Revisiting the particle-size distribution of soils: comparison of different methods and sample pre-treatments

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Summary

The choice of analytical method and sample pretreatment has significant consequences for the shape of particle-size distribution (PSD) frequency curves, and therefore for the evaluation of soil textural parameters. Here, the comparison of several granulometric methods based on different physical principles is presented: wet sieving (WS), based on gravity and the mechanical force of water, was combined with pipette (PP) sedimentation/settling velocity, Micromeritics SediGraph (MS) sedimentation/x-ray attenuation and Coulter Counter (CC) electroresistance particle counting. The Malvern Mastersizer (MM), an instrument based on laser diffraction, was used without WS. Twelve typical temperate-region soil types were chosen for this study on the basis of their mineral composition, organic matter content, conductivity and magnetic susceptibility. The modalities of PSD frequency curves obtained by different methods were compared. The results showed considerably larger clay-fraction contents determined with the sedimentation techniques, PP and MS, than that obtained by CC or MM. Statistical correlation and regression models were used to compare the fractions of clay, silt and sand obtained with different methods. Linear correlations were found in almost all cases, except those comparing clay fractions obtained by CC with those obtained by MM, PP and MS methods. These correlations were non-linear. The observed difference was attributed to the presence of aggregates and/or magnetic properties of soil particles. However, more data are needed to verify this hypothesis. The implications of sample pre-treatment with dispersant and hydrogen peroxide (H₂O₂) were evaluated by the MS and CC techniques and observed by the scanning electron microscope. H₂O₂ was found to be an efficient disaggregating agent. The use of dispersant resulted in the increased amount of the clay fraction measured by the MS method.

Introduction

Information on soil texture is fundamental for many soil studies, especially for those involving soil chemical and mineral composition (Murashkina et al., 2007), soil C content (Zhang et al., 2005), sorption characteristics (Gawlik et al., 1999), tillage characteristics (Basic et al., 2001), plant growth (Lipiec et al., 2007), erosion (Warrington et al., 2009), desertification (Su et al., 2004) and influence of soil characteristics on mine-detection techniques (Obhođaš et al., 2005; Obhođaš, 2007). Precise and comparable information on soil texture is of great importance for these studies. It is well known that the choice of granulometric method and sample pre-treatment has consequences for particle size distribution (PSD) and hence for soil texture characterization. The differences between granulometric methods have been investigated (Syvitski et al., 1991; Wu et al., 1993; Knösche et al., 1997; Konert & Vanderberghe, 1997; Beuselinck et al., 1998; Eshel et al., 2004; Dur et al., 2004; Filgueira et al., 2006; McCave et al., 2006; Goossens, 2008), but attention has rarely been paid to the modality of PSD frequency curves. The modality in frequency curves reflects different patterns of pedogenesis and has to be carefully observed prior to choosing a model for PSD interpretation.

Bimodality of PSDs is quite common and indicates two physical processes involved in soil formation, weathering of primary rocks resulting in sand and silt fractions (primary soil minerals) and weathering of sand and silt soil fractions resulting in clay fractions (secondary soil minerals). Assuming soil bimodality, Shiozawa & Campbell (1991) developed a Gaussian bimodal model for describing PSD of various soils. Condappa et al. (2008)
have shown that processes of pedogenesis in tropical and subtropical regions favour the generation of soils with bimodal PSDs. However, those of soils from temperate regions often exhibit multimodality (Pieri et al., 2006), indicating more complex pedogenesis. In addition, joining segments of the PSD obtained from techniques exploiting different particle properties to cover the necessary size spectrum adds a complication to quantitative analysis.

Some studies dealing with PSD interpretation involve description of soil texture using fractals (Comegna et al., 1998; Filgueira et al., 2006; Prosperini & Perugini, 2008). A fractal model is appropriate only to the distribution arising from a single soil-forming process, which involves only the particles that fracture as the consequence of a stress concentration on their surface. Fractal models most often can not provide adequate descriptions of the entire PSD size spectrum. Some authors use fractals only to describe the fine fraction in PSD spectra (Millan et al., 2003; Filgueira et al., 2006), whereas application to the entire PSDs may lead to fractal exponents >3 (Tyler & Wheatcraft, 1989), which have no physical meaning.

