# Soil organic matter characterisation by photometric indices or photon correlation spectroscopy: are they comparable?

GERGELY JAKAB<sup>1</sup>, Ádám RIEDER<sup>2</sup>, Anna Viktória VANCSIK<sup>1</sup> and Zoltán SZALAI<sup>1</sup>

# Abstract

Soil organic matter (SOM) is a complex component of soil that acts as basis for most of the soil forming processes. SOM characteristics, including quantity, spatial distribution, molecular size and composition, are the results of environmental effects. SOM is definitely hard to be measured in situ, therefore most investigations are based on incomplete SOM extractions or other proxies. Even though, the traditional humus concept that polymerisation degree of SOM molecules are proportional to their stability are refuted, the concerning proxies for SOM composition predictions are still in use. These are mainly based on the photometric investigations of alkali extractions. However, this extraction method received many rightful critiques, it still could be a possible alternative, since it is quite simple, cheap and represented much more SOM than water extractions. This study aimed to compare SOM composition results based on carbon-nitrogen ratio and alkali extractions measured by UV-vis spectrometry and photon correlation spectrometry on the same soil used as forest and crop field. SOM composition proxies provided inconsistent results using the NaOH extraction method compared with photon correlation. Therefore, the application of organo-mineral SOM protection theory in association with the photometric proxies seems to be difficult in the case of the investigated Luvisol. On the other hand, photon correlation spectroscopy provided results in line with the published results of the organo-mineral stabilization theory that suggested alkali extraction with special care could be a useful alternative. However, due to the known imperfections of it, the application of in situ measurement methods would be preferable.

Keywords: organic matter composition, tillage, soil carbon, dynamic light scattering

# Introduction

Soil organic matter (SOM) is an important component of soil. As a result of input (mainly plant residuals) and output (mineralization) SOM is an ever-changing holistic system that is complex and spatially diverse, therefore cannot be described or modelled adequately still today even though it is a key parameter of sustainability (JANCSOVSZKA, P. 2016). The first, widely accepted theory was the humus concept (KONONOVA, M.M. 1966), which separated SOM to single molecules based on their extent and polymerization. Main components were classified as humic, fulvic substances and humin that belonged to colloid size and polymerisation range of an increasing order respectively (STEVENSON, F.J. 1982). According to this theory the stability of a certain SOM molecule is proportional of molecular extent, polymerisation and aromaticity. This way the process of humification was presumed to be constructed more complex molecular structures to be more resistant against mineralisation. The proxies applied to measure SOM composition, therefore based on humic substance solubility in various solvents (KONONOVA, M.M. 1966).

In recent times studies proved that SOM highly interacted with the mineral phase of the soil, creating various types of complexes that affected SOM stability more than mo-

<sup>&</sup>lt;sup>1</sup> Geographical Institute, Research Centre for Astronomy and Earth Sciences of the Hungarian Academy of Sciences. H-1112 Budapest, Budaörsi út 45. E-mails: jakab.gergely@csfk.mta.hu, vancsik.anna@csfk.mta.hu, szalai.zoltan@csfk.mta.hu

<sup>&</sup>lt;sup>2</sup> University of Leeds, Earth Surface Science Institute, LS2 9JT Leeds, UK. E-mail: eeari@leeds.ac.uk

lecular composition alone (ZIMMERMANN, М. et al. 2007; Schmidt, M.W.I. et al. 2011). Accordingly, SOM could not be clearly classified on the basis of the humus concept (LEHMAN, J. and KLEBER, M. 2015). However, according to this theory stable SOM was directly related to the fine particles of the soil (HASSINK, J. 1997; WIESMEIER, M. et al. 2014) the role of aggregates was less clear. Six, J. et al. (2002) revealed that SOM takes a major role in forming and stabilizing these aggregates, which are thus considered to be storage vessels for SOM by protecting it from decomposition (MENG-YUN, L. et al. 2014; JAKAB, G. et al. 2016). Therefore, in general, SOM is classified to *i*) mineral phase associated, recalcitrant pool with long turnover time; *ii*) aggregate associated chemically and biologically active pool with short turnover time; iii) particulate organic matter (often called light fraction), which consists slightly degraded plant tissue and iv.) water soluble pool (FILEP, T. et al. 2015). Moreover, nowadays, the application of highly intact biochar in soils is coming to the focus (Kása, I. et al. 2016; DENCSŐ, M. et al. 2017).

Natural SOM systems can be disturbed by physical and chemical effects, such as agricultural land use. Many studies have shown that cultivation can change the structure of SOM by affecting aggregate size and stability (SPACCINI, R. and PICCOLO, A. 2013), carbon/ nitrogen (C/N) ratios (JOHN, B. et al. 2005; RIEDER, Á. et al. 2018) and soil organic carbon (SOC) quantity and distribution (FALKENGREN-GERUP, U. et al. 2006). MENG-YUN, L. et al. (2014) demonstrated that easily oxidisable organic carbon tended to be enriched in macro-aggregates instead of within microaggregates, and in addition their data confirmed aggregate breakdown in farmlands. These combined effects can lead to massive SOC loss in regions of cultivated land (PLAZA-BONILLA, D. et al. 2014; BILANDŽIJA, D. et al. 2017). In contrast, Rabbi, F.S.M. et al. (2014) demonstrated that SOC mineralization rates and protection was irrespective of aggregate size. The effect is clearer under tropical conditions while not always so obvious in the temperate zone, where the influence of global warming (Міка, J. and Farkas, A. 2017) makes the picture more complex.

