Effects of Electrolytes and Soil-to-suspension Ratios on pH in Acidic-coarse Textured Soil

Somchai Butnan¹, Pranee Sriraj², Banyong Toomsan³

ABSTRACT

Background: Soil pH is determined using a variety of methods. The key differences among them are the electrolytes and soil-to-suspension ratios. However, an optimal procedure tailored to a particular soil is required. This study, therefore, aimed to evaluate the effects of electrolytes and soil-to-suspension ratios on soil pH and to optimise pH measurement methods for acidic-coarsely textured soil.

Methods: Varied standard electrolytes (water, 0.01 M CaCl₂ and 1 M KCl) and soil-to-suspension ratios (1:1, 1:2.5 and 1:5 w/v) were used to measure the pH of thirty samples of acidic-coarsest textured soil.

Result: Soil pH values were observed in the following order: water > 0.01 M CaCl₂ > 1 M KCl. Higher soil pHs were a result of higher suspension volumes. The most optimal pH measurement method for an acidic-coarsely textured soil was obtained from the 1:2.5 soil-to-suspension ratio of 1 M KCl, which held the highest R² (0.850), as well as the lowest root mean square error (RMSE) (0.010), indicating the most precise method. An alternative method suitable for a cost-saving laboratory was the 1:1 soil-to-suspension ratio of 0.01 M CaCl₂, which owned R² of 0.766 and RMSE of 0.013, as its pH measurement was similar to those under the most optimal method.

Key words: Acid soil, Hydrogen ion concentration, Ionic strength, pH assessment, Soil reaction.

INTRODUCTION

Soil pH measurement is the standard and routine chemical laboratory for soil fertility evaluation, due to its ease of measurement and influence on other properties of agricultural soil (Minasny et al., 2011; Miller and Kissel, 2010). Soil pH affects plant nutrient availability, organic material decomposition, microbial activity, element toxicity, pollution mobility and soil weathering (Kome et al., 2018; Miller and Kissel, 2010; Kissel et al., 2009). These soil fertility properties play key roles in sustainable agriculture (Power and Prasad, 1997). Because soil pH influences most of the other soil fertility parameters, it has been named the master variable of soil science (Kome et al., 2018).

Electrolytes and soil-to-suspension ratios are the measurement factors that dominantly influence the variability of soil pH (Minasny et al., 2011). Electrolytes employed in soil pH determination include water, 0.01 M CaCl₂ and 1 M KCl; with soil-to-suspension ratios of 1:1, 1:2.5 and 1.5 w/v (Thomas, 1996). However, recommendations for measuring soil pH vary from country to country or even between laboratories. In the United States, water is used as an electrolyte (Soil Science Division Staff, 2017); however, certain laboratories recommend 0.01 M CaCl₂ (Rayment and Higginson, 1992), with a soil-to-suspension ratio of 1:1. In New Zealand, water (Metson, 1956) and 0.001 M CaCl₂ (Edmeades and Wheeler, 1990) with a soil-to-suspension ratio of 1:2.5 were recommended. Laboratories in Australia recommend water or 0.01 M CaCl₂ using a 1:5 soil-to-suspension ratio (Slattery et al., 1999; Minasny et al., 2011). In Thailand, varied soil pH measurement methods are employed among different laboratories. Water, 0.01 M CaCl₂ and 1 M KCl are used as electrolytes (Therajindakajorn, 2011; Land Development Department, 2004); with 1:1 (Land Development Department, 2004) or 1:2.5 soil-to-suspension ratios (Therajindakajorn, 2011).

Soil characteristics; e.g., texture, cation exchange capacity, organic matter content and other physicochemical properties; as well as soil management, such as the application of mineral fertilisers, manure and other soil amendments, can influence pH (Weil and Brady, 2017; McLean, 1982). Approximately 30-40% of the world’s agricultural soil is identified as acidic (Samac and Tesfaye, 2003; von Uexküll and Mutert, 1995). Agricultural soils in Thailand and more specifically Northeastern, are generally

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coarsely textured, indigenous acidic and low fertile due to their highly weathering and intensive uses in agricultural approaches (Vityakon, 2007).

