Experimental evidence of laser diffraction accuracy for particle size analysis

*Published Version:*
Bittelli, M., Pellegrini, S., Olmi, R., Andrenelli, M.C., Simonetti, G., Borrelli, E., et al. (2022). Experimental evidence of laser diffraction accuracy for particle size analysis. GEODERMA, 409(1 March 2022), 1-15 [10.1016/j.geoderma.2021.115627].

*Availability:*
This version is available at: https://hdl.handle.net/11585/841041 since: 2024-12-19

*Published:*

DOI: http://doi.org/10.1016/j.geoderma.2021.115627

# Experimental evidence of laser diffraction accuracy for particle size analysis

Marco Bittelli[1,*] , Sergio Pellegrini [2], Roberto Olmi[3], Maria Costanza Andrenelli[2], Gianluca Simonetti[4] , Emilio Borrelli[1] and Francesco Morari [4]

[1,*] Department of Agricultural and Food Sciences, University of Bologna, Italy

[2] Research Center for Agriculture and Environment, Florence, Italy

[3] Institute of Applied Physics, National Research Council, Sesto Fiorentino, Italy

[4] Department of Agronomy, Food, Natural resources, Animals and Environment,
University of Padua, Italy.

*Corresponding author

## Abstract

Laser diffraction analysis is a fast, reliable and automated method that provides detailed and highly resolved sediment particle size distribution. In recent studies, the methods were compared against independent methods based on direct observation of particles by digital imaging. The data showed that laser diffraction results were in better agreement with the digital imaging independent method than with sedimentation–based methods. However, analysis was performed over a limited number of samples. In this study, 47 soil samples with a wide range of textural properties were analyzed with Laser Diffraction, Pipette, Sieving, Sedigraph and Digital Imaging methods. Detailed statistical analysis using Altman plots and Honest Significant Difference tests demonstrated (at 95% significance) that the five methods do not show statistically significant differences for grain sizes above 100 μm. However, in the lower end of the size range, i.e. less or equal to 50 μm, Laser Diffraction showed much better agreement with the reference method selected for comparison, which was Digital Imaging. New regression equations were derived with slope coefficients for linear regressions between Pipette and Laser of 0.2952 ($R^2$ = 0.8625) for clay, 1.4261 ($R^2$ = 0.5746) for silt and 1.031 ($R^2$ = 0.6586) for sand, classified with the International Soil Science Society (ISSS) system. For the United States Department of Agriculture (USDA) classification system, the slopes were: 0.261 ($R^2$ = 0.8625) for clay, 1.3493 ($R^2$ = 0.8179) for silt and 1.063 ($R^2$ = 0.888) for sand. These data were consistent with previous studies. Based on regression and equivalent diameters, Laser Diffraction data were represented on textural triangles for classification, allowing for employing Laser Diffraction for soil classification. Two alternative for representing the Laser Diffraction data in textural triangles were employed: (1) using regression equations to convert data to be represented on the standard triangles and (2) modify the upper limit for the clay range, from 2 to 8 μm. Finally, based on the additional evidence presented in this research demonstrating that the Laser Diffraction method was more accurate than traditional sedimentation methods, it is suggested that the standards for particle size analysis be changed from sedimentation to Laser Diffraction methodologies.

**Keywords**: particle size analysis, comparison of methods, sedimentation methods, laser diffraction, digital imaging analysis, regression equations, textural triangles

## 1. Introduction

Particle size distribution (PSD) of soils is an important physical property influencing relevant soil processes such as water and heat flow (Bittelli et al., 2015). The hydraulic properties, namely the soil water retention and the hydraulic conductivity curves, are affected by PSD, which in turn affects the pore size distribution and soil structure. Thermal properties are also affected by PSD. Thermal conductivity and capacity depend on the conductivities and capacities of the individual soil solid, liquid and gas phases, which depends on mineralogy, porosity and structure. Therefore, a change in PSD affects the overall soil thermal properties (Bittelli et al., 2015).

Many methods to measure PSD have been presented in the literature and are used in practical applications (Allen, 1981; Gee and Or, 2002; Goossens, 2008; Rasmussen, 2020). Standards to measure PSD are defined depending on the field of interest. The Soil Science Society of America (SSSA) provides detailed description of the most common methods to measure PSD (Gee and Or, 2002), including dry and wet sieving, the standard pipette (P) and hydrometer methods. The American Society for Testing and Materials (ASTM) also provides standards for measuring PSD (ASTM, 1963), which are also based on sieving and sedimentation theory.

Moreover, the P method is also defined as a standard for measurement in mineral soils by the International Organization for Standardization (ISO 11277, 2009). Since sand particles, usually above 50 $\mu$m, are not measured with pipette and hydrometer, these methods are commonly coupled with dry and wet sieving for large size particles. However, Andrenelli et al. (2013) presented a methodology to be used with a sedimentation-based method (Sedigraph) to solve particles even in the 50–250 μm range by using a denser and more viscous dispersion liquid, able to maintain the Reynold number equal or below 0.21 for particles of 250 μm diameters. PSD is also a fundamental information in the field of sedimentology, where laser diffraction has become the standard method for sediment measurement (Antoine et al, 2009a; Újvári et al., 2016; Schulte et al. 2018a). Overall, the standards for measuring PSD in many fields are still based on sedimentation methods such as the pipette, hydrometer and sieving.

