SEASONAL VARIABILITY OF pH AND LIME REQUIREMENT IN SEVERAL SOUTHERN MICHIGAN SOILS WHEN MEASURED IN DIFFERENT WAYS

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY JOHNNIE B. COLLINS 1967

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SEASONAL VARIABILITY OF pH AND LIME REQUIREMENT IN SEVERAL SOUTHERN MICHIGAN SOILS WHEN MEASURED IN DIFFERENT WAYS

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Johnnie B. Collins

A Thesis

Submitted to

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#### ABSTRACT

SEASONAL VARIABILITY OF pH AND LIME REQUIREMENT IN SEVERAL SOUTHERN MICHIGAN SOILS WHEN MEASURED IN DIFFERENT WAYS

Вy

Johnnie B. Collins

The variability of soil pH and lime requirement was investigated from May through September, 1966, at nineteen soil sites representing thirteen southern Michigan soil series. The experimental errors in pH determinations were also studied. 100

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To be reasonably certain of a significant difference between individual soil pH measurements a variation greater than  $\pm 0.3$  pH is necessary. However, when mean soil pH values of a representative number of observations are compared, differences greater than  $\pm 0.15$  pH unit are likely significant.

On the average, during the wetter portion of the season, the air dry and oven dry soil pH values (measured in water) were approximately 0.5 and 0.8 pH unit lower, respectively, than the corresponding field moist pH values. However, during the drier portion of the season, differences between the average pH values measured at the three moisture conditions were less than 0.1 pH unit and non-significant. There were also no significant differences between the averages of the air dry and oven dry soil pH values measured during the season.

The field moist soil pH values measured in water showed the maximum seasonal variability and the air dry soil pH's measured in 1.0NKCl showed the least seasonal variability. The field moist pH's measured in water showed a maximum variation of 1.6 pH units and an average variation of 0.8 pH unit during the season. Similarly, the air dry soil pH's measured in 1.0NKCl showed a maximum variation of 1.0 pH unit and an average variation of less than 0.2 pH unit during the season.

The field moist soil pH values measured in water were positively and highly correlated with organic matter content. This is probably due to the combined effect of the relationships of organic matter content to field moisture content, and field moisture content to electrical conductivity. The seasonal variability of the air dry pH's measured in water were negatively and highly correlated with electrical conductivity of the samples. Most of the soil sites exhibited no seasonal variability of air dry pH's when measured in 1.0NKCL. This indicates that soluble salts are probably responsible for most of the observed seasonal variations in soil pH values.

On the average, the 0.01MCaCl<sub>2</sub> and 1.0NKCl salt solutions lowered the air dry soil pH's measured in water approximately 0.6 and 1.0 pH unit, respectively.

Regardless of method of determination, seasonal variability of lime requirement was observed on eleven of the

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nineteen soil sites. Using air dry samples, only four of the eleven sites exhibited a lime requirement during the earlier part of the season, but each of the eleven sites showed a lime requirement during mid-summer. SEASONAL VARIABILITY OF pH AND LIME REQUIREMENT IN SEVERAL SOUTHERN MICHIGAN SOILS WHEN MEASURED IN DIFFERENT WAYS

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The writer gratefully acknowledges the Graduate Assistantship provided him by Michigan State University enabling him to pursue and complete this study.

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#### INTRODUCTION

Perhaps the most important chemical test of a soil as a medium for plant growth is its pH value or "hydrogen ion activity". The solubility and availability of many nutrients are closely related to soil pH.

Determination of pH is one of the easiest and quickest operations used in soil chemical analysis. However, the use of soil pH values as expressions of acidity involve the consideration of several factors: In the first place, does the measured pH value give a true expression of the acidity of the soil in the field? Secondly, how variable is the reaction of the soil in the field throughout the year? Thirdly, how do the magnitudes of seasonal variations compare to the experimental errors encountered in pH determinations.

This study was conducted from May to September, 1966, in order to investigate: the seasonal variability of the acidity of the plow layers of thirteen soil series at nineteen sites in Southern Michigan, to observe several of the possible factors influencing the apparent seasonal variations, and to evaluate the experimental errors in the determinations of soil pH.

In evaluating the experimental errors, the effects of different operators, different pH meters and different times were considered. Consideration was given to the effect of field moist, air dry and oven dry samples on the pH measurements. Also, the pH's of the air dry samples collected during

the season 1 1.0NKC1 sol two salt so was also gi at the foll media: fie 3 · · · · water and To h tion, elec ( saturation tent of th - A Charles and the second In a lent was d and the second McLean-Sho soil texts • • • • • • • • • 1. 1. 1. 1. • 1 8 8 

the season were measured in water, in 0.01MCaCl<sub>2</sub> and in 1.0NKCl solutions in order to determine the effects of the two salt solutions on the pH measurements. Special attention was also given to the variability of soil pH values measured at the following moisture conditions and in two suspending media: field moist in water and in 0.01MCaCl<sub>2</sub>; air dry in water and in 0.01MCaCl<sub>2</sub>; and oven dry in water and in 0.01MCaCl<sub>2</sub>.

To help understand the seasonal variation in soil reaction, electrical conductivity (or salt content), percent base saturation, field moisture content, and organic matter content of the soil samples were investigated.

In addition, the seasonal variation of the lime requirement was determined and compared by the following methods: McLean-Shoemaker-Pratt buffer, exchange acidity, and pH plus soil texture.

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#### LITERATURE REVIEW

## Introduction

pH is commonly defined as the negative logarithm of the hydrogen ion activity. Methods for determining soil pH may be divided into two groups: electrometric (hydrogen electrode, quinhydrone electrode and glass electrode) and colorimetric. The hydrogen electrode (5,25) measures the e.m.f. of the equilibrium between gaseous hydrogen dispersed in platinum black and hydrogen ions in solution against the e.m.f. of a standard calomel half cell. The quinhydrone electrode (5) is based on the principle that for pH values up to 8.5, the oxidation-reduction potential between quinone and hydroquinone depends on the hydrogen ion activity in solution. The glass electrode (30) evolved from the observation that the potential between membranes of certain lowaluminum glasses and a solution is closely related to the pH of the solution. The colorimetric methods (22) makes use of suitable dyes or acid-base indicators, the colors of which change with the hydrogen ion activity.

### Seasonal Variations of soil pH

It has frequently been observed (6,7,9,18,31,33,37,41, 45,53,59,75,78,79,82,87) that pH values of soil samples taken from the same site at different times during the year show considerable variations. Studies of seasonal variation in

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Puri, <u>et.</u>

soil reaction are of much practical importance where this chemical test is used to determine the fertilizer (particularly micronutrients) and lime requirement of soils. Soil reaction is also one of the criteria used in the new soil classification system (7th Approximation) to classify certain soils at the family level, and it has very commonly been a criterion for differentiation among soil series. Therefore, an investigation of seasonal variations in soil reaction should be very useful.

## Causes of seasonal Variations in pH

Many investigations (6,7,9,18,31,43,44,45,53,78,79,82) have also been conducted in an attempt to ascertain why soil reaction fluctuates during the year, and to determine the magnitude of the apparent variation. A large number of investigators (18,43,44,53,78,82) have reported an increase in soil acidity during the summer months. In some instances (43,44, 78) a variation during the year of as much as 1.0 pH unit has been reported.

## Influence of salt content

Baver (6) attributed the increase in soil acidity during the summer months to the accumulation of soluble salts. Others (33,53,59,66,87) have reported similar findings. Puri, <u>et. al.</u> (59) and Schofield, <u>et. al.</u> (66) pointed out that "natural non-saline" soils contain varying amounts of salts, and that soil pH is altered appreciably in the presence

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and cor near th conten. of even small quantities of neutral salts. Yuan (87) found that a change in pH resulted when the soil was brought into contact with a salt solution, and that the change was accompanied by the liberation of exchangeable and hydrolytic acidity from exchangeable hydrogen and aluminum. As pointed out by Olson (53), probably one of the important factors responsible for an increase in acidity during the late spring or early summer is the relative high concentration of salts in the soil solution following the application of fertilizers. This conclusion is contrary to the results of Bell, <u>et. al.</u> (7) who found that fertilizers had no effect on seasonal changes in soil pH.

## Influence of drying, moisture content of samples or rainfall

The effects of drying and moisture content on variation of soil reaction have been the subjects of many investigations (3,6,16,19,28,41,51,52,64). Olson (53) determined the acidity on the same sample but at different moisture contents, and concluded that soil moisture may have an appreciable effect on soil pH. Chapman, <u>et. al</u>. (19) found that at moisture contents corresponding to the moisture equivalent, stable readings may be obtained provided the electrodes are well covered with the moist soil. They also found that constant and consistent readings may be obtained with the soil at or near the "sticky point," and that differences in moisture content in this general range had but little effect on the

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pH values. McGeorge (51) employed the spear type electrode and concluded that it yields values that truly reflect the acidity under any and all growing conditions, and that the readings are accurate and can be closely duplicated. Davis (28) pointed out that attempts to measure soil pH with the glass electrode below the moisture equivalent are undesirable and that there is no acceptable evidence that air dry soils are characteristically more acid or more alkaline than moist soils.

Burgess (16) pointed out that both air drying and oven drying had little or no effect on acid soils but that drying alkaline soils rendered them somewhat less alkaline. Arrhenius (3) reported the effect of drying on the pH of an alkaline soil and found that neither air drying nor drying in an oven at 100°F brought about any change in pH values. Huberty (41) conducted an experiment to determine the suitability of oven dry pH values as expressions of soil acidity. He obtained lower pH values with the oven dry samples than with the air dry samples and observed that the oven dry pH's were no more variable than the air dry pH's.

Rost (64) <u>et. al</u>. studied 144 soils developed from glacial and loessial materials and found that all but one became more acid upon air drying. Therefore, they concluded that the only reliable indication of conditions existing in the field are obtained when pH's are determined on field moist samples.

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Severa fluctuations Van Der Paap alternating that the tre ing wet and of high and observed si Experiment 7; 11 pë unit for acid soils. but indica tion, and rainfall w Influence Ther tigators ( ratio of s 1 the soil : • 1 (19,41,76 the "stic] over 1.0 j Pier <sup>soils</sup> were 1 1:2 to 1: Several investigators (6,53,82) have related seasonal fluctuations in soil pH values to variations in rainfall. Van Der Paauw (82) attributed fluctuations in soil pH to alternating periods of low and high rainfall. He observed that the trend of pH corresponds fairly closely to alternating wet and dry periods: it gradually increases in periods of high and decreases in periods of low rainfall. Baver (6) observed similar trends in soil pH at the Ohio Agricultural Experiment Station and he reported variations of 0.6 to 0.7 pH unit for alkaline soils and as much as 0.9 pH unit for acid soils. Olson (53) observed no effect of rainfall on pH but indicated that if factors such as temperature, evaporation, and others could be kept constant it is possible that rainfall would have a decided influence on soil acidity.

## Influence of soil water ratio

There has been little agreement among different investigators (2, 10,19,35,41,50,57,65,70,76) as to the proper ratio of soil to water that should be used in preparation of the soil suspension for pH measurements. Several investigators (19,41,76) agree that the increase in pH upon dilution from the "sticky point" to a soil-to-water ratio of 1:5 may be over 1.0 pH unit.

Pierre (57) found that the hydrogen activity of some soils were not affected by changing the soil-water ratio from l:2 to l:50. Further, those soils that showed a change in pH

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• : : • (1:1) ar no longer showed such differences after the soluble salts were leached out. Sharp and Hoagland (25) reported no significant differences in the pH's of soils at soil-water ratios varying from 1:2 to 1:500. Gillespie and Hurst (35) found no consistent differences in the hydrogen ion activity of soils using soil-water ratios of 1:1 and 1:2. His results varied from a minus 0.15 to a plus 0.25 of a pH unit, based on 1:1 as a standard.

Changes in soil pH with different soil-water ratios may be dependent on organic matter content, as pointed out by Arrhenius (2). This investigator found but little change with a humus rich soil, but a change of 0.9 pH unit with a sandy soil (low in organic matter), when ratios of 1:2.5 and 1:500 were compared. McGeorge (50) pointed out that the increase in soil pH with different dilutions is most rapid for soil-water ratios below 1:10. Likewise, Bradfield (10) found that the increase in pH is most rapid for soil-water ratios below 1:8.

On the basis of the above reports it became apparent that a standard soil-water ratio was needed. Therefore, in 1930, the soil reaction committee of the International Society of Soil Science (38) adopted a 1:25 soil-water ratio as the standard. However, several states have adopted a 1:1 ratio (55), and various investigators have adopted various ratios. The procedures used here for pH's in water (1:1) and in 0.01MCaCl<sub>2</sub>(1:2) are those recommended jointly by

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the American Testing and • 1 Analysis Par • • • Influence of Sever • : ' . 1 effect of 1 • ۲. . and that it : • the atmosph 7.0. Hoagl tivity of t . by increast • to ten perc Production of the second s soils is s • : ' out that w nent chang • : • bon dioxid of calcare • : arithm of pE of such • ť partial p ۲ of the pr  $-\frac{1}{2}\left(1+\frac{1}{2}\right) + \frac{1}{2}\left(1+\frac{1}{2}\right) + \frac{1}{2}\left(1+\frac{1}{2}\right$ • in water. • <sup>leasurene</sup> <sup>soil</sup> with 1 • regardles : :

the American Society of Agronomy and the American Society of Testing and Materials in Agronomy No. 9, Methods of Soil Analysis Part 2, 1965.

