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# Surface charge properties of kaolinite from Thai soils

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ABSTRACT

Kaolinite is the major clay mineral in many Thai soils and the charge characteristics of soil kaolinites have not been properly evaluated. Soil samples from sub-soil horizons of fourteen Oxisols and Ultisols from Thailand were taken for this study. Clay fractions were separated from the soils, and free iron oxides and organic matter were removed to obtain soil kaolinites. Surface charge properties of soil kaolinites and a reference kaolinite (KGa-2) were evaluated by various procedures. Permanent negative charge ($-\sigma_p$) was determined by cesium adsorption method. Point of zero charge (PZC) was measured by ion adsorption, potentiometric titration and electrophoretic mobility methods. X-ray diffraction analysis showed that kaolinites isolated from the Thai soils contain traces to small amounts of quartz, anatase, gibbsite, hydroxy-Al interlayered vermiculite (HIV) and illite. The value of $-\sigma_p$ of soil kaolinites varied between 34.9 and 145.3 $\mathrm{mmol_c\ kg^{-1}}$; excluding a few anomalous values for the kaolinites with impurities of 2:1 clay minerals, soil kaolinites have an average $-\sigma_p$ of 52 $\mathrm{mmol_c\ kg^{-1}}$. The $-\sigma_p$ on soil kaolinites was positively correlated with the specific surface area (SSA) of the samples. All kaolinites exhibited increasing negative charge and decreasing positive charge with increasing equilibrium solution pH confirming the presence of variable charge on the mineral surface. The PZNC values of soil kaolinites varies from 2.1–3.1, except for two samples where it could not determined as the CEC values were greater than the AEC values at all pH values. Potentiometric titration curves for all kaolinites exhibited variable net proton charge ($\Delta H-\Delta OH$ or $\sigma_H$) with changing equilibrium solution pH from 2 to 10. The PZSE values were slightly higher than the PZNC values of the soil kaolinites, and varied between 2.3 and 2.9. The zeta potential of all kaolinites became more negative with increasing solution pH (2 to 6) but not low enough to reach a positive value for all but one soil kaolinites; hence the IEP of soil kaolinites could not be obtained. The PZC of kaolinite from Thai soils are at lower pH than the natural pH of these soils, thus soil kaolinites carry a net negative charge under natural conditions and they have some limited ability to adsorb cations. Changes in soil pH from soil acidification, liming or addition of any other amendments or practices can substantially change the cation- or anion-exchange capacity of soil kaolinites, which may influence the availability of nutrient elements in the soils.

## 1. Introduction

Surface charge properties of kaolinite are important for nutrient availability and adsorption of toxic compounds in soils, particularly for highly weathered soils of the tropical and sub-tropical regions. Surface charge characteristics of geological kaolinites have been investigated by many researchers; however, soil kaolinites have received a little attention (Chorover and Sposito, 1995; Schroth and Sposito, 1997; Singh and Gilkes, 1992; Tombácz and Szekeres, 2006; Wieland and Stumm, 1992; Zhou and Gunter, 1992). Kaolinite are considered to carry a small proportion of constant structural charge (permanent charge) due to the isomorphous substitution of $Al^{3+}$ or $Fe^{3+}$ for $Si^{4+}$ in the tetrahedral sheet, however, most of the charge is variable occurring on the mineral's edges due to the protonation or deprotonation of exposed hydroxyl groups (Bolland et al., 1976; Tombácz and Szekeres, 2006; Zhou and Gunter, 1992). Inclusions of impurities of 2:1 clay minerals with kaolinite have been considered to contribute most of the permanent negative charge in kaolinite (Kim et al., 1996; Lim et al., 1980).

One of the most important parameters used to describe the chemical properties of variable charge minerals is point of zero charge (PZC), which is the pH at which the net mineral charge is zero or as the solution pH value when the diffuse layer charge density ($\sigma_d$) of a mineral is equal to zero (Sparks, 2003; Sposito, 2008). This is also the pH at which the total net particle charge density ($\sigma_n$) equals zero. A mineral carries a net negative charge if the solution pH is greater than its PZC and a net positive charge occurs at pH values lower than the PZC (Morais et al., 1976; Sparks, 2003). Various procedures have been used for the determination of PZC; they generally rely on ion adsorption, potentiometric titration or electrophoretic mobility (zeta potential) measurements (Appel et al., 2003; Chorover and Sposito, 1995; Phillips and Sheehan,

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2005; Zelazny et al., 1996). Ion adsorption involves the measurement of retention of an indifferent cation (such as $Na^+$, $Li^+$ and $Ca^{2+}$) and an anion (such as $NO_3^-$ and $Cl^-$) as a function of the solution pH at a fixed ionic strength; the PZNC is the pH value at which the cation exchange capacity (CEC) of a variable surface charge mineral is equal to its anion exchange capacity (AEC) (Sposito, 2008). The potentiometric titration method involves the measurement of point of zero salt effect (PZSE), which is the pH at which salt concentration has no effect on the adsorption of ions and the titration curves of varying ionic strengths intersect or crossover at this point (Sparks, 2003).