Sedimentation methods (based on Stockes' law) have been used for decades and most of the data collected in soil databases worldwide were obtained from these techniques. Sedimentation methods have many disadvantages: they provide a limited number of size classes, they are time consuming and the data are not reliable at small size classes (usually below 2 $\mu$m) because of Brownian motions and assumptions about particle shape and density are necessary. For these reason, over time, alternative methods have been proposed, such as Laser Diffraction (L) and Digital Imaging (DI). Many papers have been published with comparative studies among different methods (Wu et al., 1993; Loizeau et al., 1994; Konert and Vandenberghe, 1997; Muggler et al., 1997; Beuselinck et al., 1998; Bittelli et al., 1999; Buurman et al. 2001; Eshel et al., 2004; Pieri et al., 2006; Taubner et al., 2009; Goossens, 2008; Vdovic et al., 2010; Kun et al., 2013; Roberson and Weltje, 2014; Sherriff and Huallachain, 2015; Fisher et al., 2017; Makó et al. 2017; Bieganowski et al., 2018; Makó et al. 2019; Bittelli et al., 2019; Igaz et al.; 2020, Goraczko and Topolinski, 2020).

The results of the comparisons were sometime inconsistent, however the main conclusion from most authors was that sedimentation techniques "overestimate" the clay fraction, with respect to L that "underestimates" the clay fraction. In sedimentation, a non−spherical particle settles with the maximum cross sectional area perpendicular to the direction of motion (Krumbein, 1942). Since the theory applied to sedimentation based on Stocke's law assumes particles to be spherical, for non−spherical particles, this assumption determines a decrease in the equivalent diameter (longer settling times) with over−estimation of the clay fraction (Bittelli et al., 2019). The error introduced by this assumption is that the settling time is longer and therefore the particle is assumed to be smaller than its "true" diameter. Spherical assumption is also employed for L and the effect goes in the opposite direction, in L a non−spherical particle reflects a larger cross− sectional than a theoretical sphere of the same volume would reflect (Jonasz, 1994). This effect results in larger equivalent diameter, with under−estimation of the clay fraction, since a particle is assigned to a larger size section of the distribution.

For several years, the main question among researches was: given the established differences, are the sedimentation techniques that "overestimate" small size particles or L that “underestimates” ? In recent studies, Bittelli et al. (2019) and Yang et al. (2019) showed that when the two methods (sedimentation and L) were compared against an independent method based on direct DI analysis, sedimentation “overestimates” the small size fraction while L is in better agreement with DI.

Bittelli et al. (2019) utilized a novel imaging device that allowed for obtaining images of literally billions of soil particles, compared several methods (including sedimentation through X−ray attenuation) and concluded that sedimentation−based methods should be replaced by L as standard for PSD analysis (Bittelli et al., 2019). Shang et al., 2018 also employed DI as a direct measurement of grain-size distributions for identification of aeolian silt transport processes as an alternative technique for particle sizing. However, the study of Bittelli et al. (2019) was conducted over 11 samples and further analysis over a larger dataset is needed to corroborate the results.

Moreover, a transition toward a new methodology requires the option of still being able to use the historical data collected with sedimentation methods, which were used to create the majority of soil databases worldwide. In other words, transfer equations are necessary to compare data collected with sedimentation−based method and L. Overall, while many studies comparing experimental methods for PSD have been published, a systematic comparison over a large number of samples, using automated DI as a reference independent method, has not yet been performed. In addition, regression equations or modified limits in textural triangles are necessary to classify soils measured with L.

In this study: (1) forty seven soil samples, with a wide range of geological, pedological and textural properties, collected in different Italian pedo-climatic environments, are analysed with four techniques: Pipette and Sieving (P), Laser Diffraction (L), Digital Imaging (DI) and Sedigraph and Sieving (S); (2) a comparative analysis is performed among the samples, (3) regression equations are determined to convert data obtained from sedimentation based methods (P and S) to L and (4) textural triangles obtained from regression and with modified limits are presented for texture classification when data are obtained with L.

## 2. Materials and Methods

### 2.1 The soil samples

Forty-seven soil samples were collected in different Italian pedoclimatic environments. Table 1 lists information on sampling sites in terms of geographical coordinates, elevation, administrative region, total organic carbon content, total carbonate content, parent material and a World Reference Base (WRB) soil classification. The soils in Sardinia developed on Pleistocene alluvial deposits and are typical of a xeric moisture regime; little sodium is present on the exchange complex, and a moderate development of argic horizon may occur. The light pink-red color observed in these samples is typical of well-developed soils. Soils from Lombardy developed on fluvial and fluvioglacial deposits from the Pleistocene in the high Po valley; soil developed on clay or silt calcareous gravel debris deposits. All the soils are freely drained and deep to hard rock. Typically, in these soils the Ap horizon is characterized by loamy texture and brown yellowish color. Soils from Tuscany, despite the quite homogeneous texture, differ for parent material, geomorphology, climate and land use. The surface Ap horizon is characterized by a very low hydraulic conductivity, and the occurrence of redox mottles below 0.10 m.

Soil samples from Veneto are characterized by sandy (202) and sandy-loam texture (210, 211, 214), and they come from Cambisols and Luvisols developed on Pleistocene fluvial and fluvioglacial deposits of river Adige valley. These soils, homogeneous for parent material, morphology and land use (corn for silage and alfalfa in crop rotation), generally exhibit good to excessive internal drainage; only the soil of sample 214 is classified as Endostagnic due to the presence of surface water table.

Regarding the samples from Sicily, four come from well drained soils developed on colluvial deposits of limestone and calcarenitic substrates (193, 221, 222 and 227), with texture ranging from silty clay loam to sandy. Sample 223 belongs to a deep horizon (75-125 cm) of a moderately well drained soil developed on Oligocene clay and silty marine sediments, characterized by the common presence of redoximorphic features and slickensides. Finally, sample 225 comes from a calcareous Arenosol, developed on Quaternary aeolian sand deposits and characterized by excessively high internal drainage.

The soil classification used for representation in the textural triangles in the following sections were based on the ISSS (International Soil Science Society) and USDA (United States Department of Agriculture). In the ISSS, the clay fraction is in the range 0−2 $\mu$m, silt is in the range 2−20 $\mu$m and sand is in the range 20−2000 $\mu$m. In the USDA system, the clay fraction is in the range 0−2 $\mu$m, silt is in the range 2−50 $\mu$m and sand is in the range 20−2000 $\mu$m.

