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# On the calculation of the surface area of different soil size fractions

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## Abstract

A model that accounts for contributions to the total surface area (SA) by different size fractions of the soil is considered from a theoretical point of view. Calculations, based on continuous particle sizes and forms, explain SA mainly as a geometric SA. It is common for coarse soils to have a discrepancy between the measured SA, say inferred from adsorption of gases, and the calculated geometric area of up to two orders of magnitude. This discrepancy is removed by the present method. Size distribution is the main factor influencing the SA; taking particle forms into account resulted in a 2–3 times increase of SA. The several orders of magnitude range of grain sizes leads to crucial variations in the contributions that soil fractions make to weight, SA and number of grains. The fundamental lower limit of variation of soil properties, originating from the discrete nature of soils, is introduced. Despite the deterministic physical origin of SA, high sensitivity to the finest fractions can be considered on the environmental scale as a cause of the dual—stochastic and deterministic—nature of SA. Small variations of weight within experimental error and the fundamental limit may result in significant variations of SA, close to the same order of magnitude for coarse soils. An empirical equation (Sverdrup, 1990) relates textural data to SA at landscape scale. It is applicable to a collection of samples, while individual samples must be characterised on a probabilistic basis.

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## 1. Introduction

Most chemical processes in the environment take place at the surfaces of soil and parent rock particles. The surface area (SA) of different mineral particles constituting soil is a fundamental property that influences soil quality. It is important in determining cation exchange capacity, adsorption and release of nutrients and pollutants, water retention, etc. The SAs of the mineral components in a soil are key parameters when determining rates of dissolution, the only long-term source of base cations in soils apart from deposition; and are widely used for quantifying soil vulnerability to acid deposition, including critical load assessment and mapping. Realistic values of the bulk soil SA and con-

tributions of different mineral fractions are of great concern in geochemical applications, particularly in acidification research. Consideration of natural soil fractions having different origins allows determination of their contributions to the SA. A natural fraction can be thought of as a mineral species or group of closely related species, or a set of particles, homogeneous in some other respect, that arose due to a specific process of soil formation, such as parent rock fragmentation or wind deposition. Such fractions are characterised by continuous size distributions (SD), not bounded by the artificial limits of size classes introduced in the process of measurement. SA measurements of the individual mineral components, (Clow and Drever, 1996; White et al., 1996), are very rare, if not exceptional, due to the complex and time-consuming task of mineral particle separation. The difficulties involved in such measurements have stimulated a theoretical study of the problem.

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The ab initio calculations of the SA of a soil sample divided into size classes are usually based on the relationship (Herdan, 1953; Sverdrup, 1990)

$$A_{SCA} = \frac{6M}{\rho\phi} \sum_k \frac{\xi_k}{D_k}, \quad (1)$$

summation is performed over all size classes.  $D_k$  is the effective diameter defined as a diameter of the sphere with the same volume as the average particle for the  $k$ -th size class,  $\xi_k$  is the fraction of the sample's mass  $M$  within this class (or weight fraction),  $\rho$  is the density of the soil solid phase. Here and below all properties (Table 1) that enter any equation must be expressed in the main units of the same system of physical units, usually in SI. The multiplier  $6/D_k$  is the ratio between the SA of a sphere and its volume. The non-sphericity of soil particles is taken into account by the factor  $\phi$ , which usually has a value in the range 0.85–0.9 (Sverdrup, 1990). The area in Eq. (1) is traditionally called a geometric SA since it is believed that this assessment reflects a hypothetical smooth surface enveloping the actual soil particles. This latter assumption, as will be shown, is not valid, which is why it is termed a size class assessment [index SCA in (1)].

Size class assessment is exact at the limit of infinitely small size classes. It is also true for a limited number of size classes if the particles within each class are identical; however it is insufficient for understanding the SA of real soils. When particles are not identical and a consistent procedure for determination of the effective parameters  $\phi$  and  $D_k$  is not applied, this equation

underestimates the SA of relatively unweathered coarse textured soils by one-two orders of magnitude (Sverdrup, 1990). For more highly weathered soils and marine sediments disagreement can reach 3 orders of magnitude (Mayer and Rossi, 1982; White et al., 1996; Brantley et al., 1999). Therefore an empirical correlation equation relating weights of size classes and soil SA was suggested (Sverdrup, 1990). The relationship was recommended for use with coarse textured soils to estimate the SA when SA data for a particular soil type was lacking. It is usually used when applying the PROFILE model to northern soils (e.g. Hodson et al., 1996; Langan et al., 1996). A difference between the actual SA and the size class assessment is often attributed to surface roughness (Anbeek, 1992). Such a large effect of surface roughness seems strange and contradictory to morphological observations of mineral particle surfaces. The problem is that the corrosion pits seen on photomicrographs (Wilson, 1986; April and Newton, 1992) do not seem to be deep and are typically separated by distances larger than their width. Considering, for simplicity, a cubic particle with identical small cubic pits in a checkerboard pattern on its faces, it is found that the actual SA is twice as large as the SA of an equivalent particle without pits. This simple geometric example illustrates that the effect of surface roughness should not be notably larger than the SA of an equivalent smooth particle, unless some complicated surface structures, not confirmed by direct observations, are assumed, such as, of fractal type or hollow fibres. Blum (1994) has concluded, on the basis of atomic force microscopy, that surface topography can account for a twofold increase in surface area.

Table 1  
Abbreviations, main symbols and units

SA	surface area
SFF	surface form factor
PSD and SD	(particle) size distribution
$A$ ( $m^2$ )	surface area
$M$ (kg)	mass
$D$ (m)	particle size (diameter) or vector of particle parameters
$D_{col}$ and $D_{gr}$	colloid and gravel borders of the SD
$D_{W_{eff}}$ and $D_{mean}^{(p_2)}$	effective weight and weight average diameters
$N$	number of particles in a sample
$\rho$ ( $kg\ m^{-3}$ )	density of soil solid phase
$\phi$	non-sphericity of soil particles
$\eta$	surface form-factor
$\xi$	fraction of mass (weight) within size class
$f_{n_k}$	contribution of the $k$ -th fraction to the $n$ -th physical property of a sample
$p_n(D)$ and $F_n(D)$	probability density and cumulative probability functions for the $n$ -th property
	$n = 0$ —number of particles
	$n = 1$ —integral thickness of particles
	$n = 2$ —surface area
	$n = 3$ —mass or weight
$\sigma$ (–) and $D_0$ (m)	relative width and size parameter of the SDs

At the same time it is known that the rigorous treatment of continuous particle size distribution (PSD) results in an agreement between measured and calculated SAs within a factor of 4 (Wu et al., 1993). This paper discusses the relationships between PSD and the SA of soils using the methods of statistical physics. Contributions of individual size fractions to the SA of soils naturally arise within the approach introduced here and can be assessed. It will be shown that the large discrepancy between measured and calculated SAs is connected with the use of size class assessment for a few size classes, i.e. outside its range of applicability. Based on available experimental data for coarse textured soils, the actual soil SA area can be interpreted mainly as a geometric SA. The recent discussion in Applied Geochemistry (Hodson, 2002; Koptsik et al., 2002) stresses the topical nature of the considered problem.

A theoretical model designed to fill a gap between the present understanding of SA and the data available is introduced. The aim of the paper is to call attention to these poorly studied questions and to give experimentalists a set of tools with which integral soil properties can be studied.

## 2. Geometric surface area: theoretical treatment

Soils are highly dispersed systems and contain a huge number of particles. The number of particles in a soil sample can be roughly assessed as the mass of the sample divided by the mass of an effective particle. Assuming a sandy soil composed of  $\sim 1$  mm spherical particles (Shirazi and Boersma, 1984) of density  $2.65 \text{ g/cm}^3$  (Buol et al., 1973), a 40 g sample, typical for granulometric measurements (Vadunina and Korchagina, 1973), would contain  $\sim 3 \times 10^5$  particles. Substitution of the effective diameter that should be assessed for real soil by 1 mm results in a radical underestimate of the number of particles. The authors assessed the total number of particles for a group of young, relatively unweathered soils, developed on sandy and sandy-loam moraines after the last glaciation; such soils are widespread in northern Europe and North America (Buol et al., 1973). The number in a 40 g sample from the Kola Peninsula (Koptsik et al., 1999) was typically  $\sim 2 \times 10^{11}$  (see Section 3). For soils with a considerable clay content, the number of particles in a sample of the same weight may reach  $10^{20}$  (Wu et al., 1993). From a physical point of view soil particles are different macroscopic objects; as a matter of principle, they can be enumerated and studied separately. However, the large number of soil particles makes such an approach practically senseless. Soil properties should be explained without explicit reference to the detailed behaviour of individual particles.

Let us consider soil particles to be indistinguishable, simply because to explain bulk soil properties it is not

necessary to distinguish individual particles. The huge number of particles means that soil should be treated as a large collection of particles subject to the laws of statistical physics, where a discrete PSD can be substituted by a continuous PSD. Applicability of this substitution is discussed in books on statistical physics (e.g. Reif, 1967).

### 2.1. General relationships

A soil SA will be considered based on the distribution of particles according to their sizes as the simplest distribution. As different SDs are closely connected, in principle it is also possible to start with the distribution of particles by their SAs, volumes, masses, etc.; the approach chosen intuitively seems simpler in the same sense as a point in geometry is simpler than a surface or a volume.

The term PSD is used in two ways—in the sense of physics and mathematics and in the context of soil science and geology. In soil science the finite set of relative weights, or weight contributions of classes, defined by the interval of size of soil particles, is called the PSD. Below these are termed size classes to distinguish them from the continuous overlapping fractions of distinct physical origin. The number of classes varies for different classifications and experiments; 4–10 classes are typical. In physics or mathematics the term PSD means the SD of randomly selected soil particles and is often used in a narrower sense as a synonym of the distribution's probability density function, or frequency of occurrence. Though closely connected, the two meanings differ qualitatively; it is not possible to go from the soil definition to the physical one by an infinite increase of the number of size classes, as in the soil definition two different properties are considered—sizes and weights. Since the usage of the term PSD in the two contexts is quite different, such a usage will not cause difficulties.

The physical definition is the starting point. Let  $p_0(D)$  be the probability density function,  $p_0(D) \cdot \Delta D$  is the probability that a particle size lies within a small interval  $\Delta D$  near  $D$ ; the integral

$$\xi_0 = \int_{(D_1 < D < D_2)} p_0(D) dD \quad (2)$$

expresses the fraction of the number of particles within each class,  $D_1$  and  $D_2$  being the lower and upper size boundaries. The ensemble average, which is the average over a large collection of indistinguishable particles, with an arbitrary deterministic function  $\Phi(D)$  equals (e.g. Reif, 1967; Bickel and Doksum, 1976)

$$\Phi_{\text{mean}} = \int_{(D)} \Phi(D) p_0(D) dD, \quad (3)$$

where the integral is taken over the entire region over which  $D$  can vary. This fundamental equation of statistical

physics can be used for the calculation of various soil properties. For example, consider a hypothetical single-mineral soil fraction of spherical particles with mass  $M(D) = \rho\pi D^3/6$ , where  $\rho$  is the mineral density and  $D$  is the diameter (taken as particle size). When  $M(D)$  is put in (3) instead of  $\Phi(D)$ , we get the average mass of particles for this soil fraction,  $p_0(D)$  being the PSD of the fraction. Assume that the dependence of SA ( $A$ ) of a particle on its size ( $D$ ) for the whole soil is known. Inserting this dependence  $A(D)$  (instead of  $\Phi(D)$ ) in (3) the average SA of particles is obtained,  $p_0(D)$  characterising the bulk soil.

If the particles are divided into size classes, then the piecewise function, that equals  $p_0(D)/\xi_0$  when  $D$  is inside size class borders,  $D_1 < D < D_2$ , and otherwise equals zero, is the probability density function for this size class. Inserting this function in (3), the average value  $\Phi_{\text{mean}}^{D_1, D_2}$  of  $\Phi(D)$  can be calculated for the size class. Let  $M(D)$  be a function of additive physical character, say the mass of a particle, and  $N$  be the number of particles in the soil sample. Substituting the exact numbers of particles for the whole sample and for the size class by their average values, it follows directly from Eqs. (2) and (3) that the weight fraction, or weight content, of the class equals

$$\xi_W = \frac{(\xi_0 N) M_{\text{mean}}^{D_1, D_2}}{N M_{\text{mean}}} = \int_{(D_1 < D < D_2)} \frac{M(D) p_0(D)}{M_{\text{mean}}} dD. \quad (4)$$

Thus,  $M(D)p_0(D)/M_{\text{mean}}$  is the probability density function for weights of particles classified by their size. It is the continuous equivalent of the discrete relative weights of size classes traditionally called PSD in geology and soil science.

The number of particles in the soil sample can be estimated as

$$N = \frac{M}{M_{\text{mean}}}, \quad (5)$$

$M$  being the mass of the sample, and  $M_{\text{mean}}$  the average mass (3) of a particle. The reason for applying (5), giving the average  $N$ , is that there are always a huge number of particles in the sample. Its relative inaccuracy,  $\sim 1/\sqrt{N}$ , is small for large  $N$  (e.g. Reif, 1967). Knowing the number of particles in the sample (5), the SA of the soil contained in the sample can be calculated

$$A_{\text{total}} = N A_{\text{mean}} \quad (6)$$

or any other additive property provided its average value is known. The average SA of a particle,  $A_{\text{mean}}$ , can be calculated with Eq. (3), in a fashion similar to  $M_{\text{mean}}$ . Calculation of the SA thus boils down to computation of SA and mass averages. Below assumptions within which integrals for  $M_{\text{mean}}$  and  $A_{\text{mean}}$  can be taken and thus SA explicitly calculated will be considered.

