Environmental Engineering and Management Journal

May 2015, Vol.14, No. 5, 1125-1135
http://omicron.ch.tuiasi.ro/EEMJ/

"Gheorghe Asachi" Technical University of Iasi, Romania

COMPARISON OF PARTICLE-SIZE ANALYZING LABORATORY METHODS

Csaba Centeri[1*], Gergely Jakab[2], Szilárd Szabó[3], Andrea Farsang[4], Károly Barta[4], Zoltán Szalai[2], Zsolt Bíró[5]

[1]Szent István University, Institute of Environmental and Landscape Management, Department of Nature Conservation and Landscape Ecology, H-2100, Gödöllő, Páter K. u. 1., Hungary
[2]Hungarian Academy of Sciences, Research Centre for Astronomy and Earth Sciences, Geographical Institute, H-1112, Budapest, XI. Budaörsi út 45., Hungary
[4]University of Szeged, Department of Physical Geography and Geoinformatics, H-6720, Szeged, Egyetem u. 2., Hungary
[3]Debrecen University, Department of Physical Geography and Geoinformation Systems, 4032-Debrecen, Egyetem tér 1., Hungary
[5]Szent István University, Institute for Wildlife Conservation, H-2100, Gödöllő, Páter K. u. 1., Hungary

Abstract

Particle size distribution is one of the most influential factors of most soil physical and even some soil chemical characteristics. As modern measurement techniques are being introduced, the need for comparing new methods with older methodologies arises because comparability means data continuity. Here, three institutes conducted a comparison of particle size measurement among the laser, areometer and pipette techniques. The purpose of the comparison was to a) discover any differences among operators, laboratories, and techniques; b) identify if there were any differences and if they could be linked to soil type (e.g. high clay, loam, or sand content) or particle size range; and c) understand if the laser diffraction method gave results that were significantly larger than the other methods of any size fraction.
There was no statistically proven difference between the two operators examined based on the pipette method's result. The comparison of two of the institutes' pipette methods showed statistically significant differences for three of the eight samples tested. However, these differences only seemed to appear in the 0.01 mm to 0.02 mm particle size range. A technical comparison among all three methods resulted in significant differences in all cases except for one sample that had very high sand content and very low clay content. Finally, the laser diffraction method was analyzed to see if it measured a larger amount of the clay fraction, however, it instead overestimated the silt and the fine sand (0.01 mm to 0.02 mm) fraction, not the clay fraction.
Therefore, we conclude that different methodologies can provide significant difference in particle-size measurement. Based on the results, we recommend creating a widely accepted patent for sample preparation (disaggregation, the use of peroxide or other agents, using ultrasonic or other methods) and for measuring techniques (a set of refractive and sorption indexes, using ultrasonic during the measurement, pump speed etc.).

Key words: areometer, laser diffractometry, pipette method, soil fractions

Received: November, 2013; Revised final: October, 2014; Accepted: October, 2014

1. Introduction

Particle size plays an important role in many soil processes such as aggregate stability (Zauca et al., 2013), fluvial morphology (Cartacuzencu et al., 2014), pollution (Karbassi et al., 2014) and in various areas of life and science. Knowledge on particle size distribution is used for many purposes. Salter et al. (1966) analyzed the quantitative relationship between particle size, compaction and available water capacity. Gupta and Larson (1979) estimated soil water retention characteristics from particle size distribution, organic matter content and bulk density data. Gupta (1979) used particle-size distribution data

[*] Author to whom all correspondence should be addressed: e-mail: Centeri.Csaba@kti.szie.hu; Phone: +36 28522000/1697; Fax: +36 28410804

to predict packing density of soils with modelling. Arya and Paris (1981) predicted soil moisture content based partly on particle size distribution translated to pore-size distribution. Finally, since measuring particle-size is costly, there are increasing efforts to estimate soil particle size distribution from limited data. Skaggs (2001) estimated particle-size distribution from limited soil texture data.

Particle size distribution measurement has a long history. Lea and Nurse (1947) have previously published results on a symposium specifically organized for exchanging knowledge on particle-size analyses in 1947. The hydrometer (also called areometer) method was one of the first introduced (Bouyoucos, 1962). The original patent most likely was published in the USA, filed in 1959 and printed in 1964 (Rich, 1964). In 1965, the methodology of particle size analyzes was also published in the USA (Day, 1965).

There are several detailed descriptions of this methodology available in literature explaining soil particle size measurements as part of normal soil analysis methods (Tan, 1996) or describing particle size measurements in general (Rich, 1964). Finally, there are articles concerned about the basics of soil particle size measurements, e.g. dealing with sphere size and settling velocity (Gibbs et al., 1971).

1.1. Determination techniques

Due to its lengthy history, determination of particle size has several techniques with different grades of precision. All results are biased, however, by the fact that we can only express particle diameter referring to a sphere, yet, particles are of layered plates and sticks.

There is no common agreement on, e.g., the preparation of the samples; the methods used for the measurements or even the analysis (Nemes et al., 1999) used to evaluate the results (Kun et al., 2013; Mako et al., 2014). Sample preparation methods vary widely, and the disaggregating steps most often used are the application of sodium salts (sodium-pyrophosphate, -hexametaphosphate etc.), H_2O_2, ultrasonic treatment or heating. Kondrlová et al. (2012) reported that disaggregation in soil paste is more effective than that in dilute liquids.

1.1.1. Classical methods

In the 1980s, the pipette method was the most widely accepted method in particle size determination (Indorante et al., 1990), using a gravitational method that uses the Stoke's Law (Gee and Or, 2002). The areometer method is also based on settlement times and periodic density measurement. An areometer is an air filled glass tube that is able to measure density based on buoyancy in the suspension. The depth of immersion and the measured suspension's density in each trial allows for the opportunity to calculate the actual particle's diameter and the adherent weight in percent. The classical pipette and areometer methods have been dominant in laboratory practice for several decades (Andrenelli et al., 2013; Bouyoucos, 1927; Naguib and Bedaiwy, 2012). The areometer method was the simplest and fastest method but the pipette method was the most accurate (Naguib and Bedaiwy, 2012).

Due to the fact that both methods were time consuming, loaded with errors and needed a very large (at least 10 g) soil or sediment sample, the last 10-15 years has brought new techniques (e.g. laser diffractometry) that have begun to succeed the previous ones (Andrenelli et al., 2013; Beuselinck et al., 1998).

1.1.2. Laser diffraction

The laser diffraction technique is now used and accepted throughout the world (Eshel et al., 2004), yet, the equivalency of the results measured by classical and by laser diffraction techniques has not yet been clarified, even though some efforts have been made (Andrenelli et al., 2013; Goossens, 2008; Müller et al., 2009).

