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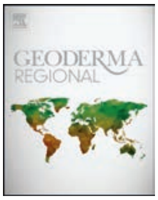

Models relating soil pH measurements in H_2O, KCl and $CaCl_2$ for volcanic ash soils of Cameroon

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ABSTRACT

Soil pH, apparently the most routinely measured soil property is an important indicator of soil quality, serves as a guide for fertilizer recommendations and liming requirements, and is an index of biogeochemical processes in terrestrial ecosystems. This study was conducted to establish relationships among different pH measurements of surface soils (0–20 cm) derived from volcanic ash parent materials in different electrolytes and soil-to-solution ratios following standard methods. Soil pH increased with increase in solution volume and for a particular soil-to-solution ratio; the trend in pH values was pH H_2O > pH 0.01 M $CaCl_2$ > pH 1 M KCl. Electrical conductivity values were very low (mean $= 0.04 \pm 0.01$ dSm^{-1}) and were highly and negatively correlated with pH H_2O and pH $CaCl_2$. pH $CaCl_2$ values were on average 0.43 units lower than those measured in water, while those measured in KCl were on average 0.73 units lower than those measured in water. Models relating different pH and EC measurements ($n = 38$) yielded R^2 values ranging from 0.774–0.978. Model validation using a dataset of 59 points gave R^2 values ranging from 0.843 to 0.958; RMSE from 0.06–0.09; MAE from 0.05–0.09 and index of agreement from 0.75–0.78. The models developed in this study are useful in quality control of pH measurements, for converting pH values of volcanic ash – derived soils in different electrolytes and soil-to-solution ratios and contribute to information necessary for the development of soil data bases at local and regional levels.

1. Introduction

Soil pH is an important indicator of soil quality (Hue, 2011). It plays a significant role in many soil processes such as solubility and availability of plant nutrients, microbial activity and decomposition of soil organic matter, sorption of contaminants and a variety of physico-chemical processes involved in biogeochemical cycling. Soil chemists have often referred to soil pH as the “master variable” because it controls ion exchange, dissolution/precipitation, reduction/oxidation, adsorption, and complexation reactions (McBride, 1994). In agricultural fields, soil pH provides information on liming and fertilizer requirements and on the effectiveness of herbicides. Additionally, soil pH is very important because it serves as an index of soil weathering and mineral transformations. Since soil pH influences many other soil parameters and is relatively easy to determine in the laboratory, it constitutes an important parameter in establishing pedotransfer functions (Seybold et al., 2009; Seybold and Libohova, 2017). Therefore, soil pH data needs to be readily interpretable, relatively precise and should not be estimated from other soil quality indicators (Seybold et al., 2003). Soil pH is one of the most measured parameters in soil analysis and different methods are usually employed, depending on the needs or objectives of the study. For example, the standard field pH measurement is performed with a 1:1 soil-to-water mixture so that comparisons of pH readings are done on an equivalent basis (Soil Science Division Staff, 2017). Thus, more dilute samples such as 1:5 soil-to-water ratio generally have a higher pH value, while less dilute samples generally have lower pH values. Secondly, other methods of measuring pH involving different electrolyte solutions are also used in soil survey for specific purposes, especially those required for some taxonomic criteria in Soil Taxonomy (Soil Science Division Staff, 2017). For example, using a 0.01 M $CaCl_2$ solution has the advantage of dampening seasonal variation in pH. That is, a concentration of 0.01 M $CaCl_2$ *is approximately equal to the salt concentration of the soil solution in many fertile soils* (*Schofield and Taylor,* 1955). This implies that even if a soil received manure or fertilizer immediately before it is sampled for soil pH determination, the error due to variation in salt concentration of the soil would be negligible if the pH measurement was done in a 0.01 M $CaCl_2$ *solution* (Kissel et al., *2009*). The role of 1 M KCl solution is to test for the presence of exchangeable Al. The absolute value of 1 M pH KCl bears a strong correlation with Al saturation. This higher concentrated salt solution displaces H^+ and Al^{3+} ions completely from the exchange complex. Aluminum, displaced by K^+ on the exchange complex, consumes OH^- ions and increases H^+ concentration. As a result, the solution pH is lowered. Generally, exchangeable aluminum is present if the pH 1 M KCl is ≤5.2. If the pH 1 M KCl is >5.2, aluminum becomes non-exchangeable due to processes such as