Considerable attention has been paid to the determination of continuous PSDs in sediments, soils etc. (Herdan, 1953; Griffiths, 1967; Allen, 1968; and references therein). However, two factors complicate the direct use of extensive experimental attempts to fit observed PSDs with continuous functions.

Firstly, though the qualitative difference between number and weight SDs is conceptually well understood, in the great majority of experimental investigations, fractions of numbers of particles are substituted by fractions of weight (Griffiths, 1967). In other words, Eq. (2) is used to fit observed PSDs, whereas Eq. (4) should be used if we want to get a PSD that not only approximates the data observed, but also allows calculation of other soil properties. Detailed studies of PSDs from 10 mm down to 40 nm, such as those by Wu et al. (1993) and Borkovec et al. (1993), are rare exceptions.

Secondly, observed PSDs are mostly fit by simple single distributions whereas soil is a mixture of different fractions. The variety of functions used and the extremely wide range of parameters (see below) only confirms that this approach, neglecting differences in fractions, can hardly describe soils as a whole. Meanwhile, the continuous experimental monitoring of the small-size end ( $D \lesssim 100 \mu\text{m}$ ) of PSD with a sedigraph shows that PSDs of more than 1000 soil and parent rock samples from different natural zones exhibit a pronounced minimum at  $D \approx 5 \mu\text{m}$  (Berezin and Voronin, 1981, 1983). The quasi-continuous sizing of particles with the light scattering technique demonstrates for young soils at least 3 well resolved peaks of weight SD in the 5–1000  $\mu\text{m}$  region (see Fig. 9, White et al., 1996). Thus, the measured PSDs should be separated in fractions according to their physical origin. Attempts to separate observed PSDs into elementary PSDs that might be physically interpreted, such as those by Shirazi et al. (1988), Shiozawa and Campbell (1991) and Buchan et al. (1993), are rare. The authors do not know of works where both of the above-mentioned points are considered.

## 2.2. Superposition model

When soil can be presented as the superposition of elementary PSDs, the probability density function equals

$$p_0(D) = \sum_k f_{0k} p_{0k}(D), \quad \left( \sum_k f_{0k} = 1 \right), \quad (7)$$

where  $f_{0k}$  is the number fraction (the relative number of particles in the  $k$ -th fraction). Inserting (7) in (3) for SA and the mass of a particle, the averages, needed for calculation of SA are obtained,

$$A_{\text{mean}} = \sum_k f_{0k} A_{\text{mean}_k}, \quad M_{\text{mean}} = \sum_k f_{0k} M_{\text{mean}_k} \quad (8)$$

Here  $A_{\text{mean}_k}$  and  $M_{\text{mean}_k}$  are the SA and mass averages for the  $k$ -th elementary fraction [calculated with their probability density function  $p_{0_k}(D)$ , also using Eq. (3)].

Elementary PSDs  $p_{0_k}(D)$  characterise individual mineral species, that were formed during geological processes and further weathered during soil formation relatively independently of each other; extremely coarse textured soil fractions are, most likely, parent rock fractions. If some of the ancient, pre-glacial, fractions are in the soil, the same mineral fractions of different age can be represented by different PSDs. Thus, theoretically the number of elementary PSDs can be expected to be larger than the number of minerals constituting the soil. However, considering a comparison of the model with the observed data, a large number of fractions mean that most of the model parameters will be statistically insignificant, or excess parameters. Technically the decomposition problem is similar to those in spectroscopy. It can not be expected that even a considerable part of the elementary PSDs can be experimentally resolved from the observed SD, represented either by a finite number of size classes, or by quasi-continuous monitoring of probability density, since the observed PSDs are smooth (e.g. Born and Wolf, 1964; Zeeman, 1977). There are two reasons to introduce the superposition model.

The first point is purely conceptual. Soils are characterised by very different spatial scales (Glazovskaya and Dmitriev, 1970; Hoosbeek et al., 2000), as are ecosystems in general (Levin, 1992). The authors shall not focus on small-scale spatial variations. Then from general considerations one can naturally expect that parameters of the true mineral and parent rock PSDs should be sample-independent—they should depend only on the geological and soil history of the sample location. In particular, such situations should be anticipated for soils formed on post-glacial and aeolian deposits. It is intended to average small-scale patterns controlled, say, by the random turbulent variation in melt streams and airflows. Thus, in many situations, parameters of SDs should be determined not for the individual samples, but for similar soils of the same effective age. Sample-dependent contributions of the fractions  $k_{0_k}$  can be determined independently from the mineralogical analysis. An approach along these lines might remove the problem of excess parameters.

Secondly, it can be expected that all or most of a few elementary PSDs, resolved from fitting (7) to the measured data, will represent several mineral components with similar PSDs. Parameters of elementary SDs are expected to be better defined (varying in a narrower range) than for single fraction models, and thus might be considered as a rough estimate of the “true” parameters. This approach will be implemented in the next section.

Remembering that  $\Phi(D)p_0(D)/\Phi_{\text{mean}}$  is the probability density function for values of the arbitrary additive

function  $\Phi(D)$  classified by particle size  $D$ , Eq. (7) can be generalised for probability density functions of SA also and weight classified by size of a particle

$$p_n(D) = \sum_k f_{n_k} p_{n_k}(D), \quad \left( \sum_k f_{n_k} = 1 \right). \quad (9)$$

Index  $n=0$  corresponds to number, 2 to SA and 3 to weight SDs; the logic of notation is the exponent in which each of these properties depends on size. Similar equations relate the corresponding cumulative probability functions  $F_n(D) = \int_0^D p_n(\bar{D}) d\bar{D}$  and  $F_{n_k}(D) = \int_0^D p_{n_k}(\bar{D}) d\bar{D}$  (e.g. Bickel and Doksum, 1976; Snedecor and Cochran, 1989), just substituting  $p_n$  by  $F_n$  and  $p_{n_k}$  by  $F_{n_k}$  in (9). Cumulative functions are convenient when fitting observed size classes (Gardner, 1956; Shiozawa and Campbell, 1991). However, the SA and weight fractions  $f_{n_k}$  are not independent. It can be shown that they are one-to-one related with the number fractions  $f_{0_k}$

$$f_{2_k} = \frac{f_{0_k} A_{\text{mean}_k}}{\sum_i f_{0_i} A_{\text{mean}_i}}, \quad f_{3_k} = \frac{f_{0_k} M_{\text{mean}_k}}{\sum_i f_{0_i} M_{\text{mean}_i}}, \quad (10a)$$

and inversely

$$f_{0_k} = \frac{f_{2_k} (A_{\text{mean}_k})^{-1}}{\sum_i f_{2_i} (A_{\text{mean}_i})^{-1}}, \quad f_{0_k} = \frac{f_{3_k} (M_{\text{mean}_k})^{-1}}{\sum_i f_{3_i} (M_{\text{mean}_i})^{-1}}. \quad (10b)$$

Combining relationships (5,6,8, and 10b) we get the SA of the soil sample

$$A_{\text{total}} = M \sum_k f_{3_k} \frac{A_{\text{mean}_k}}{M_{\text{mean}_k}}. \quad (11)$$

Here  $M$  is the sample mass,  $A_{\text{mean}_k}$  and  $M_{\text{mean}_k}$  are the average SA and mass of a particle for the  $k$ -th fraction,  $f_{3_k}$  is the fraction's relative weight. Provided that SI units are used in the calculations, the specific SA,  $A_{\text{total}}/M$ , is in  $\text{m}^2/\text{kg}$ . This equation for SA plays a central role when soil is represented as a superposition of fractions, analogous to Eq. (1) when soil is viewed as a superposition of size classes with identical particles. One can get the effective diameter for the  $k$ -th class by equating the  $k$ -th terms in  $A_{\text{SCA}}$  (1) and  $A_{\text{total}}$  (11),  $D_k = (6 M_{\text{mean}_k}) / (\rho \phi A_{\text{mean}_k})$ . The effective diameter is given only to compare the two expressions; its practical application is limited since the averages  $A_{\text{mean}_k}$  and  $M_{\text{mean}_k}$  for the size classes should anyhow be calculated first.

Results obtained up to now are rather general. Though  $D$  was termed particle size for simplicity, its size meaning is not used explicitly except in the range of integration in (2)–(4). All the above are valid if  $D$  is a multidimensional vector of parameters characterising

each particle (parameters of particle form, surface roughness, internal cavities, etc.), and integration while calculating averages is performed in this multi-dimensional space. When doing so, the only assumption made is that the soil sample is large enough to contain a huge number of particles. Within this assumption, the above equations are valid and expression (11) gives the exact value of the geometric SA of the soil. However, in order to provide expressions that are useful in practice, simplifications, or model assumptions, must be made.

### 2.3. Separation of the particle form

Soil particles have highly varying and complex forms; their linear sizes are not uniquely defined, however, this ambiguity is not very significant for the present case. Let  $D$  be an effective diameter of a particle, i.e. the diameter of a sphere of the same mineral with mass equal to the mass of the particle. Then the SA and mass of a particle equal

$$A(D) = \eta\pi D^2, \quad M(D) = \rho \frac{\pi D^3}{6}, \quad (12)$$

where  $\eta$  is an effective surface form factor (SFF; for a spherical particle  $\eta = 1$ ) and  $\rho$  is the particle density. Since the surfaces of real particles are pitted and etched (see scanning electron images of weathered particles; Wilson, 1986; April and Newton, 1992), the value  $\eta$  for real particles can be higher than the corresponding values of smooth geometric forms enveloping the particles. SFF  $\eta$  reflects both particle form and surface roughness SDs.

Assuming that for each of the elementary PSDs SFF and effective diameter are independent random variables, or equivalently that the probability density functions can be presented as the products of two functions  $p_k(\eta, D) = p_{\eta_k}(\eta) \cdot p_{D_k}(D)$  depending only on  $\eta$  and  $D$ , largely simplifies the problem. Then when calculating average SAs (3), variables  $\eta$  and  $D$  are separated and averaging by form can be made before averaging by size. This results in the enlargement of the SAs by  $\eta_{\text{mean}_k}$  times, compared with the SAs of spherical particles with the same PSDs. The authors do not know any experimental evidence directly confirming or contradicting this assumption; application of the model as a whole confirms it indirectly. An argument in favour of the assumption is that it is less rigid than the assumption commonly made about constancy of particle forms. There is no data for explicit calculation of average SFFs  $\eta_{\text{mean}_k}$ ; they will be assessed by comparing calculated and observed SAs. Assumption about separation of form and size variables allows introduction of the empirical SFFs and makes relationships (2)–(11) applicable to soil particles characterised by only one parameter—the effective diameter, thus permitting the

explicit taking into account of PSD in calculation of the SA. Eq. (12) can be understood as relating SA and diameter for particles of elementary SDs,  $\eta = \eta_{\text{mean}_k}$  being averages in particle form.

### 2.4. Elementary distributions

Practically speaking, choice of elementary SDs is not crucial. A well-approximated total PSD will result in correctly determined soil properties, regardless of which set of functions is used to represent PSD. However, knowledge of elementary PSDs is necessary for understanding the origin of soil properties.

The proper choice of elementary PSDs is a key conceptual problem for what is termed the superposition model. There is no agreed, (i.e. included in textbooks) law of PSD. When such a law is not known and the studied parameter varies in a very wide range, a log-normal distribution is usually employed (Schnoor, 1996). The Gamma and Weibull distributions (Korn and Korn, 1961; Dapples, 1975), which are in some respects similar to lognormal, seem to be other simple reasonable candidates for elementary SDs. The authors intentionally did not use fractal, or power distributions (Rieu and Sposito, 1991; Wu et al., 1993), in the superposition model, as these PSDs assume self-similarity of particles, obviously not observed for particle forms. Besides, the background fragmentation mechanism, when in each act of fragmentation some fixed fraction of newly formed particles is laid aside from further fragmentation (Matsushita, 1985), seems to be unrealistic, since weathering influences each soil particle. The simplicity is probably the main reason why a lognormal distribution was used to describe observed PSDs in many other publications (e.g. Gardner, 1956; Griffiths, 1967; Shirazi and Boersma, 1984). However, the role of a lognormal distribution for soils seems to be much larger. Dapples (1975) and Buchan (1989) noted that general physical arguments suggest the development of a lognormal PSD in weathered and deposited materials under certain natural processes. The authors chose the lognormal distribution, as physically conditioned and, probably, the most extensively studied, for assessments. The lognormal distribution results in an asymptotic limit to the geological processes involved in the formation of particles. Below the main assumptions, first discussed by Kolmogoroff (1941) for fragmentation mechanisms are repeated. The process of physical weathering is considered as a stochastic process; in each step the particle might be broken into several fragments. Probabilities of breakage and the corresponding conditional distributions for ratios of sizes of newly formed particles to the size of the parent particle are size independent for each channel of breakage. Then, disregarding the initial law of distribution, the final law of distribution after a sufficiently large number of steps will be lognormal with any desirable

accuracy. Physically speaking, as mechanical strength characteristics differ for different materials, the conditions of the Kolmogoroff theorem can be applicable only to particular elementary fractions—parent rock(s) and minerals. The simplicity and mathematical elegance of the assumption about size independence of fragmentation probabilities is a forcible argument in favour of lognormal distribution.