ZIMMERMANN, M. *et al.* (2007) published a fast procedure to separate SOM pools, that combines physical and chemical fractionation techniques, such as density separation and NaOCl oxidation. As POEPLAU, C. *et al.* (2013) pointed out in their study, this method is likely to become widely used.

Parallel with the conceptual development, the investigation methods and technics were also improved. X-ray spectromicroscopy as an important part of in situ investigations of organo-mineral interactions became more available (LEHMAN, J. et al. 2008). Increasing number of published studies are based on other in situ technics such as Raman spectroscopy and Fourier transform infrared spectroscopy, nano scale secondary ion mass spectrometry (MUELLER, C.W. et al. 2017) even though they are less widespread for routine measurements because of financial reasons. This could be the reason why humus concept proxies based on SOM solubility are still in progress. Moreover, using these extractions, more up-to-date analytical methods such as static (SLS) and dynamic light scattering (DLS) can be used to measure molecular weight and size values of SOM. Despite its efficiency, only a few studies (PALMER, N.E. and Wandruszka, R. 2001; Esfahani, M.R. et al. 2015) have applied this method. However, NaOH extraction method has received many critiques (RICE, J.A. 2001; LEHMAN, J. and KLEBER, M. 2015) it is still widely applied (WANG, K. and XING, B. 2005; CHAUDHURI, S. et al. 2013; REDDY, S. et al. 2014). Therefore, it is still a question whether the NaOH extraction based photometric proxies developed for the humus concept are applicable in combination with the organo-mineral theory.

This study aims to compare SOM composition results gained by the fractionation method of ZIMMERMANN, M. *et al.* (2007) in combination with alkali extraction as a proxy of the humus concept. Our hypothesis is that traditional photometry based results are comparable to those received using photon correlation spectroscopy. Reaching this aim the same soil under different land uses were investigated in order to determine how land use change affects SOC content and SOM composition of the various pools.

### Materials and methods

#### Study site

Soil samples were taken in 2015 near Kisbárkány, Hungary 48°00′55.3″N; 19°40′24.5″E (*Figure 1*), where the mean annual temperature is between 9–12 °C and precipitation is 600 mm (Dövényi, Z. 2010). This site was a typical example of forest clearance during the 18<sup>th</sup> century as it was widespread in the hilly parts of Hungary at that time (SZALAI, Z. *et al.* 2016). Two quite similar, slightly eroded soil profiles were sampled and described as a haplic Luvisol (IUSS WG WRB, 2015) on Oligocene siltstone (*Table 1*).

Table 1. Main parameters of the investigated topsoil\*

Parameter	Forest	Arable				
Size, μm v/v						
>200.0	0.0	0.0				
70.0-200.0	2.1	2.3				
63.0-70.0	1.5	1.7				
20.0-63.0	28.5	26.9				
2.0-20.0	53.2	51.8				
0.5–2.0	12.6	14.7				
0.5>	1.8	2.3				
Sesquioxides, m/m	14.2	-				
pH <sub>dw</sub>	6.3	6.8				
Depth of humic horizon, cm	40.0	42.0				
CaCO <sub>3</sub> , m/m	0.0	0.0				
Munsell color	10YR4/2					

\*Partly based on NÉMETH, T. and SIPOS, P. 2006.

Sampling sites were chosen on flat areas (slope steepness < 3%). Mineralogy of the soil was characterised by 40–70 per cent quartz and 5–15 per cent feldspars (SIPOS, P. 2004). The predominating clay mineral was smectite (NÉMETH, T. and SIPOS, P. 2006).



Fig. 1. Location of the sampling sites under forest and arable field Google Earth

The first profile was situated in a forest which has existed for more than 120 years, while the second was in an area which had been converted to an arable field before the  $19^{\text{th}}$  century according to the Third Military Survey of Hungary (1869–1887). Forest was dominated by *Quercus robur* with the appearance of *Ulmus campestris* < 10 per cent. Crop production on the arable field was based on autumn ploughing tillage with < 5 kg ha per year nitrogen fertilizer application in spring as an average of 20 years. Main crops were wheat, maize, rape and sunflower.

# Sampling

One sample from the forest and one sample from the crop field as composites of 9 subsamples taken from the diagonals of two 100 m<sup>2</sup> squares were collected from the 0–10 cm layer of the topsoil (RowEL, D.L. 1994). Subsamples were mixed in order to create a spatially representative sample. Samples were dried and crushed, after which the > 2,000 µm particles were removed by dry-sieving.

