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REPORT

of

COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given William Moses Shaw final oral examination for the degree of Master of Science. We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota
May 29 1917

F. J. Alway
Chairman

W. H. Hunter

William Moore.

REPORT

of

Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by William Moses Shaw for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

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May 29 191

INDICATORS OF THE LIME REQUIREMENT OF SOILS

By

William M. Shaw

A THESIS

Submitted to the Graduate School of the University
of Minnesota in partial fulfillment of the
requirements

For the Degree

of

Master of Science

St. Paul, Minnesota

May 18, 1917.

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ACKNOWLEDGEMENT

The work reported in this paper was carried out at the suggestion of Dr. F. J. Alway.

INDICATORS OF THE LIME REQUIREMENT OF SOILS.

INTRODUCTION.

The beneficial effects of lime upon the productivity of certain soils were observed in certain countries even before civilization had reached these. Thus when the Romans went to Britain they found the native Celts practising chalking of the land. This chalk they obtained in pits.

At the present time lime, in one form or ather, has become one of the most common soil amendments whenever an intensive system of agriculture is carried on in a humid region.

Experience has shown that the application of lime in the form of calcium carbonate to mineral soils very seldom results in depressing effects on the ordinary farm crops; at the same time, it has been found that many soils to which lime has been applied have not been benefited by such treatment. Where lime has a market value and where its use involves considerable investment in addition to the labor of application the question of economy will naturally arise. In answering such a question with reference to any particular case either of two means may be resorted to: field experiments with the particular soil and a particular crop, or the application of some chemical or greenhouse test that will indicate within certain limits of accuracy both the need and, if any, the amount of lime required by that particular soil.

It is evident that the results of field experiments are the most conclusive and give the only final answer to such questions. The effect of liming upon crop yields may be determined by either or both of the two factors: (1) the nature of the soil, (2) the kind of crop. Where the soil is in very poor physical condition, i.e., more or less puddled so that it remains wet and sticky for a considerable time after a rain, the benefits from liming will be shown with almost any farm crop. On the other hand, if a soil is deficient in lime, but is in good physical condition, the beneficial effects of the liming may depend entirely upon the particular crop employed in the test. Thus, if potatoes, oats and alfalfa should all be used as test crops on the same field having a very lime-deficient soil the last might be expected to show a very marked benefit, the second a slight improvement, and the first no effect at all. Again, where the soil has an abundance of lime in store the field experiments would show no benefit from liming with any of the above mentioned crops. These views have been well established by numerous experiments and are quite generally recognized.

In the field investigation of soils markedly deficient in lime the Division of Soils of the Minnesota Agricultural Experiment Station has used alfalfa as the standard crop, on account of its high degree of sensitiveness to a deficiency of lime. While one of the most valuable farm crops, it is far more dependent upon a liberal supply of lime in the soil than any other common field crop. The Division has been carrying on liming experiments in various parts of the state in cooperation with the farmers for the past two years. A record of the yields from the limed and unlimed areas has been kept. From these field experiments it appeared that the ordinary tests for the so-called "soil acidity" are not as reliable as are to be desired. Particularly striking in this respect is the disagreement between the field results and the lime requirement as determined by the various laboratory methods, in the case of the soils on the University Farm at St. Paul. The soils of these plots have shown a lime requirement with almost every chemical test employed, but in no case have they in the field shown any benefit from liming. The above circumstance emphasizes the importance of finding a simple and reliable laboratory method for determining the lime requirement. An extensive set of data on the effects of liming soils for alfalfa, together with samples from all these fields, made it possible to undertake the study of the reliability of the common laboratory methods.

HISTORICAL REVIEW.

The literature on the subject of soil acidity, and liming in general, has been amply reviewed in a number of recent papers on various phases of the subject. Especially noteworthy in this respect are a bulletin by Dr. W. Frear of Pennsylvania (12) "Sour Soils and Liming" and a paper by Hutchinson and MacLennan of the Rothamsted Station (23) entitled: "Studies on the Lime Requirement of Certain Soils". Since the appearance of the above mentioned publications a number of important contributions to the subject have been made and in this paper, therefore, I shall concern myself chiefly with the latter, but a general review of the most important methods for the estimation of lime requirements is given in advance of the more extended description of the new methods as a basis for the correlation of the latter with the former.

Two distinct and definite lines of endeavor will be noted throughout the development of the laboratory methods. The underlying principles of these are best brought out by a comparison of the two oldest and probably the two most commonly employed methods for distinguishing between calcareous and lime-deficient soils, namely: the hydrochloric acid test for soil carbonates and the litmus test for soil acidity.

The first method is based upon the fact that soils giving an effervescence on being treated with dilute hydrochloric acid always have an abundant supply of carbonates; the second rests upon a similar fact, namely: that most soils known to respond definitely to liming redden blue litmus paper. The hydrochloric acid test is based upon the examination of the soil mass for a specific ingredient, namely: earthy carbonates, or, more specifically, calcium carbonate; the litmus test, on the other hand, rests upon a chemical change brought about by the interaction of the litmus and the soil mass as a whole and, therefore, cannot properly be attributed to any specific cause. Based upon this distinction we shall recognize two general classes of laboratory methods for lime requirement in soils. The first includes all those methods which are based upon the examination of the soil mass for some specific ingredient having either a qualitative or a quantative relation to the lime requirement. The second includes all the various laboratory methods which are based upon certain general chemical phenomena, not well defined, but having some bearing upon the lime requirement.

GENERAL METHODS FOR INDICATING LIME REQUIREMENT BASED UPON THE DETERMINATION OF CARBONATES OR AVAILABLE BASES.

