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Modeling the effects of Ca^{2+} and clay-associated organic carbon on the stability of colloids from topsoils

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ABSTRACT

The goals of the study were to investigate the effects of the soil–water phase ionic strength, mainly monitored by the calcium ion (Ca^{2+}) concentration, on the stability behavior of easily dispersed topsoil colloidal clay-sized particles (<2 μm). The aggregation kinetics as a function of the Ca^{2+} concentration was monitored by measuring the increase of the particle size over time with photon correlation spectroscopy. The critical coagulation concentrations (*CCC*) of Ca^{2+} were measured. The Hamaker constants (*A*) characterizing the attractive chemical properties of the topsoil colloid surface were thus scaled according to the Derjaguin, Landau, Verwey, Overbeek (DLVO) theory by taking into account the electrokinetic behavior of the particles, measured by the ζ-potential. Effective values for the Hamaker constants of topsoil clay-sized colloids, clay minerals, and metal oxides were calculated by referring to reported values for crystalline silica or sand (quartz) particles. Potential-energy diagrams of interacting topsoil clay-sized colloids were calculated. The primary energy maximum and secondary energy minimum were used for modeling the aggregation kinetics along the Ca^{2+} concentration by employing Marmur's model. Coagulation in the secondary energy minimum can only explain the aggregation efficiency of topsoil colloids at low Ca^{2+} concentrations (<2 mM Ca^{2+}) under unfavorable electrostatic conditions. The effect of surface-associated organic matter on the colloidal electrosteric stability was also investigated by comparing the topsoil colloid stability after the removal of organic matter.

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1. Introduction

The dispersion of colloidal particles <2 μm from the clay-sized soil fraction, which mainly includes aluminosilicates and oxides, modifies the soil aggregate structure and contributes to soil–water erosion. An exposure of the encapsulated organic carbon (OC) to microbial processes can lead to an increase in mineralization and emission of CO_2. A rapid transport of such water-dispersible colloids (WDC) through preferential pathways in the soil porous structure has been considered as a potential mechanism for contamination by chemicals tightly bound to the associated organic matter with WDC [1–3].

The release and transport of WDC in agricultural soils is conditioned by the hydrodynamic water flow and the solution chemistry. Chemical conditions such as the presence of organic matter, varying pH, electrolyte concentration, and sodium adsorption ratio (SAR), which measures the relative distribution of monovalent and divalent cations, are also crucial factors for the concentration of mobile WDC [2–9]. In a general way, the effects of the solution chemistry on the stability behavior of the colloidal particles can be modeled by the Derjaguin, Landau, Verwey, Overbeek (DLVO) theory, which considers two types of coagulation: at close surface contact, in the primary energy minimum, and at large to moderate separation distances, in the secondary energy minimum., Recent experimental and theoretical results on the deposition and reentrainment of relatively large-sized latex particles and microorganisms at silica material surfaces have demonstrated the importance of the relatively weak and reversible coagulation in the secondary energy minimum for particle mobility in saturated porous media [10–17].

The goals of the study are to investigate the effects of the soil water phase ionic strength, mainly monitored by the calcium ion (Ca^{2+}) concentration, on the stability behavior of easily dispersed colloidal particles (<2 μm) from the soil clay fraction of German agricultural topsoils. In the same way, the stability behavior of soil clay constituents is also investigated. The potential-energy diagrams of DLVO theory were first established from the experimental estimations of the Stern potential and Hamaker constant (*A*). The importance of the secondary minimum energies for modeling the coagulation efficiency (W^{-1}) was thus investigated by employing Marmur's model [18].The effect of surface-associated organic matter on the colloidal stability was also investigated by comparing the topsoil colloid stability after the removal of organic matter.

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2. Materials and methods

2.1. Fractionation of soil colloids

Soil samples were collected at Merzenhausen (*M*) in the Cologne–Aachen embayment (orthic luvisol, silty loam soil), at Bad Lauchstädt (*L*) in the central German area (haplic chernozem, silty loam soil) and at Scheyern (*S*) in the Bavarian tertiary hill area (dystric cambisol, loamy soil). See other soil characteristics in Supporting material (Table S1). The top 10-cm layer was sampled. The sample was air-dried. Stones and large pieces of plant material were removed by hand after sieving soils through a 5-mm sieve.

All soil phase fractionations in water were conducted gently in duplicate as follows. One hundred grams of air-dried soil was added to a 1000-ml Duran bottle (Schott, Germany) containing 200 ml of distilled water and shaken using a horizontal shaker (150 rpm) for 6 h. Then 600 ml of distilled water was added before starting sedimentation [19]. Separate containing nonsettling colloid is obtained after a 12-h sedimentation time at room temperature. This easily dispersed colloidal soil fraction was collected by high-speed centrifugation (10,000*g*; 90 min) of the suspension without any filtration. The pristine soil colloidal fraction was thus freeze-dried for the analysis of organic carbon and thermal oxidation. The organic carbon (OC) content and *z*-average diameter (d_z) of the pristine topsoil colloids (M_c, S_c and L_c) are reported in Table 1. It must be noted that 3–7% of the total soil mass was easily dispersed in water [19], which is much less than the soil clay mass fraction (15–22%), (Supporting material, S.1).