Another physical limiting condition concerns extremely small particles. Mathematically, the Kolmogoroff process of disruption of soil particles is indefinite; however, it is limited by other physical and chemical processes. When soil particles become small enough, close to the colloid border  $D_{\text{col}}$ , they either become mobile and are washed away from soil with the water flow, or they are effectively removed from the infinite disruption process by aggregation, coagulation, etc. Let us assume for simplicity that the removal of particles from a considered set of primary minerals is very sharp, takes place at the colloid border  $D_{\text{col}}$ , and may be described by the step function (1 when  $D > D_{\text{col}}$ , 0 otherwise). This assumption is confirmed by an observed (Wu et al., 1993) plateau of cumulative PSD at  $D \lesssim 0.1\text{--}0.2 \mu\text{m}$  and by aggregation of particles with  $D < 0.1 \mu\text{m}$ , observed within 0.5 h of sonification.

Let us assume that the soil has already reached textural maturity in the context of physical weathering considered here. Then, accounting also for the gravel border of particle sizes,  $D_{\text{gr}}$ , for the  $k$ -th elementary fraction the probability density functions for the number (index  $n=0$ ) of particles, SA ( $n=2$ ) and weight ( $n=3$ ) of particles classified by their sizes, equal

$$p_{n_k}(\sigma_k, D_{0_k}; D) = \Xi_{n_k} D^{n-1} \exp\left(-\frac{\ln\left(\left(D/D_{0_k}\right)^2\right)}{2\sigma_k^2}\right),$$

when  $D_{\text{col}} < D \leq D_{\text{gr}}$ ,

$$p_{n_k}(\sigma_k, D_{0_k}; D) = 0, \quad \text{when } D \leq D_{\text{col}} \text{ or } D > D_{\text{gr}}. \quad (13)$$

For brevity these 3 functions are called (13, and their sums relating to soil as a whole) number, SA and weight SDs. Exact expressions for normalising the constant  $\Xi_{n_k}$  and the most probable, average and root-mean-square deviation (width  $D_{\text{std}}$ ) diameters are presented in the Appendix. Parameter  $D_{0_k}$  has the dimension of size and controls size-dependent properties of PSD, the dimensionless parameter  $\sigma_k$  characterises its relative width. Diameters when SDs reach maximums depend linearly on  $D_{0_k}$ . Widths of PSDs depend on  $D_{0_k}$  approximately linearly; deviation is significant at the ends of PSDs. Relative width  $D_{\text{std}}/D_{\text{mode}}$  depends weakly on  $D_{0_k}$  and approximately equals  $\exp\left(\frac{3}{2}\sigma^2\right)\sqrt{\exp(\sigma^2)-1}$  for all SDs. As modification of SDs at the colloid and gravel borders

is in a sense only a correction of the tails of SDs, the number SD ( $n=0$ ) is called “truncated lognormal”. Probability densities (13) can be also applied to size classes equating  $D_{\text{col}}$  and  $D_{\text{gr}}$  with size class borders.

Given the number SDs (13,  $n=0$ ) and, thus, knowing the average SAs (A3) and masses (A4) of particles, the SA (11) of soil can be written as

$$A_{\text{total}} = 6M \sum_k \left( \frac{\eta_{\text{mean}_k}}{\rho_k} \frac{f_{3_k}}{D_{\text{mean}_k}^{(p_3)}} \exp(\sigma_k^2) \frac{C_{2k} C_{4k}}{C_{3k}^2} \right). \quad (14)$$

Here  $\eta_{\text{mean}_k}$  are average SFFs,  $D_{\text{mean}_k}^{(p_3)}$  are weight average diameters (the upper index reminds us that particle diameter is averaged with the weight SD (13,  $n=3$ )). The correction factors  $C_{n_k}$ , connected with truncation of lognormal distribution at the low and high size boundaries, are given in the Appendix (A2). The terms in (14) are grouped to show common features and distinctions from the size class assessment (1).

## 2.5. Example of calculation

Now the authors repeat in brief the major conceptual steps and consider a numerical example. Fitting the sum of weight SDs (9,  $n=3$ , or the corresponding cumulative functions) with the observed weights of size classes, parameters of elementary PSDs and their weight content are determined. Then it is possible to either directly calculate total SA by (14) or determine within a general system the average SA and masses of particles for the elementary number SDs (9,  $n=0$ ), and finally determine the soil SA by (11). The average SA and mass, cumulative probability functions and other relationships useful for comparison of truncated lognormal distribution(s) with experimental data are summarised in the appendix. Calculation within the general system, being only slightly longer, helps to better understand soil properties.

If one is interested only in the SAs (11) and (14), it is convenient to take units widely used in soil SA research. Taking sample mass  $M$  in g, and size (parameter  $D_0$ ) in  $\mu\text{m}$ , then the scaling factors are exactly matched and Eqs. (11) and (14) give specific soil SA  $A_{\text{total}}/M$  in  $\text{m}^2/\text{g}$ . Here the standard system is considered, using SI units.

Let us calculate the SA of a hypothetical soil consisting of spherical particles ( $\eta = 1$ ) characterised by SDs (13) with parameters  $D_0 = 2.8 \times 10^{-16} \mu\text{m} = 2.8 \times 10^{-22} \text{m}$ ,  $\sigma = 3.8$ ,  $D_{\text{col}} = 0.2 \mu\text{m} = 2 \times 10^{-7} \text{m}$ ,  $D_{\text{gr}} = 5 \text{mm} = 5 \times 10^{-3}$ ; the density of soil particles  $\rho = 2.65 \text{g/cm}^3 = 2.65 \times 10^3 \text{kg/m}^3$ . These are the parameters of a single-fraction PSD that fits one of the measured PSDs analysed in the next section. This is an effective, uniquely wide PSD; such PSDs, as will be discussed below, do not make sense as elementary PSDs. However, this extreme case clarifies a role of the

truncation correction and demonstrates several features of the PSD on one example.

The classical (unlimited particle sizes) lognormal distribution will be considered first, then the correction factors  $C_n=1$  ( $n=0,1,\dots$ ). Expressions for the average SA (Appendix, A3) and mass (A4) of particles give  $A_{\text{mean}}^{(cl)} = \eta\pi D_0^2 \exp(2\sigma^2) = 1 \cdot \pi \cdot (2.8 \times 10^{-22} \text{ [m]})^2 \cdot \exp(2 \times 3.8^2) = 8.6 \times 10^{-31} \text{ m}^2$  and  $M_{\text{mean}}^{(cl)} = \rho(\pi/6)D_0^3 \exp(\frac{9}{2}\sigma^2) = (2.65 \times 10^3 \text{ [kg/m}^3]) \cdot (\pi/6) \cdot (2.8 \times 10^{-22} \text{ [m]})^3 \cdot \exp(\frac{9}{2} \cdot 3.8^2) = 5.1 \times 10^{-34} \text{ kg}$  (dimensions are in square brackets). A one gram sample ( $M=10^{-3} \text{ kg}$ ) contains  $N^{(cl)} = M/M_{\text{mean}}^{(cl)} = (10^{-3} \text{ [kg]}) / (5.1 \times 10^{-34} \text{ [kg]}) = 2.0 \times 10^{30}$  particles, its SA  $A_{\text{total}}^{(cl)} = N^{(cl)} \cdot A_{\text{mean}}^{(cl)} = (2.0 \times 10^{30}) \cdot (8.6 \times 10^{-31} \text{ [m}^2]) = 1.7 \text{ m}^2$ . The specific SA of this hypothetical medium is  $1.7 \text{ m}^2/\text{g}$ ; by itself this value might seem reasonable at first glance. The fractions ( $A7^{(cl)}$ ) of the number and SA of colloid particles equal  $F_0^{(cl)}(D_{\text{col}}; \sigma, D_0) = 1.0$  (99.9...%, 18 (!) successive 9),  $F_2^{(cl)} = 0.92$ , showing that the number and SA of particles are dominated by colloid particles, while their weight content  $F_3^{(cl)} = 0.0082$  is negligible. Inclusion of particles with  $D < D_{\text{col}}$  in the PSD results in a non-physically small average particle (its mass is by 3 orders of magnitude smaller than the rest mass of an electron) and an astronomically high number of particles. Thus, this PSD can not be used to assess soil properties.

Now the truncated SD (13) will be considered. Values of the correction functions (A2)  $C_0=1.1 \times 10^{-19}$ ,  $C_2=0.081$ ,  $C_3=0.60$  (error functions can be calculated using tables (e.g. Abramowitz and Stegun, 1964) or, more conveniently, in mathematical packages, such as Mathematica, Maple or Matlab). For the truncated SD the average particle SA (A3) and mass (A4) equal  $A_{\text{mean}} = A_{\text{mean}}^{(cl)} \cdot C_2 / C_0 = (8.6 \times 10^{-31} \text{ [m}^2]) \cdot 0.081 / (1.1 \times 10^{-19}) = 6.2 \times 10^{-13} \text{ m}^2$  and  $M_{\text{mean}} = M_{\text{mean}}^{(cl)} \cdot C_3 / C_0 = (5.1 \times 10^{-34} \text{ [kg]}) \cdot 0.60 / (1.1 \times 10^{-19}) = 2.7 \times 10^{-15} \text{ kg}$ . The truncation has returned physical sense to these properties. The number of particles and SA of one gram of soil  $N = M / M_{\text{mean}} = (10^{-3} \text{ [kg]}) / (2.7 \times 10^{-15} \text{ [kg]}) = 3.7 \times 10^{11}$  and  $A_{\text{total}} = N \cdot A_{\text{mean}} = (3.7 \times 10^{11}) \cdot (6.2 \times 10^{-13} \text{ [m}^2]) = 0.23 \text{ m}^2$ . So, specific soil SA is  $0.23 \text{ m}^2/\text{g}$ , an order of magnitude smaller than for the parent non-truncated SD.

The separation of particle size and form variables and the choice of probability density functions for mineral particle fractions are the main theoretical assumptions for introduction of the superposition model of the soil SA. Simplifications made in the next section serve mainly for illustrative purposes. To understand if the model is applicable to soils, conceptually the most controversial (from the point of view of statistical physics) case of a low specific number of soil particles—coarse textured soils will be considered. It will be shown that even without fitting of empirical SFFs the model removes the 1–2 orders of magnitude divergence between the measured and calculated SA of coarse textured soils.

### 3. Application of the model: results and discussion

#### 3.1. Parameters of distributions

In order to determine the reasonable physical range of parameters of elementary PSDs the weight SD of the previous section was applied to fit the discrete PSDs (Koptsik and Teveldal, 1995) for soils characteristic of the Kola Peninsula (northernmost Europe). Cumulative relative weights, or relative weights of particles with sizes  $D < D_{\text{size border}}$ , of 8 successive size classes (ending with the gravel fraction,  $D_{\text{size border}} = \{2, 63, 125, 250 \mu\text{m}, 0.5, 1, 2, \text{ and } 5 \text{ mm}\}$ ) were first fitted independently for each sample by single elementary weight cumulative functions ( $A9, n=3$ ) or by a sum of two of them. To minimise the number of free parameters, the relative widths  $\sigma$  of the two elementary PSDs were set to be equal. To fit observed weight fractions, nonlinear least squares optimisation of the parameters of the PSDs was performed using the simplex search method (Nelder and Mead, 1964). In all cases the colloid border was fixed at  $D_{\text{col}} = 0.2 \mu\text{m}$  (Gedroits, 1975). Twenty-three observed PSDs were fitted. As densities of soil minerals vary in a relatively narrow range  $2.5\text{--}3.2 \text{ g/cm}^3$  (Hurlbut and Klein, 1977), it was assumed for simplicity that all soil minerals have equal density,  $2.65 \text{ g/cm}^3$  (Soil Survey Manual, 1993). The hidden inner cavities of particles were neglected.

Half of the observed PSDs were fitted by a single truncated lognormal distribution ( $r^2 \geq 0.9$ , where  $r$  is the correlation coefficient between observed and calculated weight fractions). The width parameter  $\sigma$  of SD changes in the range  $0.4\text{--}4$ . This range for  $\sigma$  might at first glance seem to be moderate; however, as  $\sigma$  influences SDs (13) through the common exponential multiplier  $\exp(-\ln((D/D_0)^2)/(2\sigma^2))$ , it greatly influences the SDs. If colloid correction had not been taken into account, the total SA of the widest PSD would have been overestimated by more than one order of magnitude (see previous section).

About half of the observed PSDs could be decomposed into two single truncated lognormal distributions ( $r^2 \geq 0.9$ ), while the other PSDs were more complex. However, the range for the parameters was notably narrower: the width  $\sigma$  lay in the range  $0.4\text{--}1.1$ , both parameters  $D_0$  lay within the limit borders of size classes and varied by only one order of magnitude. Compared with the previous cases, these two PSDs might be viewed as physically determined. Buchan et al., 1993 have concluded that the sum of two lognormal distributions seems to be an optimum model for the PSD in several studied models. The nearness of the lognormal distribution to the SD (13,  $n=3$ ; see below) forms, in the authors' opinion, the physical background of this observation.

