Soil pH Measurement is on the Menu Today: Salt or No Salt

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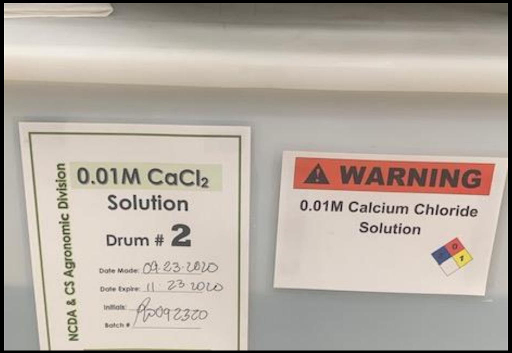
Soil pH

"The determination of the hydrogen-ion activity or pH of soils is by far the most commonly made soil test. It is widely used by soil testing labs and county agents for estimating lime needs of soils" (Peech, 1966).

Low pH, Al toxicity

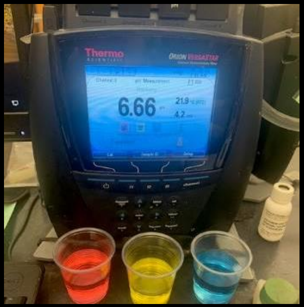
pH Analysis Today

- 1:1, 1:2, saturated paste, di H_2O, salt
- ALP, 2023
  - 1:1 – 63 labs (74%) → H_2O
  - 1:1 – 22 labs (26%) → 0.01 M $CaCl_2$
- NAPT, 2023
  - 1:1 – 74 labs (80%) → H_2O
  - 1:1 – 19 labs (20%) → 0.01 M $CaCl_2$



pH Analysis Today

- 2-point calibration buffers 4 and 7 common
- Stirring and measurement in suspension
  - Speeds the equilibrium and reading



- Wide range of equilibration times
  - 10, <u>15</u>, 30, 60, up to 120 minutes
- Automation using robots is prevalent
- Rinsing of electrodes

Definition and Measurement of pH

$$pH = -\log [H^+]$$

$$pH = -\log a_{H^+}$$

EMF (voltage) measured potentiometrically

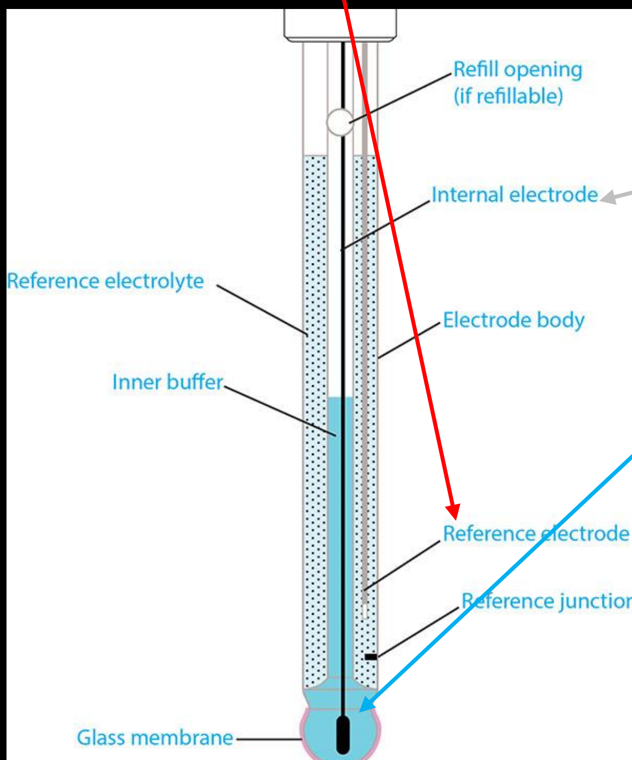
Measured by glass electrode – silver chloride electrode system

$$Ag \mid AgCl_2, KCl_{(sat)} \overset{E_j}{\parallel} \text{test solution} \mid \text{glass} \mid 0.1M\ HCl, AgCl_2 \mid Ag$$

Combination Electrode for pH

half cell $\qquad E_j \qquad$ half cell

$Ag \mid AgCl_2, KCl_{(sat)}$ || test solution || $glass \mid 0.1M\ HCl, AgCl_2 \mid Ag$



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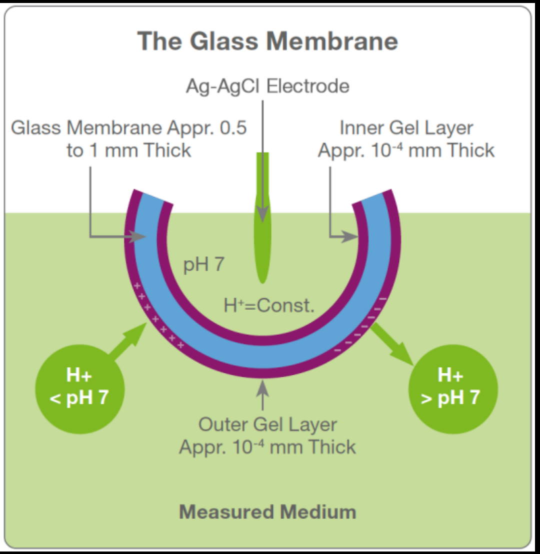
ATC
Probe

Glass Bulb…Sensing H^+

- Ion specific electrode – H^+ only
- Potential (voltage) Δ
  - Inside membrane - constant potential
    - Internal reference electrode
  - Outside membrane - unknown potential
- Voltage difference
  - Measured @ meter



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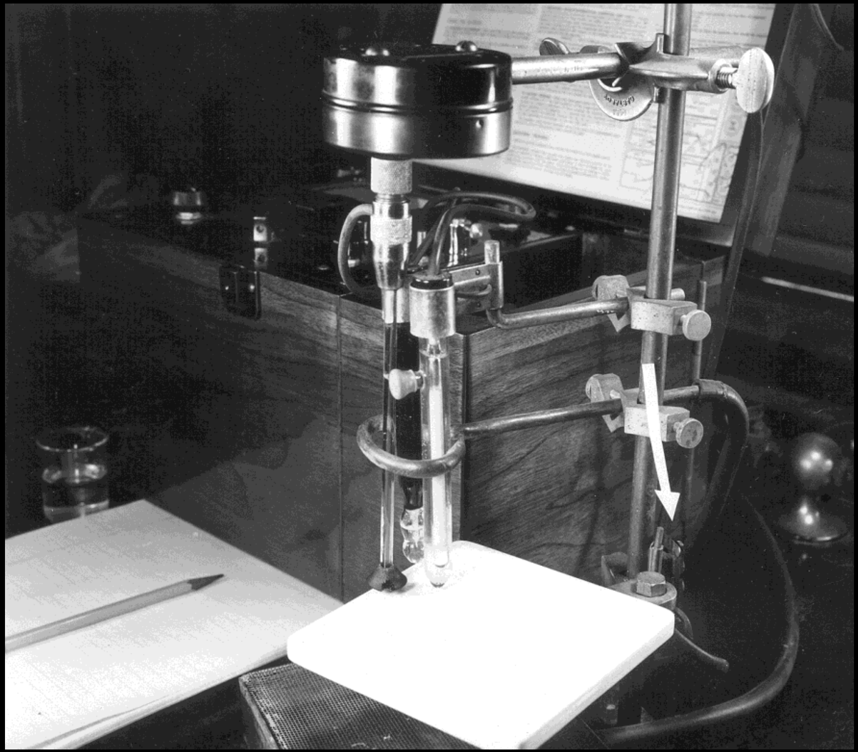
Factors Affecting Measurement

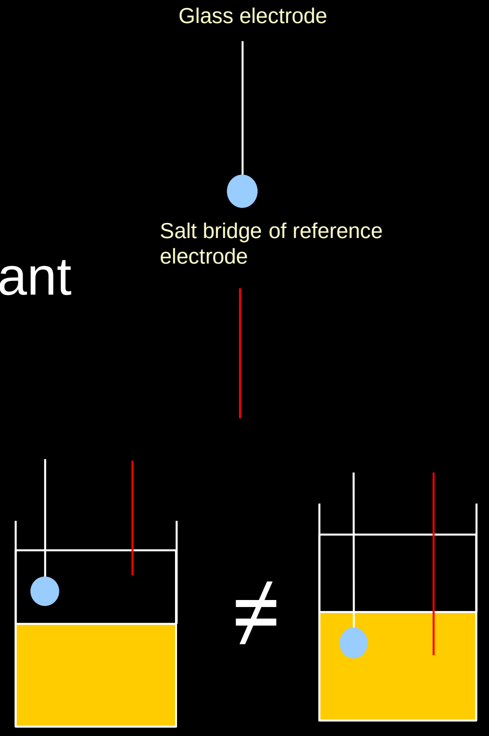
- Carbon dioxide
- Soil drying
- Equilibration time
- Soil to water ratio
- Junction potential
- Suspension effect
- Salt content



