

# IMPROVED RELIABILITY OF SOIL PH MEASUREMENT USING MECHANICAL STIRRING

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## Abstract

A review of the analytical methodology to determine soil pH adopted by agricultural laboratories in New Zealand demonstrated that no single procedure is currently adopted. Differences in procedures include; the settling time, manual versus robotic reading, pH probe types, position of probes during measurement and stirring vs. not stirring while reading. Test measurement trials where soil pH readings were taken using four different electrode positions (within the soil supernatant, soil/supernatant interface, directly in the soil sediment and at a set height in a stirred soil/water slurry), showed these factors had a marked affect on measurement uncertainty.

The practice of stirring the samples while taking pH measurements creates a homogeneous soil suspension and resulted in greater measurement reliability and precision. It is proposed that these improvements will also lead to an improved alignment of results between different laboratories.

The adoption of a single, referenced procedure for the measurement of soil pH using mechanical stirring while readings are taken is recommended for New Zealand agricultural laboratories.

## Introduction

The measurement of the concentration of acidity in soil (soil pH) is one of most commonly determined soil parameters because of its influence on soil chemistry and plant growth. Factors influenced by soil pH include availability of elements, rates of element adsorption/desorption, rates of mineral dissolution, mineralization of organic matter and changes in soil water holding capacity.

An early reference to soil pH measurement in the New Zealand Soil Bureau Bulletin 12 (Metson, 1956) details a procedure based on a 1: 2.5 soil: water suspension. The method was adopted from the recommendations of the Soil Reaction Committee of the International Society of Soil Science (1930). Metson describes pH measurement of the soil suspensions “making three or four readings for each sample with brief stirring between each”. This method was largely adopted by the New Zealand Soil Bureau in a later publication (Blakemore et al, 1987) with a significant change of procedure. The change stipulated that the suspension be “stirred vigorously” and “left to stand overnight”. The pH measurement of this settled suspension was then taken “without stirring”. This method has been adopted as method 4A3 by Rayment and Lyons (2011) in their publication *Soil Chemical Methods – Australasia*. It is noted in the same publication that the more widely adopted method for Australian laboratories, method 4A1 is based on a soil:water ratio of 1:5 and the requirement for “ the suspension to be mechanically stirred during measurement to minimise changes in electrode potential associated with suspension effects and positioning of electrodes”.

The change from using two probes, to ones that combine both the reference and glass electrodes within the one body is a change that has not been accompanied by changes to methods indicating the targeted positioning of the combination electrode in settled soil suspensions.

The advent of robotics in modern laboratories has meant the exact positioning of the pH electrode in relation to the sediment zone and supernatant is not possible because variations in organic matter result in considerable variation in the height of the sediment interface. It has been demonstrated that placing the electrode within the settled sediment of a soil with a high CEC, the resultant pH is generally lower than the reading taken from the supernatant. This has been termed the sediment effect. Conversely, readings taken in the sediment for soils with a net positive charge and a greater proportion of dissociated hydroxyl to hydrogen ions can give higher pH readings than the supernatant (Coleman and Thomas 1967).

A survey of the conditions of analysis employed by various New Zealand laboratories undertaking pH measurements was conducted by Massey University (L. D. Currie 2011, pers comm). This showed that no single procedure was being adopted. It is against this background that the authors undertook a series of measurements to determine the effect of changing the position of the electrodes on the reliability of pH analysis.

### **Method and Experimental**

98 soils were chosen to represent a variety of generic soil types, geographical regions and to provide a wide dynamic range of pH measurements. All soils were air dried at 40°C for 16 hours and ground to pass a 2 mm sieve opening. A standard procedure was used to prepare the soil suspensions for all treatments. Preparation was based on soil:water suspensions at a ratio of 1:2.5 (v/v) by taking 10 mL of soil and 25 mL water. Immediately after the addition of the water the suspensions were thoroughly mixed on an orbital shaker for 5 minutes at 200 rpm. pH readings were taken at  $20 \pm 2^\circ\text{C}$  within 4 hours after mixing. Measurements were taken using a Eutech Instruments pH 510 pH meter equipped with an Orion, Ross Sure Flow pH electrode and calibrated using proprietary buffer solutions at pH 4.01, 7.00 and 10.00. Results were recorded for each sample and treatment once the reading had stabilised.