Compared with classical measurements such as sieving, sedimentation or image analysis, laser diffraction offers valuable advantages:

- low sample need,
- short analysis times (Loizeau et al., 1994),
- good reproducibility and precision (Jonkers et al., 2009),
- simple calibration (Frake et al., 1998),
- large measuring range – very detailed classification (Buurman et al., 1997),
- high flexibility.

An additional benefit is the possibility of a very detailed classification of particle sizes (Buurman et al., 1997).

The refractive index of the soil particles is a key parameter needed for proper interpretation using the Mie theory on the measured data, especially in the smaller particle size range (<10μm) (Arriaga et al., 2006). Since soil is a very heterogeneous material it is hard to find an adequate refractive index value, which represents the whole material.

Although the methods are based on different principles, there is an express need to translate the results to a common ground. The best correlation between the pipette and laser method was found in the case of sand, while clay seemed to be the most problematic component (Di Stefano et al., 2010). According to Konert and Vandenberghe (1997) the laser method consistently underestimates the ratio of clay fraction (<2 μm) because of the lamellar shape of some clay minerals and because of the refractive index effect. They found that the clay fraction (<2 μm) measured using the sedimentation method is equivalent to the fraction below 8μm measured using the laser method. Finally, Beuselnick et al. (1998) also underline the role of particle shape in the clay fraction.

The objective of this study is to compare the results of various methods used on different soils. The purpose of this comparison is to a) discover any differences among operators, laboratories, and

techniques; b) identify any differences and if these could be linked to soil type (e.g. high clay, loam, or sand content) (Buchan, 1993), or particle size range; and c) understand if the laser diffraction method gives results that are significantly larger than the other methods of any size fraction (Beuselinck et al., 1998; Goossens, 2008).

2. Experimental

Eight soil samples of topsoil (0-10 cm) were collected from various regions of Hungary (Fig. 1). The samples represent a wide pallet of soil texture and soil structure. In some samples there was not any relevant aggregating agent among the coarse particles (i.e. TUR, KMA, Table 1).

In other samples higher clay content was found with significant additional inorganic and humus colloid content that resulted in more stable aggregates (i.e. samples from the BOR, GFH and GAH (Table 1)).

Three institutions participated in the measurements, in which eight samples were collected from seven locations and three analysis methods were used. Codification of all information is in Table 1.

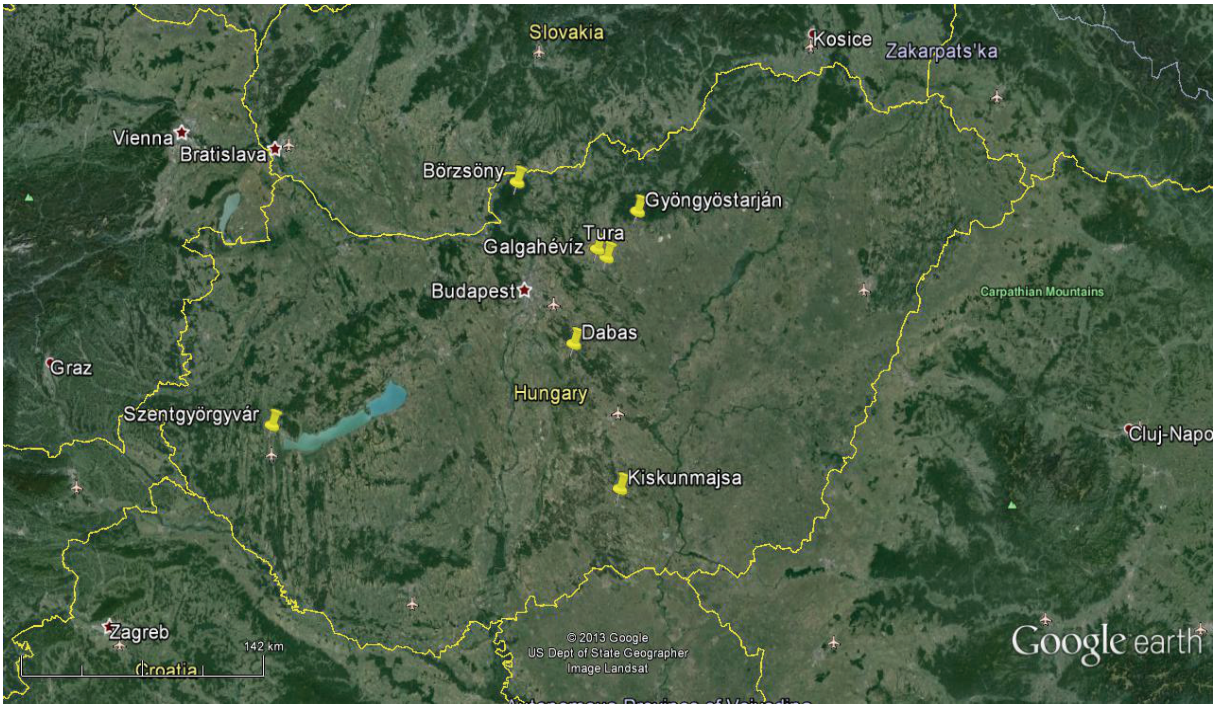

Fig. 1. Sampling sites in Hungary

Table 1. Encoding of participating institutes, sampling sites and repetitions

Participating institutes	***Code***
Geographical Institute, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences	F
University of Debrecen	D
University of Szeged	S
Sampling sites	***Code***
Börzsöny Mountain	BOR
Dabas	FES
Galgahévíz	GAL
Gyöngyöstarján, Mátra Mountain, lower slope section	GAH
Gyöngyöstarján, Mátra Mountain, upper slope section	GFH
Kiskunmajsa	KMA
Szentgyörgyvár, Zala Hills	SZG
Tura	TUR
Measurement method	***Code***
Laser method	L
Pipette method, laboratory staff No. 1.	
Pipette method, laboratory staff No. 2.	
Repetitions	
Repetition 1	
Repetition 2	

2.1. The Laser Particle Sizer Analysette 22 MicroTech method applied

During the preparation process rganic matter was not removed from the soil. Sample preparation was applied using sodium pyrophosphate to disperse the aggregated particles into elemental grains according to the Hungarian patent (MSZ 08-0205-1978) for particle sizing. 20 g of sample (air-dried) was dispersed in 25 ml of sodium pyrophosphate (0.5 n) for 24 hours.

