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Unraveling the size distributions of surface properties for purple soil and yellow soil

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ABSTRACT

Soils contain diverse colloidal particles whose properties are pertinent to ecological and human health, whereas few investigations systematically analyze the surface properties of these particles. The objective of this study was to elucidate the surface properties of particles within targeted size ranges (i.e. >10, 1–10, 0.5–1, 0.2–0.5 and <0.2 μm) for a purple soil (Entisol) and a yellow soil (Ultisol) using the combined determination method. The mineralogy of corresponding particle-size fractions was determined by X-ray diffraction. We found that up to 80% of the specific surface area and 85% of the surface charge of the entire soil came from colloidal-sized particles (<1 μm), and almost half of the specific surface area and surface charge came from the smallest particles (<0.2 μm). Vermiculite, illite, montmorillonite and mica dominated in the colloidal-sized particles, of which the smallest particles had the highest proportion of vermiculite and montmorillonite. For a given size fraction, the purple soil had a larger specific surface area, stronger electrostatic field, and higher surface charge than the yellow soil due to differences in mineralogy. Likewise, the differences in surface properties among the various particle-size fractions can also be ascribed to mineralogy. Our results indicated that soil surface properties were essentially determined by the colloidal-sized particles, and the <0.2 μm nanoparticles made the largest contribution to soil properties. The composition of clay minerals within the diverse particle-size fractions could fully explain the size distributions of surface properties.

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Introduction

Particle size distribution is a fundamental soil property that is commonly used to estimate other soil properties and processes, such as water retention characteristics (Guber et al., 2003; Henderson et al., 2005; Wösten et al., 2001), erosion capacity (Cheng et al., 2007; Guo et al., 2007; Wischmeier and Mannering, 1969), and transmission and distribution of nutrients and pollutants (Li and Pang, 2014; Six et al., 2002; Wang and Keller, 2008; Wang et al., 2006). Numerous studies

have demonstrated that soil surface properties profoundly influence these soil properties and processes (Bower and Gschwend, 1952; Ding et al., 2010; Frhstorfer et al., 1993; Jenny and Reitemeier, 1934; Jiang et al., 2011; Li et al., 2010a; Petersen et al., 1996). Of course, the surface properties of soil and the particle size distribution should be interrelated.

Previous studies involving surface properties of soil particles in the sand (20–2000 μm), silt (2–20 μm) and clay (<2 μm) fractions have generally indicated that specific surface area (Dolinar, 2012; Ersahin et al., 2006; Petersen et

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al., 1996) and surface charge number (Ersahin et al., 2006; Yu, 1976) for a given soil are inversely related to particle size. In contrast to the substantial number of studies that have analyzed the surface properties of larger particles, studies on detailed size distributions of surface properties in the soil clay fraction ($<2\ \mu\text{m}$) are rather scarce. Nevertheless, many soil processes are determined by the nature of the clay fraction (Hillel, 1998; Kiem and Kögel-Knabner, 2002; Saggar et al., 1999; Wu et al., 2012; Yonekura et al., 2013). In this size fraction, soil particles within the nanoscale or colloidal range ($<1\ \mu\text{m}$) are vital and ubiquitous components in natural systems including soils, water, and atmospheric aerosol (Brunekreef and Russell, 2009; Schmidt, 2010). By virtue of their small size, high surface area and abundant surface defects, colloidal-sized particles are involved in the adsorption, migration and transformation of chemical contaminants, heavy metals, and nutrients (Grolimund et al., 1996; McCarthy and Zachara, 1989; Ryan and Elimelech, 1996; Wilkinson and Lead, 2007), which are key factors in several environmental problems (e.g., soil erosion, water eutrophication, heavy metal pollution and air pollution). Moreover, ingestion of fine-sized soil particles associated with many trace metals (Ajmone-Marsan et al., 2008; Madrid et al., 2008) and organic contaminants (Luo et al., 2011) through the water or air can even pose special risks to human health. Therefore, there is an increasing interest in extraction and characterization of colloidal-sized particles, especially natural nanoparticles in soils (Bakshi et al., 2014; Calabi-Floody et al., 2011; Li et al., 2010b; Li et al., 2012; Tian et al., 2014). For example, Calabi-Floody et al. (2011) extracted nanomaterials from the clay fraction of an Andisol and compared the zeta potential of these particles. However, little information on the systematic characterization of surface properties and mineralogy of soil colloidal particles in different size ranges was reported. Clearly, this information can provide insight into the interactions of colloidal-sized particles with environmental pollutants and ultimately clarify the role of colloidal particles in environmental problems.