Though all soils studied were characterised by low, but non-zero clay contents, both single and two-fraction



models predicted a practically zero content of the clay class, the most significant class when explaining SA. Due to the crude size classification used, the small-sized elementary fraction(s) could not be determined when treating each sample individually, as parameters of the finest fraction were controlled by small errors. To solve this problem, an integrated approach was applied. The soils studied were developed on tills and glaciofluvial deposits after the last glaciation (late Pleistocene) about 10 ka. The PSD is mainly controlled by fragmentation processes accompanying the movement and melting of the glacier; initial conditions at the site of final deposition exert more control on the PSD of coarse textured soils than breakage resulting from their subsequent evolution (Middleton, 1970; Dapples, 1975). In accordance with this observation the elementary PSDs were considered to be characteristic for the entire region, and the only sample-specific parameters were the relative weights of the fractions.

All samples were fitted as one data set. The introduction of 4 or 5 elementary fractions allowed a reasonable description of the data: the parameters of these two representations were close and, thus, might be viewed as physically determined. The main advantage was a reasonable description of all the samples and a better fit of the small-size end of the PSD compared with a single- or two-fraction individual approach. The squared correlation coefficient  $r_{\text{all}}^2 = 0.9$  for all the data, and for individual samples  $r_{\text{sample}}^2 > 0.7$ . The parameters of the PSDs of the 4-fraction representation and the relative weight contributions of fractions to size classes are presented in Table 2 for the International and USDA systems. Instead of  $D_0$ , more easily perceived characteristics are given: the effective weight diameter ( $D_{W_{\text{eff}}}$ , A5), or diameter of a sphere of the same material with mass equal to the average mass of a particle, and the weight average

diameter ( $D_{\text{mean}}^{(p_3)}$ , A6). The calculated clay content, remained lower than the observed and fit badly ( $r_{\text{clay}}^2 = 0.1$ ). As can be seen, the clay class was controlled by the tail of the silt-sized elementary PSD. As result, the 4-fraction representation underestimated the role of small particles in the PSD. Addition of the fifth PSD to the fit, while only slightly increasing the overall agreement, led to a good approximation of the clay content ( $r_{\text{clay}}^2 = 0.9$ ). The parameters of 3 coarse elementary fractions remained practically unchanged, the silt-sized elementary PSD shifted to larger sizes ( $D_0$  was increased 1.5 times). Though the clay-sized elementary fraction can be interpreted as the large-side tail of the weight SD, the small  $D_{W_{\text{eff}}} = 0.03 \mu\text{m}$  implies that this fraction can not be viewed as physically determined. The small clay content and the crude size class borders prevented reliable determination of this fraction. Introduction of the fifth PSD caused overfit of the clay content, and the 5-fraction model overestimated the role of small particles. Since the content of fine particles is represented in opposite ways by the 4- and 5-fraction models, the models will be used for lower and upper estimates of SA.

The parameters of PSDs, determined and derived from the literature, are presented in Fig. 1. The parameters were derived as described in the Appendix, neglecting the truncation correction as it plays a relatively minor role in the weight SD (the lognormal distribution, used to fit measured weights of size classes, can be excellently approximated with (13,  $n=3$ )). The lognormal transformation of the y-axis is in line with the dependence of characteristic diameters of elementary PSDs on  $\sigma^2$  (see the Appendix). The parameters determined are in accordance with the literature: the addition of derived parameters only extends the parameter domain. The parameters of the single-fraction model showed a trend (Fig. 1a; the solid line is the fitted

Table 2  
Parameters of 4 elementary distributions and their size classes for soils from the Kola Peninsula

No.	$\sigma = 0.42$ $D_{W_{\text{eff}}} (\mu\text{m})$	Weight contributions (%) of elementary fractions to size classes ( $\mu\text{m}$ ), international system							
		<2	2–6	6–20	20–60	60–200	200–600	600–2000	2000–6000
1	2.3	17.3	78.0	4.71	0	0	0	0	0
2	100	0	0	0	2.77	80.2	17.0	0.02	0
3	360	0	0	0	0	2.18	70.3	27.5	0.03
4	2400	0	0	0	0	0	0	12.3	87.7
No.	$\sigma = 0.42$ $D_{\text{mean}}^{(p_3)} (\mu\text{m})$	Weight contributions (%) of elementary fractions to size classes ( $\mu\text{m}$ ), USDA system							
		<2	2–50	50–100	100–250	250–500	500–1000	1000–2000	2000–5000
1	3.3	17.3	82.7	0	0	0	0	0	0
2	150	0	0.941	23.3	68.9	6.82	0.09	0	0
3	510	0	0	0.01	6.84	49.6	40.0	3.46	0.03
4	3100	0	0	0	0	0	0.25	13.3	86.5

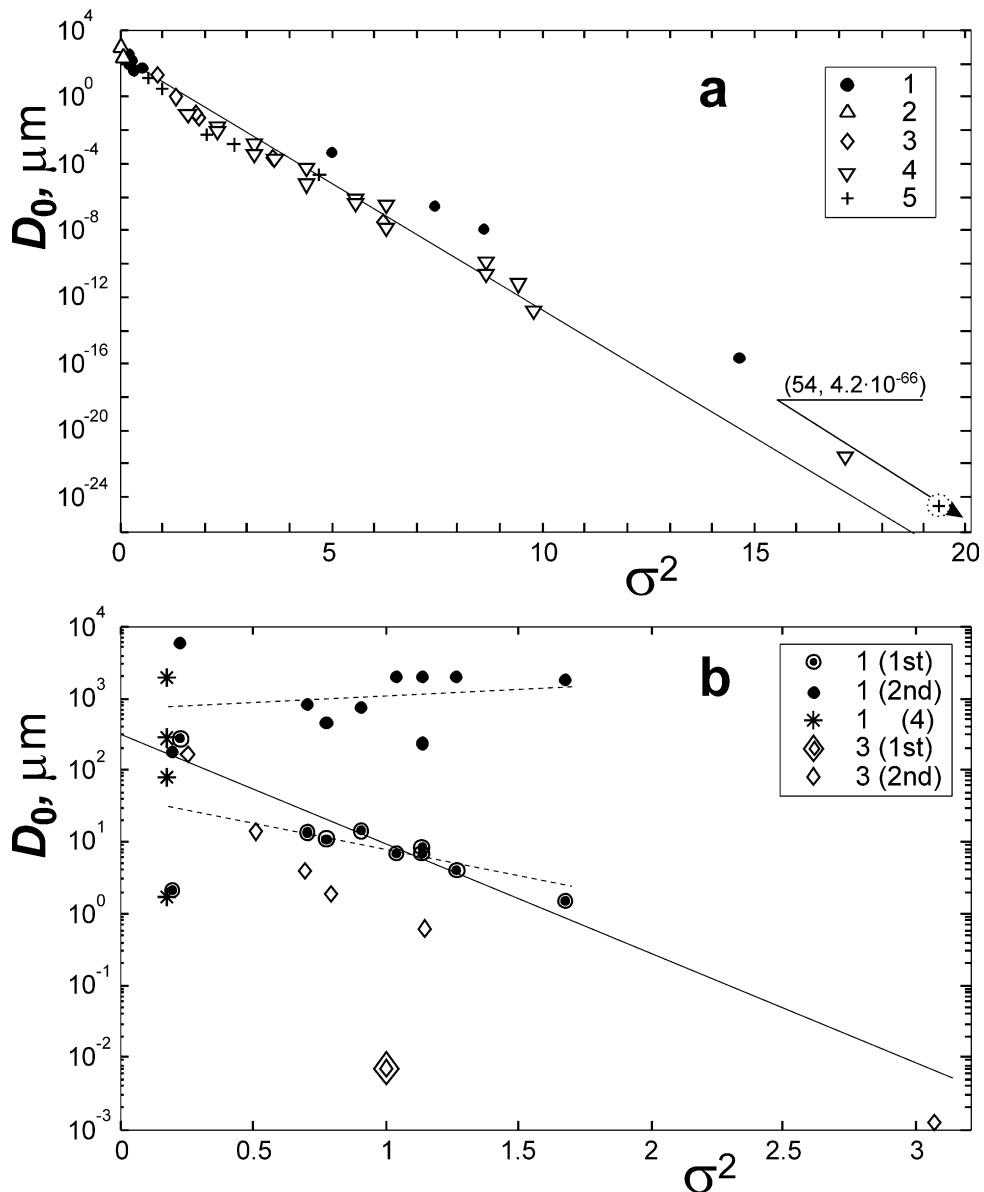


Fig. 1. Parameters of elementary distributions when soils are represented as single fractions (a) and as sums of several fractions (b). 1—present study, 2—Gardner (1956), 3—Shiozawa and Campbell (1991), 4—Buchan (1989), 5—Shirazi et al. (1988). The solid line is an isoline of equation  $D_{\text{mean}}^{(p_3)} = 300 \mu\text{m}$ , dashed lines are linear trends.

isoline  $D_{\text{mean}}^{(p_3)} = 300 \mu\text{m}$  for the non-truncated SD). The main difference between the soils is in the width of the PSDs. Grouping of points along this line revealed the similarity of the soils: the  $D_{\text{mean}}^{(p_3)}$  values were approximately equal for all fitted single-fraction soils. The 95% confidence interval for  $D_{\text{mean}}^{(p_3)}$  was 200–450  $\mu\text{m}$ . The slope of the isoline ( $-7/2$ ) was close to the slope of the linear trend ( $-3.1 \pm 0.1$ ). The residual sum of squared errors was only 1.5 times higher than for the linear trend, and

according to Mallows'  $C_p$  test (Mallows, 1973; Snedecor and Cochran, 1989) the isoline better fitted the data.

The parameters of the single-fraction model varied widely, the size parameter by several tens of orders of magnitude, whereas the border limits of the size classes varied by only 4 orders of magnitude. The size parameter of the widest PSD (Shirazi et al., 1988) was by tens of orders of magnitude smaller than any conceivable size in physics. Obviously, such a wide range of parameters reflected only the effective character of wide

PSDs. The parameters of several-fraction representations (Fig. 1b) varied within a significantly lower range. Most of the size parameters lay within the border limits of size classes. The two outliers and a different trend in the parameters found by Shiozawa and Campbell (1991) were, probably, connected with the fact that the finest fraction was not fitted to the data but fixed for all samples. In this sense the procedure was closer to determination of a single fraction. That is why behaviour of their coarse fraction partly resembled single-fraction behaviour (the solid line is the same as in Fig. 1a). When both fractions were freed, the size parameters had a tendency to independence from  $\sigma$  (dashed lines) and varied only within one order of magnitude for each of the fractions. Representation of the PSD as several fractions resulted in lower values of  $\sigma$  and better defined size parameters. This result gives a hope that the several-fraction representation of the PSD might be physically determined.

### 3.2. Number of particles

Knowing the parameters of elementary PSDs and thus the average grain masses (A4) of soil fractions, the authors determined the elementary number fractions (10b), and calculated the overall average mass (8) of particle and the number of particles (5) in the samples. The wide single-fraction PSDs that, most likely, approximated the sums of several fractions were characterised by a high number of particles. When these wide ( $\sigma > 2$ ) single-fraction approximations were not considered, the number of particles grew with the number of elementary fractions by which the PSD was represented, from  $\sim 5 \times 10^7$  (the minimum was 600,000) particles in a 40 g sample for the single-fraction model to  $\sim 2 \times 10^{11}$  for the 4-fraction representation of the soil. This increase in the number of particles is because the more terms that are retained in the representation of soil as elementary fractions, the better fine classes that control the number of particles are fitted. The numbers given by the 4-fraction representation were lower than the true numbers of particles since this representation underestimated the clay content. The upper estimate of the number of particles given by the 5-fraction model was  $\sim 5 \times 10^{13}$ . The intentionally wary choice of numeric value for the colloid border probably resulted in an underestimation of the number of particles.

The suggested general system of calculations is based only on the assumption of the applicability of continuous PSDs to the description of soil properties. By showing on the example of the Kola soils that the number of soil particles is huge even for coarse textured soils the validity of the approach and the applicability of the general expression (11) for SA to soils has been proved.

The large number of particles means that there is no alternative to the explicit determination and description of a continuous PSD when relating soil texture with

other soil properties. While conceptually probably everybody admits this, quantitatively soils are mostly analysed into a small number of size classes. The theoretical analysis of soil in a few size classes explicitly contradicts the concept of a huge number of soil particles. Light scattering methods (Hulst van de, 1957), giving a (quasi)continuous PSD, become more and more popular in soil research. A gap between the conceptual and scattering particle sizing approaches to soil, on the one hand, and the theoretical understanding of the relationship between size classes and the SA of the soil, on the other, becomes clear. Quantitative studies of the number of soil particles are very rare. Two of the first detailed investigations by Wu et al. (1993) and Borkovec et al. (1993) should be noted. However, as they used fractal approximation, the contributions of individual soil fractions could not be assessed.

