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Salt Concentration and Measurement of Soil pH

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Abstract: The measured value of soil pH depends in part on the laboratory procedures used, such as the soil–solution ratio and soil solution electrolyte composition. One of the most significant factors affecting the measured value of soil pH is the electrolyte concentration of the soil solution. Since electrolyte concentration of agricultural soils can vary greatly during the year and between years, the date of sampling can result in highly variable pH values for samples with the same percentage of base saturation when soil pH is measured in deionized water. For example, we found a different relationship between extractable calcium (Ca) and pH (1:1 in deionized water) for about 18,000 soil samples from the same geographic area taken during winter of 2 years, differing in winter rainfall. On average, samples taken during the wetter year had higher pH for a given value of extractable Ca, consistent with a reduced ionic strength (more leaching) in the wet year. In a comparison of pH in water with pH in 0.01 M calcium chloride ($CaCl_2$) for 1,186 soil samples received from clients, the median difference in pH was 0.67. It is notable that 20% of the samples had a difference of >0.8 and 10% had a difference of >0.9 pH units. Some samples with differences larger than the median may not receive a lime recommendation when needed because of the erroneously high pH reading in water caused by low ionic strength. The stability of pH readings in 0.01 M $CaCl_2$ essentially eliminates this problem.

Keywords: Acid soils, calcium chloride pH, pH

INTRODUCTION

In routine soil testing, one of the most important measurements is soil pH. In areas with acid soils, a recommendation to apply lime is based on

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soil pH being less than a critical value that depends on the crop to be grown. If soils are poorly buffered, an accurate measurement is especially important because pHs drop more easily to levels at which aluminum (Al) and manganese (Mn) toxicities may occur.

Although the measurement of soil pH is relatively simple in practice, the measured value for any soil sample depends in part on the laboratory procedures used, such as the soil–solution ratio, the electrolyte composition of the soil solution, stirring vs not stirring during measurement, and position of the calomel electrode during measurement for samples not being stirred (Sumner 1994; Thomas 1996). One of the most significant factors that affect the measured value of soil pH is the electrolyte concentration of the solution, especially when soil pH is measured in deionized water (pH_{H2O}). Sumner noted that relatively small increases in the salt concentrations from typical crop fertilization rates often cause decreases of more than 0.5 pH units in the pH_{H2O}. He cited data from Adams (1984), who found that the pH_{H2O} of an Alabama Ultisol was reduced by 0.7 pH units by a typical crop fertilization rate, without a corresponding increase in total acidity. The decrease in pH_{H2O} was considered to be due to the salt added in the fertilizer. Biological reactions can also affect pH_{H2O}, not only because of the acidity that results from nitrification and other reactions but also because of the increase in soil solution ionic strength that results from the acid-producing reactions (Liu et al. 2008). Black (1993) noted that an increase in soluble salts can have a pronounced effect on the measured values in soil pH_{H2O} but no appreciable effect on the titratable acidity in the soil.

Date of sampling during the year would be expected to affect the measured values of soil pH, because the amount of salt in the soil solution would be heavily influenced by crop production inputs and the weather. In the southeastern United States, the soil solution would be relatively low in salts during the primary soil testing season for summer crops (January through March) because of the typically high winter rainfall, sandy soils, and time (several months) since the last fertilizer application. Higher soil pH_{H2O} due to lower salt levels would therefore be expected for samples taken during the winter time period. In support of this idea, Shuman et al. (1983) found that pH measured in water was always lower when samples were taken in the fall (typically the driest time of year) compared to winter samples. In addition, the amount of winter rainfall varies between years in the southeastern United States, causing variable leaching of the soil solution. As a result, when measured in water, soil pH may also be different between years because of weather-related changes in the salt concentration of the soil solution, even though a soil may have the same amount of total acidity and the same levels of calcium and magnesium.