Given the diverse nature of soils, each soil necessitates a tailored approach for pH measurement. This principle holds true for acid-coarsely textured soil, an important soil type found in tropical regions, which required a particular pH measurement procedure. The objective of this study was therefore to evaluate the effects of electrolytes and soil-to-suspension ratios on pH of typically acid-coarsely textured soil.

MATERIALS AND METHODS

Soil

In order to achieve an inherently acid-coarsely textured soil with a diverse pH range, this study focused on isohyperthermic Aeric Kandiaquults, which are naturally acidic soil commonly found in Northeast Thailand. These soils were subjected to varying amounts of cricket feces-derived liming material. Thirty soil samples were examined, then air-dried and subsequently sieved through a 2-mm sieve before laboratory analyses. The physicochemical properties of the soil are presented in Table 1.

pH measurement methods

Two factors of soil pH measurement methods were investigated; electrolytes (water, 0.01 M CaCl$_2$ and 1 M KCl) and soil-to-suspension ratios (1:1, 1:2.5 and 1:5 in w/v). The ionic strengths ($I$) of 0.01 M CaCl$_2$ and 1 M KCl were equivalent to 0.03 M and 0.5 M, respectively, regarding the calculation procedure demonstrated by Lehmann et al. (1996) and Sposito (2008):

$$I = \frac{1}{2} \sum^n_{i=1} z^2_i c_i$$

Where, $z_i$ and $c_i$ = valency and molar concentration of an ion i.

The soil-to-suspension ratios of 1:1, 1:2.5 and 1:5 were achieved by adding 5, 12.5 and 25 ml of each electrolyte to 5 g of soil, respectively. Soil pH was subsequently determined following the standard method described by McLean (1982). Briefly, a soil suspension was agitated for 30 min, then allowed to settle for 30 min before the pH of the suspension was measured on a pH meter (Eutech PC 700, Thermo Fisher Scientific, Massachusetts, USA).

Laboratory measurements for initial soil properties

Electrical conductivity (EC) was measured in a soil-to-water ratio of 1:5 w/v. Soil organic carbon determination was performed using the Walkley and Black method (Nelson and Sommers, 1982). Total nitrogen was determined by the Kjeldahl method (Bremner and Mulvaney, 1982) on a micro-Kjeldahl distillation apparatus (Pro-Nitro S 4002851, JC Selecta, Barcelona, Spain). Phosphorus was extracted using a Bray-2 solution and determined via a UV-Vis spectrophotometer (Hitachi U-5100, Hitachi High-Tech Corporation, Tokyo, Japan) using a wavelength of 820 nm (Jones, 2001). Cations of K, Ca, Mg and Na, were extracted in 1 N NH$_4$OAc at pH 7 (Pansu and Gautheryou, 2006) and measured on a flame atomic absorption spectrometer (Agilent 240FS AA, Agilent Technologies, California, USA). The effective cation exchange capacity (ECEC) was achieved by the sum of K, Ca, Mg and Na, according to Ketterings et al. (2014). Soil texture was assessed using the pipette method (Kroetsch and Wang, 2008). Hydrogen ion concentrations in the soil were achieved using the titrimetry method following Pansu and Gautheryou (2006).

Statistical analysis

Delta pH ($\Delta$ pH) was obtained from the difference between pH measurements under differing soil-to-suspension ratios within the same electrolyte. Regression analysis, through the PROC GLM procedure (SAS Institute Inc., 2004), evaluated the relationships of EC with $\Delta$ pH and pH measured under a soil-to-suspension ratio with H$^+$ concentration. The error of each method was estimated by the root mean square error (RMSE), which is defined as:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\hat{y}_i - y_i)^2}$$

Where, $\hat{y}_i$ and $y_i$ are the soil pH measurements obtained by each method and H$^+$ concentration, respectively. Statistical significance was at $p$≤0.05.