Soils are composed of abundant clay minerals with constant-charge surfaces. Each kind of clay mineral has specific surface properties, and expansive clay minerals seem to have a dominant influence on soil properties due to their high specific surface area and surface reactivity. Given that the contents and proportions of mineralogical constituents are different in various soil fractions (Huang, 2000; Tsao et al., 2013), the mineral composition should be an important influence factor of the size distributions of soil surface properties. Nevertheless, the lack of the accurate determinations of different surface properties for soil particles within a targeted size range under the same experimental conditions handicaps the valid evaluation of their relationship with soil mineralogy, and ultimately hinders the quantitative assessment of their role in reactions and processes in soils. Fortunately, the combined determination method (Li et al., 2011) in this paper compensates for this shortage.

In this article, special attention was directed to yellow soil and purple soil, which are widespread in southwestern China. We systematically measured the surface properties and mineralogy of soil particles in different size ranges (i.e., >10 , $1\text{--}10$, $0.5\text{--}1$, $0.2\text{--}0.5$ and $<0.2\ \mu\text{m}$) for these soils, with the aims

(1) to clarify the size distributions of surface properties for different kinds of soils, (2) to identify the composition of clay minerals in various particle-size fractions, and (3) to elucidate the relationship between surface properties and soil mineralogy in the size distribution.

1. Materials and methods

1.1. Separation and collection of soil particles within different size ranges for the tested soils

The yellow soil (Ultisol) and purple soil (Entisol) were collected from Chongqing, Southwestern China ($29^{\circ}45'\text{N}$, $106^{\circ}19'\text{E}$). Soil samples were taken from a depth of 0–20 cm within the profile, air dried at room temperature, gently crumbled and passed through a 2 mm mesh sieve to remove plant roots, stones and other large substances. A portion of each soil sample was used for basic chemical property analysis. The pH of the bulk soil suspension was measured at a soil/solution ratio of 1:2.5 in both ultrapure water and 1.0 mol/L KCl solution using a pH electrode. The organic matter content was measured by the potassium dichromate oxidation method (Yang et al., 2008). The cation exchange capacity was measured with the exchange method (Hu et al., 2000), and the free Fe oxide was determined by the citrate-bicarbonate-dithionite method (Lu, 2000). All the selected chemical properties of the bulk soils are displayed in Table 1.

Another portion of each soil sample was prepared for subsequent extraction of particles in different size fractions. Soil particles in size fractions of >10 , $1\text{--}10$, $0.5\text{--}1$, $0.2\text{--}0.5$ and $<0.2\ \mu\text{m}$ were subsequently isolated according to the following procedure. First, air-dried soil particles for the purple soil and yellow soil were treated with 30% hydrogen peroxide (H_2O_2) to remove the associated organic matter (Calabi-Floody et al., 2011; House and Farr, 1989). The procedure involved ultrasonically dispersing the particles in ultrapure water, adding an appropriate amount of H_2O_2 solution to the suspension, heating at 60°C for 16 hr with intensive stirring, and washing away the excess H_2O_2 with ultrapure water. Then the obtained soil suspension was oven-dried at 75°C and passed through a $<0.25\ \text{mm}$ mesh sieve. Second, 50.0 g of the obtained soil particles was treated with 0.01 mol/L KOH solution in 500 mL of ultrapure water to adjust the pH value to 7.5. The suspension was then ultrasonically dispersed at a frequency of 20 kHz for 30 min by a probe-type ultrasonic homogenizer (Scientz-IID, Ningbo Scientz Biotechnology Co., Ltd., Zhejiang, China), before diluting to 5000 mL with ultrapure water. Finally, soil particles $<10\ \mu\text{m}$ were extracted

Table 1 – Basic chemical properties of two tested soils.