The hydrochloric acid test for carbonates previously referred to has been known and generally used ever since the early days of the chemical investigation of soils and rocks. It has frequently been used as a qualitative test to precede more elaborate methods of analysis. Until recently no careful observations had been made as to the applicability of this test as an indicator of the lime requirement. Bandi (5, 1914) reports experiments on lime determination in agricultural soils by more recent methods, using also the hydrochloric acid test. His studies had reference to the power of sustaining and developing the growth of azotobacter and he concluded that the simple hydrochloric acid test is generally sufficient and that if a soil effervesces with this acid it is in no need of lime. As regards the lower limits of the effervescence test there is very little information. Shorey (44) has tested 63 samples containing various amounts of carbonate and found that where the calcium carbonate content was below 0.40 per cent no effervescence was observed. Since 0.25 per cent calcium carbonate content was the next lowest in the series, the inference is that "this test as ordinarily used in the field would be negative where the calcium carbonate content was less than 0.30 or 0.40 per cent".

A further extension and more definite application of these general methods to the lime requirement has been shown in the introduction of various methods for the estimation of the more active forms of lime and more especially the calcium carbonatecontent of soils.

Hollenan (19) in 1892 proposed the estimation of available lime by extracting a soil with carbon dioxide saturated distilled water for 24 hours, and suggested that where clay soils upon such treatment yield 0.15 per cent or less of CaO liming should prove beneficial. The proposed method was subjected to a critical examination by Wheeler (54) in 1900. He selected two soils, a sand and a clay, which had shown marked benefits from liming as indicated by increased yields of the beet crops. He found the determination discordant with the field results, the amount of lime removed in the higher case being only about one-fifth of that below the point at which Holleman concluded that lime would be useful.

During the period of 1889 to 1903 a number of methods based largely upon the amounts of acid-extractable CaO, with or without MgO, have been proposed, principally by German chemists. None of these have found any practical application.

A method for the estimation of lime in an available state by the use of a neutral salt was proposed by Meyer ([illegible]) in 1900. This consists of treating 10 gms. of soil with 100 cc. of a 10 per cent ammonium chloride solution for at least three hours and then determining the amount of lime dissolved. In 1909 Weibull (53) checked up this method by a correlation of the nitrifying power of the soils tested. He found that this method is applicable only when the organic matter of the soil, as indicated by loss on ignition, is taken into consideration. According to his observations ordinary soils giving 3 to 6 per cent loss upon ignition and less than 0.30 per cent soluble lime are acid in character and possess a low nitrifying power. In alkaline soils the ratio of lime to loss upon ignition was found to be 1.20 or higher, and where it fell below 1.20 the soils were acid. The method was also tested out by Christensen and Larson (10) in 1911 in connection with extensive liming experiments conducted by the Danish "Lime Committee". The results were only fairly concordant. The ammonium chloride method as proposed by Meyer has been adopted by the California Experiment Station, where it is used "as a measure of the carbonate and humate of lime present by comparing it with the precipitate obtained from a soil whose percentage of lime has been correctly ascertained".

Important data bearing upon the relation between the content of (acid soluble) lime and the natural fertility of the land have been gathered in this country and in Europe. These will be recorded here in view of the recurring interest in such relationship.

Hilgard (18) even in 1860 attempted to establish the relation between the calcareous nature of the soils, as shown by their natural flora, and their lime content. According to his data a sandy soil should contain no less than 0.1 per cent CaO. Whereas in clay soils it should be not less than 0.6 per cent in order to possess the advantages of a calcareous soil. He further states:

"This is apparent to the eye in that the dark tinted humus characteristic of truly calcareous lands does not appear in clay soils until the lime percentages rise to nearly 1.0 per cent, while in sandy lands much smaller amounts (say 0.2 per cent) will produce this effect."

From a correlation of the crop producing power of the German soils and their chemical composition as ascertained by analysis with strong acids Maercker (31, 1896) arrived at a practical rating of soils by their chemical ingredients. According to the lime content he recognizes the following classes:

	Clay soils Per cent	Sandy soils Per cent
Poor	Below 0.1	Below .05
Medium	0.1 - .25	.10 - .15
Normal	.25 - .50	.15 - .20
Good	.50 - 1.0	.20 - .30
Rich	Above 1.0	Above .30

In England the lime content has been studied in connection with the development of the "finger-and-toe" disease on cruciferous crops which is considered a positive indication of an acid condition of a soil. From analyses made by Hall (16) and those quoted by him it appears that this disease develops in soils with a lime content as high as .31 per cent for sands and .39 per cent for clays, while in soils with a lime (CaO) content of .52, .43 and .89 per cent conditions were found unfavorable for the spread of the above disease, but no reference is made as to the texture of the soils quoted.

Wheeler (54, p. 84) tested out this method upon Rhode Island soils and found that it furnished no reliable guide to the lime requirement of these as determined by field trials with beets.

While the acid-soluble CaO is generally determined in the course of the chemical analysis of soils, the amount so found is not ordinarily regarded as an indication of the lime requirement.

Hall (16) emphasizes the fact "that the factor required is not the calcium, but the amount of carbonate that will serve as a base in the soil" and concludes that the carbon dioxide evolved on treating the soil with an acid is the only measure in estimating the earth carbonates.

Snyder (45, p. 9)states his criterion for the lime requirement of soils in the following: "Soils which contain from .3 to .5 per cent or more of lime and from .1 to .4 per cent combined carbon dioxide and are not strongly charged with alkali salts, are reasonably well supplied with active lime compounds". If, however, the soil contains only from .01 to .02 per cent of carbon dioxide and a similar amount of sulphur dioxide then the lime is probably present as a silicate, in which case the soil may stand in need of a lime fertilizer."