## Influence of CO2 pressure in the atmosphere

Several investigators (39,57,61,85) agree that the effect of increased carbon dioxide is to decrease soil pH, and that its effect at the partial pressure prevailing in the atmosphere is very small in soils having pH values below 7.0. Hoagland, et. al. (39) found that the hydrogen ion activity of the suspension of acid soils is not markedly affected by increasing the carbon dioxide content of the suspension up to ten percent, but that the acidity of a slightly aklaline soils is slightly increased by such treatment. They pointed out that when the original conditions are restored no permanent change in soil reaction could be attributed to the carbon dioxide. Whitney and Gardner (85) found that the pH of calcareous soils is a straight-line function of the logarithm of the carbon dioxide pressure and concluded that the pH of such soils, measured after equilibration with known partial pressures of  $CO_2$ , should give a better indication of the probable pH range in the field than the pH measured in water. In the U.S. salinity laboratory (61), the pH measurements are ordinarily made after equilibration of the soil with the carbon dioxide pressure of the atmosphere, regardless of the soil to water ratio used.

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It has been reported that plants may influence seasonal changes in soil reaction by removing bases from the exchange complex during the growing season (75). Relationships between pH and base saturation have been the subject of many investigations (48,49,58,72). Morgan (52) pointed out that the relationship between pH and percent base saturation may be fairly constant within a soil type, but that it may vary widely between soil types. Mehlich (48,49) studied the base saturation and pH relationships and concluded that this relationship is almost solely influenced by the nature of the exchange complex. For montmorillonitic soils base saturation of the complex at pH 7.0 is practically complete; whereas for kaolinitic soils at the same pH value only 50 to 80 percent of the colloids are base saturated. The base saturation relationships are very useful in classifying soils in the new soil classification system (7th Approximation).

#### Influence of absorbed aluminum

It has been reported by several investigators (13,20, 24,40,46,62,63,67.70,80,83) that in very acid soils aluminum contributes to soil acidity. On the breakdown of clay, aluminum contributes to soil acidity. On the breakdown of clay, aluminum is released and absorbed on the exchange complex. The hydrolysis of aluminum results in the formation of hydroxy-aluminum ions and hydrogen ions, thereby increasing the apparent soil acidity.

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#### Influence of organic matter

Several investigators (1,12,15,34,68,69,74,84) have studied the organic matter content and organic acids of soils in relation to variations in soil reaction. They concluded that the organic matter acts as a buffer, whereas the organic acids accumulated under anaerobic conditions may slightly influence soil acidity.

#### Influence of time interval between preparation and pH measurements

The time interval between preparing the suspension and making the determination in relation to changes in soil pH values has been the subject of several investigations (4,29, 50). Working with alkaline soils, McGeorge (50) concluded that the pH decreases with an increase in the time interval. Contrary to the above, Bailey (4) used boiled distilled water, a 1:2 and 1:4 soil-water ratio, field moist and air dry samples, and concluded that the pH of the suspension was not affected by the length of time the water was in contact with the soil sample. Bailey's conclusion was substantially in agreement with the results of Dean and Walker (29).

#### <u>Comparisons of various colorimetric methods for pH measurements</u>

At the present time, the colorimetric method for pH determination is primarily confined to field test kits. Mason <u>et.al.</u> (47) compared several pH field kits based on their cost, accuracy and adaptability for rapid use. They found that the reproducibility of pH values as indicated by the several field

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kits were influenced by the following: (1) experience of operator, (2) purity of chemicals and proper adjustment of pH, (3) cleanliness, (4) contamination, (5) and manipulation of soil extract. In most colorimetric techniques, the pH of an aqueous soil extract is usually measured. Woodruff (84), however, has recently proposed a colorimetric method based on measurement of the pH of a 0.01MCaCl<sub>2</sub> extract of soil in an attempt to fix the salt concentration of the soil and thus minimize the variation in soil pH due to fluctuation in the amount of soluble salts.

#### Accuracy of glass electrode measurements

At present, the glass electrode is the most extensively used electrometric method for pH determinations. It is standard equipment in most laboratories and it may be line or battery operated.

The reproducibility of pH values with the glass electrode has been the subject of several investigations (19,23, 25,54,55,59,60,66). Chapman, <u>et. al</u>. (19) found that readings with the glass electrode were stable, constant and consistent at moisture contents corresponding to the moisture equivalent and/or the sticky point; providing the electrodes were well covered with the moist soil and there was good contact. They reported a maximum variation of 0.08 pH unit with a loam soil, and a range of 0.4 pH unit with a clay loam soil at the above moisture content.

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Hox : are usual lower moi e ¢ pH values than that measured ٢ Were still is inter of hydro. metric m cannot b differer Were 0.] were O. liquid. P the jun trodes ٢ t not exc • ٢ ¢ ¢ , be avo: , <sup>Salt</sup> bj į clear ; ments ( in a o, to the

<sup>soil</sup> su

However, soil pH measurements with the glass electrode are usually made in dilute suspensions rather than at the lower moisture contents. Coleman, <u>et. al.</u> (25) observed that pH values obtained for a stirred soil suspension was lower than that of the supernatant liquid and that the pH value measured when the electrodes were pressed into the sediments were still lower. He concluded that the measured e.m.f. which is interpreted in terms of pH includes two terms, the activity of hydrogen ions and a junction potential, and that potentiometric measurements of the pH of soil suspensions or pastes cannot be entirely attributed to soil acidity. For twelve different soils they reported that the pH of the suspensions were 0.1 to 0.9 pH units lower and the pH of the supernatant liquid.

Peech, <u>et. al.</u> (55) pointed out that the error due to the junction potential when both the glass and calomel electrodes are immersed in the flocculated soil suspension should not exceed 0.25 pH unit. They indicated that the error may be avoided in flocculated soil suspensions by placing the salt bridge or the conventional type calomel electrode in the clear supernatant liquid and the glass electrode in the sediments or partly settled suspension.

Schofield, <u>et. al.</u> (66) proposed the measurement of pH in a  $0.01MCaCl_2$  solution. They indicated that the error due to the junction potential could thus be minimized because soil suspensions are flocculated in  $0.01MCaCl_2$ . Also, they

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pointed ou ution over equivalent solution ( tent. The independer saline so ¢ Cla ۲ potential the clear the error ionic st Dolar. e Хэ sonal va (59). 7 imiluend tions an soil th in the ' ٠

pointed out that the pH in  $0.01MCaCl_2$  is independent of dilution over a wide range, and that  $0.01MCaCl_2$  is approximately equivalent to the total electrolyte concentration of the soil solution of a non-saline soil at optimum field moisture content. Therefore the observed pH in  $0.01MCaCl_2$  should be independent of the initial amount of salts present in nonsaline soils.

Clark (23) found that the errors due to the junction potential were not eliminated by placing the KCl bridge in the clear supernatant liquid. However, he indicated that the errors are essentially eliminated by insuring that the ionic strength of the salt in solution is less than 0.005 molar.

Many European workers have attempted to minimize seasonal variations in soil pH values by measuring pH in 1N KCl (59). They have indicated that pH values in 1N KCl are less influenced by changes in biological and meteorological conditions and thus reflect a more intrinsic characteristic of the soil than the soil pH measured in water, as is commonly done in the United States.

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• This soil serie . were mine; (Houghton irainage well to p samples m t tion of e irainaze, Vegetatic Table 2. Th laps. F: bire, na and pH w gravel r e nick are •

#### EXPERIMENTAL PROCEDURE

#### Location of sites

This study was initiated in May, 1966, using thirteen soil series and nineteen sites. All of the series and sites were mineral soils except one which was an organic soil (Houghton muck). The texture of the surface, and the natural drainage of the soils varied from clay loam to sand and from well to poorly drained, respectively. The pH's of air dry samples measured in water varied from 5.2 to 8.0. The location of each site is given in Table 1, and the texture, natural drainage, degree of erosion, percent slope, direction of slope, vegetation or crop, and area studied at each site are given in Table 2.

The general soil areas were located by the use of soil maps. From these areas, plots with uniform topography, texture, natural drainage, vegetation or crop, color of surface and pH were selected. The sites selected were not close to gravel roads, dead furrows, lime or manure piles, or burned muck areas.

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Table 1. Location of plots

Soil Site	County	Two.
Blount	Clinton	Watertown
Ceresco No. 1	Ingham	Meridian
Ceresco No. 2	Ingham	Meridian
Colwood No. 1	Clinton	Bath
Colwood No. 2	Clinton	Bath
Chelsea*	Clinton	Victor
Hillsdale No. 1	Ingham	Leslie
Hillsdale No. 2	Ingham	Meridian
Houghton	Clinton	Bath
Lapeer	Ingham	Keridian
Lapeer	TIONE .	
Nekoosa No. 1	Clinton	Bath
-	-	
Nekoosa No. 1	Clinton	Bath
Nekoosa No. 1 Nekoosa No. 2	Clinton Clinton	Bath Beth
Nekoosa No. 1 Nekoosa No. 2 Oakville	Clinton Clinton Ingham	Bath Bath Meridian
Nekoosa No. 1 Nekoosa No. 2 Oakville Fewamo No. 1	Clinton Clinton Ingham Clinton	Bath Bath Meridian Watertown
Nekoosa No. 1 Nekoosa No. 2 Oakville Pewamo No. 1 Pewamo No. 2	Clinton Clinton Ingham Clinton Clinton	Bath Bath Meridian Watertown Eagle
Nekoosa No. 1 Nekoosa No. 2 Oakville Fewamo No. 1 Pewamo No. 2 Plainfield	Clinton Clinton Ingham Clinton Clinton Shiawassee	Bath Bath Meridian Watertown Eagle Woodhull

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\*Formerly called Graycalm. Graycalm is now restricted to Northern Michigan

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### Table 1. Continued

NE 1, SW 1,	NW 🔒,	Sec. 6	5,	T5N,	RGW
NW ½, NW ½,	NW 4,	Sec.	36,	T4N,	RlW
NE $\frac{1}{2}$ , NE $\frac{1}{2}$ ,	NE 1.	Sec.	35,	T4N,	R1W
NE 14, NE 14,	NE ½,	Sec. 2	22,	T5N,	RIW
NE $\frac{1}{4}$ , NE $\frac{1}{4}$ ,	NE 1.	Sec. 2	23.	T5N,	RIW
se ½, nw ½,	SW 1,	Sec.	31,	<b>T3</b> 6N,	RlW
NE 1, SE 1,	NW Ż.	Sec. 2	24,	TIN,	RlW
SW 1, NE 1,	SW Ż,	Sec.	30,	T4N,	RIV
NE 1, NE 1.	NE 2,	Sec. 1	14,	T5N,	RIW
SW 14, SW 14,	NE 1.	Sec. 1	19,	T4N,	R2W
NE 1, NE 2,	NE 2.	Sec. 2	22,	T5N,	RlW
SE 4, SE 4,	SW į,	Sec. 2	24,	T5N,	RIW
SN 4, NW 4,	NE 1.	Sec. 2	22,	T4N,	RlW
NW 1, NW 1,	NW 2.	Sec.	6,	T5N,	R3W
SW 4, SE 4,	NE 1.	Sec.	1,	T5N,	R47
SE 1, SE 1,	NW 1.	Sec. 2	20,	T7N,	RlE
SW 1/2, NE 1/2,	SW 14,	Sec.	30,	T4N,	RlW
SE 🛓, SE 🕌,	NE 1.	Sec. 2	24,	T5N,	RlW
SE 1/4, SE 1/4,	SW 1.	Sec.	4,	T7N,	R4W

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Table	2.	Texture, degree of erosion, percent slope,
		direction of slope, crop or vegetation and
		natural drainage of the 19 sites used in
		the study.

Soil Site	Texture (Surface)	Degree of Erosion	% Slope
Blount	Clay Loam	(1) Slight (0)	(A) 0-23 (A)
Ceresco No. 1	Sandy Loam	None (0)	(A) (A)
Ceresco No. 2	Sandy Loam	None (1)	(A) (A)
Colwood No. 1	Loam	Slight	0-2,5
Colwood No. 2	Loam	(1) Slight	(A) 0-2%
Chelsea	Sand	(1) Slight	(A) 0-2% (₽)
Hillsdale No. 1	Sandy Loem	(1) Slight	(B) 3-63
Hillsdale No. 2	Sandy Loam	(1) Slight	(B) 3-63
Houghton	Muck	(0) None	(A) 0-2,3
Lapeer	Sandy Loam	(1) Slight	(A) 0-2,%
Nekoosa No. 1	Sand	(1) Slight	(A) 0-2%
Nekoosa No. 2	Sand	(1) Slight	(B) 0-2%
0akv111e	Sand	(1) Slight	(E) 3-6,2
Pewamo No. 1	Clay Loam	(1) Slight	(A) 0-2,%
Pewamo No. 2	Clay Loam	(1) Slight	(A) 0-2%
Plainfield	Sand	(2) Moderate	(E) 3-6%
Spinks No. 1	Loamy Sand	(1) Slight	(B) 3-6,3
Spinks No. 2	Loamy Sand	(1) Slight	(E) 3-6だ
St. Clair	Clay Loam	(1) Slight	(в) 3-6,5

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### Table 2. Continued

Direction of Slope	Crop or Vegetation	Natural <u>Drainage</u>	Area of Flot
Southern	Corn	Imperfect*	40 ft. x 50 ft.
Southern	Grass	Imperfect	50 ft. x 50 ft.
Southern	Grass	Imperfect	50 ft. x 60 ft.
South Western	Grass	Foor	30 ft. x 80 ft.
Southern	Grass	Foor	40 ft. x 50 ft.
South Western	Grass	Well	100 ft. x 100 ft.
South western	Alfalfa	Well	60 ft. x 80 ft.
Southern	Grass	Well	40 ft. x 60 ft.
Southern	Sod	Poor	100 ft. x 200 ft.
Southern	Grass	Well	40 ft. x 50 ft.
South western	Grass	Imperfect	40 ft. x 100 ft.
Southern	Grass	Imperfect	30 ft. x 100 ft.
South western	Fasture	well	30 ft. x 80 ft.
South western	Corn	Poor	100 ft. x 200 ft.
Southern	Alfalfa	Poor	100 ft. x 200 ft.
South western	Grass	Well	30 ft. x 70 ft.
South western	Alfalfa	Well	50 ft. x 80 ft.
Southern	Corn	Well	80 ft. x 40 ft.
Southern	Alfalfa	Well	40 ft. x 60 ft.

