determine the basic soil physical and chemical properties and to characterize the soil organic and mineral phases, the following methods were used:

- determination of soil pH (distilled water and KCl) and $CaCO_3$ content
- determination of total and dissolved organic carbon content and dissolved nitrogen content using a TOC/TN analyser (TOC-L, TN-L, Shimadzu)
- determination of solid phase total nitrogen content by the Kjeldahl method
- determination of cation exchange capacity
- determination of Fe, Mn and Al concentration in dithionite–citrate–bicarbonate extracts and in acid ammonium oxalate extracts using a microwave plasma atomic emission spectrometer (MP-AES 4200, Agilent Technologies)
- determination of the soil texture by the pipette method
- determination of soil mineral components (particularly clay minerals) and functional groups of SOM using a Fourier-transform infrared spectrometer (Bruker Vertex 70) and calculation of indexes (e.g. aromaticity index) from the selected characteristic absorption bands
- qualitative and quantitaive determination of minerals in the clay fraction (<2 μm) of soils using an X-ray powder diffractometer (Rigaku Miniflex 600)
- determination of changes in $\delta^{13}C$ values of soils and maize residues during the 163-days incubation period using an isotope ratio mass spectrometer (Delta plus XP, Thermo Finnigan) and the application of $\delta^{13}C$ values of soils and maize residues for the separation of the different sources of soil respiration (basal respiration, residue mineralization, priming effect) and the quantification of the amount the stabilized crop residue

The decomposition of the SOM was studied using a 163-days incubation. Maize residues were added to the soils in order to affect the SOM decomposition dynamics and get natural ^{13}C enrichment for $\delta^{13}C$ analysis. The samples were kept in an incubator at 20°C for 163 days at 70% field capacity. The soil respiration was measured at specified intervals (on day 3, 8, 15,

30, 51, 79, 107, 135 and 163) and trapped in 2M NaOH and quantified by titration with 1M HCl. Another aliquot of NaOH was mixed with $2MSrCl_2$ to get $SrCO_3$ for $\delta^{13}C$ analysis.
Carbon mineralization kinetics was modelled by fitting a first-order two pools model on the CO_2 efflux values. The decomposition rate constants of the model were determined by the linearization of the equation applying the method of residuals. The relationships between the organic and mineral phases versus the mineralization parameters (cumulative CO_2 efflux, amount of maize residue stabilized, priming effect, decomposition rate constant and mean residence time) of the soils were analysed by Pearson's correlation and linear regression analyses. The difference among the soils were determined by a one-way ANOVA with post hoc Tukey test.

3. Theses

1. My research proved that the mineral composition of the solid phase of the soil has a greater effect on the decomposition (or rather on the stabilization) of organic matter than the clay content of the soils.
2. While international literature sources emphasize the importance of swelling clay minerals in the stabilization of soil organic matter, according to my results, Al and Fe oxides and illite content may play a more important role than these minerals.
3. My research proved that both divalent (Fe^{2+} and Mn^{2+}) and trivalent (Al^{3+}, Fe^{3+}) ions play an important role in the chemical stabilization of soil organic matter. This is due to the cationic bridges formed between organic materials and polyvalent metal ions according to the literature. Although literature data primarily emphasizes the importance of Fe^{3+}, Al^{3+} was found to be having a stronger organic matter stabilizing effect in the Hungarian soils investigated.
4. My research proved that soil environment (pH), the quality of organic matter (C/N ratio) and the physical and mineral properties of the solid phase of the soils all influence the decomposition rate constant of the easily mineralizable carbon pool.
5. My research proved that although the decomposition rate constant of the slowly mineralizable carbon pool is not sensitive to most of the studied environmental factors and their changes, the aluminum and illite content of soils significantly modified the decomposition of this carbon pool.
6. My research proved that the C/N ratio of soils is essential for the development of priming effect. In soils having the highest C/N ratio, a negative priming effect was observed, whereas soils having lower C/N ratio a positive priming effect was identified.

7. Based on my results, it is likely that as a result of land use change and the use of conservation agro technology, more effective stabilization of carbon is expected in areas (except for hydromorphic areas) where the mineral phase of the soil facilitates it.

4. Conclusions

The texture of soils alone cannot be considered as the sole controlling factor in a complex system such as soils where many other parameters can determine the turnover of organic matters. This was confirmed by my research where not only the texture or clay content of the soils, but also the chemical composition of the mineral phase proved to be an essential factor in the decomposition of organic matter. Strong correlation was found between the inhibition of SOM decomposition, that is, the stabilization of SOM and the amount of certain mineral types of soils (Al and Fe oxides and illite) - moreover, these correlations were stronger than between the SOM decomposition and the clay content of soils. Furthermore, the decomposition rate constant of the slow C pool was found to be not affected by the texture of soils, whereas the Al and illite content of the soils proved to be significant stabilizing factors. This confirms the importance of studying the mineral composition of soils to obtain better knowledge on SOM stabilization processes.

5. Published papers written in the framework of this Ph.D. dissertation

Zacháry, D., Filep, T., Jakab, G., Varga, G., Ringer M., Szalai, Z., 2018. Kinetic parameters of soil organic matter decomposition in soils under forest in Hungary. GEODERMA REGIONAL 14 Paper: e00187. https://doi.org/10.1016/j.geodrs.2018.e00187

Zacháry, D., 2018. Applications of stable carbon isotopes in soil science with special attention to natural ^{13}C abundance approach. HUNGARIAN GEOGRAPHICAL BULLETIN 68, 3−19. https://doi.org/10.15201/hungeobull.68.1.1

6. Other publications written in the framework of this Ph.D. dissertation

Jakab, G., Hegyi, I., Fullen, M., Szabó, J., **Zacháry, D.,** Szalai, Z. 2018. A 300-year record of sedimentation in a small tilled catena in Hungary based on $\delta^{13}C$, $\delta^{15}N$, and C/N distribution. JOURNAL OF SOILS AND SEDIMENTS 18, 1767-1779.

