



## Silicic acid as a dispersibility enhancer in a Fe-oxide-rich kaolinitic soil clay



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### ABSTRACT

In soils, dispersion is a crucial step preceding the loss of clay-sized particles by surface run-off and leaching, which in turn results in soil degradation. Despite the fact that silicic acid is common in soil solutions, its effect on aggregation stability of fine sized particles in soils has not been detailed. Here we examined the effect of silicic acid on dispersion of a kaolinitic soil clay fraction rich in Fe-oxides (8.5%) at different pH values by combining dynamic light scattering for particle sizing and test tube experiments for examination of particles in suspension. Adsorption of silicic acid on the clay fraction was characterized by batch adsorption experiments and effects on surface charge by zeta potential ( $\zeta$ ) measurements over a pH range from 2 to 11. We found that silicic acid adsorbed onto clay and co-existing Fe oxides, made  $\zeta$  more negative, and thereby counteracted aggregation of the clay fraction. Silicic acid showed its most effectivity for maintaining dispersion at a pH range of 4 to 6. Beyond this pH range, dispersion was either strongly favored or prevented, and the effect of silicic acid on dispersion was obscured. Given the ubiquitous presence of silicic acid in soils, our findings regarding its impact on aggregation stability have important implication for conservation of acidic soils.

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### 1. Introduction

Bare soils without protective vegetative cover face serious clay loss due to surface runoff, particularly if dispersion of aggregates is favored. The dispersive effect of negative electrolytes (e.g. anions, humic substances) through interaction with 1:1 clay minerals (such as kaolinite), via enhancement negative surface charge and thereby repulsive forces between dispersed particles, has been well established (Frenkel et al., 1992; Kretzschmar et al., 1998; Nguyen et al., 2009; Nguyen et al., 2013). However, although dissolved silicic acid is among the most common compounds of the soil solution (Dietzel, 2000), its effect on clay dispersion is poorly documented.

In natural environments, silicic acid in pore solution may derive from chemical weathering of primary silicates, clay minerals or phytolith dissolution (Frayse et al., 2006; Nguyen et al., 2014), and exists as monomeric silicic acid ( $\text{H}_4\text{SiO}_4$ ) or as polymeric silicic acid, formed by linkage via silicon-oxygen-silicon bonds. This polymerization may build up dimeric ( $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ ), trimeric ( $\text{Si}_3\text{O}_5(\text{OH})_3^{3-}$ ) or tetrameric ( $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ ) silica. Polymers up to 10 silicon atoms are called oligomeric or low-molecular-weight silica. pH is one of the first important factors regulating formation of silicic acid species in solution. In alkaline

solutions, polymeric silicic acids are predominant, whereas they are unstable in neutral and acidic solutions and can be decomposed to the monomeric form within several hours (Dietzel, 2000). Concentrations of silicic acid in soil solution can reach up to 2 mM (Karthanasis, 2002) but are more commonly in the range of ca 0.1 to 0.6 mM (Epstein, 2001; Sommer et al., 2006). Silicic acid in soils is typically immobilized by adsorption to Al and Fe oxides (Wonisch et al., 2008; Haynes, 2014) and clay minerals (Keller et al., 2012), while the remainder in solution can be subject to leaching.

The platelet-shaped 1:1 dioctahedral clay minerals have two different surface reaction sites, basal planes and edges. The basal surface is believed to carry permanent negative charges due to isomorphous substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  (Ma and Eggleton, 1999). In these 1:1 clays, the substitution has a much smaller extent than in the 2:1 layer silicates smectite, vermiculite and illite. The edge sites of kaolinite platelets consist of  $\equiv\text{SiOH}$  and  $>\text{AlOH}$  groups, for which the charge properties are regulated by adsorption or dissociation of protons or adsorbed cations/anions, as occurs with metal oxides (van Olphen, 1977). In acidic solutions at  $\text{pH} < \text{pH}$  point of zero charge (pzc), adsorption of protons creates positive edge charges, resulting in attraction and linkages between the positively-charged edge surface and the negatively-charged basal surface. This produces the voluminous, so-called “card house” structures, forming aggregates of low density (Tombácz and Szekeres, 2006). The presence of Fe oxides, which is typical for highly weathered soils containing 1:1 clay minerals, can be a factor enhancing clay

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aggregation (Goldberg and Glaubig, 1987; Lagaly, 2006) by providing more positively-charged sites and promoting clay – Fe oxide bonding by electrostatic interactions. Adsorption of silicic acid onto clay particles was described by (Yariv and Cross, 1979), however the possible mechanisms, i.e. electrostatic interactions, cation bridging and ligand exchange, were not developed in detail. On the other hand, Fe oxides can absorb silicic acid by ligand exchange reactions, in which hydroxyl groups of the Fe oxides are replaced (Hiemstra et al., 2007; Jordan et al., 2007). This clearly suggests that adsorption of silicic acid onto Fe oxide-clay mixtures is likely, and that sorption could possibly interfere with aggregation and favor dispersion. Here we describe studies of silicic acid's effect on dispersibility of a Fe-oxide-rich, kaolinitic soil clay sample that may point toward a potential avenue for reducing clay loss from soils.