Soil types	pH	Organic matter content (g/kg)	CEC ($\text{cmol}_{(-)}/\text{kg}$)	Free iron oxides (g/kg)
Purple soil	7.1	18.5	32.0	4.21
Yellow soil	4.4	2.85	11.9	10.4
CEC: cation exchange capacity.				

and collected by sedimentation under gravity, according to Stokes' Law (Jia et al., 2013; Li et al., 2010b; Tian et al., 2013; Tsao et al., 2013; Xiong et al., 1985), and the residue ($>10\ \mu\text{m}$) was weighed after drying to a constant weight in an oven at 75°C . The particles in the $<10\ \mu\text{m}$ size fraction were then treated as the original material to successively extract the particles in size fractions of <1 , <0.5 and $<0.2\ \mu\text{m}$ by the same treatment mentioned above. To validate the method for extraction of fine clay particles, the size (hydrodynamic) distribution of the extracted $<0.2\ \mu\text{m}$ soil particles for both purple soil and yellow soil was measured with the dynamic light scattering technique as shown in Fig. 1. It was found that in fact the extracted particles were mainly distributed in the range of <200 – $250\ \text{nm}$ in diameter. Thus our extraction method was valid. Table 2 provides the percentages of particles with different size fractions (i.e., >10 , 1 – 10 , 0.5 – 1 , 0.2 – 0.5 and $<0.2\ \mu\text{m}$) by weight.

1.2. Surface properties and soil mineralogy analyses

Surface properties of soil particles within a targeted size range were measured using the combined determination method (Li et al., 2011). First, H-saturated samples were prepared by washing the soil particles several times with a $0.1\ \text{mol/L}$ HCl solution and then with ultrapure water repeatedly until the solution was free of Cl^- in suspension. Second, about $5.0\ \text{g}$ of the oven-dried H-saturated sample was added successively with an equal volume (depending on the surface charges of the sample) of $0.02\ \text{mol/L}$ $\text{Ca}(\text{OH})_2$ solution and NaOH solution into a $150\ \text{mL}$ triangular bottle. Several drops of $0.1\ \text{mol/L}$ HCl solution were used to adjust the pH of the suspension to 7.0 after intensive shaking for $24\ \text{hr}$. The suspension was centrifuged and the supernatant was collected after another $24\ \text{hr}$ of shaking. Third, the final pH and the activities of Na^+ (a_{Na}^0) and Ca^{2+} (a_{Ca}^0) in bulk solution were measured by H-ion, Na-ion and Ca-ion selective electrodes, respectively. Then the absorbed quantities of Na^+ (N_{Na}) and Ca^{2+} (N_{Ca}) (i.e., differences between the added and remaining quantities of Na^+ and

Table 2 – Particle size distribution of the two soils.

Materials	Particle size (μm)				
	>10	1 – 10	0.5 – 1	0.2 – 0.5	<0.2
Purple soil	36.3%	27.4%	14.1%	5.44%	16.8%
Yellow soil	34.9%	28.8%	6.10%	9.86%	20.3%

Ca^{2+}) on charged particle surfaces were measured. By introducing the experimental data into the following Eqs. (1)–(5) (Li et al., 2011; Liu et al., 2010), the specific surface area, surface charge, surface potential, and electrostatic field strength at the surface for different particle size fractions of the soils were calculated.