Table 1
Properties of pristine topsoil colloids.

Soils[a]	OC content, g kg^{-1}	d_z, nm
M_c	20	640
S_c	24	780
L_c	43	510

[a] Merzenhausen (*M*), Scheyern (*S*), Bad Lauchstädt (*L*).

2.2. Clays

Montmorillonite (d_z, 540 nm) and kaolinite (d_z, 1300 nm) were prepared by procedures described elsewhere [20,21]. Gibbsite (d_z, 700 nm) and goethite (d_z, 560 nm) were obtained after synthesis (gibbsite [22,23], goethite [24]). Colloidal fractions of crushed sand quartz F32 (d_z, 620 nm) from Quarzwerke GmbH (Frechen, Germany) were obtained according to the same fractionation procedure as that for soil colloids. In the same way, a fine fraction of illite (d_z, 670 nm) from Cs-Ker Illit Bt (Bekecs, Hungary) was obtained. Other chemicals were Merck products. Water purified through Millipore filters was used in all experiments.

2.3. Thermal oxidation

The removal of organic carbon from the pristine topsoil colloids was performed by thermal oxidation to obtain the corresponding mineral phases [25]. The thermal oxidation of the various soils and soil fractions was performed at 400 °C with an OC removal efficiency of about 95%.

2.4. Organic carbon analysis

The total carbon (TC) of the colloidal soil fraction and bulk soils was measured with a CHNS analyzer (LECO System). The total organic carbon (TOC) content is obtained after the correction of TC from the inorganic carbon content. Average values were obtained from three replicate measurements of soil samples. The relative standard deviation is better than 5%.

2.5. Photon correlation spectroscopy

The photon correlation spectroscopy (PCS) measurements were performed using a Malvern ZetaSizer 4 equipped with a 5 mW He–Ne laser ($\lambda = 632.8$ nm). Measurements were made at a scattering angle of 90°. The monomodal cumulant method of the ZetaSizer 4 software was used to analyze the correlation function. An averaged translational diffusion constant was thus obtained, from which an equivalent spherical hydrodynamic diameter (*z*-average diameter, d_z) for the particles was calculated. Dispersion concentrations varied from 0.05 to 0.2 g/L.

2.6. ζ-Potential measurement

For the electrokinetic studies by microelectrophoresis, a Laser Zee Meter (Pen Kem Model 501) was used.

The Smoluchowski equation

$$\zeta = u\eta/\varepsilon, \qquad (1)$$

was applied where ε is the permittivity ($\varepsilon = \varepsilon_r\varepsilon_0$) and η is the viscosity of the medium used to transform the microelectrophoretic mobility (u) into ζ-potential, which is justified according to the relative size of the colloidal particles (radius $r = d_z/2$) and their electrochemical double layers (κ^{-1}, the Debye–Hückel length), $\kappa r \geqslant 20$. Dispersion concentrations varied from 0.05 to 0.2 g/L. Measurements were performed in individually prepared solutions for each Ca^{2+} concentration after a waiting time of at least 2 h.

2.7. pH

pH measurements were made with an Expandable ionAnalyser EA 940 from Orion Research. The pHs of the soil colloidal dispersions were in the range of pH 5.5–6.5. In the case of metal oxide dispersions, a pH of about 5 for goethite and gibbsite and a pH of about 10 for quartz were adjusted far from isoelectric points (point of zero charge [26]: goethite, pH^0 8.4–9.4; gibbsite, pH^0 8–9; quartz, pH^0 3.7). In the case of illite, kaolinite and montmorillonite, the pH was also adjusted at about 10, far from the isoelectric point of the clay platelet edge sites (pH^0 6–7).

3. Results and discussion

3.1. Colloidal topsoil parameters of stability

3.1.1. Aggregation kinetics and critical coagulation concentration (CCC) determination

The effects of organic matter and calcium ions on the aggregation kinetics of the negatively charged topsoil colloids were investigated by measuring the particle size with photon correlation spectroscopy (PCS) along the calcium concentration before and after the removal of the associated organic matter (see Supporting material, S.2). In Fig. 1, the aggregation kinetics are shown under Brownian motion conditions of the pristine L_c topsoil colloid. The d_z values, measured by photon correlation spectroscopy, are plotted against time [27–29].

It can be seen that an increase of the $CaCl_2$ salt concentration in a range above 0.5 mM accelerates the particle aggregation up to a maximum rate at about 3 mM while the pH remains constant at about pH 5.5.

Under these Ca^{2+} concentration conditions, there is a screening of the repulsive electrical forces, and the rapid aggregation kinetics (k_{afast}) is assumed to be close to a pure diffusion-controlled

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