

Importance of soil interparticle forces and organic matter for aggregate stability in a temperate soil and a subtropical soil

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ABSTRACT

Soil organic matter (SOM) and interparticle forces, including the electrostatic repulsive force (ERF), surface-hydration repulsive force (SHRF) and van der Waals attractive force (vDWAF), play crucial roles in aggregate stability. However, few studies investigated their coupled effects on aggregate stability in variably charged soils, in which soil particle interactions are more complex than in permanently charged soils due to the coexistence of positive and negative charges and the variable surface charge characteristics. Therefore, this study aims to: 1) investigate the combined effects of soil solution pH and the overlapping of electric double layers (EDLs) between positively charged Fe/Al (hydro)oxides and negatively charged SOM on the ERF and aggregate stability before (control) and after SOM removal and after straw incubation for 240 days; and 2) evaluate the importance of soil interparticle forces and SOM for aggregate stability in a permanently charged temperate soil (Vertisol) and a variably charged subtropical soil (Ultisol). Soil aggregate stability was determined by measuring the release of small particles ($w(<d)\%$) after aggregate breakdown at different KCl concentrations (10^{-1} to 10^{-5} mol L⁻¹). Soil solution pH was adjusted by varying KCl concentration. In both soils, the $w(<d)\%$ increased exponentially with the net force of the soil interparticle forces. However, in contrast to the Vertisol, the $w(<d)\%$ of the differently treated Ultisol showed almost no change before the KCl concentration decreased to 10^{-2} mol L⁻¹ and continuous changes after the KCl concentration decreased to 10^{-2} mol L⁻¹. In addition, the differences in the $w(<d)\%$ between the SOM removal treatment and the control and straw incubation treatments were much larger in the Ultisol than in the Vertisol. In the Ultisol, the ERF did exhibit little and continuous increase over the whole range of tested pH. When considering the impact of the overlapping of oppositely charged EDLs between Fe/Al (hydro)oxides and SOM, a much stronger reduction in ERF was observed in the control and straw incubation treatments and at lower KCl concentrations. Consequently, in both the Vertisol and Ultisol, aggregate stability is essentially controlled by the soil interparticle forces, whereas the effects of soil solution pH and the overlapping of oppositely charged EDLs between SOM and Fe/Al (hydro)oxides on the ERF must be considered in variably charged soils (i.e. Ultisol). Moreover, SOM can play a more important role in aggregate stability in subtropical soil than in temperate soil.

1. Introduction

Stable aggregates are crucial to the improvement of soil permeability and reduction of soil erosion. Essentially, the breakdown or stabilization of soil aggregates is the result of the interaction of the external and internal soil forces. Hence, aggregate breakdown during rainfall is generally ascribed to soil external forces such as raindrop impact and the shear strength of flowing water, or soil internal forces

such as slaking produced by compressed air in the aggregate, physicochemical dispersion caused by osmotic stress, differential swelling of clay minerals and hydrophobic interactions caused by hydrophobic substances such as lipids and waxes (Dal Ferro et al., 2012; Le Bissonnais, 1996; Levy et al., 2003; Sadeghi et al., 2017). However, according to Hu et al. (2015), slaking, differential clay swelling and flowing water are probably not the main mechanisms of aggregate breakdown. The raindrop impact pressure is only approximately

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0.1–0.3 MPa (Nearing et al., 1987) and the osmotic stress pressure is estimated to be <0.25 MPa (Xu et al., 2015b), both of which seem too weak to destroy dry aggregates. Moreover, although hydrophobicity can improve soil aggregate stability, it is greatly influenced by soil water content and will disappear after soil becomes wet (Doerr and Thomas, 2000), and may not be the most significant factor (Dal Ferro et al., 2012).

Recently, based on the viewpoint of colloidal surface chemistry, some studies note that soil aggregate stability is intrinsically determined by three interparticle forces including the electrostatic repulsive force (ERF), the van der Waals attractive force (vDWAF) and the surface-hydration repulsive force (SHRF) or Lewis acid-base repulsive force (Calero et al., 2017; Hu et al., 2015; Li et al., 2013; Xu et al., 2015a; Yu et al., 2017). The ERF is produced by the overlapping of electric double layers (EDLs) of two adjacent particles of the same charge, and the vDWAF is generated due to the electromagnetic effects of the molecules that make up the particles (Liang et al., 2007). The SHRF originates from the interaction between clay surfaces and adjacent water molecules (Low, 1987) and is practically identical to the Lewis acid-base repulsive force (van Oss, 2006), which results from the excess in hydration pressure generated by the motion and orientation restrictions of water molecules on colloidal surfaces (Calero et al., 2017). These three forces can produce a repulsive or attractive interparticle pressure as high as 10–100 MPa that is thought to be much stronger than the external or internal forces on soil described above and, therefore, ought to determine also soil aggregate breakdown (Hu et al., 2015; Xu et al., 2015a). Previous studies demonstrated that water infiltration, splash erosion and soil colloid or particle transport are also strongly influenced by the interactions of these three interparticle forces (Carstens et al., 2018; Gong et al., 2018; Hu et al., 2018b; Li et al., 2013; Yu et al., 2016). However, the above results were mainly achieved from permanently charged soils that are usually distributed in temperate regions and are dominated by negatively charged 2:1 clay minerals. Little is known about the role of soil interparticle forces in aggregate stability in variably charged soils that are generally distributed in tropical and subtropical regions and are dominated by positively charged Fe/Al (hydro)oxides and negatively charged 1:1 clay minerals (e.g., kaolinite).

Compared to temperate soils, soil particle interactions may be more complex in tropical and subtropical soils due to the coexistence of positive and negative charges and the variable surface-charge characteristics (Qafoku et al., 2004; Yu, 1997). For instance, Li et al. (2018) recently reported the unexpected phenomenon that variable-charge soil aggregates (KCl saturated) always seem to be stable and do not disperse in different concentrations of KCl solution even under very low ionic strength (10^{-4} mol L⁻¹). In permanently charged temperate soils, such a low ionic strength usually implies a strong ERF between soil particles (more than 10 MPa) and results in an intensive aggregate breakdown (Hu et al., 2015). This distinct behavior of variably charged soils probably can be explained by the mechanism of the overlapping of EDLs of oppositely charged soil particles (Barber and Rowell, 1972; Qafoku and Sumner, 2002; Xu et al., 2014). According to this mechanism, a portion of the surface positive and negative charges will be balanced due to the overlapping of EDLs around oppositely charged 1:1 clay minerals and Fe/Al (hydro)oxides (Qafoku and Sumner, 2002; Xu et al., 2014). Therefore, despite the ionic strength being quite low, the ERF may be still weak and soil aggregates can remain stable. Hence, it is necessary to consider the impact of the overlapping of oppositely charged EDLs when studying the relationship between soil interparticle forces and aggregate stability in tropical and subtropical soils. In addition, the quantity of soil surface charge is more sensitive to the pH of the soil solution in variably charged soils than in permanently charged soils (Yu, 1997), thus, the influence of pH on the ERF should also be considered in tropical and subtropical soils.

Moreover, it is now generally believed that soil organic matter (SOM) plays a more important role in the stabilization of aggregates in

permanently charged temperate soils than in variably charged tropical and subtropical soils (Denef and Six, 2005; Peng et al., 2015; Six et al., 2004). However, SOM is a main source of negative charge in tropical and subtropical soils, that bear a much larger number of surface charges than 1:1 clay minerals of the same mass (Yu, 1997). This fact implies that the overlapping of oppositely charged EDLs is stronger between SOM and Fe/Al (hydro)oxides than between 1:1 clay minerals and oxides and, therefore, the ERF can be weakened more severely in the presence of SOM. In temperate soils, in which the overlapping of oppositely charged EDLs is negligible, SOM weakens the ERF mainly through organo-mineral interactions (Yu et al., 2017). Thus, in tropical and subtropical soils, SOM may weaken the ERF more strongly through its additional impact on the overlapping of oppositely charged EDLs except for organo-mineral interactions. In other words, SOM may play a more important role in aggregate stability in tropical and subtropical soils than in temperate soils.

Consequently, this study aims to explore the role of soil interparticle forces in aggregate stability, to investigate the combined effects of soil solution pH and the overlapping of oppositely charged EDLs between Fe/Al (hydro)oxides and SOM on the ERF between soil particles and to evaluate the importance of SOM in the stabilization of aggregates in variably charged soils. A comparative study between temperate and subtropical soils will contribute to a better understanding of the relationship between soil interparticle forces and aggregate stability in variably charged soils.

2. Materials and methods

2.1. Materials and treatments

A temperate soil presumably dominated by permanent charge and a subtropical soil presumably dominated by variable charge were collected from Suixi (Anhui province, China; 36°37'N, 116°46'E) and Yingtan (Jiangxi province, China; 28°21'N, 116°10'E), and are classified as an Vertisol and an Ultisol, respectively, according to the USDA soil classification (Soil Survey Staff, 2003). The Vertisol is dominated by montmorillonite, chlorite, kaolinite and illite, and the Ultisol is dominated by Fe/Al (hydro)oxides and kaolinite, thus, the Vertisol and Ultisol are presumed to be a permanently charged soil and a variably charged soil, respectively. The pH values of the Vertisol and Ultisol were 6.34 and 4.62, respectively, and the clay, silt and sand contents of Vertisol and Ultisol are 26.8%, 41.5% and 31.7%, and 44.3%, 29.0%, and 26.7%, respectively.

