Salt Concentration and Measurement of Soil pH
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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). One of the most significant factors that affects the measured value of soil pH is the electrolyte concentration of the solution. Sumner noted that relatively small increases in the salt concentrations from typical crop fertilization rates often cause decreases of over 0.5 pH units in the measured soil pH. He cited data from Adams (1984), who found that the soil pH in water of an Alabama Ultisol was reduced 0.7 pH units by a typical crop fertilization rate, and without a corresponding increase in total acidity. The decrease in pH was considered to be due to the salt added in the fertilizer.

Effect of soil solution concentration on soil pH. Since 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 molar 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 and 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 molar. 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 system.

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 Molar and higher, there was an approximately linear decrease in pH to the highest concentration of 1 Molar. The pH in water was 6.0, whereas at a concentration of 0.01 molar, the pH was just under 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 120 lb K_2O and 150 lb N per acre gave salt levels of 0.006 Molar, assuming that all fertilizer was incorporated into the top 10 cm of soil, the soil bulk density was approximately 1.5 g cm^{-3} and that the lab procedure would employ a soil:solution ratio of 1:1. Even if a soil received manure or fertilizer 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 K were applied as described above, the final concentration of salt if the solution used in the procedure was 0.01 M would be 0.01 + 0.006 = 0.016M. 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 units. 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 above. 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.
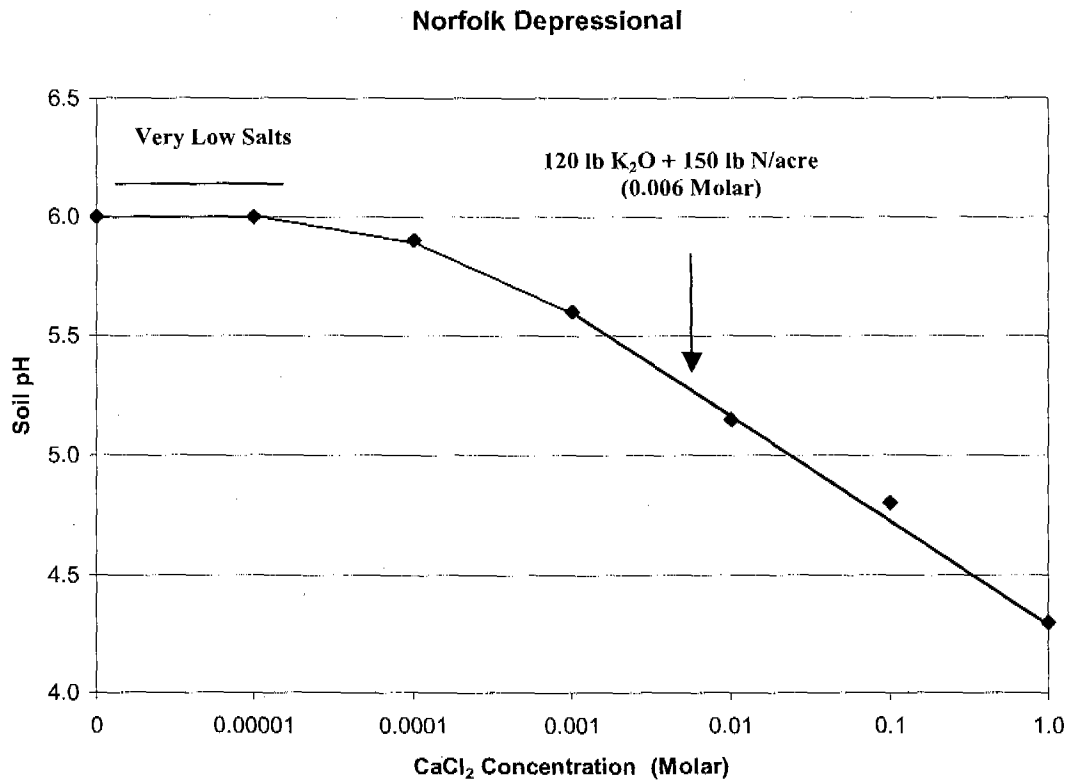
Norfolk Depressional

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

Seasonal variation in soil pH measured in water. 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 US, 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 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.

Effect of winter rainfall on soil pH values. The amount of winter rainfall varies between years in the Southeast 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 two years, a relatively dry Winter of 1998-99 (13.1 inches of rain at Plains, GA) and the relatively wet winter of 2000-2001 (21.7 inches of rain at Plains, GA). 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 two years (Figure 2). The wetter winter (2000-2001) consistently had less Mehlich I calcium, especially at the upper pH ranges than was the case for the drier (and warmer by 1.7 C) winter. The number of samples analyzed during the two years was similar (18,551 in 1998-99 and 18,574 in 2000-2001).