$$\varphi_0 = -2RT/(2\beta_{\text{Ca}} - \beta_{\text{Na}})/F \times \ln[(a_{\text{Ca}}^0 N_{\text{Na}})/(a_{\text{Na}}^0 N_{\text{Ca}})] \quad (1)$$

$$\sigma = \text{sgn}(\varphi) \sqrt{\frac{\varepsilon RT}{2\pi}} \left[a_{\text{Na}}^0 \left(e^{\frac{\beta_{\text{Na}} F \varphi}{RT}} - 1 \right) + a_{\text{Ca}}^0 \left(e^{\frac{2\beta_{\text{Ca}} F \varphi}{RT}} - 1 \right) + (a_{\text{Na}}^0 + 2a_{\text{Ca}}^0) \left(e^{\frac{F \varphi}{RT}} - 1 \right) \right] \quad (2)$$

$$E = 4\pi\sigma/\varepsilon \quad (3)$$

$$S = \frac{N_{\text{Na}} K}{m a_{\text{Na}}^0} e^{\frac{\beta_{\text{Na}} F \varphi}{RT}} = \frac{N_{\text{Ca}} K}{m a_{\text{Ca}}^0} e^{\frac{2\beta_{\text{Ca}} F \varphi}{RT}} \quad (4)$$

$$\text{SCN} = 10^5 S \sigma / F \quad (5)$$

where

$$\beta_{\text{Ca}} = -0.0213 \ln(I^{0.5}) + 1.2331$$

$$\beta_{\text{Na}} = 0.0213 \ln(I^{0.5}) + 0.7669$$

$$m = 0.5259 \ln(c_{\text{Na}}^0/c_{\text{Ca}}^0) + 1.992$$

where, φ_0 (V) is the surface potential; σ (C/dm^2) is the surface charge density; E (V/dm) is the electrostatic field strength at surface; S (dm^2/kg) is the specific surface area; SCN (mol/kg) is the surface charge number; R ($\text{J}/(\text{K}\cdot\text{mol})$) is the universal gas constant; T (K) is the absolute temperature; F (C/mol) is the

Fig. 1 – Particle size distribution of soil particles in the $<0.2\ \mu\text{m}$ size fraction.

Faraday constant; Z is the charge of each ion species; β_{Na} and β_{Ca} are the corresponding modification factor of Z for Na^+ and Ca^{2+} , respectively; κ (1/dm) is the Debye–Hückel parameter; ε is the dielectric constant ($8.9 \times 10^{-10} \text{ C}^2/(\text{J}\cdot\text{dm})$ for water); I (mol/L) is the ionic strength, c_{Na}^0 (mol/L) and c_{Ca}^0 (mol/L) is equilibrium concentration of Na^+ and Ca^{2+} in bulk solution, respectively.

X-ray diffraction (XRD) analysis was conducted to determine soil mineralogy, especially for the clay mineral types (Tsao et al., 2013; Wang et al., 2006). The soil clay mineral compositions of the samples studied were detected and analyzed by the Bioelements Analysis Laboratory (College of Resources and Environment, Southwest University) with an X-ray diffractometer (XD-3, Beijing Purkinje General Instrument Co., Ltd., Beijing, China).

2. Results and discussion

2.1. Mineralogy of the clay minerals of the various particle-size fractions

The results of the semi-quantitative analysis of clay minerals for soil particles in different size fractions are displayed in Table 3. On one hand, the contents and proportions of minerals were different in the different soils. Quartz, mica, kaolinite, illite and vermiculite were found to exist in soil particles for both purple soil and yellow soil, whereas montmorillonite and albite were only detected in purple soil particles. Additionally, for a targeted size range, the purple soil particles contained more abundant expansive clay minerals (i.e., vermiculite and montmorillonite) as compared with the yellow soil particles. On the other hand, prominent differences of mineralogical constituents were observed in soil particles for different size fractions. Specifically, the larger purple soil particles of the size range $>1 \mu\text{m}$ had abundant soil primary minerals (albite and quartz), while the colloidal-sized particles contained more secondary clay minerals, which have higher surface charge and larger specific surface area. The composition of the secondary clay minerals varied remarkably among the 0.5–1, 0.2–0.5 and $<0.2 \mu\text{m}$ size fractions in purple soil particles. In particular, for fractions in the smallest particle-size range ($<0.2 \mu\text{m}$), over half of the clay minerals were expansive clay minerals. Similarly, for the yellow soil, plenty of quartz particles were present in the $>10 \mu\text{m}$ and 1–10 μm size fractions. In the colloidal-sized

particles, vermiculite and illite gradually increased in relative abundance as the particle size range decreased from 0.5–1 μm to $<0.2 \mu\text{m}$. Our results are consistent with the observations of Tsao et al. (2013). In their study, the content of soil primary minerals (i.e., quartz) decreased with decreasing particle size, while the content of secondary clay minerals (i.e., kaolinite) rapidly increased with the decline of particle size.