\* "Imperfectly drained" and "somewhat poorly drained" are synonymous expressions of the natural drainage conditions of a soil.

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#### Collection of samples

Uniformity of the pH at each site was ascertained by the variability of pH among six individual cores and a composite sample which consisted of 20 cores. The six individual cores were 3 inches in diameter and extended to a depth of 6 to 8 inches (the plow depth). The 20 cores of the composite sample were one inch in diameter and extended to a depth of 6 to 8 The six cores were collected by dividing each plot inches. into six equal parts and taking a core from the center of each of the six parts. The 20 cores of the composite sample for each site were taken according to Extension Bulletin E-498 of the Cooperative Extension Service of Michigan State University (71). Two sub-samples were taken from each of the six individual cores and from the composite sample, and the pH's were determined with the glass electrode in a 1:1 soilwater suspension, Table 3.

After the sites or plots were located and established, the plow layer or upper 6 to 8 inches of each plot was sampled about the fifteenth of each month. Ten of the sites were sampled from May through September the other sites were sampled from June through September. One composite sample was collected from each plot each month in the same way the first composite sample of each plot was collected.

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#### Preparation of samples

The composite samples were well mixed in a plastic pail. After uniform mixing, a sub-sample was taken from the original sample of each site and placed in a plastic bag. After the sub-sample from each site was brought into the laboratory, part of it was refrigerated at about 40°F. until the field moist pH's could be determined and the remainder was placed on a laboratory bench and allowed to air dry. The samples were covered with wrapping paper, while air drying, in order to prevent contamination by dust particles. Determinations of pH on the air dry samples were made after three or four weeks of air drying. The pH of the field moist samples were determined from one to three days after collection of the samples. A portion of the field moist sample from each plot was dried in an oven for 24 hours, at approximately 100-110°F, and the pH's of these oven dried samples were also determined.

#### METHODS OF ANALYSIS

All samples were crushed and sieved through a two millimeter screen prior to analysis, and all determinations were run in duplicate, except where otherwise indicated.

#### Soil reaction

The hydrogen ion activity was determined with a Beckman Zeromatic pH meter and with the Hellige-Truog colorimetric kit at the following moisture statuses: field moist, air dry, and oven dry.

All pH measurements made with the glass electrode were on samples with the soil water ratios as indicated, on a weight basis. Glass electrode pH's of the oven dry and field moist samples were measured in a 1:1 soil  $-H_20$  suspension and in a 1:2 soil - 0.01MCaCl<sub>2</sub> suspension. The hydrogen ion activities of the air dry samples were also measured in a 1:2 soil -1NKCl suspension, in addition to the above two suspensions. The suspensions were each allowed to equilibrate for fifteen minutes with several intermittent stirrings.

#### Cation exchange capacity

The cation exchange capacities were determined by saturating the exchange complex with sodium ions (lN NaAc, at pH8.2) and replacing the sodium ion with ammonium ions (lN NH4Ac) (42). The sodium in dilute solution was determined with a

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Coleman flame photometer, and expressed as m.e./100 grams of soil.

#### Total exchangeable metallic cations

The total exchangeable bases were determined by the titration method as described by Bray and Willhite (42).

#### Electrical conductivity

The total soluble salt content was estimated by the electrical conductivity method as described by Greweling and Peech (36). A Solu-Bridge soil tester (Model RD-15) was used and the specific conductance was expressed as mhos x  $10^{-5}/cm$ .

#### Organic matter content

Total organic matter was determined by the ignition and weight loss method as described by Mitchell (42).

#### Lime requirement

Lime requirement was evaluated by the following three methods:

- 1. Shoemaker, et. al., buffer method (73).
- 2. pH Texture method (77).
- 3. Exchange acidity determined by difference between cation exchange capacity and total exchangeable metablic cations.

The lime requirements as determined by the above three methods were compared.

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#### RESULTS AND DISCUSSION

## Evaluation of the errors encountered in the measurements of soil pH with the glass electrode

To evaluate the errors in soil pH measurements with the glass electrode, consideration was given to: (1) the variability of the pH's of several standard laboratory check samples measured repeatedly during the period of this study, (2) the effects of different operators, different pH meters and different times on the pH's of five air dry soil samples, and the reproducibility of soil pH measurements made on these air dry samples: in water, in  $0.01MCaCl_2$  and in 1.0NKCl, (3) the variations in duplicate pH measurements made on composite field moist samples from each of the 19 sites, compared to the variability of duplicate measurements made on six core samples from each of these sites.

# Variability of pH measurements made on standard laboratory check samples during the season

pH values of the check samples used in this investigation were each measured several times during this study from May to October and approximately on the same dates that the pH's of the nineteen soil sites were measured. In addition, these pH measurements were not always made by the same operator and the measurements were not always made with the same pH meter on the different dates.

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Variability of pH values measured during this study for each of three of the standard check samples are illustrated in Figure 1. Check sample No. 1 has the highest pH value and it showed the least variability. pH values of this check sample fluctuated only 0.1 pH unit from time to time during this study. The maximum and minimum pH values for each of the other two check samples were observed during the earlier and latter part of this study, respectively. Figure 1. Differences between the maximum and minimum pH values for each check sample were 0.3 pH unit or less. Variations of the pH's of the other three check samples were comparable and similar to the variations, as illustrated in Figure 1, of check samples number 2 and 6.

The standard deviations of the means for the individual check samples ranged from a low of 0.07 to a high of 0.22 pH unit (Table 3). The combined standard error of the difference between the "known mean pH values and the measured mean pH values was  $\pm$  0.075. Twice this value will judge significance at the 0.05 probability level. By this criterion none of the measured mean pH values of the check samples differed significantly from their known pH values. However, it is interesting that all the observed means were less than the known values: on the average this difference was 0.09 pH unit. It is concluded that differences between mean soil pH values of a group of represen-

-23-

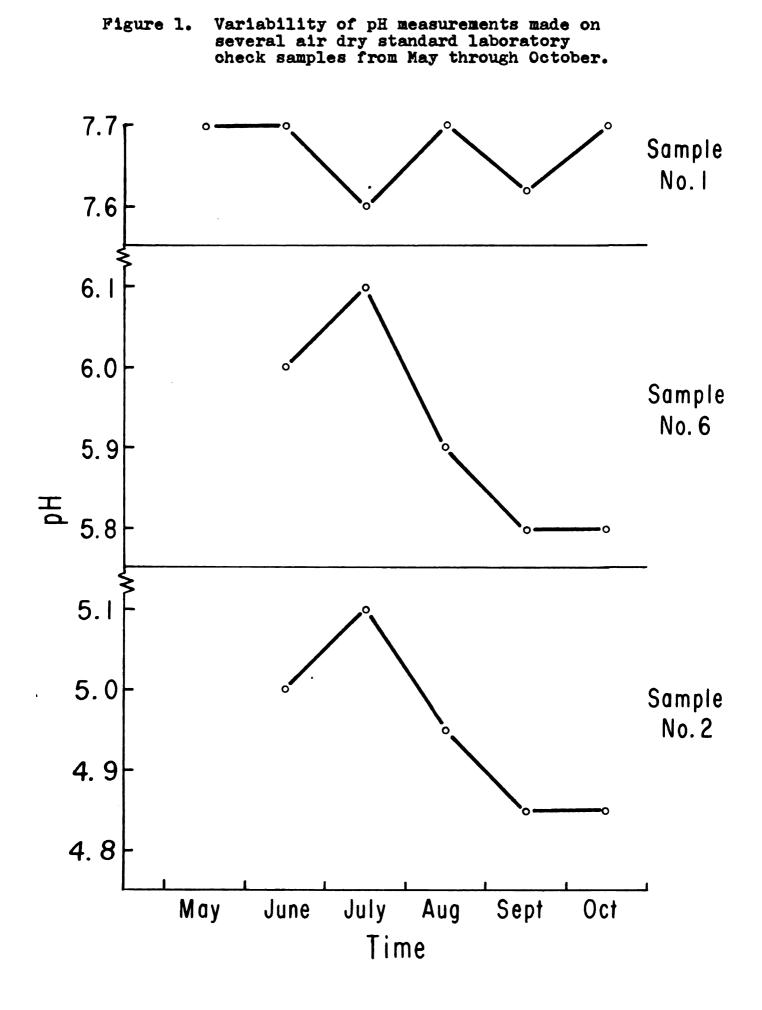


Table 3.	"Known pH Values" and variability of pH
	measurements made on standard laboratory check samples from May to October, 1966.

Sample Number	"Known mean pH Values"	Number of pH measur- ments	Means and standard deviations of pH measurements
l	7•75	13	7.68 <u>+</u> 0.07
2	5.05	12	4.94 <u>+</u> 0.17
3	6.0	10	5•94 <u>+</u> 0•22
4	5•9	10	5•75 <u>+</u> 0•17
5	5•7	9	5.68 <u>+</u> 0.16
6	6.05	5	5.90 <u>+</u> 0.14

tative observations may be significant when the differences are greater than  $\pm$  0.15 pH unit.

#### Effects of different operators and different pH meters on the variability of the pH's of five air dry soil samples

The pH's of one air dry sample from each of five of the nineteen soil sites used in this study were measured repeatedly to evaluate various possible sources of experimental errors in the pH measurements. The textures of these five samples ranged from loamy sand to clay loam, and their reaction, measured in water, ranged from a pH value of 6.0 to a pH value of 7.4.

Three operators measured the pH's of the five soil samples with one pH meter on the same day in the following suspending media: water, 0.01MCaCl<sub>2</sub> and 1.0NKCl. A three way analysis of variance (5 soils, 3 operators, and 3 suspending media) was performed on the data; soils and media were considered fixed and operators random in that analysis, Table 4. Significant differences were found for all main effects and a soil by media interaction, Table 4. Therefore, the variability of soil pH measurements made by different operators must be considered in studies of this type.

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Table 4.		(5 soils, 3	for a three way operators, 3 sus-
	pondring m	cuiu/•	

Source of Variance	Degrees of Freedom	Means Squared
Soil	4	1.96**
Operator	2	0.13**
Soil X operator	8	0.01
Suspending media	2	3.62**
Soil X Suspending Media	a 8	0.04*
Operator X Suspending Media	4	0.01
Error	16	0.01

**\*\*** Significant at probability less than 0.01

\* Significant at probability less than 0.05

The pH's of the five soil samples were measured in the three suspending media by one operator using two different pH meters on the same day. The maximum average difference between the two pH meters was 0.06 pH unit, Table 5. This is not a significant difference. Thus it appears that variations in pH measurements made under these conditions with the different pH meters are not important.

#### Reproducibility of soil pH measurements made in H2C, in 0.01MCaCl2 and in 1.01MCl by one operator using one pH meter on the same day.

One operator employed the same pH meter and made ten pH measurements on each of the five soil samples at hourly intervals on one day. On the average the standard deviations of the measurements made in water, in 0.01MCaCl2 and in 1.0NKCl were  $\pm 0.08$ ,  $\pm 0.07$ , and  $\pm 0.08$  pH unit respectively, Table 5. It is concluded that there are no significant differences in the reproducibility of soil pH values measured in the three suspending media. This conclusion is contrary to the proposal of Schofield <u>et. al.</u> (66) who indicated that soil pH measurements made on air dry samples in 0.01MCaCl<sub>2</sub> are more reproducible than measurements made in water. However, the possibility remains that seasonal variations in soil pH's may be less in 0.01MCaCl<sub>2</sub> than in water even though individual determinations are no more reproducible.

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Summary of the variability in the pH's
of five air dry soil semples measured
in water, in 0.01MCaCl <sub>2</sub> and in 1.0MKCl.
(

Suspending Media	Nean pH for each operator	Mean pH of each meter		
WATER	(1) 6.80 (2) 6.50 (3) 6.68	(1) 6.64 (2) 6.70		
Standard deviation(s)	+0.11 pH unit	<u>+</u> 0.04 pH unit		
Standard error of the mean $(S\overline{x})$	<u>+</u> 0.03 pH unit	<u>+</u> 0.01 pH unit		
0.01MCaCl <sub>2</sub>	(1) 6.44 (2) 6.22 (3) 6.30	(1) 6.28 (2) 6.24		
Standard deviation(s)	<u>+</u> 0.12 pH unit	<u>+</u> 0.03 pH unit		
Standard error of the mean $(S\overline{x})$	<u>+</u> 0.03 pH unit	<u>+</u> 0.01 pH unit		
1.0NKC1	(1) 5.74 (2) 5.62 (3) 5.78	(1) 5.84 (2) 5.90		
Standard deviation(s)	<u>+</u> 0.03 pH unit	<u>+</u> 0.04 pH unit		
Standerd error of the mean (S <del>x</del> )	<u>+</u> 0.02 pH unit	<u>+</u> 0.01 pH unit		

## Table 5. Continued

_		standard dev the mean of					5 soils
Nec	n pH		<u>S</u>		SX		
(1) (2) (3)	6.20 7.36 6.95	+0.03 +0.05 +0.09	pΗ ι	unit	<u>+</u> 0.025 +0.016 +0.028	рΗι	ınit
(4)	6.20	<u>+</u> 0.09	рН и	unit	<u>+</u> 0.028	pH ı	unit
(5)	6.6 <b>1</b>	<u>+</u> 0.0?	pH ı	unit	<u>+</u> 0.022	r Eq	unit
(1) (2) (3)	5•79 6•97 6•67	<u>+</u> 0.09 <u>+</u> 0.06 <u>+</u> 0.05	pΗι	unit	<u>+0.028</u> +0.019 +0.016	pH 1	unit
(4)	5.78	<u>+</u> 0.08	рН и	unit	<u>+</u> 0.025	рН ι	unit
(5)	6.30	<u>+</u> 0.08	рΗι	unit	<u>+</u> 0.025	pH ı	unit
(1) (2) (3)	5.40 6.70 6.20	<u>+</u> 0.08 +0.03 +0.09	pH u	unit	+0.025 +0.025 +0.028	pΗι	init
(4)	5.28	<u>+</u> 0.03	рН и	unit	<u>+</u> 0.025	рН и	unit
(5)	5•75	<u>+</u> 0.06	pH U	Unit	<u>+</u> 0.019	рН и	unit

#### Variability of soil pH values measured in 0.01MCaCl\_ with one pH meter by one operator on two different dates.

The pH's of all the airdry samples from each of the nineteen soil sites used in this study were measured in  $0.01MCaCl_2$  on two different dates. The regression of March 21 values on April 13 values was calculated (Figure 2): y = 0.04 + 0.99x. The standard error of the estimates equals 0.15 pH unit. To judge what may be a real difference between soil pH measurements, twice the standard error of the estimate was employed or 0.30 pH units. This will judge significance at approximately the 0.05 probability level.