Russell (37, p. 3) points out instances where the growth of alfalfa is directly dependent upon the calcium carbonate content of the soil. According to his findings this crop did well on soils containing 0.6 and 0.8 per cent of calcium carbonate, but was a failure where this was as low as 0.07 to 0.2 per cent.

Hall and Russell (22) report a considerable number of soils having very little or no calcium carbonates but giving a neutral reaction, and Hutchinson and MacLennan (23, p. 97) call attention to the risk of starting field trials on the mere basis of a low carbonate content of the soil.

Hopkins (21, Table 15) reports a large number of the soils showing no calcium carbonate content, yet having only a negligible lime requirement, varying from 30 to 100 pounds per acre.

The eastern loess soils of Nebraska, according to analyses reported by Alway and Rost (2, p. 414) contain only negligible amounts (.01 to .02 per cent)of carbon dioxide, but produce excellent crops of alfalfa.

Shorey, et al. (44) have recently reported a detailed study of the different forms of calcium, as shown by the following outline:

Not dissolved by 4% HCl - Difficultly decomposable silicates

Determined

(by difference)

Total CaO

(Determined)

Not dissolved by 2% HCl:
(Determined by difference)=Easily decomposed calcium silicates

Dissolved by 4% HCl

Dissolved by 2% HCl

1. $CaCO_3$ (calculated from found CO_2
2. $CaSO_4$ (calculated from found SO_3 in water solution
3. Calcium humates (Determined by difference.)

They analyzed 63 samples representing 23 soil types from 19 different states according to this scheme, and found no relation between the calcium carbonate content of the soil and its reaction to litmus. They call particular attention to one soil type of which the samples showed only a trace of carbon dioxide but which was recognized as well adapted to alfalfa. These authors suggest that the reaction of a soil may be influenced by the amount of easily decomposable calcium silicates as well as by that of calcium carbonates.

CLASS II. CHEMICAL TESTS AS INDICATORS.

In this group the litmus test, already referred to, has been most extensively used. It consists in bringing blue litmus paper of a good grade into contact with the soil in a moderately moist condition and leaving it for a certain length of time (usually for 5 minutes) and then recording the tint of the test paper. This test generally affords a distinction between acid and neutral or alkaline soils and in some instances the degree of acidity can be surmised from the intensity of the pink color and also the time required for the change in color to take place. Various objections have been raised against the use of the litmus test, one being that the effect of the carbonic acid in the soil may produce a pink color where the soil is in reality not acid. This objection has been answered by Wheeler (54, p. 67) who states: "so long as a liberal amount of calcium carbonate is present in a soil the presence of carbonic acid tends to increase rather than to lessen the tendency toward an alkaline reaction (a point proved by us experimentally in the laboratory) it must be evident that the indication of acidity afforded by blue litmus paper is sufficient to show a deficiency of carbonate of lime or other basic ingredients in soils".

Barlow (6) has attempted to definitely correlate the intensity of the pink coloration and the rapidity of change of color of the litmus paper with the lime requirement as determined by the Veitch method. In order to facilitate the observation of the color changes Barlow has modified the ordinary procedure by placing the litmus paper upon a glass plate and then placing on top of this the soil previously moistened. Using this method he made 10 determinations of 10 different soils to find the length of time it would take soils of different lime requirement to produce a definite color change. His data show that there is no definite relation between the lime requirement as determined by the Veitch method and the time required to produce a distinct change in color.

While there are doubtless a great number of field experiments based upon the litmus paper test the results reported are not of such a nature as to make direct comparison possible. In summarizing the results obtained from comparing the litmus test with field trials Wheeler (54, p. 87) expresses his view that "This method is highly effective in the hands of a close observer who has had much experience in testing soils of known character". Some observations in this regard have also been made by Kellerman (25, p. 5) in connection with the study of legume inoculation. He found that "A red litmus reaction was shown in every case where the growth (of alfalfa) was poor and the plants on these areas were always devoid of nodules, while no reaction was obtained from the good portion of the field where nodules were found upon the roots".

The present generally accepted view of the value of the litmus paper test is summarized in Frear's (12) statement "This is the test now most generally in use. The color contrast is indicative only of the fact that the soil is, or is not acid. The degree of acidity is not definitely established by this means".

The introduction of laboratory methods for the determination of lime requirement of soils other than the litmus paper test began less than two decades ago. Müntz in France, Tacke in Germany, and Wheeler in the United States were the pioneers, each in his respective country. The last two worked contemporaneously, during the period of 1895-1897, while the work of Müntz was somewhat earlier. The greatest amount of work in devising laboratory methods for the determination of the lime requirement has been done in the United States, while Germany, England and Japan have followed in the order mentioned. Very little is found in the literature to indicate that similar work is being prosecuted in other countries.

The work of Wheeler has three elements of importance:

1 - It is the pioneer work on the subject.

2 - Field experiments were used as the basis of checking the laboratory methods.

3 - Attention was called to two distinct factors determining the need of lime, namely: the physical and the chemical defects and it was pointed out that any method which takes into account only the chemical defects cannot be expected to agree in all cases with the crop results (54, p. 86) The last point is especially important since it predicted the limiting factor of all the methods based upon chemical reactions alone for determining the actual lime-need of a soil.

The methods checked up by Wheeler, besides those already mentioned, were the Müntz method, the Tacke method, the total humus, the colorimetric humus determination and the ammonia adsorption method. These methods will be briefly described.

The Tacke method (47) consists of bringing a soil into contact with a suspension of $CaCO_3$ and determining the carbon dioxide freed from it by the soil. Hydrogen is passed over the soil to remove the residual carbon dioxide before the suspension is added and continued for at least two and a half hours after the addition of the carbonate. The carbon dioxide is absorbed in N/10 NaoH and determined titrimetrically, after the addition of $BaCl_2$ with N/10 HCl and the use of phenolphthalein as an indicator. The reation between the soil and carbonate is allowed to take place at room temperature.