RESULTS AND DISCUSSION

Effects of electrolytes and soil-to-suspension ratios on soil pH

Soil pH varied depending upon the electrolytes and soil-to-suspension ratios (Fig 1). Under the same soil-to-suspension ratio, soil pHs were observed in descending order: water > 0.01 M CaCl$_2$ > 1 M KCl. Decreased pH, measured in CaCl$_2$ and KCl solution relative to those in water, resulted from a greater dissociation of H$^+$ from exchangeable sites replaced by Ca$^{2+}$-derived Ca$^{2+}$ and KCl-derived K$^+$, bringing about increased aqueous H$^+$ (Kome et al., 2018; Minasny et al., 2011). Meanwhile, water suspension determined mainly existing H$^+$ in soil solution and readily dissociated H$^+$ (Wilke, 2005). The pH in KCl, which was lower than that in CaCl$_2$, resulted from the higher ionic strength of 1 M KCl ($I = 0.5$ M) than that of 0.01 M CaCl$_2$ ($I = 0.03$ M) rendering more substantial H$^+$ displacement of the electrolytes (Edmeades and Wheeler, 1990). Ionic strength consists of the combining functions of the concentration of an ion and its valency (Lehmann et al., 1996; Sposito, 2008). The higher ionic strength of an electrolyte produced the higher replacing power of an ion derived from that electrolyte in replacing H$^+$ on the exchangeable sites of soil colloid surfaces (Sposito, 2008; Hao et al., 2019).

Increasing suspension volumes brought about increased soil pH in all electrolytes (Fig 1). Kome et al. (2018) and Merl et al. (2022) determined that raised suspension volumes decreased H$^+$ concentrations, termed the dilution effect.
Increased EC significantly decreased $\Delta$ pH regardless of the type of electrolyte (Fig 2), indicating that the differences in soil pH, resulting from the different soil-to-suspension ratios, lowered with rising ionic strength. Notably, the ionic strength increased as EC increased (Dolling and Ritchie, 1985). Miller and Kissel (2010) and Kome et al. (2018) stated that declined $\Delta$ pH under increased EC was attributed to the salt effect. The higher EC was attributed to higher concentrations of cations and anions in soil (Miller and Curtin, 2008). The excess cations might displace the high amount of H$^+$ and Al$^{3+}$ on the exchangeable sites of soil colloidal surfaces, either low or high suspension volume (Sumner, 1994). The results implied that the soil-to-suspension ratios significantly affect soil pH measurement, particularly in low fertile soils which exhibit low EC (Sumner, 1994; Dolling and Ritchie, 1985), similar to the tropical coarsely textured soil studied herein. However, this result was not the case for $\Delta$ pH$_{1:5,1:2.5}$ in 1 M KCl, which has yet to be explained.