Before the evaluation of soil aggregate stability and the determination of surface charge properties, both Vertisol and Ultisol samples were subjected to three treatments: (1) soils were kept unaltered (hereafter called control treatment). (2) Soils were oxidized with 30% H₂O₂ to remove SOM (hereafter called SOM removal). (3) Soils were mixed with <0.25 mm rice straw particles (straw/soil: 25 g: 500 g) and incubated for 240 days (hereafter called straw incubation). The detailed procedures of SOM removal and soil incubation are described in Yu et al. (2017). The soil organic carbon (SOC) concentrations of soils subjected to different treatments were measured by oxidation with potassium dichromate (Walkley and Black, 1934).

2.2. Preparation of soil aggregates

In order to quantitatively evaluate the relationship between soil interparticle forces and aggregate stability, soil samples of the three Vertisol and Ultisol treatments were first saturated with KCl and homogenized and 1–5 mm KCl-saturated aggregates were prepared according to the method of Yu et al. (2017). Taking the control treatment of the Ultisol as an example, dry soil samples (600 g) were weighed into a 5-L beaker and washed by dispersion, agitation, centrifugation, and decantation with four 5-L portions of 0.5 mol L⁻¹ KCl solution, then with three portions of deionized water. The wet soil

samples were then homogenized as thoroughly as possible, oven-dried at 60 °C and ground through nested 1- and 5-mm sieves to collected 1–5 mm soil aggregates (hereafter termed as KCl-saturated aggregates).

2.3. Evaluation of soil aggregate stability

To quantitatively assess the aggregate stability of the differently treated Vertisol and Ultisol, the quantities of released small particles ($w(<d)\%$) of <10, <5 and <2 μm diameter after the breakdown of 1–5 mm aggregates were determined according to the method of Xu et al. (2015a) and Hu et al. (2015). Taking the control treatment of the Ultisol as an example, 10 g of 1–5 mm KCl-saturated dry aggregates were transferred into a 500-ml cylinder filled with 10^{-1} , 10^{-2} , 10^{-3} or 10^{-5} mol L⁻¹ KCl solutions (three replicates). After the aggregates were immersed for 2 min, the cylinder was slowly and carefully inverted two times within 2 min. Then, the mass percentage ($w(<d)\%$, $d = 10, 5$ or $2 \mu\text{m}$) of the released small particles of <10, <5 or <2 μm diameter to the total mass of aggregates after aggregate breakdown was measured according to the pipette method (based on the Stokes' law). The pH of the suspension was then determined.

2.4. Surface charge analysis

The combined determination method was applied to measure the surface charge properties of differently treated Ultisol and Vertisol (Ding et al., 2015; Li et al., 2011; Tang et al., 2015; Yu et al., 2017). Briefly, oven-dried (60°C) and crushed (<0.25 mm) H⁺-saturated samples of differently treated Ultisol and Vertisol samples were prepared by washing first with 0.1 mol L⁻¹ HCl and then with deionized water according to the method of Yu et al. (2017). Three replicates of 5.0-g H⁺-saturated soil samples from each treatment were then weighed into three 150-ml triangular bottles and equal volumes (approximately 20–40 ml) of 0.01 mol L⁻¹ Ca(OH)₂ solution and 0.016 mol L⁻¹ NaOH solution were added. Because pH affects the soil surface charge properties more strongly in variably charged soils than in permanently charged soils, after shaking for 24 h (25 °C), the pH values of the differently treated Vertisol suspensions were all adjusted to 7.0 with 1 and 0.1 mol L⁻¹ HCl solutions, while the pH values of differently treated Ultisol suspensions were adjusted to the corresponding mean pH values that were recorded after the measurement of $w(<d)\%$. The suspensions were shaken again until the equilibrium pH (pH_e) value approached 7.0 for the Vertisol or the corresponding recorded pH values for the Ultisol. The suspensions then were centrifuged and the supernatants were collected. The quantities of Ca²⁺ and Na⁺ adsorbed on soil particles were determined by measuring the activities and concentration of Ca²⁺ and Na⁺ in the supernatants using ion-selective electrodes (Leici PXSJ-216F, Shanghai, China). Finally, the surface charge density (σ_0 , C m⁻²), the surface charge number (Q_s , cmol_c kg⁻¹), and the specific surface area (SSA, m² g⁻¹) were calculated by introducing the measured data into the following equations (Li et al., 2011):

$$\sigma_0 = \text{sgn}(\varphi_0) \left[5 \frac{\varepsilon RT}{\pi} \left[\alpha_{\text{Na}}^0 \left(e^{\frac{\beta_{\text{Na}} F \varphi_0}{RT}} - 1 \right) + \alpha_{\text{Ca}}^0 \left(e^{\frac{2\beta_{\text{Ca}} F \varphi_0}{RT}} - 1 \right) + (\alpha_{\text{Na}}^0 + 2\alpha_{\text{Ca}}^0) \left(e^{\frac{F \varphi_0}{RT}} - 1 \right) \right] \right] \quad (1)$$

$$Q_s = 10^5 \frac{S \sigma_0}{F} \quad (2)$$

$$\text{SSA} = \frac{N_{\text{Na}} \kappa}{m \alpha_{\text{Na}}^0} e^{\frac{\beta_{\text{Na}} F \varphi_0}{2RT}} \times 10^{-2} = \frac{N_{\text{Ca}} \kappa}{m \alpha_{\text{Ca}}^0} e^{\frac{2\beta_{\text{Ca}} F \varphi_0}{RT}} \times 10^{-2} \quad (3)$$

$$m = 0.529 \ln \left[(\alpha_{\text{Na}}^0 + \alpha_{\text{H}}^0) / \alpha_{\text{Ca}}^0 \right] + 1.992 \quad (4)$$

where ε (C² J⁻¹ dm⁻¹) is the dielectric constant; R (J mol⁻¹ K⁻¹) is the gas constant; T (K) is the absolute temperature; α_i^0 (mol L⁻¹) is the activity of the i th cation ($i = \text{Ca}^{2+}$, Na^+) in the bulk solution; F

(C mol⁻¹) is the Faraday constant; $\beta_{\text{Na}} = 0.0213 \ln(I^{0.5}) + 0.7669$, $\beta_{\text{Ca}} = -0.0213 \ln(I^{0.5}) + 1.2331$, I is the ion strength in bulk solution; N_i (mol g⁻¹) is the total number of the i th cation ($i = \text{Ca}^{2+}$, Na^+) adsorbed on the soil particle surfaces; κ (1/dm) is the Debye-Hückel parameter, here $\kappa = (4\pi F^2 \sum Z_i^2 \alpha_i^0 / \varepsilon RT)^{1/2}$, Z_i is the cation valence; α_i^0 is the equilibrium concentration of the i th cation ($i = \text{Na}^+$, H^+ and Ca^{2+}) in bulk solution.

2.5. Calculation of soil interparticle forces

The electrostatic repulsive pressure (P_E) (MPa), the van der Waals attractive pressure (P_{vdw}) (MPa) and the surface hydration repulsive pressure (P_h) (MPa) in KCl-saturated aggregates can be calculated according to the following equations (Hou et al., 2009; Li et al., 2013):

$$P_E = \frac{2}{1010} RT c_0 \left\{ \cosh \left[\frac{Z_i F \varphi(\lambda/2)}{RT} \right] - 1 \right\} \quad (5)$$

$$P_{vdw} = -\frac{A_{\text{eff}}}{6\pi} (10\lambda)^{-3} \quad (6)$$

$$P_h = 3.33 \times 10^3 e^{-5.76 \times 10^9 \lambda} \quad (7)$$

where c_0 (mol L⁻¹) is the equilibrium concentration of the cation in the bulk solution; λ (dm) is the distance between two adjacent soil particles; and $\varphi(\lambda/2)$ (V) is the potential at the middle of the overlap of the electric double layers of two adjacent soil particles which can be calculated by (Hou et al., 2009; Li et al., 2013):

$$\frac{\pi}{2} \left[1 + \left(\frac{1}{2} \right)^2 e^{\frac{2Z_i F \varphi(\lambda/2)}{RT}} + \left(\frac{3}{8} \right)^2 e^{\frac{4Z_i F \varphi(\lambda/2)}{RT}} \right] - \arcsin \frac{Z_i F \varphi_0 - Z_i F \varphi(\lambda/2)}{2RT} = \frac{1}{4} \lambda \kappa e^{-\frac{Z_i F \varphi(\lambda/2)}{2RT}} \quad (8)$$

where $\kappa = (8\pi F^2 \alpha_i^0 / \varepsilon RT) 1/2$ for 1:1 type electrolytes, φ_0 (V) is the surface potential which can be calculated by:

$$\varphi_0 = \frac{2RT}{Z_i F} \ln \left(2 \frac{c_i}{\bar{c}_i} \right) \quad (9)$$

where \bar{c}_i (mol L⁻¹) is the average concentration of the i th cation in the EDLs and is defined as $\bar{c}_i = \frac{kQ_s}{SSA} \times 10^{-3}$. The A_{eff} (J) is the soil effective Hamaker constant in aqueous solution that can be estimated by determining the dry end of soil water characteristic curves using a dew-point potentiometer (WP4-T, Decagon Devices, Pullman, WA) according to the method of Tuller and Or (2005). The detailed determination procedures for the A_{eff} value can be found in Yu et al. (2017). The determined A_{eff} values of the control, SOM removal and straw incubation treatments of the Vertisol and Ultisol were 8.79×10^{-20} , 6.16×10^{-20} and 10.73×10^{-20} J and 6.30×10^{-20} , 3.38×10^{-20} and 7.13×10^{-20} J, respectively.