Note that expansive clay minerals have larger specific surface area and higher surface charge, and that montmorillonite has the largest specific surface area and highest surface charge, so the differences in mineralogical compositions among particles and soils should lead to differences in their surface properties, as will be confirmed in the discussion below.

2.2. Surface properties and interaction forces of the various particle-size fractions

2.2.1. Surface properties

For both variably and permanently charged soil, under a given pH condition, the surface properties were independent of solution composition and concentration, except for surface potential (Li et al., 2011). In our experiments, the pH conditions were approximately constant, thus the corresponding surface properties of particles in different size fractions are shown in Table 4.

Table 4 shows that the size distribution of surface properties for the two soils was perfectly consistent with the changing trends of mineralogical components among particles and soils. Smaller purple soil particles were observed to have larger specific surface area. Briefly, specific surface area dramatically increased from $2.76 \times 10^3 \text{ dm}^2/\text{g}$ to $42.1 \times 10^3 \text{ dm}^2/\text{g}$ as particle size decreased from $>10 \mu\text{m}$ to $<0.2 \mu\text{m}$. Likewise, the yellow soil exhibited a distinct increase in specific surface area with the decline in particle size, except for particles in the 1–10 μm and 0.2–0.5 μm size fractions. Although colloidal-sized particles in the size range $<1 \mu\text{m}$ exhibited a specific surface area one order of magnitude larger than that of the particles in the size range $>1 \mu\text{m}$ for both soils, the specific surface area of colloidal-sized particles for the purple soil was larger than that for the yellow soil.

The charge on the surface of particles for the two soils increased significantly with decreasing particle size, such that the surface charge of particles in the smallest size range ($<0.2 \mu\text{m}$) was two orders of magnitude higher than that in the

Table 3 – Semi-quantitative analysis of clay compositions in various particle-size fractions for the two soils.

Materials	Particle size (μm)	Quartz	Mica	Kaolinite	Illite	Montmorillonite	Vermiculite	Albite
Purple soil	>10	+++	++	–	+	–	+	+++
	1–10	+++	+++	–	+	–	+	++
	0.5–1	++	+++	+	++	–	++	+
	0.2–0.5	++	+++	+	+++	–	–	+
	<0.2	+	++	–	++	++	+++	+
Yellow soil	>10	+++++	+	–	–	–	–	–
	1–10	++++	++	–	+	–	–	–
	0.5–1	–	++++	+	++	–	+	–
	0.2–0.5	+	+++	+	+++	–	++	–
	<0.2	+	++	+	+++	–	++	–

Symbols of –: trace or not detected; +: $<10\%$; ++: 10%–25%; +++: 25%–50%; ++++: 50%–75%; +++++: $>75\%$.

Table 4 – Surface properties of the original soil and particles within different size ranges.