Schofield and Taylor (1955) recommended that soil pH be measured in 0.01 M calcium chloride (pH_{CaCl2}), because its concentration approximates the salt concentration of the soil solution in many fertile soils. Because small changes in ionic strength of the soil solution may change soil pH significantly without changes in titratable acidity, this may be an even more important reason to measure pH routinely in 0.01 M calcium chloride. To minimize these errors, Rayment and Higginson (1992) recommended the measurement of pH at a soil–solution ratio of 1:1 using 0.01 M $CaCl_2$ for soils of Australia. The objective of this study was to evaluate errors in soil pH_{H2O} due to weather and environment and show how measurement of pH_{CaCl2} can reduce those errors for soils in the southeastern United States.

MATERIALS AND METHODS

Effect of Soil Solution Calcium Chloride Concentration on Soil pH

Because calcium is typically the cation of highest concentration in the soil solution, we studied how soil pH was affected by the concentration of calcium chloride that varied from zero to 1 M concentration. Three soils from the coastal plain of Georgia that varied in their organic matter and clay contents were selected for the study, and each was prepared to be relatively salt free by leaching with 15 cm of deionized water in a Buchner funnel. The soils were then air dried, reground, and sieved through a 2-mm sieve. Soil pH was measured in a soil–solution ratio of 1:1, using calcium chloride solutions of 0, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 0.1, and 1 M. Soil pH was determined on triplicate samples starting with samples at the lowest concentrations of calcium chloride and proceeding to the highest concentrations. Soil pH was measured using a Labfit AS-3000 robotic pH analyzer.

Effect of Winter Rainfall on Soil pH Values

Soil pH_{H2O} (1:1 soil–water) and Mehlich I–extractable calcium were in past years determined routinely on soils submitted by clients to the University of Georgia (UGA) Soil, Plant, and Water Laboratory. These data are stored in the laboratory database and are available for analysis. Extractable calcium was determined by Mehlich I extraction (Southern Cooperative Series 1983), followed by determination of calcium in the extract by inductively coupled plasma (ICP)–emission spectroscopy. Soil pH_{H2O} was also determined as described in Southern Cooperative Series (1983). Data from the Southwest Georgia Extension District from two contrasting seasons were compared, one relatively dry year with 33 cm of rain during the November through March time period (1998–99) and the other with 55 cm of rainfall during November through March (2000–1). Data of both pH and extractable calcium were averaged within ranges of pH_{H2O} to allow for easy comparison of the 2 years. The number of samples analyzed during the 2 years was similar (18,551 in 1998–99 and 18,574 in 2000–1).

Comparison of pH Measured in Water vs. pH Measured in 0.01 M Calcium Chloride

This study was carried out to gain a better understanding of the differences between soil pH measured in water compared to those measured in 0.01 M calcium chloride. The pH was determined for 1,186 soil samples selected at random from those submitted by clients in the state of Georgia for the time period from early January until mid-July 2004. Soil pH was measured using a Labfit AS-3000 robotic pH Analyzer (Labfit, Australia) using a soil–solution ratio of 1:1 in two separate analysis of each sample using deionized water and 0.01 M calcium chloride.

RESULTS AND DISCUSSION

Effect of Soil Solution Calcium Chloride Concentration on Soil pH

Results were similar for all soils; therefore, only the results from the soil Norfolk Depressional are shown here (Figure 1). There was relatively little effect on the measured values of soil pH at the three lowest concentrations of calcium chloride. At concentrations of 0.001 M and higher, there was an approximately linear decrease in pH to the highest concentration of 1 M. The pH in water was 6.0, whereas at a concentration of 0.01 M, the pH was just less than 5.2, a drop of about 0.8 pH units. Measurement of pH in a solution of 0.01 M calcium chloride was recommended by Schofield and Taylor (1955), because its concentration approximates the salt concentration of the soil solution in many fertile soils. As can be noted in Figure 1, the concentration of salt from fertilizer added as muriate of potash and ammonium nitrate at typical agronomic rates of 135 kg dipotassium oxide (K_2O) and 170 kg nitrogen (N) per hectare gave salt levels of 0.006 M, assuming that all fertilizer was incorporated into the top 10 cm of soil, the soil bulk density was 1.5 $g\,cm^{-3}$, and the laboratory procedure would employ a soil–solution ratio of 1:1. Even if a soil received manure or fertilizer