Beckman Model G

Electrode Placement & Junction Potential

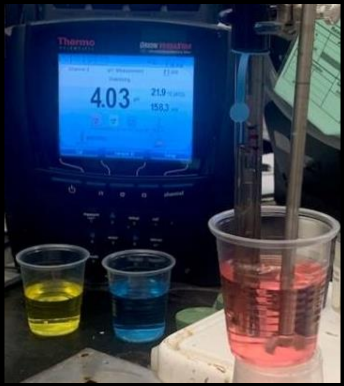
- Desire a stable Ej potential
- Mobility / diffusion of K^+, Cl^- in soil (charged system)
- High Ej possible if electrode in sediment
- Very sandy, low EC soil → Ej of concern
- Suggestions from Sumner
  - Use narrow soil:water ratio
  - Allow suspension to settle, reference in supernatant
  - No stirring…questions why this is done
  - Use of salt pH – 1 M KCL or 0.01 M $CaCl_2$



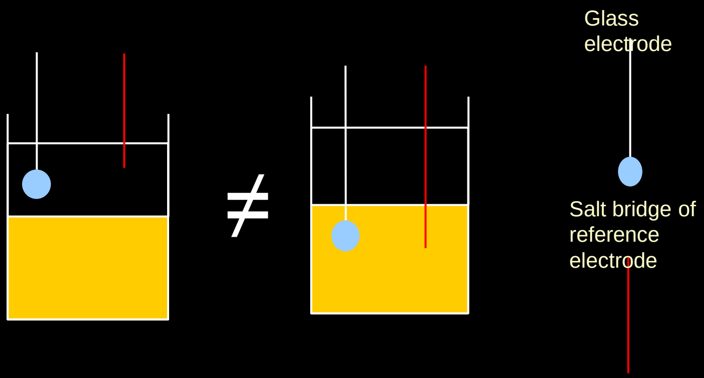
Sumner. 1994 Measurement of Soil pH: Problems and Solutions. Commun. Soil Sci Plant Anal., 40: 179 – 187.

Other Considerations on pH Measurement

- Reading pH in buffers; supernatant or soil suspension
  - Consider the differences in EC and potential electrode response



	EC (ds/m)
4 buffer	4.7
7 buffer	7.8
0.01 M $CaCl_2$	2.4



Miller and Kissel, 2010, SSSAJ, 74: 310-316.

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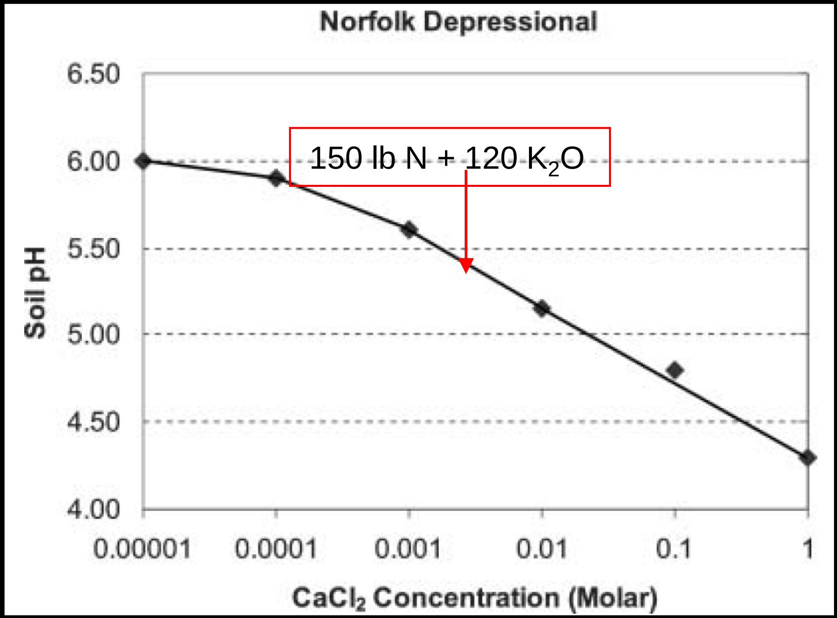
Recommendation for pH Measurement

- Electrode stability / measurement depends on salt strength
- Low EC soils, high pH bias in water (graphs)
- 0.01 M $CaC1_2$ recommended to ~ EC of fertile soils
  - Schofield and Taylor, 1955; Sumner, 1994



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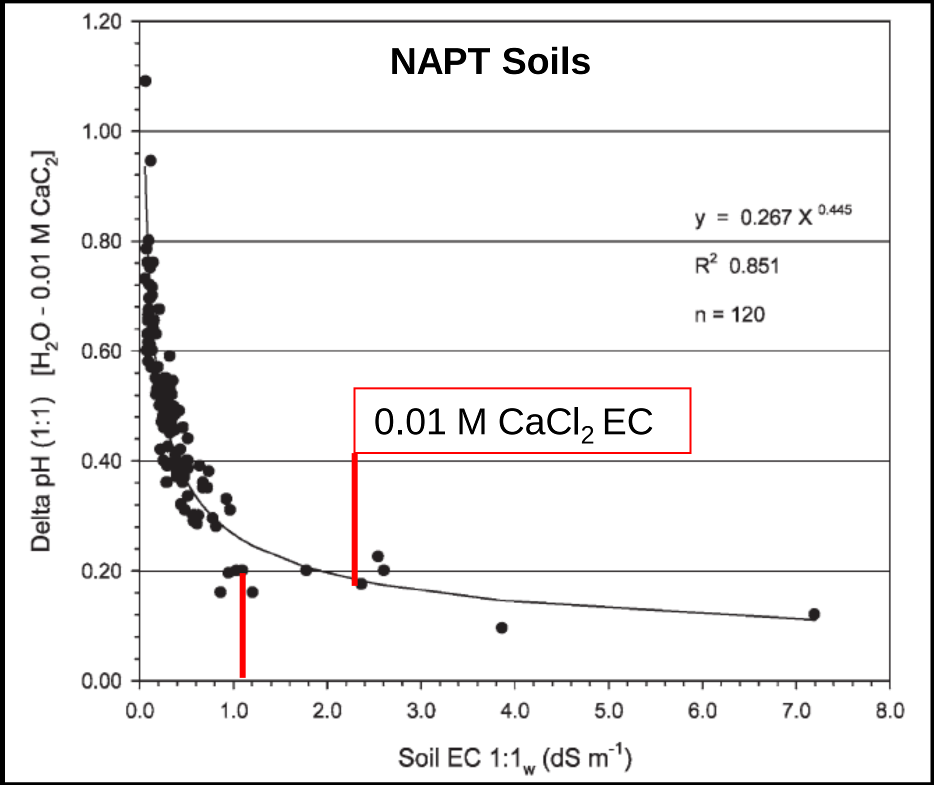

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In working with consultants and farmers, my perspective on pH…..