After the disaggregation the suspension was leached through a 500 μm sieve in order to remove the coarse fraction then measured in the diffractometer. During the four-minute long measurement process permanent ultrasonic disaggregation was applied (Madarász et al., 2012; Makó et al., 2014). The volume of the coarse fractions (>500 μm) were calculated on the basis of the sieving results

The "Analysette 22" applies a helium-neon laser with a wavelength of 655 nm, below 5 mW for measurement (Fritsch GmbH, 2005). The diffracted beams are gathered by a Fourier lens onto the detector. The calculating routine is based on the Mie theory (Mie, 1908) to predict particle-size distribution from the intensity of the diffracted light pattern. The particles are groupped into 102 separate size classes. One calculation is an average of 180 scans of the sample hence no repetitions are needed.

2.2. The Köhn-pipette method

Measurements were taken on the basis of Buzás (1993) according to the Hungarian patent for particle size distribution (MSZ-08-0205-1978, 1978).

The soil samples after the preparation process (i.e. sieving with Ø=0.2 mm mesh size and organic matter (OM) removal with H_2O_2) were placed into a mortar with water then continuous rubbing was applied. At the end of the process, the smallest size fraction was poured into a sedimentation vessel. This procedure was repeated until the complete desappearence of the fine particles in the mortar was reached. The suspension was expanded to 1000 ml applying distilled water. In order to prevent coagulation 10 ml 0.2 M sodium-oxalate was added since aggregation is hardly pH dependent (Zauca et al., 2013). The settling time of 10 cm-s was used for calculation within the suspension. After the perfect settlement of the finest (<0.001 mm) fraction, the pipetted samples were dried at 105 °C and weighted.Comparing the dry weights of the individual pipetted samples to that of the initial amount of soils, particle size distribution was received.

2.3. The areometer method applied

This method is based on Stokes' law as well. Preparation was similar to the pipette method: first, organic matter was removed by oxidation with H_2O_2, and an air-dried sample of a minimum of 100 g was sieved until it was 0.063 mm in diameter. If there was any cohesion between particles, continuous rubbing was applied. Suspension was made from 20-60 g samples (the quantity depended on the plasticity index) in small steps: after wetting samples they were mixed and tempered repetedly in order to reach individual particles. Consecutively, the moisture of the original sample was determined with gravimetry. We added 0.5-1 g sodium-pyrophosphate to the suspension to prevent coagulation, and then added distilled water until a total volume of 1000 cm^3 was achieved.

Settlement started and the main different compared to pipette method was the measurement of settling speed. Here, the density of soil suspension must be and was measured at different times (30 s until 24 h) by the areometer (Buzás, 1993; MSZ 14043/3: 1979).

2.4. Statistical analyses

We compared the different methods (areometer, pipette, laser diffraction) to reveal whether the ratio of the fractions were different. We used the Kruskal-Wallis test for the comparison and we conducted a *post hoc* test to explore which methods differed from the others using the Mann-Whitney test (Sokal and Rohlf, 1969).

Furthermore, the pipette method was applied in two institutes (University of Debrecen and University of Szeged); thus, we analyzed the difference between the results by fractions with the Mann-Whitney test and calculated the Monte Carlo p (permutation test of 9999 repetitions). We calculated the effect size for each comparison that quantified the magnitude of difference in a standardized and comparable way (Cohen, 1992). Its values ranged from 0 to 1 indicating the importance of an effect (0 meant the lack of any effects and 1 signed perfect effect (Field, 2009)).

The Kruskal–Wallis test is most commonly used when there is one categorical variable and one ratio/ordinal variable—the latter does not meet the normality assumption of an ANOVA, it is the non-parametric analogue of a one-way ANOVA.

Like most non-parametric tests, it is performed on ranked data, so data observed in scale level are converted to their ranks in the overall data set: the smallest value gets a rank of 1, the next smallest gets a rank of 2 etc. (McDonald, 2009). The Mann–Whitney U-test's independent variable is limited to categorical variables with only two values. It is the non-parametric analogue to Student's t-test (McDonald, 2009).

The Chi-square test is used to determine if a single categorical variable has the same distribution in 2 (or more) distinct populations from 2 (or more) samples. The Chi-square (λ^2) test assesses the independence of two variables and also, how well a

theoretical model or set of a priori probabilities fits a set of data (goodness of fit). In both cases the test is typically thought of as a nonparametric procedure involving observed (O) and expected (E) frequencies.

The expected frequencies may be determined either theoretically or empirically. The basic formula for calculating λ^2 is given by Eq. (1).

$$\lambda^2 = \sum\left[\frac{(0-E)^2}{E}\right] \quad (1)$$

3. Results and discussion

3.1. Comparison of the results of measuring particle size distribution by two operators in the laboratory using the pipette method

The results of two laboratory personnel were compared in the case of the pipette method in order to analyze the influence of "human factors". This trial was only done at the Debrecen University. The results of measurements by these two laboratory operators are in Table 2.According to the χ^2 test there was no significant difference between the results of measuring particle size distribution by the two laboratory operators (Table 3).

Due to fractions having non-detectable amounts of smaller particles, the sample KMA was the closest to the significant difference ($p<0.05$) regardless of the fact that it was a soil dominated by sand with minimal proportions of other fractions.

Analysis of the "human factor" helped us to disclose the effect of personal attitude towards the measurements. The next step was to compare the results of the two universities using the pipette method.

3.2. Comparison of the results of measuring particle size distribution in two institutes using the pipette method

The results of the measurements with the pipette method used by the University of Debrecen and the University of Szeged are seen in Table 4.

Statistical analysis of the results with the λ^2 test proved differences in the case of 3 of the 8 examined soil samples (Fig. 2):

- in the case of the soil sample from the volcanic Börzsöny Mountain (BOR),
- the soil sample from the volcanic Mátra Mountain (GAH, lower section of the slope) and
- the soil sample from the sandy lowlands of the Galga Creek (TUR) (Table 5).

In all three cases with significant differences there were the largest differentiations in the case of the sand fraction. Szeged University consequently measured much less of the fine fraction than the University of Debrecen and twice as much of the coarse sand fraction. This means that – regardless of using the same patent – Szeged University did not manage to disaggregate the coarse sand particles.