#### Soil fractionation

The ZIMMERMANN fractionation method was improved by POEPLAU, C. et al. (2013) and in its present form widely used and accepted. The authors decided to use this method for compatibility reasons to the RothC model (COLEMAN, K. and JENKINSON, D.S. 1996) for possible further application. Fractionation procedures were as follows, 30 g of each sample were taken to 150 ml of distilled water then ultrasonic dispersion with 22 J/ml was applied. Then the samples were wet-sieved over a 63 µm screen in order to separate the sand, aggregate and particulate organic matter (POM) fraction from the rest of the sample. Particles < 63 mm were centrifuged (at 3,500 RPM for 15 min) in order to separate the silt and clay (s+c) and the dissolved (DOC < 0.45 mm) fraction (POPLEAU, C. *et al.* 2013). After the centrifugation the liquid component including DOC was decanted, whereas the solid phase was considered as s+c fraction. 1 g of the s+c fraction was oxidized with 6 per cent NaOCl in order to determine the resistant SOC (rSOC) content. Finally, the >63 mm fraction was separated by density. The heavy fraction (> 1.8 g cm<sup>-3</sup>) contained the sand and aggregates (S+A), while the light fraction (< 1.8 g per cm<sup>3</sup>) was POM.

#### UV-Vis spectroscopy

For SOM extraction the most traditional alkali solution method was applied since this was quite simple and therefore, still in use in recent studies (NIEROP, K.G.J. *et al.* 2001). 40 mL 0.5 M NaOH were added to 4 g of sample, which were then shaken for 24 h according to the method of GALANTINI, J. A. *et al.* (2004) under non reductive conditions. Following this step, the solvent was centrifuged at 3,500 RPM for 15 min (SZALAI, Z. *et al.* 2016) and right after that measured by photometry in order to avoid oxidation and recombination.

A Shimadzu UV-3,600 spectrophotometer was used to measure the absorbance values of the extractions depending on the wavelength. The total spectrum was recorded from 180 nm to 1,000 nm wherein the  $E_2/E_3$  (245/265 nm),  $E_4/E_6$  (400/600 nm) and Ultraviolet Absorbance Ratio Index URI (210/254 nm) ratios were calculated as they are in connection with SOM composition (TAN, K.H. 2003; Guo, M. and CHOROVER, J. 2003; HER, N.G. *et al.* 2008; NADI, M. *et al.* 2012).

## Dynamic light scattering

This method was chosen since it needed the same alkali SOM extraction as the photometric method did, therefore independently from extraction method the results were directly comparable with each other. DLS measurements were made using a Malvern Zetasizer Nano instrument where 0.5 M NaOH was determined as the solvent and extracted SOM was determined as the substance. Measurements were carried out right after the extraction process as it was described at photometric measurements. The resulting histograms are based on volumetric percentage of the averages of at least three repetitions. (In case of high diversity two additional repetitions were created.)

#### SOC, particle size and pH measurement

Soil organic carbon (SOC) and total nitrogen TN data were achieved applying a Tekmar Dohrmann Apollo 9,000N instrument, which used dry combustion at 800 °C (SZALAI, Z. et al. 2016). This instrument is additionally capable of measuring solid state samples, and so there was no need for prior sample preparation (BUURMAN, P. et al. 1996). Particle sizes of the bulk samples were determined in a range of 0.2-2000 µm using a Fritch Analysette 22 Microtech laser diffractometer by applying 0.5 M sodium pyrophosphate and 15 min ultrasonic treatment for disaggregation (CENTERI, Cs. et al. 2015). The device provided 105 size classes those were grouped to 10 according to the USDA system (Table 1). pH values were determined using a potentiometer according to BUURMAN, P. et al. (1996).

#### Statistical analysis

SOC, DOC and TN values were determined as three repetitions at least. If SD exceeded 10

per cent additional measurements were carried out. Normality of the data was checked using Shapiro-Wilks test and transformation was carried out if that was needed. Differences among the averages were tested using one-way ANOVA with post hoc Tukey test. Since POM had one order higher values this fraction was excluded from the ANOVA for SOC and TN.

# **Results and discussion**

# *Sand* + *Aggregate fractions and SOC distribution*

The most relevant component of the bulk soil was in aggregated form and was classified as S+A by the fractionation under both land uses. The ratio of aggregates was higher under forest vegetation (*Table 2*). This ~ 10% difference did not highlight relevant changes so we cannot conclude that it was generated by land use conversion. In contrast, there was a difference between the SOC concentration of S+A, POM and bulk soil under forest and arable land, as under forest the SOC concentration is twice as much as under arable land use in all these fractions.

It is in accordance with the results of FALKENGREN-GRERUP, U. *et al.* (2006) approximately 48 per cent of the SOC has mineralized under arable use due to intensive cultivation during the last ~200 years (*Table 2*).