Table 1

Soil organic carbon (SOC) concentrations of the Vertisol and Ultisol before and after the removal of soil organic matter (SOM) or straw incubation for 240 days (mean ± standard deviation).

Soil type	SOC (g kg ⁻¹)		
	Control	SOM removal	Straw incubation
Vertisol	10.45 ± 0.33b	1.62 ± 0.54c*	18.23 ± 0.83 a
Ultisol	9.76 ± 0.33b	1.33 ± 0.23c	19.41 ± 0.77 a

* Different lowercase letters indicate significant differences between different treatments at $p < 0.05$ ($n = 3$).

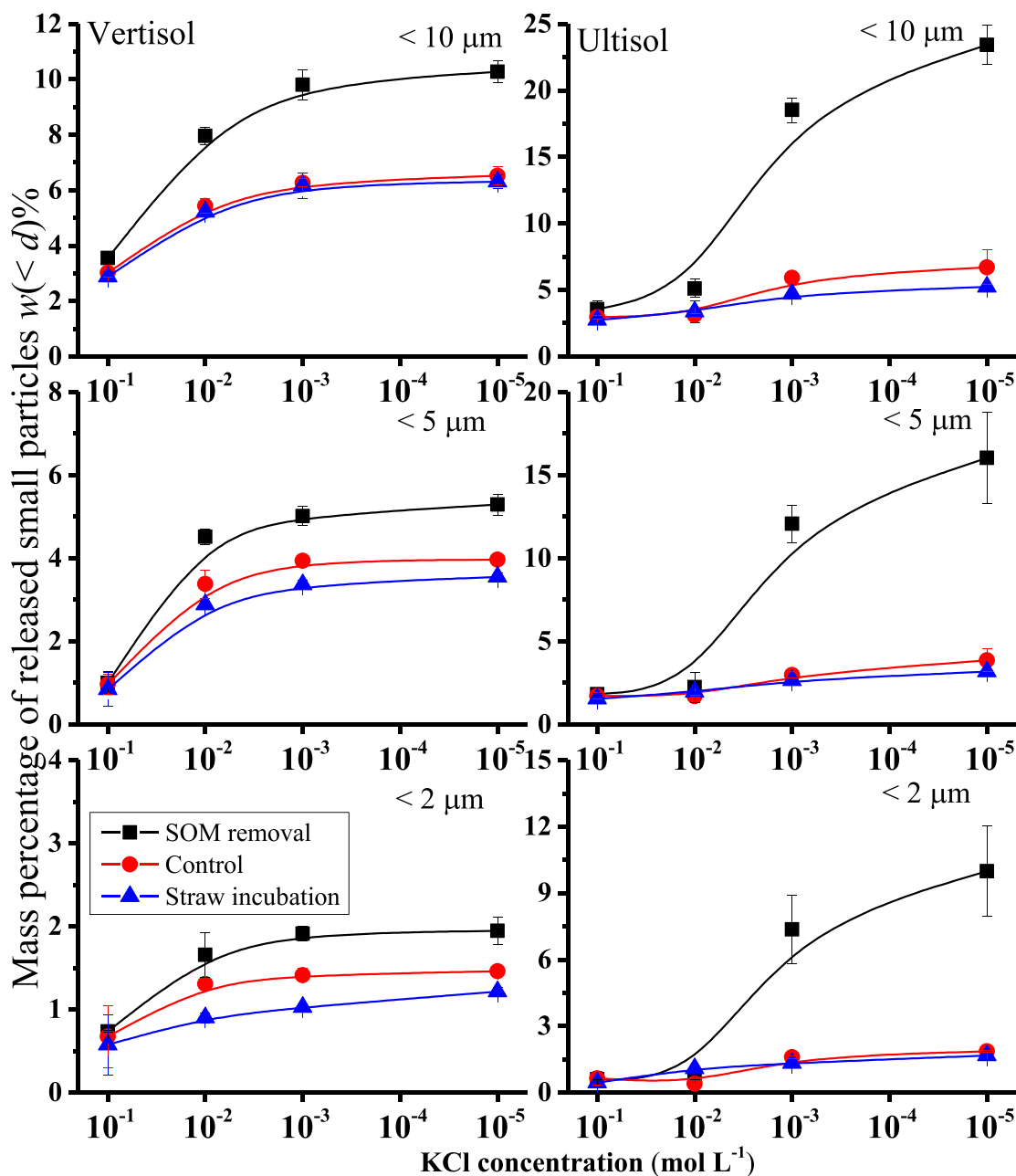


Fig. 1. Variation in the mass percentage of released small particles of <10 , <5 , and $<2 \mu\text{m}$ diameter ($w(<d)\%$, $d = 10, 5$ or $2 \mu\text{m}$) to the total mass of aggregates after aggregate breakdown with different KCl concentration for differently treated Vertisol and Ultisol. Error bars represents the standard deviation ($n = 3$).

3. Results

3.1. SOC concentrations of differently treated Vertisol and Ultisol

After oxidation with H_2O_2 , the SOC concentrations of the Vertisol and Ultisol were significantly decreased from 10.45 and 9.76 g kg^{-1} to 1.62 and 1.33 g kg^{-1} , respectively (Table 1). By contrast, after incubation with straw for 240 days, the SOC concentrations of Vertisol and Ultisol were significantly increased to 18.23 and 19.41 g kg^{-1} , respectively. For the same treatment, there was no significant difference in the SOC concentration between the Vertisol and Ultisol.

3.2. Soil aggregate stability at different KCl concentrations

For differently treated Vertisol, the quantities of released small particles ($w(<d)\%$, $d = 10, 5$ or $2 \mu\text{m}$) from 1 to 5 mm KCl-saturated aggregates were smallest at $10^{-1} \text{ mol L}^{-1}$ KCl solution (Fig. 1). With the decrease in KCl concentration, the $w(<d)\%$ of differently treated Vertisol sharply increased until the KCl concentration decreased to $10^{-3} \text{ mol L}^{-1}$, after which the $w(<d)\%$ did not change significantly. In addition, when the KCl concentration was $10^{-1} \text{ mol L}^{-1}$, there was no significant difference in the $w(<d)\%$ among the differently treated Vertisol. However, when the KCl concentration was $<10^{-1} \text{ mol L}^{-1}$,

Table 2
pH of the KCl-saturated aggregates of the three Vertisol and Ultisol treatments at different KCl concentrations (mean \pm standard deviation).

Soil type	Treatment	pH KCl concentration (mol L ⁻¹)			
		10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁵
Vertisol	SOM removal	6.1 \pm 0.1	6.4 \pm 0.1	7.1 \pm 0.1	7.5 \pm 0.1
	Control	5.7 \pm 0.0	6.2 \pm 0.0	6.7 \pm 0.1	7.1 \pm 0.1
	Straw incubation	6.0 \pm 0.1	6.3 \pm 0.1	7.0 \pm 0.1	7.4 \pm 0.1
Ultisol	SOM removal	5.0 \pm 0.0	5.3 \pm 0.0	5.8 \pm 0.0	6.3 \pm 0.0
	Control	4.5 \pm 0.0	4.9 \pm 0.0	5.6 \pm 0.0	6.2 \pm 0.0
	Straw incubation	4.5 \pm 0.0	5.0 \pm 0.0	5.6 \pm 0.0	6.1 \pm 0.0

the $w(<d)$ % was significantly increased after removal of SOM and decreased after incubation with straw for 240 days compared to the control treatment of Vertisol, despite there was no significant difference between the straw incubation and control treatments in the $w(<10\ \mu\text{m})$ %. With the decrease in KCl concentration, the differences in the $w(<d)$ % among differently treated Vertisol also sharply increased until the KCl concentration decreased to 10⁻³ mol L⁻¹ after which there was almost no change in the differences.

