



Improving clay content measurement in oxidic and volcanic ash soils of Hawaii by increasing dispersant concentration and ultrasonic energy levels



Joshua H.S. Silva^a, Jonathan L. Deenik^{a,*}, Russell S. Yost^a, Gregory L. Bruland^{b,1}, Susan E. Crow^b

^a Tropical Plant and Soil Sciences Department, University of Hawaii at Mānoa, 3190 Maile Way, St. John 102, Honolulu, HI 96822, USA

^b Natural Resources and Environmental Management Department, University of Hawaii at Mānoa, 1910 East-west Rd, Sherman 101, Honolulu, HI 96822, USA

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ABSTRACT

Quantifying clay content is a fundamental step in predicting and managing soil behaviors such as nutrient and water retention. However, clay measurements are underestimated when using standard methods of dispersion in soils rich in oxides and volcanic ash-derived non-crystalline minerals. Increasing levels of the chemical dispersant and ultrasonic energy are two simple techniques found to increase dispersion and clay measurements in temperate soils, but their effects are less known for oxidic and volcanic ash soils. In this study we investigated the effects of increasing dispersion concentration and ultrasonic energy on clay measurements for a range of oxidic and volcanic ash soils from Hawaii. While doubling and tripling the standard sodium hexametaphosphate concentration of 0.441 g L⁻¹ did not increase estimates of clay content, increasing levels of ultrasonic energy up to 1600 J mL⁻¹ significantly increased measured clay content for all oxide and volcanic ash soils. The response to ultrasonication was dependent on soil carbon, oxide content, and surface charge, with more energy needed to disperse soils higher in carbon, oxides, and positive charge. Scanning electron microscopy revealed damage to the sand fraction in some soils when ultrasonicated, but the extent of this damage was viewed as negligible. Porous sand-sized particles resembling pumice grains were also observed in some soils, suggesting that conventional particle size analysis and clay interpretations may not adequately describe surface related behaviors.

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1. Introduction

Clay content measurements are often used to predict soil behavior in lieu of missing data or costly and time-consuming measurements (Minasny and Hartemink, 2011). Clay particles (diameter < 2 μm) are characterized by high specific surface area (Borggaard, 1983; Carter et al., 1965; Perrott, 1977; Wada, 1985) and, as a result, greatly influence water retention (Nagendran and Angayarkanni, 2010), cation exchange capacity (Banin and Amiel, 1971; Curtin and Rostad, 1997), phosphorus retention (Cox, 1994; Wiriyakitnateekul et al., 2005), and carbon and nitrogen storage (Wichern and Joergensen, 2009). Given its central role in soil behavior, clay content is used in pedotransfer functions that quickly estimate soil properties such as water content at field capacity (Gaiser et al., 2000) or cation exchange capacity (Curtin and Rostad, 1997), as well as in larger models like the Revised Soil Loss Equation that estimates soil erosion (RUSLE Development Team, 2001). Thus, quantifying the abundance of clay-sized particles has been an important step in predicting and managing soil behavior.

The first step in quantifying clay content involves the dispersion of soil aggregates into discrete sand, silt, and clay-sized particles by chemical and physical treatments. However, in highly weathered oxide-rich soils of the tropics and volcanic ash soils composed of non-crystalline minerals, bonding between oxides and organic matter (Alekseeva et al., 2009; Igwe et al., 2009), electrostatic attraction among oxide and non-crystalline minerals (Huygens et al., 2005; Uehara and Gillman, 1981), or irreversible drying of non-crystalline gels leads to the formation of stable silt and sand size aggregates, which resist dispersion when using standard procedures (Nanzoyo et al., 1993; Uehara and Gillman, 1981). The tendency of these soils to resist standard dispersion techniques often leads to the underestimation of clay content (Gee and Or, 2002; Nanzoyo et al., 1993) and discrepancies between clay measurement and its relationship to soil behavior. To demonstrate the problem, let us present data for two soils from the National Cooperative Soil Survey (2013) with similar clay measurements: a highly weathered Acroperox from Hawaii with oxidic mineralogy and measured clay of 122 g kg⁻¹; and a Haploxeralf from the Central Valley, California with similar measured clay, but composed of high activity clay minerals. As expected for a soil with low clay content, the Haploxeralf showed a low water content at the permanent wilting point (68 g kg⁻¹). In contrast, the Acroperox showed nearly three times the water content at permanent wilting (202 g kg⁻¹), suggesting a soil with high clay

* Corresponding author.