Soil magnetism and soil conductivity are often not determined. The need for these types of information has arisen in relation to soil properties that adversely affect detection of landmines. Magnetic properties of some soils severely affect metal detector sensing, preventing their use for landmine clearance. Frequency-dependent magnetic susceptibility (K_{LF} - K_{HF}) indicates the ‘magnetic viscosity’ of the soil particle which affects the sensing of the electrical instrument. Tite & Linnington (1975) and Hannam & Dearing (2008) found that Terra Rossa soils overlying limestone beds can have large frequency-dependent magnetic susceptibility caused by the presence of ferro-minerals in the clay fraction. Magnetic susceptibility of the soil may be caused by a subgroup in the clay fraction containing ferromagnetic particles of size 0.5–1 μm that contain only one magnetic domain, having as a consequence higher magnetic susceptibility when compared with larger particles. For this reason, haematite and goethite, minerals typically present in Terra Rossa soils, exhibit a pronounced magnetic viscosity regardless of the fact that the magnetic characteristics of these minerals are weak and usually do not contribute to soil magnetism. The magnetic susceptibility effects on PSD needs to be resolved.

In addition to the effects introduced by the methods, the preparation of samples is an important factor that contributes to measurement reliability (Matthews, 1991; Chappell, 1998). Common preparations for determination of PSDs include removal of organic matter, carbonates and/or iron oxides, ultrasonication and addition of a dispersant (McManus, 1988). However, it is not always advisable to use all of these. The choice should correspond to the aim of the investigation and type of material to be analysed (Matthews, 1991).

The present study examines the reliability of several methods (and combinations thereof) for PSD determination, exploiting various particle properties of a variety of temperate soils, subjected to selected pretreatments, and examines their variability.

**Materials and methods**

**Sample determination and preparation**

Twelve soil samples were chosen to represent typical soils from temperate regions. These were selected from a number of samples collected from cleared landmine sites in previous studies (Obhoďaš et al., 2005; Obhoďaš, 2007). All samples were dried at 105°C and sieved through a 200-μm ASTM sieve to eliminate gravel and large organic debris. A portion of each sample was homogenized in an agate mortar. The mineralogical composition of homogenized samples was analysed with a Philips ‘X’Pert’ vertical x-ray goniometer (PANalytical, B.V., Almelo, the Netherlands). The determination of carbonate minerals was performed by acid digestion, (ONORM L 1084, 1999) and the organic matter (OM) content was determined as weight loss on ignition. Soil conductivity was measured in a stirred water suspension made of 1 g of soil in 200 ml of deionized water (conductivity 1.9 ± 1.2 μS cm⁻¹) using a YSI 5563 sensor (YSI Ltd., Fleet, UK). The soil volumetric magnetic susceptibility was measured with a Bartington MS2 B-Coil susceptibility meter (Bartington Instruments, Witney, UK) at the frequencies of K_{LF} = 458 Hz and K_{HF} = 4580 Hz, which provided an indication of the volumetric frequency-dependent magnetic susceptibility (K_{LF} – K_{HF}).

**Grain-size analyses**

The soil samples were suspended in deionised water, ultrasonicated for five minutes and then analysed by pipette (PP), Micromeritics SediGraph 5100 (MS) (Micromeritics Instrument Corporation, Norcross, GA, USA) and Coulter Counter TA II (CC) (Coulter Electronics, Hialeah, FL, USA) in combination with wet sieving, and by the Malvern Mastersizer 2000 (MM) (Malvern Instruments, Malvern, UK). Texture classes of the soil samples, determined from the resulting PSDs, were categorized according to the German soil texture classification system (Bormann, 2007). A short description of each of these methods is given below.