Similar variation trends in $w(<d)$ % were also found for the Ultisol (Fig. 1). For differently treated Ultisol, the $w(<d)$ % increased with the decrease in KCl concentration. Compared to the control treatment, the $w(<d)$ % was significantly increased after SOM removal, while it was decreased after incubation with straw, and the differences in the $w(<d)$ % among differently treated Ultisol increased with the decrease in KCl concentration. However, Fig. 1 also shows three clear differences between the Ultisol and Vertisol. First, with the decrease in KCl concentration, the $w(<d)$ % of differently treated Ultisol had almost no change until the KCl concentration was <10⁻² mol L⁻¹. Second, compared to the Vertisol, with the decrease in KCl concentration, the $w(<d)$ % of differently treated Ultisol and the differences in $w(<d)$ % among the three treatments could still largely increase even when the KCl concentration was <10⁻³ mol L⁻¹. Finally, the differences in the $w(<d)$ % between the SOM removal treatment and the control and straw incubation treatments were significantly larger in the Ultisol than in the Vertisol, especially when the KCl concentration was <10⁻² mol L⁻¹. Table 2 shows the recorded pH values of differently treated KCl-saturated aggregates of Vertisol and Ultisol for different concentrations of

KCl solutions. For all soils, the pH gradually decreased with the increase in KCl concentration.

3.3. Surface charge properties of the differently treated Vertisol and Ultisol

The measured results show that for both the Vertisol and Ultisol under the same application condition of KCl concentration (or concentration range), SOM removal significantly decreased the specific surface area (SSA) while it significantly increased the surface charge density (σ_0) compared to the control treatment (Table 3). In contrast, incubation with straw for 240 days significantly increased the SSA and slightly decreased the σ_0 in both soils. After removal of SOM, surface charge number (Q_s) also significantly decreased in the Vertisol, but it only showed a slight decrease in the Ultisol under the same application condition of KCl concentration. Table 3 also suggests that, in differently treated Ultisol, the values of both Q_s and σ_0 gradually increased when the pH_e increased from 5.0, 4.5 and 4.6 to 6.3, 6.2 and 6.1 (or when the applicable KCl concentration decreased from 10⁻¹ to 10⁻⁵ mol L⁻¹). Even so, the largest Q_s and σ_0 of differently treated Ultisol at the highest pH_e values were substantially smaller than those of the Vertisol. However, compared to the SOM removal treatment, σ_0 only decreased by 8.5% and 11.3% for the control and straw incubation treatments of the Vertisol, respectively. In contrast, σ_0 greatly decreased in average by 29.1% and 35.8% for the control and straw incubation treatments of the Ultisol, respectively.

3.4. Soil internal forces within KCl-saturated aggregates of differently treated Vertisol and Ultisol

3.4.1. P_E in KCl-saturated aggregates of differently treated Vertisol and Ultisol

In all soils, at a given distance (λ) between two adjacent soil particles, the electrostatic repulsive pressure (P_E) increased by decreasing KCl concentration (Fig. 2). However, the pattern of increase in P_E of the Ultisol was quite different from that of the Vertisol. In differently treated Ultisol, at a given λ , the P_E could increase continuously at a high rate with the decrease in KCl concentration, even when the KCl concentration was <10⁻³ mol L⁻¹. For example, at $\lambda = 0.5$ nm, when the KCl concentration decreased from 10⁻¹ to 10⁻², 10⁻² to 10⁻³ and 10⁻³ to 10⁻⁵ mol L⁻¹, the P_E increased by 0.75, 0.41 and 0.38, 1.56, 1.00 and 0.99 and 2.03, 1.74 and 1.02 MPa for the SOM removal, control and straw incubation treatments of the Ultisol, respectively.

Table 3

The soil specific surface area (SSA), surface charge number (Q_s) and surface charge density (σ_0) of differently treated Vertisols and Ultisols which were determined at different equilibrium pH (pH_e) values and the corresponding concentration (or concentration range) of the KCl solution (C_{KCl}).

Soil type	Treatments	C_{KCl} (mol L ⁻¹)	pH_e	SSA (m ² g ⁻¹)	Q_s (cmol _c kg ⁻¹)	σ_0 (C m ⁻²)	
Vertisol	SOM removal	10 ⁻¹ –10 ⁻⁵	7.0	61.4 \pm 1.1 c*	19.13 \pm 0.24 b	0.301 \pm 0.009 a	
	Control	10 ⁻¹ –10 ⁻⁵	7.0	94.9 \pm 2.0 b	27.05 \pm 0.33 a	0.275 \pm 0.002 b	
	Straw incubation	10 ⁻¹ –10 ⁻⁵	7.0	98.3 \pm 1.8 a	27.14 \pm 0.02 a	0.267 \pm 0.005 b	
Ultisol	SOM removal	10 ⁻¹	5.0	56.6 \pm 2.5 c	4.08 \pm 0.41 a	0.070 \pm 0.010 a	
		10 ⁻²	5.3	58.8 \pm 1.6 c	5.30 \pm 0.08 a	0.087 \pm 0.004 a	
		10 ⁻³	5.8	55.7 \pm 1.0 c	6.57 \pm 0.58 a	0.114 \pm 0.008 a	
		10 ⁻⁵	6.3	58.2 \pm 1.8 c	8.81 \pm 0.35 a	0.146 \pm 0.010 a	
		Control	10 ⁻¹	4.5	84.2 \pm 2.2 b	4.31 \pm 0.08 a	0.049 \pm 0.002 b
	Control	10 ⁻²	4.9	85.6 \pm 1.2 b	5.37 \pm 0.06 a	0.061 \pm 0.000 b	
		10 ⁻³	5.6	84.8 \pm 2.0 b	7.02 \pm 0.24 a	0.080 \pm 0.004 b	
		10 ⁻⁵	6.2	80.4 \pm 2.2 b	8.93 \pm 0.33 a	0.107 \pm 0.004 b	
		Straw incubation	10 ⁻¹	4.6	94.5 \pm 8.2 a	4.39 \pm 0.04 a	0.045 \pm 0.004 b
		10 ⁻²	5.0	94.2 \pm 9.3 a	5.37 \pm 0.05 a	0.055 \pm 0.005 b	
		10 ⁻³	5.6	95.1 \pm 4.3 a	7.33 \pm 0.24 a	0.075 \pm 0.005 b	
		10 ⁻⁵	6.1	96.0 \pm 8.6 a	9.10 \pm 0.33 a	0.092 \pm 0.012 b	

* Different lower case letters indicate significant differences between different treatments under the same application condition of KCl concentration range or values at $p < 0.05$ ($n = 3$). The σ_0 , Q_s and SSA were calculated according to the Eqs. (1), (2) and (3), respectively.

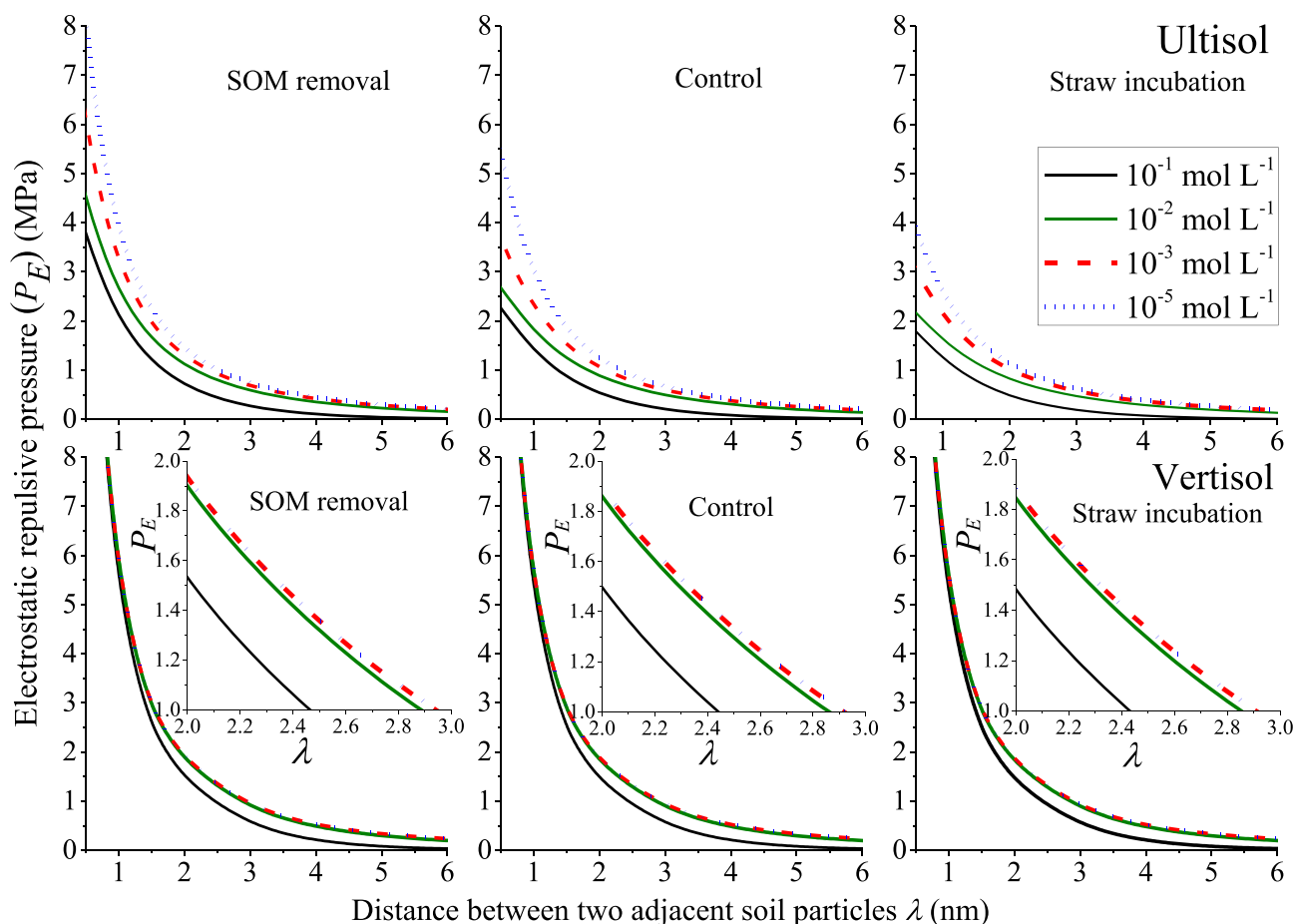


Fig. 2. Distribution of the electrostatic repulsive pressure (P_E) of differently treated Vertisol and Ultisol at different KCl concentrations.