Filep, T., **Zacháry, D.,** Balog, K., 2016. Assessment of soil quality of arable soils in Hungary using DRIFT spectroscopy and chemometrics. VIBRATIONAL SPECTROSCOPY 84, 16-23.

Zacháry, D., Szalai, Z., Filep, T., Kovács, J., Jakab, G., 2017. Magyarországi talajok CO_2 dinamikájának vizsgálata laboratóriumi inkubációs kísérletben. In: Szigyártó, IL; Szikszai, A (szerk.) XIII. Kárpát-medencei Környezettudományi Konferencia, Kolozsvár, Románia, Ábel Kiadó, 110-115.

Szalai, Z., Szabó, J., Kovács, J., Mészáros, E., Albert, G., Centeri, Cs., Szabó, B., Madarász, B., **Zacháry, D.,** Jakab, G., 2016. Redistribution of soil organic carbon triggered by erosion at field scale under subhumid climate, Hungary. PEDOSPHERE 26, 652-665.

Zacháry, D., Filep, T., Balázs, R., Király, Cs., Ringer, M., Jakab, G., 2019. The role of clay mineral composition in the stabilization of SOM in soils under forest in Hungary. 8th International Symposium on Interactions of Soil Minerals with Organic Components and Microorganisms (ISMOM), Seville, Spanyolország, absztrakt kötet, 48-49.

Zacháry, D., Jakab, G., Filep, T., Ringer, M., Szalai, Z., 2017. Effect of soil parameters on the decomposition rate of soil organic carbon in Hungarian forest soils. 6th International Symposium on Soil Organic Matter: Healthy soils for sustainable agriculture: the role of SOM, absztrakt kötet, 402.

Zacháry, D., Szalai, Z., Filep, T., Kovács, J., Jakab, G., 2017. CO_2 dinamics and priming effect of different Hungarian soils based on laboratory incubation experiment. Geophysical Research Abstracts 19 Paper: EGU2017-14830.

Zacháry, D., Szalai, Z., Jakab, G., Németh, T., Sipos, P., Filep, T., 2016. Preliminary results on the influence of mineralogy on the turnover rates of SOM from different Hungarian soils. Geophysical Research Abstracts 18 Paper: 7542.

Zacháry, D., Szalai, Z., Jakab, G., Filep, T., 2015. Effect of mineralogy on the turnover rates of SOM of different Hungarian soils. 5th International Symposium on Soil Organic Matter, p. 231.

Zacháry, D., Jakab, G., Filep, T., Molnár, M., Szalai, Z., 2018. Study on the turnover time of different soil organic matter fractions from Hungary. Geophysical Research Abstracts 20 Paper: EGU2018-1265.

7. Other important publications

Jakab, G., Filep, T., Király, Cs., Madarász, B., **Zacháry, D.,** Ringer, M., Vancsik, A., Gáspár, L., Szalai, Z., 2019. Differences in mineral phase associated soil organic matter composition due to varying tillage intensity. AGRONOMY, 9 Paper: 9110700.

Rieder, Á., Madarász, B., Szabó, J.A., **Zacháry, D.,** Vancsik, A., Ringer, M., Szalai, Z., Jakab, G., 2018. Soil organic matter alteration velocity due to land-use change: a case study under conservation agriculture. SUSTAINABILITY 10, Paper: 943.

Jakab, G., Madarász, B., Szabó, J.A., Tóth, A., **Zacháry, D.,** Szalai, Z., Kertész, Á., Dyson, J., 2017. Infiltration and soil loss changes during the growing season under ploughing and conservation tillage. SUSTAINABILITY 9, Paper: 1726.

Zacháry, D., Szabó, J., Jakab, G., Pál, T., Kiss, K., Kovács, J., Szalai, Z. 2017. Effect of different pretreatment procedures on the particle size distribution results Geophysical Research Abstracts 19 Paper: EGU2017-15252.

7. References

Ahn, M.Y., Zimmerman, A.R., Comerford, N.B., Sickman, J.O., Grunwald, S., 2009. Carbon mineralization and labile crganic carbon pools in the sandy soils of a north Florida watershed. Ecosystems 12, 672–685.

Barré, P., Fernandez-Ugalde, O., Virto, I., Velde, B., Chenu, C., 2014. Impact of phyllosilicate mineralogy on organic carbon stabilization in soils: Incomplete knowledge and exciting prospects. Geoderma 235–236, 382–395.

Hassink, J., 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. Plant Soil 191, 77–87.

Lal, R., 2004. Soil carbon sequestration impacts on global climate change and food security. Science (80-.). 304, 1623–1627.

Procter, A.C., Gill, R.A., Fay, P.A., Polley, H.W., Jackson, R.B., 2015. Soil carbon responses to past and future CO2 in three Texas prairie soils. Soil Biol. Biochem. 83, 66–75.

Wattel-Koekkoek, E.J.W., Buurman, P., Van Der Plicht, J., Wattel, E., Van Breemen, N., 2003. Mean residence time of soil organic matter associated with kaolinite and smectite. Eur. J. Soil Sci. 54, 269–278.