The Müntz (35) method for determining free humic acids consists in treating 20 gms. of soil with 50 cc. concentrated ammonia. This is allowed to stand from 2 to 3 days in a warm place, after which water is added to make one liter, the mixture is shaken up and allowed to settle. 500 cc. of supernatant liquid is made strongly acid with concentrated hydrochloric acid and the resulting precipitate collected, dried, weighed, incinerated and weighed again, the loss between the two weighings being considered the amount of "free humic acids". Wheeler (54, p. 73) found that the strength of the ammonia did not materially influence the results of this method.

The total humus was determined by treating the soil with 1 per cent HCl until the lime was leached out and washing the soil free of acid. From this point the procedure follows the method of Müntz, described above.

The colorimetric method of humus determination is exactly the same as outlined under the Müntz method with the difference that instead of precipitating with acid the humus solution is concentrated or diluted so as to match a color indicating a certain lime requirement, the amount of dilution or concentration in comparison with the standard thus giving the comparative lime requirement of the soil under investigation.

Titration methods were tried with lime water and with ammonium hydroxide. With the former 1.0 gram of soil was treated with 50 cc. standard lime-water and shaken occasionally for 24 hours, filtering off the supernatant liquid, adding an excess of standard hydrochloric acid and titrating back with the lime water with corralline as an indicator. It was found that better results were obtained when larger quantities of lime water were used. Still better results were obtained from the use of ammonium hydroxide. This method consisted in treating 15 gms. of soil with 100 cc. N/10 ammonium hydroxide and 100 cc. of distilled water at the ordinary temperature for about 42 hours with occasional shaking. The supernatant liquid was acidified with standard acid, N/2 - (5 cc. to every 20 cc. of ammonia solution), the liquid made up to a certain volume, and an aliquot titrated against ammonium hydroxide using coralline as indicator.

The results that agreed most closely with the crop tests were obtained by titrating the ammonia absorbed by the soil. Fairly concordant results were also obtained by the Müntz free humic acid method and by the comparison of the color of the ammonia extracts with such an extract from a soil of a known lime requirement.

In 1902 Hopkins, Pettit and Knox (20) proposed the use of a method involving extraction with neutral salt solutions. Upon treating a soil with a salt solution the difficultly soluble acids "apparently unite with the mineral base, liberating the mineral acid, or an acid salt which, of course, is perfectly soluble, and whose titrating power furnishes a very satisfactory basis for determining the total acidity of the soil. Originally a 5 per cent solution of sodium chloride was recommended, but later this was changed to a normal solution of potassium nitrate. The method, as later modified and tentatively adopted by the Association of Official Agricultural Chemists (4) is as follows. 100 gms. of soil is placed in a 400 cc. bottle, 250 cc. N/1 potassium nitrate is added, the bottles are stoppered and shaken for 3 hours in a shaking machine, or every five minutes by hand, and allowed to stand over night. 125 cc. of the clear supernatant liquid is drawn off, boiled ten minutes to expel carbon dioxide, cooled, and titrated with standard sodium hydroxide solution, using phenolphtalein as an indicator. The total acidity is obtained by multiplying the titration by a factor of 2.5.

No specific green-house or field experiments with liming could be found where this method has been used as the basis of the experiment. Dr. Frear (12, p. 104) states that in his experience "Soils acid to litmus do not all show acidity with the Hopkins reagent". Regarding the chemistry involved in this method Veitch (52) states "There is practically no reaction between the organic matter and the salt solution whereby difficultly soluble organic acids are dissolved", and adds "If it be found by experience that the sodium chloride method is a measure of the acidity or lime requirement of soils, then we must conclude that the water insoluble organic acids play no part in soil acidity".

In 1902 Veitch presented the lime water method for determination of lime requirement of soils. This method claims the distinction of approximating more closely to the natural process involved in the field in neutralizing soils by the aid of lime. From the above it will be seen that the very same reagents had been tested out by Wheeler and not found successful on account of a somewhat different procedure. The method as originally outlined by Veitch (51) consisted in treating portions of 10 grms. of soil in platinum dishes with various amounts of standard lime water, water was added to make about 75 cc. and the mixture immediately evaporated to dryness on a steam bath. The contents were transferred to Jena flaska with exactly 100 cc, distilled water. The flasks were allowed to stand over night, the contents well shaken and immediately filtered. 50 cc. of the clear filtrate was placed in a Jena beaker and boiled down to about 10 cc. or until it showed a pink color with phenlphthalein. The three different quantities of lime water taken sufficed for orientation. Within the limits set by the first trial a second set of determinations was made in the same manner, until in the last determination the difference between the acid-reacting and alkaline portions was not greater than 2 cc. of the standard calcium hydroxide solution. The smallest amount of lime water taken to produce an alkaline reaction of the extract on such treatment was taken as the basis of the lime requirement of the soil. With soils of unknown character a preliminary test was applied. This consisted in the same treatment as above described with one sample, leaving out the lime water and the evaporation on the steam bath. When the extract from such preliminary test appeared alkaline the soil was considered as not deficient in lime. If the extract did not give an alkaline reaction the lime water test was carried out as described.

This method has been quite generally recognized as the only reliable indicator of the lime requirement. The only objection raised against it has been the great amount of time consumed and the requirement of no slight degree of skill on the part of the analyst.

Albert (1) proposed a method based upon the absorptive capacity of the soil for bases. This method consists in treating 20-50 grams of air dry soil with 200 cc. of water in a Jena flask. From 50 to 100 cc. of N/5 barium hydroxide is run in from a burette and 10 grams of solid ammonium chloride added. The flask is fitted immediately to a condenser and the contents boiled for 20-25 minutes. The ammonia is collected in N/10 acid and titrated with sodium alizarin sulphonate as indicator. Suchting and Arnd (46) found that results obtained by this method are not consistent.