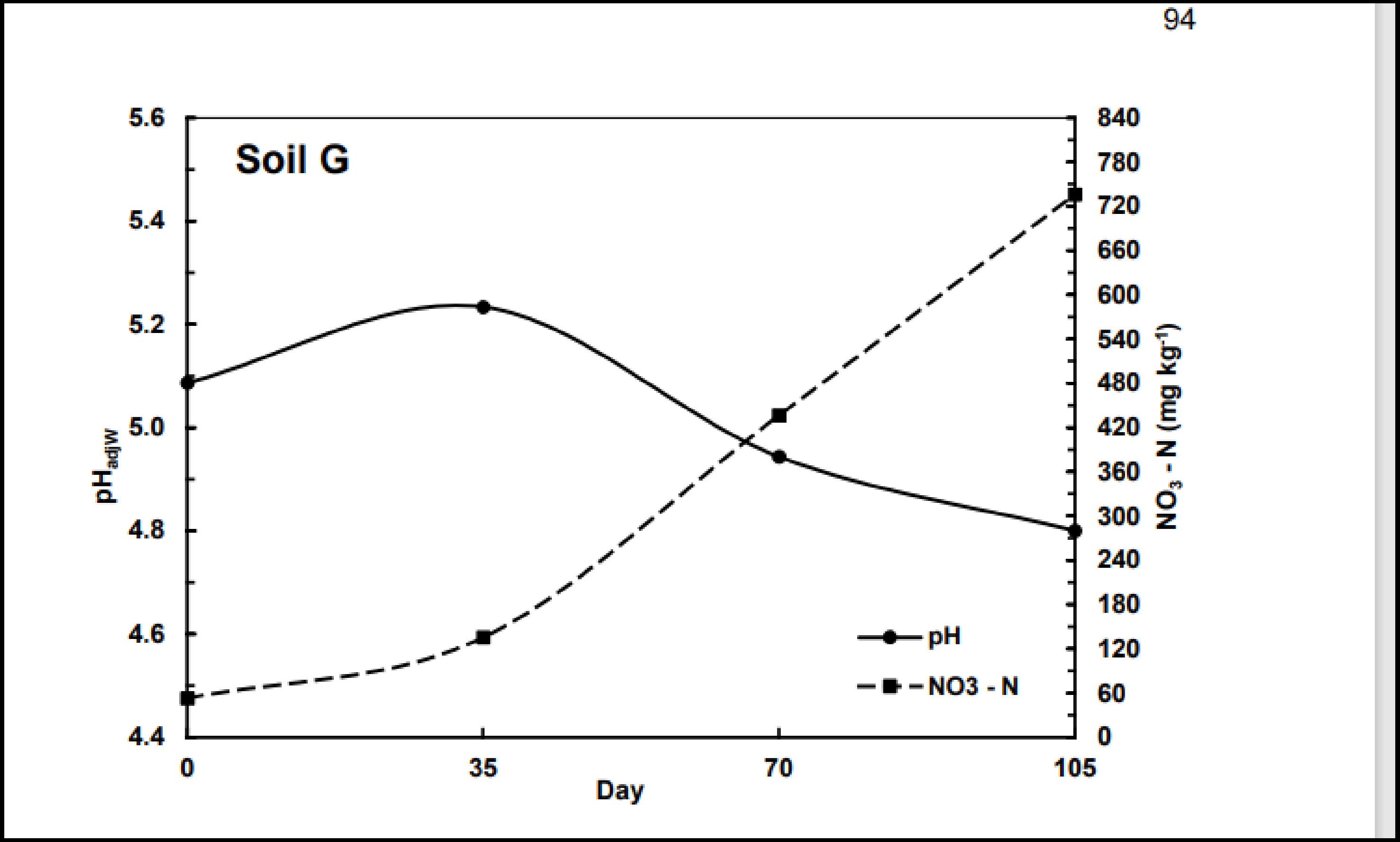
Most challenged and questioned measurements in soil testing labs today is pH and the lime requirement.

Why is my pH 5.5 when it was 5.6 and I applied lime?

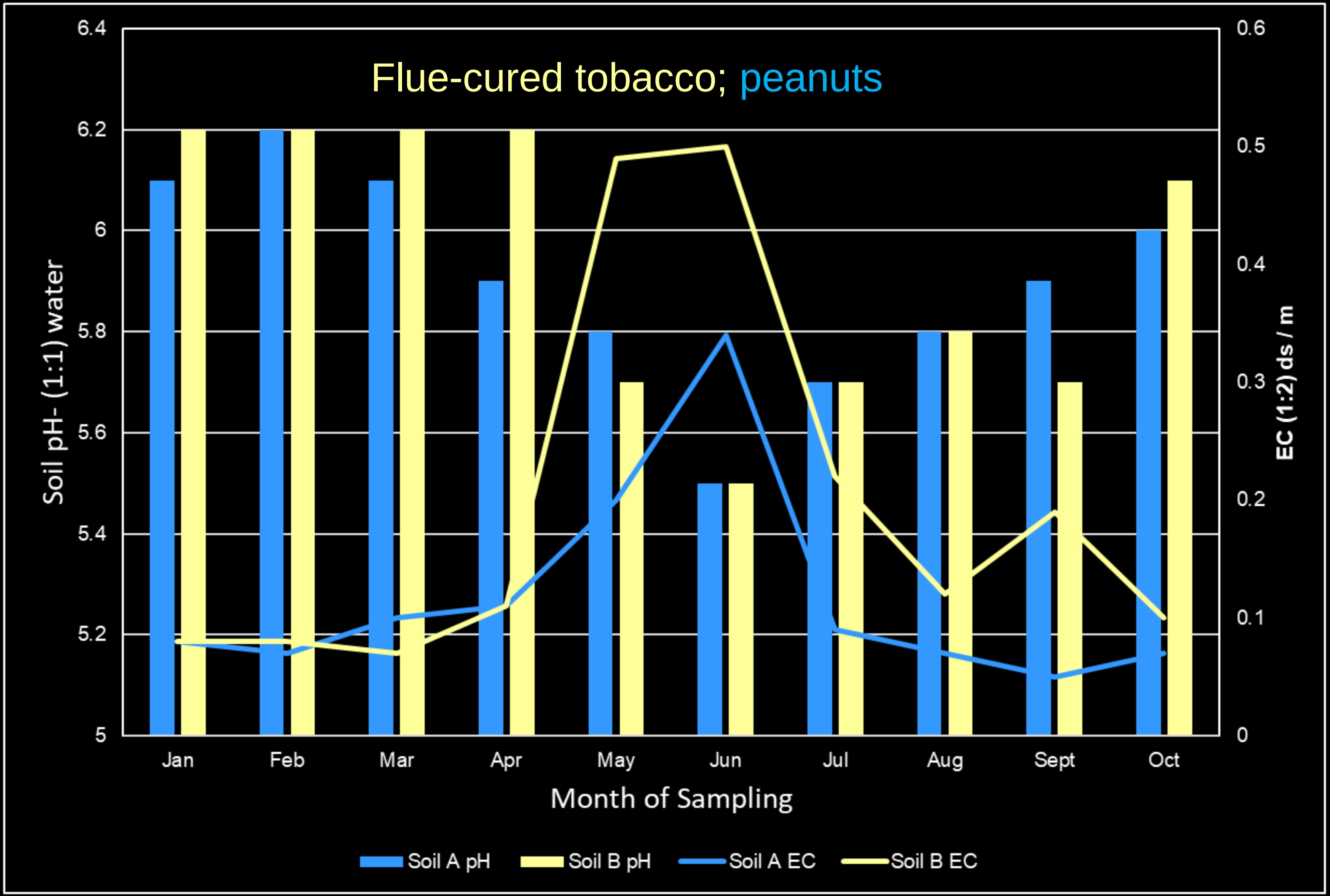
Why is pH fluctuating???

pH Fluctuates in Season?