TABLE 1 HERE

## *2.2* Particle size analysis

### *2.2.1* Pipette

The analysis with the pipette method followed the standard procedure of the Soil Science Society of America (Gee and Or, 2002). The procedure followed the following phases: 1) weighing 10 g of air dried soil sample < 2 mm; 2) soil dispersion with 10 mL of a solution of Calgon (0.2% vol); 3) distilled water addition up to a final volume of 250 $cm^3$; 4) agitation of the suspension with horizontal agitator for at least 12 h (150 rpm); 5) cleaning of the suspension at 250 μm with distilled water; 6) topping up the passing fraction to the reference volume of 500 $cm^3$ with distilled water; 7) analyzing the soil suspension volume (20 $cm^3$). Since another sedimentation based method was used (the Sedigraph) to standardize the procedure, some other specifications have been adopted as indicated in Andrenelli et al. (2013). No pre-treatment for soil organic matter removal has been carried out. In that regard, Matthews (1991) maintains that the choice of including removal of organic matter, carbonates and/or iron oxides should correspond to the aim of the investigation and type of material to be analyzed. Moreover, Schulte et al. (2016) investigated the effect of HCl pretreatment on LD for sediments. They found that pretreating post-depositional modified aeolian sediments with HCl may result in misleading grain size distributions and should be avoided in standard analyses of loess–paleosol-sequences. The soil samples used for sedimentation, were prepared into a suspension previously passed through 250 μm sieve; the wet sieving procedure was employed to determine the sands larger than 250 μm, but also the fine and very fine sand fractions, after that silt and clay analysis was completed. Sieving was also performed at 50, 100, 250, 1000 and 2000 $\mu$m. All measurements were replicated three times.

### *2.2.2.* Sedigraph

Particle size by sedimentation was also measured with the Sedigraph (Micromeritics Inc.) for automated analysis with X-ray diffraction. The Sedigraph uses a paralleled X-ray beam to detect changes in suspended sediment concentration during settling. Samples of 5 g of bulk soil (< 2 mm) were used to obtain a soil suspension passed through a 250 μm wet sieve to detect medium, coarse and very coarse sands. Eighty-six size classes were obtained from the

Sedigraph analysis in the size interval between 0.35 and 250 μm, while three data points were obtained at 500, 1000 and 2000 μm with sieves. All soil suspensions were replicated three times and automatically loaded by Mastertech auto-sampler. Sample preparation and analytical procedure followed the suggestion of Andrenelli et al. (2013) for the analysis of the curve between 50 and 250 μm, therefore adopting a solution of Calgon (0.2%) in sucrose (50%) to assure the conformity to the Stokes law. The initial part of the curve was analyzed by Sedigraph, starting from a soil suspension passed through 250 μm, but adopting a solution of Calgon (0.2%) in distilled water to reduce the occurrence of Brownian motions. To obtain an accurate solution of Stokes law, particle density was measured for each sample using a helium pycnometer. The device is equipped with a software for data acquisition and automatic data analysis. The measurements were repeated three times for each sample.

### *2.2.3.* Laser diffraction

L analysis was performed with a light scattering apparatus (Malvern Mastersizer 2000, England), equipped with a 2 mW Helium-Neon laser with a wavelength of 633 nm. The apparatus has active beam length of 2.4 mm, and it operates in the range 0.02 to 2000 μm. L analysis provided eighty-eight size classes in the interval between 0.012 and 2000 μm. For each sample, four sub-samples of the soil suspension prepared according to Gee and Or (2002) were introduced into the sample bath in small increments until the obscuration value fell within the range of 10–20%. The Mie theory used to render the data requires the adoption of an absorption coefficient and a refraction index. According to Ozer et al. (2010) the values of RI and AC of 1.55 and 0.1, respectively were suggested for laser diffraction in naturally soils. As also reported by Jonasz, (1987); Eshel et al., (2004) and Bittelli et al. (2019), a value of RI=1.5 provides reliable results in most mineral soils, which was used in this study. The samples did not present significant concentrations of iron oxides that would justify the use of significantly different values for the RI.

### *2.2.4.* Automated image analysis

The device Morphologi G3S (Malvern Inc., England) was used for DI analysis. This instrument is based on direct optical observation of particles, therefore the smallest measurable particles provides information down to 0.3 μm in size (Morphologi G3, Malvern, 2016), using the highest magnification lenses. One-hundred and twenty six size classes were obtained in the size interval between 0.3 and 2000 μm. The CE diameter was selected, which is the area of circle created by summing the areas of the pixels of the collected image (Allen, 1981). Two grams of samples were collected and dispersed in 300 ml of Calgon solution (in conformity with the pretreatment for the pipette method) with a ratio of dispersion of 1:150. Each sample was separated into two sub-samples, the silt-clay (SC) and the sand fraction (Sa). The dispersion was then included in a centrifuge at 15,000 rpm for 5 min. After centrifugation the samples were sieved at 50 µm to separate and measure the silt and sand fraction, from the sand fraction. From the dispersion (without the sand fraction), and during stirring (to avoid deposition), 200 µL were collected and dispersed into deionized water (1:100). While keeping the solution in agitation and mixing in deionized water, 100 µL were collected and placed over the microscope slide. It was verified with particular care during the experiment, from visual inspection and pre-treatment, that all aggregates were destroyed and only the actual PSD (not micro-aggregate size distribution) was measured. The Morphologi G3S is a very accurate and precise instrument, which addressed and solved many problems related to optical particle size measurement. Moreover, it provides many morphological information useful for sediment and soil analysis. Contamination of dust or particles was avoided by working in very clean and sterilized condition. The measurement of the Sa and SC fraction was replicated four times. Since two different magnifications (lenses) are used for the analysis, the fractional distribution was obtained by a weighting function as described in Bittelli et al. (2019). The two distributions were then combined, to obtain a complete cumulative distribution.