Lyon and Bizzell (28) have compared the Albert method with the Veitch lime water test and found much lower results by the former. After introducing a number of changes in the procedure of the Albert method they found a fair agreement between the results of the two methods. Since the modified Albert method is much more rapid than the Veitch they proposed its general adoption. The modified Albert method consists in using 25 grams of soil in a Jena Kjeldahl flask, moistened with 50 cc. boiled distilled water and 50 cc. N/10 $Ba(OH)_2$ is added. The contents are digested over a steam bath for one hour; 150 cc. of distilled water and 5 grams of solid ammonium chloride are added, the flasks are connected with a nitrogen distillation apparatus and heated. The distillate (150 cc.) is collected in N/10 acid and titrated, using methyl orange as an indicator. The strength of 50 cc. $Ba(OH)_2$ is determined by direct titration with the same indicator. The difference between the two titrations represents the $Ba(OH)_2$ absorbed by the soil. On account of the slightly decomposing effect of the soil upon the ammonium chloride it is necessary to run a blank consisting of the soil and ammonium chloride, omitting the barium hydroxide solution and a correction thereof made in the determinations. Hutchinson and MacLennan (23, p. 89) criticise the method because it does not take into consideration the appreciable quantities of ammonia formed by heating a soil with barium hydroxide alone and on account of other errors to which the method is exposed, they regard the method as of very little value.

A method very similar to that of Hopkins has recently been proposed by Daikuhara (11) the only differences being that KCl instead of KNO_3 is used and the factor for the first titration is 3.5 instead of 2.5. It appears from Daikuhara's own work that his method offers no advantage over the Hopkins, since he shows (11, p. 29) that KNO_3 gives almost identical results.

Loew (27) suggests the use of potassium or sodium acetate for determining the lime requirement of clay soils. The method consists in digesting .50 grams of finely ground soil with 200 cc. of neutral 1 per cent solution of acetate salt at room temperature for 24 hours with frequent shaking. 100 cc. of the filtrate is titrated against standard NaOH solution.

Jones (24) has proposed a very simple method for the estimation of lime requirement of soils by the use of calcium acetate. His method consists in grinding 5.6 grams of soil with 0.5 grams of calcium acetate to a fine powder. Just enough water is added to make a stiff paste, the grinding continued for a few seconds, 30 cc. of more water is added and the mixture well stirred. The whole is transferred to a 200 cc. measuring flask and made up to a volume about 160 cc; this is allowed to stand for about 15 minutes with occasional shaking, then made up to 200 cc. and filtered. The first 10 or 15 cc. of the filtrate are rejected and then 100 cc. of the filtrate is taken for titration with phenolphthalein. The reading, multiplied by (2 x 1.8 x 1000) gives the number of pounds of lime, (as $CaCO_3$) per acre of two million pounds of soil.

In his study of the influence of sulphur upon soil acidity

Lint (26) applied the Jones method and found that the results compared very favorably with those obtained by the Veitch method.

A method in which the soil is allowed to react with a solution of calcium bicarbonate has recently been developed by Hutchinson and MacLennan (23)consisting in the following: A stock solution of calcium bicarbonate is prepared by passing a current of carbon dioxide into a suspension of calcium carbonate in distilled water. A large excess of calcium carbonate must be used to furnish enough fine particles to readily go into solution. The treated carbonate is then diluted with one-third of its volume of distilled water and filtered, the filtrate having a concentration of N/50.

For an actual determination 10 to 20 grams of soil are placed in a bottle of 500-100 cc. capacity together with 200-300 cc. of approximately N/50 solution of calcium bicarbonate, prepared as above described. After displacing the air in the bottle by a current of carbon dioxide the bottle is placed in a shaking machine for 3 hours. Then the contents are filtered. A portion of the filtrate equal to half of the original amount of solution used is titrated with N/10 acid, using methyl orange as indicator. The difference indicates the amount of calcium carbonate absorbed, each cc. of N/10 acid being equal to 5 mgms. of calcium carbonate. A solution of bicarbonate weaker than N/10 causes an appreciable lowering of the results.

MacIntire (29) proposes a modification of the above method, placing 10 grams of fine earth, under 0.5 mm., in a porcelain evaporating dish, adding 150 cc. of the stock bicarbonate solution and evaporating to a thin paste. The mixture is stirred first when the calcium carbonate is precipitated and again when it reaches a volume of 50-75 cc. Next the soil is washed into a 300 cc. Erlenmeyer flask by means of carbon dioxide-free distilled water, making the volume about 60 cc. A series of flasks are then connected with a shaking device (as described in Tenn. Agri. Expr. Sta. Bul. 107, p. 161), 5 cc. of 85 per cent phosphoric acid added and the liberated carbon dioxide determined by passing of the gas through 25 cc. of 4 per cent sodium hydroxide in a Camp absorption tower, the air passing into the system being, of course, first purified of carbon dioxide. Carbon dioxide-free distilled water is used to increase the volume of 25 cc. sodium hydroxide to an amount sufficient to cover the beads before the passage of carbon dioxide through the absorbent solution. A vacuum of 4 inches is maintained in the apparatus during the 30 minutes of agitation and aspiration. The amount of calcium carbonate in 100 cc. of the carbonate solution is determined by boiling off the excess of dissolved gas and decomposing the precipitated carbonate by the above procedure. The difference between the added and the residual carbonate in the soil is then determined. According to a later publication of MacIntire(29) the residual carbonates may be liberated by bringing the soil and acid to boiling for <u>one minute</u> with passage of purified air during boiling and for 30 minutes subsequently. It is also suggested that the carbon dioxide may be determined gravimetrically as well as by the double titration method.