While the number of soil particles is huge for the whole soil and for fine soil fractions, it is not necessarily the case for the coarsest fractions. It is the case for the Kola soils. The number of particles in a soil fraction can be calculated by multiplying its number fraction (10b) by the total number of particles. The number of particles of the coarsest fraction (Table 2) was only  $\sim 1000$  for the samples considered. Consider a monolithic sample, divided into two parts after sampling. Though both samples were formed under exactly the same conditions of formation/deposition of particles, the number of particles in the same fractions of the two samples must differ. The inevitable, connected with the discrete character of PSD, fluctuation in the number of particles is of the order  $\sqrt{N_k}$  (e.g. Reif, 1967),  $N_k$  being the number of particles in the fraction considered in each sample (since  $\sqrt{N_k} \ll N_k$ ,  $N_{k1} \simeq N_{k2}$ ). A rough estimate of the variation  $\Delta N$  was also made in the following numerical experiment concerning the PSDs of spherical particles. A set of random lognormal distributions with the same parameters was first computed. Then, for each SD, particles satisfying truncation limits were added one by one until the fixed weight was achieved. For PSDs from Table 2 and  $N = 1000$ –400,000 standard deviation  $\text{std}(N) \approx \sqrt{N}$ .

Knowing the mean number  $N_k$  and the dispersion  $\sqrt{N_k}$  of the number of particles, the relative fluctuation of weight of this fraction can be estimated, connected with the fluctuation of the number of particles, as  $(M_{\text{mean}} \sqrt{N_k}) / (M_{\text{mean}} N_k) = \sqrt{N_k} / N_k$ ; it is greatest for the coarsest fraction. As the size parameters of elementary PSDs notably differ, this value for the coarsest fraction is much larger than for any other. For the coarsest fraction of Kola 40 g samples the relative fluctuation of the fraction's weight was ca. 5%, the absolute fluctuation was  $\sim 1\%$ .

As the space in between particles of the coarsest fraction(s) is filled with finer fractions, variation of the weight of the fine fractions is controlled by the variation of weight of the coarsest fraction(s). Assuming that the

weight content of the coarsest ( $K$ -th) fraction is sufficient, so that the fundamental limit on variation of the fraction's weight content  $\Delta_{3K} = f_{3K} \sqrt{N_k/N_k}$  is notably larger than for the previous size fraction. Then the variations in the weight content of other fractions are governed by this fraction. Consider a cavity remaining in the place of one of the coarsest fraction particles ideally removed from the soil. The free volume will be filled with particles from its immediate surroundings. As volumes of the neighbouring particles are on the average much smaller than the volume of the removed particle, they can be considered in the first approximation as a continuous effective medium that is filling in the cavity. The volume of particles of some fraction filling in the cavity in this approximation is proportional to the volume content of this fraction in the cavity neighbourhood. Neglecting the difference between weight and volume fractions, the additional weight of the  $k$ -th fraction ( $k = 1, 2, \dots, K-1$ ) compensating the random change of weight content  $\Delta_{3K}$  of the coarsest fraction can be assessed in this approximation as  $\Delta_{3k} = -f_{3k} \Delta_{3K}$ . Thus for fractions for which average weights are equal within an order of magnitude, variations of weight content are also roughly equal. For fractions poorly represented in soil, the weight variation is moderated by the content of the fraction.

This assessment of the fundamental lower limit of variation in the fraction content, based on the idea of local flows of particles of fine fractions as a whole, is limited since it implies that all soil mineral particle fractions were formed in one process of particle breakage/deposition. Variations in finest fractions of aeolian origin, deposited on the formed substrate of coarse fractions and then migrating through it with rainwater flow, will most likely not follow this assessment; variations of successively deposited different non-mixing size fractions are also a subject of separate assessment. This simplest model of formation of fraction content variations was used just to show that variations in the weight content of fine fractions can be of the order of variation of the coarsest fraction. As small as this might seem at first glance, this variation is not negligible, as its role in soil properties controlled by SA is largely increased (see below).

### 3.3. Relative contributions

Absolute values of calculated soil SA depend linearly on the unknown effective SFFs. Relative number, SA and weight contributions of the elementary fractions will be considered first, since they are less sensitive to this factor.

The probability density functions (13) of a single elementary fraction for number, SA and weight SD, are shown (Fig. 2) for a typical single-fraction width parameter  $\sigma = 0.7$ ; the effective weight diameter is chosen to be small enough ( $D_{W_{\text{eff}}} = 2$ ,  $D_{\text{mean}}^{(p_3)} = 5.3 \mu\text{m}$ ) to show

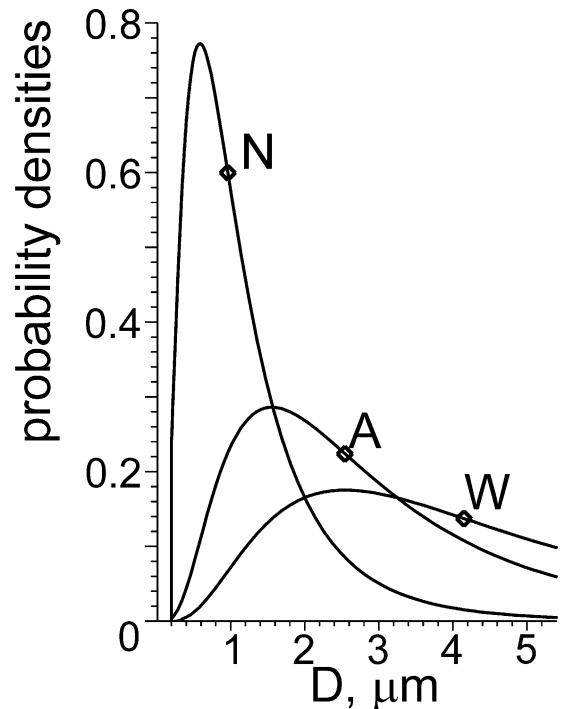


Fig. 2. Probability density functions of an elementary mineral fraction for number ( $N$ ), surface area ( $A$ ) and weight ( $W$ ) of particles classified by their sizes ( $\sigma = 0.7$ ,  $D_{W_{\text{eff}}} = 2 \mu\text{m}$ ,  $D_{\text{mean}}^{(p_3)} = 5.3 \mu\text{m}$ ,  $D_{\text{col}} = 0.2 \mu\text{m}$ ). Diamonds mark medians of distributions.

graphically the colloid border of the SDs. This PSD was explained by 15 wt.% of clay, the remaining 85% of the weight belonging to the silt class (in both International and USDA classifications). Note that for a single PSD the probability density function for the SA does not depend on its effective SFF. Each of the 3 functions is asymmetric, with their medians (marked with diamonds) shifted to the right of the most probable diameter, and is similar to the classical lognormal distribution. The dependence of all 3 functions (13) on the effective diameter of the particle is similar: this is determined by the common exponential multiplier  $\exp(-\ln((D/D_0)^2)/(2\sigma^2))$ , that sharply decreases in both tails of the SD (when  $D_{\text{col}} < D \ll D_0$  and  $D \gg D_0$ ), and a slowly changing power function of the diameter, which modifies the behaviour of the probability density in the range of significant nonzero values of the multiplier. Though the 3 functions (13) depend on the diameter in a similar fashion, conceptually it is significant that only one of them can be viewed as being independent; the two others can be obtained by multiplication by some power of  $D$  and renormalization.

The similarity of dependencies appears in the excellent approximation of any of them by a lognormal distribution [or equivalently, by the common multiplier of

(13)] with the same width parameter  $\sigma$  and a changed  $D_0$ . The maximal difference between the actual probability density and the function approximating it within the domain of single-fraction parameters (Fig. 1) is several ( $\sim 7$ – $10$ ) orders of magnitude smaller than the greatest probability density. Such a small difference, much less than experimental errors, means that the suggested form of distribution and the lognormal, previously used to fit weights of soil size classes, should agree in goodness of fit. Thus, the two forms of weight SDs can be transformed into one another without any loss of experimental information.

Physically it is significant that the probability function for SA is shifted towards smaller diameters than the probability function for weights and is characterised by a sharper maximum (Fig. 2). The probability function for the number of particles is further shifted towards smaller diameters and is the sharpest. As a result of these shifts, the abrupt step in number SD at  $D = D_{col}$  can not be noticed for the SA and weight SDs at the chosen graphical scale. The notable shift of the number SD to the left is the physical cause of the weight SD characteristics: the effective weight diameter is more than two times smaller than the weight median diameter. Both the shift and the sharpening of SDs are highly sensitive to the dimensionless width parameter  $\sigma$ . The ratios of the characteristic diameters and widths of PSDs, defined by the mean-square-root deviation from the average value, for the number, SA and weight SDs are approximately equal to  $1:\exp(2\sigma^2):\exp(3\sigma^2)$  (exact expressions are given in the Appendix). For wide SDs ( $\sigma > 1.2$ ) these changes are drastic, and all 3 probability densities can be shown only with nonlinearly compressed (say, logarithmically transformed) axes.

For a mixture of elementary fractions probability densities are typically distributed in a wider range of diameters. As a result, the relocation of the probability densities of the number, SA and weight of particles along the diameter axis is even more striking. Effective weight diameters for the two elementary fractions, presented in Fig. 3, equal 5 and 50  $\mu\text{m}$  ( $D_{\text{mean}}^{(p_3)} = 13$  and 130  $\mu\text{m}$ ),  $\sigma = 0.7$  for both PSDs; SFFs of the distributions are taken as equal. Solid lines show total probability densities; dotted lines represent the contributions of elementary SDs to them. At small diameters the total probabilities coincide with the corresponding contributions of the fine fraction, while at large diameters they are completely controlled by the coarse fraction. The change in the size parameter of elementary PSDs by only one order of magnitude results in the transformation of the 4% contribution of the fine fraction to total weight to its 30% contribution to SA, and to its 98% contribution to number of particles (Fig. 3). The coarse fraction is shown in the number probability function as a slight, indistinguishable to the eye, change in the

shoulder line; to visualise the contribution, it is also shown in the insertion as a 20 times amplified curve.

The redistribution of probability densities can be illustrated at the qualitative level. The dependence of the SA and weight probability densities on particle size differ from the number probability density by the  $D^2$  ( $A(D)$ ) and  $D^3$  ( $M(D)$ ) multipliers, respectively [see Eqs. (4) and (12)]. Thus, in the vicinity of the density peaks at  $D = D_0 \exp((n-1)\sigma^2)$ , the ratios of the probability densities of the coarse (index 2) to fine (1) fractions for the SA and weight SDs are larger by  $(D_{0_2}/D_{0_1})^2$  and  $(D_{0_2}/D_{0_1})^3$  times than for the number SD (for equal width parameters of the two PSDs). This simple assessment of coarse to fine fraction ratios works for narrow well-resolved fractions (with the accuracy of 4 significant digits in the example of Fig. 3, when both PSDs are far from the truncation borders). The SA and weight SDs differ by the  $1/D$  multiplier, causing the SA to

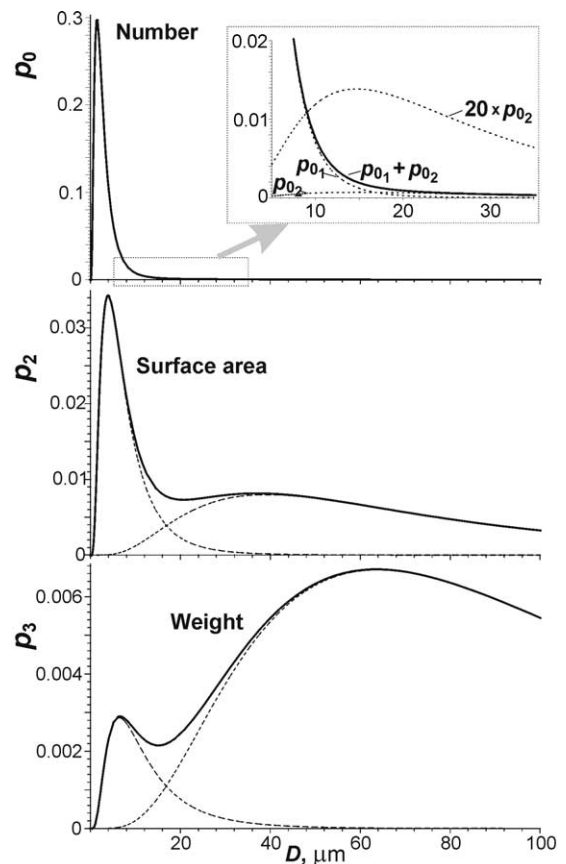


Fig. 3. Probability density functions of a mixture of two mineral fractions for number (upper curve), surface area (middle curve) and weight (lower curve) of particles classified by their sizes. Contributions of elementary fractions ( $\sigma = 0.7$ ,  $D_{W_{\text{eff}1}} = 5$ ,  $D_{W_{\text{eff}2}} = 50$   $\mu\text{m}$ ,  $D_{\text{col}} = 0.2$   $\mu\text{m}$ ) are shown by dotted curves.

weight fraction ratio to decrease approximately as  $D_{01}/D_{02}$  for coarse to fine fractions. Thus, the redistribution of probability densities is notably increased when the ratio of size parameters  $D_0$  increases. By particle sizing with the weight SD, inevitably more attention is paid to coarse fractions while when studying soil SA consideration should be given to fine fractions. The drastic transfer of probability density within the range of particle sizes when moving from one SD to another suggests that all of these 3 SDs should be experimentally measured. Reconstruction of two SDs from one might cause significant errors in the tails of the SDs. The drastic changes within the SD stress the necessity of averaging particle properties with the number SD and not with the weight SD.