Materials	Particle size (μm)	pH	Specific surface area (10 ³ dm ² /g)	Surface charge density (10 ^{−3} C/dm ²)	Surface charge number (cmol _c /kg)	Electrostatic field strength at surface (10 ⁸ V/m)
Purple soil	>10	6.94	2.76 ± 0.06 a	3.05 ± 0.49 a	9.96 ± 0.57 a	4.30 ± 0.69 a
	1–10	6.78	3.31 ± 0.01 a	5.56 ± 0.35 b	19.6 ± 0.8 b	7.85 ± 0.50 b
	0.5–1	7.23	16.3 ± 0.2 b	2.81 ± 0.11 a	47.3 ± 1.1 c	3.96 ± 0.16 a
	0.2–0.5	7.32	19.9 ± 0.1 b	3.77 ± 0.01 a	77.6 ± 0.4 d	5.32 ± 0.01 a
	<0.2	7.25	42.1 ± 0.1 c	2.42 ± 0.19 a	104 ± 1 e	3.41 ± 0.27 a
Yellow soil	>10	7.27	7.05 ± 0.01 b	0.0944 ± 0.001 a	0.693 ± 0.060 a	0.133 ± 0.009 a
	1–10	7.17	4.07 ± 0.01 a	0.634 ± 0.026 b	2.68 ± 0.09 b	0.891 ± 0.016 b
	0.5–1	7.13	17.3 ± 0.2 d	0.609 ± 0.014 b	10.8 ± 0.2 c	0.844 ± 0.011 b
	0.2–0.5	7.05	12.7 ± 0.1 c	1.13 ± 0.31 c	14.4 ± 1.2 d	1.60 ± 0.43 c
	<0.2	7.00	18.5 ± 0.6 d	1.42 ± 0.09 c	27.2 ± 1.4 e	2.00 ± 0.13 c

Data are means ± standard deviation of three replicates; significant differences between treatments at $p < 0.05$ are indicated with different letters.

largest size range (>10 μm). Moreover, for a given particle-size fraction, the surface charges in the purple soil were much higher than in the yellow soil. For example, the surface charge in the >10 μm size fraction for the purple soil (9.96 cmol_c/kg) was 14 times higher than that in the yellow soil (0.693 cmol_c/kg).

The yellow soil and purple soil particles exhibited completely different trends in the size distributions of surface charge density and electrostatic field strength at the surface. The purple soil particles in the size range 1–10 μm held the highest surface charge density (5.56×10^{-3} C/dm²) and the strongest electrostatic field at the surface (7.85×10^8 V/m), while no significant differences of these two properties were detected among particles within other size ranges. Unlike the purple soil, the surface charge density and electrostatic field strength at the surface for the yellow soil increased significantly with decreasing particle size, and the two properties in the <0.2 μm size fraction was fifteen times higher than in the >10 μm size fraction.

Furthermore, the contributions of an individual particle-size fraction to the specific surface area and surface charge number of the entire soil can be calculated using Eqs. (6) and (7) and the results are displayed in Table 5:

$$\alpha_{iS} = \frac{(r_i \times S_i)}{\sum r_i \times S_i} \times 100\% \quad (6)$$

$$\alpha_{iSCN} = \frac{(r_i \times SCN_i)}{\sum r_i \times SCN_i} \times 100\% \quad (7)$$

where, α_{iS} and α_{iSCN} are the contribution rates of an individual particle-size fraction (i) to the overall specific surface area and surface charge, respectively, which has limits of 0–100%; r_i is the weight percentage of particles in this particle-size fraction (Table 2); S_i (dm²/g) and SCN_i (cmol_c/kg) are the specific surface area and surface charge of particles in this particle-size fraction (Table 4).

Clearly, more than 80% and 60% of specific surface area as well as 75% and 85% of surface charge came from the colloidal-sized particles of the size range <1 μm for the two soils, respectively, indicating that surface properties of the entire soil were essentially determined by the nature of the colloidal-sized particles, even though the mass of these particles can be merely a few percent of the total (Table 2).

Furthermore, although fractions in the smallest particle-size range <0.2 μm only comprised less than one fifth of the bulk soil, approximately half of the specific surface area and surface charge of the entire soil came from these particles, indicating that the smallest particles played an extremely crucial role in the overall soil properties.