Moreover, SOC distribution among fractions has also varied substantially between

	Forest			Arable		
Soil fraction	Soil mass, %	SOC, g/kg	Proportion of SOC weighted with soil mass, %	Soil mass, %	SOC, g/kg	Proportion of SOC weighted with soil mass, %
S+A <sup>1</sup>	83.8	18.8	76.0	71.7	9.0	39.6
POM <sup>2</sup>	1.8	182.8	15.8	8.8	94.2	50.7
s+c <sup>3</sup> (rSOC) <sup>4</sup>	7.2	19.7 (4.8)	6.8	7.2	17.7 (10.7)	7.8
DOC <sup>5</sup> + (loss)	0.0 (7.3)	0.005 (n. a.)	0.0 (1.4)	0.0 (12.3)	0.005 (n. a.)	1.9
Bulk soil	_	25.4			13.3	-

Table 2. Carbon content and fractional distribution of the samples fractionated by the ZIMMERMANN, M. et al. (2007) method

<sup>1</sup>Sand and Aggregates, <sup>2</sup>Particulate Organic Matter, <sup>3</sup>silt and clay; <sup>4</sup>resistant Soil Organic Carbon; <sup>5</sup>Dissolved Organic Carbon; n. a. = no data.

the two land use types. Both S+A and POM fractions contained approximately half of their SOC content under arable field compared to the forest soil.

This changes could be the result of both mineralization and a lower degree of formation (JOHN, B. *et al.* 2005) beyond the potential soil erosion under both land uses. S+A had a much higher SOC loss than might be predicted on the basis of decreasing aggregate stability (lower ratio of S+A), which consequently implies that there might be some additional/secondary aggregating agent besides SOM, such as sesquioxides (BARTHES, B.G. *et al.* 2008). SOC content of the finest fraction (s+c) seemed to be decreasing as well because of tillage operations, even though this change was not significant (*Figure 2*).

In contrast, in this fraction, the volume of resistant SOC increased significantly, which suggested the overrepresentation of chemically active SOC in mineralization. Moreover, tillage could improve SOM conservation on the mineral phase as it was reported by FORTUNA, A. *et al.* (2003). SOC solubility did not change, and DOC presented less than 1 per cent under both land uses.



*Fig.* 2. Differences among SOM fractionated by the ZIMMERMANN, M. *et al.* (2007) method concerning soil organic carbon (SOC) content. Whiskers indicate standard deviation. Same letters indicate groups with no difference at p < 0.05 level. – s+c = silt and clay; rSOC = resistant soil organic carbon; DOC = dissolved organic carbon; S+A = sand and aggregates; bulk = bulk soil; Particulate organic matter (POM) is excluded from this figure because of a higher magnitude value.

#### TN content of the fractions

TN distribution compared to that of SOC revealed the higher proportion (~ 40%) of dissolved component under both land uses (*Table 3*). The high volume of water soluble N content in topsoil of the forest does not necessarily indicate inorganic N but could be the result of increased microbiological activity (CHATIGNY, M.H. 2003).

TN content of the bulk soils decreased (p<0.01) under cultivation, although TN related to the finest size fractions (s+c, rSOC) did not changed significantly (*Figure 3*). This was in line with the classic SOM saturation theory of HASSINK, J. (1997) and WIESMEIER, M. *et al.* (2014) who emphasized the role of <20µm fraction in SOM conservation. Therefore, the TN difference of the bulk soils was solely due to the TN loss of aggregates under cultivation (*Table 3*) (GOEBEL, M. *et al.* 2005). The proportion of POM N increased by 5 times under cultivation, which increase is 3 times higher compared to carbon.

An additional SOM loss opportunity was detected wherein SOM was dissolved in sodium polytungstate (SPT). The potential error caused by this process is relatively unknown, although CROW, S.E. *et al.* (2007) estimated it to be up to 26 per cent.



*Fig.* 3. Differences among SOM fractionated by the ZIMMERMANN, M. *et al.* (2007) method concerning total nitrogen (TN) content. Whiskers indicate standard deviation. Same letters indicate groups with no difference at p < 0.05 level. – s+c, rSOC, DOC, S+A, POM, bulk = For explanation see *Fig.* 2. POM is excluded from this figure because of a higher magnitude value.

	Forest			Arable		
Soil fraction	Soil mass, %	TN, g/kg	Proportion of TN weighted with soil mass, %	Soil mass, %	TN, g/kg	Proportion of TN weighted with soil mass, %
S+A <sup>1</sup>	83.8	0.9	51.7	71.7	0.5	27.7
POM <sup>2</sup>	1.8	4.5	5.2	8.8	4.1	24.8
s+c <sup>3</sup> (rSOC) <sup>4</sup>	7.2	1.2 (0.2)	5.6	7.2	1.1 (0.1)	5.4
DOC <sup>5</sup> + (loss)	0.0 (7.3)	0.1 (n. a.)	0.0 (37.7)	0.0 (12.3)	0.1 (n. a.)	42.1
Bulk soil	-	1.4	-	-	1.0	_

Table 3. Nitrogen content and fractional distribution of the samples fractionated by the ZIMMERMANN, M. et al. (2007) method

<sup>1</sup>Sand and Aggregates, <sup>2</sup>Particulate Organic Matter, <sup>3</sup>silt and clay; <sup>4</sup>resistant Soil Organic Carbon; <sup>5</sup>Dissolved Organic Carbon; n. a. = no data.

#### C/N ratios of the fractions

Most fractions had a C/N ratio between 10 and 20, which is usual for temperate SOM (BRONICK, C.J. and LAL, R. 2005). As it was expected lowest values were related to the water soluble components, while outstanding high C/N values were found in the POM (of forest's soil) and rSOC (of arable field's soil) fractions (*Figure 4*), even though significant differences at p<0.05 were only found under forest.