### *2.3.* Statistical Analysis

The statistical problem consists in the comparison of four measurement methods for PSD: DI, L, P and S. The measurement concerned a total of 47 samples, each consisting in a variable number of measurements in the range 0−2000 $\mu$m. For comparing purposes, the measurements have been re−aggregated in six classes of particle sizes: (0-2] $\mu$m, (2-20] $\mu$m, (20-50] $\mu$m, (50-100] $\mu$m, (100-250] $\mu$m, (250-2000] $\mu$m. Therefore, there is a total of 282 measurements for each of the four methods and two classifications: method and particle size. Measurement is the quantitative variable, the other two are classification factors. For this statistical problem, pairwise analysis with Bland−Altman plots was used to compare measurement techniques (Bland and Altman, 1999). For quantitative investigation the analysis of variance (ANOVA) was performed, as was regression analysis. The statistical analysis was performed by writing a code with the R software.

## 3. **Results and Discussion**

### *3.1.* Particle Size Distribution

Particle size distributions were compared for different methods by plotting cumulative distribution functions (CDF) and by performing a statistical analysis of size classes. For comparison, the instruments output was selected such that all four methods had the same value of particle size (same x axis). P and S had less particle size classes in the clay range. For size classes above 250 $\mu$m, only four classes were represented 250, 500, 1000 and 2000 $\mu$m. Specifically: P presented the following limits: 2, 20, 50, 100, 250, 1000 and 2000 $\mu$m. The P sedimentation method was used for the 2 and 20 limits, while 50, 100, 250, 1000 and 2000 $\mu$m were obtained by sieving. L displayed 88 classes in the range 0.01-2000 $\mu$m, DI displayed 126 classes in the range 0.3-2000 $\mu$m and S presented 86 classes in the range 2-250 $\mu$m, the values at 500, 1000 and 2000 $\mu$m were obtained by sieving. As described above S, although being a sedimentation-based method, provided data larger than 20 $\mu$m and up to 250 $\mu$m because the methodology presented by Andrenelli et al. (2013) was employed. With this choice of size classes, the four methods are perfectly comparable since each exact cumulative value is compared for exactly the same size value. Clearly, not every method has the same number of data values, however the size data (x-axis value) of P are exactly the same in the L and DI data series, since many data points are collected. As examples, Figure 1 depicts the CDF for fifteen representative samples, having different textural properties and distributions.

FIGURE 1. HERE

Figure 2 depicts PSD of six size classes for the fifteen soil samples, for P, L, DI and S. All the soil samples with high clay content displayed the same behavior with P and S largely overestimating the amount of small size fractions. These differences are particularly evident in samples 65, 83, 101, 180, 182, 189, 216, 221 and 223. However, the statistical analysis confirmed this behavior for the majority of the 47 samples analyzed. Clearly, samples with small size fractions did not displayed such striking differences as also depicted in Figure 1.

Differences were found also within the methods based on sedimentation (P and S) but, as shown below, the differences were not statistically significant. These differences are due to the experimental methodologies used for measurement. P is based on the collection of a sample of liquid (with the dispersed particles) at a given depth within a cylinder after a prescribed amount of time (Allen, 1981; Gee and Or, 2002; Bittelli et al., 2015). S measures the attenuation of X-rays during the sedimentation process and then derives PSD from changes in particle concentration. While the fundamental law is the same, Stockes' law for sedimentation, the experimental procedure is different. For this reason, the two methods are producing slightly different results. However, they are consistent in overestimating the amount of small particle when compared to L and DI.

FIGURE 2. HERE

Generally, all samples display the same behavior, with the sedimentation–based methods (P and S) largely overestimating the amount of small size particles, when compared to L, which, on the other hand, was in agreement with the reference DI method. Although Figure 1 and 2 are depicting representative examples, the detailed statistical analysis presented below confirmed these results for the entire dataset.

### *3.2. Statistical analysis*

The performance of the different methods can be investigated on a pairwise base. Denoting by $s_1$ and $s_2$ the measurement obtained in the whole size range by any couple of two methods, a first assessment of the relative performance of those two methods can be obtained. The first step is to plot the difference $s_1 - s_2$ as a function of the mean values $(s_1 + s_2)/2$, which corresponds to the so−called Bland−Altman plots (Bland and Altman, 1999), frequently employed to compare two measurement techniques. Figure 3 depicts those comparisons for all the size ranges combined. It is noteworthy how DI,L display less differences, with respect to DI,P and DI,S. On the other hand, the two sedimentation-based methods (P,S) are in good agreement.

FIGURE 3. HERE

Similar plots can be obtained for the six size classes. Four examples, for four size classes, are shown in Figure 4. Four size classes were selected for clarity in the plot representation, however the pair-wise comparison was performed for the six classes presented in Figure 2. The figure title indicates the pairs, for instance DI, L is the comparison between Digital Imaging and Laser, and so forth. The first class [0-2] $\mu$m clearly shows a similarity between L and DI methods and a similarity between P and S in the same class. An analogous behavior is observed in the second and third class, while for the larger size classes (above 50 $\mu$m) the differences among methods are less pronounced. These results confirm that DI and L are in better agreement for small size particles, with respect to the sedimentation-based methods P and S.

FIGURE 4. HERE

To better understand the relationship between the different combinations of factors (4 measurement methods, 6 size classes) a two−way variance analysis (ANOVA) on the measurements could be applied. Unfortunately, one of the assumptions needed for a correct ANOVA is violated: the residuals are approximately normally distributed but homogeneity of variance is not fulfilled. However, it is possible to consider one class at a time and apply one−way ANOVA, if homogeneity of variance is fulfilled, or employ non−parametric tests like Kruskal−Wallis if there is not homogeneity of variance (Siegel and Castellan, 1988). In the lower−sizes classes, for example in the (0,2] interval, the data variances are rather different in the four method groups. However, the standard deviations in the groups are proportional to the group means. A logarithmic transformation of the data was applied to reduce the variance inhomogeneity of residuals (Dunn, 1964).