Based on the specific surface area (S) and surface charge number (SCN) of soil particles within different size ranges calculated above (Table 4), under a given concentration of a single 1:1 or 2:1 electrolyte solution, the surface potential of those soil particles can be calculated with Eqs. (8) and (9), respectively (Li et al., 2011):

1:1 Electrolyte solution:

$$\varphi_0 = -2RT/(ZF) \times \ln(2a^0/\tilde{c}) \quad (8)$$

2:1 Electrolyte solution:

$$\varphi_0 = -2RT/(ZF) \times \ln(\sqrt{3}a^0/\tilde{c}) \quad (9)$$

where:

$$\tilde{c} = SCN \times \kappa/S$$

and

$$\kappa = \sqrt{8\pi F^2 \left(\frac{1}{2} \times \sum a^0 Z^2 \right) / (\epsilon RT)}$$

where, $\tilde{c}$ (mol/L) is the average concentration of any given cation species in the diffuse layer, and a^0 (mol/L) is the

Table 5 – Contribution rates of the various particle-size fractions to the specific surface area and surface charges.

Particle size (μm)	Specific surface area		Surface charge number	
	Purple soil	Yellow soil	Purple soil	Yellow soil
>10	8.13%	25.3%	9.68%	2.80%
1–10	7.35%	12.1%	14.4%	8.96%
0.5–1	18.6%	10.9%	17.9%	7.64%
0.2–0.5	8.75%	12.8%	11.3%	16.4%
<0.2	57.2%	38.9%	46.8%	64.2%

equilibrium concentration of this cation species in bulk solution, which is defined as 0–1 mol/L in this study.

A significant negative logarithmic trend was evident for surface potential with increasing electrolyte concentrations for the two soils (Fig. 2). The surface potential of soil particles in a 1:1 electrolyte solution exceeded that in a 2:1 electrolyte solution under the same electrolyte concentration and particle-size fraction conditions. At any given electrolyte concentration, great differences of surface potential were found among various particle-size fractions, and the purple soil and yellow soil had almost reversed variation trends in the size distribution of surface potential. For instance, in the 0.01 mol/L 1:1 electrolyte solution, the surface potential in the >10, 1–10, 0.5–1, 0.2–0.5 and <0.2 μm size fractions for the purple soil particles were –0.209, –0.235, –0.198, –0.213 and –0.190 V, respectively. Thus the sequence was φ_0 (1–10 μm) > φ_0 (0.2–0.5 μm) > φ_0 (>10 μm) > φ_0 (0.5–1 μm) > φ_0 (<0.2 μm) for the purple soil. However, the corresponding surface potentials of particles within the targeted size ranges for the yellow soil were –0.0242, –0.122, –0.119, –0.150 and –0.163 V, respectively, and the sequence therefore was φ_0 (<0.2 μm) > φ_0 (0.2–0.5 μm) > φ_0 (1–10 μm) > φ_0 (0.5–1 μm) > φ_0 (>10 μm) for the yellow soil. Combining Eqs. (3) and (4), we can see the differences of surface potential of particles in different size fractions stem from their surface charge density, and the sequence of surface charge density (Table 4) was in good agreement with that of the surface potential for the two soils.

2.2.2. Assessment of electrostatic repulsive pressure between adjacent particles

After quantitatively characterizing the surface properties of particles in various size fractions, it was possible to evaluate the interactions among particles within a targeted size range. For example, the electrostatic repulsive pressure between adjacent soil particles in a single 1:1 or 2:1 electrolyte solution can be calculated (Ducker et al., 1992) as:

$$P_{\text{EDL}}(d) = 2/101 \times RTa^0 \{ \cosh[Z F \varphi(d/2)/(RT)] - 1 \} \quad (10)$$

where $P_{\text{EDL}}(d)$ (atm) is the electrostatic repulsive pressure and d is the distance between two adjacent particle surfaces. The potential at the mid-point of the two adjacent particle surfaces ($\varphi(d/2)$) can also be calculated (Hou et al., 2009; Li et al., 2009) as:

$$\frac{\pi}{2} \left[1 + \left(\frac{1}{2} \right)^2 e^{\frac{2ZF\varphi_0(\frac{d}{2})}{RT}} + \left(\frac{3}{8} \right)^2 e^{\frac{4ZF\varphi_0(\frac{d}{2})}{RT}} \right] - \arcsin \frac{e^{\frac{ZF\varphi_0 - ZF\varphi(d/2)}{2RT}}}{2} = 1/4 \times d k e^{\frac{ZF\varphi_0(\frac{d}{2})}{RT}} \quad (11)$$

For electrolyte concentration 0.01 mol/L, the surface potential (φ_0) of particles in a given size fraction is calculated by Eqs. (8) and (9). Integrating Eqs. (10) and (11), the electrostatic repulsive pressure of soil particles for different distances between two adjacent particle surfaces was calculated (Fig. 3).