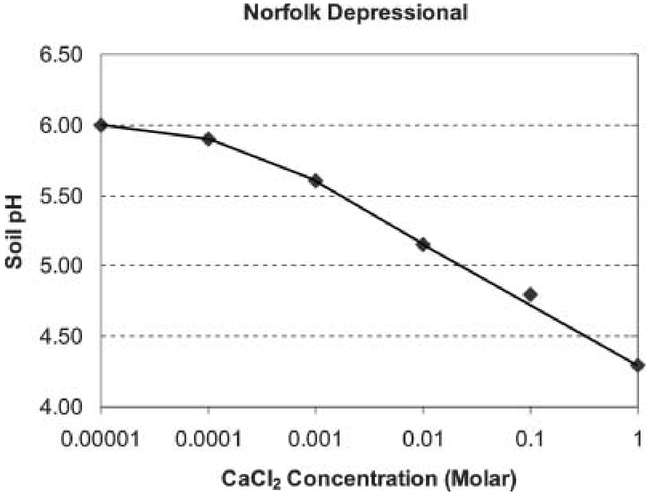


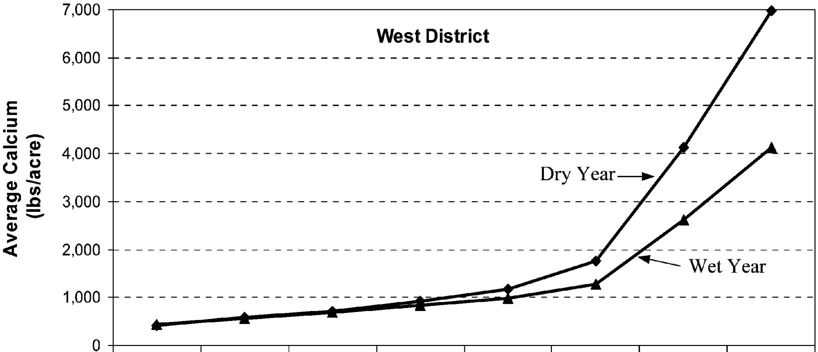
Figure 1. Soil pH of Norfolk Depressional sandy loam (1.41% organic C), as affected by calcium chloride solution concentration.

immediately before it was sampled for measurement of pH, the error due to variation in salt content of the soil would be considerably less if the measurement of pH was carried out in 0.01 M calcium chloride. For example, if rates of N and potassium (K) were applied as described previously, the final concentration of salt, if the solution used in the procedure was 0.01 M, would be $0.01 + 0.006 = 0.016$ M. As can be noted in Figure 1, the pH of the Norfolk Depressional would be approximately 5.15 when measured at a concentration of 0.01 M. When measured at a salt concentration of 0.016 M, the soil pH would only drop an additional 0.1 pH unit. This compares to a difference of 0.8 pH units when deionized water is used for the measurement of pH of the Norfolk Depressional with and without the addition of N and K fertilizer at the rates given previously. Although fertilizer is more typically applied after soil analysis, manures are sometimes applied prior to sampling of soil, and they often contain considerable salt that can affect the measurement of pH in water.

Effect of Winter Rainfall on Soil pH Values

The amount of winter rainfall varies between years in the southeastern United States, causing variable leaching of the soil solution. As a result, when measured in water, soil pH may also be different between years due to weather-related changes in the salt concentration of the soil solution, even though a soil may have the same amount of total acidity and the same levels of calcium and magnesium. This is illustrated by a comparison of data of soil pH as a function of calcium extracted by Mehlich I for the winter sampling period for 2 years, a relatively dry winter of 1998–99 (33 cm of rain at Plains, Georgia) and the relatively wet winter of 2000–1 (55 cm of rain at Plains, Georgia). Only UGA soil test results from the West Extension District (the most intensive crop production area) are shown, but results were similar for the other two south Georgia districts. When soil test results for the average Mehlich I calcium were plotted against the average pH for each pH range, we found different relationships for the 2 years (Figure 2). The wetter winter (2000–1) consistently had less Mehlich I calcium, especially at the upper pH ranges, than the drier (and warmer by 1.7 °C) winter.