An additional test on group pairs was used to further corroborate the results, by performing three pairwise Wilcoxon−Mann−Whitney tests (Siegel and Castellan, 1988). Applying the Bonferroni correction for multiple comparisons, the *null hypothesis* (concerning the equality among the mean ranks of the four methods) cannot be rejected at a level 0.05 only for the differences among DI and L, and P and S, respectively. It was therefore computed a Tukey (1948) Honest Significant Difference (HSD) test and plotted in Figure 5, depicting the Tukey HSD plots in the classes 0-2, 2-20, 20-50, 50-100, 100-250 and 250-2000 $\mu$m.

FIGURE 5 HERE

The results confirm what was found from the Bland−Altman plots. The 95% difference intervals, among the four methods, are not statistically significant for grain sizes above 100 $\mu$m. In the lower end of the size range, i.e. less or equal to 50 $\mu$m, L method is in much better agreement with the “reference method”, the DI methods.

### *3.3. Regression analysis*

Having established that the L method provides more accurate measurements of PSD, it is now important to determine regression equations among L and P. The determination of linear regressions is important since most of the databases in geology, sedimentology, pedology, geo−technical engineering and soil sciences, were created with data obtained from sedimentation−based techniques in addition to sieving. To transition toward L as a standard method, as proposed by Bittelli et al. (2019), equations are necessary to compare data and results. For instance, if a measurement of a soil sample is performed today with L, how does it compare to data for another soil already measured in the past with sedimentation-based and sieving methods?

The regression is performed between P and L, since among sedimentation methods P is more common and the majority of the data collected in the past were measured with this method. Although databases also contain data collected with another common sedimentation method, the hydrometer, our statistical analysis showed that P and S did not present statistically significant differences. The S employ a quite different methodology (X-rays attenuation) to exploit Stokes' law, nevertheless no significant differences were found when compared to P. Although the hydrometer was not used and tested in this study, it is expected to obtain similar results if hydrometer was compared to P and S, since the hydrometer's principle is based on measurement of fluid density variations during sedimentation, exploiting again Stokes' law. On the other hand, the S is a more recent and expensive methodology that did provide a higher resolution of PSD (Andrenelli et al, 2013) and it was therefore selected for a more detailed analysis of sedimentation methods.

Regression analysis was performed for the main three particle size classes (clay, silt and sand) and for the two most common classification systems in soil science: the ISSS (International Soil Science Society) and USDA (United States Department of Agriculture). As described above, the fairly large number of samples were selected to represent a wide range of textural classes and geological substrates, as listed in Table 1.

FIGURE 6. HERE

Figure 6 and 7 depicts data and regression equations for L versus P and vice versa. The linear equation fitting procedure was performed by forcing the intercept to zero. This choice slightly reduced the value of $R^2$, but makes the conversion of data much easier and general, when applied to data where the values of the predicted variable is unknown. Moreover, in some cases when clay fractions were very small, the regression would lead to negative values of mass (a non−physical result), therefore the intercept was set to zero to avoid this problem. In this study, when regressions between L and P were performed, a value of 3.66 for the slope coefficient was found for clay (Figure 6). Taubner et al. (2009), that also compared P and L, reported a slope coefficient of 3.089.

The slope coefficients for the regressions between P and L (Figure 7) were the following for ISSS: 0.2952 ($R^2 = 0.8625$) for clay, 1.4261 ($R^2 = 0.5746$) for silt and 1.031 ($R^2 = 0.6586$) for sand. For the USDA classification the slopes were: 0.261 ($R^2 = 0.8625$) for clay, 1.3493 ($R^2 = 0.8179$) for silt and 1.063 ($R^2 = 0.888$) for sand. Konert and Vandenberghe (1997) obtained a value for the slope coefficient of 0.361, for the regression between P and L, while Eshel et al. (2004) reported a value of 0.345, for the clay fraction. The differences in the regression coefficients are likely due to differences in the pre-treatments and experimental methodologies employed in the different studies. Moreover, differences could arise from using, for instance, L devices built by different manufacturers.

However, it is noteworthy that the slope coefficient for the clay fraction obtained in this study is similar to published data, indicating that L determines a measurement of clay content that is about a third of the one obtained by sedimentation methods. This difference is then reflected in slope coefficients larger than 1 for silt (the mass fraction that are not classified as clay because particles larger than 2 $\mu$m, moves then into the silt fraction). Finally, the slope coefficients for sand are very close to one, indicating that the amount of sand measured with P and L is very similar.

Slope coefficients for silt in the ISSS and USDA classification were clearly different. This difference is due to the fact that the size limit for the USDA is larger (2-50 $\mu$m) than the ISSS (2-20 $\mu$m), which is a class affected by the differences between the two methods.

Overall, these results provide additional evidence that particle shape is the main factor determining differences between the methods, as also discussed by Konert and Vandenberghe (1997); Eshel et al. (2004); Pieri et al. (2006); Bittelli et al. (2019).

FIGURE 7. HERE

Clearly, the regression coefficients obtained by different studies presented in the literature cannot be the same, given the different soil samples and pre-treatments employed. However, it is remarkable that several studies (Konert and Vandenberghe, 1997; Eshel et al., 2004; Taubner et al., 2009) were consistent in reporting an over−estimation by P of about 3 times the value obtained by L. For example, a clay content of 10 % with L would correspond to about 30 % with P, although this value depends on the mineral properties of the clay particles as pointed out by Schulte and Lehmkuhl (2018). Overall, it is quite a dramatic difference, with consequences for soil classification, particle-size studies and other applications, as described below.