Table 2. The results of particle size analysis using the pipette method from two laboratory operators at the Debrecen University; the averages of three parallel measurements are given

Site codes	*Particle size categories (mm)*											
	<0.002		*0.002-0.005*		*0.005-0.01*		*0.01-0.02*		*0.02-0.05*		*0.05-2*	
	(%)											
	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2
BOR	4.8	5.0	3.4	5.6	8.1	9.6	13.2	12.9	20.8	21.7	49.7	45.3
GAH	29.2	30.1	13.8	16.0	13.2	11.4	14.3	12.6	16.8	18.5	12.7	11.6
GFH	27.4	23.9	14.0	17.1	14.4	13.3	15.9	13.0	14.9	17.7	13.3	15.1
SZG	6.9	7.3	8.8	8.6	12.1	11.6	17.3	17.1	28.0	27.6	26.8	28.0
TUR	29.2	26.4	12.8	14.7	12.4	11.7	14.7	11.5	17.6	20.3	13.3	15.6
KMA	0.0	0.3	0.0	0.1	0.0	0.1	1.9	0.2	3.5	1.4	94.7	97.9
FES	7.2	6.0	4.7	5.0	6.5	7.15	10.1	11.2	20.0	22.3	51.6	48.35
GAL	6.8	7.3	7.7	8.1	11.1	10.8	18.4	18.1	37.0	34.3	19.0	21.5

P1= laboratory staff No. 1., P2= laboratory staff No. 2.

Table 3. The results of statistical analysis of the differences between particle size measurements of two laboratory operators using the pipette method

Sample code	*Results of χ^2 test*
D_BOR_P	χ^2=0.874, df=5, NS
D_GAH_P	χ^2=0.539, df=5, NS
D_GFH_P	χ^2=1.246, df=5, NS
D_SZG_P	χ^2=0.049, df=5, NS
D_TUR_P	χ^2=1.043, df=5, NS
D_KMA_P	χ^2=2.747, df=5, NS
D_FES_P	χ^2=0.437, df=5, NS
D_GAL_P	χ^2=0.304, df=5, NS

NS = not significant at p<0.05 level (critical value: 11.07)

Table 4. The results of particle size analysis using the pipette method at the University of Debrecen (D) and the University of Szeged (S)

Site codes	*Particle size categories (mm)*											
	<0.002		*0.002-0.005*		*0.005-0.01*		*0.01-0.02*		*0.02-0.05*		*0.05-2*	
	(%)											
	S	D	S	D	S	D	S	D	S	D	S	D
BOR	4.67	4.88	2.35	4.30	1.96	8.68	4.25	13.04	6.62	21.14	80.14	47.96
GAH	38.76	29.56	11.13	14.68	10.03	12.50	7.42	13.58	1.09	17.46	31.57	12.22
GFH	36.43	26.02	14.09	15.20	10.94	13.96	9.60	14.76	11.59	16.04	17.36	14.02
SZG	9.90	7.06	7.74	8.72	10.41	11.86	12.60	17.22	24.74	27.86	34.61	27.28
TUR	18.33	28.06	10.44	13.54	10.00	12.12	10.21	13.40	17.07	18.68	33.95	14.20
KMA	0.40	0.15	1.82	0.05	0.11	0.05	0.74	1.03	0.20	2.43	96.73	96.30
FES	11.78	6.70	6.36	4.80	7.33	6.76	8.90	10.52	15.59	20.92	50.04	50.30
GAL	10.15	6.98	5.53	7.86	8.11	10.98	12.38	18.26	32.70	35.94	31.14	19.98

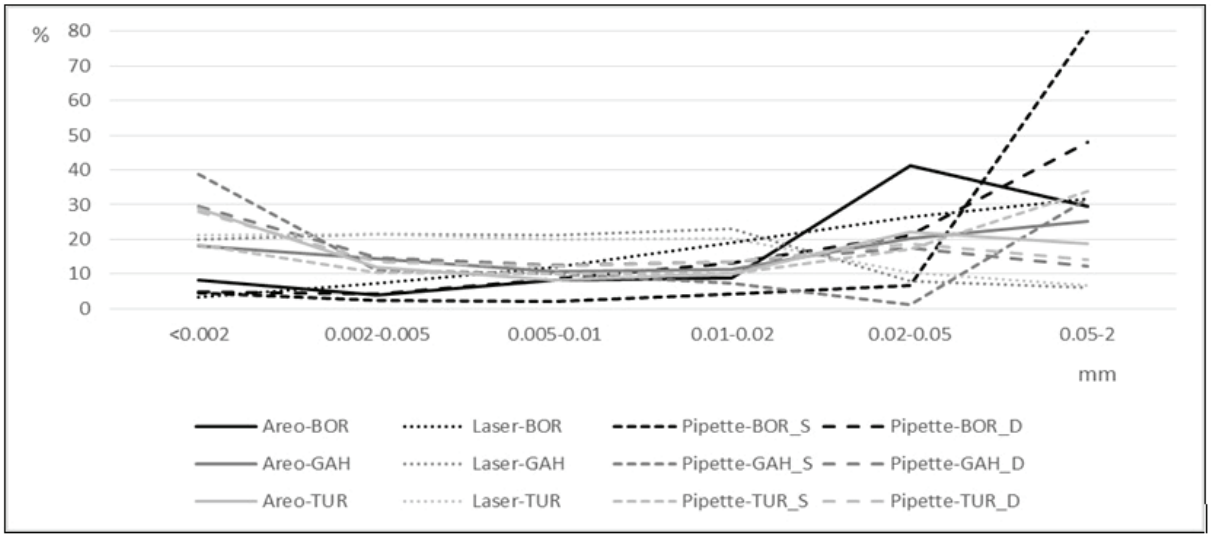

Fig. 2. Particle size curves of the samples having significant differences with the λ^2 test

Table 5. The results of the statistical analysis from the comparison of particle-size measurements using the pipette method of 8 soils of Hungary from two institutes

Site codes	*Results of χ^2 test*	*Site codes*	*Results of χ^2 test*
BOR	χ^2=24.96, df=5, p<0.001	TUR	χ^2=11.248, df=5, p<0.05
GAH	χ^2=26.795, df=5, p<0.001	KMA	χ^2=3.735, df=5, NS
GFH	χ^2=4.311, df=5, NS	FES	χ^2=2.55, df=5, NS
SZG	χ^2=2.396, df=5, NS	GAL	χ^2=5.144, df=5, NS

NS = not significant

This phenomenon occurred only in the case of these three samples. This might lead us to the assumption that there are environmental effects responsible for these results. One common environmental factor is the andesite parent material in the case of BOR and GAH, however TUR has a loess sand parent material. Furthermore, GFH differs from GAH in the rate of erosion, so the majority of the environmental background is similar. This is the case with the materials that help glue the soil particles in larger aggregates. If the reason of weak disaggregation by any of the participating laboratories is because of the big clay or TOC content, then GFH and GAH should have behaved similarly. On the other hand, selective erosion of the soil organic matter might cause differences in aggregate stability (Navas et al., 2009) and thus can lead to weak(er) disaggregation by a laboratory.

