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A Brief Study on Using pH_{H_2O} to Predict pH_{KCl} for Acid Soils

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Abstract

pH_{KCl} and pH_{H_2O} are two basic necessary indexes to reflect the acidity of asoil. Predicting pH_{KCl} directly from pH_{H_2O} could save the cost of laboratory work. In this study, the values of pH_{KCl} and pH_{H_2O} of 442 and 310 horizon samples from 126 and 98 soil profiles (0 - 120 cm in depth) surveyed from 2014 to 2015 in Guangxi and Yunnan were used to establish the optimal correlation model between pH_{KCl} and pH_{H_2O}. The results showed that: 1) pH_{KCl} is lower than pH_{H_2O}, pH_{KCl} was 0.07 - 1.99 units with a mean of 0.99 units lower than pH_{H_2O} for Guangxi, while 0.03 - 1.90 units with a mean of 0.89 lower than pH_{H2O} for Yunan. 2) There is significant positive correlation between pH_{KCl} and pH_{H_2O}, the optimal correlation models between pH_{KCl} (y) and pH_{H_2O} (x) for Guangxi and Yunnan are $y = 0.1963x^2 - 1.0512x + 4.338$, $R^2 = 0.836$, $p < 0.01$ and $y = 1.5882e^{0.1859x}$, $R^2 = 0.769$, $p < 0.01$, respectively, and the values of MAE and RSME of the models are 0.13 and 0.36 for Guangxi, 0.08 and 0.28 for Yunnan, respectively. There are significant negative correlations between pH_{KCl} with exchangeable H^+ and Al^{3+} ($R^2 = 0.487, 0.716$, $p < 0.01$), and pH_{KCl} is dominated by exchangeable Al^{3+}, followed by exchangeable H^+, and their contribution to pH_{KCl} were 71.1% and 28.7%, respectively.

Keywords

Predicting Model, pH_{KCl}, pH_{H_2O}, Correlation, Influential Factors, Acid Soil

1. Introduction

pH is a basic but important property of soil, it can influence soil other physicochemical properties, microorganism activities and plant growth. For an acid soil (pH < 7.0), usually containing more potential exchangeable Al^{3+} and H^+, pH measured by KCl extraction (here expressed as pH_{KCl}) is conventionally used to indicate soil acidity together with pH measured by water extraction (here expressed as pH_{H_2O}) [1]. Moreover, pH_{KCl} is also used to identify Alice property ($pH_{KCl} \le 4.0$) or Alice evidence ($pH_{KCl} \le 4.5$) in soil taxonomy [2] [3].

It is well known that there is internal relationship between pH_{KCl} and pH_{H_2O}, but so far little information is available on the quantitative correlation between pH_{KCl} and pH_{H_2O}, possibly due to the easiness in measuring pH_{KCl} as pH_{H_2O} in the laboratory. However, it is still worthy predicating pH_{KCl} directly from pH_{H_2O} on the special conditions, for examples, when there is no information of pH_{KCl} for soils in the historical literatures, or to save time and cost for a massive measurement in the laboratory. Meanwhile, some studies showed that soil pH is dominated by exchangeable Al^{3+}, followed by the exchangeable H^+ for acid soils in south China [4] [5], and exchangeable base, the contents of SOC and clays may also influence soil pH [6] [7] [8] [9], however, it is still unclear that the quantitative contribution of these influential factors to soil pH.

Thus, soil dada of Guangxi and Yunnan in South China obtained in 2014-2015 were used in this study in order to: 1) establish the optimal correlation model between pH_{KCl} and pH_{H_2O}, and 2) to quantitatively identity the contribution of exchangeable H^+, exchangeable Al^{3+}, exchangeable base, SOC and clay contents to soil pH.

2. Methods and Materials

2.1. Data of Soil Indexes

Soil Series Database of the National S & T Special Basic Project of Soil Series Survey and Compilation of *Soil Series of China* (Nos. 2008FY110600 & 2014FY110200) were used in this study. After the comparison of the data completeness of pH_{KCl}, pH_{H_2O}, exchangeable H^+, exchangeable Al^{3+}, exchangeable base, SOC and clay contents, and the elimination of abnormal data according to method of $\mu \pm 3\sigma$, 442 and 310 horizon samples from 126 and 98 soil profiles (0 - 120 cm in depth) surveyed from 2014 to 2015 in Guangxi and Yunnan (see **Figure 1**) were used to setup the optimal correlation model between pH_{KCl} and pH_{H_2O}, while 110 horizon samples from 30 soil profiles in Yunnan were adopted to quantitatively disclose the influence of exchangeable H^+, exchangeable Al^{3+}, exchangeable base, SOC and clay contents on soil pH.