# Variability of field moist pH values within each of the nineteen soil sites.

pH values of the first composite sample collected and each of the six single core samples collected from 1/6 of each plot are presented in Table 6. These pH values were measured in water with one pH meter, by one operator on the same day. The determination standard deviation for the sites ranged from a low of 0.096 to a high of 0.169 pH unit, and for the combined analysis it was 0.138 pH unit. Thus we conclude that the determination variability is consistent from site to site. The individual F statistics for testing the variability among cores within each plot were all non-significant. In fact, the F tests deviated only slightly from 1.0. From this we can conclude that the variability in the pH measurements of a particular soil site is due mainly to determination rather than to sampling.

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Figure 2. Comparison of pH values of all the air dry samples from the 19 sites measured in 0.01MCaCl<sub>2</sub> on two dates.

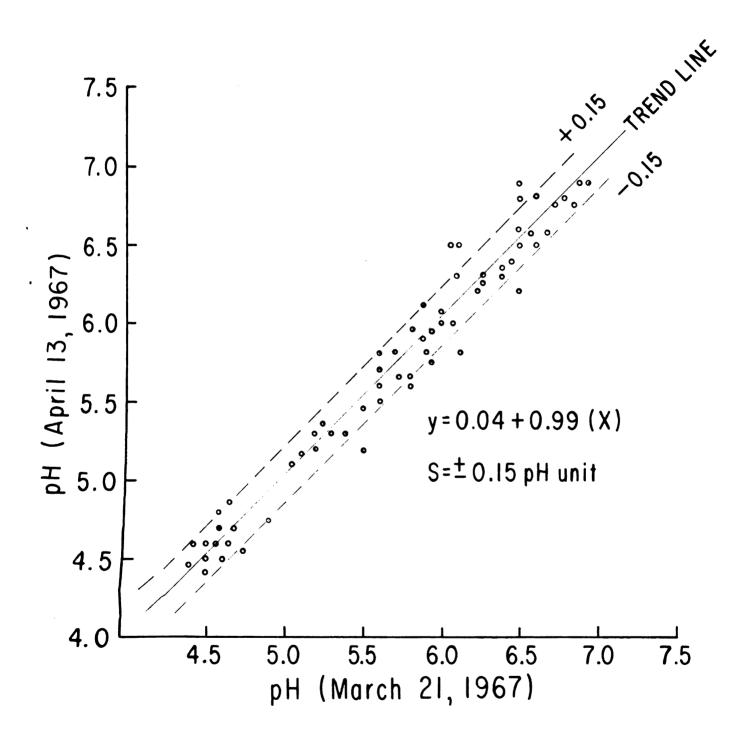


Table 6.	Variations in the pH's of the composite
	and single core samples collected in the
	initial sampling of each plot

Field Moist pH values - 1:1 Soil-H20 Ratio, by Weight

	Compos	site	Sin	gle Co	ores (	3 in.	in di	ameter)
Soil Site	Sample (20 cores, Soil Site 14 in. in diameter		K0.1		No.2		No.	3
Blount	7.0	7.2	7.2	7.0	7.1	6.9	7.2	7.0
Ceresco No.1	7•9	8.1	8.0	8.2	8.0	7.8	8.2	8.0
Ceresco No.2	7•9	7•7	8.0	8.1	7.6	7.8	8.0	7.3
Colwood No.1	8.0	8.2	8.2	8.2	8.0	8.3	8.0	8.2
Colwood No.2	8.0	7.8	7.6	7.8	7.9	7.6	7.8	7.8
Chelsea	5.8	5.6	5•9	5.6	5.6	5.6	5.8	5.6
Hillsdale No.l	6.7	6.9	6.5	6.7	6.6	6.7	6.6	6.8
Hillsdale No.2	6.2	6.2	6.3	6.0	6.2	6.4	6.3	6.1
Houghton	6.9	7.0	7.1	7.1	7.1	6.9	7.2	7.0
Laper	7.4	7.4	7•3	7•3	7•3	7•5	7•3	7•4
Nekoosa No.1	6.8	7.0	ó <b>.</b> 9	6.7	6.9	7.2	6.8	6.8
Nekoosa No.2	7•7	7•9	7.6	7.8	7•9	7•7	7•7	7.6
Oakville	6.4	6.3	6.2	6.4	6.3	6.1	6.4	6.2
Pewamo No. 1	7•5	7•5	7.4	7.6	7•7	7•5	7.6	7•4
Fewamo No. 2	7•5	7•3	7•4	7•4	7.6	7.4	7.6	7.6
Plainfield	6.0	6.3	6.1	6.3	6.2	6.0	6.3	6.1
Spinks No. 1	6.4	6.7	6.8	6.6	6.6	6.4	6.7	6.7
Spinks No. 2	6.6	6.8	6.6	6.6	6.7	6.5	6.9	6.7
St. Clair	7•5	7•5	7.4	7.6	7•7	7•5	7.4	7.6

. No	.4	No	•5 ·	No.6		Neans and Determination
7,2	7.2	6.9	7.2	7.1	7.1	Standard Deviations $(S_D)$ 7.09 ± 0.134
8.1	8.0	8.0	7.8	7•9	7•9	7.99 <u>+</u> 0.122
7.9	7•7	7•7	7.8	7.8	8.0	7.84 <u>+</u> 0.135
8.2	7•9	8.3	8.1	7•9	8.1	8.11 <u>+</u> 0.155
7.8	7.6	7.8	7.6	7•9	7•7	7.76 <u>+</u> 0.144
5.7	5•9	5•7	5.6	5.6	5.6	5.68 <u>+</u> 0.125
6.5	6.5	6.7	6.5	6.8	6.6	6 <b>.6</b> 5 <u>+</u> 0 <b>.</b> 122
6.3	6.3	6.1	6.1	6.4	6.2	6.22 <u>+</u> 0.122
7.0	6.9	7.0	6.8	7.1	7.1	7.01 <u>+</u> 0.099
7.4	7.2	7•3	7•3	7.4	7•5	7•35 <u>+</u> 0•096
7.1	6.9	6.9	6.7	7.1	6.9	6.91 <u>+</u> 0.144
7.6	7•7	7•7	7•9	7•7	7.6	7.72 <u>+</u> 0.104
6.4	6.2	6.5	6.3	6.3	6.1	6.31 <u>+</u> 0.122
7.6	7.6	7•5	7•3	7•5	7•3	7.50 <u>+</u> 0.119
7•5	7•7	7•7	7•5	7•5	7•3	7.50 <u>+</u> 0.119
6.0	6.3	6.3	6.0	6.0	6.1	6.14 <u>+</u> 0.169
6.4	6.5	6.7	6.5	6.7	6.7	6.60 <u>+</u> 0.127
6.5	6.7	6.7	6.9	6.9	6.7	6.70 <u>+</u> 0.131
7.6	7.6	7•7	7•5	7.4	7•5	7.54 <u>+</u> 0.110
				Co	mbined S	0.133

Summary

On the basis of the above, it is evident that pH measurements made on a particular soil sample varied when measured under the different conditions stated above (Tables 3, 4, 5 and 6 and Figures 1, 2). The greatest variations of soil pH values occurred under those conditions where measurements were not always made with the same pH meter and by the same operator on the same date, Table 3. However, in most instances the standard deviations of pH values measured on the same soil samples under the various conditions were approximately  $\pm$  0.15 pH unit or less (Tables 3, 4, 5 and 6 and Figure 2).

Therefore, a variation of  $\pm 0.3$  pH unit is considered necessary to be certain of a probable significant difference between individual soil pH measurements. This range of variability satisfactorily includes the errors encountered in the individual measurements of the pH's of the soils used in this study. However, when mean soil pH values of a group of representative observations are compared then differences greater than  $\pm 0.15$  pH unit may be significant, Table 3.

> Influence of moisture conditions and suspending media on seasonal variability of soil pH values

Data on soil pH's determined at two moisture conditions with the Truog kit, and at three moisture conditions and in

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several suspending media with the glass electrode are presented in Table 7 in the Appendix, for each of the sites on each sampling date. Statistical deductions for these data are presented in Figures 3, 4 and 5.

Ten of the nineteen soil sites used in this study were sampled for five months, May through September, and the other sites were sampled for four months, June through September. On the nine sites sampled for only four times the seasonal trends were similar to those of the other ten sites during that period.

# Influence of moisture condition on seasonal variability of soil pH values measured in water and in 0.0MCaCl<sub>2</sub> with the glass electrode

The field moist soil pH data showed a continuous decrease in values as the season progressed, Figure 3. Because of the lower pH's observed on the standard laboratory samples below pH 6.5 after August 15, as shown in Figure 1, the pH readings on the field moist and oven dry samples measured in  $H_20$  were corrected by adding 0.1 pH units to the September readings that were below pH 6.5. Soil pH values measured at this moisture condition in water and in 0.01MCaCl<sub>2</sub> were 0.81 and 0.47 pH units lower, respectively, at the end of the season, in September than at the beginning of the season, in May. On the other hand, the air dry and oven soil pH values tended to show a cyclic seasonal trend.

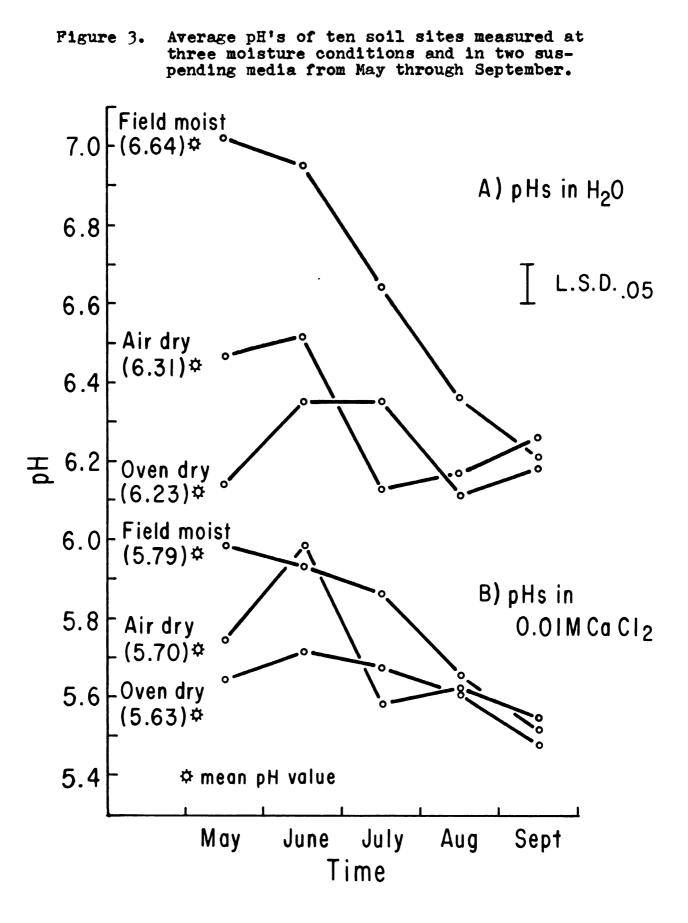
Differences between average soil pH values at the three

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moisture conditions were 0.08 pH unit or less in both water and 0.01MCaCl<sub>2</sub> at the end of the season, Figure 3. These differences are not significant. However, differences between soil pH values measured at the three moisture conditions are significant at certain times during the earlier part of the season. The calculated L.S.D. at the 5% level is equal to 0.1 pH unit, Figure 3. This calculation was based on a site by time by moisture condition interaction.

During this period, the air dry and oven dry soil pH values measured in water were as much as 0.55 and 0.88 pH units lower than the corresponding field moist pH values, respectively, Figure 3A. Similarly, the air dry and oven dry soil pH's measured in 0.01MCaCl<sub>2</sub> were as much as 0.28 and 0.34 pH units lower than the corresponding field moist pH values, respectively, Figure 3B.

During the season, there were no consistent significant differences between the air dry and oven dry soil pH values measured in either of the two suspending media, Figure 3. On the average, the oven dry soil pH values were less than 0.1 pH unit lower than the air dry soil pH values measured in either water or 0.01MCaCl<sub>2</sub>. The average of the 0.01MCaCl<sub>2</sub> pH's were lower than the mean pH values measured in water at the following moisture conditions by the following amounts: field moist; 0.85 pH unit; air dry; 0.60 pH unit; and oven dry; 0.61 pH unit.