E-mail address: jdeenik@hawaii.edu (J.L. Deenik).

¹ Present address: Biology and Natural Resources Department, Principia College, 1 Maybeck Pl, Elsah, IL 62028, USA.

content. For the California soil with high activity clays, one can assume standard procedures successfully dispersed soil particles to produce accurate clay measurements. For the oxidic Acriferox, however, the discrepancy between low measured clay and high 1500 kPa water content is an artifact of the dispersion methodology; in an oxide-rich soil, clay aggregates are not fully dispersed and thus measured as silt or sand particles, but continue to impart clay-like behavior to the soil. This discrepancy is widespread for soil rich in oxide and non-crystalline minerals, justifying the ongoing need to find alternatives to standard dispersion techniques that improve clay determination.

Standard procedures in particle size analysis subject the soil to chemical treatment to disperse clay aggregates. Manipulating the type of chemical dispersant has been proposed as a way to improve dispersion in dispersion resistant soils. However, replacing sodium hexametaphosphate (NaHMP) with sodium hydroxide (de Carvalho et al., 1988; Neto et al., 2009; Zhang et al., 2005) or lithium hydroxide (Mauri et al., 2011; Rodrigues et al., 2011) did not improve clay determination. Manipulating dispersant concentration has also been investigated as a way of potentially increasing clay dispersion. Although studied less extensively than dispersant type, increasing dispersant concentration, specifically NaHMP, was found to increase dispersion and measured clay in soils dominated by smectite, kaolinite, and quartz minerals (Mishra et al., 2011; Zhang et al., 2005), suggesting that it may be a simple improvement to the established method. However, these experiments did not include the problematic highly weathered oxidic and volcanic ash soils of the tropics.

The standard procedure for particle analysis includes mechanical shaking to assist the dispersion process (Gee and Or, 2002). Manipulating the shaking time has shown limited success in improving dispersion in an oxide-rich Alfisol (Ogunwole et al., 2001), while adding coarse sand to the dispersant solution increased measured clay in Brazilian Oxisols (Korah et al., 2009; Tavares-Filho and Magellan, 2008). However, adopting these two approaches for routine analysis are likely impractical due to long shaking times (>24 h) and the added labor and time associated with the pre- and post-treatment steps in the coarse sand method.

Ultrasonication, a rapid technique that physically separates soil aggregates using sound waves, has shown promise as an attractive alternative to standard shaking treatments. Several experiments demonstrated that ultrasonication not only produced higher measurements of clay than 10 to 16 h of shaking, but also physically dispersed soils more quickly, with times at which clay plateaued ranging from 5 to 30 min (Edwards and Bremner, 1967; Gregorich et al., 1988; Yang et al., 2009). Increasing ultrasonication energy levels also led to increased aggregate dispersion and measured clay values in many studies (Asano and Wagai, 2014; Edwards and Bremner, 1967; Gregorich et al., 1988; Hunter and Busacca, 1989; Morra et al., 1991; Oorts et al., 2005; Roscoe et al., 2000; Sá et al., 2002; Yang et al., 2009), but the energy level at which clay measurements plateaued differed among soil types. These energy levels ranged from 90 to 300 J mL⁻¹ in Ustox soils (Roscoe et al., 2000; Sá et al., 2002), 400 J mL⁻¹ in Vitrand and Cryand soils (Hunter and Busacca, 1989), and up to 1500 J mL⁻¹ in Inceptisols and Entisols (Gregorich et al., 1988; Kaiser et al., 2012). Asano and Wagai (2014) studied even higher energies of 5000 and 10,000 J mL⁻¹ in an Andisol, but energies exceeding 400 to 1500 J mL⁻¹ have been observed to damage primary soil particles (Hunter and Busacca, 1989; Kaiser et al., 2012). Despite these findings on a range of soil types, the effects of increasing ultrasonication energy levels for highly weathered oxide and volcanic ash soils are less understood. Additionally, aside from Asano and Wagai (2014) and Sá et al. (2004), no other attempts have been made to link differences in ultrasonic treatment levels to key aggregating agents, such as oxide and carbon contents or charge properties.