2.2. Methods to Determine Soil Indexes

For soil indexes adopted in this study, pH_{H_2O} and pH_{KCl} were determined by potentiometer method after water extraction (soil: water is 1:2.5) and 1 $mol \cdot L^{-1}$ KCl extraction, respectively. Exchangeable H^+ and Al^{3+} by neutralization titration method after 1 $mol \cdot L^{-1}$ KCl extraction, exchangeable base by drying neutralization titration method after 1 $mol \cdot L^{-1}$ NH_4OAc extraction, SOC by volume method after K_2CrO_4 digestion, and clay content by pipet method [1].

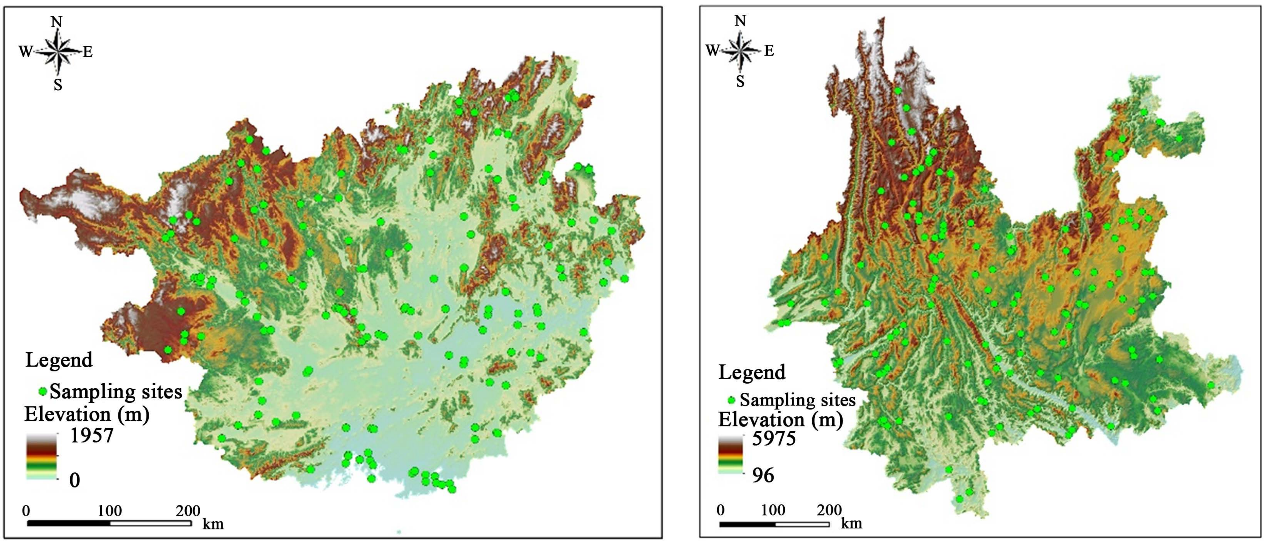

Figure 1. Sites of soil profiles in Guangxi (left) and Yunnan (right) surveyed from 2014 to 2015.

2.3. Data Processing, Modeling and Mapping

Microsoft Excel 2016 and IBM Statistics SPSS 20.0 were used for data processing, modeling and mapping.

3. Results

3.1. Statistical Information of Soil Indexes

Table 1 showed that soil pH_{KCl} ranged from 2.41 to 6.51 for Guangxi and from 3.21 to 5.91 for Yunnan, with a mean of 4.27 for Guangxi and 4.20 for Yunnan, respectively, which prove further that the soils in South China are generally acid [10] [11].

It is well known that pH_{KCl} is lower than pH_{H_2O} because KCl could extract more Al^{3+} from soil particles than water [1], however, **Table 1** showed that the lower extents are different in different regions, for examples, pH_{KCl} was 0.07 - 1.99 units with a mean of 0.99 units lower than pH_{H_2O} for Guangxi, while 0.03 - 1.90 units with a mean of 0.89 units lower than pH_{H_2O} for Yunnan.