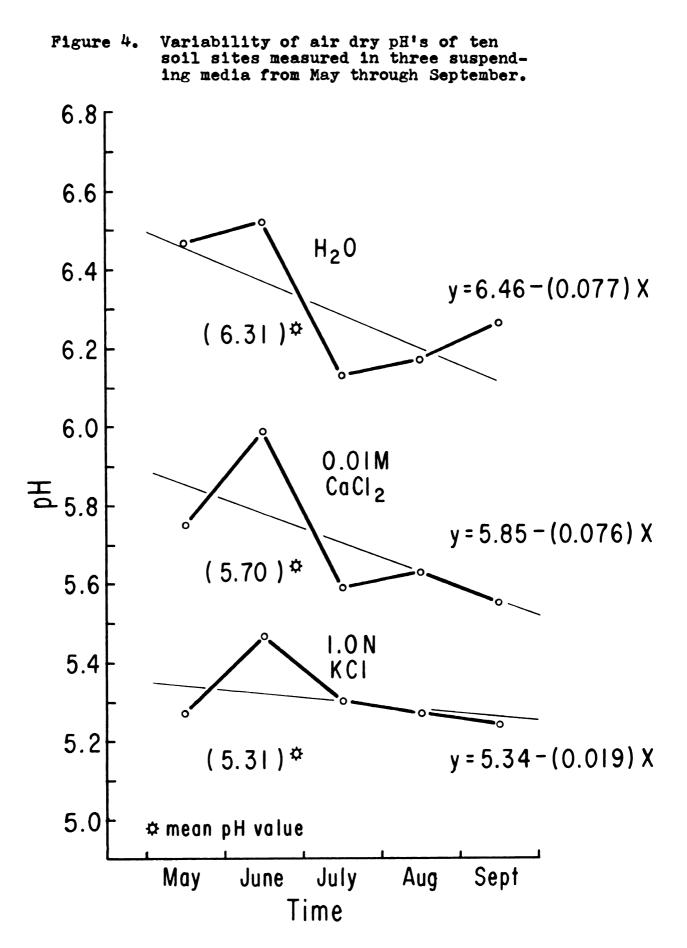


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Comparison of the variability of the air dry
pH's of soil samples collected from May through
September when measured in H<sub>2</sub>O, in 0.01MCaCl<sub>2</sub>
and in 1.0NKCl with the glass electrode.
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The average air dry soil pH values measured in water, in 0.01MCaCl<sub>2</sub> and in 1.0NKCl showed a cyclic seasonal trend in the pH's of the ten sites studied for five months, Figure 4. The May pH values were lower, on the average, than the June pH values for the ten sites.

The average pH values measured in water were the highest at all times during the season and the 1.0NKCl pH's were lowest for the entire season. On the average, pH's measured in 0.01MCaCl<sub>2</sub> and in 1.0NKCl were approximately 0.6 and 1.0 pH units lower, respectively, than pH's measured in water. However, the 0.01MCaCl<sub>2</sub> pH's were 0.5 pH lower than the water pH's at the more alkaline end of the pH scale and 0.8 pH unit lower at the more acid end of the pH scale. Similarly the 1.0NKCl pH's were 0.9 and 1.1 pH units lower than the water pH's at the more alkaline and acid ends of the pH scale, respectively.

There were no significant differences between the seasonal variability of the average air dry pH values measured in water and in  $0.01MCaCl_2$ , Figure 4. This is contrary to the proposal of Schofield <u>et. al</u> (66) who have indicated that air dry soil pH values measured in  $0.01MCaCl_2$  show less seasonal variability than the corresponding pH values measured in water. However, the  $0.01MCaCl_2$  solution did reduce the



seasonal variability of field moist pH values compared to those measured in water, Figure 3. The field moist soil pH values measured in water and in 0.01MCaCl<sub>2</sub> were 0.81 and 0.47 pH units lower at the end of the season (September) than at the beginning of the season (May), respectively.

pH values measured in 1.0NKCl showed the least seasonal variability, Figure 4. This is in agreement with the findings of many European workers who have reported that soil pH values measured in 1.0NKCl are less influenced by changes in biological and meteorological conditions and reflect a more intrinsic characteristic of the soil than soil pH values measured in water (59).

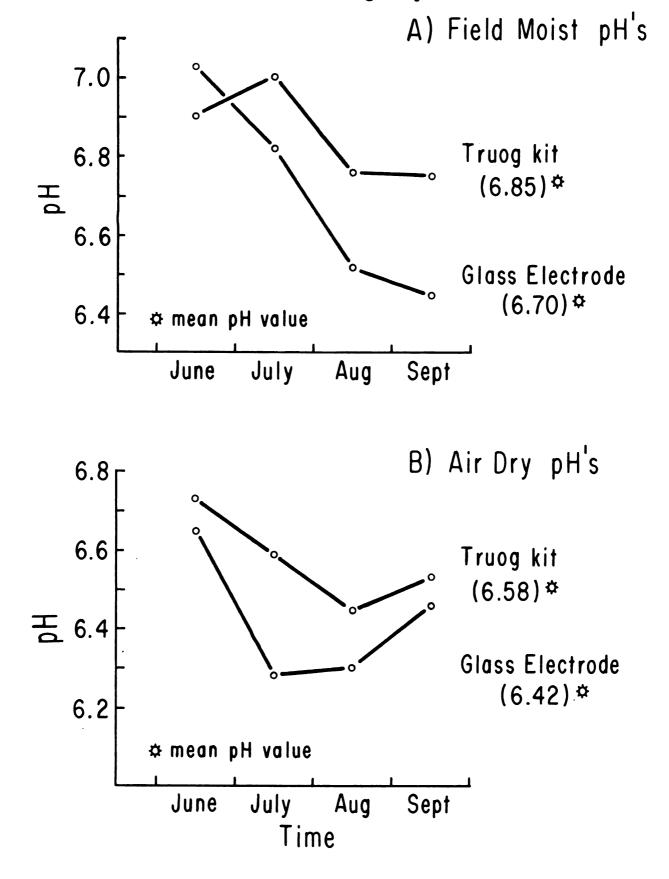
### <u>Comparison of the seasonal variability of field</u> <u>moist and air dry soil pH values measured with</u> <u>the Truog kit and with the glass electrode</u>

On the nineteen soil sites sampled four times, the field moist and air dry soil pH values determined with the Truog kit showed seasonal trends similar to those of the corresponding pH values measured with the glass electrode, Figure 5. On the average, air drying lowered the field moist soil pH values determined with the Truog kit approximately 0.3 pH unit during the season. The Truog kit showed less seasonal variability in pH's, on the average, than the glass electrode, particularly on field moist soil samples.

On the average, differences between the field moist soil pH values measured in water with the Truog kit and with

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Figure 5. Comparison of average field moist and air dry pH values of nineteen soil sites measured with the Truog Kit and in water with the glass electrode from June through September.



the glass electrode increased as the season progressed to a maximum difference of approximately 0.3 pH unit at the end of the season, Figure 5A. Figure 5B shows that the air dry soil pH values measured with the Truog kit during the season were approximately 0.2 pH unit higher, on the average, than the corresponding pH values measured in water with the glass electrode. The air dry pH values showed an upward trend in September with the Truog and glass electrode methods, indicating a cyclic trend back toward the higher pH values early in the season.

#### Summary

Regardless of suspending media, the field moist soil pH's showed a steady decrease in values as the season progressed, and the oven dry and air dry pH's showed a cyclic seasonal trend, Figures 3 and 4. However, it is apparent that soil pH measurements are influenced by the moisture condition of the sample and the suspending media.

At the beginning of the season, in May, the oven dry pH's measured in water were as much as 0.88 pH unit lower than the corresponding field moist pH values. Differences between the mean of the air dry and oven dry pH values measured in water and in 0.01MCaCl<sub>2</sub> were not significant. At the end of the season, there were also no significant differences between pH values measured at the three moisture conditions in water or in 0.01MCaCl<sub>2</sub>, Figure 3.

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Field moist pH values measured in 0.01MCaCl<sub>2</sub> showed less seasonal variability than the corresponding pH's measured in water. However, the oven dry and air dry pH's measured in 0.01MCaCl<sub>2</sub> were just as variable as the corresponding pH's measured in water, Figure 3. The air dry pH's measured in 1.0NKCl showed less seasonal variability than the corresponding pH's in water or in 0.01MCaCl<sub>2</sub>, Figure 4.

The 0.01MCaCl<sub>2</sub> pH's were lower than the mean pH values measured in water at the following moisture conditions by the following amounts: Field moist, 0.85 pH unit; and oven dry, 0.61 pH unit. The air dry pH's measured in 0.01MCaCl<sub>2</sub> and in 1.0NKCl were 0.6 and 1.0 pH unit lower, respectively, than the corresponding pH's measured in water, Figure 4.

On the average the field moist pH values determined with the Truog kit were as much as 0.3 pH unit higher than the corresponding pH values measured in water with the glass electrode at the end of the season, in September, Figure 5A. However, on the average, the air dry pH's determined with the Truog kit were 0.2 pH unit higher than the pH values measured in water with the glass electrode, Figure 5B.

# <u>Several factors influencing the</u> seasonal variability of soil pH values

The field moist pH values, measured in water, of all the nineteen soil sites studied showed seasonal variability (Table 7), as illustrated in Figure 3 for the ten sites. However, only

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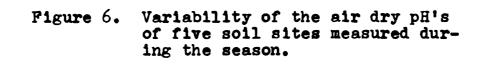
fourteen of the sites showed seasonal variability of soil pH when the air dry pH's measured in water were considered, Table 7. Variations of the pH's of the other five sites (Chelsea, Hillsdale No. 2, Houghton, Oakville and Pewamo No. 1) measured during the season fell within the range of the experimental error,  $\pm$  0.3 pH unit, deduced in this study. Even though differences between the pH values for each of these five sites measured during the season were not significant, it appears that there may be a seasonal trend similar to that illustrated in Figure 4, as shown in Figure **6**.

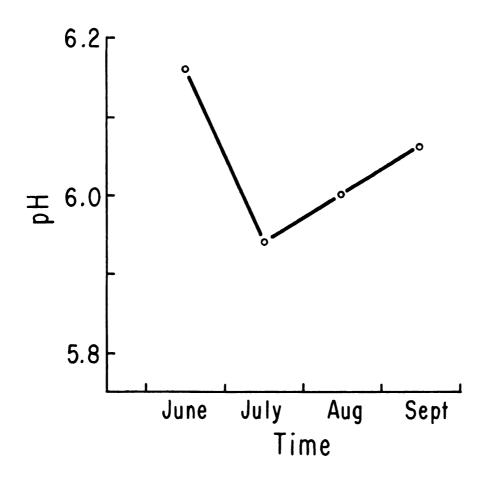
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Seasonal variations of the field moist pH values measured in water ranged from 0.5 pH unit for Chelsea to 1.6 pH unit for Pewamo No. 1, Table 7. The seasonal variations of the corresponding air dry soil pH values ranged from 0.5 pH unit for Nekoosa No. 1 to 0.9 pH unit for Pewamo No. 1, Table 7.

Tohelp explain these seasonal variations in soil pH measurements the field moisture content, the total exchangeable metallic cations, the electrical conductivity and the organic matter content were determined on each sample collected from each site during the season. These data for each site and for each month are presented in Table 8 in the appendix.

In addition, the cation exchange capacity of each site was determined on one of the samples from each site. The





percent base saturation and the exchange acidity were calculated using the cation exchange capacities and the exchangeable metallic cations. It was assumed that there were no changes in the cation exchange capacity of each site during the season. The cation exchange capacity, the calculated percent base saturation and the calculated exchange acidity for each site are shown in Table 8B in the appendix.

Statistical analyses of these data were made under the supervision of Dr. C. E. Cress in the Crop Science Department with the assistance of Mrs. N. Galuzzi and the Computer Laboratory. The resulting significant correlations between the pH's and these soil properties are shown in Table 9.

Electrical conductivity and organic matter percentage were negatively and positively correlated, respectively, with soil pH's, Table 9. The negative correlation shows that the increase in electrical conductivity, due probably to the presence of soluble salts, is associated with decreases in soil pH values. There is also a significant increase in field moist soil pH's with an increase in the moisture percentage. These two relationships may thus be direct corollaries of increasing the salt concentrations and diluting their influences on soil pH's, respectively.

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Table 9 Significant simple correlations between seasonal variability of soil pH and field moisture percentage, base saturation percentage, electrical conductivity and organic matter content.

Correlation of field moist pH's measured in water with:

Field moisture percentage ..... r = +0.285\*Base saturation percentage ..... r = +0.493\*Electrical conductivity ..... r = -0.336\*Organic matter content .... r = +0.592\*Base saturation and organic matter percentages .... r = +0.638\*

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Correlation of air dry pH's measured in water with:

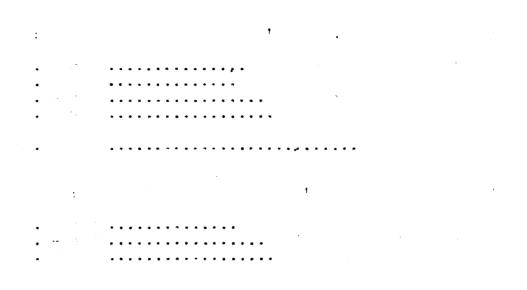
Base saturation percentage ..... r = +0.532\*Electrical Conductivity ..... r = -0.815\*Organic matter content ..... r = +0.094\*

Correlation of field moisture percentage with:

Electrical conductivity r = 90.73\*Organic matter percentage r = 0.76\*

\*Significant at 5% level

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Seasonal variations of electrical conductivity and organic matter content were highly correlated with field moisture percentage, Table 9. This helps to explain why organic matter gave the highest correlation between seasonal variability of the field moist soil pH values and the lowest correlation between the seasonal variability of the air dry soil pH values. This is due to the fact that organic matter influences the amount of moisture present at the field moist condition and to the dilution effect of increased moisture on the soluble salts present.