- Biological activity



Seasonal Fluctuations in Soil pH



Data from Growing Season

EC and pHw after leaching with of water

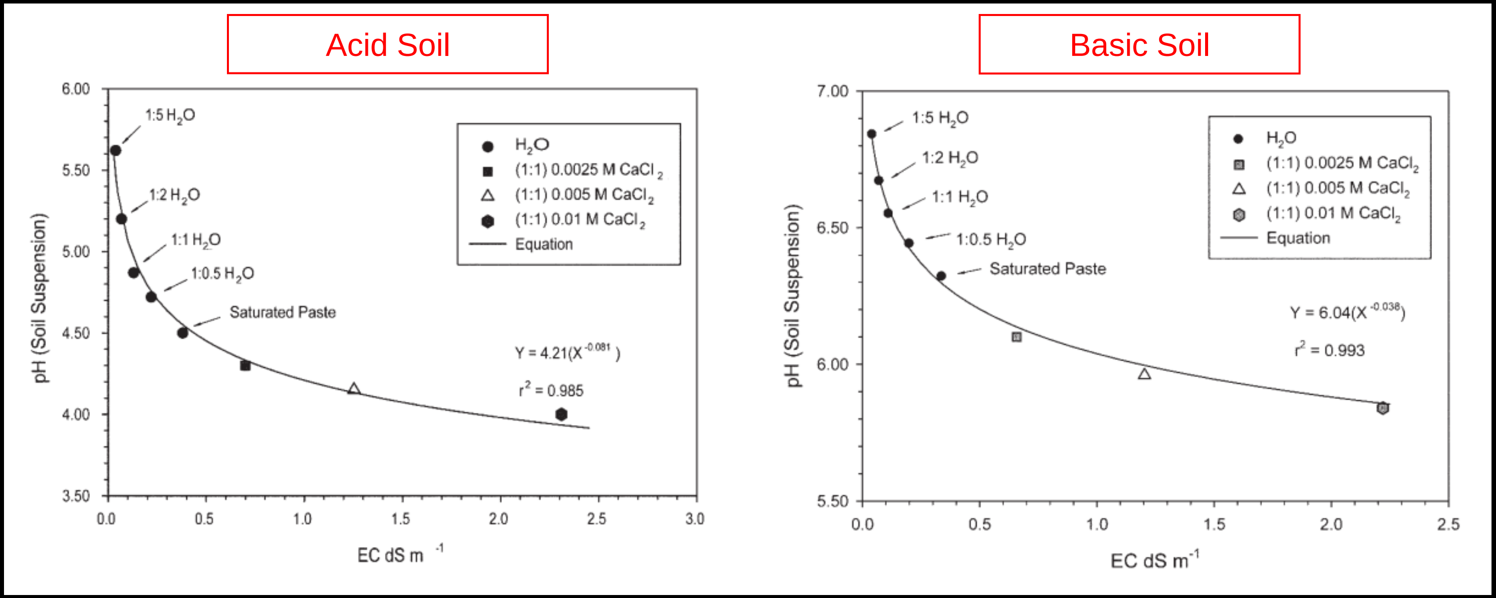
FY / PC ID	Crop	HM	CEC	BS	pH[a]	pH_{leach}[b]	pH Diff	EC[a]
		%	meq / 100 cc	%				ds / m
18 / 103	Soybean	0.4	2.6	55	5.2	5.4	0.2	0.05
18 / 257	Soybean	0.7	5.9	82	6.2	6.3	0.1	0.08
18 / 83	Soybean	1.3	10	81	6	6.1	0.1	0.09
18 / 18	Tobacco	0.6	5.6	82	5.9	6.1	0.2	0.15
18 / 123	Sweet potato	0.3	2.1	55	5	5.4	0.4	0.16
18 / 239	Corn	0.4	5.5	76	5.6	6.1	0.5	0.23
18 / 325	Sweet potato	0.8	4.1	76	5.5	6.1	0.5	0.26
18 / 15	Tobacco	0.5	7.2	79	5.4	5.8	0.4	0.59
18 / 36	Corn	4.4	21.9	87	5.9	6.4	0.5	0.61
17 / 2267	Corn	4.6	7.3	44	4.5	5.2	0.7	0.61
18 / 421	Sweet potato	0.7	5.5	76	5.1	5.9	0.8	0.64
17 / 2295	Corn	4.4	14.6	78	5.3	5.9	0.6	0.74

[a] Soil pH and EC (1:2) of sample measured during analysis.
[b] Soil pH measured in deionized water after leaching with 30 mL of deionized water

Explanation of Salt Effect on pH Depression

- Acid soils, Ca^{+2} from $CaCl_2$ displaces H^+ & Al^{+3}
- High pH soils – see the same but this explanation cannot be used

EC changed by increase in $CaCl_2$ or change in soil:water ratio



- Reinforces Ej potential error associated with salt strength

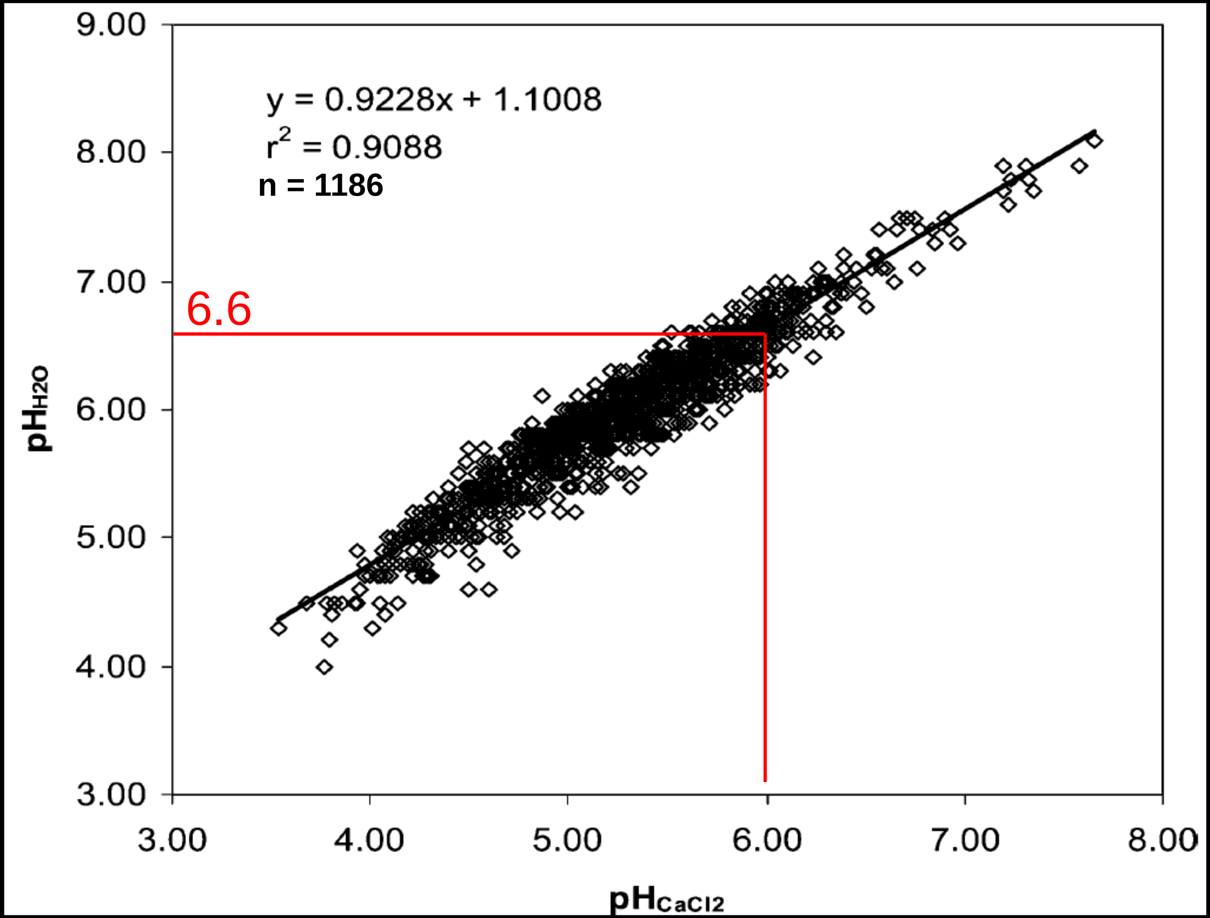
Miller and Kissel, 2010, SSSAJ, 74: 310-316.

UGA Study Salt pH

- Data from 18,500 samples each period
  - Similar soil types, same geographic region
- Two contrasting seasons studied
  - Dry (1998-1999) – 33 cm rain
  - Wet (2000-1) – 55 cm rain
- Higher pHw for a given level of Mehlich 1 Ca in wet year
  - Consistent with lower ionic strength affecting measure
- 1186 chosen randomly from Jan – July 2004
  - pH_{CaCl2} vs pH_{H2O}

Kissel, et al. 2009. Commun. Soil Sci Plant Anal., 40: 179 – 187.