### *3.4. Textural triangles*

Representation of the data obtained from P (red dots) and L (blue crosses), on the ISSS and USDA textural triangles, is depicted in Figure 8. Plates (A) and (B) indicates soil classification for the ISSS and USDA respectively, for samples measured with L (blue crosses) and P (red circles). Plates (C) and (D) indicates soil classification for the ISSS and USDA systems, for samples obtained from regression of L data to P, (blue crosses) and Pipette (red circles). The regression coefficients used for the transformation are indicated in Figure 6. To represent the data on the triangles, the clay, silt and sand fractions obtained with L were multiplied by the regression coefficients and then plotted on the textural triangles. The representation on the textural triangles was performed by using the R software by Moeys (2018).

FIGURE 8. HERE

Because of the differences described above, current classification triangles applied to L data would lead to unrealistic classification (see plates A and B). For instance, none of the samples would belong to fine texture classes such as Clay, Clay loam, Silty clay, Sandy clay or Sandy clay loam. Clearly, this is due to the much smaller amount of fine particles measured by L. While L provides more accurate measurements, L data represented onto the traditional textural triangles would not accurately represent soil properties and classes.

Originally, soil classification was based on the mass ratio of the three classes, but also on other soil features such as mechanical properties: consistence, cohesion, resistance to deformation and plasticity. These features, for instance, help pedologists, geologists and soil scientists to obtain a quick field assessment of soil texture by manual inspection of samples (Birkeland, 1984). These sample features are determined by the mineralogical, chemical and physical properties of minerals, type of clay mineral and other crystalline material. A classification that would classify most soils as coarse materials would clearly provide an inaccurate soil classification.

For this reason, it is important to provide regression coefficients to represent particle size data obtained from L into textural triangles.

Plates (C) and (D) in Figure 9 depicts the results of the transformation by regression. Clearly, the data obtained from regression of L data are not perfectly matching the ones obtained with P, and they could not since the regression analysis had coefficients not equal to 1. However, the L data are now positioned in the original textural classes. It is however remarkable to notice that the three classes that were not represented before by the P (Silty clay, Silty clay loam and Silty loam for the ISSS) are still not represented in the new regressed representation with L (Plate C).

Clearly, the advantages of using L have been discussed at length in previous publications and in this research. The effort to represent the L data on texture triangles is motivated by the necessity to obtain a realistic soil classification, in accordance with current databases used worldwide. If the purpose of particle size analysis is not soil classification, such as researches and applications in sedimentology, geology, soil chemistry, rheology, soil physics and others, this transformation is not necessary and the original L data can be used.

### *3.5. Equivalent limits*

An alternative to applying regression equations to L data and then plotting the transformed data on the textural triangle is to change the equivalent limits for the clay fraction.

This approach was originally proposed by Konert and Vandenberghe (1997). Because of the over−estimation of the clay fraction by sedimentation methods and to avoid confusion, Konert and Vandenberghe (1997) recommended not to read the upper limit of the clay range at 2 $\mu$m when L methods are used. In their work, they analysed equivalent limits for particles of different shapes with respect to the spherical assumption, using disc−shaped particles and other shapes (page 533 in their paper). Their calculations corresponded very well with their experimental results, which showed a correspondence of the 2 $\mu$m pipette analysis with the 8 $\mu$m diameter in the L analysis. Therefore, they proposed to set the upper limit of the clay fraction not at 2 $\mu$m but at 8 $\mu$m. This transformation results in assigning a larger fraction of the mass distribution to the clay range, therefore with cumulative distribution more similar to the ones obtained with P. Antoine et al. (2009b) also found that particle size comparison between P and L showed that the classical cuts at 2, 20 and 50 μm, used with the sieve and pipette method, corresponded respectively to approximately 4.6, 22.7 and 63 μm. This concept was applied and tested in this research to assign the L data to three classes with the following limits: the clay fraction is in the range 0–8 $\mu$m, silt is in the range 8–50 $\mu$m and sand is in the range 20–2000 $\mu$m. The upper limits were selected consistent to the USDA triangle since the upper limit for silt is 50 $\mu$m. Using the ISSS triangle would have determined a fairly narrow range for silt (8–20 $\mu$m). The three classes (clay, silt and sand) were then computed from the cumulative curves for L and plotted on the triangle. Figure 9 depicts the modified triangle, with red circles for P and green crosses for L.

It is noteworthy how the soils are distributed across the triangle with realistic classifications. As pointed out by Konert and Vandenberghe (1997) the upper limit of 8 $\mu$m may be affected by the soil mineralogy and clay type, therefore it is a general value that corresponded well with theory and their experimental results, but it may change depending on the soil samples. In any case, the traditional upper limit of 2 $\mu$m for clay was also empirically selected, since clay particles can display a large variety of sizes and shapes, and it can therefore be changed. However, the necessity exists only if, as in the case shown here, soils are classified using ternary diagrams.

FIGURE 9. HERE

To further evaluate the relationship between the clay percentage obtained by P and the one obtained from L by selecting the size clay size limits in the range at 0−8 $\mu$m, a scatter plot was drawn (Figure 10). A good correlation was found with $R^2 = 0.873$.

FIGURE 10. HERE

## 4. Conclusions

L analysis is a faster and automated method that provides many advantages with respect to classic sedimentation methods. For this reason, for about three decades, researches were performed to investigate the differences between the methods. Results consistently pointed toward very significant differences between the methods. The question was: which method provides a ”true” measurement?

With the technological development of robotic, automated, optical microscopes to observe and record literally billions of soil particles, it was possible to perform independent particle size measurements from direct observations. Direct observation with DI was assumed to be the reference

(”true”) method for comparisons. In a recent paper, Bittelli et al. (2019) compared L and sedimentation for eleven samples, assuming direct observations with DI as a reference method. The research demonstrated that L provides more accurate measurements when compared to classic sedimentation methods.