In contrast, at a given λ (for example at $\lambda = 2$ nm, small graphs in Fig. 2), although the P_E of differently treated Vertisol could also increase considerably when the KCl concentration decreased from 10^{-1} to 10^{-2} mol L $^{-1}$, the P_E showed only a small change when the KCl concentration was $<10^{-2}$ mol L $^{-1}$. Specifically, when the KCl concentration was $<10^{-3}$ mol L $^{-1}$, the P_E of differently treated Vertisol showed no change. Fig. 2 also shows that compared to the control treatment of the Ultisol, at a given λ , the P_E could be greatly decreased after incubation with straw and greatly increased after SOM removal at the same KCl concentration. However, compared to the Ultisol, the differences in P_E at the same λ among differently treated Vertisol were much smaller under the same KCl concentration.

To illustrate the impact of varied pH at different KCl concentrations on P_E in the Ultisol, the P_E values of differently treated Ultisol and Vertisol at $\lambda = 2$ nm under different KCl concentrations shown in Fig. 2 were plotted in Fig. 3. Note that the P_E values of differently treated Ultisol (solid symbols in Fig. 3) were calculated based on the surface charge parameters (Table 3) that were determined at different pH_e values. The hollow symbols in Fig. 3 are the P_E values of differently treated Ultisol that were calculated based only on the surface charge parameters at the pH_e values of 6.3, 6.2 and 6.1 to illustrate the situation without an impact of pH. Fig. 3 suggests that, if the influences of varying pH at different KCl concentrations on soil surface charge properties and P_E are not considered, the variation in P_E with KCl concentration of the Ultisol would be the same as that of the Vertisol. Namely, the P_E between two adjacent soil particles would sharply increase when the KCl solution concentration decreased from 10^{-1} to 10^{-2} mol L $^{-1}$, and it would not increase after the KCl concentration decreased to 10^{-3} mol L $^{-1}$ (the dashed lines in Fig. 3). In contrast, when the pH impact is considered, the P_E values of differently treated

Ultisol would continuously increase when the KCl concentration decreased from 10^{-1} to 10^{-5} mol L $^{-1}$ (full lines in Fig. 3).

3.4.2. P_{vdw} and p_h in KCl-saturated aggregates of differently treated Vertisol and Ultisol

The calculated van der Waals attractive pressures (P_{vdw}) suggest that for both the Vertisol and Ultisol, SOM removal decreased the P_{vdw} between two adjacent soil particles while straw incubation had the opposite effect when compared to the control treatment (Fig. 4). In addition, for the same treatment, the value of P_{vdw} was much larger in Vertisol than in Ultisol. Since it is difficult to accurately measure the surface hydration repulsive pressure (P_h) of different soils at present, the P_h was assumed to be the same for differently treated Vertisol and Ultisol in this study. The calculated values suggest that the P_{vdw} would be equal to the P_h when the λ is about 1.3, 1.4 and 1.2 nm and 1.4, 1.5 and 1.3 nm for the control, SOM removal and straw incubation treatments of the Vertisol and Ultisol, respectively.

3.4.3. Net pressures in KCl-saturated aggregates of differently treated Vertisol and Ultisol

By combining the results of P_E (Fig. 2), P_{vdw} and P_h (Fig. 4), the net pressures ($P_{net} = P_E + P_{vdw} + P_h$) of differently treated Vertisol and Ultisol were obtained. Fig. 5 shows that, at a given λ , the P_{net} increased with the decrease in KCl concentration in all soils. In differently treated Ultisol, at a given λ , the P_{net} could increase continuously at a high rate when the KCl concentration decreased from 10^{-1} to 10^{-5} mol L $^{-1}$. However, in differently treated Vertisol, the P_{net} at a given λ showed only a small change when the KCl concentration was $<10^{-2}$ mol L $^{-1}$. For both Vertisol and Ultisol, the P_{net} value increased after SOM removal while it decreased after incubation for 240 days with straw

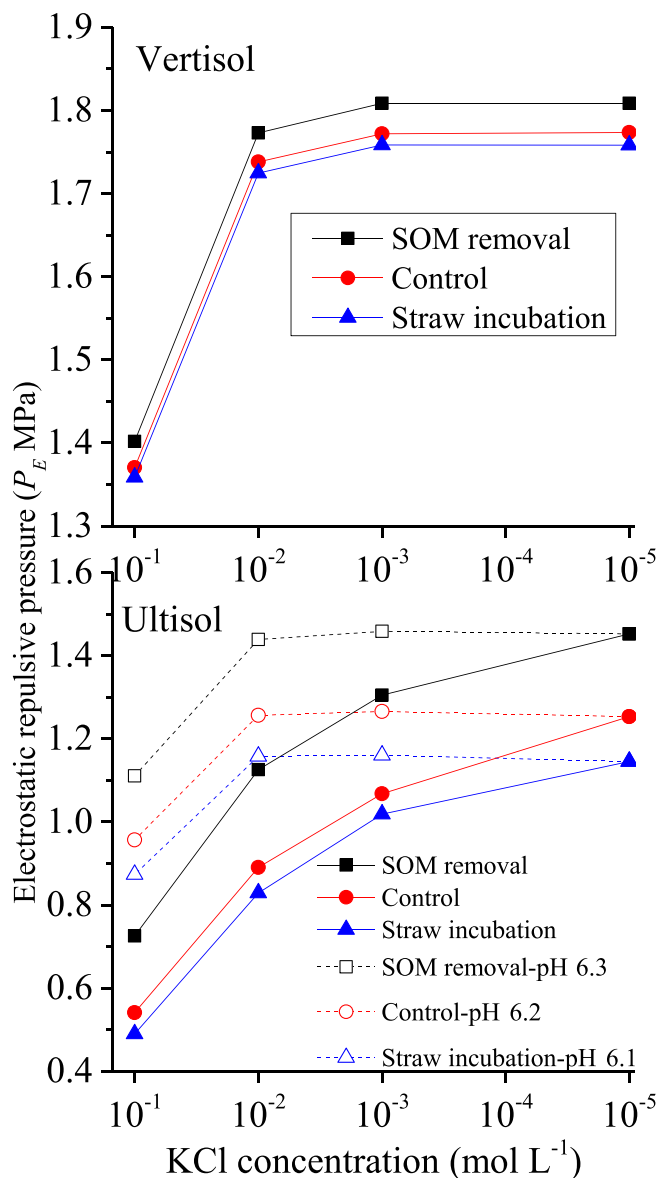


Fig. 3. Relationship of electrostatic repulsive pressure (P_E) between two adjacent soil particles at a distance of 2 nm and KCl concentration for differently treated Vertisol and Ultisol. Solid or hollow symbols indicate the P_E values of differently treated Ultisol that were calculated based on the surface charge parameters that were determined at different pH_e values or only at the pH_e values of 6.3, 6.2 and 6.1 in Table 3.

addition compared to the control treatment. Specifically, the differences in P_{net} between the SOM removal treatment and the control and straw incubation treatments were much larger in the Ultisol than in the Vertisol.