The contributions of elementary fractions fitted to real PSDs to the number of particles, SA and weight vary within a wide range. To bridge the gap between the representation of soil as the sum of continuous fractions not bounded by artificial size class limits and the traditional representation as size classes, the fitted number, SA and weight fractions are presented in both ways in Table 3 for two samples. One sample is represented by a single fraction, one by two elementary fractions. The 4 size classes are the same as will be used in the empirical Eq. (15); the SFFs are assumed equal. The elementary PSDs, fitted to measured size classes ( $\text{index}^F$ ), are presented in the upper sub-rows for each type of SD. The extremely small, immeasurable, calculated classes are retained in the table to illustrate changes between the 3

SDs. Both continuous weight SDs describe the observed weights of size classes highly significantly: the squared coefficients of correlation ( $r^2$ ) between the fitted and observed classes are larger than 0.99 for the samples. For the two-fraction sample the approximately equal weight fractions are transformed to a 97% contribution of the finer elementary fraction to the SA and a 100% contribution (with 5 significant digits) to the number of particles. In the traditional representation of soil this behaviour is exhibited as a 6 times increase in the ratio SA:weight and a 2 times increase of the ratio number:SA for the silt class. For the clay class the increase of the ratios is more than 100 and 300 times, respectively.

Though all measured size classes (the M-rows for the two PSDs in Table 3) were characterised by a low, but non-zero, clay content, this could not be explained as the tails of the fitted coarse SDs. Within the model considered here, this implies a small admixture of elementary fraction(s) of smaller size to be present in the soils. The existence of the third, clay-sized, fraction is conceptually significant to understand soil SA.

Analysis of measured cumulative curves (Wu et al., 1993) has shown that weight fractions, determined for the same samples with different physical methods, disagree by several percent; the methodological errors increase for small particles due to the hydration effect. While analysing the number of soil particles the authors showed that the physical limit on the fluctuations of fraction contents for coarse textured soils might be close

Table 3

Calculated number, surface area and weight fractions and size classes for two one-two fraction samples from the Kola Peninsula

Parameters and type of distribution		Elementary fractions (%)			Contributions (%) of size classes ( $\mu\text{m}$ )					
		$f_1^A$	$f_2^F$	$f_3^F$	<2	2–63	63–250	250–2000	2000–5000	
$D_{W_{\text{eff}}}$ , $\mu\text{m} \rightarrow$		1	39	2400						
$\sigma = 0.84$	Number	F <sup>a</sup>	0	100 <sup>b</sup>	7.39E-4	1.12	95.5	3.36	0.0266	1.11E-4
		A	99.9	0.0604	4.47E-7	98.1	1.92	0.00203	1.61E-5	6.73E-08
	Surface area	F	0	97.3	2.74	0.0036	54.4	39.3	4.26	2.03
		A	53.9	44.8	1.26	38	41	18.1	1.96	0.935
	Weight	F	0	36.5	63.5	2.87E-5	8.95	21.3	10.6	59.1
		A	1	36.1	62.9	0.385	9.47	21.1	10.5	58.5
M					1.3	6.6	21.7	11.1	59.3	
$\sigma = 0.43$	$D_{W_{\text{eff}}}$ , $\mu\text{m} \rightarrow$		1	380						
		Number	F	0	100	–	1.20E-28	0.0247	38.1	61.9
	A	100	1.84E-4	–	98.8	1.22	7.00E-5	1.14E-4	6.31E-10	
	Surface area	F	0	100	–	3.78E-33	6.79E-4	12.1	87.9	0.0141
		A	79.2	20.8	–	72.6	6.59	2.52	18.2	0.00293
	Weight	F	0	100	–	1.60E-35	8.60E-5	5.46	94.5	0.0692
A		1	99	–	0.829	0.171	5.40	93.5	0.0685	
M					1.2	0.2	3.2	92.1	3.3	

<sup>a</sup> A, F, M. The fitted (F) distributions of measured size classes (M) and the fitted distributions with the artificial addition (A) of 1 wt.% of clay fraction.

<sup>b</sup> Contributions are presented with 3 significant digits accuracy. This and similar values are smaller than the true 100%.

by an order of magnitude to this value. One per cent of the total weight was taken as the lower limit of the typical accuracy of the experimental determination of weight fractions. One wt.% of the clay-sized hypothetical fraction, with  $D_{W_{eff}} = 1 \mu\text{m}$  and breadth the same as for coarse fractions, was artificially mixed with the fitted PSDs (lower sub-rows ( $\wedge$ ) in Table 3). The clay contents, produced by the mixture, were even smaller than those observed. While the weight fractions and classes remained practically unchanged, the SA and number SDs changed drastically: more than 50% of the soil SA and 99.9% of the number of particles originated from this “small” admixture. A notably higher occurrence of layered minerals in the clay classes (Koptsik and Tevel-dal, 1995) is typical for soils (Buol et al., 1973). It is confirmed by direct analysis of particle forms (Wu et al., 1993, Hodson et al., 1998). Based on these observations of forms, the SFFs for clay-sized layered particles might be expected to be an order of magnitude larger than for coarse fractions. When the added fraction is layered, the same SA changes are characteristic for  $\sim 0.1\%$  weight content, or if the added fraction is more diffuse and/or coarse. Thus, a small change in clay content, of the order of the experimental error, might bring about a notable change in the SA of coarse textured soils.

Fine particles can be revealed more clearly with X-ray measurements. Berezin and Voronin (1981) and Buchan et al. (1993) noticed that the content of fine particles inferred from X-ray absorption significantly over-estimated the result compared with classical weight measurements. As absorption of X-rays is controlled (e.g. Kitaigorodskii, 1950) by the sum of particle sizes in the beam, this fact is naturally explained within the developed approach. Properties of the integral thickness SD (13,  $n=1$ ) are between those of SA and number SDs. This explains why all soils, including coarse-textured, are characterised by the pronounced peak for the clay-sized components in the probability density function determined from X-ray attenuation (Berezin and Voronin, 1983).

The authors complete consideration of the relative contributions by illustrating differences (Fig. 4) in the number, SA, and weight probability densities using data for one of the Kola soils, for which weights of classes were represented as 4 elementary fractions (Table 2). To reflect a wide range of differences, the logarithmic-logarithmic scale is chosen. The vertical lines at both sides of the SDs are truncation steps to zero (zero to be plotted at minus infinity on the logarithmic scale). This realistic case summarises all main features of the SDs that were discussed with simple examples in this section. The positions of fraction probability peaks are gradually shifted to smaller sizes from weight (Fig. 4i, W) to SA (A), then to integral thickness (not shown) and to number (N) SD. These shifts (positions of weight peaks are marked with arrows on the number SD) are visually less

impressive than those in Figs. 2 and 3. This is a combined effect of the narrower PSDs and of the chosen compressed scale. The redistribution of probability densities, when going from weight to SA and then to number SD, are, on the other hand, much more impressive. As can be seen from Fig. 4i, the difference of maximum probabilities of the finest and coarsest fractions increased from 2 orders of magnitude for weight to 5 (note,  $5-2=3$ ;  $D_{0_4}/D_{0_1} = 10^3$ ) for SA and to 11 ( $11-2=3^2$ ) orders of magnitude for the number SD. The area under a fraction’s probability density curve (plotted on the linear-linear scale) determines contribution of this fraction to the property. The relative enhancements of the number and SA contributions of 4 size fractions are shown in relation to the coarsest fraction (Fig. 4ii). The differently hatched left and right half of a bar represents respectively the exact ratio of the contribution and its simple approximation (the ratio  $D_{0_4}/D_{0_k}$  for SA and  $(D_{0_4}/D_{0_k})^3$  for number of particles). The differences, hardly noticeable on a logarithmic scale, are

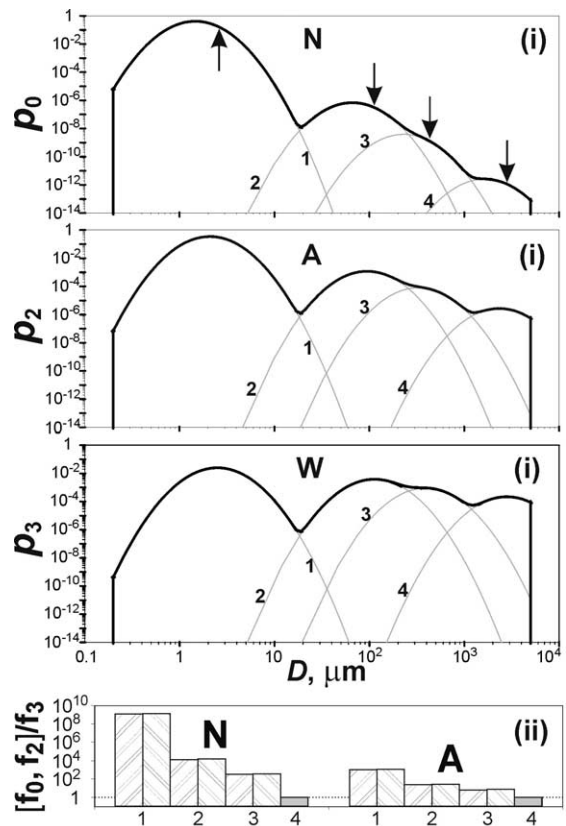


Fig. 4. Probability density functions (i) for the number (N), surface area (A) and weight (W) distributions separated into 4 size fractions (Table 2) and relative to weight enhancements (ii) of the number and surface area elementary fractions for one of the Kola samples. Parameters of the elementary fractions are given in Table 2.

controlled by truncation corrections. The contribution of the finest determined fraction (dominated by silt-size particles, Table 2) to SA is more than 3 orders of magnitude larger than to weight. The relative significance for SA of the clay-sized fraction, for which parameters were not determined due to its minor weight percentage, must be significantly larger.

A relatively minor, linear, alteration of the SFFs influences the redistribution of the probability density between the SA peaks. The difference in the effective SFFs, that in most situations for coarse textured soils can not be notably higher than the average value  $\eta \lesssim 4$  (estimated in the next subsection), may result in less than an order of magnitude change in the contributions of the elementary fractions to the total SA. On the other hand, alteration of the size parameters, which change for the several-fraction representation of PSDs by 3 orders of magnitude, results in a change in the contribution of the finest grain size fraction to the SA by 3 orders of magnitude. Thus, the conclusion is that the consistent consideration of PSD is more significant for calculation of the soil SA than consistent estimation of particle forms.

This conclusion is based on analysis of relatively unweathered coarse textured soils, in which the observed clay class mainly originates as tails of coarser fractions. For more highly weathered ancient soils, developed on silt and clay deposits, the clay-sized grain fraction might be expected to dominate the PSD. In this case the influence of SFF on SA, though remaining smaller than the influence of PSD, might be notably more significant than for coarse textured soils. However, highly weathered soils are a subject for separate investigation.

### 3.4. Absolute values of surface area

As a first step, total SA (14) was calculated supposing a spherical form for all particles ( $\eta_k = 1$ ). As the exact SA was not measured, the area assessed was chosen with an empirical equation (Sverdrup and Warfvinge, 1995; Sverdrup, 1996)

$$A_{\text{emp}} = \left( \sum_{k=1}^4 P_k \xi_k \right) \frac{\rho_{\text{soil}}}{\rho_0}, \quad (15)$$

as a reference value. Eq. (15) gives the SA of soil in a unit volume,  $\rho_{\text{soil}}$  is soil density,  $\rho_0 = 1 \text{ g/cm}^3$  is a reference density. Here  $\xi_k$  are weight fractions, the upper borders of 4 size classes equal to 2, 60, 250 and 2000  $\mu\text{m}$ , the corresponding coefficients  $P_k$  equal to 8, 2.2, 0.3, 0.05 ( $\text{m}^2/\text{cm}^3$  soil). Each of the weight fractions  $\xi_k$  entering into this equation was calculated as the difference of the  $k$ - and  $(k-1)$ -th cumulative fractions (9, elementary cumulative fractions by (A7),  $n = 3$ ). Dividing

(15) by  $\rho_{\text{soil}}$  (1.2–1.4  $\text{g/cm}^3$  for the Kola soils) units of measurement are converted to those in which SA (14) was calculated.

It was decided to use (15) since the Kola soils are close in age and are derived on similar bedrock and in similar climatic conditions. It is presumed that this equation, first derived for southern Swedish soils, has a wider range of applicability and describes the SA of coarse textured northern soils reasonably well (Sverdrup et al., 1990; Sverdrup and Warfvinge, 1995). Applicability of this equation to Scottish soils was opposed by Hodson et al. (1998). However, Koptsik et al. (2002) argue that the data of Hodson et al. (1998) satisfy the empirical equation after exclusion of outliers. The average absolute value of the deviation of the measured SA from the empirical is ca. 30%; even for outliers it is only 110–140%. It should be remembered that the divergence between the present theoretical explanation of geometric SA [size class assessment (1)] and the measured SA of coarse textured soils is 1–2 orders of magnitude. Taking into account the poor present theoretical understanding of the SA, the SA, calculated with the correlation Eq. (15), is sufficient when trying to understand its origin, to explain it, say, within a factor of 2; this is termed reference area below.