Due to the lower C/N values of crops compared to those of the forest litter (Cools, N. *et al.* 2014), C/N arable field POM was lower, since this fraction referred to the most recent non degraded SOM. The most extreme value was found in the rSOC fraction of the arable field, which could not be interpreted adequately.

# Photometric indexes

The absorbance value at 280 nm revealed a consistent pattern that highlighted only the quantitative difference between each pair (*Figure 5*). Absorbance values normalized to SOC content prove that absorbance is not a direct function of SOC content. Since this property would be a proxy of aromaticity, the results suggested the same order of fractions under both land use types which was in contrast with both the results of C/N ratio of



Fig. 4. C/N values of the SOM fractionated by the ZIMMERMANN, M. *et al.* (2007) method under various land uses. Same letters indicate groups with no difference at p < 0.05 level. – s+c, rSOC, DOC, S+A, bulk, POM = For explanation see Fig. 2.



*Fig.* 5. Absorbance values of SOM solutions (in 0.5 M NaOH) at 280 nm fractionated by the ZIMMERMANN, M. *et al.* (2007) method. Abs/SOC is the absorbance value normalized to the SOC content of the sample. – s+c, rSOC, S+A, POM = For explanation see *Fig.* 2.

this study and the SOM stabilization theory of SCHMIDT, M.W.I. *et al.* (2011) and LEHMANN, J. and KLEBER, M. (2015). Moreover, LÜTZOW, M. *et al.* (2006) pointed out that aromaticity is not necessarily indicative of higher resistance against degradation, especially in the most resistant clay associated fraction.

URI revealed different results compared to the  $E_2/E_3$  and  $E_4/E_6$  indexes. The only significant tendency regarding the URI is that the S+A fraction has the highest value under both land uses, which could refer to the higher proportion of aliphatic SOM components within the aggregates (*Figure 6*). The reason of extremely high value at arable S+A is unknown.

The trend of  $E_2/E_3$  and  $E_4/E_6$  were different, even though both of them were presumed to be a proxy of SOM polymerisation degree.  $E_4/$ E<sub>6</sub> indicated that the average polymerization degree of SOM is the highest in POM and lowest in the finest mineralogical fraction. This is in accordance with the traditional humus concept (Kononova, M.M. 1966), but contradicts the results of CHAUDHURI, S. et al. (2013) who reported a tendentious decrease in  $E_4/E_6$  value with maturation. Almost similar but they have got different values, which was also reported by NADI, M. et al. (2012). E<sub>2</sub>/E<sub>3</sub> did not indicate relevant differences among the fractions. Moreover, there was no considerable difference between the two land use types either.



*Fig.* 6. Photometric index values of SOM fractionated by the ZIMMERMANN, M. *et al.* (2007) method under different land uses URI = Ultraviolet Ratio Index;  $E_2/E_3$ = ratio between absorbance values at 254 and 365 nm;  $E_4/E_6$  = ratio between absorbance values at 465 and 665 nm; s+c, rSOC, S+A, POM = For explanation see *Fig.* 2.

#### Results of molecular size distribution

Most investigated organic substances had a polydisperse molecular size distribution. The histograms were bi-, trimodal or possessed even more peaks that referred to the heterogeneous compositions of SOM in each fraction (*Figure 7*).

There were trimodal distribution at both land uses concerning the POM fraction. The two higher molecular sized peaks were situated at the same size under both forest and crop field, whereas the lowest peak that dominated the forest sample was shifted upward under crop field. In general, this comparison implied that the forest had the relatively lower molecular-sized POM composition; however, there was no relevant difference measured by the photometric indexes.

In the aggregate fraction (S+A), the size difference between the forest and arable samples was the highest with a very wide range of large molecular sizes under the forest. Moreover, under forest, as it was expected, this fraction had the highest molecular size values compared to the others as was also reported by (TAN, K.H. *et al.* 2003). In case of S+A, the average molecular size was significantly lower under the arable land, even though photometric indexes revealed the opposite tendency.

However, the highest peaks indicated nearly the same modulus value in both cases at approximately 550–600 nm, though the distribution is obviously different regarding the s+c fraction. The arable sample seemed to be much more diverse, and was shifted to the lower size direction, although no changes were indicated by C/N ratio.

Concerning the rSOC in either case, the main peak was shifted downwards and became narrower compared with those of the whole s+c fraction. This suggested that oxidation (hypochlorite treatment for labile fraction removal) diminished the molecular size in both cases, however, the more intensive degradation occurred under the forest. Accordingly, *i*) oxidization could degrade SOM molecules in a wide size range; *ii*) molecular sizes rang-



*Fig. 7.* Soil organic matter molecular size distributions of the studied fractions (ZIMMERMANN, M. *et al.* 2007) under different land uses. Spectra are averages. – s+c, rSOC, S+A, POM = For explanation see *Fig. 2.* 

ing from 300–350 nm seemed to be more resistant, although other narrow peaks appeared depending on land use variations.

These spectra did not substantiate the results obtained from the photometric indexes, even though they were in line with the results of organo-mineral theory (i.e., POM is the direct function of plant cover, and aggregates contain the largest SOM molecules – MANZONI, S. and PORPORATO, A. 2009; BURD, A.B. *et al.* 2015).