3.5. Relationship between the quantity of released small particles ($w(<d)$) and the net pressure (P_{net}) in the Ultisol and Vertisol

The relationship between the $w(<d)$ % (Fig. 1) and the P_{net} at $\lambda = 2$ nm (Fig. 5) was established. Fig. 6 shows that the $w(<10 \mu\text{m})$ %, $w(<5 \mu\text{m})$ % and $w(<2 \mu\text{m})$ % were significantly and positively related to the P_{net} and that the $w(<d)$ % increased exponentially with P_{net} in both the Ultisol and Vertisol. In addition, for the same soil, the SOM removal treatment has the largest $\Delta w/\Delta P_{net}$ ratio, followed by the control and straw incubation treatments. Take the $w(<10 \mu\text{m})$ % as an example. When the KCl concentration decreased from 10^{-1} to 10^{-5}

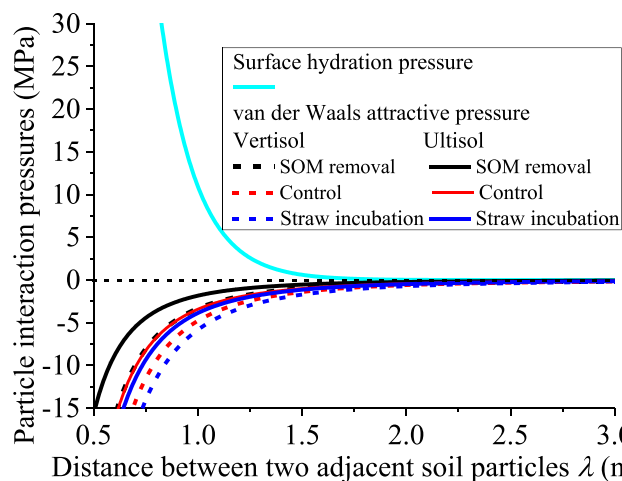


Fig. 4. Distribution of surface hydration repulsive pressure (P_h) and van der Waals attractive pressure (P_{vdw}) as function of the distance between two adjacent particles of differently treated Vertisol and Ultisol.

mol L^{-1} , the P_{net} increased by 0.73, 0.71 and 0.65 MPa and 0.41, 0.40 and 0.40 MPa for the SOM removal, control and straw incubation treatments of the Ultisol and Vertisol, respectively. Correspondingly, the $w(<10 \mu\text{m})$ % increased by 19.9%, 3.7% and 2.5% and 6.7%, 3.5% and 3.4% for the SOM removal, control and straw incubation treatments of the Ultisol and Vertisol, respectively. As a result, the $\Delta w(<10 \mu\text{m})/\Delta P_{net}$ ratios of the SOM removal, control and straw incubation treatments of the Ultisol and Vertisol were 27.3, 5.3 and 3.8 and 16.5, 8.7 and 8.6, respectively. Above data also suggest that for the same SOM removal treatment, the Ultisol has a much larger $\Delta w/\Delta P_{net}$ ratio than the Vertisol.

4. Discussion

4.1. Role of soil interparticle forces in aggregate stability in permanently and variably charged soils

The breakdown of soil aggregates during rainfall is often ascribed to the mechanical breakdown of the raindrop and the attendant flowing water (Le Bissonnais, 1996; Sadeghi et al., 2017). However, in this study, there was clearly no influence of raindrops and the shear strength of flowing water was weak. Hu et al. (2015) demonstrated that, under the condition of weak external impact force (for example, when the aggregate is immersed in a shallow and static aqueous solution) a soil aggregate can still be thoroughly destroyed within a few seconds. These authors further proved that, even considering raindrop impact, the contribution of soil internal forces to splash erosion that begins with the breakdown of soil aggregates can reach 65–80% (Hu et al., 2018a). Thus, in agreement with Hu et al. (2015, 2018b), also in this study, soil aggregate breakdown is also likely caused mainly by soil internal forces.

In addition, hydrophobic interactions caused by hydrophobic substances, slaking because of compressed air, differential swelling of clay minerals and physicochemical dispersion due to osmotic stress are also widely thought to be the main mechanisms of soil aggregate breakdown (Dal Ferro et al., 2012; Le Bissonnais, 1996; Wu et al., 2017). However, soil hydrophobicity is greatly affected by soil water content and its effect disappears when soil becomes wet (Doerr and Thomas, 2000). According to the study of Peng (2004), which determined the water infiltration rate of 10–20 mm aggregates of the same Ultisol, at least 90 mm³ water can infiltrated into the aggregates during 2 min. As much smaller aggregates (1–5 mm) were used and they had been immersed in the water for 2 min, the influence of hydrophobicity on aggregate breakdown can probably be neglected in this study. In addition, since

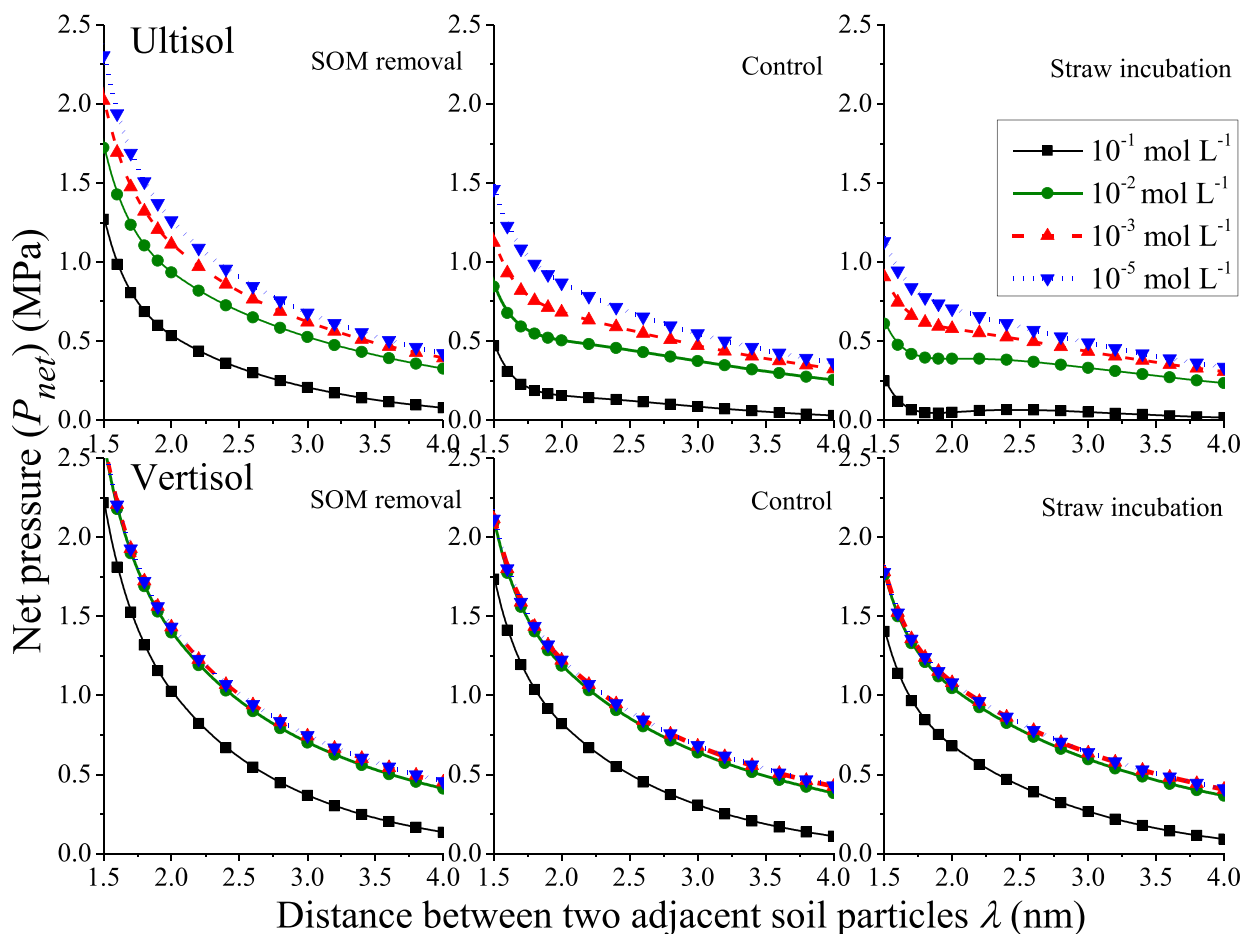


Fig. 5. Distribution of net pressures ($P_{net} = P_E + P_{vdw} + P_h$) of differently treated Vertisol and Ultisol at different KCl concentrations.

the used 1–5 mm KCl-saturated aggregates were homogenously prepared, for the same treatment of a given soil, the volume of trapped air within aggregates and the swelling characteristic should be the same. Besides, the clay mineral swelling is primarily due to the surface-water interaction or surface hydration repulsive force (SHRF) (Low, 1981),

which is independent of the type and concentration of the electrolyte solution (Israelachvili and Adams, 1978). Accordingly, the influences of slaking and differential swelling ought to remain unchanged at different concentrations of electrolyte solutions (Hu et al., 2015; Yu et al., 2017). In other words, slaking and differential swelling cannot explain the