**Pipette method.** Ten grams of soil sample suspended in 1 litre of deionised water were passed through a set of American Society for Testing and Materials (A.S.T.M.) sieves (1000 – 32 μm). The transmitted suspension was then poured into a 1-litre graduated cylinder and allowed to settle. Successive aliquots of 10 cm³ were extracted from the suspension at the time intervals calculated for a specific particle diameter (according to Stokes’ law), dried and weighed. The PSD of particles <32 μm was calculated on a mass basis.

**Micromeritics SediGraph.** Ten grams of dry sample were suspended in water, sieved (1000 – 63 μm sieves) and the transmitted suspension was allowed to settle. Granulometric distribution of particles in the suspension was determined by measuring the X-ray attenuation during sedimentation in the instrument’s cell. The PSD of this portion of the sample (<63 μm)
was determined, on a mass basis, from the X-ray attenuation during sedimentation.

**Coulter Counter.** Samples were wet-sieved as described for the pipette method. An aliquot of the transmitted suspension was withdrawn and mixed with 0.15 M NaCl solution (conductivity = 15659.6 μS cm⁻¹). The suspension was drawn through a tube of 70-μm aperture. Two electrodes placed either side of the tube aperture provide a direct current electrical field. As a particle passes through the measurement tube, it changes the resistance between the electrodes. This produces a short voltage pulse of a magnitude proportional to the particle volume. The detectable size-range for this aperture was 1–32 μm, and below this size the PSD function was graphically extrapolated by the operator. The segment of the PSD obtained from sieving (>32 μm) was then joined to the segment from the CC expressed on a volume basis.

**Malvern Mastersizer.** One gram of dry sample was suspended in 50 cm³ of redistilled water. Approximately 5–10 cm³ of that suspension was placed in a dispersion unit containing 800 ml of tap water. The intensity of scattered light from the laser, scattered at different angles from the different particles, was measured with a series of detectors. Particle size was calculated on a volume basis using the Mie theory and proprietary software. A refractive index of 1.53 was used as a model parameter.

**Sample disaggregation and dispersion procedures**

Four suspensions of selected samples were prepared as: (i) original sample suspended in deionised water (10 g dm⁻³), (ii) original sample suspended in 0.1% solution of dispersant (sodium hexametaphosphate), (iii) sample treated with 15% H₂O₂ solution, and (iv) sample treated with H₂O₂, and then suspended in 0.1% dispersant solution. The PSDs were measured by the MS and CC methods. Subsequently, suspensions were allowed to settle and after six days 10-ml aliquots were withdrawn from the top of each suspension. Sample aliquots were air-dried on the glass tiles, coated with graphite, and inspected at 20 kV by a TS 5136 MM scanning electron microscope (SEM; Tescan, Cranberry Township, PA, USA).

**Mathematical methods**

Median (d50), average particle sizes (APD), Pearson product-moment correlation coefficients (r) used with the 0.95 confidence level, coefficients of determination (R²)and probability of error (p) were calculated from the PSDs. The fractions of sand, silt and clay obtained from the various methods were correlated pair-wise for the 12 samples. The resulting parameters a and b are the slope and the intercept of the linear regression equations (Y = aX + b), while c and d are the parameters of the logarithmic regression equations (Y = (c)logX + d). For the 0.95 confidence level, a statistically significant correlation corresponds to r ≥ 0.576 (for N = 12 and N-2 degrees of freedom). APD was calculated according to the model:

\[ \bar{x} = \sum_{i} w_i x_i / 100, \]

where \( w_i \) is a fraction of \( x_i \) in percentages, and \( x_i \) is an average particle diameter of ith size.