Fractions were also compared after the assessment of the sample sites. Measurements with the pipette method in the two institutes appeared to be similar at each fraction except between the range of 0.01-0.02 mm. In this fraction, measured values had differing inter-quartile ranges (Fig. 3).

Nevertheless, in spite of non-significant results, fractions of 0.002-0.005, 0.02-0.05 and 0.05-2 mm reflected a large effect (r=-0.60) indicating the variability of the results (Table 6).

Although the differences in the case of 0.005-0.01, 0.02-0.05 and 0.05-2 mm fractions were not significant, these effect sizes (r = -0.37) can be considered as “moderate”, according to Field (2009).

The areometer method was only used at the University of Szeged while laser diffractometry method was only used at the Geographical Institute (RCSES).

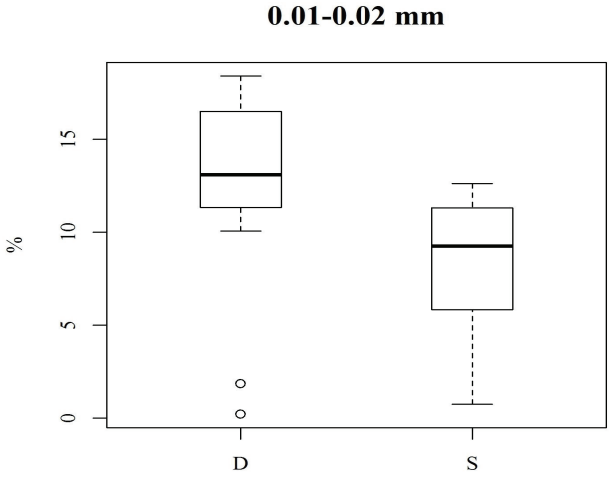

Fig. 3. Differing interquartile ranges in 0.01-0.02 mm fraction, using the pipette method at the University of Debrecen and the University of Szeged

3.3. The results and discussion of particle size analyses with all methods used

In this section analyses of all methods (pipette, areometer and laser diffractometry) used is shown (Table 7). The results, shown in Table 7, differed from all previous data because in this case an average value was used for the formerly analyzed pipette method, except for the sites BOR, GAH and TUR where there were significant differences between the results of the two institutes using the pipette method.

The comparison including all methods (laser, pipette and areometer) resulted in significant differences in all cases except KMA (Table 8). In the case of the measurements with laser diffractometry, smaller particles (<20 μm) were present in larger proportion (except in case of KMA) than in the case of measuring with pipette or areometer methods.

This is of high importance as sample preparation of laser measurement did not included the oxidation of OM. Based on this measurement, we can assume that organic aggregate bindings have a larger relevance in micro-aggregates than in larger ones. Although, Watteau et al. (2012) found the largest SOC content in the fraction of 50-200 μm, inorganic carbon dominates in the fraction of 2-20 μm. This therefore confirms the efficiency of ultrasonic treatment (only in case of laser measurements) as it was able to separate the aggregates without oxidization of OM. Based on Madarász et al. (2012), ultrasonic has the best separating efficiency in the whole fraction range; here, it performed well in the sand fraction.

The results from the Debrecen University measured with the pipette method were closer to the results measured with the laser diffractometry than those measured at the Szeged University, and can be seen from the smaller differences (smaller λ^2 values and significance levels). This explained the former statistical analysis where only the pipette method was analyzed: the Debrecen University measured smaller amounts from coarser fractions and larger amounts of the finer fractions as well as in the case of the results using the laser diffractometry.

3.4. Comparison of the accuracy of methods in the analyzed fractions (methods versus fractions)

We found significant differences among the applied methods in the case of fractions between 0.002-0.05 mm (Table 9) except between the areometer and pipette methods, which had no significant differences; however, laser diffraction differed from both traditional methods. Effect sizes also identified statistically proven differences on the results of laser diffraction. Significant differences of the paired analysis corresponded with those revealed in the Kruskal-Wallis test.

The results revealed that laser diffraction overestimated the silt fraction (0.002-0.005 and 0.005-0.01 mm fractions) and fine sand fraction (0.01-0.02 mm) during the comparison of the results with the areometer and pipette methods; furthermore, from loess to the coarser fractions this method measured less than the others (Fig. 4).

This means that—regardless of the sample preparation-laser diffraction also underestimates the clay fraction in this case (with the inclusion of all methods). This kind of underestimation has been mentioned by various authors (Beuselinck et al., 1998; Di Stefano et al., 2010; Konert and Vandenberghe 1997; Loizeau et al., 1994; McCave et al., 1986; Pieri et al., 2006). Differences were significant in all cases except clay (<0.002 mm) and coarse sand (0.05-2 mm).

Table 6. Comparison of the measurements of the pipette method conducted at the University of Szeged and Debrecen University

	Measured fraction sizes (mm)					
	<0.002	***0.002-0.005***	***0.005-0.01***	***0.01-0.02***	***0.02-0.05***	***0.05-2***
Median (DU)	7.02	8.29	11.42	13.49	19.80	23.63
Median (SZU)	10.96	7.05	9.05	9.25	13.59	34.28
Mann-Whitney U	26.00	27.00	18.00	9.00	18.00	20.00
Sig.	0.53	0.60	0.14	0.02*	0.14	0.21
Effect size	-0.16	-0.13	-0.37	-0.60	-0.37	-0.32

**p<0.05*

Table 7. The results of particle size analyses by all methods (pipette, areometer and laser) and all participating institutes (University of Szeged, University of Debrecen and Hungarian Academy of Sciences- Geographical Institute)

Site codes	*Particle size fractions (mm)*											
	<0.002		*0.002-0.005*		*0.005-0.01*		*0.01-0.02*		*0.02-0.05*		*0.05-2*	
	(%)											
	A	**L**	**A**	**L**	**A**	**L**	**A**	**L**	**A**	**L**	**A**	**L**
BOR	8.2	3.4	3.8	7.3	8.1	11.9	9.0	19.0	41.4	26.6	29.5	31.8
GAH	18.2	20.1	14.5	21.4	10.6	21.3	11.2	23.0	20.3	8.0	25.3	6.2
GFH	20.6	21.0	9.4	22.4	10.1	21.5	11.5	20.1	16.3	9.2	32.3	5.8
SZG	15.0	9.7	9.6	17.4	8.0	20.5	15.4	20.5	30.5	16.6	21.5	15.3
TUR	29.0	21.1	11.9	21.6	8.1	19.9	10.0	20.3	22.3	10.5	18.8	6.7
KMA	0.0	1.1	0.0	1.3	0.0	1.6	1.5	1.6	4.1	1.7	94.4	92.7
FES	15.5	7.3	6.1	12.1	5.4	14.2	6.5	15.4	26.5	12.4	40.0	38.7
GAL	11.4	14.7	6.4	18.3	11.0	16.2	15.0	19.0	32.1	19.5	24.2	12.2