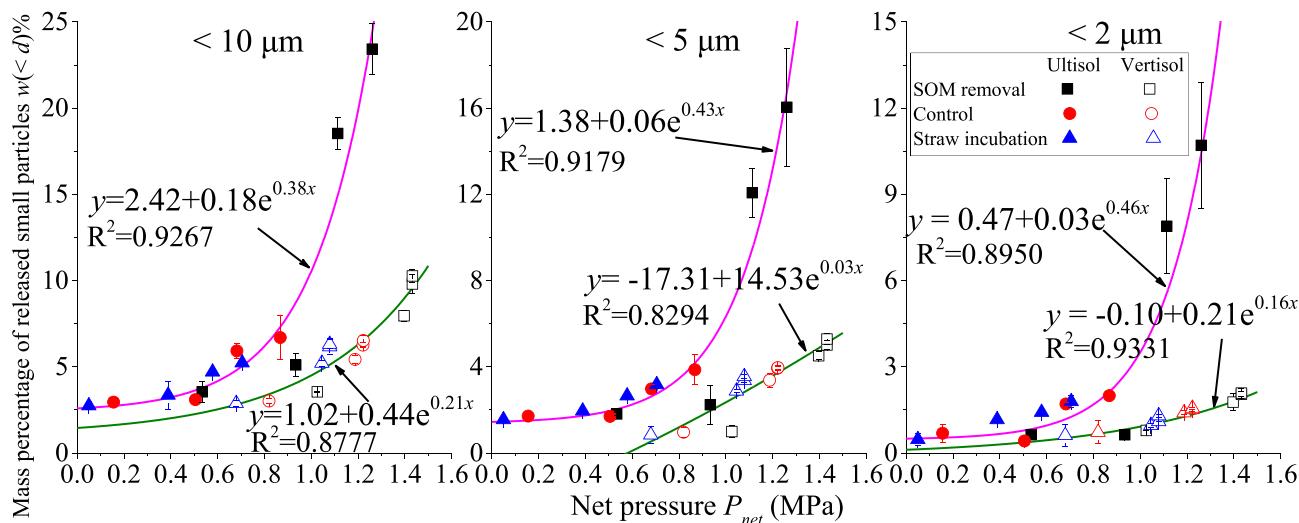


Fig. 6. Relationship between the mass percentage of released small particles ($w(<d)\%$, $d = 10, 5$ or $2 \mu\text{m}$) of differently treated Vertisol and Ultisol and the net pressure (P_{net}) at a distance of 2 nm between two adjacent soil particles. Magenta and green lines are the fitted curves for the Ultisol and Vertisol, respectively. Error bars represents the standard deviation ($n = 3$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

variation in the quantities of released small particle ($w(<d)\%$) with the KCl concentration in differently treated Vertisols and Ultisols.

Additionally, the compressed air pressure is <0.1 MPa (Zaher et al., 2005) and the osmotic stress is <0.25 MPa (Xu et al., 2015b). However, even for the SOM removal treatment of the Ultisol, which had the weakest van der Waals attractive force (vDWF) among the different soils, the value of van der Waals attractive pressure (P_{vdw}) was more than 14 MPa (absolute value) at a distance of 0.5 nm ($\lambda = 0.5$ nm) between two adjacent soil particles. Thus, compressed air pressure (slaking) and osmotic stress cannot overcome the vDWF between soil particles to break dried aggregates. In contrast, Figs. 2 and 4 suggest that at $\lambda = 0.5$ nm, the value of surface hydration repulsive pressure (P_h) was more than 184 MPa and the electrostatic repulsive pressure (P_E) at 10^{-5} mol L $^{-1}$ KCl solution could approach 8 MPa for the SOM removal treatment of the Ultisol. Obviously, the interactions of the electrostatic repulsive force (ERF), the vDWF and the SHRF between soil particles should play a more important role in aggregate breakdown in both the Vertisol and Ultisol than hydrophobic interaction, slaking, differential swelling and osmotic stress. The results presented in Fig. 6 further suggest that aggregate stability is essentially determined by soil interparticle forces in both the Vertisol and Ultisol. The same exponential relationship between the $w(<d)\%$ and the P_E or the $P_E + P_h$ was also found in other permanently charged soils (Hu et al., 2015; Yu et al., 2017). Li et al. (2018) also reported an exponential relationship between soil erosion intensity and P_E in a variably charged soil. It can be seen that soil interparticle forces play a universal and critical role in aggregate stability in both permanently and variably charged soils.

However, compared to the Vertisol, the Ultisol still showed three distinct differences in the variation of $w(<d)\%$ with KCl concentration (Fig. 1): (1) in contrast to the Vertisol, the $w(<d)\%$ showed no significant increase from 10^{-1} to 10^{-2} mol L $^{-1}$ but continuously and largely increased from 10^{-2} to 10^{-5} mol L $^{-1}$ in the Ultisol; (2) the differences in the $w(<d)\%$ between the SOM removal treatment and the control and straw incubation treatments were much larger in the Ultisol than in the Vertisol; and (3) the differences in the $w(<d)\%$ could still largely increase even when the KCl concentration was $<10^{-3}$ mol L $^{-1}$ in the Ultisol. These differences indicate that some extra factors must have a significant influence on the interactions of soil interparticle forces in variably charged soils.

4.2. Effect of pH on ERF between soil particles in variably charged Ultisol

The first obvious difference between the Ultisol and Vertisol is likely caused by the varied pH at different concentrations of KCl solutions, and it will be discussed in detail below.

According to the calculation results presented in Fig. 3, if the influence of pH on soil surface charge properties and ERF of the Vertisol and Ultisol is not considered, then the $w(<d)\%$ will change with KCl concentration as follows: (1) the $w(<d)\%$ should be the smallest at 10^{-1} mol L $^{-1}$, and (2) with the decrease in KCl concentration, the $w(<d)\%$ will sharply increase until the KCl concentration decreases to 10^{-3} mol L $^{-1}$, after which the $w(<d)\%$ should show no change. Fig. 1 clearly suggests that for the Vertisol, the variations in $w(<d)\%$ with KCl concentration can align very well with the predictions of the above theoretical calculations. Therefore, despite the variation in pH with the KCl concentration for differently treated Vertisol (Table 2), the variation in the $w(<d)\%$ with KCl concentration can be still primarily explained by the ERF (Figs. 2 and 3) that are calculated from one set of surface charge parameters at the same pH_e of 7.0 (Table 3). In other permanently charged soils, the same variation in the $w(<d)\%$ with the electrolyte concentration was also reported (Hu et al., 2015, 2018b; Xu et al., 2015), and the variation can also be primarily explained by the ERF being calculated from only one set of surface charge parameters. Thus, this pH effect probably can be ignored in permanently charged soils. However, for the differently treated Ultisol, the second prediction of the above theoretical calculations is clearly contrary to the

experimental results of the variation in the $w(<d)\%$ with KCl concentration (Fig. 1) and, therefore, cannot explain the first obvious difference between the Ultisol and Vertisol.

Contrary, if the pH effects on soil surface charge properties, P_E and P_{net} of the Ultisol are considered, according to the calculations shown in Figs. 2, 3 and 5, the P_E and P_{net} at a given λ would continuously increase from 10^{-1} to 10^{-5} mol L $^{-1}$. Specifically, when the λ is less than approximately 1 nm, the P_E values only showed small increases with a KCl concentration decrease from 10^{-1} to 10^{-2} mol L $^{-1}$ (Fig. 2). These results indicate that the $w(<d)\%$ of differently treated Ultisols may show no significant change from 10^{-1} to 10^{-2} mol L $^{-1}$ and a continuous and large increase from 10^{-2} to 10^{-5} mol L $^{-1}$. Clearly, these theoretical calculations can primarily explain the variations of $w(<d)\%$ with the KCl concentration for differently treated Ultisol (Fig. 1). It is well known that changes in pH can significantly affect particle surface charge (Chorom et al., 1994), which in turn affect the stability of colloids and soil aggregates (Chorom and Rengasamy, 1995; Nguetkam and Dultz, 2014; Regelink et al., 2015). Moreover, due to the large content of Fe/Al oxides and hydroxides, the pH effect on surface charges is more significant in variably charged soils than in permanently charged soils (Yu, 1997). Hence, the first difference in the variation in the $w(<d)\%$ with KCl concentration between the Ultisol and Vertisol is obviously a consequence of varying pH. Therefore, when studying the role of soil interparticle forces on aggregate stability in variably charged soils, the influence of the soil solution pH on ERF must be considered.

4.3. Effect of the overlapping of EDLs between SOM and Fe/Al (hydro) oxides on ERF in variably charged Ultisol

The second and third obvious difference between the two soils are that 1) the differences in $w(<d)\%$ between the SOM removal treatment and the control and straw incubation treatments were much larger in the Ultisol than in the Vertisol, and 2) the differences could still increase largely even when the KCl concentration was $<10^{-3}$ mol L $^{-1}$ in the Ultisol (Fig. 1). These two differences were actually caused by the change in the $w(<d)\%$ being quite small in the KCl concentration range of 10^{-1} to 10^{-5} mol L $^{-1}$ in the control and straw incubation treatments compared to the SOM removal treatment of Ultisol (Fig. 1). This result is similar to that of the reported odd phenomenon that the breakdown of KCl-saturated aggregates did not increase when the KCl concentration decreased from 1 to 10^{-4} mol L $^{-1}$ for a variably charged soil without removal of SOM (Li et al., 2018). The question then arises of how to explain these very stable aggregates of variably charged soils.