**Results and discussion**

**Soil characteristics**

Table 1 shows the characteristics of the 12 samples, obtained by the XRD analysis. Samples were composed mainly of

<table>
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<th>Il / M</th>
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<th>Ka</th>
<th>S</th>
<th>H / G</th>
<th>CaCO₃</th>
<th>OM</th>
<th>Soil type</th>
<th>Dry soil density</th>
<th>Conductivity</th>
<th>K₇F</th>
<th>K₉F</th>
<th>K₇F - K₉F</th>
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<td>+</td>
<td>+</td>
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<td>+</td>
<td>-</td>
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Q = quartz; Chl = chlorite; Il / M = illite/muscovite; F = feldspars; Ca = calcite; Ka = kaolinite; S = smectite; H / G = haematite/goethite.
quartz, chlorite, K-feldspars, mica and clay minerals. A substantial amount of calcite was detected in samples 6–12. The quantitative analysis of carbonate minerals using the acid-digestion method was consistent with the XRD analysis. Samples 1–5 contained 0.4–1.4%, samples 6 and 7 contained less than 10%, and samples 8–12 contained 10–55% of carbonates (CaCO₃). The organic matter content (OM) ranged from 1.1 to 12.0% (by weight). The conductivity varied between 5.7 and 56.3 μS cm⁻¹ and the frequency-dependent magnetic susceptibility between 0.8 and 49.0 × 10⁻⁵ (SI units).

**Soil texture**

The shapes of the PSD frequency curves (Figure 1a,b), average particle diameters (APD), median diameters (d₅₀) (Table 2) and soil texture classes (Figure 2) obtained from analysed soil samples clearly show a dependence on the method used to obtain them. In general, the main differences can be described as a more pronounced multimodality of PSD frequency curves obtained by splicing sieve analysis to those of CC, MS and PP, compared with those obtained in their entirety using laser diffraction (MM). Minima at the meeting point of PSD from sieve analysis with that of the CC, MS or PP were common and well-pronounced for the soils containing a dominant silt fraction. This can be explained (i) as a ‘methodological break’ (a discontinuity between joining segments of the PSD obtained by techniques that exploit different physical properties of particles) and (ii) by the decreased efficiency of the techniques at their boundaries of effective use. At the coarse end, the greater mass of the particles makes them more difficult to keep in suspension during analysis, resulting in an underestimate of that particular grain size. In addition, sieves have decreased accuracy for grain sizes below 50 μm (Gee & Bauder, 1986). They prevent or allow the randomly oriented platy particles (which can exist in the range of 32–63 μm) to pass through the screen under the mechanical force of water. Platy particles that manage to pass through the sieve of smallest mesh size, on the basis of their two smallest dimensions, will settle in fluid with their longest dimensions oriented tangentially to their motion during a settling process in methods such as MS and PP. This enhances their apparent size, relative to a particle of the same equivalent spherical diameter. Accordingly, passing such particles through the CC aperture may produce a pulse height assigned to the equivalent spherical volume larger than the smallest mesh size of the sieves, and categorize them to a class size above the upper limit of detection of the CC.

Settling techniques, MS and PP, had increases in clay fraction with a minimum in the PSD at 2 ± 1 μm (Figure 1). This effect arises from the departure of particle shape and density from those used in the application of Stokes’ law, the neglect of particle diffusion and convective disturbances so that all solids remaining in suspension at the end of the prescribed settling period are included within the smallest size class. In the range where Stokes’ law is applicable, 1–100 μm (Duck, 1994), particle shape and variations in density, arising from pore fluid inclusions in small aggregates or among the various minerals present, serve to distribute material
Table 2 Average particle-size diameter (APD) and median diameter (d50) for measured soil samples obtained by pipette (PP), Coulter Counter (CC), Micromeritics SediGraph (MS) and Malvern Mastersizer (MM) methods

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<tr>
<th>Location</th>
<th>PP</th>
<th>CC</th>
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<th>PP</th>
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into size classes close to that defined by the selected implementation of Stokes’ law.

Implementation of Stokes’ law (Equation 2) requires a solids density that is unlikely to represent all the materials in the sample and serves to define the size axis of that part of the PSD:

\[ v = \frac{(\rho_p - \rho_f) g d^2}{18 \mu} , \]  

where \( v \) is the settling velocity, \( \rho_p \) is the particle density, \( \rho_f \) is the fluid density, \( g \) is the acceleration due to the gravity, \( d \) is the particle diameter and \( \mu \) is the dynamic viscosity of the fluid.