The application of DI allowed us extend the original analysis of Bittelli et al. (2019) to a larger number of samples. A detailed statistical analysis was carried out to further investigate the differences among experimental methods. The results are consistent with previous findings confirming the large over−estimation of small size classes by sedimentation methods with respect to L. DI was assumed as a reference method and employed for comparison. L was in much better agreement with DI, that sedimentation methods. In particular, the differences were important in small size ranges, but not statistically significant above 100 $\mu$m in particle size.

Since the majority of databases in soil science, pedology, sedimentology and geology were created by using data collected with sedimentation−based methods, it is important to be able to convert data from L to sedimentation and vice versa. Moreover, soil should be still classified according to international standards. In this research regression equations are derived and used to convert data from L to P and represent the samples over the two main textural triangles used in soil science, the ISSS and USDA. Regression equations were derived from experimental data, to relate data obtained from P and L. Correlations and coefficients were consistent with previous published data, although it is suggested here, with respect to previous publications, to set the intercept to zero to avoid unrealistic estimations of negative masses for small mass fractions in the clay range.

Two approaches were then proposed to classify samples and represent them on textural triangles. First, the regression equations can be applied to the L data to be represented on triangles. The second approach is to modify the upper limit for clay from 2 to 8 $\mu$m and classify as clay the particles comprised in the range 0 - 8 $\mu$m. The computation of cumulative curves and distribution is easy since L provides many size classes, including the one with upper limit at 8 $\mu$m. The silt fraction will be comprised between 8 and 50 $\mu$m if the USDA triangle is used. It is suggested to utilize the USDA triangle, since with the ISSS triangle the silt range would be between 8 and 20 $\mu$m, a narrow range that leads to a small silt mass fraction. It can be noted how the soils are distributed across the triangle with realistic classifications, indicating that the upper limit for clay at 8 $\mu$m is a reliable limit as indicated by Konert and Vandenberghe (1997). Moreover, a good correlation was found between the clay fraction computed with P with the 2 $\mu$m upper limit for clay, and the one for L with the upper limit at 8 $\mu$m. The use of fixed limits clearly depends on the purpose of the study and application, as Schulte et al. (2018b) pointed out that, for instance, in sedimentology fixed limits should be avoided, since genetic processes cannot be reconstructed based on a single proxy value describing grain size such as the mean, median, or other relationship between fine and coarse fractions.

Finally, based on the additional evidence presented here about the better accuracy of L with respect to traditional sedimentation methods, it is suggested to change the standards for PSD analysis from sedimentation to laser diffraction methodologies.

## Acknowledgement

We thank Valentino Polchi for technical support with the instrumentation.

## References

Allen, T., 1981. Particle Size Analysis. 3rd ed. ed., Chapman and Hall, London.

Andrenelli, M., Fiori, V., Pellegrini, S., 2013. Soil particle-size analysis up to 250 $\mu$m by x-ray granulometer: device set-up and regressions for data conversion into pipette-equivalent values. Geoderma 192, 380–393.

Antoine, P., Rousseau, D.-D., Moine, O., Kunesch, S., Hatté, C., Lang, A., Tissoux, H., Zöller, L., Dezember 2009a. Rapid and cyclic aeolian deposition during the Last Glacial in European loess: a high-resolution record from Nussloch, Germany. Quaternary Sci. Rev. 28, 2955-2973.

Antoine, P., Rousseau, D.D., Fuchs, M., Hatte, C., Gauthier, C., Markovic, S.B., Jovanovic, M.,Gaudenyi, T., Moine, O., Rossignol, J., 2009b. High-resolution record of the last cli-matic cycle in the southern Carpathian Basin (Surduk, Vojvodina, Serbia). Quat. Int. 198, 19–36.

ASTM, 1963. Standard test method for particle-size analysis of soils. D422–63 , West Conshohocken, PA.

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

Birkeland, P., 1984. Soils and Geomorphology. Oxford University Press, Oxford, United Kingdom.

Bieganowski, A., Ryzak, M., Sochan, A., Makó, A., Barna, G., Hernádi, H., 2018. Beczek, M.; Polakowski, C. Laserdiffractometry in the measurements of soil and sediment particle size distribution. Adv. Agron. 151,215–279.

Bittelli, M., Andrenelli, M., Simonetti, G., Pellegrini, S., Artioli, G., Piccoli, I., Morari, F., 2019. Shall we abandon sedimentation methods for particle size analysis in soils ? Soil Til. Res. 185, 34–46.

Bittelli, M., Campbell, G., Flury, M., 1999. Characterization of particle size distribution in soils using a fragmentation model. Soil Sci. Soc. Am. J. 63, 782–788.

Bittelli, M., Campbell, G.S., Tomei, F., 2015. Soil Physics with Python. Transport in the Soil-Plant-Atmosphere Continuum. First edition ed., Oxford University Press, Oxford, United Kingdom.

Bland, J., Altman, D., 1999. Measuring agreement in method comparison studies. Stat. Methods Med. Res. 8, 135–160.

Buurman, P., Pape, Th., Reijneveld, J.A., de Jong F. and van Gelder, E., 2001. Laser-diffraction and pipette-method grain sizing of Dutch sediments correlations for fine fractions of marine, fluvial, and loess samples. Neth. J. Geosci. 80, 2, 49-57.

Fisher, P., Aumann, C., Chia, K., O'Halloran, N., Chandra S., 2017. Adequacy of laser diffraction for soil particle size analysis. PLoS One, 1-20. https://doi.org/10.1371/journal.pone.0176510

Dunn, O., 1964. Multiple comparisons using rank sums. Technometrics, 6,

241–252.