Results with the pipette method*	*<0.002*	*0.002-0.005*	*0.005-0.01*	*0.01-0.02*	*0.02-0.05*	*0.05-2*
	(%)					
S_BOR_P	4.67	2.3	2.0	4.3	6.6	80.1
D_BOR_P	4.88	4.3	8.7	13.0	21.1	48.0
S_GAH_P	38.76	11.1	10.0	7.4	1.1	31.6
D_GAH_P	29.56	14.7	12.5	13.6	17.5	12.2
GFH_P	28.99	14.9	13.1	13.3	14.8	15.0
SZG_P	7.87	8.4	11.4	15.9	27.0	29.4
S_TUR_P	18.33	10.4	10.0	10.2	17.1	33.9
D_TUR_P	28.06	13.5	12.1	13.4	18.7	14.2
KMA_P	0.23	0.6	0.1	0.9	1.7	96.4
FES_P	8.15	5.2	6.9	10.1	19.4	50.2
GAL_P	7.88	7.2	10.2	16.6	35.0	23.2

*A = areometer method, L = laser diffractometry; *Because of the significant differences between the results of measurements at two universities in case of the BOR, GAH and TUR samples, these three samples participate with two data, respectively.*

Table 8. The results of the statistical analyses of all methods used

Site codes	*The result of χ^2 test*	*Site codes*	*The result of χ^2 test*
BOR_S	χ^2=81.692, df=10, p<0.001	TUR_S	χ^2=42.217, df=10, p<0.001
BOR_D	χ^2=21.061, df=10, p<0.05	TUR_D	χ^2=23.895, df=10, p<0.01
GAH_S	χ^2=64.673, df=10, p<0.001	KMA	χ^2=7.575, df=10, NS
GAH_D	χ^2=32.831, df=10, p<0.001	FES	χ^2=23.173, df=10, p<0.05
GFH	χ^2=34.242, df=10, p<0.001	GAL	χ^2=21.789, df=10, p<0.05
SZG	χ^2=22.466, df=10, p<0.05		

Table 9. Comparison of all methods used for particle size measurements

Particle size classes		*<0.002*	*0.002-0.005*	*0.005-0.01*	*0.01-0.02*	*0.02-0.05*	*0.05-2*
Chi-Square		0.347	6.923	13.975	11.831	6.459	3.467
Sig.		0.841	**0.031**	**0.001**	**0.003**	**0.040**	0.177
Effect size	Areometer-Pipette	-0.055	-0.046	-0.222	-0.143	-0.216	-0.007
	Areometer-Laser	-0.108	-0.498*	-0.633*	-0.592*	-0.458*	-0.336
	Pipette-Laser	-0.039	-0.315*	-0.402*	-0.401*	-0.203	-0.229

***bold**: p<0.05 for the Kruskal-Wallis test; *: p<0.05 for the Mann-Whitney test*

All differences resulted from the altering ratios of fractions measured by laser diffractometry. Data of the pipette and areometer methods did not differ significantly.The sample from Kiskunmajsa (KMA) was one of the samples that significantly differed from the others due to its high sand content. Laser diffractometry resulted 94.4%; the pipette method resulted 98.1%; while the areometer method resulted 98.5% of the 0.02-2 mm fraction.

Results showed that laser diffractometry underestimated the sand fraction, however, in the case of laser diffractometry measurements, the fraction above 500 μm was also measured with sieving. It is widely acknowledged that sieving in the 0.02-2 mm fraction is the most accurate. It means that the difference is a result of sample preparation and not the measurement itself. Ultrasonic preparation did a better disaggregation of bigger aggregates.

Regardless of this fact, in our case, more measurements and comparisons may be needed to find the best method for sand measurements. In the clay fraction of the sample of KMA, the laser method resulted the highest value of 1.1% while the areometer did not find any of this fraction and the pipette method found 0.2%. The reason for the better performance of the laser method (again) is the preparation with the ultrasonic method.

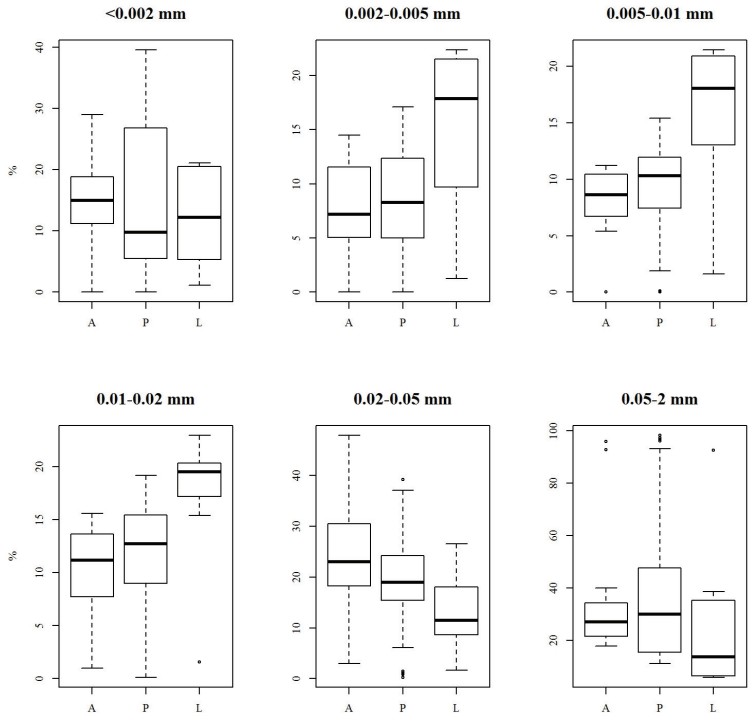

Fig. 4. Interquartile ranges of soil fractions by determination methods (for significance see Table 10)
(A: areometer method; P: pipette method; L: laser diffractometry)

The BOR sample was a special sample. Its soil formed on volcanic parent material, including a high amount of organic matter: a sample oily to the touch. This sample requires attention in the 0.002-0.02 fraction: the pipette method from the Szeged University resulted in d 8.6%, while the Debrecen University resulted in 26%, the areometer method resulted in 21% and laser diffractometry resulted in 38%.

In the clay fraction (<0.002 mm) of the sample of BOR, the laser method provided the lowest value—as expected—because the laser method consistently underestimates the ratio of clay fraction. Vdovic et al. (2010) found that laser method results in lower amounts of the clay fraction compared to the results of sedimentation methods.