Another reason is that a solids density of 2.65 g cm\(^{-3}\) is often used with Stokes’ law in its application to soils and sediments, but according to Clifton et al. (1999) particle density may vary in a sample from 1.66 to 2.99 g cm\(^{-3}\). Recently, Virto et al. (2008) have shown that the silt fraction found in silty temperate soils actually consists of un-complexed, non-occluded light organic matter, non-occluded primary silt-size minerals and stable silt-size aggregates with densities between 1.6 and 2.5 g cm\(^{-3}\). In addition, aggregates often contain a significant pore volume, which decreases their density and prolongs settling time (Trew- week & Morgan, 1977) in relation to a solid particle of the same dimensions.

If we assume a range of particle densities as 1.6 < \( \rho_p < 2.65 \) g cm\(^{-3}\), fluid density of \( \rho_f = 1.0 \) g cm\(^{-3}\) and dynamic fluid viscosity \( \mu = 0.01 \) g cm\(^{-1}\) s\(^{-1}\), Stokes’ law (Equation 2) for particles of 30 \( \mu \)m in diameter will give settling velocities from

Figure 2 Texture classes of measured soil samples obtained by four granulometric methods presented in texture triangles. Texture classes are: Ss = pure sand, Sl = loamy sand, St = clayey sand, Su = silty sand, Ls = sandy loam, Lts = clayey sandy loam, Ts = sandy clay, Us = sandy silt, Ut = clayey silt, Lt = clayey loam, Su = silty sand, Sl = loamy sand, Shs = loamy silty sand, Uu = pure silt, Uls = loamy sandy silt, Lu = silty loam, Tu=silty clay, Ti = loamy clay, Tt = pure clay, 2 = slightly, 3 = medium, 4 = highly.
Revisiting the particle size distribution of soils

0.0294 cm s\(^{-1}\) to 0.0785 cm s\(^{-1}\). Hence, the 30-μm particles, having \(\rho = 1.6\) g cm\(^{-3}\), need 5.67 minutes to settle to the depth of 10 cm, while 2.65 g cm\(^{-3}\) particles need 2.12 minutes. The porosity and irregular shape of aggregates will additionally prolong their settling time. Therefore, the minima in PSD frequency curves obtained by settling techniques can reflect the presence of low-density particles and irregular, heterogeneous aggregates reported in fractions of smaller dimensions. The more pronounced multimodality of PSD frequency curves obtained by settling techniques, caused most probably by irregular shape and heterogeneous densities of particles and aggregates, can be observed in Figure 1(a,b).

In contrast to settling techniques, the CC technique may underestimate the clay fraction content. The weak electrolyte solution used in this technique can promote aggregation of clay particles in spite of ultrasonic dispersion pretreatment and continuous stirring during the measurement. In addition, any particles much smaller than approximately 5% of the aperture diameter may pass undetected because the instrument sensitivity decreases rapidly below this size. The combination of the PSD from CC with that from sieve analysis involves joining a size scale based on an equivalent spherical diameter with that of a mesh size provided directly by the sieves. The usual practice of joining of these two segments does not include conversion of CC-derived volume percentage (% Vol) to mass percentage (% Mass) or vice versa because a representative solid density is used.

The volume and the mass percentages are related as:

\[
\% \text{ Vol} = \frac{\rho(\text{soil})}{\rho(\text{s.particle})} \% \text{ Mass},
\]

where \(\rho(\text{soil})\) represents the average soil density and \(\rho(\text{s.particle})\) is the density of a certain size fraction; the conversion of CC data to a mass basis (or vice versa) requires selection of an appropriate solids density for a given fraction, which determines the relative amplitude of this segment of the overall PSD. If the range of densities reported by Virto et al. (2008) is used, 2.65 g cm\(^{-3}\) for clay and \(1.6 < \rho < 2.65\) g cm\(^{-3}\) for silt, then the shape of the PSD curve will be modified accordingly. The assumption of greater particle density in the silt fraction will influence the shape of the PSD frequency curve in the region closer to the sand fraction, whereas the assumption of lower particle density will influence the region closer to the clay fraction.