Salt Effect on pH Using 0.01M $CaCl_2$



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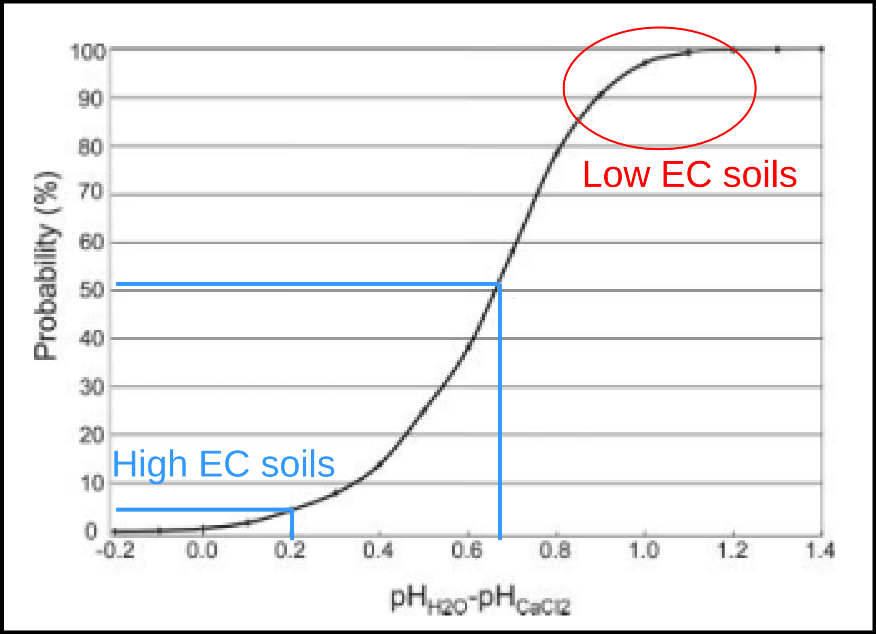
Cumulative Probability of Difference in pH
$pH_w – pH_{CaCl2}$

- 50% soils
  - Δ pH = 0.67
- 5% soils, Δ pH < 0.2 units
  - High EC soils
- 20% soils, Δ pH > 0.8 units
  - Low EC soils
  - Lime needed but no LR due to error



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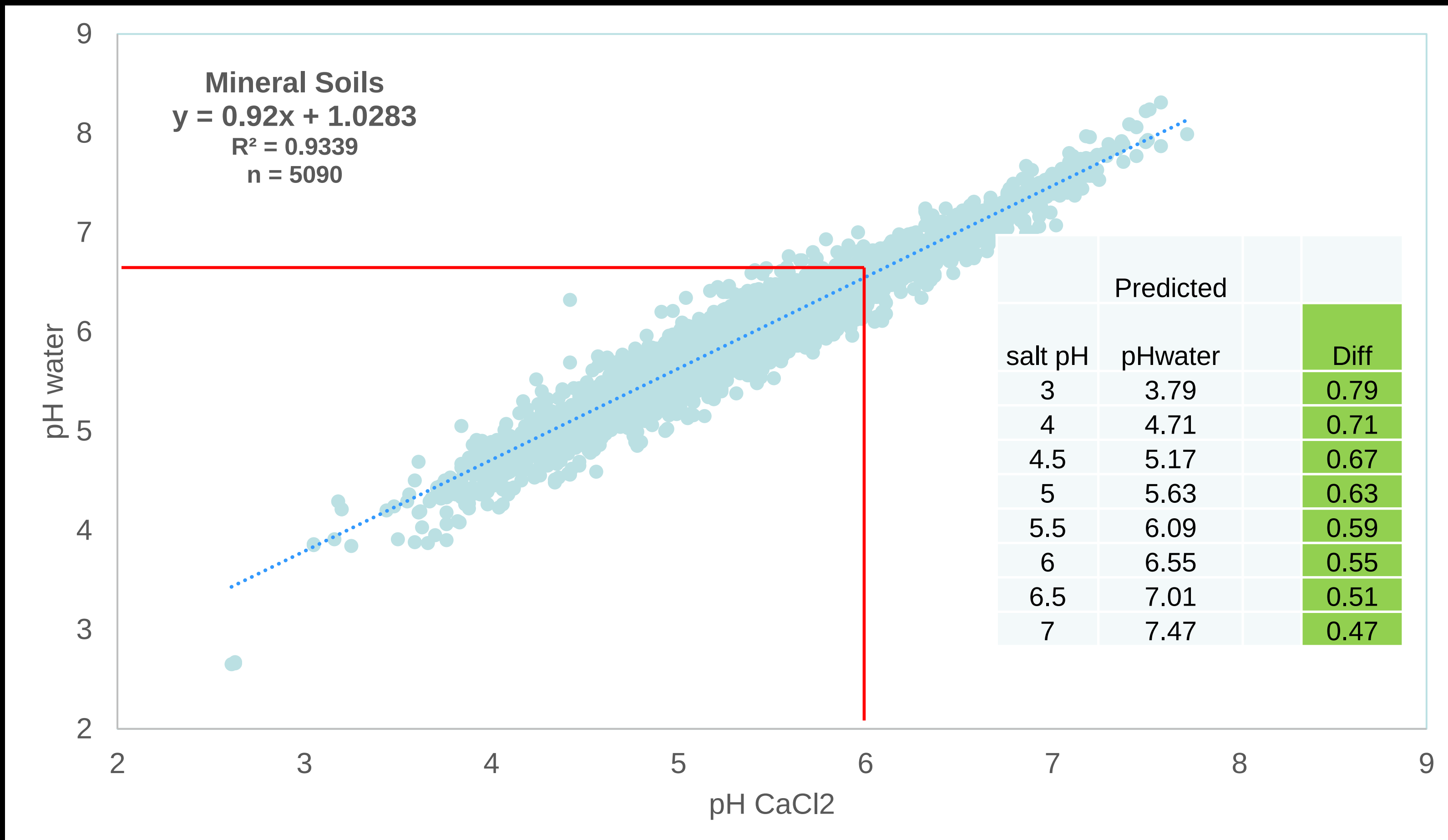
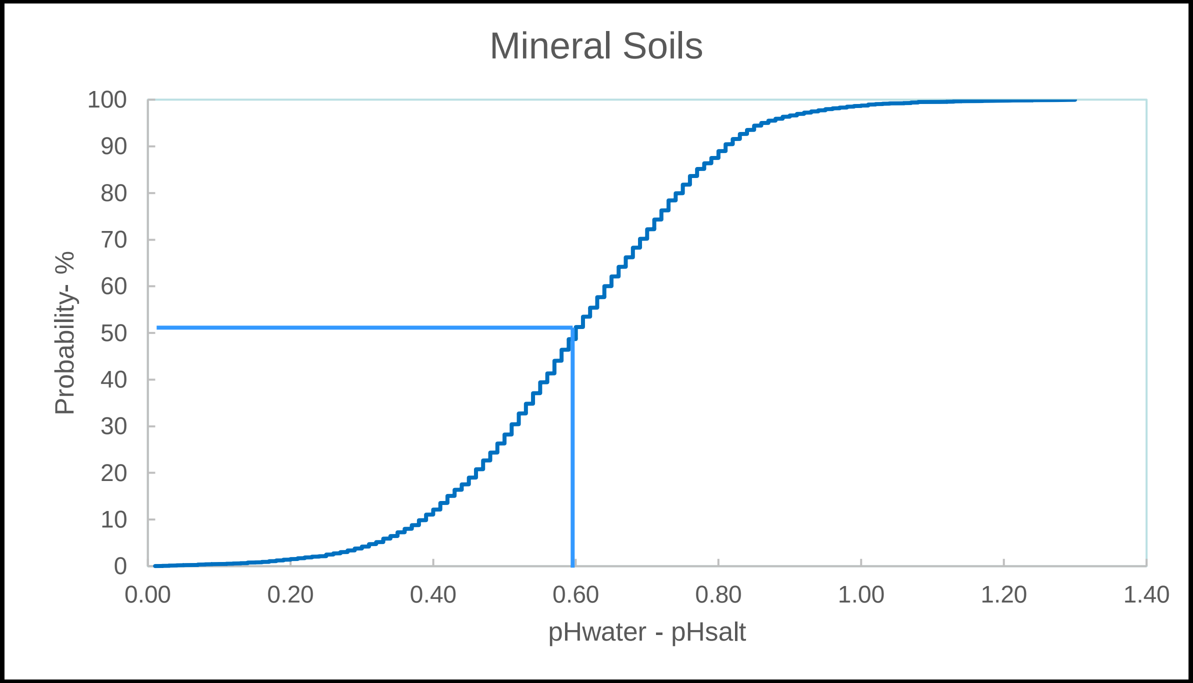
Salt Effect on pH Using 0.01M $CaCl_2$
North Carolina Data



	Predicted		
salt pH	pHwater		Diff
3	3.79		0.79
4	4.71		0.71
4.5	5.17		0.67
5	5.63		0.63
5.5	6.09		0.59
6	6.55		0.55
6.5	7.01		0.51
7	7.47		0.47