SOM compositions of the soil fractions under arable land and forest were comparable, but quite different (*Figure 8*). SOM of the crop field demonstrated substantial diversity, both the highest-and lowest-sized SOM molecules were associated with POM. In this case SOM molecules were found to have a more or less continuous size distribution, whereas under forest the fractions seemed to be clustered around certain size values.



Fig. 8. SOM molecular size distribution of different fractions (ZIMMERMANN, M. et al. 2007) under arable (A) and forest (B) land uses. – s+c, rSOC, S+A, POM = For explanation see Fig. 2.

# Conclusions

Even though OM input and land use are presumed to be the primary driving forces of soil aggregation and SOM composition, no relevant difference was found in the volume of aggregation and aggregate stability due to former forest clearance and cultivation, however SOC and TN concentrations decreased significantly in the investigated smectite rich Luvisol. Therefore, the binding capability of this particular soil was presumed to be the function of rather SOM composition than SOC content. In contrast silt and clay associated SOM quantity did not change significantly. SOM composition proxies provided inconsistent results using the NaOH extraction method. Therefore, the application of organo-mineral SOM protection theory in association with the photometric proxies seems to be difficult in the present case.

On the other hand, photon correlation spectroscopy provided results in line with the published results of the organo-mineral stabilization theory that suggested alkali extraction with special care could be a useful alternative for such soils. However, due to the known imperfections of it, the application of in situ measurement methods would be preferable.

#### REFERENCES

- BARTHÈS, B.G., KOUAKOUA, E., LARRÉ-LARROUY, M.C., RAZAFIMBELO, T.M., DE LUCA, E.F., AZONTONDE, A., NEVES, C.S.V.J., DE FREITAS, P.L. and FELLER, C.L. 2008. Texture and sesquioxide effects on waterstable aggregates and organic matter in some tropical soils. *Geoderma* 143. (1–2): 14–25.
- BILANDŽIJA, D., ZGORELEC, Ž. and KISIĆ, I. 2017. Influence of tillage systems on short-term soil CO<sub>2</sub> emissions. *Hungarian Geographical Bulletin* 66. (1): 29–35.
- BRONICK, C.J. and LAL, R. 2005. Soil structure and management: a review. *Geoderma* 124. (1–2): 3–22.
- BURD, A.B., FREY, S., CABRE, A., ITO, T., LEVINE, N.M., LØNBORG, C., LONG, M., MAURITZ, M., THOMAS, R.Q., STEPHENS, B.M., VANWALLEGHEM, T. and ZENG, N. 2015. Terrestrial and marine perspectives on modelling organic matter degradation pathways. *Global Change Biology* 22. (1): 121–136. DOI:10.1111/ gcb.12987

- BUURMAN, P., VAN LAGEN, B. and VELTHORST, E.J. (eds.) 1996. Manual for soil and water analysis. Leiden, The Netherlands, Backhuys Publishers.
- CENTERI, CS., JAKAB, G., SZABÓ, SZ., FARSANG, A., BARTA, K., SZALAI, Z. and Bíró, Zs. 2015. Comparison of particle-size analysing laboratory methods. *Environmental Engineering and Management Journal* 14. (5): 1125–1135.
- CHATIGNY, M.H. 2003. Dissolved and water-extractable organic matter in soils: A review on the influence of land use and management practices. *Geoderma* 113. (3–4): 357–380.
- CHAUDHURI, S., MCDONALD, L.M., SKOUSEN, J. and PENA-YEWTUKHIW, E.M. 2013. Soil organic carbon molecular properties: effects of time since reclamation in a minesoil chronosequence. *Land Degradation & Development* 26.(3): 237–248. DOI: 10.1002/ldr.2202
- COLEMAN, K. and JENKINSON, D.S. 1996. RothC-26.3 – A Model for the turnover of carbon in soil. In *Evaluation of Soil Organic Matter Models*. Eds.: POWLSON, D.S., SMITH, P. and SMITH, J.U., NATO ASI Series I: Global Environmental Change 38. Berlin–Heidelberg, Springer, 237–246.
- COOLS, N., VESTERDAL, L., DE VOS, B., VANGUELOVA, E. and HANSEN, K. 2014. Tree species is the major factor explaining C:N ratios in European forest soils. *Forest Ecology and Management* 311. 3–16.
- CROW, S. E., SWANSTON, C. W., LAJTHA, K., BROOKS, J.R. and KEIRSTEAD, H. 2007. Density fractionation of forest soils: methodological questions and interpretation of incubation results and turnover time in an ecosystem context. *Biogeochemistry* 85. 69–90.
- DENCSŐ, M., TÓTH, E., GELYBÓ, GY., KÁSA, I., HOREL, Á., RÉKÁSI, M., TAKÁCS, T., FARKAS, CS., POTYÓ, I. and UZINGER, N. 2017. Changes in the moisture content and respiration of a calcareous sandy soil after combined treatment with biochar and compost or mineral fertiliser. Agrokémia és Talajtan 66. (1): 79–93. (In Hungarian with English abstract.)
- Dövényi, Ż. (ed.) 2010. *Inventory of microregions in Hungary*. Budapest, MTA FKI. (In Hungarian.)
- ESFAHANI, M.R., STRETZ, H.A. and WELLS, J.M.M. 2015. Abiotic reversible self-assembly of fulvic and humic acid aggregates in low electrolytic conductivity solutions by dynamic light scattering and zeta potential investigation. *Science of the Total Environment* 537. 81–92.
- FALKENGREN-GRERUP, U., BRINK, D.J. and BRUNET, J. 2006. Land use effects on soil N, P, C and pH persist over 40–80 years of forest growth on agricultural soils. *Forest Ecology and Management* 225. 74–81.
- FILEP, T., DRASKOVITS, E., SZABÓ, J., KOÓS, S., LÁSZLÓ, P. and SZALAI, Z. 2015. The dissolved organic matter as a potential soil quality indicator in arable soils of Hungary. *Environmental Monitoring and Assessment* 187. 1–12.