The relatively low correlation between seasonal variability of soil pH values and percent base saturation may be partially due to the presence of soluble salts which will be counted in the exchangeable cations but will tend to decrease rather than increase the pH. However, the air dry pH's of eight of the sites (Blount, Ceresco No. 1, Colwood No. 2, Hillsdale No. 1, Nekoosa No. 1, Pewamo No.1, Plainfield and Spinks No. 2) also showed seasonal variability when measured in 0.01MCaCl<sub>2</sub>, Table 7. Two of the sites, Blount and Hillsdale No. 1, showed seasonal variability even when measured in 1.0NKCl, Table 7. These indicate that other factors besides electrical conductivity are responsible for the observed variations in the measured pH values of some soils. However electrical conductivity, believed to be largely a reflection of salt content, is responsible for most of the seasonal

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variability of the pH's of most of the soil sites used in this study.

It was assumed that there were no significant seasonal variations in the cation exchange capacities. However, there were variations of as much as ten percent, in the organic matter percentages during the season. Therefore, it is possible that the cation exchange capacities also varied seasonally. Seasonal variability of the cation exchange capacities may partially account for the relatively low correlation between seasonal variations of soil pH values and the base saturation percentages, as calculated in this study.

#### Seasonal variability

#### of lime requirement

The variation of lime requirement was evaluated on air dry samples collected from eleven sites by the following three methods: pH plus texture, SMP or buffer and exchange acidity. Lime requirement was determined on all air dry soil samples with pH values less than 6.5 when measured in water with the glass electrode. These data are presented in Table 10 and the variations of the average lime requirements for four months (June through September) are illustrated in Figure 7.

On the average, the pH plus texture method showed the maximum seasonal variability of lime requirement, which was approximately 1.0 ton per acre, Figure 7. The maximum average

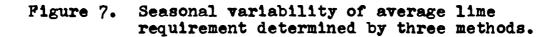
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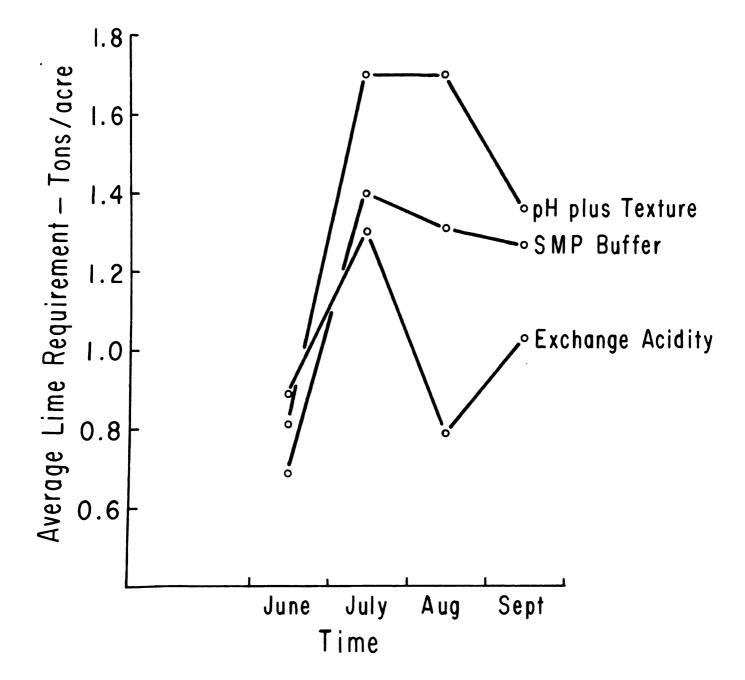
variations in lime requirements by the buffer method during the season were more comparable to but greater than those in the exchange acidity method, Figure 7. The pH plus texture and S.M.P. buffer methods showed a cyclic seasonal trend in lime requirement, with the maximum in mid-summer (July), Figure 7. Contrary to these the lime requirement evaluated by the exchange acidity method tended to fluctuateless during the season.

Seven of the eleven soil sites with evident lime requirement had zero lime requirement at the beginning of the season or in May, Table 10. However, each of the eleven sites exhibited maximum lime requirement in July or in August. The maximum difference in lime requirement evaluated by the pH plus texture method was 2.5 tons per acre for Hillsdale No. 2. Similarly, the maximum difference in lime requirement determined by the S.M.P. buffer method was 2.3 tons per acre for Pewamo No. 1. However, the maximum seasonal difference in lime requirement for any soil studied was with use of the exchange acidity method on samples collected from Pewamo No. 1. Here the lime requirement varied from 0.0 early in the season to 4 tons per acre in July, Table 10.

Thus, it is concluded that the seasonal variability of lime requirement should be considered when lime recommendations are made.

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## SUMMARY AND CONCLUSIONS

A study of the seasonal variability of the pH's and lime requirements of several soils in Southern Michigan was conducted. The experimental errors in pH determinations were evaluated. Results of chemical and physical soil analyses were studied and correlations of those results with pH differences were calculated to determine the relationship of several soil properties to the seasonal variability of soil pH values.

The results of this study are summarized as follows:

- 1. To be reasonably certain of a significant difference between individual soil pH values, a variation greater than  $\pm$  0.3 pH unit is necessary. However, when mean soil pH values of a representative number of observations are compared, differences greater than  $\pm$  0.15 pH unit are likely significant.
- 2. Field moist soil pH values measured in water usually showed marked seasonal variability. A maximum variation of 1.6 pH units was observed, and the average seasonal variation was approximately 0.8 pH unit. The highest and lowest pH values were early in the season and at the end of the season, respectively. The correlation between organic matter content and season variability of these pH values was the highest of the correlations with the soil factors studied. This is probably due to the combined

effects of the relationships of organic matter content to field moisture content, and field moisture content to electrical conductivity.

- On the average, during the wetter portion of the 3. season, the air dry and oven dry pH values measured in water were approximately 0.5 and 0.8 pH unit lower, respectively, than the corresponding field moist pH values. During the drier part of the season, differences between average pH values measured at the three moisture conditions were less than 0.1 pH unit and non-significant. Air dry and oven dry pH values measured on samples collected during the drier portion of the season may be better expressions of the pH in the field than the corresponding pH values measured on samples collected during the wetter part of the Therefore, when soil pH values are inseason. terpreted for various purposes the moisture conditions and the time of collection of the soil samples should be considered.
- 4. Only four of eleven soil sites exhibited a lime requirement during the early part of the season, based on air dry samples, but each of the eleven sites showed a lime requirement during the middle of the summer. A maximum seasonal variation of 4 tons per acre was observed for an individual site,

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using the exchangeable hydrogen method for lime requirement. Therefore, the time of sampling and the method for estimating lime requirement are factors that should be considered in making lime requirements recommendations.

5. The relative magnitude of the seasonal variability of soil pH values, measured in both water and in  $0.01MCaCl_2$ , at the three moisture conditions is as follows: field moist > oven dry  $\cong$  air dry. Drying soil samples in an oven facilitates the time and space necessary for drying. Therefore, it appears that oven dry soil samples are best adapted for routine pH determinations.

- 6. On the average,  $0.01MCaCl_2$  and 1.0NKCl lowered air dry soil pH values measured in water approximately 0.6 and 1.0 pH unit, respectively. The relative order for the seasonal variability of air dry pH's measured in the three suspending media is as follows:  $H_20$ > 0.01MCaCl\_2>1.0NKCl. However, for some soils the 0.01MCaCl\_2 pH's were just as variable as the pH's measured in water.
- 7. Field moist soil pH values determined with the Truog kit showed less seasonal variability than the corresponding pH values measured in water with the glass electrode. However, on the average, the Truog pH values were higher than the pH values

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measured in water with the glass electrode. On the average field moist and air dry soil pH values determined with the Truog kit were not more than 0.3 and 0.2 pH unit higher, respectively, than the corresponding glass electrode pH values. The Truog kit is also well adapted for field work, especially soil survey. Therefore, the Truog kit, as it is commonly used by soil surveyors in Michigan, appears to be a satisfactory field kit for pH determinations.

- 8. Soil pH values measured in 1.0NKCl were the least variable during the season and appeared to reflect an intrinsic characteristic of the soil. Therefore, these pH values may be very useful in reseasch work and soil classification, especially in classifying soils at the family level in the 7th approximation. These pH values may also aid in making lime requirement recommendations that are relatively free of seasonal influences.
- 9. Seasonal variability of air dry soil pH values measured in water were negatively and highly correlated with electrical conductivity of the samples. Also, most of the soil sites exhibited no seasonal variability of soil pH values when measured in 1.0NKCL. This indicates that soluble salts are probably responsible for most of the observed

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seasonal variability of soil pH values. However, two of the nineteen soil sites showed seasonal variations even when measured in 1.0NKCl, so soluple salts cannot explain all of the seasonal variations in pH's.

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10. Further study is needed to determine what and how other soil properties influence the seasonal variability of soil pH values and lime requirements of soils.

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APPENDIX

Tab**le** 7

Soil reaction measured at three moisture conditions and in several suspending media for each site on each sampling date

A. Nay sampling

Field Moist pH's

1.11

Soil	Truog	Glass	Electrode
Site	Kit	H <sub>2</sub> 0	<b>0.</b> 01MCaCl <sub>2</sub>
Blount Ceresco(No.l) Hillsdale(No.l) Houghton Lapeer Nekoosa(no.l) Oakville Pewamo(No.l) Plainfield Spinks(No.l)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

### Air Dry pH's

	Truog Kit	Gl H <sub>2</sub> 0	ass Electrode 0.01MCaCl <sub>2</sub> .	1.ONKC1
Blount Ceresco(No.1) Hillsdale(No.1) Houghton Lapeer Nekoosa(No.1) Oakville Pewamo(No.1) Plainfield Spinks(no.1)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.6 7.5 6.0 6.6 7.2 6.7 5.9 6.9 5.5 5.8	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5.15.16.36.44.95.05.65.76.06.05.65.64.34.25.55.54.24.34.84.9

#### Oven Dry pH's

	U	Glass	Electrode 0.01MCaCl <sub>2</sub>
	п	20	
Blount	6.2	6.2	5.7 5.7
Ceresco(No.l)	7.0	6.9	6.5 6.5
Hillsdale(No.l)	5.8	5.7	5.2 5.2
Houghton	6.1	6.2	5.9 5.9
Lapeer	6.7	6.7	6.0 6.0
Nekoosa(No.1)	6.5	6.5	5.8 5.8
Oakville	5.4	5.5	4.8 4.7
Pewamo(No.1)	6.6	6.6	6.0 6.0
Plainfield	5.1	5.1	4.5 4.5
Spinks(No.1)	5.8	5.8	5.1 5.2

	Table 7.	Cortinue	ad				
	B. June S						
	Field Mois						
<u>Soil_Site</u>		<u>g Kit</u>			Lass El	ectrod	.e 'a <b>(</b> "]
				<u>H</u> 2		0.01MC	
Blount Ceresco No. 1 Ceresco No. 2 Colwood No. 1 Colwood No. 2 Chelsea Hillsdale No. 2 Houghton Lapeer Nekoosa No. 1 Nékoosa No. 1 Nékoosa No. 2 Oakville Fewamo No. 1 Pewamo No. 2 Flainfield Spinks No. 1 Spinks No. 2 St. Clair	8.0 7.4 7.4 5.9 6.6 7.0 5.2 7.1 7.5 5.4	7.004492409521026464 7.004492409521026464		7.1072976205382356376	37375667777677566 	09886412216895557 75664556666466455	6.6 7.0 5.9 6.8 5.5  6.6 6.9 5.5  6.5 5.5  6.5 5.5  6.5  5.5  6.3
	<u>Air Dry</u>	pH's					
	Truo	<u>s Kit</u>	<u>H</u> 20	0.01	LI.CaCl <sub>2</sub>	<u>1.0</u>	HRC1
Blount Ceresco No. 1 Ceresco No. 2 Colwood No. 1 Colwood No. 2 Chelsea Hillsdale No. 2 Houghton Lapeer Nekoosa No. 1 Nekoosa No. 1 Nekoosa No. 2 Oakville Fewamo No. 1 Fewamo No. 2 Flainfield Spinks No. 1 Spinks No. 2 St. Clair	6.7 8.0 8.0 7.8 7.8 7.8 5.8 5.0 7.6 7.6 7.5 6 7.5 6 7.5 6 6 .5 8 6 .5 8 5 6 7.5 8 6 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 8 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5	6.8 8.00 8.00 5.20 6.06 7.60 7.50 6.55 7.60 7.50 6.55 7.50 6.50 7.50 6.50 7.50 7.50 7.50 7.50 7.50 6.50 7.50 7.50 7.50 7.50 7.50 7.50 7.50 7	7.5 7.5 7.5 7.5 6.2 9.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7		7098898503467230890		6.434201842504330924 6.4645456564554455

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	Table	7.	Continued
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# B. June Semple