4 replicate batches of the 98 samples comprising 10 mL volumes of each soil were dispensed in duplicate into 50 mL cups. 25 mL of water was added to each sample, they were mixed and the pH measurements taken. The four batches were analysed separately, on different days and using a different electrode placement to represent each treatment. The treatments were; within the soil supernatant, soil/supernatant interface, directly in the soil sediment and at a set height in a mechanically stirred soil/water suspension.

### **Results and Discussion**

It was apparent from the respective treatments that there was no appreciable bias between the different probe positions (Figure 2). However based on the comparison of the means of the duplicate tests and their respective variances, the results show that the stirring treatment has a significantly (Bartlett's test  $p = <0.001$ ) lower variance than the other treatments (Figures 1) and supports the hypothesis that the creation of a homogenous soil suspension while pH readings are taken is more robust and reproducible. Daily soil pH measurements of internally generated quality control samples at this laboratory using the stirring option endorse this observation. After the introduction of stirring there was a noticeable improvement in measurement precision in comparison to previous data based on settled soil suspensions.

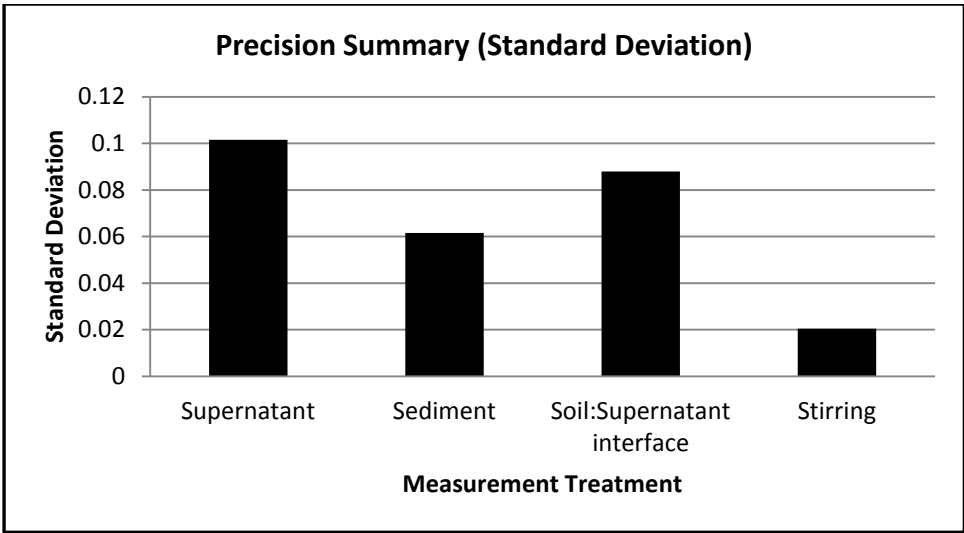


Figure 1. Measurement precision based on analysis of variance expressed as the standard deviation of measurement.

Sample results for each treatment charted against the average for all treatments showed the different electrode positions gave different slopes (Figure 2). However the increased measurement uncertainty for all treatments using the settled soil suspensions (Figures 4,5 and 6) led the authors to the conclusion that the adoption of stirring while reading would result in improved inter and intra laboratory precision.