It appeared that the colloid correction should be taken into account in two cases: firstly, for fine mineral particle fractions (clay-sized and fine silt-sized), and secondly, when the entire observed PSD can be fitted by a wide single lognormal curve. Physically the latter case means that in some situations the actual sum of a large number of elementary PSDs can be approximated with reasonable accuracy by a single lognormal distribution. In both cases the scope of the colloid correction is the same—to remove from consideration super-fine particles that can not be retained in soil at the predicted frequencies. The finest particles contribute noticeably to the SA and colloid truncation prevents overestimation of the total SA. In all other cases the influence of colloid correction is negligible.

SA (14), calculated within single- and two-fraction representations of soil, notably fits the reference area better than it does size class assessment (1). However, both these representations, leading to zero clay classes, notably underestimate SA.

First consider soil particles to be spherical. The 4- and 5-fraction representations of soil gave lower and upper estimates of the SA of spherical particles that were the same as for soil PSD. The average ratio of the reference SA (15) to the calculated (14) equalled 4 for the 4-fraction representation of soil (Fig. 5, data set 1,  $r^2 = 0.75$ ). In the case of the upper estimate (5 fractions) the value of the calculated SA almost coincided with that of the reference one; however its relative variation was larger ( $r^2 = 0.45$ ). These results agree well with those of Wu et al. (1993) and Borkovec et al. (1993), obtained with an entirely



different approximation of PSD. Thus, a conceptually simple account of SD alone, without consideration of particle form or surface roughness, immediately decreases the discrepancy between the calculated and reference SAs by one order of magnitude. The consistent description of soil particles, continuously changing in size, is thus quite important to explain geometric SA.

It is stressed that the SAs were assessed from the distribution of particle weight by size of particle, or independently from SA measurements. No surface specific parameters were considered. Compared with the alternative of ab initio calculation—sieve class assessment, the coincidence between the calculated and reference values is quite impressive. The discrepancy for the 4-fraction representation of the soil can be explained by 3 factors: (i) non-sphericity of particle forms, (ii) surface roughness and (iii) the contribution of the clay fraction.

Treatment of the ratio of the two areas as uniformly controlled by the 4 PSDs suggests that effective SFFs are to the same extent larger than for a sphere,  $\eta \approx 4$ . The SFFs correspond to particle flakiness of ca. 30; such a large flakiness could hardly remain unnoticed with the naked eye for the prevailing coarse sand fractions. However, as the amount of layered particles increases with decrease of particle size, the effect of the particle form of the fine fractions is important in interpreting the discrepancy. The particle flakiness observed by Hodson et al. (1998) for similar coarse textured soils, also developed on granitic bedrock, equalled 80 and 15 within the clay and silt classes. The corresponding SFFs  $\eta$  were 8 and 3, respectively; it was assumed that these values are characteristic also for the Kola soils. The elementary PSDs of the 4- and 5-fraction representations were well resolved, and the clay and silt classes were dominated by fractions with the corresponding size parameter. As a result, these SFFs characterised the finest fractions and not the entire clay and silt classes, as was interpreted by Hodson et al. (1998). Assigning the silt SFF ( $\eta = 3$ ) to the finest fraction of the 4-fraction representation and assuming particles of other fractions to be spherical, resulted in the growth of the SA by 2.5 times. Thus the flakiness of particles, independently measured for similar soils, allowed SA to be explained geometrically within a factor of two on average.

The remaining discrepancy ( $\sim SA$ ) between the calculated and reference areas was the maximum that could be attributed to surface roughness. As the effect of the true clay fraction was not considered in the assessment, the contribution of surface roughness was in all probability smaller. This conclusion about the relatively minor effect of surface roughness agrees with micro-morphological, including atomic force microscopic, observations and simple geometric expectations (see Introduction).

Note that clay could not be reliably determined in the 5-fraction model. That was because the size parameter

of the finest fraction was practically unrestricted by the silt and sand fractions and became unreasonably small for covering variation in the observed clay weights. By considering both the SA and weights of classes in the fit the parameters of the two finest fractions were refined. The SFFs of the two fractions were fixed in line with particle form observations by Hodson et al. (1998). The size parameters were  $D_{01} = 0.82$  and  $D_{02} = 4.9 \mu\text{m}$ ; the width parameter and size parameters of the 3 coarsest fractions practically coincided with those of the 4-fraction representation (Table 2). The calculated SA (14) is shown in Fig. 5 (data set 2,  $r^2 = 0.55$ ). As should be expected for fitted data, the trend line (dashed) coincides with the  $45^\circ$  line for equal calculated and reference SAs. This refinement stresses the high sensitivity of the SA to the content of fine soil fractions. On average, 2 wt.% of the clay fraction controlled 80% of the SA ( $\sim 0.5 \text{ m}^2/\text{g}$ ). As surface roughness was not considered, the “true” size parameter of the first fraction is, most probably, larger and that of the second fraction smaller than obtained in the representation. Note also that the contribution of the clay-sized fraction is not outstanding. The SA of a hypothetical soil with the same density consisting of the clay fraction only is ca.  $20 \text{ m}^2/\text{g}$ , more than an order of magnitude smaller than for layered minerals (Greenland and Mott, 1978). Thus, the SA of coarse textured soils is highly sensitive to the clay content. Spatial variations in the weight content of the finest elementary fraction, about equal to an experimental error or fundamental limit of weight variation, result in

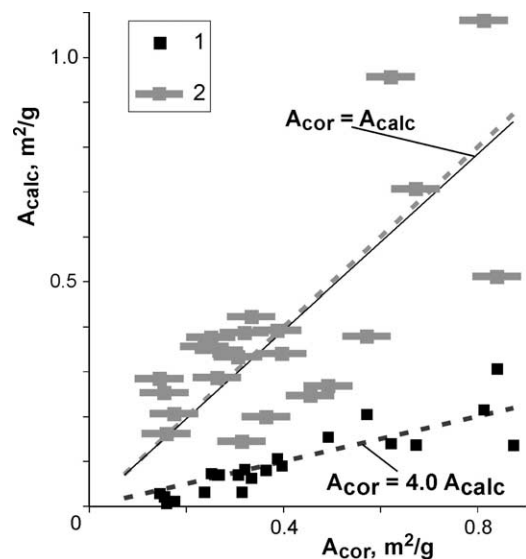


Fig. 5. Surface area (14,  $A_{\text{calc}}$ ) vs. calculated with the correlation according to Eq. (15,  $A_{\text{cor}}$ ). 1. 4 fractions, spherical particles; 2. 5 fractions,  $\eta_1 = 8$ ,  $\eta_2 = 3$ ,  $\eta_{(3-5)} = 1$ , other parameters of the distributions from Table 2.

variation of the SA close to its value by an order of magnitude.

While the conclusion about the fundamental limit of SA variation was made while considering the geometric SA of mineral particles, the methodological value of its derivation is notably wider. This conclusion depends on only two assumptions—on the existence of several natural fractions within one of the soil components and on the low number of elementary units of the coarsest fractions. It may be hypothesised that a low number of large macromolecular aggregates in the organic covering of mineral particles is important for the SA of native soils, especially for fine-textured soils.

Though, with the data considered here, the authors could not determine all the above-mentioned contributions to the SA in a unique way, by comparing these 3 cases ranges were determined for the contributions of surface roughness and clay-sized particles to the SA of the Kola soils. The realistic coincidence of the calculated and reference SAs implies that the SA of coarse textured soils can be reasonably explained as a geometric SA.

### 3.5. Relationships with simple assessments

Now, when reasonable values for SA have been obtained, it becomes clear why the simple Eq. (1) for SA fails when estimating SA within broad size classes. The problem is that calculation of the SA could have been started from the continuous analogy of this equation, obtained at the limit of infinitely decreasing size of classes. It can be shown that the result would be exactly the same—the main Eq. (11) for the SA obtained by superposition of soil fractions. Thus, Eq. (1) for a geometric SA is simply a numerical assessment within a finite set of size classes of the soil SA, as calculated in the previous subsection. The cause of the failure is very simple: the crude size classes. Below imperfections in size separation, such as minor weight admixture of fine particles, which can also notably increase the SA of coarse classes are not considered.

Consider a 4-fraction hypothetical soil with PSDs characteristic for Kola soils, but with spherical particles. The exact SA of each size class of this medium can be calculated as described above (setting the colloid and gravel borders to size class limits) and compared with the corresponding term of Eq. (1). For the size classes of Eq. (15) the difference is most pronounced for silt. The problem is that the size classes are too broad in comparison with the characteristic widths of the elementary PSDs contributing to them. This is why particles can not be viewed as identical within size classes. As result, the calculated SA (1) for the hypothetical soils is significantly smaller than the true one. The difference is most pronounced for the silt class, the most extensive on the logarithmic scale, for which the ratio of the two areas for the 4-fraction soil is typically about 10 and

reaches 35. Recalculating the SAs (1) with an increased number of size classes, it is seen that to assess the SA with 1% accuracy the silt class should be subdivided into 8 and the clay class into 5 subclasses. On the whole, soil should be divided into at least 22 size classes of equal breadth on the logarithmic scale. When the size classes used are fine enough to properly assess the SA of spherical particles, Eq. (1) (applied by Hodson et al. (1998) to only 4 classes) can be used. Only then can SFFs be introduced for individual classes and applied to (1) to real soils. The estimate of the required number of size classes depends mostly on the breadth of the elementary fractions constituting soil and the rough size classification used. However, the quasi-continuous measurement of the weight SD of young Modesto soils, developed on similar bedrock (White et al., 1996, Fig. 9), exhibited well-resolved peaks, seen with the naked eye. Simulation of these peaks showed similar widths, thus confirming the conclusion about the required number of size classes.

To relate the SA and SD of soil with an equation like (1) requires a large increase of the number of soil classes. This increase implies a significant expansion of experimental work, including direct observations of particle forms and measuring the SAs of classes. From this point of view, the suggested decomposition of soil into elementary fractions is an alternative that simplifies the task.

The parameters of elementary PSDs should certainly depend on the soil type and region studied. In line with the opinion that initial conditions at the site of deposition exert the main control on the PSD, let us assume that this dependence is not too rigid. Then, the range of applicability of the elementary fractions determined is wider than for the Kola soils. Close PSDs can be expected for the widespread soils developed after the last glaciation on sandy and sandy-loam moraines. For such soils the authors suggest the use in independent research of the PSDs determined as the first approximation. Then, the time-consuming task of the decomposition of the weight SD into elementary fractions (requiring some grounding in programming) can be reduced to a much simpler task. Weights of classes can be decomposed in least square means into a basic 4 calculated fractions (Table 2). This task can be solved by methods of linear algebra in many packages, including electronic worksheets, such as Excel. One should only remember that elementary PSDs do not form a complete orthonormal basis; thus, perfect coincidence between observed and calculated values can not be expected. Constraints not considered within linear methods ( $\sum f_{3k} = 1$ ,  $f_{3k} > 0$ ) should be applied manually for solution.

The authors applied this simplified procedure to the data of Hodson et al. (1998). Since no information on the gravel fraction was available and thus the coarsest

fraction could not be determined, 4 fine fractions of the 5-fraction model was used in the decomposition. The calculated SA of spherical particles was only 3.5 times smaller than the measured soil SA and the correlation coefficient was twice as large as for empirical Eq. (15) applied to the whole set. These results are in line with the results discussed above.

The 4-member model might be viewed as a foundation of the empirical Eq. (15). Indeed, the calculated weights of 4 classes are expressed as linear combinations of 4 elementary fractions  $f_{3i}$ . Solving this system of equations,  $f_{3i}$  can be expressed as linear combinations of sieved fractions  $\xi_i$ . Inserting the solution in the main equation, Eq. (14), for the SA we get a linear equation similar to the empirical one; its coefficients  $B_i$  depend only on the parameters of elementary fractions. Using the parameters of the 4 fine fractions of the 5-fraction representation, the coefficients  $B_i$  for clay and silt, that determine SA, agree within a factor of 3 with the corresponding coefficients  $P_i$  of Eq. (15). However, the agreement is only semi-quantitative: the two other coefficients significantly underestimate the coefficients of the empirical equation.

By this treatment the authors also show that the high sensitivity of soil SA to the content of fine fractions is the main cause of its high spatial variability. The cloud-like character of the SA dependence on soil texture seems to be one of the main background points that caused the recent discussion (Hodson, 2002; Koptsik et al., 2002). The authors stated in the discussion that Eq. (15) for SA should be better interpreted in terms of statistical physics: relatively unweathered soils that developed on granitic parent material in a cool humid climate for a large collection of soils should be described by Eq. (15). It is not reasonable to view (15) as applicable to an exact sample as it assesses the SA in a statistical sense only. The present considerations provide a theoretical basis for this statement. It is the dispersed and multi-particulate character of a soil that is the physical origin of the stochastic contribution to the soil SA.