If measured values of soil pH in water were more exact and independent of soil solution composition, more than 18,000 samples should give a similar relationship between pH and soil calcium that does not vary by year. Because the average soil type sampled should not vary, the average relationship between Mehlich I extractable calcium and pH of soils in the region should be the same each year. Apparently, the different relationship that emerged between the 2 years was due to a more dilute soil solution in the wetter year, resulting in a higher pH at any



	pH <5.5	pH 5.5-5.9	pH 6.0-6.4	pH 6.5-6.7	pH 6.8-7.0	pH 7.1-7.4	pH 7.5-7.8	pH >7.8
◆ Average Ca 11/1/98 - 3/31/99	419	583	721	912	1,176	1,769	4,133	6,982
#Samples 11/1/98 - 3/31/99	1,994	4,441	8,851	2,173	768	251	54	19
▲ Average Ca 11/1/00 - 3/31/01	438	573	701	842	984	1,269	2,625	4,126
#Samples 11/1/00 - 3/31/01	1,124	3,269	8,560	3,322	1,658	606	107	28

Figure 2. Average Mehlich I extractable calcium as related to soil pH for soil samples analyzed for the West Extension district in Georgia for the period 1 November 1998 to 31 March 1999 and for the period 1 November 2000 to 31 March 2001.

given level of soil calcium (or, as shown in Figure 2, a lower Mehlich I calcium for a given pH range).

Based on the results shown in Figure 1, time of sampling during the year would be expected to affect the measured values of soil pH, because the amount of salt in the soil solution would be heavily influenced by crop production inputs and the weather. In the southeast United States, the soil solution would be relatively low in salts during the primary soil testing season for summer crops (January through March) because of the typically high winter rainfall, sandy soils, and time (several months) since the last fertilizer application. Higher soil pH (measured in water) due to lower salt levels would therefore be expected for samples taken during the winter time period. In support of this idea, Shuman et al. (1983) found that pH measured in water was always lower when samples were taken in the fall (typically the driest time of year) compared to winter samples. As would be suggested from the previous discussion, measuring pH in 0.01 M calcium chloride would provide more stable readings of pH and reduce the variability due to management and seasonal variation in weather, especially rainfall.

Comparison of pH Measured in Water vs. pH Measured in 0.01 M Calcium Chloride

The results from that comparison are shown in Figure 3. A linear equation provides a quantitative comparison between the two methods. At a pH of 4.50 in 0.01 M calcium chloride (pH_{CaCl2}), the average water pH from the regression was 5.25, a difference of 0.75 pH units. At a pH of 6.0 in 0.01 M $CaCl_2$, the average water pH from the regression was 6.64, a difference of 0.64 pH units.

It is also of interest to characterize the variation in values of pH_{H2O}–pH_{CaCl2}. To describe the variation of pH for the data shown in Figure 3, pH values in 0.01 M $CaCl_2$ were subtracted from those in water for each sample. The differences were then placed in rank order from the lowest to the highest, and then the fractional probability for each (n / N + 1) was also calculated and the data plotted. In this procedure, n is the rank order from low to high, and N is the total number of observations. The results of cumulative probability of (pH_{H2O}–pH_{CaCl2}) are shown in Figure 4. For our set of data, approximately 5% of the samples had (pH_{H2O}–pH_{CaCl2}) values of less than 0.2 pH units, indicating that a relatively small proportion of the soil samples had relatively high soil solution salt contents. At the other extreme, approximately 20% of the samples had differences in pH greater than 0.8, and 10% had a difference greater than 0.9 pH units. It should be noted that the difference in pH at the 50% probability level was approximately 0.67 pH units.