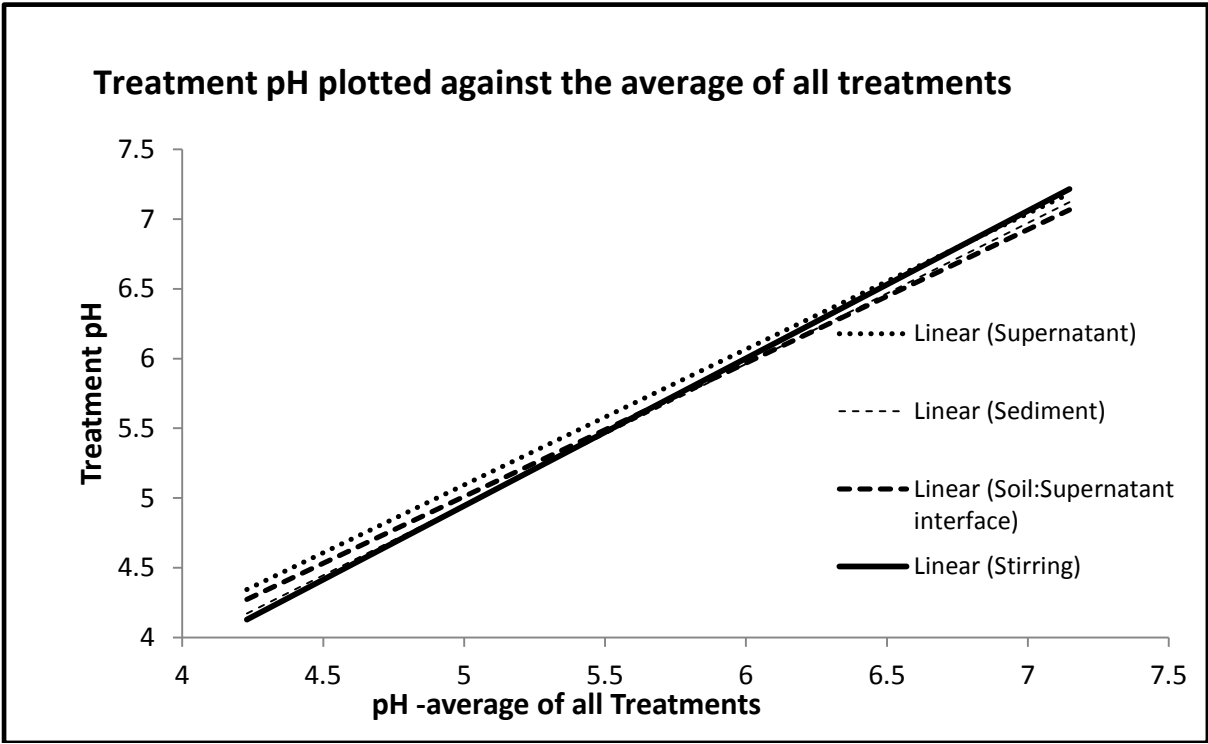


Figure 2. Regression analysis for pH measurements for each sample and treatment against the mean pH for each sample across all treatments.

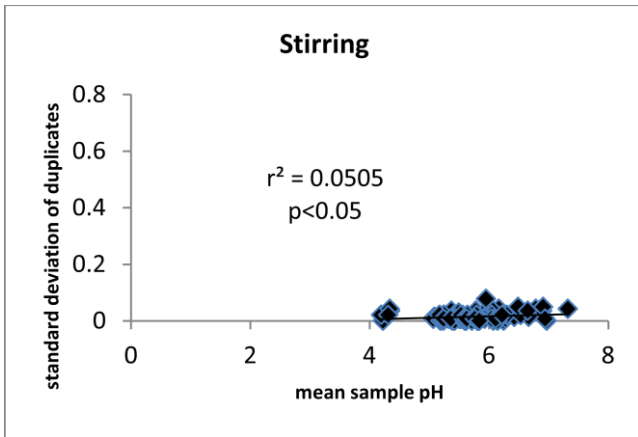


Figure 3.