The analysis of electrostatic repulsive pressure in Fig. 3 shows a significant negative logarithmic decrease with increasing

Fig. 2 – Surface potential of soil particles within different size ranges under different concentrations of a single 1:1 or 2:1 electrolyte solution. P: purple soil, Y: yellow soil.

distance between two adjacent particle surfaces. The difference of electrostatic repulsive pressure between soil particles in different size fractions became more significant at smaller distances from the particle surface. Generally, smaller soil particles had stronger electrostatic repulsive pressure between adjacent particles for the two soils when the other conditions were the same. In addition, under the same size fraction and electrolyte composition conditions, the electrostatic repulsive pressure between the purple soil particles was very much higher than that between the yellow soil particles.

The above discussion showed that, the high charge densities for different particle-size fractions could produce a strong electric field around particles, and this electric field would further produce strong electrostatic repulsive pressure between adjacent particles in soil aggregates, which would result in soil aggregate breakdown, making small clay particles easier to disperse in water to form a suspension. Finally, through the flow of the suspension, fine soil particles along with adsorbed nutrients and contaminants would flow into other natural systems.

Hu et al. (2015) have quantitatively analyzed how the electrostatic repulsive pressure between clay particles of the same purple soil in our study influenced soil aggregate breakdown, and found that, after aggregate breakdown, the small particles released (separate and micro-aggregates) with a diameter $<2\ \mu\text{m}$ exponentially increased with the increase of electrostatic repulsive pressure, indicating that the surface properties of clay particles strongly influence soil aggregate

stability. Moreover, Li et al. (2013) further studied the relationship between transport ability of soil particles during rainfall and the surface potential of soil particles for the same purple soil in this study. They found that, with the increase of surface potential, the intensity of particle transport during rainfall sharply increased, implying that the electrostatic repulsive pressure determined the intensity of soil transport in natural systems.

In conclusion, the surface properties of various particle-size fractions, especially the electrochemical properties at the particle surface for the smaller soil particles, would strongly influence clay particle interactions in natural soil, and thus influence soil aggregate stability and soil erosion. By virtue of the fact that most of the nutrients and contaminants are transported to the earth surface water via small soil particles, especially the colloidal- and nano-size particles (Sumner, 1999; Yang et al., 2009), understanding the size distributions of surface properties for soil particles, especially for colloidal-sized soil particles, would be an important issue in soil and water environments.

3. Conclusions

The size distribution of surface properties of soil particles is closely related to soil particle transport during rainfall, thus this is an important issue in soil and water environments.

Fig. 3 – Electrostatic repulsive pressure of soil particles within different size ranges under different distances between two adjacent particle surfaces in a single 1:1 or 2:1 electrolyte solution. P: purple soil, Y: yellow soil.

This study was conducted to clarify the surface properties and soil mineralogy of various particle-size fractions (i.e., >10, 1–10, 0.5–1, 0.2–0.5 and <0.2 μm) for two typical soil species in Southwestern China. Up to 85% of the surface charges and specific surface area came from colloidal-sized particles in the size range <1 μm , and the smallest particles <0.2 μm contributed the largest proportion (~50%) to these surface properties, implying that colloidal-sized soil particles, especially the smallest soil nanoparticles, played a decisive role in overall soil surface properties. Additionally, the variation of the contents and proportions of soil secondary clay minerals in various particle-size fractions for the two soils were consistent with the change trends of their surface properties, indicating that surface properties of different particle-size fractions depended on their clay mineral compositions.

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