In comparison with the other techniques, the MM technique considerably underestimates the clay and fine silt fractions and shifts the distribution towards larger sizes. Such shifting was also observed by other authors (Konert & Vandenberghe, 1997; Eshel et al., 2004; McCave et al., 2006; Pieri et al., 2006), who attributed the underestimate of the fine fraction to the liability of

![Figure 3](image-url)
the laser technique to interpret the platy particles as spheres. They also considered the influence of different optical model applications (Mie and Fraunhofer theories) and measurement parameters, such as the selection of absorbance and relative refractive index in the Mie theory. However, there was agreement that the shape or sphericity of the particles is of prime importance in measuring the grain size by the laser technique. In addition, in a continuous flow of particles, the projected cross-sectional area of a non-spherical particle averaged over all the particle’s possible orientations relative to the direction of the beam is larger than that of a sphere with an equal volume (Jonasz, 1991).

The shift toward larger sizes by the MM technique is exemplified by samples 4, 5, 7, 9 and 12 (Figure 1). The common characteristic of these samples is their large OM content, which was a possible cause of aggregation. Because no sieving was applied, we can assume that this could be the additional reason why the two-step techniques show a greater content of fine fractions. The shaking and the mechanical force of water applied during sieving could break the aggregates more efficiently than ultrasonication alone, enhancing the contribution of the fractions <32/63 \( \mu \text{m} \).

The parameters of linear regression analyses of the sand, silt and clay fractions obtained by the various techniques (Table 3) suggest a reasonably good fit, with correlation coefficients (\( r \)) of > 0.76, which suggests a good statistical significance.

However, these results differ from those obtained by others (Konert & Vandenberghe, 1997; Eshel et al., 2004; Pieri et al., 2006). We confirm, as these authors have observed, that universally applicable mathematical relationships between the PSD frequency curves, or fractions thereof, obtained by the various methods, cannot be established. Such relationships are influenced strongly by sample pretreatment techniques, the instrument type and measurement parameters. Should the need arise to compare, or merge, soil texture databases comprising PSDs from these various techniques then suitable mathematical relationships for inter-conversion between these are desirable.

Regression analysis of the clay fraction obtained by CC and those obtained by the other methods showed non-linear relationships (Figure 4). Samples 3, 7, 9 and 12 contributed the most to this non-linearity. The observed non-linearity cannot be attributed to the soil particle conductivity because the conductivity measurements showed that the differences are too small (see Table 1) in comparison with the conductivity of the electrolyte (15 660 \( \mu \text{S cm}^{-1} \)), and therefore could not have any effects on CC sensing. The potential causes of the observed non-linear relationship are discussed below.

The non-linear regressions, presenting correlation of clay fraction obtained by CC with that of PP, MS and MM, are shown in Figure 4. Samples contributing to the non-linearity in the regressions (3, 12, 9 and 7) had a large magnetic susceptibility (\( K_{\text{LF}} - K_{\text{HF}} \)), which was 9.1, 11.7, 27.2 and 49.0 \( \times 10^{-5} \text{ SI} \), respectively. The remaining eight samples had \( K_{\text{LF}} - K_{\text{HF}} \) values that were less than 5.0 \( \times 10^{-5} \text{ SI} \) (Table 1).

In the study involving the influence of soil characteristics on different landmine detection techniques (Obhoda, 2007), it was observed that soils showing volumetric frequency-dependent magnetic susceptibility (\( K_{\text{LF}} - K_{\text{HF}} \)) larger than 25 \( \times 10^{-5} \text{ SI} \), had a very strong effect on the performance of the metal detectors used for landmines. Hence there is a possibility that particles with magnetic properties interact with the electrical field in the CC aperture, reducing the voltage pulse produced by its passage. Such a particle would be classified as having a smaller size than those associated with its actual volume, thus contributing to the increase in the clay-size region of the PSD.