**Table 1**: Descriptive statistics of pH measured in different electrolytes and soil-to-suspension ratios and other physicochemical characteristics of the soil (n = 30).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH$_{\text{water}}$ (1:1)</td>
<td>5.17</td>
<td>6.54</td>
<td>5.73</td>
<td>0.42</td>
</tr>
<tr>
<td>pH$_{\text{water}}$ (1:2.5)</td>
<td>5.31</td>
<td>6.48</td>
<td>5.81</td>
<td>0.35</td>
</tr>
<tr>
<td>pH$_{\text{water}}$ (1:5)</td>
<td>5.89</td>
<td>6.68</td>
<td>6.26</td>
<td>0.23</td>
</tr>
<tr>
<td>pH$_{\text{CaCl}_2}$ (1:1)</td>
<td>4.55</td>
<td>6.12</td>
<td>5.15</td>
<td>0.47</td>
</tr>
<tr>
<td>pH$_{\text{CaCl}_2}$ (1:2.5)</td>
<td>4.85</td>
<td>6.15</td>
<td>5.32</td>
<td>0.38</td>
</tr>
<tr>
<td>pH$_{\text{CaCl}_2}$ (1:5)</td>
<td>4.84</td>
<td>5.99</td>
<td>5.41</td>
<td>0.33</td>
</tr>
<tr>
<td>pH$_{\text{KCl}}$ (1:1)</td>
<td>4.37</td>
<td>6.25</td>
<td>5.09</td>
<td>0.56</td>
</tr>
<tr>
<td>pH$_{\text{KCl}}$ (1:2.5)</td>
<td>4.45</td>
<td>6.30</td>
<td>5.11</td>
<td>0.58</td>
</tr>
<tr>
<td>pH$_{\text{KCl}}$ (1:5)</td>
<td>4.60</td>
<td>6.27</td>
<td>5.23</td>
<td>0.51</td>
</tr>
<tr>
<td>EC (1:5)</td>
<td>0.08</td>
<td>0.36</td>
<td>0.17</td>
<td>0.08</td>
</tr>
<tr>
<td>ECEC (cmol/kg)</td>
<td>1.57</td>
<td>3.46</td>
<td>2.19</td>
<td>0.55</td>
</tr>
<tr>
<td>SOC (g/kg)</td>
<td>3.65</td>
<td>4.52</td>
<td>4.01</td>
<td>0.27</td>
</tr>
<tr>
<td>TN (g/kg)</td>
<td>0.31</td>
<td>0.47</td>
<td>0.39</td>
<td>0.03</td>
</tr>
<tr>
<td>P (mg/kg)</td>
<td>52.5</td>
<td>356.3</td>
<td>126.4</td>
<td>104.4</td>
</tr>
<tr>
<td>K (mg/kg)</td>
<td>0.10</td>
<td>0.56</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>Ca (mg/kg)</td>
<td>1.11</td>
<td>2.23</td>
<td>1.55</td>
<td>0.29</td>
</tr>
<tr>
<td>Mg (mg/kg)</td>
<td>0.15</td>
<td>0.62</td>
<td>0.29</td>
<td>0.16</td>
</tr>
<tr>
<td>Na (mg/kg)</td>
<td>0.12</td>
<td>0.16</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>Soil texture</td>
<td>Loamy sand</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig 1**: Mean values of soil pH measured in water, 0.01 M CaCl$_2$ and 1 M KCl at soil-to-suspension ratios of 1:1, 1:2.5 and 1:5. Error bars indicate the standard deviation.
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Optimal methods in soil pH measurement

Regression analysis between pH and $H^+$ concentrations, as well as their $R^2$ and RMSE were employed to evaluate the optimal pH measurement method for acidic-coarse textured soil (Fig 3A-I). Increasing the suspension volumes decreased $R^2$ and increased RMSE of the pH measured in water (Fig 3A, B, C) and 0.01 M CaCl$_2$ (Fig 3D, E, F). The results indicated that higher suspension volumes lowered

Fig 2: Relationships of electrical conductivity with ΔpH measured in water (A): 0.01 M CaCl$_2$ (B); and 1 M KCl (C).

Fig 3: Exchangeable $H^+$ concentrations as related to soil pH measurements within different electrolytes: water (A, B, C), 0.01 M CaCl$_2$ (D, E, F) and 1 M KCl (G, H, I) at the soil-to-suspension ratios of 1:1, 1:2.5 and 1:5 ($n = 30$).
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precisions of the pH measured in these two electrolytes. Our findings were in line with those of Kome et al. (2018), who demonstrated that increasing the suspension volumes from the soil-to-suspension ratios of 1:2.5 to 1:5 resulted in lower prediction precision, as assessed by $R^2$, which decreased from 0.957 to 0.921 in water and from 0.855 to 0.844 in 1 M KCl. A more constant equilibrium of H$^+$ and Al species in lower soil suspension volumes might bring about a higher precision measurement method than that of the higher volume counterparts. The instability of H$^+$ and Al in soil has been reported to affect the equilibrium of soil suspension (Dahlgren and Walker, 1994), which may influence the precision of the pH measurement within the current study.