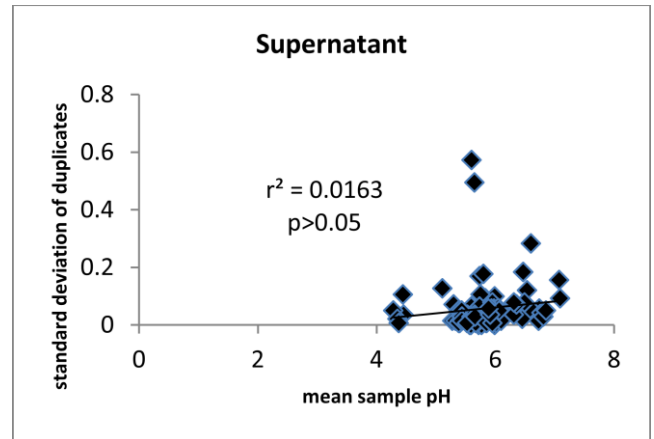


Figure 4.

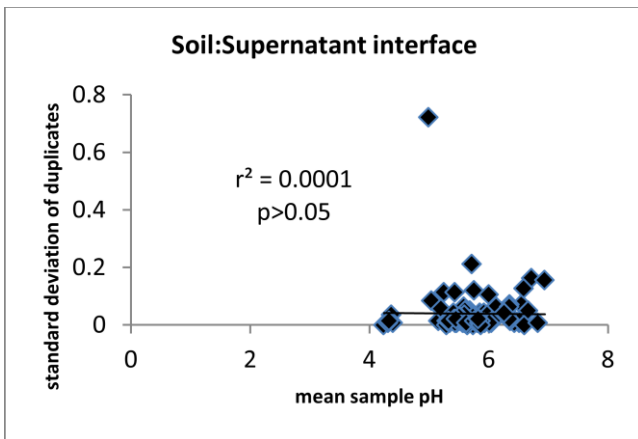


Figure 5.

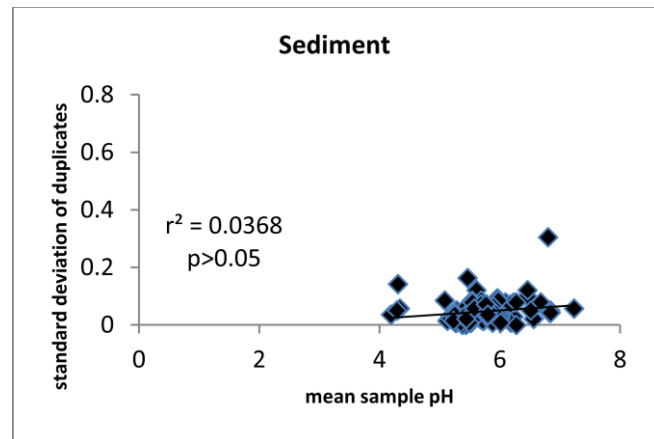


Figure 6.

*Figures 3,4,5 and 6: For each of the treatments, the sample means were calculated from the duplicate pH readings and plotted against their respective standard deviations.*

A further factor for consideration is the wider use of robotics for taking soil pH measurements. Using robotics it is difficult to position the electrode within a defined zone due to changes in the height of the sediment caused by variations in soil characteristics. This factor is particularly the case for laboratories taking their measurements in the narrow zone at the soil sediment/supernatant interface.

### **Conclusion**

The adoption of more regular and extensive soil testing by the modern farm enterprise to more finely tune fertiliser and soil amendment inputs requires the contract laboratory to provide reliable and reproducible results. It is also in the interest of the agricultural market that inter-laboratory agreement is continuously improved to account for customers that change their laboratory provider.

It is incumbent on laboratories to review analytical methodology and to increase the robustness and reproducibility of techniques where possible. This is particularly important for empirical tests like soil pH. The authors recommend that the current New Zealand method be altered to adopt common measurement conditions including the practice of stirring the soil/water suspension while pH readings are taken.

## **References**

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