Gaither (13) has proposed what is known as the Vacuum method for determination of lime requirement. It has since been used (3 and 38) at the Ohio Experiment Station, where the method originated. It is essentially a modification of the Tacke procedure for the determination of acidity in peat soils. The principal difference lies in the fact that the reaction between the calcium carbonate and the soil is brought about by the application of heat under reduced pressure. From this point on it becomes a question of the proper means of the recovery and estimation of the carbon dioxide evolved from the reaction mixture. The procedure for the recovery and estimation of the carbon dioxide has been adapted from the Marr(32) procedure for the determination of soil carbonates with only slight modification. The principal advantages of this method over the original Tacke method is considered to be the standardization of conditions under which the reaction can be controlled. It is also claimed that there is no organic matter attacked which has been shown to be the case with the Tacke method and also with the other methods of carbonate determinations.

Bouyoucos (7), employing the same reagent as in the Veitch method, but adopting an entirely new procedure, has developed a method which, he claims, will show not only the total lime requirement of a soil, but also the nature of the acidity as well, i.e., whether it is due to free acids or acid salts or to the unsaturated hyrated aluminum silicates. The method is based on the following assumptions - 1. That if a soil contains a soluble acid or acid salt its freezing point rises more or less regularly and gradually with the increase in the amount of $Ca(OH)_2$ added until the points of neutralization and saturation are reached and then it begins to fall. 2. If on the other hand a soil contains neither a soluble acid nor an acid salt but possesses an absorptive power for lime, due probably to the unsatisfied silicate compounds and organic matter, the freezing point remains constant as more and more of $Ca(OH)_2$ is added to the soil, until the absorptive power is satisfied, and then commences to fall. 3. Finally, if the soil contains no soluble acid or acid salt and has no absorptive power for lime, i.e., if it is already both neutral and satisfied, then the freezing point starts to fall almost immediately upon the addition of a small amount of $Ca(OH)_2$.

Sharp and Hoagland (42) have recently proposed the use of the hydrogen ion concentration as a measure of soil acidity, but the experimental work with it has been so far too limited to test its value.

Truog's Zinc sulphide test has been extensively used in thislaboratory (49). This method is based upon the reaction that takes place when an acid soil comes into contact with zinc sulphide, resulting in the liberation of hydrogen sulphide, which in turn, being allowed to react upon lead acetate paper causes the formation of the black sulphide of lead. For each determination 10 grams of soil is placed in an 300 cc. Erlenmeyer flask, 1 gram of hydrated calcium chloride and 0.1 gram of zinc sulphide added, 100 cc. of distilled water poured in, the contents well shaken and heated by the aid of a Bunsen burner, the flame being adjusted so that it will not cause the contents to boil over. The boiling is continued just one minute, then a strip of filter paper saturated with lead acetate solution is placed over the mouth of the flask and boiling continued for exactly two minutes longer, at the end of which time the paper is promptly taken off and allowed to dry. The amount of lead sulphide appearing against the white background of the paper causes a darkening proportional to the amount of hydrogen sulphide evolved, which Truog assumes to be proportional to the degree of acidity of the soil. By comparing these test papers with those obtained with standard soils we may secure a rough quantitative determination of the acidity.

Where a large number of samples are to be tested by this method it is found more convenient to prepare a stock solution of calcium chloride containing the zinc sulphide in suspension, so that each 10 cc. of the solution will contain the amounts needed for one test. Care should be taken that no acid has gotten to the reagents which can be best ascertained by first running a blank determination.

The test has proven to be very sensitive and to give concordant results. Its greatest advantage lies in the fact that the test papers can be mounted and preserved for future reference.

COMPARISON OF METHODS

It will be noted that whenever a new method is proposed it is customary to present it in comparison with one or more of the older well known methods. Two objects may be served by such comparisons. One is to show that, while the presented method offers many advantages in technique, manipulation, etc., the results obtained do not materially depart from those obtained by the older, more cumbersome methods. The other is to prove the superiority of the new test by showing that the results obtained are more in accord with the known behavior of the soil than those obtained by any of the methods with which the comparison is made. Bearing that in mind it would seem highly interesting to find out the concordance of the conclusions drawn with regard to certain methods by the various authors. With this object in view, the tables presented by various investigators will be next quoted, the generalization drawn from each notes, and then a correlation of the claims attempted.

Table I - Comparison by Hutchinson and MacLennan (23, p. 93)

Method	Acidity expressed as $CaCO_3$ required to neutralize the soils (Per cent)				
	Chelsea soil	Millbrook soil	Oundle soil	Woburn soil	Craibstone soil
Jones	0.045	0.045	0.018	0.232	0.161
Hopkins	0.012	0.006	0.002	0.244	0.030
Lyon & Bizzell	-	-	-	0.226	0.436
Veitch	-	-	-	0.204	0.407
Hutchinson & MacLennan	Nil	0.020	Nil	0.260	0.430

The authors make the following comment "Where the soil reaction is presumably due to the presence of acid mineral compounds, as in the case of the Woburn soil, the methods proposed by Jones and Hopkins give results closely approaching those obtained by other methods, but this agreement no longer holds when the reaction or lime requirement is due to other causes, as in the Craibstone soil. It is interesting to note that in both cases the bicarbonate method gives data agreeing well with those from the more laborious Lyon and Bizzell and the Veitch test.

Table II - Comparison of the different methods by MacIntire using Tennessee soils.