West District

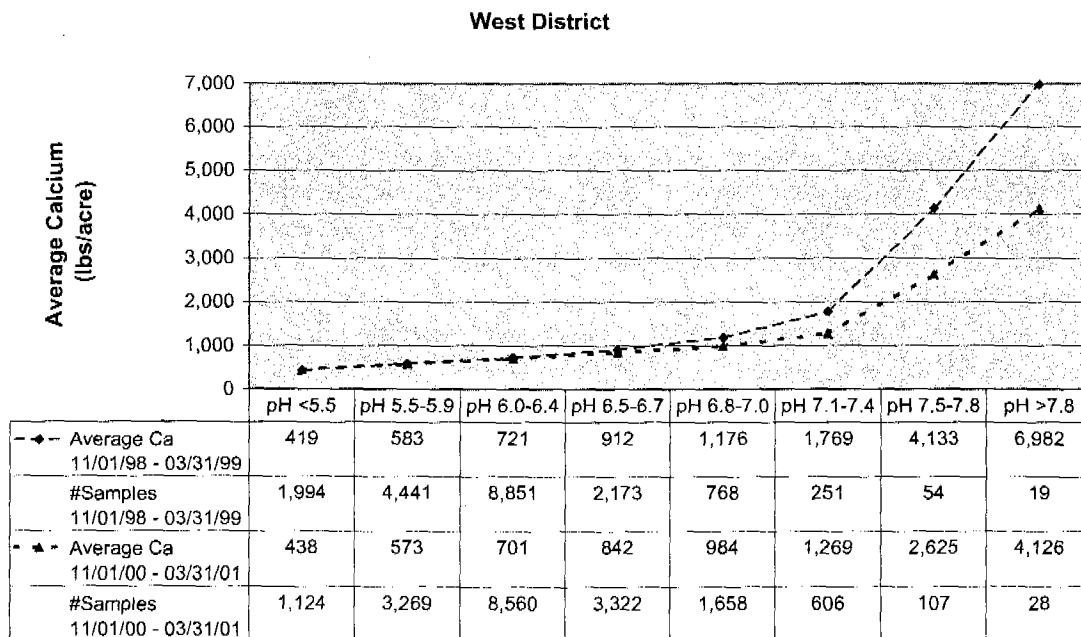|	pH <5.5	pH 5.5-5.9	pH 6.0-6.4	pH 6.5-6.7	pH 6.8-7.0	pH 7.1-7.4	pH 7.5-7.8	pH >7.8
Average Ca 11/01/98 - 03/31/99	419	583	721	912	1,176	1,769	4,133	6,982
#Samples 11/01/98 - 03/31/99	1,994	4,441	8,851	2,173	768	251	54	19
Average Ca 11/01/00 - 03/31/01	438	573	701	842	984	1,269	2,625	4,126
#Samples 11/01/00 - 03/31/01	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 November 1, 1998 to March 31, 1999and for the period November 1, 2000 to March 31, 2001.

If measured values of soil pH in water were more exact and independent of soil solution composition, over 18,000 samples should give a similar relationship between pH and soil calcium that does not vary by year. Since the average soil type sampled should not vary, ie, 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 two years was due to a more dilute soil solution in the wetter year, resulting in a higher pH at any given level of soil calcium (or as shown in Figure 2, a lower Mehlich I calcium for a given pH range).

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 approximately 3000 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. 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 (pH1), 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.
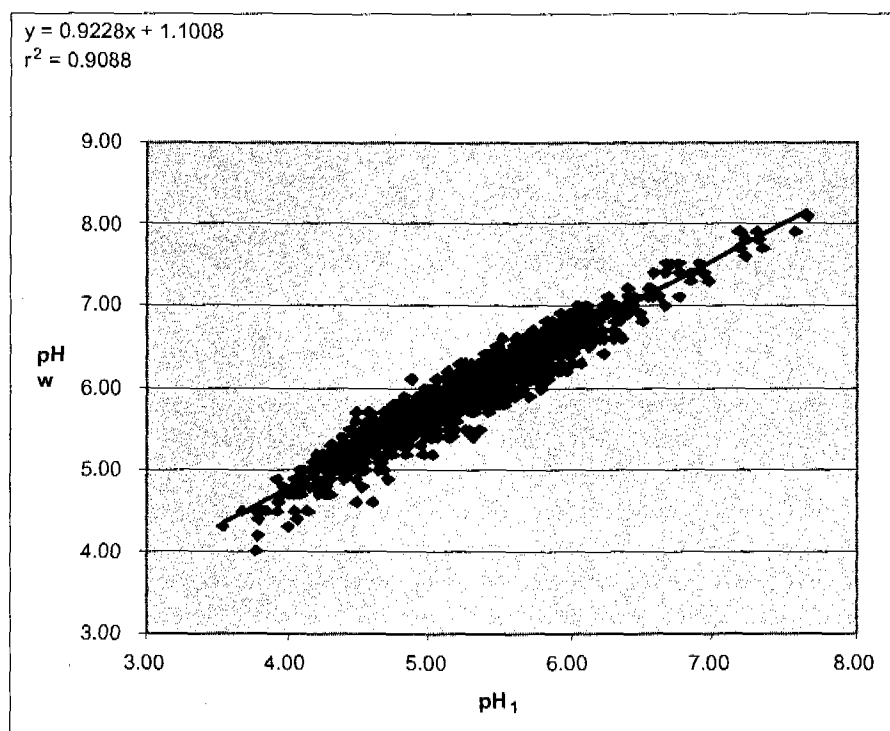