Ionic strength increased as the suspension volume increased (Sonmez et al., 2008). Increases in the ionic strength of particularly variably charged soil brought about increased negative and positive charges (Black and Campbell, 1982). At a higher ionic strength, due to higher electrolyte concentration, Dahlgren and Walker (1994) demonstrated that Al and H$^+$ on the exchangeable sites were displaced and then released into the aqueous phase of the soil suspension by cations. The displaced Al in the aqueous phase consequently hydrolysed, producing additional H$^+$ as $\text{Al}^{3+} + \text{H}_2\text{O} = \text{Al(OH)}^{2+} + \text{H}^+$ (Adams, 1971). Dahlgren and Walker (1994) claimed that the H$^+$ product rapidly adsorbed onto a negative charge which increased due to the increasing ionic strength. Withdrawal of H$^+$-rendered lower H$^+$ activity in the aqueous phase, causing further hydrolysis of aqueous Al and, as a result, manifesting supersaturation and precipitation of Al species. Positively charged Al species were then adsorbed on the negative charges. This process reasoned that the equilibrium of suspension with a higher ionic strength was less constant, resulting in less precision of the higher suspension volumes in the pH measurements.

The highest $R^2$ (0.850) and lowest RMSE (0.010) were observed in pH$\text{KCl}(1:2.5)$ (Fig 3H). As soil pH is the determination of H$^+$ concentration in soil (McLean, 1982), the optimal method for soil pH measurement in an acidic-coarse textured soil used in the current study was pH$\text{KCl}(1:2.5)$. However, due to the high amount of the chemical KCl used to prepare 1 M KCl (74.55 g KCl/L), the soil pH measurement of pH$\text{KCl}(1:2.5)$ would be costly. An alternative method, suitable for a cost-saving laboratory, was the soil pH measurement in 0.01 M CaCl$_2$ with the soil-to-suspension ratio of 1:1 ($\text{pH}_\text{CaCl}_2(1:1)$), as their pH values were similar to those measured in pH$\text{KCl}(1:2.5)$ (Fig 1), concomitant with a low amount of CaCl$_2$ (1.47 g CaCl$_2$/L). The soil pH measurement method of pH$\text{CaCl}_2(1:1)$ owned $R^2$ of 0.766 and RMSE of 0.013 (Fig 3D).

CONCLUSION

The results demonstrate that the descending order of soil pH, measured in water > 0.01 M CaCl$_2$ > 1 M KCl. The pH increased with increasing suspension volumes in all three electrolytes.

Decreasing the suspension volumes increased the precision of pH measurement, where water and 0.01 M CaCl$_2$ were utilised as the electrolytes. The most optimal pH method recommended for soil fertility evaluation of an acidic-coarsely textured soil was the soil-to-suspension of 1:2.5 in 1 M KCl. The alternative method suggested for a cost-saving laboratory was the pH measurement in 0.01 M CaCl$_2$ at a ratio of 1:1.

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Conflict of interest: None.

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Conflict of interest: None.

أساسيات المكونات الكيميائية ونسبة التورم في الأرض الرطبة السهيلة المطردة

النتائج تظهر أن Precision من pH الم量 في حالة ماء > 0.01 M CaCl$_2$ > 1 M KCl. pH يزيد مع زيادة معدة الحبوب في جميع البتلات الكيميائية.

الخلاصة

تظهر النتائج أن الترتيب الذي يشير إلى تركيبة pH من الأرض، المدفوع في ماء > 0.01 M CaCl$_2$ > 1 M KCl. pH يزيد مع زيادة معدة الحبوب في جميع البتلات الكيميائية.

المراجعات


None.