Soil	$CaCO_3$ per 2,000,000 lbs. of soil			
	MacIntire lbs.	Veitch lbs.	Tacke lbs.	Hutchinson & MacLennan lbs.
Clay subsoil	14400	7420	8850	7020
Swamp silt	15420	11428	19900	10220
River-bottom silt loam	10620	7536	9850	5320
Average	13480	8794	12866	7520

The author's comment is to the effect that in the Hutchinson and MacLennan method the carbonated water depresses the reaction and gives less carbonate decomposition than is effected at room temperature by the agitation of a soil with calcium carbonate in CO_2 free water as by the Tacke method. He further points out experiments with the Veitch method performed by Gardner and Brown (14) and also those of Hutchinson and MacLennan (22) with their own method, which go to show that neither of the above methods indicate the maximum lime requirement of a soil, and, consequently, the higher figures obtained by the proposed method must be accepted as being more in accord with the actual lime requirement of soils.

Ames and Schollenberger of the Ohio station employed soils taken from the fertilizer plots of the Wooster Farm. The soil of this farm is described as a silt loam, largely derived from sandstone and shale. "As far as its history is known, it contains no natural supply of $CaCO_3$ and each year it becomes increasingly difficult to secure a satisfactory growth of clover unless lime is applied". To study the specific effect of liming only a half of each fertilizer plot has been limed. The liming was done in 1903 at the rate of (CaO) 1875 pounds per acre and in 1909 ($CaCO_3$) 2000 pounds. The samples for the experiments were taken from the first six inches in 1912. The treatment of the plots had been as follows: 0 - Check, 2 - and phosphate, 3 - potassium chloride, 5 - sodium nitrate, 11 - a complete fertilizer, 24 - ammonium sulphate and a complete fertilizer, 26 and 29 - bone meal and basic slag, respectively, as the phosphorus form in complete fertilizers. Table III shows the lime requirement as found by the different methods, Table IV the degree to which the original need for lime appeared to have been satisfied and Table V the change in the requirement in the course of 6 years.

Table III - Comparison of methods by Ames and Schollenberger, using Wooster Farm Soils.

Plot	$CaCO_3$ present: pounds per acre	Reaction to litmus	Lime requirement in pounds per acre: Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
0	-	Decidedly acid	3400	2000	3500	2925	7300
0 + Lime	150	" "	100	Alkaline	2200	1700	4900
2	-	" "	2640	2000	5850	2700	7800
2 + Lime	225	" "	80	Alkaline	2400	975	3800
3	-	" "	3240	2000	3550	3025	-
3 + Lime	450	" "	200	Alkaline	2650	1600	-
5	-	" "	3040	1200	3550	2550	6200
5 + Lime	575	" "	120	Alkaline	2500	1250	4225
11	-	" "	3080	1800	3850	2825	7100
11 + Lime	300	" "	90	Alkaline	2500	1375	5900
24	-	" "	4240	3000	4000	2700	8300
24 + Lime	00	" "	260	200	2850	1475	5700
26	-	" "	2940	2000	3700	2250	7350
26 + Lime	250	" "	360	Alkaline	2900	1325	4050
29	-	" "	2560	1200	3600	2250	6600
29 + Lime	300	" "	150	Alkaline	2100	1075	4050
18	-	" "	2760	2600	4200	3100	8500
18 + Lime	-	" "	120	Alkaline	2[illegible]50	1950	5200

Table IV - Proportion of the original lime requirement satisfied by lime treatment, as indicated by the different methods.

No. of soil	Method: Hopkins P. ct.	Veitch P. ct.	MacIntire P. ct.	Hutchinson P. ct.	Vacuum P. ct.
0	97	100	36	41	32
2	97	100	37	60	51
3	94	100	25	47	-
5	96	100	29	50	31
11	97	100	35	51	17
24	94	93	28	45	31
26	87	100	21	41	45
29	94	100	41	52	38
18	95	100	29	37	39

Table V - Comparison of lime requirement in same plots sampled in 1896 and again 6 years later.

Fertilizer used	Year	Lime requirement: Hopkins Pounds	Veitch Pounds	MacIntire Pounds	Hutchinson Pounds
Ammonium sulphate	1896	750	4000	3000	1750
" "	1912	4240	3000	4000	2700
None	1896	625	4000	2700	1575
"	1912	[illegible]440	2000	3550	2925

In comparing the results of the various methods with the actual responses to lime, shown by the growth of clover, these authors conclude that both the Veitch and the Hopkins methods lead to erroneous results, and that the others are more reliable. In regard to the vacuum method they state: "for many soils naturally supplied with calcium carbonate and which gave an alkaline reaction with litmus paper, results by this method indicate a further need of lime. This would seem to indicate that the results obtained for lime requirement are probably too high and that the method would not be applicable to soils in general.

Table VI - Comparison of vacuum with dilute nitric acid method(38)

Series of Plots	Excess lime requirement of the unlimed over the limed halves					Excess bases soluble in N/5 Nitric acid over limed
	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum	
Sec.D,5 yr.rot.-0-6"	622	913	521	543	1081	952
Sec.D,5 yr.rot.-0-12"	1054	-	-	-	1960	1524
Lime Ext.6 tons-0-12"	-	-	-	-	1500	1919
" " 13 " -0-12"	-	-	-	-	1964	1995

Schollenberger, in a later publication, however, states: "That the vacuum method has been studied at greatest length, the results obtained, while not remarkably close, indicate that this is the most reliable method of those studied, which is at the same time universally applicable". The results of the Hutchinson and MacLennan and the MacIntire methods are considered to be only half the proper value. The Veitch method apparently gives most excellent results, but experiments are too few to draw general conclusions. The data in Table VI are from the later publication mentioned.