- FORTUNA, A., HARWOOD, R.R. and PAUL, E.A. 2003. The effects of compost and crop rotations on carbon turnover and the particulate organic matter fraction. *Soil Science* 168. (6). 434–444.
- GALANTINI, J.A., SENESI, N., BRUNETTI, G. and ROSELL, R. 2004. Influence of texture on organic matter distribution and quality and nitrogen and sulphur status in semiarid Pampean grassland soils of Argentina. *Geoderma* 123. (1–2): 143–152.
- GOEBEL, M., BACHMANN, J., WOCHE, S.K. and FISCHER, W.R. 2005. Soil wettability, aggregate stability, and the decomposition of soil organic matter. *Geoderma* 128. (1–2): 80–93.
- GUO, M. and CHOROVER, J. 2003. Transport and fractionation of DOM in soil columns. *Soil Science* 168. 108–118.
- HASSINK, J. 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant and Soil* 191. 77–87.
- HER, N.G., AMY, G., SOHN, J. and GUNTEN, U. 2008. UV absorbance ratio index with size exclusion chromatography (URI-SEC) as an NOM property indicator. *Aqua* 57. (1): 35–46.
- IUSS Working Group WRB 2015. World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. Rome, FAO.
- JAKAB, G., SZABÓ, J., SZALAI, Z., MÉSZÁROS, E., MADARÁSZ, B., CENTERI, CS., SZABÓ, B., NÉMETH, T. and SIPOS, P. 2016. Changes in organic carbon concentration and organic matter compound of erosion-delivered soil aggregates. *Environmental Earth Sciences* 75. 144–155.
- JANCSOVSZKA, P. 2016. Sustainable development goals (SDGs). *Tájökológiai Lapok* 14. (2): 71–181. (In Hungarian with English abstract.)
- JOHN, B., YAMASHITA, T., LUDWIG, B. and FLESSA, H. 2005. Storage of organic carbon in aggregate and density fractions of silty soils under different types of land use. *Geoderma* 128. (1–2): 63–79.
- KÁSA, I., MOLNÁR, S. and HOREL, Á. 2016. Net changes in nitrification in cultivated soil as a function of temperature and the type and concentration of biochar. Agrokémia és Talajtan 65. (2): 297–311. (In Hungarian with English abstract.)
- KONONOVA, M.M. 1966. Soil Organic Matter. Its Nature, its Role in Soil Formation and in Soil Fertility. Oxford, Pergamon Press.
- LEHMANN, J. and KLEBER, M. 2015. The contentious nature of soil organic matter. *Nature* 528. 60–68.
- LEHMANN, J., SOLOMON, D., KINYANGI, J., DATHE L., WIRICK, S. and JACOBSEN, C. 2008. Spatial complexity of soil organic matter forms at nanometre scales. *Nature Geoscience* 1. 238–242.
- LÜTZOW, M., KÖGEL-KNABNER, I., EKSCHMITT, K., MATZNER, E., GUGGENBERGER, G., MARSCHNER, B. and FLESSA, H. 2006. Stabilization of organic matter

in temperate soils: mechanisms and their relevance under different soil conditions – a review. *European Journal of Soil Science* 57. (4): 426–445. DOI:10.1111/ j.1365-2389.2006.00809.x