Previous work suggests that ultrasonication shows promise as an alternative to standard dispersion techniques in the improvement of clay content determination. Our work compares dispersant concentration

manipulation and ultrasonication treatments in their effectiveness to improve clay content determination in dispersion resistant soils common to the humid tropics. To address these gaps in knowledge, the objectives of our study were the following: 1) evaluate the effect of increasing chemical dispersant concentration on clay content determination for oxide and volcanic ash soils that resist dispersion; and 2) evaluate the effect of increasing ultrasonication energy levels on clay content measurements. We hypothesize that resistance to dispersion is proportional to concentrations of iron and aluminum oxides, carbon, and positive charge based upon the important roles these constituents play in aggregation (El Swaify, 1980; Huygens et al., 2005; Igwe et al., 2009; Li et al., 2005).

2. Materials and methods

2.1. Soils and sample preparation

The sample set consisted of ten soils from Hawaii and one from California (Salinas series), representing diverse soil mineralogy, degrees of weathering, and suggested differences in dispersion resistance (Table 1). Four soils (Lualualei, Leilehua, Hali'i, and Hilo series) were utilized for the dispersant concentration experiment. For the ultrasonication experiment and seven additional soil types were included for a total of eleven soils to broaden the range of soil mineralogy. The Lualualei and Salinas soils, in which the clay fraction was composed of 2:1 clay minerals that disperse easily, served to validate the integrity of our methods, and they were used to evaluate potential damage from high concentration and energy levels. Soils were collected from the 0 to 15 cm depth on agricultural lands that were not in production at the time of collection, with dominant vegetation being grasses such as guinea grass (*Megathyrsus maximus* Jacq., formerly *Panicum maximum* Jacq.). The soil samples, except for the Andisols, were air dried at ambient conditions over two days, sieved to <2 mm, and used for further analyses. As Andisols are known to irreversibly dry (Nanzyo et al., 1993), these soils were sieved to <2 mm in field-moist conditions and stored at approximately 5 °C in sealed containers to prevent moisture loss.

Table 1
Soil taxonomic classification and mineralogy.

Series	Taxonomic classification ^a	Mineralogy ^b
Lualualei	Fine, smectitic, isohyperthermic Typic Gypsiteorrerts	N/A
Salinas	Fine-loamy, mixed, superactive, thermic Pachic Haploxerolls	MI, MT, KK
Leilehua	Very-fine, ferruginous, isothermic Ustic Kanhaplohumults	HE, GE, GI, KK, MI
Moloka'i	Very-fine, kaolinitic, isohyperthermic Typic Eutrotorrox	GE, GI, HE, KK
Wahiawa	Very-fine, kaolinitic, isohyperthermic Rhodic Haplustox	FE, HE, KK, MI, MG, MS, QZ ^c
Pa'aloa	Very-fine, sesquic, isothermic, humic Rhodic Kandiodox	N/A
Kapa'a	Very-fine, sesquic, isohyperthermic Anionic Acrudox	N/A
Hali'i	Fine, ferruginous, isothermic Anionic Acriferox	GE, GI, HE, KK
Hilo	Medial over hydrous, ferrihydritic, isohyperthermic Acrudoxic Hydrudands	GE, GI, KK, NC
Honoka'a	Hydrous, ferrihydritic, isothermic Acrudoxic Hydrudands	GI, KK
Maile	Hydrous, ferrihydritic, isothermic Acrudoxic Hydrudands	GE, MS ^c , NC, OP, PR ^c , QZ ^c

^a Taxonomic information retrieved from Soil Survey Staff. (2013).

^b Mineralogical data retrieved from the National Cooperative Soil Survey (2013). Abbreviations for mineralogy are as follows: GE = goethite, GI = gibbsite, HE = hematite, KK = kaolinite, MI = mica, MG = magnetite, MS = muscovite, MT = montmorillonite, NC = non-crystalline, OP = opaques, PR = pyroxene, QZ = quartz, N/A = not available.

^c Denotes trace amounts detected.

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