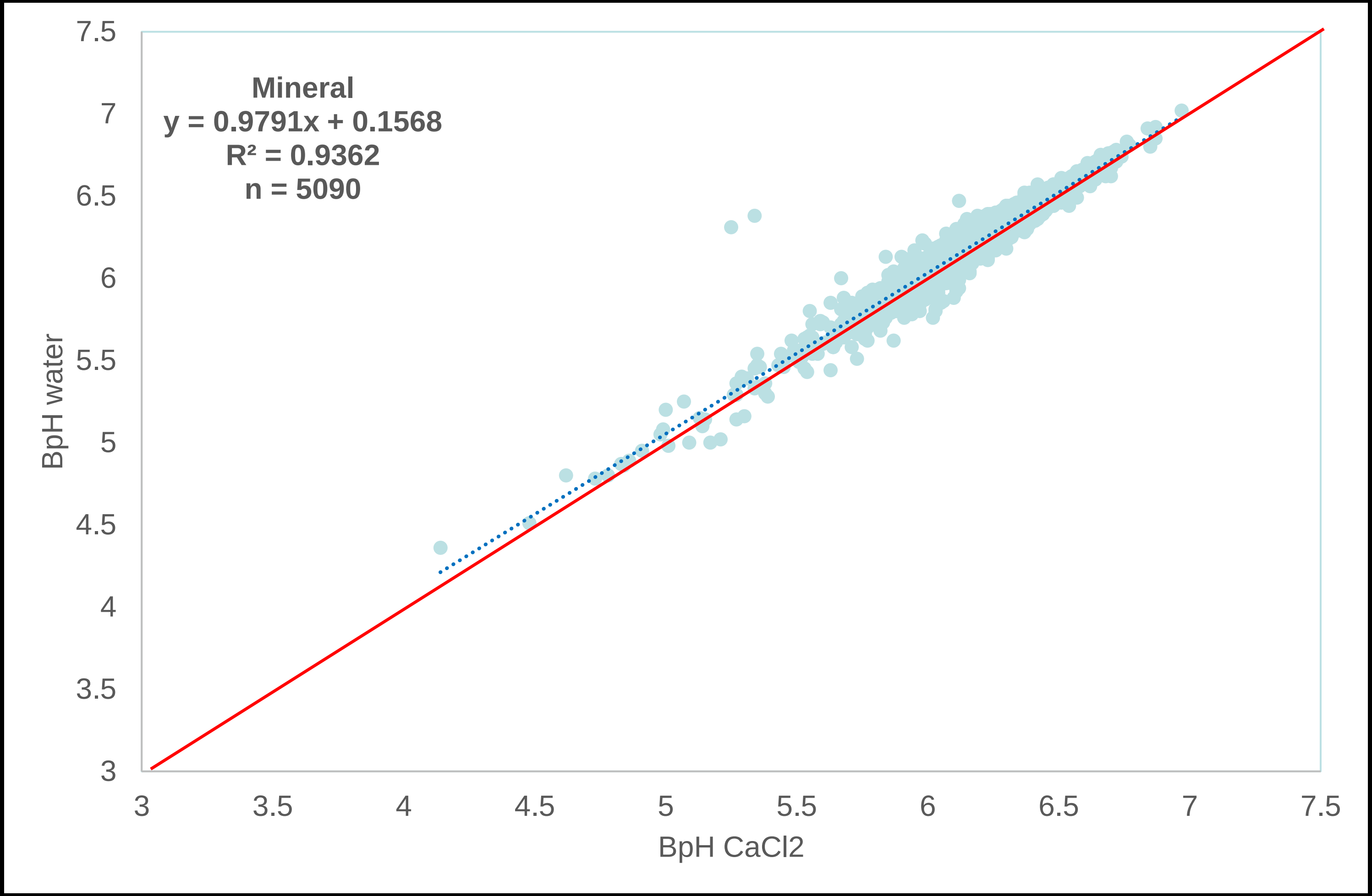
NCDA, FY 2015, 2018 data.

Cumulative Probability of Difference in pH North Carolina $pH_w - pH_{CaCl2}$



- Small % of samples with < 0.2 difference – high EC soils
- 20% soils Δ pH > 0.8 units, significant low EC soils where lime may be needed but not getting a rec.

Salt Effect on BpH Using 0.01M $CaCl_2$
NC Mehlich BpH Data



NCDA, FY 2015, 2018 data.

NCDA Lime Equation

$pH_{adj} = pH_s + 0.6$

Lime (t/ac) = $Ac \times [(pH_{target} – pH_{adj}) / 6.6 – pH_{adj}]$

Example: $pH_s = 4.8$, $pH_{adj} = 5.4$

Lime = 2.0 x [(6.0 – 5.4) / 6.6 – 5.4]

= 2.0 x [0.6 / 1.2]

= 1.0 t/ac

Grower Education

Importance of Adequate Soil pH

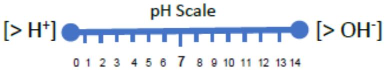
Soil pH and lime recommendations are the most widely used soil test information generated by the NCDA&CS Soil Testing Laboratory. NC soils are naturally acidic (low pH) and require adequate lime for pH management. If acidity is uncorrected, low nutrient availability and poor root growth often result in reduced yields. The pH desired for optimum root growth and nutrient availability is associated with soil class in NC as follows.

Target pH used for most crops as related to soil class by NCDA&CS soil testing.

Soil Class	Desired pH
Mineral	6.0 – 6.5
Mineral-Organic	5.5
Organic	5.0

What is pH and Measurement of Soil pH?

The concentration of hydrogen ions (H^+) in the soil is measured as pH. Remember that water is H_2O, which is essentially a combination of one H^+ ion and one OH^- ion (HOH). Pure water has a **neutral pH of 7** on the pH scale of 0 to 14. A pH less than 7 (< 7.0) is referred to as acidic (more H^+ than OH^-) and a pH greater than 7.0 (> 7.0) is alkaline or basic (more OH^- than H^+). Plants grow best when there is enough acidity to keep nutrients soluble, but without pH being too low to harm roots. Most soils in the southeastern US are acid with pH < 7.0. In the laboratory, a pH combination electrode is used along with a meter to measure H^+ ions. The meter serves as a voltmeter that measures an

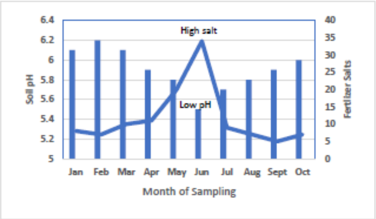


electrical current that depends on the balance of H^+/OH^- ions in a solution. The electrode and the ionic solution complete a circuit, like that of a battery.

Until recently, the standard pH method used by the NCDA&CS Soil Testing Laboratory was a 1:1, soil:water by volume ratio. One part air-dried soil (about 2 teaspoons) is mixed with one part deionized water (about 2 teaspoons) in a small plastic cup to make a slurry that equilibrates for one hour. The electrode and meter are calibrated using buffer solutions of known pH (pH 4, 7, and 10). The electrode is rinsed, placed into the soil/water slurry and stirred; after a few seconds, a reading on the meter stabilizes to supply the actual pH of the soil.

What Affects pH Measurement?

Electrodes require a certain amount of salt to operate correctly, just like a battery needs acid and salt to operate. **When dissolved salt concentrations in soil are very low, instability in the electrode occurs.** This is concerning since all fertilizers are salts and the amount of fertilizer left in the soil after plant uptake and leaching, especially in sandy soils, can vary within a growing season and from season to season. The figure below provides an example of fluctuations in pH from January through October as influenced by salt content in a NC peanut field. **Notice that soil pH (represented by bars) is generally higher when fertilizer salts (shown by line graph) are lower.**



In recent years, some growers and consultants have questioned significant, unexpected differences in pH from year to year and within growing seasons. Typically soils sampled in the early fall after a dry summer will tend to have lower pH readings than soils sampled later in the winter after significant rainfall. The differences seen are largely due to the presence or absence of fertilizer salts. How can we improve on pH measurement given this concern?

A Better Approach in pH Measurement

Measuring pH in a dilute salt solution such as 0.01 M calcium chloride ($CaCl_2$) instead of water is a way to mediate the pH salt effect. **This approach will keep the electrode more stable from the adverse effects of low salt and give a more consistent pH measurement for a given field during the year and from year to year, while still capturing any real changes in acidity.**

Results of North Carolina's Study of Salt pH

Results from a study of approximately 7,000 soils from three soil classes across North Carolina indicate that using the dilute salt (0.01 M $CaCl_2$) lowers the pH measurement by an average of 0.6 units. For example, a soil pH of 5.7 measured in water would result in a pH of 5.1 if measured in $CaCl_2$ solution. Our results are supported by the University of Georgia's soil testing lab that found the same 0.6 unit difference. NCDA&CS chemists have noticed significant improvement in the performance of pH electrodes/meters with this change. When compared to our previous pH method, lime recommendations with the new method: 1) will be lower when salts are high and 2) will be higher when salt levels are low.