Aggregation of small particles, some initially below detectable size, in the suspension fed to the aperture in the CC, is promoted by the electrolyte environment. It is possible that aggregation has contributed to the PSDs of samples 3, 7, 9 and 12, which contain greater concentrations of OM than the others. As the sensitivity of the CC method diminishes at the lower boundary, some sub-micron particles may remain undetected unless they contribute to aggregates at the size above this boundary (>2 \( \mu \text{m} \)). There is evidence that the liquid component (pore fluid) of an aggregate is not detected by the CC (which measures only the particulate matter) and that the volume of such an aggregate may be underestimated (Treweek & Morgan, 1977) because the disruption of the aggregate in the brief, but intense, shear as it passes through the aperture. This increases the voltage pulse width at the expense of its height. Thus there is a failure to detect some material contained in aggregates during transit through the aperture. Unless this can be

### Table 3 Linear regression parameters obtained for fractions of sand, silt and clay analysed by different methods for 0.95 confidence level

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th></th>
<th>Silt</th>
<th></th>
<th>Clay</th>
<th></th>
<th>APD</th>
<th></th>
<th>d50</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a )</td>
<td>( b )</td>
<td>( R^2 )</td>
<td>( r )</td>
<td>( a )</td>
<td>( b )</td>
<td>( R^2 )</td>
<td>( r )</td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>MM</td>
<td>0.8</td>
<td>14.3</td>
<td>0.83</td>
<td>0.91</td>
<td>0.8</td>
<td>16.1</td>
<td>0.65</td>
<td>0.81</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MS</td>
<td>1.0</td>
<td>—0.1</td>
<td>0.99</td>
<td>0.99</td>
<td>0.9</td>
<td>—0.3</td>
<td>0.95</td>
<td>0.97</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CC</td>
<td>1.0</td>
<td>0.1</td>
<td>0.98</td>
<td>0.99</td>
<td>1.0</td>
<td>3.4</td>
<td>0.92</td>
<td>0.96</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MM</td>
<td>0.8</td>
<td>13.8</td>
<td>0.86</td>
<td>0.93</td>
<td>0.9</td>
<td>14.7</td>
<td>0.72</td>
<td>0.85</td>
<td>0.04</td>
<td>0.1</td>
</tr>
<tr>
<td>MS</td>
<td>1.0</td>
<td>—0.1</td>
<td>0.98</td>
<td>0.99</td>
<td>0.9</td>
<td>1.6</td>
<td>0.91</td>
<td>0.95</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>MM</td>
<td>0.8</td>
<td>14.4</td>
<td>0.83</td>
<td>0.91</td>
<td>0.8</td>
<td>18.0</td>
<td>0.64</td>
<td>0.80</td>
<td>0.03</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\( PP = \) pipette, \( CC = \) Coulter Counter, \( MS = \) Micromeritics SediGraph, \( MM = \) Malvern Mastersizer \( a = \) line slope, \( b = \) line intercept \( (Y = aX + b) \), \( R^2 = \) coefficient of determination, \( r = \) correlation coefficient, \( APD = \) average particle diameter and \( d50 = \) median.
Figure 4  Correlations of clay fractions obtained by CC and the other three methods.

Effects of sample pre-treatment

The PSD frequency curves obtained by MS and CC techniques, following various pretreatments of samples 1 and 12 (Figures 5 and 6), show that these resulted in an increase in the clay fraction detected by MS in comparison with those reported earlier (Figure 1a,b). It appears that H₂O₂ disrupted the aggregates, releasing many small particles, and dispersant had a similar effect, both reducing particle settling. The combined effect of both dispersant and H₂O₂ was cumulative, increasing the proportion of the <1 μm material by more than 30%, suggesting that this combination promoted disaggregation of particles. The clay fractions detected by CC doubled after pre-treatment with H₂O₂ alone and in combination with dispersant (Figures 5b, 6b), indicating the effective action of H₂O₂ on disaggregation of the material bound with oxidizable organic matter. The effect of dispersant alone was negligible, indicating that destruction of organic matter was necessary in order for it to contribute an effect in the electrolyte environment within the CC.