### Cven Dry pH's

<u>Soil Site</u>	Glass I <u>H<sub>2</sub>0</u>	Electrode <u>0.01MCmCl</u> 2
Blount Ceresco No. 1 Ceresco No. 2 Colwood No. 1 Colwood No. 2 Chelsea Hillsdale No. 1 Hillsdale No. 2 Houghton Lapeer Nekoosa No. 1 Nekoosa No. 1 Nekoosa No. 1 Pewamo No. 2 Plainfield Spinks No. 1 Spinks No. 2 St. Clair	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.4       6.3         6.6       6.7         6.6       6.7         6.6       6.7         6.6       6.7         6.6       6.7         6.6       6.7         6.6       6.7         6.6       6.7         6.6       6.4         4.6       4.5         5.0       5.6         6.0       5.6         5.5       5.6         6.0       5.6         7.6       6.1         4.6       5.4         5.5       5.6         6.0       5.4         6.0       5.6         6.0       5.6         5.4       5.6

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Table 7. Continued

### C. July Sampling

	Field 1	<u>Soist p</u>	H'S	<u>Oven</u>	Dry pl's
Soil Site	fruog Kit	Glass H <sub>2</sub> 0	Electrode 0.01MCaCl <sub>2</sub>	Glass H <sub>2</sub> 0	Electrode 0.011.CaCl <sub>2</sub>
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Hillsdale No.2 Houghton Lapeer Nekoosa No.1 Nekoosa No.2 Oakville Pewamo No.1 Pewamo No.2 Flainfield Spinks No.1 Spinks No.2 St. Clair	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.7 7.7 7.5 4.9 6.0 7.1 2.9 6.1 8.2 3 6.0 7.5 6.1 8.2 3 6.7 7.5 6.7 7.5 6.7 7.5 6.7 7.5 6.7 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7	6.2 6.6 8 6.5 9.2 8 4.5 2.5 0 9.3 9 8 3 4 5.6 6 5.5 9.3 9 8 3 4 5 6 4 5 6 4 5 6 4 5 6 4 5 6 6 6 6 6 6	6.8 7.7 7.4 5.6 6.1 8 7.7 7.4 5.6 6.1 8 2.4 1930 5.6 6.5 6.5 6.5 6.5	6.4 7.1 7.0 6.7 4.8 5.1 6.7 4.8 5.1 6.5 5.1 6.5 5.2 4.9 5.1 5.2 4.9 5.1 5.1 5.1 5.1 5.1 5.1 5.1 5.1 5.1 5.1

# Air Dry pH's

	Tru	og	1	Glass Electro	de	
	Ki	t	<sup>H</sup> 2 <sup>0</sup>	0.01MCaCl <sub>2</sub>	1.01	KC1
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Hillsdale No.2 Houghton Lapeer Nekoosa No.1 Nekoosa No.1 Nekoosa No.2 Oakville Pewamo No.1 Pewamo No.2 Flainfield Spinks No.2 St. Clair	6.700050800505580616	6000078080507402837 67567566	6.777655930395071712 7.6.55567665665566	6.3 98 6.25 4.25 5.62 5.64 5.25 5.64 5.25 5.8 5.64 5.25 5.8 5.8 5.8 5.8 5.8 5.8 5.8 5.8 5.8 5.	3044124089613362123 5.5556455455555555555555555555555555555	9154235290704470034 566664556564554555

# Table 7. Continued

### D. August Sompling

# Field Moist pH's

### Cven Dry pH's

Blount $6.5$ $6.7$ $6.3$ $5.9$ $6.2$ $5.8$ Ceresco No.1 $7.5$ $7.5$ $7.7$ $6.7$ $7.4$ $6.9$ Ceresco No.2 $8.0$ $8.0$ $7.3$ $6.3$ $7.1$ $6.7$ Colwood No.1 $7.5$ $7.6$ $7.4$ $6.4$ $7.4$ $6.7$ Colwood No.2 $7.0$ $7.4$ $6.3$ $6.9$ $5.8$ Chelsea $5.5$ $5.6$ $5.4$ $4.5$ $5.3$ $4.6$ Hillsdale No.1 $5.7$ $5.8$ $5.6$ $5.0$ $5.2$ $4.7$ Hillsdale No.2 $6.0$ $6.0$ $6.0$ $5.0$ $5.6$ $5.1$ Houghton $7.0$ $7.0$ $6.6$ $6.1$ $6.4$ $6.0$ Lapeer $7.0$ $7.0$ $6.9$ $6.1$ $6.6$ $5.9$ Nekoosa No.1 $7.0$ $7.0$ $6.9$ $6.1$ $6.6$ $5.9$ Nekoosa No.2 $7.0$ $7.0$ $6.9$ $6.2$ $6.5$ $6.2$ Oakville $5.7$ $5.6$ $4.6$ $5.2$ $4.6$ Pewamo No.1 $6.3$ $6.3$ $6.2$ $5.7$ $6.1$ $5.7$ Pewamo No.2 $7.0$ $7.0$ $7.0$ $6.5$ $6.8$ $6.4$ Plainfield $5.5$ $5.5$ $5.3$ $4.4$ $5.1$ $4.5$	Soil Site	Truog Kit	Glass Electrode H <sub>2</sub> 0 0.01MCaCl <sub>2</sub>	Glass Electrode H <sub>2</sub> 0    0.01MCaCl <sub>2</sub>
Spinks No.1         7.0         7.0         6.2         5.8         6.2         5.8           Spinks No.2         6.0         6.0         6.2         5.4         5.8         5.3           St. Clair         7.0         7.0         6.6         6.0         5.7	Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Hillsdale No.2 Houghton Lapeer Nekoosa No.1 Nekoosa No.2 Oakville Pewamo No.1 Pewamo No.2 Plainfield Spinks No.1 Spinks No.2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$7 \cdot 7$ $6 \cdot 7$ $7 \cdot 3$ $6 \cdot 3$ $7 \cdot 4$ $6 \cdot 3$ $7 \cdot 4$ $6 \cdot 3$ $5 \cdot 4$ $4 \cdot 5$ $5 \cdot 6$ $5 \cdot 0$ $6 \cdot 6$ $6 \cdot 1$ $7 \cdot 2$ $6 \cdot 3$ $6 \cdot 9$ $6 \cdot 2$ $5 \cdot 6$ $5 \cdot 0$ $6 \cdot 9$ $6 \cdot 2$ $5 \cdot 6$ $5 \cdot 7$ $7 \cdot 3$ $4 \cdot 4$ $6 \cdot 2$ $5 \cdot 7$ $7 \cdot 3$ $4 \cdot 4$ $6 \cdot 2$ $5 \cdot 7$ $7 \cdot 3$ $4 \cdot 4$ $6 \cdot 2$ $5 \cdot 4$	7.4 $6.9$ $7.1$ $6.7$ $7.4$ $6.7$ $7.4$ $6.7$ $6.9$ $5.8$ $5.3$ $4.6$ $5.2$ $4.7$ $5.6$ $5.1$ $6.7$ $6.3$ $5.6$ $5.1$ $6.7$ $6.3$ $6.5$ $6.2$ $5.2$ $4.6$ $5.2$ $4.6$ $5.2$ $4.6$ $5.2$ $4.5$ $6.5$ $6.2$ $5.2$ $4.5$ $6.5$ $5.2$ $5.1$ $4.5$ $5.8$ $5.3$

# Air Dry pH's

	Tru Ki		H20	Glass Electrode 0.01MCaCl <sub>2</sub>	1.01	WKCl
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Hillsdale No.2 Houghton Lapeer Nekoosa No.1 Nekoosa No.2 Oakville Pewamo No.1 Pewamo No.2 Plainfield Spinks No.1 Spinks No.2	6 • 5 0 5 6 5 5 0 5 8 6 0 0 5 4 0 7 • 5 • 5 5 5 6 7 6 6 5 6 7 5 6 6	8 7 7 0 4 8 7 5 0 5 9 8 0 8 3 7 6 6 5 6 5 6 5 6 5 6 5 6 5 6 5 6 5 6 5	6.239004494867617211 6.239004494867617211	6.7 6.6 4.8 5.8 5.0 6.3 5.2 5.2 5.2 5.4 5.7 6.4 5.4 5.4 5.4 5.4 5.4 5.4 5.4 5.4 5.4 5	566664445656455454 566664445656455454 54	5666644456071208019
St. Clair	6.5	6.5	6.3		5.1	5.2

#### E. September Samuling

#### Field Noist pH's

Oven Dry pH's\_

21610	10120 p	<u>n s</u>	CVE	
Truog Kit				Electrode 0.01MCaCl <sub>2</sub>
8.0 7.5 7.2 5.7 6.6 7.2 6.6 7.2 6.6 7.2 6.6 7.5 6.6 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 6.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7	7•539796941648252 •556667566556	6.467628122646934538 6.467628122646934538	7.0 7.1 7.4 7.9 5.9 7.9 4.9 4.3 8.3 2 1.3	6.6 5.6 6.5 6.6 5.2 8 1 1 1 5 7 8 2 5 4 5 6 4 5 8 2 5 4 5 6 4 5 6 4 5 6 4 5 6 4 5 6 4 5 6 4 5 6 5 6
	Air	Dry pH's		
Truog Kit				1
7.5 7.0 7.0 5.5 6.3 6.5 6.3 6.4 6.8 6.5 6.4 6.8 6.5 6.4 6.8 6.4 6.8 6.5 6.4 6.8 6.5 6.4 6.8 6.5 6.4 6.8 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5 6.5	6.9 7.4 7.4 7.6 5.4 5.5 5.9 7.6 5.9 6.2 7.6 5.9 7.6 5.9 7.6 5.9 7.6 5.9 7.6 5.9 7.5 6.2 5.9 5.9 5.9 5.9 5.9 5.9 5.9 5.9 5.9 5.9	6.5 6.4 6.5 6.6 6.5 4.8 5.2 6.1 5.5 6.8 5.3 4.8 5.5 6.8 5.2 4.8 5.5 6.8 5.2 4.8 5.2 5.3 6.8 5.2 4.8 5.2 5.3 5.3 6.8 5.3 6.2 5.3 5.5 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.3 6.8 5.5 5.8 6.8 5.5 5.8 6.8 5.5 5.8 6.8 5.8 5.8 6.8 5.8 5.8 5.8 6.8 5.8 5.8 5.8 5.8 5.8 6.8 5.8 5.8 5.8 5.8 6.8 5.8	6.3 6.2 6.1 4.0 4.3 5.9 5.2 5.0 4.3 5.2 5.0 4.3 5.2 5.0 5.2 5.2 5.2 5.2 5.1 5.3 tandard la	6.2 6.0 4.0 4.0 5.6 5.9 5.1 6.0 4.2 5.1 5.1 5.1 5.1 5.3 boratory
	Truog Kit 7.0 7.0 7.5 7.5 8.0 8.0 7.5 7.5 7.2 7.2 5.8 6.0 6.7 6.6 6.9 7.0 6.5 6.9 7.0 7.0 6.5 7.0 7.0 7.0 6.5 7.0 5.5 6.5 6.5 7.0 7.0 7.0 7.5 7.5 7.0 7.0 5.5 6.5 6.3 6.4 6.5 6.4 6.5 6.5 6.5 6.5 6.5 6.5 6.5 5.5 6.5 5.5 6.0 6.5 7.0 6.5 7.0 7.0 7.0 7.0 7.5 7.5 7.0 7.0 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.0 7.0 7.5 7.5 7.5 7.5 7.0 7.0 7.5	Truog KitGlass $H_20^*$ 7.07.07.57.66.45.76.56.86.96.86.96.5 <td>Kit<math>H_20*</math><math>0.01ECaCl_2</math>7.07.07.06.67.57.56.86.48.08.07.56.77.27.27.36.65.86.05.95.26.76.65.74.86.56.45.95.16.86.96.66.27.07.06.96.26.36.56.45.96.45.95.16.86.96.67.07.06.96.26.36.56.45.96.56.56.46.56.56.46.56.56.27.07.06.36.56.56.27.07.06.37.07.06.37.07.06.37.57.57.36.47.57.57.57.36.47.07.07.66.55.57.07.07.07.66.55.57.65.57.65.44.46.36.55.55.56.66.96.16.36.36.45.55.55.55.36.45.95.55.56.56.56.56.56.56.56.56.5<td>Truog KitGlass <math>H_20^*</math>Class <math>0.01KCaCl_2</math>Glass <math>H_20^*</math>7.07.07.06.67.07.57.56.86.47.18.08.07.56.67.17.57.57.56.77.47.27.27.36.67.07.86.05.95.25.96.76.65.74.85.56.56.45.95.15.96.86.96.66.26.77.07.06.96.26.96.36.56.45.66.47.07.07.16.46.96.05.95.65.96.36.97.07.16.46.96.05.95.65.24.45.36.56.25.36.97.07.06.35.55.65.24.45.36.3Air Dry pH'sTruog Class Electrode H20NumberH200.01NCaCl_21.0NKC7.07.06.96.56.27.57.57.46.56.37.57.46.56.37.57.46.56.37.57.46.56.15.55.65.56.44.44.06.36.46.56.56.15.97.5</td></td>	Kit $H_20*$ $0.01ECaCl_2$ 7.07.07.06.67.57.56.86.48.08.07.56.77.27.27.36.65.86.05.95.26.76.65.74.86.56.45.95.16.86.96.66.27.07.06.96.26.36.56.45.96.45.95.16.86.96.67.07.06.96.26.36.56.45.96.56.56.46.56.56.46.56.56.27.07.06.36.56.56.27.07.06.37.07.06.37.07.06.37.57.57.36.47.57.57.57.36.47.07.07.66.55.57.07.07.07.66.55.57.65.57.65.44.46.36.55.55.56.66.96.16.36.36.45.55.55.55.36.45.95.55.56.56.56.56.56.56.56.56.5 <td>Truog KitGlass <math>H_20^*</math>Class <math>0.01KCaCl_2</math>Glass <math>H_20^*</math>7.07.07.06.67.07.57.56.86.47.18.08.07.56.67.17.57.57.56.77.47.27.27.36.67.07.86.05.95.25.96.76.65.74.85.56.56.45.95.15.96.86.96.66.26.77.07.06.96.26.96.36.56.45.66.47.07.07.16.46.96.05.95.65.96.36.97.07.16.46.96.05.95.65.24.45.36.56.25.36.97.07.06.35.55.65.24.45.36.3Air Dry pH'sTruog Class Electrode H20NumberH200.01NCaCl_21.0NKC7.07.06.96.56.27.57.57.46.56.37.57.46.56.37.57.46.56.37.57.46.56.15.55.65.56.44.44.06.36.46.56.56.15.97.5</td>	Truog KitGlass $H_20^*$ Class $0.01KCaCl_2$ Glass $H_20^*$ 7.07.07.06.67.07.57.56.86.47.18.08.07.56.67.17.57.57.56.77.47.27.27.36.67.07.86.05.95.25.96.76.65.74.85.56.56.45.95.15.96.86.96.66.26.77.07.06.96.26.96.36.56.45.66.47.07.07.16.46.96.05.95.65.96.36.97.07.16.46.96.05.95.65.24.45.36.56.25.36.97.07.06.35.55.65.24.45.36.3Air Dry pH'sTruog Class Electrode H20NumberH200.01NCaCl_21.0NKC7.07.06.96.56.27.57.57.46.56.37.57.46.56.37.57.46.56.37.57.46.56.15.55.65.56.44.44.06.36.46.56.56.15.97.5

samples below pH 6.5 after August, as shown in Fig.1, the pH readings on the field moist and oven dry samples measured in H20 were corrected by adding 0.1 pH units to the September readings that were below pH 6.5. • • •

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Table 8A Field moisture percentage, total exchangeable metallic cations electrical conductivity and organic matter content measured during the season, for each soil site.