Table 1 also showed that only pH_{H_2O} of Guangxi presented as normal distribution ($\pm 0.1 <$ skewness $< \pm 0.1$), while pH_{H_2O} of Yunnan, pH_{KCl} of Guangxi and Yunnan as extremely-skewed normal distribution (skewness $> \pm 0.3$), The values of kurtoses of pH_{H_2O} and pH_{KCl} of both Guangxi and Yunnan ranged from −0.44 to 0.42, indicating the probability density curves of pH_{H_2O} and pH_{KCl} were very flat (kurtosis < 0.67) [12].

3.2. Optimal Correlation Model between pH_{KCl} and pH_{H_2O}

IBM Statistics SPSS 20.0 is used to find the optimal correlation between pH_{KCl} and pH_{H_2O}. It can be seen from **Figure 2** that: 1) The values of R^2 showed again that there was significant positive correlation between pH_{KCl} and pH_{H_2O} for both Guangxi and Yunnan ($p < 0.01$). 2) The optimal correlation models were

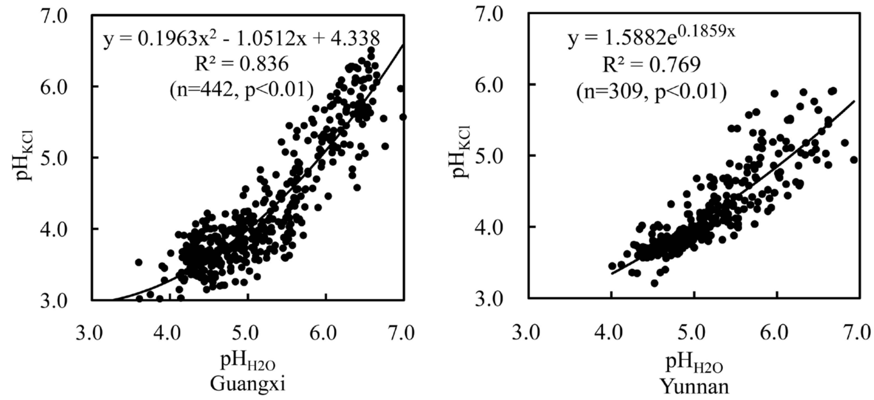

Figure 2. Optimal correlation models between measured pH_{KCl} and pH_{H_2O}.

Table 1. Statistical information of measured soil pH_{KCl} and pH_{H_2O}.

Region	Parameter	Minimum	Maximum	Mean	St. D	Skewness	Kurtosis
Guangxi	pH_{H_2O}	2.77	6.99	5.16	0.82	0.01	−0.36
(n = 442)	pH_{KCl}	2.41	6.51	4.27	0.89	0.74	−0.44
Yunnan	pH_{H_2O}	4.01	6.93	5.19	0.60	0.68	−0.21
(n = 310)	pH_{KCl}	3.21	5.91	4.20	0.56	1.05	0.42

different in Guangxi and Yunnan, quadratic model is found for Guangxi while exponential model for Yunnan, which may be attributed to the differences in climatic condition, soil types and land use types of the two regions. Values of MAE and RSME showed that the model accuracies were different in Guangxi and Yunnan, and the model accuracy is higher for Guangxi than Yunnan (**Figure 3**).

3.3. pH_{H_2O} Threshold for $pH_{KCl} \leq 4.0$ or 4.5

It is our concern to know pH_{H_2O} corresponding to $pH_{KCl} \leq 4.0$ or 4.5, which is the threshold of Alice property or Alice evidence in soil taxonomy. It can be seen from **Table 2** that the estimated pH_{KCl} would be most likely lower than 4.0 or 4.5 when the measured $pH_{H_2O} \leq 5.0$ or 5.5 for a soil in south China judged from the optimal correlation models in **Figure 2**.

Here, pH_{H_2O} and pH_{KCl} dada of 211horizons of 58 acid soil profiles surveyed from 2009 to 2010 in Guangdong were used to validate the proposed pH_{H_2O} threshold (≤5.0 or ≤5.5), the results showed that pH_{KCl} was within 3.08 - 4.21 (n = 173, pH_{KCl} of 98.6% soil samples lower than 4.0) and from 3.08 - 5.00 (n = 202, pH_{KCl} of all soil samples lower than 4.5) with a mean of 3.67 or 3.74 respectively when $pH_{H_2O} \leq 5.5$ or 5.0, indicating the proposed pH_{H_2O} thresholds are reliable.