The MS was found to be more sensitive to different pre-treatments than CC in terms of the fine fraction increase and
pronounced multimodality. Micrographs of the specimens from the supernatant liquid of four suspensions of sample 1, subjected to various pretreatments, following 6 days of settling (Figure 7), indicate that aggregate structures several microns in size were present after ultrasonication. Particles/aggregates with more distinct edges arose from dispersant addition (but no change in size), and a structure-free, amorphous mass of small particles occurred in the presence of both H_2O_2 and dispersant. Assuming that particles would behave according to Stokes’ law, and putting aside for the moment the particle diffusion and convection caused by temperature changes that occur in the suspension, the supernatants should have contained only particles <0.4 μm.

Dissimilar settling from suspension was indicated by the concentrations of the particles in the supernatant liquids, which were 0.03, 0.18, 0.07 and 0.35 g litre\(^{-1}\), respectively. Large concentrations of suspended particles (0.18 and 0.35 g litre\(^{-1}\)) were found in the supernatant liquids following treatment with dispersant and dispersant combined with H_2O_2. The dispersant caused the delay in settling, enabling the particles to remain in suspension in the water column for longer.

It appears that H_2O_2 was the only agent effective in disrupting the aggregates, whereas dispersant increased the clay fraction determined by MS as a consequence of an increase in inter-particle repulsive forces. In contrast, application of the dispersant did not alter the PSD function and results remained within the range of instrument reproducibility.

The combination of H_2O_2 and dispersant pre-treatment produced larger increases in the clay fraction determined by MS, but the effect of that combination was not so apparent with CC analyses. In part, that may be because small particles were liberated which were smaller than the detectable range of the CC.

Sample pre-treatment clearly influences the outcomes of size analyses below around 60 μm. Chena & Plante (2006) have shown that aggregates made of clay and OM do not exhibit the same properties as free clay and free OM. The authors stated that organo-mineral complexes must be regarded as conceptual entities because the energies required to fully disperse the clay-size fraction are likely to render the results meaningless in natural systems and are also likely to result in the breakdown of intact organic or mineral particles. The use of various sample pre-treatments for research needs to be guided by its purposes because the complete disintegration of soil aggregates is difficult and arbitrary. Partial disruption may occur during handling and within some particle size instrumentation sampling systems.

**Conclusion**

Multimodal soil PSDs may arise from more than one soil-forming process and as artefacts of particle-size analysis. Distributions obtained by combination of data from two methods exploiting different particle properties over adjoining size ranges may produce a minimum in a PSD frequency curve at the junction. Settling techniques do not resolve details of the PSD below approximately 2 μm. All unsettled material is usually lumped together and may produce an additional mode. In contrast to these techniques, the CC and MM techniques underestimate the clay content as a result of the failure to detect small particles and the solids content of aggregates torn apart during detection in the former (CC), and as a result of a relative overestimate of the silt and sand fractions in the latter (MM).

Methods based on electrical counting, presented here by the CC method, appear to underestimate the clay fraction in soils compared with other methods. This may arise from two possible effects, insensitivity to fine particles and a reduced response due to particle magnetism. These two effects are not mutually exclusive and require more extensive investigation of model systems and a wider variety of soils.

The use of dispersant alone does not appear to result in the most significant changes in soil sample PSDs using the methods reported here. The oxidizing agent H_2O_2 appears to be affective in increasing the clay content within PSDs through disruption of aggregates bound with organic material. Addition of dispersant following H_2O_2 treatment facilitates further disaggregation. The sequence and variety of pre-treatments coupled with the conditions...
imposed during analysis suggest that a wide combination of methods is needed to examine the detailed properties of regions within the soil particle size spectrum.

Acknowledgements

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