The isoelectric point (IEP) method is based on electrophoretic mobility measurement; IEP is the pH at which there is no movement of mineral or soil particles in response to an applied electric field i.e. the electrophoretic mobility of a mineral is zero.

A large majority of Thai soils are highly weathered and the clay fraction is often dominated by kaolinite (Darunsontaya et al., 2010; Kanket et al., 2005; Wisawapipat et al., 2010; Yoothong et al., 1997). Kaolinite in highly weathered Thai soils have been reported to contain a range of crystal morphologies such as euhedral hexagonal to anhedral plates, laths and tubes (Hart et al., 2003; Kanket et al., 2005; Trakoonyingcharoen et al., 2006). Similarly, a range of cation exchange capacity (CEC) values have been observed for kaolinite isolated from Thai soils and the variability in the CEC of soil kaolinites has been attributed to the specific surface area (SSA) and crystal size of the mineral (Kanket et al., 2005; Trakoonyingcharoen et al., 2006; Wisawapipat et al., 2010). However, little is known about the nature and characteristic of charge on kaolinite in Thai soils. This study was therefore aimed to (i) assess the permanent and variable

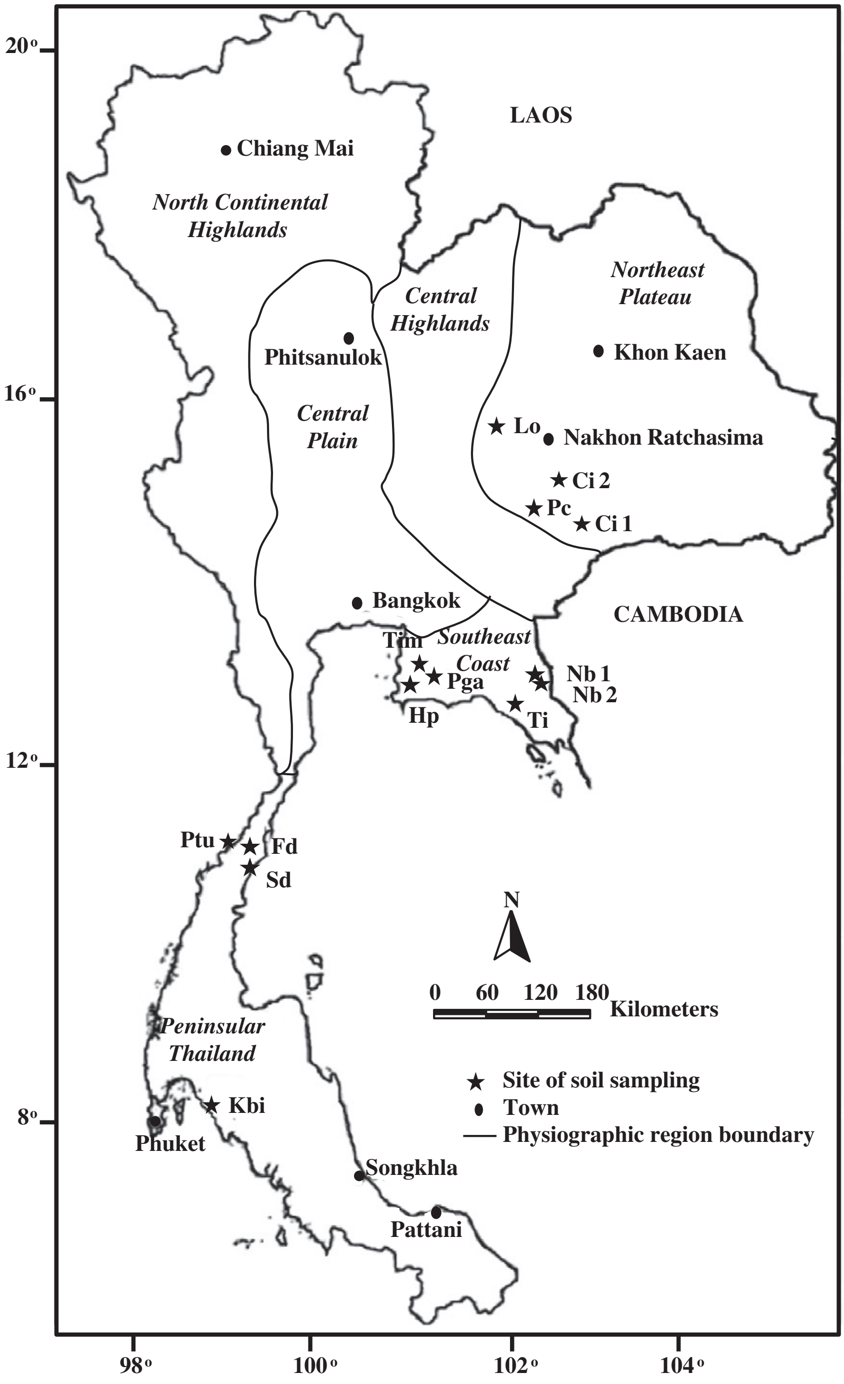

**Fig. 1.** A map showing the sites for the soils in Thailand used in the study.