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hydrolysis, polymerization and precipitation (USDA-NRCS, 2005). Thus, a 1 M KCl solution is used to infer aluminum saturation levels in some great groups of Oxisols (e.g., Acrudox). If the criteria are met, aluminum toxicity may be a concern and so, proper management options will be used. Furthermore, the comparison of pH 1 M KCl with pH H_2O provides an assessment of the nature of the net charge on the colloidal system. The numerical difference in the values of pH measured in 1 M KCl and H_2O (pH KCl – pH H_2O) is referred to as the delta pH. When this difference is negative, the colloid has a net negative charge (cation exchange capacity), and when positive, it has a net positive charge (anion exchange capacity). Additionally, a 1 M NaF solution is used to infer the presence of short-range order minerals such as allophanes and it is used in defining the criteria for the isotic mineralogy class (Soil Science Division Staff, 2017).

In most laboratories of soil analysis in Cameroon, routine soil pH measurements are often performed following the AFNOR standard NF X-31-103 (1988), which recommends a 1:2.5 soil-to-water ratio, and the International standard NF ISO 10390 (1994) which recommends a 1:5 soil-to-water ratio. However, the latter is not commonly used, likely because soil pH data obtained from measurements with 1:2.5 soil-to-water ratio are given more preference to inform on soil acidity levels and nutrient availability (i.e. mostly for soil fertility investigations and fertilizer recommendations). However, the influence of electrolyte concentration on soil pH measurements has been reported in many studies (Hossner, 2008) and have found great application in various domains such as in the harmonization of global soil maps (Libohova et al., 2014); in developing pedotransfer functions (Libohova et al., 2014; Minasny et al., 2011); and for guiding on soil analysis in the laboratory (Kalra, 1995; *Kissel* et al., 2009; *Thomas,* 1996).

Volcanic ash soils are among the most fertile soils of Cameroon and are intensively used for agricultural production. However, information on the chemical properties of these soils, notably soil pH, is sparse. Therefore, the objective of this work was to determine the pH of volcanic ash soils from Cameroon in different solutions and soil-to-solution ratios in order to establish their relationships with one another using statistical models. To our knowledge, such models do not exist for volcanic ash soils of Cameroon. The relationships are meant to guide on pH measurements in routine laboratory analyses and to contribute to information necessary for developing soil data bases.

2. Materials and methods

2.1. Description of study site, soil sampling and sample preparation

In this study, soil samples were collected from the surface (0–20 cm) horizons of cultivated farmlands in different locations along the slopes of mount Kupe (located between latitudes 4°43′N and 4°52′N and longitudes 9°38′ E and 9°47′ E) in southwest Cameroon. The study area has a tropical wet (Af) climate with two main seasons: the rainy season which spans from March to November (mean annual rainfall = 3095.6 mm) and the dry season from November to March (mean annual temperature = 25.2 °C), based on long-term climatic data (1984–2014). The dominant parent materials in the sampling area consist of tuff, scoria and pumice, originating from recent volcanic activity. The soils are young and belong to the soil orders Andisol, Inceptisol and Entisol, characterized by low bulk density (generally <0.9 Mg m^{-3}), high organic carbon contents and a sandy texture. The sampling points were distributed over different topographic landscapes (hill tops, valleys, slopes, flat land) at different altitudes ranging between about 400–900 m above sea level. A total of 98 samples were collected randomly using a soil auger. Sampling was done in the dry season, during the month of December in 2017. Samples were stored in polythene bags and labeled with indelible markers. The samples were air-dried at room temperature away from direct sunlight, crushed using a porcelain mortar and pestle, and then sieved through a 2 mm sieve to separate the fine earth fraction (< 2 mm) from the coarse fraction.