3.4. Contribution of Influential Factors to Soil pH

Table 3 showed the statistical information of values of pH_{KCl}, clay, SOC, free Fe_2O_3, exchangeable H^+, Al^{3+} and base of 110 horizon samples of 30 soil profiles

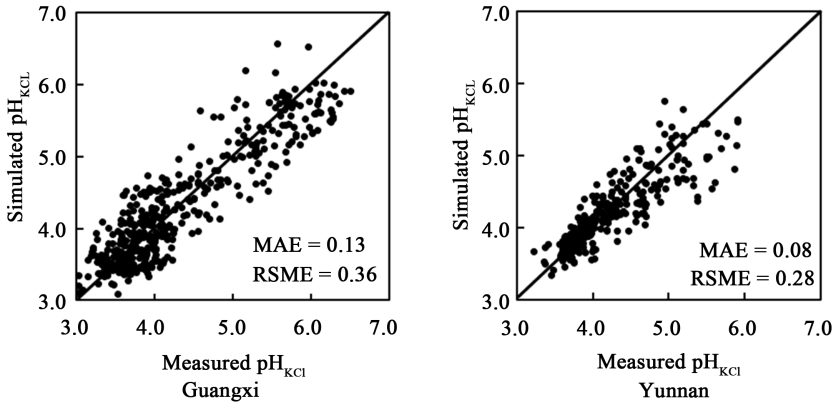

Figure 3. Comparison between simulated and measured pH$_{KCl}$. MAE is mean absolute error, while RMSE is root mean square error.

Table 2. pH$_{H_2O}$ thresholds for pH$_{KCl}$ ≤ 4.5 or 4.0.

pH$_{KCl}$	pH$_{H_2O}$	
	Guangxi	Yunnan
≤4.5	5.51	5.60
≤4.0	5.02	4.97

Table 3. Statistics of basic properties of soil samples of Yunnan (n = 110).

Soil indexes	pH$_{KCl}$	Clay g·kg^{-1}	SOC g·kg^{-1}	Free Fe_2O_3 g·kg^{-1}	H^+ cmol (+) kg^{-1}	Al^{3+} cmol (+) kg^{-1}	Exchangeable base cmol (+) kg^{-1}
Mean	3.81	413	11.01	52.27	0.25	5.29	2.47
S.D.	0.22	102	8.85	29.50	0.41	2.93	2.14

in Yunnan. **Table 4** showed Pearson correlation coefficients between pH$_{KCl}$ with other soil indexes. It can be seen that there were extremely significant correlations between pH$_{KCl}$ with exchangeable H^+ and Al^{3+}, while significant correlation between pH$_{KCl}$ with exchangeable base, which indicate that exchangeable Al^{3+}, H^+ and base are the influential factors of soil pH, and their optimal correlation models with pH$_{KCl}$ were all in quadratic form (see **Table 3** and **Figure 4**).

The linear regression model between pH$_{KCl}$ with exchangeable Al^{3+}, H^+ and base was obtained by using IBM Statistics SPSS 20.0 as pH$_{KCl}$ = 4.087 − 0.448H^+ − 0.042Al^{3+} − 0.001 Base ($R = 0.764$, $R^2 = 0.583$, $F = 49.41$, $p < 0.01$), which could be simplified as pH$_{KCl}$ = 4.087 − 0.448H^+ − 0.042Al^{3+} since the exchangeable base could be neglected.

The linear regression model between pH$_{KCl}$ with the normalized exchangeable H^+ and Al^{3+} was obtained as pH$_{KCl}$ = 4.064 − 0.211H^+ − 0.522 Al^{3+} ($R = 0.763$, $R^2 = 0.581$, $F = 49.08$, $p < 0.01$). The contribution of Al^{3+} and H^+ to pH$_{KCl}$ were 71.1% and 28.7% after normalizing the coefficients of Al^{3+} and H^+, which indicate further pH$_{KCl}$ is mainly dominated by exchangeable Al^{3+}, followed by exchangeable H^+ [4]-[9].