It has been suggested that organo-mineral complex content is positively related to SOC concentration (Garrido and Matus, 2012). Thus, according to the measured SOC concentration in Table 1, we can assume that, in both the Vertisol and Ultisol, the organo-mineral complex contents of the three treated soil samples followed the order of straw incubation treatment > control treatment > SOM removal treatment. According to Yu et al. (2017), organo-mineral interactions can increase the vDWF and decrease the ERF between soil particles in aggregates. Meanwhile, primary soil particles can be bound together by SOM through organo-mineral interactions to form silt-sized assemblages or microaggregates (Denef and Six, 2005; Calero et al., 2017). As a result, the more organo-mineral complexes are present, the more stable the aggregates are, resulting in fewer small and primary particles that are released after the breakdown of soil aggregates. This is the primary reason why the breakdown of soil aggregates decreased with the increase in SOM content in the Vertisol (Fig. 1). However, the much smaller $w(<d)\%$ of the control and straw incubation treatments of Ultisol at concentrations of 10^{-3} and 10^{-5} mol L $^{-1}$ KCl cannot merely be explained by organo-mineral interactions. For example, the SOM content of the variably charged soil in Li et al. (2018) was merely 5.6 g kg $^{-1}$, but the $w(<d)\%$ at KCl solution concentrations of 1 to 10^{-4} mol L $^{-1}$ were always zero. In addition for organo-mineral interactions,

there must be other mechanisms that cause aggregates with such stability to break up under different concentrations of KCl solutions in the control and straw incubation treatments of Ultisol.

Note that a basic property of tropical and subtropical soils is the coexistence of positively charged Fe/Al (hydro)oxides and negatively charged 1:1 clay minerals (Yu, 1997; Qafoku et al., 2004). In aqueous environments, positively and negatively charged EDLs will be developed on the surfaces of Fe/Al (hydro)oxides and 1:1 clay minerals (Barber and Rowell, 1972; Yu, 1997; Qafoku and Sumner, 2002). When the soil suffers intensive leaching (such as during rainfall or irrigation), the ionic strength of the soil solution will decrease, while the counter anions and cations in the positively and negatively charged EDLs will diffuse into the soil solution (Qafoku and Sumner, 2002; Xu et al., 2014). As a result, positively and negatively charged EDLs around Fe/Al (hydro)oxides and 1:1 clay minerals will expand and overlap with each other (Qafoku and Sumner, 2002; Xu et al., 2014). When the oppositely charged EDLs are overlapped, a portion of the positive and negative charges on the surfaces of the Fe/Al (hydro)oxides and 1:1 clay minerals will be neutralized (Barber and Rowell, 1972; Qafoku and Sumner, 2002; Xu et al., 2014). Therefore, a decrease in soil surface charges due to the overlapping of oppositely charged EDLs will weaken the ERF between soil particles and enhance aggregate stability. Previous studies also suggested that the degree of overlapping of oppositely charged EDLs is greatly affected by electrolyte concentration, namely, the lower the electrolyte concentration is, the stronger the overlapping of oppositely charged EDLs will be (Hou et al., 2007; Li and Xu, 2008; Li et al., 2016). In turn, this finding means that despite the ERF is still increasing with decreasing electrolyte concentration, it may only show a small increase in variably charged soils. Hence, the $w(<d)$ % of the control and straw incubation treatments of the Ultisol only showing small increases as the KCl concentration changes from 10^{-1} to 10^{-5} mol L $^{-1}$ (Fig. 1) is essentially because of the influence of the increasing overlapping of oppositely charged EDLs on the ERF between soil particles.

Previous studies, however, have usually focused on the overlapping of oppositely charged EDLs between Fe/Al (hydro)oxides and clay minerals (Barber and Rowell, 1972; Qafoku and Sumner, 2002; Hou et al., 2007; Li and Xu, 2008; Li et al., 2016). Compared to the control and straw incubation treatments of the Ultisol, the soil mineralogy clearly did not change after the removal of the SOM. However, the $w(<d)$ % of the Ultisol could still dramatically increase when the KCl concentration decreased from 10^{-2} to 10^{-5} mol L $^{-1}$ after removal of SOM (Fig. 1). This result clearly suggests that the very stable soil aggregates of the control and straw incubation treatments of Ultisol cannot be explained by merely considering the overlapping of oppositely charged EDLs between Fe/Al (hydro)oxides and clay minerals.

In variably charged soils, SOM carries a larger number of negative surface charges than do the 1:1 clay minerals of the same mass (Yu, 1997). Therefore, the overlapping of oppositely charged EDLs between SOM and Fe/Al (hydro)oxides should be stronger than between 1:1 clay minerals and (hydro)oxides. This finding means that the decrease in surface charge and the attenuation of ERF due to the overlapping of oppositely charged EDLs will also be larger and stronger in the presence of SOM. Table 3 shows that, when the KCl concentration decreases from 10^{-1} to 10^{-5} mol L $^{-1}$, σ_0 increases by 0.076 C m $^{-2}$ for the SOM removal treatment of Ultisol, while it only increased by 0.058 and 0.047 C m $^{-2}$ for the control and straw incubation treatments, respectively. As a result, when the KCl concentration decreased from 10^{-1} to 10^{-5} mol L $^{-1}$, the P_E at $\lambda = 0.5$ nm between the two adjacent soil particles increased by 4.3 MPa for the SOM removal treatment of the Ultisol, while it did only increase by 3.2 and 2.4 MPa for the control and the straw incubation treatments, respectively (Fig. 2). It can be seen that in addition to the interaction of oppositely charged EDLs between clay minerals and Fe/Al (hydro)oxides, the overlapping of oppositely charged EDLs between SOM and Fe/Al (hydro)oxides also plays a crucial role in the much weaker breakdown of soil aggregates of variably charged soils in neutral electrolyte solutions.

4.4. Importance of SOM in aggregate stability in variably charged soils

According to the well-known aggregate hierarchy theory, SOM plays a much more important role for aggregate stability in temperate soils than in tropical and subtropical soils where it only plays a partial role (Denef and Six, 2005; Oades and Water, 1991; Peng et al., 2015; Six et al., 2004). This is because in tropical and subtropical soils, stable aggregates can be directly formed through electrostatic attractive forces between positively charged Fe/Al oxides and hydroxides and negatively charged 1:1 clay minerals. For this reason, there is less dependence on SOM for aggregate formation (Six et al., 2004; Denef and Six, 2005). However, the much larger differences in $w(<d)$ % in the Ultisol than in the Vertisol between the SOM removal treatment and the control and straw incubation treatments (Fig. 1) clearly suggest that SOM can play a more important role in the stabilization of aggregates in tropical and subtropical soils. Based on the previous discussions, these contrary results may be caused by the aggregate hierarchy theory ignoring the influence of SOM on the overlapping of differently charged EDLs and soil interparticle forces. This is because the viewpoint about aggregate formation of tropical and subtropical soil in this theory is the transfer of the traditional concept of the overlapping of oppositely charged EDLs on positively charged Fe/Al oxides and hydroxides and negatively charged 1:1 clay minerals (Qafoku and Sumner, 2002).

Interestingly, the aggregate hierarchy is generally thought to exist only in temperate soils and is not present in tropical and subtropical soils (Oades and Waters, 1991; Six et al., 2004; Denef and Six, 2005; Peng et al., 2015). In this study, the results shown in Fig. 6 clearly suggest that the aggregate stability in both temperate and tropical and subtropical soils is controlled by soil interparticle forces. Hence, the interactions of the ERF, the SHRF and the vDWF between soil particles probably play more fundamental roles than the aggregate hierarchy in the formation and stabilization of soil aggregates for different soil types. Despite KCl-saturated soil cannot be found under natural conditions, the results of this study suggest that to increase soil aggregate stability, the net repulsive force between soil particles should basically be reduced. Our results indicate furthermore that the impact of soil organic matter in tropical and subtropical soil might be underestimated on the base of previous/common concepts. In this regard, our study showed that in case SOM is severely degraded, more serious soil erosion may occur in tropical and subtropical soils than in temperate soils.

5. Conclusions

In both permanently charged temperate soil and variably charged subtropical soil, aggregate stability is essentially controlled by the interactions of the electrostatic repulsive force (ERF), the surface hydration repulsive force (SHRF) and the van der Waals attractive force (vDWF) between two adjacent soil particles in the aggregates. However, in variably charged soils, a decrease in soil solution pH due to the increase in electrolyte concentration can gradually reduce the surface charge number (Q_s) and the surface charge density (σ_0) and thus weaken the ERF. In addition, the increasing overlapping of electric double layers (EDLs) of positively charged Fe/Al (hydro)oxides and negatively charged soil organic matter (SOM) can also distinctly weaken the ERF. As a result, in contrast to permanently charged soils, variably charged soils can lack aggregate breakdown before KCl concentration decreases to 10^{-2} mol L $^{-1}$ and show a continuous and distinct increase in aggregate breakdown after the KCl concentration decreases to 10^{-2} mol L $^{-1}$. Moreover, the aggregates of variably charged soils that contain a certain SOM can keep high stability in different concentrations of neutral electrolyte solutions. This study suggests that the effects of soil solution pH and overlapping of oppositely charged EDLs between SOM and Fe/Al (hydro)oxides on the ERF have to be considered in variably charged soils, and SOM can play a much more important role in aggregate stability in tropical subtropical soils than in temperate soils.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2019.114088>.

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