#### A. May Sampling

Soil Site	Field Noisture %	Total exchange- able metallic cations (me./100g.)	Electric Conducti (mhos x1		Organic Natter %
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Houghton Hillsdale No.2 Lapeer Nekoosa No.1 Nekoosa No.1 Nekoosa No.2 Cakville Pewomo, No.1 Fewomo No. 2 - Plainfield Spinks No.1 Spinks No.2 St. Clair	-	9.49 18.49  36.29 2.26  4.86 3.22 0.67 15.69 	12 20  31 31 3 14 15  0 15  0 15 	16 18  31 12 10 13  0 15  0 3 	5.30 7.80  92.20 2.01  4.70 1.01  1.02 6.03  0.70 1.20
	B. Jun	e Sampling			
Blount Ceresco No.1 Ceresco No.2 Colwood No.2 Colwood No.2 Chelsea Houghton Hillsdale No.2 Lapeer Nekoosa No.1 Nekoosa No.2 Cakville Pewomo No.1 Pewomo No.1 Pewomo No.2 Flainfield Spinks No.1 Spinks No.2 St. Clair	16.87 $20.83$ $25.96$ $16.09$ $28.81$ $6.75$ $71.93$ $14.62$ $9.46$ $10.36$ $6.03$ $6.26$ $4.93$ $19.73$ $22.13$ $4.23$ $10.96$ $5.71$ $15.33$	14.27 $18.49$ $19.83$ $19.09$ $15.40$ $1.29$ $39.96$ $2.26$ $2.64$ $4.85$ $1.49$ $2.66$ $0.89$ $16.13$ $15.13$ $0.81$ $2.43$ $2.97$ $11.13$	30 18 4 12 20 0 26 0 0 10 0 10 0 30 9 2 5 3 12	34 13 2 9 20 0 30 0 0 30 0 0 8 0 10 0 26 13 4 5 1 12	5.10 7.90 8.00 4.50 6.02 1.40 91.50 2.12 2.40 4.80 1.00 2.03 6.13 6.13 6.03 6.13 6.02 1.23 1.13 5.12

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C. July Sempling

Soil Site	Field Koisture	Total exchange- able metallic cations (me./100g.)	Electric conducti (mhos x1	vity	Creanic Patter S
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Houghton Hillsdale No.2 Lapeer Nekoosa No.1 Nekoosa No.2 Cakville Fewomo No.1 Pewomo No.2 Flainfield Spinks No.2 St. Clair	15.17 $20.26$ $23.08$ $17.99$ $16.56$ $9.62$ $75.03$ $10.09$ $9.93$ $8.33$ $5.65$ $8.30$ $4.37$ $17.46$ $17.36$ $3.39$ $9.47$ $6.25$ $11.33$	12.93 19.59 19.38 19.08 15.40 1.29 40.93 2.26 4.07 4.85 3.19 4.43 1.56 14.84 14.25 1.62 4.05 2.06 11.13	32 19 20 21 16 4 28 5 8 18 11 26 0 30 20 0 17 10 13	36 19 22 13 20 22 52 16 12 20 24 0 15 10 13	$\begin{array}{c} 4.90\\ 8.10\\ 8.20\\ 4.30\\ 6.10\\ 1.40\\ 92.30\\ 1.93\\ 2.41\\ 5.00\\ 1.93\\ 2.41\\ 5.00\\ 1.93\\ 2.41\\ 5.00\\ 1.93\\ 2.55\\ 6.00\\ 1.30\\ 1.25\\ 5.05\end{array}$
	D. Augus	st Sampling			
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Houghton Hillsdale No.2 Lapeer Nekoosa No.1 Nekoosa No.2 Oakville Fewomo No.1 Pewomo No.2 Plainfield Spinks No.1 Spinks No.2 St. Clair	15.40 $15.73$ $19.97$ $6.67$ $13.4$ $4.84$ $66.59$ $11.15$ $14.09$ $4.29$ $9.29$ $6.61$ $4.87$ $13.29$ $20.05$ $2.87$ $5.87$ $5.42$ $11.93$	11.28 $22.69$ $22.08$ $17.76$ $12.32$ $1.07$ $40.93$ $2.26$ $5.32$ $4.87$ $3.62$ $5.76$ $3.34$ $17.91$ $19.43$ $2.33$ $5.34$ $2.04$ $11.13$	29 21 21 22 0 79 21 18 11 8 9 0 32 4 0 19 9 19	33 21 23 27 26 0 81 15 13 17 6 11 0 30 6 0 17 7 19	$\begin{array}{c} 4.90\\ 8.00\\ 7.91\\ 4.11\\ 5.94\\ 1.22\\ 92.40\\ 1.88\\ 2.39\\ 4.90\\ 1.21\\ 1.90\\ 0.99\\ 6.53\\ 6.10\\ 0.83\\ 1.27\\ 1.30\\ 5.18\end{array}$

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E.	September	Sampling
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Soil Site	Field Moisture %	Total exchange- able metallic cations (me./100g.)	con	ctrical ductivity s x10 <sup>-5</sup> /cm)	Organic Matter ぽ
Blount Ceresco No.1 Ceresco No.2 Colwood No.1 Colwood No.2 Chelsea Houghton Hillsdale No.2 Lapeer Nekoosa No.1 Nekoosa No.2 Oakville Pewomo No.1 Pewomo No.1 Pewomo No.2 Plainfield Spinks No.1 Spinks No.2 St. Clair		13.45 $21.38$ $17.67$ $18.64$ $15.30$ $1.94$ $40.93$ $3.17$ $4.42$ $5.85$ $2.93$ $6.09$ $2.23$ $15.61$ $15.11$ $2.08$ $2.03$ $2.04$ $11.13$	34 19 17 18 12 52 6 12 10 0 4 0 21 27 0 2 0 13	32 17 23 18 18 16 58 4 18 12 0 2 0 19 33 0 2 0 19 33 0 2 0 15	4.80 7.80 7.92 4.00 5.83 1.31 91.60 1.70 2.38 4.72 1.20 2.10 1.10 6.43 6.05 0.77 1.25 1.28 5.19
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Table 2B. Cation exchange capacity of each site, and the base saturation percentage and exchange acidity of each site measured during the season.

		tion	MA			INE
Soil Site	cap	0	Base Sa- turation	Exchange acidity (mc/100m)	Base Sa- turation	Exchange acidity (me/100g)
Blount	15.2	** 14.7	63.68	5.41	95•5	0.68
Ceresco No.1	24.5	***25.1	80.8	6.31	80.8	6.31
Ceresco No.2	23.1	***23•3			85.7	3.32
Colwood No.1	21.2	*21.7			89.2	2.36
Colwood No.2	25.5	***25•5			60.4	10.10
Chelsea	7.2	<b>*</b> 7.01	****		18.3	5•77
Houghton	108	*** <b>1</b> 03	33.6	71.71	37.0	68.04
Hillsdale No.l	6.7	** 7.1	32.8	4.64	32.8	4.64
Hillsdale No.2	9.2	<b>**</b> 9.2			28.7	6.56
Lapeer	8.7	*** 9.2	54.0	4.09	54.2	4.05
Nekoosa No <b>.l</b>	6.5	*** 6.13	50.7	3.09	23.7	4.82
Nekoosa No.2	6.9	*** 7.0			38.3	4.29
Oakville	4.3	*** 4.4	15.2	3•73	20.5	3.46
Pewano No. 1	28.3	**29.4	54.4	13.16	55.9	12.72
Pewamo No. 2	32.4	**31.3			47.5	16.67
Flainfield	3.5	*** 3.85	12.6	3.21	22.0	2.87
Spinks No. 1	6.5	** 6.68	38.84	4.03	36.9	4.15
Spinks No. 2	<b>3.</b> 98	** 4.3	_ ~ ~ ~ ~		71.8	1.17
St. Clair	15.2	**15.6	~ ~ ~ ~ ~ ~		72.3	4.27

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Measured on samples collected in July
Heasured on samples collected in August

\*\*\* Measured on samples collected in September

# Table 83. Continued

JULY Base	: Exchange	AUGUST Base	Exchange	SEPTEMB: Base	ER Exchange
Saturation	acidity (me/100g)	Saturation $\frac{3}{5}$	acidity (me/100g)	Saturation	
. 86.94	2.02	75.26	3.67	89.7	1.50
79.02	5.21	91.5	2.11	86.2	3.42
85.7	3.32	95.2	1.12	76.2	5.53
89.2	2.32	83.0	3.64	87.1	2.75
60.4	10.10	48.3	13.13	60.4	10.20
18.3	5.77	15.2	5.99	27.5	5.12
37•9	68.07	37•9	68.07	37.9	68.07
32.8	4.64	32.8	4.64	45.9	3•73
47.9	5.13	57.8	3.88	47.9	4.73
54.5	4.05	54.7	4.03	65.7	3.05
50.7	3.12	57•5	2.69	47.4	3.33
63.7	2.52	82.9	1.19	86.9	0.86
35.8	2.79	76.7	1.01	51.2	2.12
51.3	14.01	62.2	10.94	54.4	13.24
44.8	17.65	61.1	12.37	47.5	16.69
44.0	2.06	62.9	1.35	56 <b>.</b> 5	1.30
61.5	2.54	81.2	1.25	30.7	4.56
49.7	2.03	49.7	2.10	19.7	2.10
72.3	4.33	72.3	4.27	72.3	4.27

Table 10. Seasonal variability of lime requirement (Tons/acre) determined by the pH plus texture, SMF buffer and exchange acidity methods as determined on air dry samples from 11 of the sites representing 9 soils.

<u>Soil Site</u>	pH plus texture	MAY SLP Buffer	exchange <u>acidity</u>	pH plus texture	JUKE SMP <u>buff</u> er	exchange acidity
Blount	0.0	0.0	0.0	0.0	0.0	0.0
Chelsea	0.0	0.0	0.0	1.50	1.51	2.22
Hillsdale No. l	1.50	1.51	1.53	1.50	1.27	1.53
Hillsdale No. 2	0.0	0.0	0.0	2.50	1.51	2.31
Nekoosa No. 1	L 0.0	0.0	0.0.	0.0	0.0	0.0
Oakville	1.50	1.15	1.39	1.50	1.27	1.23
Pewamo No. 1	0.00	0.00	0.00	0.00	0.00	0.00
Plainfield	1.50	1.15	1.18	1.50	1.15	1.02
Spinks No. 1	1.50	1.27	1.50	0.50	0.96	1.40
Spinks No. 2	0.0	0.0	0.0	0.0	0.0	0.0
St. Clair	0.0	0.0	0.0	0.0	0.0	0.0

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pH plus texture	JULY SKP buffer	exchange acidity	pH plus texture	AUGUST SIF buffer	exchange scidity
0.0	0.0	0.0	2.00	1.51	0.37
2.00	1.69	2.22	2.00	1.69	2.33
2.50	1.69	1.53	3.00	1.51	1.53
2.50	1.51	1.43	2.50	1.93	1.02
0.50	1.15	0.95	0.0	0.0	<b>C</b> •0
1.50	1.27	0.95	1.50	1.27	0.0
2.00	2.05	4.06	2.00	1.93	2.52
2.00	1.51	0.62	2.00	1.15	0.30
1.50	1.69	0.60	0.50	0.96	trace
0.50	1.15	trace	0.50	0.96	trace
2.00	1.51	0.58	2.00	1.51	0.58

# Table 10 Continued

	ST	EPTEMEER	
Soil Site	pH plus texture	SNP Euffer	exchange acidity
Elount	0.00	0.0	0.0
Chelsea	2.00	1.51	1.39
Hillsdale No. 1	2.50	1.51	1.14
Hillsdale No. 2	2.50	1.51	1.43
Nekoosa No. 1	0.51	1.15	0.56
Oakville	1.50	1.51	0.62
Pewamo No. 1	2.00	2.29	3.62
Plainfield	2.00	1.27	0.41
Spinks No. 1	1.50	1.69	1.60
Spinks No. 2	0.50	1.51	trace
St. Clair	0.0	0.0	0.0