The adsorption of silicic acid and its consequent effect on clay dispersion may be more pronounced in acidic, variable-charged soils, since the point of zero charge for the most common Fe oxides, goethite and hematite, is between pH 6.5–9 (Kosmulski, 2014). Therefore, we examined dispersion of a clay fraction, separated from a Fe-oxide-rich, kaolinitic soil from an area with strong progress in soil formation of the Red River Basin (RRB) in Vietnam. As Fe and Al oxides in the clay fraction might interact with silicic acid and modify colloidal properties of the oxide-clay mixture, the role of these oxides can be identified by using a clay fraction from which these oxides were removed by pre-treatment with dithionite citrate bicarbonate (DCB). Batch adsorption experiments were performed to determine the silicic acid loading capacity of the separated clay sample as a function of pH. We employed a method of dynamic light scattering (DLS) developed from studies conducted by Kretzschmar et al. (1998) to examine aggregation kinetics of the clay fractions in the presence of silicic acid as functions of pH and electrolyte background. Since the surface charge is the most important parameter for particle aggregation, zeta potentials ( $\zeta$ ) were utilized to evaluate the effect of silicic acid adsorption on clay, surface charge properties, and colloidal suspension stability. The findings from this study regarding its impact on aggregation stability can help to develop techniques for conservation of acidic soils.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Site description

The study site is located on the experimental station of the Northern Mountainous Institute for Agriculture-Forestry Technology and Science in Phu Ho, Phu Tho province (21°26' N lat, 105°15' E long), in the central Red River Basin, Vietnam (Fig. 1). The station was founded in 1918 as the first tea research center in Indochina. It is located on a hilly area of approximately 250 ha with an elevation ranging from 50 to 300 m. The soil is an Ultisol and has been used for tea cultivation (*Camellia sinensis*) for hundreds of years. The climate is warm and humid (continental) with an average temperature of 23.5 °C and an average relative humidity of 85%. Average annual precipitation is 1700 mm and is distributed fairly evenly throughout the year.

#### 2.1.2. Processing of soil sample and separation of clay fraction

The soil sample was taken from the humus-rich surface horizon (0–25 cm depth), air-dried, and passed through a 2 mm sieve. The pH of the fine soil sample was determined using 0.2 M KCl ( $w/v = 1:2.5$ ). The particle-size distribution was determined by the pipette method. Organic-C was quantified using an elemental analyzer (PerkinElmer 2400 Series II CHNS/O). Oxalate treatment was used to extract “active” forms (non-crystalline) of Al and Fe oxides whereas dithionite citrate bicarbonate (DCB) treatment was performed to examine crystalline forms of Al and Fe oxides (Jackson et al., 1986; Pizarro et al., 2008). Fe and Al in solution were determined by ICP-OES (PE 7300 V - ICP, PerkinElmer). Chemical composition of the fine soil sample was analyzed via the



**Fig. 1.** Sampling site within the experimental station of the Northern Mountainous Institute for Agriculture-Forestry Technology and Science (NOMAFSI), Phu Ho, Phu Tho, Vietnam (Image source: UN FAO AQUASTAT (derived from HydroSHEDS), GMS, EOC, UN FAO GAUL, NASA SRTM).

particle-induced X-ray emission (PIXE) method, using a tandem accelerator proton beam (5SDH-2 Pelletron accelerator system, National Electrostatics Corporation, USA, installed at the Vietnam National University, Hanoi).

Fine soil was dispersed by agitating overnight in deionized water. The clay fraction ( $<2 \mu\text{m}$ ) was separated by sedimentation and decantation. The clay fraction obtained is referred to as “original clay”, whereas “DCB-treated clay” is a term implying the original clay fraction, from which Fe oxides were removed by DCB treatment. Both the original and DCB-treated clay fractions were used in the batch adsorption experiments, light scattering, and  $\zeta$  measurements in order to determine the role of Fe oxides in affecting clay colloidal properties. The original freeze-dried clay fraction was used for determination of particle micromorphology by SEM (FEI Quanta 600 FEG, USA). Mineral phases were determined by powder X-ray diffraction (Bruker AXS D5005, Germany) with oriented samples on glass slides. FTIR measurements were taken using a Nicolet™ iS™5 FT-IR (Thermo Scientific, USA) at ambient conditions with potassium bromide (KBr) as the diluent to determine the surface groups of the clay fraction.

#### 2.1.3. Preparation of silicic acid solutions

Solutions of silicic acid were prepared by dissolving 0.5 g of pure silica gel with a particle size of 0.15 mm (Fisher Scientific Company, USA) in 500 mL of 0.05 M NaOH by stirring at 70 °C for 3 h. The resulting solution was kept at room temperature for 3 d and was subsequently neutralized by adding the same amount of 0.05 M HCl. Dissolved Si was quantified by the molybdate blue method using a UV-Vis spectrophotometer (L-VIS-400, Labnics Company, Fremont, CA, USA), and then diluted to different target concentrations by adding a suitable amount of 0.05 M NaCl.

### 2.2. Methods

#### 2.2.1. Establishing batch adsorption experiments

The adsorption of silicic acid to the original clay and DCB-treated clay fraction was determined at an electrolyte background of 0.05 M NaCl in the pH range from 2 to 11. Stock suspensions of the clay fraction ( $10 \text{ g L}^{-1}$ ) were prepared prior to the experiment. The clay suspension was transferred in 5-mL amounts into plastic tubes. Aliquots of 28 mL of 3.5 mM silicic acid solution (prepared as mentioned above) were added to the suspensions. To each of these mixtures 17 mL of solutions of hydrogen chloride (0.05 M HCl), sodium chloride (0.05 M NaCl) and sodium hydroxide (0.05 M NaOH)

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