They suggest disaggregating the samples with peroxide. However, the pipette method resulted in almost the same low percentage (both universities—Szeged and Debrecen—measured a low value of 4.7 and 4.9%). Both the laser and pipette methods resulted low values compared to the areometer method measuring 8.2% of the clay fraction. Using the peroxide in the pipette method seems inefficient to clay fraction as the ultrasonic also separated that amount of clay if we compare it from the 8 μm threshold.

In addition, in the case of the sample from BOR, the pipette method of Szeged found significantly higher amounts of the sand (0.02-2mm) fraction (86%) compared with the pipette method of Debrecen (69.1%) and the areometer method of Szeged (70.9%) and the laser diffractometry of the Geographical Institute (58.4%).

4. Conclusions

The comparison of the operators did not yield significant differences according to the χ^2 test. The analyses conducted here were suitable for proving the reliability of the operators, and checking the size of the error in the examined cases. The one-on-one analysis of the fractions versus the operators yield results show the fractions where larger differences appear. This means that special attention must be paid in those cases in order to reduce overall error of the measurements.

Classical methods performed similar results but the areometer method resulted in the smallest interquartile range for the clay fraction. The results of the pipette method showed that generally there are no significant differences in most of the fractions. The pipette method resulted in the lowest amount of the clay fraction (<0.002 mm) and the highest amount of the coarse sand fraction (0.05-2 mm), while in all other cases its results were between the results of the aerometer and the laser methods. Beuselinck et al. (1998) found similar results—the pipette method has the best performance in the 63μm< fraction while laser method had the biggest standard deviations in this fraction.

The aerometer method can be utilized for understanding the processes and to give recommendations to decrease errors during the

measurements as, e.g., it had the smallest interquartile range for the clay fraction.

The reason of the significant difference among particle size measurements was the laser method (but not with lower amount of clay fraction). However it is known from the work of various authors that the laser method underestimates the amount of the clay fraction and in the presented cases it resulted only in some of the samples and not in all of them. In the cases where there were no differences in the amount of clay fraction measured with the three methods, there were definitely micro-aggregates left disaggregated during the measurements with the laser method. Therefore, we can state that the differences in the results were caused by sample preparation. Generally we found that the laser method overestimates the 0.002-0.02 mm and underestimates the >0.02 mm fraction compared with the other two methods. There is no evidence among any of the 3 methods that all of the aggregates could disintegrate into particles. Ultrasonic preparation is the most effective method as it illustrated that if a 0.02-2 mm fraction is disaggregated, it causes a much higher percentage of 0.002-0.02 fraction. However, even the ultrasonic preparation is insufficient to break down micro-aggregates, therefore the 0.002-0.02 fraction will include the separated macro-aggregates and thus those will not be the part of the clay fraction.

Soil samples with different texture and humus content did not show unified tendency among the methods in measuring the clay content, so it is not possible to create a decent connection with the methods. It is advisable to use a different protocol for different soil groups (e.g. large clay content, large sand content, large humus content, large iron content as a specific correlation may be valid for them. These protocols are investigated in the comparisons of the other existing methods, being found that removal of organic matter did not significantly affect the measured grain size distribution (in the case of only two samples).

Although these results are relevant, they have not yet been analyzed in the required number to provide general scientific statements. Additional work is needed in order to have a standard way of comparing laser diffraction results to pipette and areometer results.

Based on the results, we recommend creating a widely accepted patent for sample preparation (disaggregation, the use of peroxide or other agents, using ultrasonic or other methods) and for measuring techniques (a set of refractive and sorption indexes, using ultrasonic during the measurement, pump speed etc.). Without this patent, the results of the laser method in different countries are not comparable. Creating the patent has utmost importance as the laser method today is used widely and more frequently.

References

Andrenelli M.C., Fiori V., Pellegrini S., (2013), Soil particle-size analysis up to 250μm by X-ray granulometer: device set-up and regressions for data conversion into pipette-equivalent values, *Geoderma*, **192**, 380-393.

Arriaga F.J., Lowerly B., Mays M.D., (2006), A fast method for determining soil particle size distribution using a laser instrument, *Soil Science*, **171**, 663-674.

Arya L.M., Paris J.F., (1981), A physicoempirical model to predict the soil moisture characteristic from particle-size distribution and bulk density data, *Soil Science Society of America Journal*, **45**, 1023-1030.

Beuselinck L., Govers G., Poesen J., Degraer G., Froyen L., (1998), Grain-size analysis by laser diffractometry: comparison with the sieve-pipette method, *Catena*, **32**, 193-208.

Bouyoucos J.B., (1962), Hydrometer method for making particle size analysis of soils, *Agronomy Journal*, **54**, 464-465.

Buchan G.D., Grewal K.S., Claydon J.J., Mcpherson R.J., (1993), A Ccomparison of sedigraph and pipette methods for soil particle-size analysis, *Australian Journal of Soil Research*, **31**, 407-417.

Buurman P., Pape Th., Muggler C., (1997), Laser grain-size determination in soil genetic studies 1.Practical problems, *Soil Science*, **162**, 211-218.

Buzás I. (Ed.), (1993), *Soil and Agrochemistry Analysing Method Book No. 1, Physical, Hydrological and Mineralogy Analyses of Soils (in Hungarian)*, Inda 4231 Publishing, Budapest, Hungary.

Cartacuzencu S., Lazar I., Nedeff V., Lazar G., (2014), Technical solution to reduce soil erosion produced by Tazlau river in Tarata perimeter, Romania, *Environmental Engineering and Management Journal*, **13**, 1971-1978.

Cohen J., (1992), Statistical power analysis, *Current Directions in Psychological Science*, **1**, 98-101.

Day P.R., (1965), *Particle Fractionation and Particle-Size Analyses*, In: *Methods of Soil Analyses, Part I. Part 1. Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling,* Black C.A. (Ed.), **9**, 545-567.

Di Stefano C., Ferro V., Mirabile S., (2010), Comparison between grain-size analyses using laser diffraction and sedimentation methods, *Biosystem Engineering*, **106**, 205-215.

Eshel G., Levy G.J., Mingelgrin U., Singer M.J., (2004), Critical evaluation of the use of laser diffraction for particle size analysis, *Soil Science Society of America Journal*, **68**, 736-743.

Field A., (2009), *Discovering Statistics*, SAGE Publications, London.

Frake P., Gill I., Luscombe C.N., Rudd D.R., Waterhouse J., Jayasoorya A.A., (1998), Near-infrared mass median particle size determination of lactose monohydrate, evaluating several chemometric approaches, *Analyst*, **123**, 2043-2046.