Eshel, G., Levy, G., Mingelgrin, U., Singer, M., 2004. Critical evaluation of the use of laser diffraction for particle-size distribution analysis. Soil Sci. Soc. Am. J. 68, 736–743.

Gee, G., Or, D., 2002. Particle-size analysis, in: Dane, J.H., Topp, G.C. (Eds.), Methods of soil analysis, Part 1. Agron. Monogr. ASA, Madison, WI, pp. 255–293.

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.

Goraczko, A., Topolinski, S., 2020. Particle size distribution of natural clayey soils: A discussion on the use of laser diffraction analysis (LDA). Geosciences 10 (2), 55.

Igaz, D., Aydin, E., Šinkovičová, M., Šimanský, V., Tall, A., Horák, J., 2020. Laser Diffraction as an Innovative Alternative to Standard Pipette Method for Determination of Soil Texture Classes in Central Europe. Water, 12, 1232. https://doi.org/10.3390/w12051232

Jonasz, M., 1994. Nonsphericity of suspended marine particles and its influence on light scattering. Limnol. Oceanogr. 32, 1059–1065.

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.

Krumbein, W., 1942. Settling velocity of flume behavior of nonspherical particles. Trans. Am. Geophys. Union 41, 621–633.

Kun, Á., Katona, O., Sipos, G., Barta, K., 2013. Comparison of Pipette and Laser Diffraction Methods in Determining the Granulometric Content of Fluvial Sediment Samples. J. Environ. Geog. 6, 3-4, 49-54.

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., Tóth, G., Weynants, M., Rajkai, K, Hermann, T. ,Tóth, B.,2017. Pedotransfer functions for converting laser diffraction particle-size data to conventional values. Eur. J. Soil Sci. 68, 5, 769-782.

Makó, A., Szabó, B., Rajkai, K., Szabó, J., Bakacsi, Zs., Labancz, V., Hernádi, H., Barna, Gy., 2019. Evaluation of soil texture determination using soil fraction data resulting from laser diffraction method. Int. Agrophys., 33, 445-454.

Matthews, M.D., 1991. The effect of pretreatment on size analysis. In: Syvitski, J.P.M. (Ed.), Principles, Methods and Applications of Particle Size Analysis. Cambridge University Press, Cambridge, MA pp. 368.

Moeys, J., 2018. The soil texture wizard: R functions for plotting, classifying, transforming and exploring soil texture data. http://www.R-project.org , 1–104.

Muggler, C., Pape, T., Buurman, P., 1997. Laser grain-size determination in

soil genetic studies 2. clay content, clay formation, and aggregation in some brazilian oxisols. Soil Sci. 162, 219–228.

Ozer, M., Mehmet, O., Nihat, S.I., 2010. Effect of particle optical properties on size distribution of soils obtained by laser diffraction environment. Eng. Geosci. 16 (2), 163–173.

Pieri, L., Bittelli, M., Rossi, P., 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.

Roberson S. and Weltje G. J., 2014. Inter-instrument comparison of particle-size analysers. Sedimentology 61, 1157–1174

Sherriff, S.C., Huallachain, D.O., 2015. Consequences of using different soil texture determination methodologies for soil physical quality and unsaturated zone time lag estimates. J. Contam. Hydrol. 182, 16-24.

Siegel, S., Castellan, N., 1988. Nonparametric statistics for the behavioral sciences. Mc GrawHill, New York.

Shang Y., A. Kaakinen, C.J. Beets, M.A. Prins, 2018. Aeolian silt transport processes as fingerprinted by dynamic image analysis of the grain size and shape characteristics of Chinese loess and Red Clay deposits. Sediment. Geol. 37, 36-48.

Schulte, P., Lehmkuhl, F., Steininger, F., Loibl, D., Lockot, G., Protze, J., Fischer, P., Stauch, G., 2016. Influence of HCl pretreatment and organo-mineral complexes on laser diffraction measurement of loess-paleosol-sequences. Catena 137, 392-405.

P. Schulte, Lehmkuhl, F., 2018a. The difference of two laser diffraction patterns as an indicator for post-depositional grain size reduction in loess-paleosol sequences, Palaeogeogr. Palaeocl. 509,126-136.

Schulte, P., Sprafke, T., Rodrigues, L., Fitzsimmons, K.E., 2018b. Are fixed grain size ratios useful proxies for loess sedimentation dynamics? Experiences from Remizovka, Kazakhstan, Aeolian Res., 31 (2018), pp. 131-140

Rasmussen, C., 2020. Particle Sizing in Geosciences: Explanation of Various Techniques and Pre-treatments. Aarhus University, Denmark. E-book url: https://ebooks.au.dk/aul/catalog/book/374

Taubner, H., Roth, B., Tippkoutter, R., 2009. Determination of soil texture: Comparison of the sedimentation method and the laser-diffraction analysis. J. Plant Nutr. Soil Sci. 172, 161–171.

Tukey, J., 1948. Comparing individual means in the analysis of variance. Biometrics 5, 99D114.

Újvári, G., Kok, J.F., Varga, G., Kovács, J., 2016. The physics of wind-blown loess: Implications for grain size proxy interpretations in Quaternary paleoclimate studies. Earth Sci. Rev. 154, 247-278.

Vdovic, N., Obhada, J., Pikelj, K., 2010. Revisiting the particle-size distribution of soils: comparison of different methods and sample pre-treatments. Eur. J. Soil Sci. 61, 854–864.

Wu, Q., Borkovec, M., Sticher, H., 1993. On particle-size distributions in soils. Soil Sci. Soc. Am. J. 57, 883–890.

Yang, Y., Wang, L., Wendroth, O., Liu, B., Cheng, C., Huang, T., Shi, Y., 2019. Is the laser diffraction method reliable for soil particle size distribution analysis? Soil Sci. Soc. Am. J. 83, 2, 276–287.