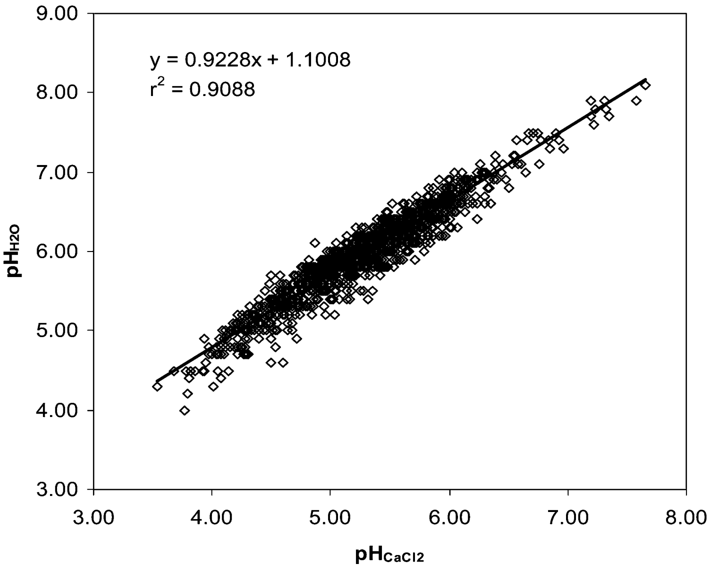


Figure 3. Comparison of 1:1 soil pH when measured in water with soil pH measured in 0.01 M $CaCl_2$ for the 1186 randomly selected samples submitted to the UGA soil testing laboratory for routine soil analysis from January to July 2004.

Implications for Soil Analysis

Soil pH measurements are most sensitive to small differences in soil solution salt concentration at very low soil solution salt levels. If soil pH

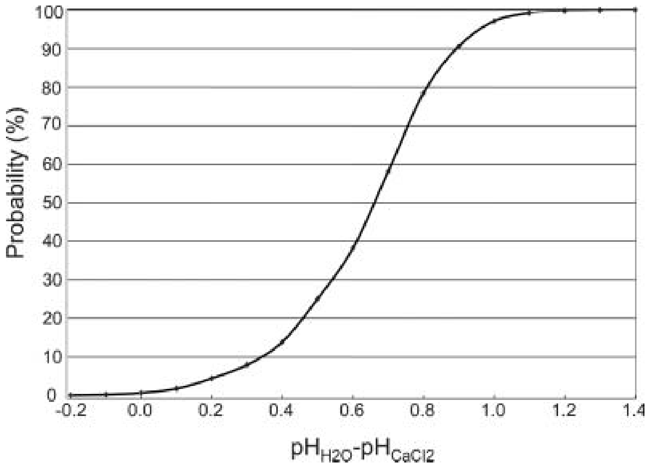


Figure 4. Cumulative probability of the differences in pH ($pH_{H2O} - pH_{CaCl2}$) for the 1186 routine soil samples shown in Figure 3.

is measured in 0.01 M $CaCl_2$, soil pH readings will be more stable both within a season and between years, because the normal seasonal or yearly differences in soil solution salt concentration are small compared to the 0.01 M concentration used in the measurement. The differences in pH values between the two methods discussed here (pH_{H2O}–pH_{CaCl2}) provide useful information about the impact that variation in soil solution salt contents have on lime recommendations when pH is measured in water.

The median soil sample from our tests had a difference in pH (pH_{H2O}–pH_{CaCl2}) of approximately 0.67. However, it is the 20% of samples with a pH difference of 0.8 or greater that are most troublesome, because they are likely to need a lime recommendation yet not receive it if the measured pH is slightly more than the target pH. Not receiving a lime recommendation when needed is an especially troubling problem for samples taken from fields that are poorly buffered and highly spatially variable. In these cases, the field areas with the lowest pH are at high risk for sensitive crops to develop aluminum and manganese toxicity.

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