The different scales of description—the macroscopic field scale and the scale of a sample—should not be mixed up. A correlation relationship observed on the landscape scale is of statistical type, while dynamical laws govern a sample. The complementary character of the two scales and types of laws is typical for complex systems (Pattee, 2000). The principal qualitative distinction between dynamical and statistical laws is not unique for soil science; Planck (1960) and Schrödinger (1944) discussed it for physics and biology. The application by Hodson et al. (1998) of the statistical correlation Eq. (15) to individual soil samples is methodologically erroneous. The observed differences in the SA are neither large nor strange—the spatial variability is just the same as is given by nature. If mechanisms of SA formation, if individual samples, are the

focus of investigation, as far as can be seen, the general approach discussed above is the only valid one. This is just the consequence of the huge number of soil particles. On the other hand, if properties of a macroscopic soil object (polypedon, soil within catchment or region) are in focus and samples are studied only as a means of assessment, then the use of Eq. (15) seems reasonable. That is the main field of applicability of empirical models (e.g. Hoosbeek et al., 2000); such usage was implied by the authors of the equation when suggesting it for critical loads assessment (Sverdrup et al., 1990).

The approach to calculation of the SA developed here does not remove the problem of its spatial variability (compare e.g. the present Fig. 5 and Fig. 1 in the paper by Koptsik et al., 2002). Within the macroscopic approach, the highly variable component of the mineral particle SA can be viewed as random in the same sense as flipping a coin is usually viewed as a random event rather than as the deterministic result of detailed knowledge of the initial conditions of the coin. The conclusion about the relative contributions of the stochastic and deterministic components of the SA for coarse-textured soils agrees with simple assessments. Using the correlation SA (15) as an environmental gradient, it may be inferred (see Fig. 1 in Koptsik et al., 2002) that the inherent uncertainty in the soil SA is about its average value by an order of magnitude. This conclusion is also confirmed for boreal forest soils by direct observation of spatial variability of soil SA within a uniform unit, the polypedon (Oreshkina, 1983).

Soil scientists seem to come very close to the hypothesis about the fundamental limits of variation when studying soils with geostatistical methods. However, the nonzero nugget variances of semivariograms, observed for the majority of soil properties, are usually connected with measurement errors (e.g. Hoosbeek et al., 2000). While relating the nuggets with processes inherent in the soil itself, with the soil fundamental limits, influences the paradigm of soil description. If fluctuations in properties are inevitable, natural characteristics of single soil samples, then a deterministic description of soil is possible only in the statistical sense and a description of individual samples can be probabilistic only.

#### 4. Conclusions

A so-called superposition model capable of accounting for the contributions of soil fractions of distinct sizes to SA is introduced and theoretically considered. Three physically most important distributions, number, SA and weight of soil particles, classified by their sizes, are discussed. The authors are not aware of other superposition models of PSD which explain additive soil properties. When no assumptions are made about the SD, the SA relationships obtained provide a theory of

the geometric SA of mineral particles. By showing that the number of soil particles is huge, even for coarse textured soils, the validity of this general approach is demonstrated. To get practical results, size fractions are described by truncated lognormal distributions that can be theoretically viewed as controlled by physical weathering. Relationships obtained within this approximation are presented at a level needed for quantitative estimations, and allow independent SA assessment. The introduced model was applied to soil texture data for sandy podzols developed on tills and glaciofluvial deposits after the last glaciation in the Kola Peninsula. The calculated SA was compared with that given by a correlation equation (Sverdrup, 1990) in giving the best description of the measured values. The SA of coarse textured soils was explained as a geometric SA, as the area of a hypothetical smooth surface enveloping the actual soil particles. Taking into account continuous particle size and form distributions reduced by nearly two orders of magnitude the gap between measured and calculated SAs, assuming identity of particles within soil texture size classes. The failure of the last assessment to give a geometric SA, is connected with the use of crude size classes that are insufficient to reflect the continuous variation in sizes of soil particles, and with the imperfection of size separation procedures. To adequately assess a geometric SA with ca. 1% accuracy the number of size classes should be increased by at least 5 times. The choice of a physically based continuous PSD simplifies the description of a soil because a noticeably lower number of components is needed to compare with the number of size classes representing a soil.

Parameters of elementary PSDs, determined by considering weights of size classes, agree with those that can be derived from the literature. The reduction of parameter variation, when soil is decomposed into several fractions, is incredibly great; it reaches  $\sim 10^{20}$  compared with that of a single-fraction model. The size parameters are within the size limits of soil grains and are robust to the addition of a new fraction except in the vicinity of its size parameter. The physically determined reduction of the parameter range suggests that several-fraction decompositions can adequately explain integral soil properties.

PSD is the main factor that controls the SA of coarse textured soils. By taking into account the particle forms for clay-sized layered minerals that were poorly represented in soils, the SA increased by 2–3 times. The effective SFFs of particles of coarse textured soils are only several times larger than for spheres. The span of particle sizes through several orders of magnitude causes crucial, also several orders of magnitude, changes in the contributions that size fractions make to the integral soil properties. The radical changes in the SDs of weight, SA and number of particles suggest that the SDs should be simultaneously measured.

The model semi-quantitatively supports the correlation Eq. (15) that relates SA and soil texture. The equation seems to be a reasonable way of relating SA to limited data on soil texture. However, the equation should be interpreted in a statistical physics sense: it is applicable only to macroscopic soil objects or to a collection of samples but not to the individual samples themselves. The high sensitivity to the fine fraction content can be viewed at a more general, environmental level of knowledge as a physical cause of the inherent in SA stochastic component, which is averaged by the correlation equation.

The number of particles of the coarsest fraction that is countable contributes noticeably to variations of soil properties. The fundamental lower limit of variation of weight, controlled by the discrete nature of soil, may be  $\sim 1\%$  for coarse textured soils, i.e. of the order of experimental error. The SA is highly sensitive to the content of small-sized mineral fractions; on average, 2 wt.% of the clay fraction contributed 80% of the SA. While the variation in weight of the finest mineral fraction may seem small, within experimental error and the fundamental limit of variation, the corresponding variation in SA is quite significant. For coarse textured soils the variation is close to the average value by an order of magnitude. The high variability of many surface-controlled properties of soils is believed to be related to the fundamental limit of variation of soil that is controlled by the number of particles of the coarsest fractions (mineral or organic) of the soil.

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### Appendix. Truncated lognormal distribution

The authors consider the properties of an ensemble of uniform particles without inner cavities. Probability density functions for the distribution of number, SA, and weight of particles classified by their sizes ( $n=0, 2$  and 3, respectively), are given by Eq. (13). The normalising multipliers equal

$$\Xi_n = \frac{\exp(-2\sigma^2)}{\sqrt{2\pi}\sigma D_0^n C_n(\sigma, D_0, D_{\text{col}}, D_{\text{gr}})}, \quad (\text{A1})$$

where functions

$$C_n(\sigma, D_0, D_{col}, D_{gr}) = \frac{1}{2} \operatorname{erf} \left( \frac{\ln \left( \frac{D_{gr}}{D_0} \right) - n\sigma^2}{\sqrt{2}\sigma} \right) - \frac{1}{2} \operatorname{erf} \left( \frac{\ln \left( \frac{D_{col}}{D_0} \right) - n\sigma^2}{\sqrt{2}\sigma} \right). \quad (A2)$$

The expressions for  $\Xi_n$  are exact expressions for the classical lognormal distribution except for the factors  $C_n$ , which are caused by the colloid and gravel border correction;  $\operatorname{erf}(x)$  is the error function. Each of the correction functions  $C_n$  is the difference between the corresponding cumulative probability functions (A6<sup>(cl)</sup>) of the corresponding non-truncated basis distribution at  $D_{gr}$  and  $D_{col}$ . In the limiting case, when  $D_{col}$  approaches zero and  $D_{gr}$  is infinitely increased, each of the summands in (A2) approaches  $\frac{1}{2}$  and  $C_n = 1$ .

For an ensemble of particles with density  $\rho$  and effective surface form-factor  $\eta$ , the average SA

$$A_{\text{mean}} = \eta\pi D_0^2 \exp(2\sigma^2) \cdot \frac{C_2(\sigma, D_0, D_{col}, D_{gr})}{C_0(\sigma, D_0, D_{col}, D_{gr})}, \quad (A3)$$

and the mass of a particle

$$M_{\text{mean}} = \rho \frac{\pi}{6} D_0^3 \exp\left(\frac{9}{2}\sigma^2\right) \cdot \frac{C_3(\sigma, D_0, D_{col}, D_{gr})}{C_0(\sigma, D_0, D_{col}, D_{gr})}. \quad (A4)$$

The effective weight diameter, or the diameter of a sphere, made of material with the same density  $\rho$ , for which the mass equals  $M_{\text{mean}}$ ,

$$D_{W_{\text{eff}}} = D_0 \exp\left(\frac{3}{2}\sigma^2\right) \cdot \sqrt[3]{\frac{C_3(\sigma, D_0, D_{col}, D_{gr})}{C_0(\sigma, D_0, D_{col}, D_{gr})}}. \quad (A5)$$

The weight average diameter, or the diameter averaged with the weight distribution  $p_3(D)$ ,

$$D_{\text{mean}}^{(p_3)} = D_0 \exp\left(\frac{7}{2}\sigma^2\right) \cdot \frac{C_4(\sigma, D_0, D_{col}, D_{gr})}{C_3(\sigma, D_0, D_{col}, D_{gr})}. \quad (A6)$$

In all the examples, these values were used instead of  $D_0$  as they can be more easily “felt” by soil scientists, accustomed to the distribution of weight of particles by their size. Eqs. (A5) and (A6) relate  $D_{W_{\text{eff}}}$  and  $D_{\text{mean}}^{(p_3)}$  with  $D_0$  in a unique fashion. Characteristic diameters—the most probable ( $D_{\text{mode}}$ ), average ( $D_{\text{mean}}$ ) and root-mean-square deviation ( $D_{\text{std}}$ )—are summarised in Table A1 for these 3 distributions.

Cumulative probability functions for the distribution of number, SA and weight of particles by their sizes are given by

$$F_n(D; \sigma, D_0, D_{col}, D_{gr}) = \frac{C_n(\sigma, D_0, D_{col}, D)}{C_n(\sigma, D_0, D_{col}, D_{gr})}, \quad (A7)$$

where  $C_n$  are correction functions (A2). In the limiting case of the basic non-truncated distribution this expression simplifies to

$$F_n^{(cl)}(D; \sigma, D_0) = \frac{1}{2} \operatorname{erf} \left( \frac{\ln(D/D_0) - n\sigma^2}{\sqrt{2}\sigma} \right) + \frac{1}{2}. \quad (A7^{(cl)})$$

*Relationship with the traditional lognormal fit of weight distribution*

The classical lognormal distribution

$$\mathcal{P}_W(\sigma, X_0; X) = \frac{1}{\sqrt{2\pi}\sigma X} \exp\left(-\frac{(\ln X - \ln X_0)^2}{2\sigma^2}\right) \quad (A8)$$

has been rather often used to fit the observed weights of size classes, and its parameters  $X_0$  and  $\sigma$  can be found in the literature. The authors intentionally changed the notion of particle diameter to  $X$  in order to stress the conceptual difference between this distribution and the number distribution (formally, this equation coincides (neglecting the colloid and gravel border corrections) with (13) when  $n=0$ ). Conceptually, this distribution is only effective, and it can not be used for the determination of macroscopic soil physical properties. However, it can approximate the true weight distribution (13,  $n=3$ ) very closely. The relationship between the parameters of

Table A1

Characteristic diameters for distributions of number, surface area, and weight of particles classified by their size

Distribution	$D_{\text{mode}}^a$	$D_{\text{mean}}$	$D_{\text{std}}$
$p_0(\sigma, D_0; D)$	$D_0 \exp(-\sigma^2)$	$D_0 \exp\left(\frac{1}{2}\sigma^2\right) \frac{C_1}{C_0}$	$D_0 \exp\left(\frac{1}{2}\sigma^2\right) \sqrt{\exp(\sigma^2) \frac{C_1}{C_0} - \left(\frac{C_1}{C_0}\right)^2}$
$p_2(\sigma, D_0; D)$	$D_0 \exp(\sigma^2)$	$D_0 \exp\left(\frac{5}{2}\sigma^2\right) \frac{C_2}{C_1}$	$D_0 \exp\left(\frac{5}{2}\sigma^2\right) \sqrt{\exp(\sigma^2) \frac{C_2}{C_1} - \left(\frac{C_2}{C_1}\right)^2}$
$p_3(\sigma, D_0; D)$	$D_0 \exp(2\sigma^2)$	$D_0 \exp\left(\frac{7}{2}\sigma^2\right) \frac{C_3}{C_2}$	$D_0 \exp\left(\frac{7}{2}\sigma^2\right) \sqrt{\exp(\sigma^2) \frac{C_3}{C_2} - \left(\frac{C_3}{C_2}\right)^2}$

<sup>a</sup> When maximums are reached between the two outer borders of particle size distribution ( $D_{col} < D_0 \exp(-\sigma^2)$ ,  $D_0 \exp(2\sigma^2) < D_{gr}$ ).

coinciding effective and true weight distributions can be found by equating their mode diameters (Table A1):

$$D_0 = X_0 \exp(-3\sigma^2); \quad (\text{A9})$$

the width parameters  $\sigma$  coincide for both distributions. Therefore, the parameters of the number distribution (13,  $n=0$ ) might be assessed from an available log-normal fit.

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