Figure 3. A comparison of 1:1 soil pH when measured in water with soil pH measured in 0.01 M CaCl$_2$ for subsample of approximately 3000 samples submitted to the UGA soil testing laboratory for routine soil analysis during January to July 2004.

It is also of interest to characterize the variation in values of pH_{H2O}- pH_{CaCl2}. In order 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. 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 values of less than 0.2 pH units, differences 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 of greater than 0.8. It should be noted that the difference in pH at the 50% probability level was approximately 0.67 pH units.
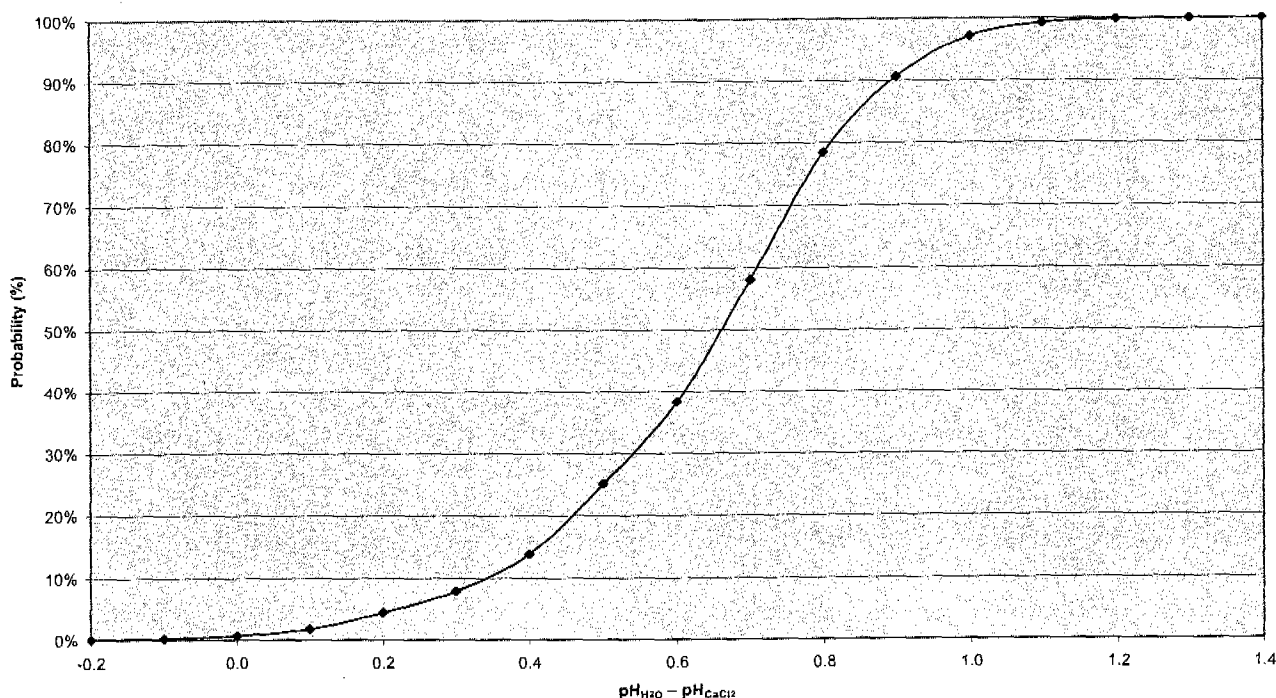

Figure 4. Cumulative probability of the differences in pH pH (pH_{H2O}- pH_{CaCl2}) for the approximately 3000 routine soil samples shown in Figure 3.

Implications on 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 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 molar 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 above 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 in the southeastern United States.

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