2.2. Laboratory analysis

Soil pH of the <2 mm fraction was measured in distilled deionized water, 1 M KCl, and 0.01 M $CaCl_2$ in soil-solution ratios of 1:1, 1:2.5 and 1:5 following standard procedures for soil pH determination as described by Pansu and Gautheyrou (2006), using an AI1201 PH60-E Premium digital pH meter (Apera Instruments, Columbus, Ohio, USA) bearing a glass electrode and a reference electrode, which had previously been calibrated with buffer solutions of pH 4 and 7. The 1 M KCl solution was prepared by dissolving 745.6 g of KCl in 10 L of distilled water, while the 0.01 M $CaCl_2$ was prepared by dissolving 14.7 g of $CaCl_2{\cdot}2H_2O$ in 10 L of distilled water. All reagents (KCl and $CaCl_2{\cdot}2H_2O$) used were of analytical grade. All measurements were carried out at room temperature (varying between 23.1 and 25.6 °C). In order to minimize the influence of contact time between solution and soil on soil pH readings, all measurements were done after 30 min of agitation following recommendations made by Qiu and Zhu (1986). For all pH measurements, soil samples of 10 g were used in order to effectively cover the junction of the combination electrode by the supernatant liquid, especially for 1:1 soil-to-solution ratios. Soil electrical conductivity (EC) was measured in a 1:5 soil-to-water ratio using a WTW 8120 conductivity meter, model number LF 521 (Wissenschaflich-Technische-Werkstätten, Weilheim IOB, Germany) expressed in dS m^{-1}. A standard solution of 0.01 N KCl was used to calibrate the conductivity meter.

2.3. Statistical analysis

Descriptive statistics, statistics of dispersion, normality of distribution and measure of central tendencies were carried out for soil pH data in different electrolytes and soil-to-solution ratios. Variability in soil pH was analyzed using the coefficient of variation. Simple linear regression analysis was performed with $pH_{1:5}$ $CaCl_2$, $pH_{1:5}$ H_2O, $pH_{1:1}$ KCl and $pH_{1:2.5}$ KCl as the dependent variables to test their overall relationship with $pH_{1:1}$ H_2O, $pH_{1:2.5}$ H_2O, $pH_{1:1}$ KCl and $pH_{1:2.5}$ KCl as independent variables. Data splitting using a cross-validation technique was used to validate the generated models. The linear models were calibrated using 38 soil samples. To evaluate the performance of the models, we used the coefficient of determination (R^2), the root mean square error (RMSE), the mean absolute error (MAE) and the index of agreement (*D*). The coefficient of determination is defined as the square of the Pearson's product-moment correlation coefficient and describes the proportion of the total variance in the observed data that can be explained by the model (Legates and McCabe, 1999). R^2 is given by;

$$R2=\left[\frac{\sum_{i=1}^{n}(O_i-O_{av})(P_i-P_{av})}{\left[\sum_{i=1}^{n}(O_i-O_{av})^2\right]^{0.5}\left[\sum_{i=1}^{n}(P_i-P_{av})^2\right]^{0.5}}\right]^2 \qquad (1)$$

R^2 ranges from 0.0 to 1.0, with higher values indicating better agreement.

Table 1
Descriptive statistics of the training and validation data used in the study ($n = 98$).

	Minimum	Maximum	Mean	Std. Error	Std. Deviation	CV (%)
$pH_{1:1}$ H_2O	5.22	6.42	5.84	0.02	0.23	3.94
$pH_{1:2.5}$ H_2O	5.34	6.48	5.93	0.02	0.22	3.71
$pH_{1:5}$ H_2O	5.38	6.55	6.00	0.02	0.21	3.50
$pH_{1:1}$ KCl	4.44	5.55	5.08	0.02	0.21	4.13
$pH_{1:2.5}$ KCl	4.51	5.69	5.19	0.02	0.21	4.05
$pH_{1:5}$ $CaCl_2$	5.00	6.11	5.57	0.02	0.21	3.77
ΔpH	−1.02	−0.49	−0.74	0.01	0.09	12.16
EC (dS/m)	0.02	0.13	0.04	0.01	0.02	50.00

Notes: ΔpH = $pH_{1:2.5}$ KCl - $pH_{1:2.5}$ H_2O.

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