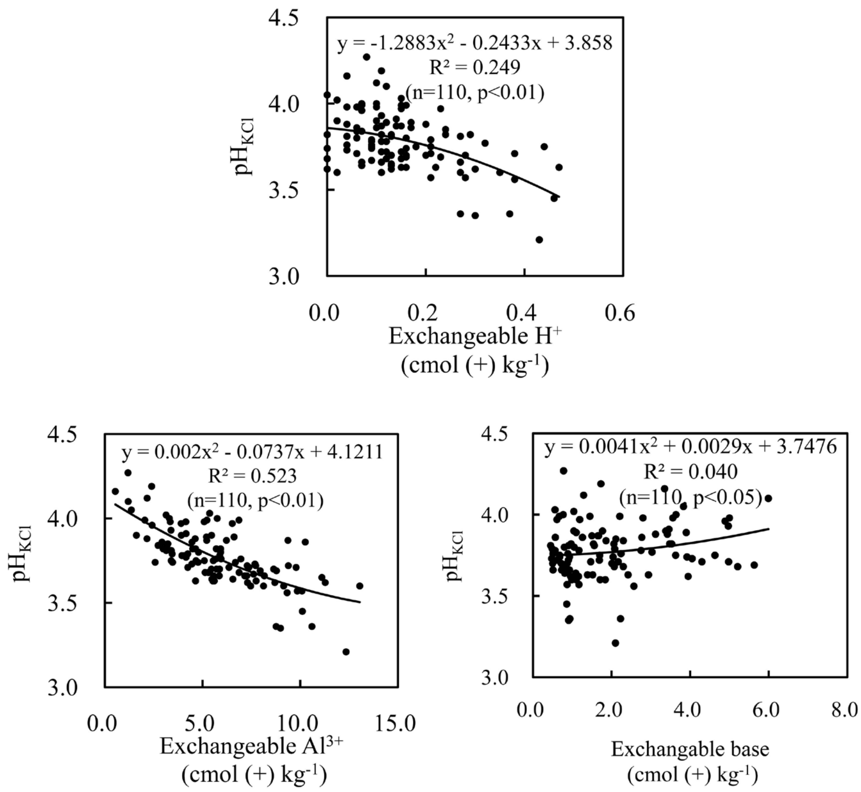

Figure 4. Optimal correlation models between pH_{KCl} with exchangeable H^+, Al^{3+} and base.

Table 4. Pearson correlation coefficients between pH_{KCl} and other indexes (n = 110).

Soil indexes	Clay	SOC	H^+	Al^{3+}	BS	Free Fe_2O_3
pH_{KCl}	0.011	−0.048	−0.487**	−0.716**	0.194*	0.117

**Significant at 0.01 level, *Significant at 0.05 level.

3.5. Discussion

Soil acidification is a natural process in tropical and subtropical regions due to higher rate of weathering and leaching under hot and humid climatic conditions [13] [14] [15], it is accelerated greatly due to acidic deposition and excess application of acid fertilizer in agricultural system [16] [17] [18] [19]. Our data showed that soil pH_{KCl} ranged from 2.41 to 6.51 for Guangxi and from 3.21 to 5.91 for Yunnan, which proves further that the soils in South China are generally acid [6] [10] [11].

Although it is well known that pH_{KCl} certainly has inner relation with pH_{H_2O}, so far there is no quantitative model between the two indexes. Our study not only proved further the quantitative relation between pH_{KCl} and pH_{H_2O}, but also established the correlation models and further found that the correlation models are different in different regions, it is useful to predict soil pH_{KCl} directly from pH_{H_2O} when there is no available information of pH_{KCl} or to save time and cost for a massive measurement in the laboratory.

Our study found the optimal correlation models between soil pH and exchangeable Al^{3+} and H^+ are in quadratic form, other studies showed the optimal correlation models between soil pH and exchangeable acid are different, which include power [8] or quadratic forms [9]. Different optimal models may be attributed to the differences in climatic conditions, soil types and land use types for the different studied regions.

Studies already proved that the main form of exchangeable acidity is found in the form of exchangeable Al^{3+} in acid soils and disclosed the mechanism of soil acidification [6] [19] [20] [21] [22]. Our study showed that the content of Al^{3+} of soil samples in Yunnan were 5.29 ± 2.93 cmol (+) kg^{-1}, higher than H^+, which was 0.25 ± 0.41 cmol (+) kg^{-1}, meanwhile, exchangeable Al^{3+} has more significant correlation (R^2 = 0.716) with soil pH compared with exchangeable H^+ (R^2 = 0.487), Thus, it is normal that exchangeable Al^{3+}contributes more (71.1%) to soil pH compared to exchangeable H^+ (28.7%).

4. Conclusion

By using the database of soil properties of Guangxi and Yunnan, this study discloses that pH_{KCl} is meanly 1.0 unit lower than pH_{H_2O}. There is significant positive correlation between pH_{KCl} and pH_{H_2O}, but the optimal correlation models are in quadratic or exponential forms for different regions. There are significant negative correlations between pH_{KCl} with exchangeable H^+ and Al^{3+}, and exchangeable Al^{3+} and H^+ contribute 71.1% and 28.7% to soil pH, respectively.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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