Fritsch GmbH, (2005), *Operating Instructions*, Laser Particle Sizer analysette 22 MicroTec.

Gee G.W., Or D., (2002), *Particle-Size Analysis*, In: *Methods of Soil Analysis, Part 4. Physical methods*, Dane J.H., Topp G.C. (Eds.), Madison, WI, Soil Science Society of America, 255-293.

Gibbs R.J., Matthews M.D., Link D.A., (1971), The relationship between sphere size and settling velocity, *Journal of Sedimentary Petrology*, **41**, 7-18.

Goossens D., (2008), Techniques to measure grain-size distributions of loamy sediments: a comparative study of ten instruments for wet analysis, *Sedimentology*, **55**, 65-96.

Gupta S.C., (1979), A model for predicting packing density of soils using particle-size distribution, *Soil Science Society of America Journal*, **43**, 758-764.

Gupta S.C., Larson W.E., (1979), Estimating soil water retention characteristics from particle size distribution, organic matter percent, and bulk density, *Water Resources Research*, **15**, 1633-1635.

Indorante S.J., Hammer R.D., Koenig P.G., Follmer L.R., (1990), Particle size analysis by a modified pipette procedure, *Soil Science Society of America Journal*, **54**, 560-563.

Jonkers L., Prins M.A., Brummer G.J.A., Konert M., Lougheed B.C., (2009), Experimental insights into laser diffraction particle sizing of fine-grained sediments for use in palaeoceanography, *Sedimentology*, **56**, 2192-2206.

Karbassi A., Nasrabadi T., Rezai M., Modabberi S., (2014), Pollution with metals (As, Sb, Hg, Zn) in agricultural soil located close to Zarshuran gold mine, Iran, *Environmental Engineering and Management Journal*, **13**, 1971-1978.

Kondrlová E., Igaz D., Horák J., (2012), Determination of sample preparation method for laser diffraction: from suspension towards soil paste, *Plant Production (Növénytermelés)*, **61**, 275-278.

Konert M., Vandenberghe J., (1997), Comparison of laser grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction, *Sedimentology*, **44**, 523-535.

Kun Á., Katona O., Sipos Gy., Barta K., (2013), Comparison of pipette and laser diffraction methods in determining the granulometric content of fluvial sediment samples, *Journal of Environmental Geography*, **6**, 49-54.

Lea F.M., Nurse R.W., (1947), *Permeability Methods for Fineness Measurements,* Symposium on Particle Size Analysis, Transactions of the Institution of Chemical Engineers, vol. **25,** Institution of Chemical Engineers, London, 47-56.

Loizeau J., Arbouille D., Santiago S., Vernet J., (1994), Evaluation of a wide range laser diffraction grain size analyser for use with sediments, *Sedimentology*, **41**, 353-361.

Makó A., Rajkai K., Hernádi H., Hauk G., (2014), Comparison of different settings and pre-treatments in soil particle size distribution measurement by laser-diffraction method, *Soil Science and Agricultural Chemistry (Agrokémia és Talajtan)*, **63**, 19-28.

McCave I.N., Bryant R.J., Cook H.F., Coughanowr C.A., (1986), Evaluation of a laser diffraction size analyzer for use with natural sediments, *Journal of Sedimentology and Petrology*, **56**, 561-564.

McDonald J.H., (2009), *Handbook of Biological Statistics* 2nd Ed., Sparky House Publishing, Baltimore, Maryland, USA.

Mie G., (1908), Contributions to the optics of turbid media, especially colloidal metal solutions, Leipzig (in German), *Annals of Physics (Annalen der Physik)*, **330**, 377-445.

Madarász B., Jakab G., Szalai Z., Juhos K., (2012), Examination of sample preparation methods for the laser grain size analysis of soils with high organic matter content, (in Hungarian), *Soil Science and Agricultural Chemistry, (Agrokémia és Talajtan),* **61**, 381-398.

Müller H.W., Dohrmann R., Klosa D., Rehder S., Eckelmann W., (2009), Comparison of two procedures for particle-size analysis: Köhn pipette and X-ray granulometry, *Journal of Plant Nutrition and Soil Science*, **172**, 172-179.

MSZ-08-0205, (1978), Analysis of soil physical properties and water management (in Hungarian), Hungarian Patent No. *MSZ-08-0205.*

Naguib M., Bedaiwy A., (2012), A simplified approach for determining the hydrometer's dynamic settling depth in particle-size analysis, *Catena*, **97**, 95-103.

Navas A., Gaspar L., López-Vicente M., Machín J., (2009), Patterns of soil carbon and nitrogen in relation to soil movement under different land uses in mountain farmland fields (South Central Pyrenees), *Catena,* **94,** 43–52.

Nemes A., Wösten J.H.M., Lilly A., Oude Voshaar J.H., (1999), Evaluation of different procedures to interpolate particle-size distributions to achieve compatibility within soil databases, *Geoderma*, **90**, 187-202.

Pieri L., Bittelli M., Pisa P.R., (2006), Laser diffraction, transmission electron microscopy and image analysis to evaluate a bimodal Gaussian model for particle size distribution in soils, *Geoderma*, **135**, 118-132.

Rich T., (1964), Particle size measurements, US Patent, No. *3,138,029*.

Salter P.J., Berry G., Williams J.B., (1966), The influence of texture on the moisture characteristics of soils: III. Quantitative relationships between particle size, compaction and available water capacity, *Journal of Soil Science*, **17**, 93-98.

Skaggs T.H., (2001), Estimating particle-size distribution from limited soil texture data, *Soil Science Society of America Journal*, **65**, 1038-1044.

Sokal R.R., Rohlf F.J., (1969), *Introduction to Biostatistics,* W. H. Freeman and Company, 2nd edition, New York.

Tan K.H., (1996), *Soil Sampling, Preparation and Analysis*, 1st ed., Marcel Dekker, New York.

Vdovic N., Obhodas J., Pikelj K., (2010), Revisiting the particle-size distribution of soils: comparison of different methods and sample pre-treatments, *European Journal of Soil Science*, **61**, 854-864.

Watteau F., Villemin G., Bartoli F., Schwartz C., Morel J.L., (2012), 0-20 μm aggregate typology based on the nature of aggregative organic materials in a cultivated silty topsoil, *Soil Biology & Biochemistry*, **46**, 103–114.

Zauca D.C, Stătescu F., Pavel L.V., (2013), Soil structure and water-stable aggregates, *Environmental Engineering and Management Journal*, **12**, 741-746.