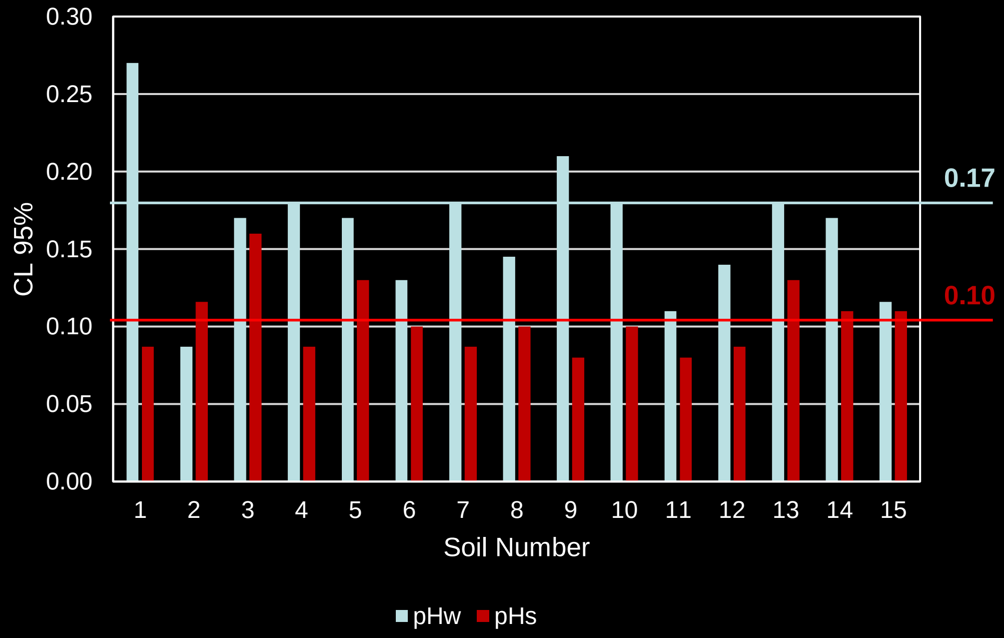
Report and Recommendation Changes

The Soil Testing Section began measuring soil pH in a dilute salt (0.01 M $CaCl_2$) on September 5, 2017. The pH on the soil test report will be a more precise value for a given field from season to season. The reported pH has a positive adjustment of 0.6 units as determined in our study. The lime recommendation will use this reported pH (with adjustment) in the lime equation. The estimated exchangeable acidity (Ac value) that is reported remains unchanged.

The soil test report looks the same and essentially clients will not notice any change. With our new pH measurement, more consistent pH values will be given regardless of presence or absence of fertilizer salts that fluctuate seasonally with rainfall. **The result for growers will be more precise pH values and lime recommendations.**

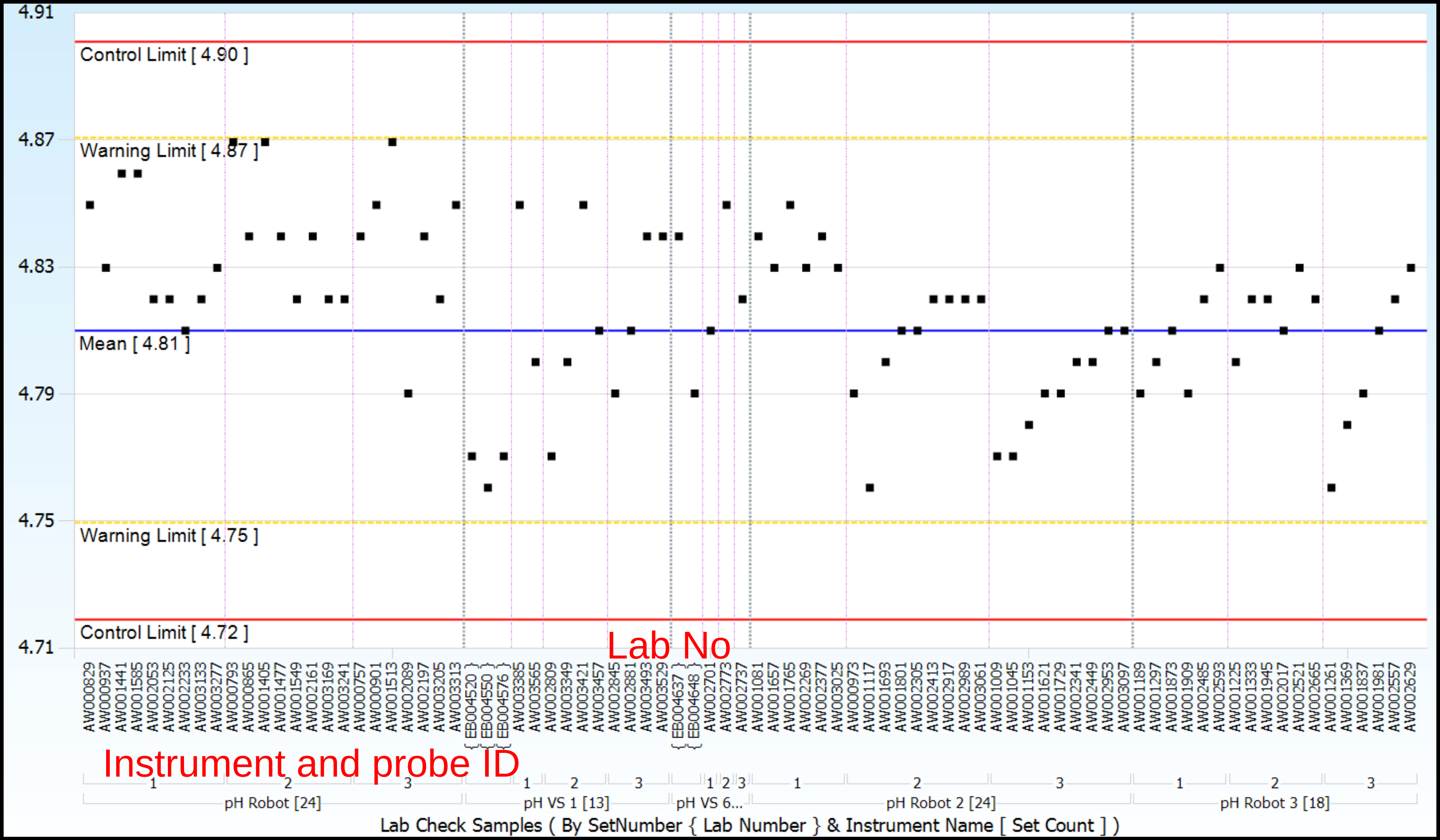
Precision of Salt Measurement

- 15 soils - ISTA 2019 lab database
  - n = 19 labs pH_w
  - n = 9 labs pH_s
- Median data from 3 measures of pH / lab
- 95% confidence limits (CL)