- MANZONI, S. and PORPORATO, A. 2009. Soil carbon and nitrogen mineralization: Theory and models across scales. *Soil Biology and Biochemistry* 41. (7): 1355–1379.
- MENG-YUN, L., QING-RUI, C., YAN-BING, Q., JING, L. and TAO, C. 2014. Aggregation and soil organic carbon fractions under different land uses on the tableland of the Loess Plateau of China. *Catena* 115. 19–28.
- MIKA, J. and FARKAS, A. 2017. Sensitivity of inland water bodies, natural vegetation and agriculture to weather extremes and to climate change. *Tájökológiai Lapok* 15. (2): 85–90. (In Hungarian with English abstract.)
- MUELLER, C.W., HOESCHEN, C., STEFFENS, M., BUDDENBAUM, H., HINKEL, K., BOCKHEIM, J.G. and KAO-KNIFFIN, J. 2017. Microscale soil structures foster organic matter stabilization in permafrost soils. *Geoderma* 293. (1–2): 44–53.
- NADI, M., SEDAGHATI, E. and FULEKY, GY. 2012. Evaluation of humus quality of forest soils with two extraction methods. *International Journal of Forest*, *Soil and Erosion* 2. (3): 124–127.
- NÉMETH, T. and SIPOS, P. 2006. Characterization of Clay Minerals in Brown Forest Soil Profiles (Luvisols) of the Cserhát Mountains (North Hungary). Agrokémia és Talajtan 55. 39–48. (In Hungarian with English abstract.)
- NIEROP, KGJ, VAN LAGEN, B. and BUURMAN, P. 2001. Composition of plant tissues and soil organic matter in the first stages of a vegetation succession. *Geoderma* 100. (1–2): 1–24.
- PALMER, N.E. and WANDRUSZKA VON, R. 2001. Dynamic light scattering measurements of particle size development in aqueous humic materials. *Fresenius' Journal of Analytical Chemistry* 371. 951–954.
- PLAZA-BONILLA, D., ALVARO-FUENTES, J. and CANTERO-MARTÍNEZ, C. 2014. Identifying soil organic carbon fractions sensitive to agricultural management practices. *Soil & Tillage Research* 139. 19–22.
- POEPLAU, C., DONA, A., DONDINI, M., LEIFELD, J., NEMOD, R., SCHUMACHER, J., SENAPATI, N. and WIESMEIER, M. 2013. Reproducibility of a soil organic carbon fractionation method to derive RothC carbon pools. *European Journal of Soil Science* 64. 735–746. DOI: 10.1111/ejss.12088
- RABBI, F.S.M., WILSON, B.R., LOCKWOOD, P.V., DANIEL, H. and YOUNG, I.M. 2014. Soil organic carbon mineralization rates in aggregates under contrasting land uses. *Geoderma* 216. (1–2): 10–18.
- REDDY, S., NAGARAJA, M.S., PUNITH RAJ, T.S., POLICE PATIL, A.S. and DHUMGOND, P. 2014. Elemental Analysis,  $E_4/E_6$  Ratio and Total Acidity of Soil Humic and Fulvic Acids From Different Land Use Systems. Annals of Plant and Soil Research 16. (2): 89–92.

RICE, J.A. 2001. Humin. Soil Science 166. 848-857.

- RIEDER, Á., MADARÁSZ, B., SZABÓ, J.A., ZACHÁRY, D., VANCSIK, A., RINGER, M., SZALAI, Z., and JAKAB, G. 2018. Soil Organic Matter Alteration Velocity due to Land-Use Change: A Case Study under Conservation Agriculture. *Sustainability* 10. 943. 1–11.
- Rowel, D.L. 1994. *Soil science: methods and applications*. London, Prentice Hall. 350 p.
- Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S. and Trumbore, S.E. 2011. Persistence of soil organic matter as an ecosystem property. *Nature* 478. 49–56. DOI:10.1038/nature10386
- SIPOS, P. 2004. Geologic and pedogenic effects on heavy metal distributions in forest soils from the Cserhát Mountains and the Karancs area, NE Hungary. Acta Geologica Hungarica 47.(4): 411–429.
- SIX, J., CONANT, R.T., PAUL, E.A. and PAUSTIAN, K. 2002. Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. *Plant and Soil* 241. 155–176.
- SPACCINI, R. and PICCOLO, A. 2013. Effects of field managements for soil organic matter stabilization on water-stable aggregate distribution and aggregate stability in three agricultural soils. *Journal of Geochemical Exploration* 129. 45–51.

- STEVENSON, F.J. 1982. Humus Chemistry. Genesis, Compositions, Reactions. 2<sup>nd</sup> edition. New York, Wiley and Sons Inc.
- SZALAI, Z., SZABÓ, J., KOVÁCS, J., MÉSZÁROS, E., ALBERT, G., CENTERI, CS., SZABÓ, B., MADARÁSZ, B., ZACHÁRY, D. and JAKAB, G. 2016. Redistribution of Soil Organic Carbon Triggered by Erosion at Field Scale Under Subhumid Climate, Hungary. *Pedosphere* 26. (5): 652–665.
- TAN, K.H. 2003. Humic Matter in Soil and the Environment Principles and Controversies. New York, Marcel Dekker Inc. USA
- WANG, K. and XING, B. 2005. Structural and sorption characteristics of adsorbed humic acid on clay minerals. *Journal of Environmental Quality* 34. 342–349. DOI:10.2134/jeq2005.0342
- WIESMEIER, M., HÜBNER, R., SPÖRLEIN, P., GEU, U., HANGEN, E., REISCHL, A., SCHILLING, B., VON LÜTZOW, M. and KÖGEL-KNABNER, I. 2014. Carbon sequestration potential of soil in southeast Germany derived from stable soil organic carbon saturation. *Global Change Biology* 20. 653–665.
- ZIMMERMANN, M., LEIFELD, J., SCHMIDT, M.W.I., SMITH, P. and FUHRER, J. 2007. Measured soil organic matter fractions can be related to pools in the RothC model. European Journal of Soil Science 58. 658–667.