pHs Control Chart Data - NCDA

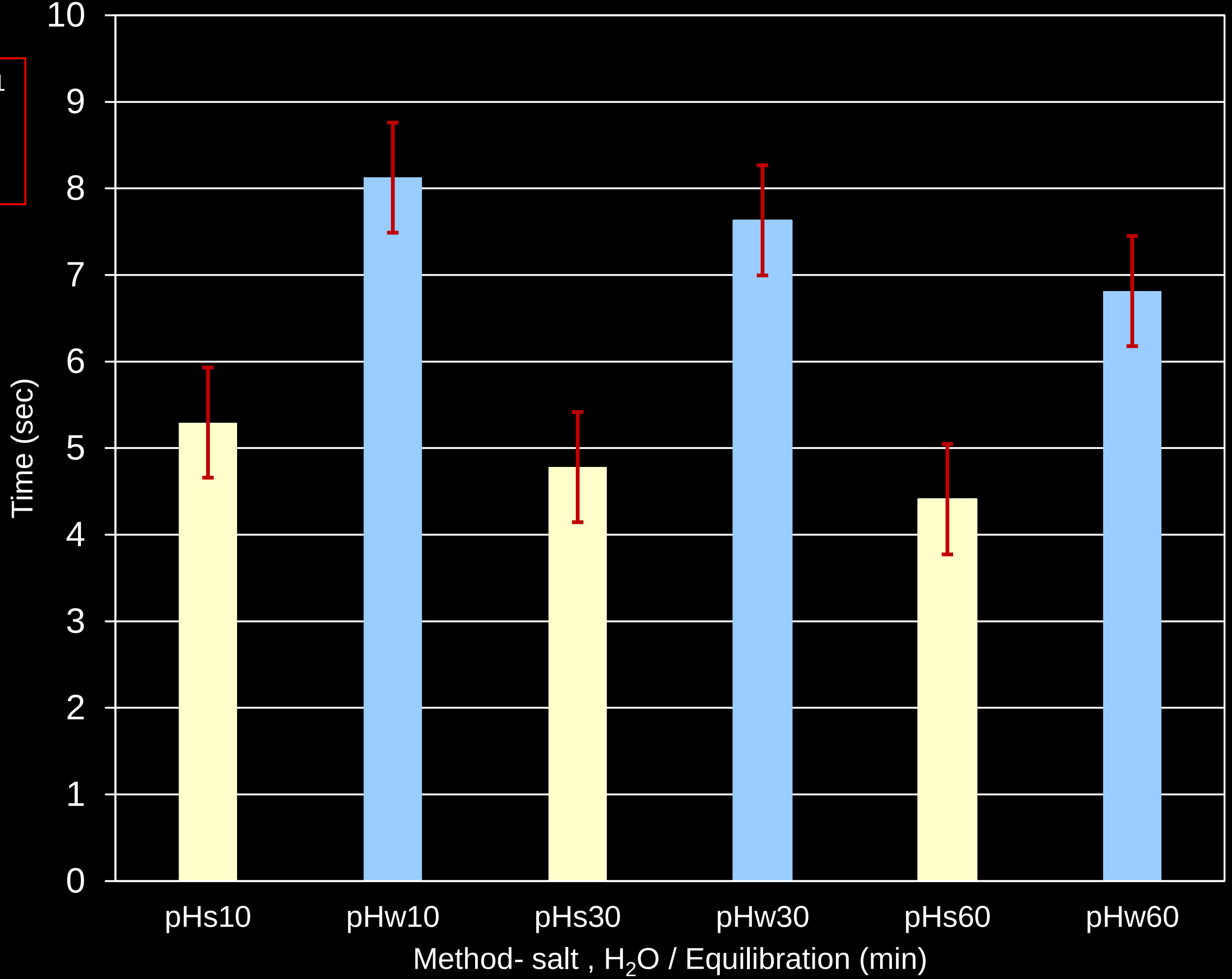
1 check per 36 samples random; 2844 samples analyzed



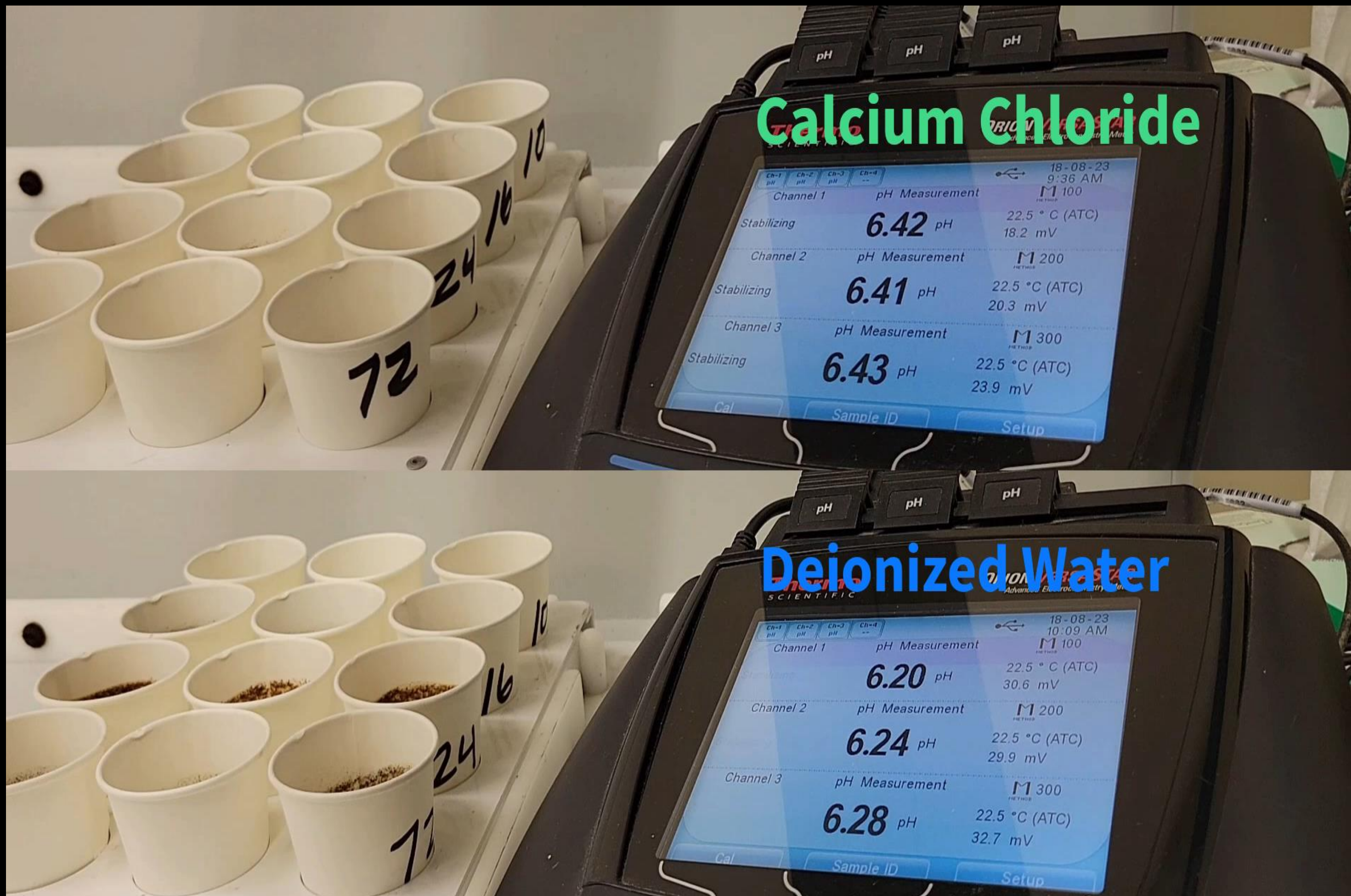
Speed of Measurement

pHs vs pHw – Variable Equilibration Time

EC = 0.03 ds m^{-1}
pHs = 4.15
pHw = 4.74

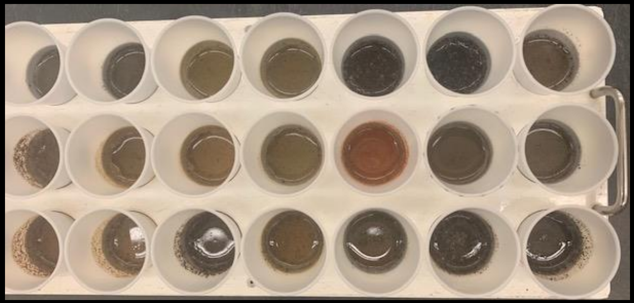


Stability and Speed



Closing Remarks

- Simplicity in pH measurement but…..
- EC affects measurement….junction is important
- Salt measurement
  - Very robust measurement of pH
  - More stable within a season and between years
  - Provide better lime requirements low EC soils
  - Improves precision
  - Increases speed in equilibrium of measurement
  - Consider environment client face seasonally / soil types
- Control chart data is advised
- Used different QC samples daily



References

- Kissel, et al. 2009. Salt concentration and measurement of soil pH. Comm. Soil Plant Anal. 40:179-187.
- Miller and Kissel. 2010. Comparison of soil pH methods on soils of North America. SSSAJ. 74:310-316
- Peech at al. 1953. The significance of potentiometric measurements involving liquid junction in clay and soil suspensions. Proc. SSSAJ. 17:214-218.
- Sumner. 1994. Measurement of soil pH: problems and solutions. Comm. Soil Plant Anal. 25:859-879.
- Wescott, C. C. 1978. pH measurements. Academic Press, Inc.

THANK YOU!

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