Table VII - Comparison of Bouyoucus and Veitch methods, by Bouyoucus

Soil No.	Description of Soil	Bouyoucus method Pounds	Veitch method Pounds
No. 3	(Heavy silt loam - gray)	6,730.8	560
No. 4	(Heavy silt loam - black)	10,096.2	0
No. 15	(Light silt loam - gray)	10,096.2	3,780
No. 16	(Coarse sand - brown)	3,926.3	1,890

It is obvious that the results obtained with the Bouyoucos method are extremely high, compared with the Veitch method. The author makes note of this by stating that the indication obtained by his method does not necessarily show the lime requirement needed for optimum crop production, and that field trials would be required to ascertain the relation between the indication and the lime required for optimum growth of a particular crop. The only claim the author maintains for his method is that it shows the maximum lime requirement to neutralize the acidity and to satisfy the absorptive capacity of a soil.

Since the comparisons of methods cited from various investigators employed widely differing types of soils, a comparison of results of the findings of one investigator with those of any other is hardly possible, but the general conclusion may be drawn that the Veitch method is the one most frequently used as a standard and it finds favorable comparison with both the Lyon and Bizzell and the bicarbonate method. The Lyon and Bizzell method gives results fairly comparable with those obtained by the Veitch. The Hopkins method Ames and Schollenberger found gives uniformly higher results, while in the hands of Hutchinson and MacLennan they were variable.

The Hutchinson and MacLennan bicarbonate method gives results agreeing with those of the Veitch method, both according to the data given by its authors and by MacIntire, while, according to Ames and Schollenberger they appear variable and generally higher.

The MacIntire, Vacuum and Bouyoucus methods give uniformly higher results than the Veitch.

VEGETATION AND FIELD EXPERIMENTS.

Although liming experiments have been carried on in great numbers in various states of the Union, and on a great variety of soils under varying treatments, they afford very few data of value for our present purpose, for the reason that in very few of them have the field results been correlated with the degree of acidity of the soil as determined by any method. The correlation of field results with the lime requirement as indicated by any of the laboratory methods has of late become an important part of the study of acid soils.

The relation between lime requirement of some Danish soils and the percentage of lime soluble in ammonium chloride, a method described above, can be seen from field experiments recorded by Christensen and Larsen (10).

Table VIII - Danish Liming experiments.

Percentage of lime (CaO) soluble in NH_4 Cl.	Number of experiments	Results of field experiments Lime response: Positive P. ct.	Negative P. ct.	Doubtful P. ct.	None and doubtful P. ct.
0 - 0.05	16	87	6	6	13
.06 - .10	16	87	6	6	13
.11 - .15	17	65	24	12	35
.16 - .20	15	40	40	20	60
.21 - .25	17	24	65	12	76
.26 - .30	8	0	88	13	100
over .30	27	11	81	8	89

The Veitch test has been studied at the Pennsylvania Experiment station by Gardner and Brown, and later by White.

Gardner and Brown (14) have performed vegetation experiments with red clover on acid soils to which enough lime had been applied to supply the deficiency indicated by the Veitch method, and also at a rate of one ton per acre in excess of this amount. The results have been summarized by Frear (12, p. 176) and are shown below.

Table IX - Comparison of laboratory tests with field trials by Pennsylvania station.

Number of plots in the average	Average lime requirement per acre	Relative weights of green crops: Unlimed	Limed: Veitch	Limed: Veitch & 1 ton
	Pounds			
121	None	100	-	103
13	190	100	102	110
6	843	100	115	131
4	1,395	100	197	222

White (55) in his study of the effect of varied amounts of limestone upon the growth and composition of sorrel and clover, started with an acid soil of a lime requirement of 5200 pounds of calcium carbonate, as determined by the Veitch method and added various amounts of lime up to an excess of 10 tons above neutral. His results as far as the growth of clover is concerned show that a considerable growth was obtained when the acidity was reduced to 1600 pounds calcium carbonate required, the maximum growth being obtained with an excess of 2 to 3 tons over the Veitch requirement, and higher applications caused a gradual depression of the yield.

Daikuhara (11, p. 36) states that he had carried out pot experiments consisting of growing various crops on acid soils to which varied amounts of lime had been added. The optimum lime content of each soil had thus been obtained and compared with the lime requirement of those soils as indicated by the potassium chloride (Daikuhara) test. The results, reported in Table X, are strikingly concordant:

Table X - Daikuhara's comparison of the lime requirement indicated by his method with the optimum amount as found by vegetation tests, using Japanese soils.

Soils	Optimum amount of $CaCO_3$ Grams	Lime requirement by author's test Grams
Niigata	1.80	1.60
Gifu	1.30	.93
Shiga	2.80	2.56
Yoshino	3.40	3.78

Hutchinson and MacLennan (23, p. 96) compared the yields obtained from the permanent barley plots of the Woburn Experiment Station with the lime requirement as indicated by their test. The results given in the table below they considered to indicate a general concordance of the results of their method.

Table XI - Comparison of the bicarbonate indication with field results.

Soil	$CaCO_3$ required - 1914 P.ct. $CaCO_3$	Yield in bu. - 1913
1	0.260	0
2	.140	11.9
3	-	34.3
4	.043	16.3
5	.183	-
6	-	31.5
7	.140	13.1
8	.190	-
9	-	31.6
10	.123	6.7

Schollenberger (38) used clover in some pot experiments in connection with the Vacuum test. In his comparisons he makes use of this test in an indirect and somewhat complicated manner, comparing the field results with the "per cent total lime requirement satisfied". This value he obtained by a series of analyses including the estimation of N/5 acid soluble bases, determination of carbonates, and the lime requirement by the Vacuum method. After reducing these components to the calcium carbonate equivalent, the formula: -

$$\frac{\text{Lime requirement}}{\underset{\text{(N/5 acid soluble)}}{\text{bases}} + \underset{\text{(by vacuum)}}{\text{lime requirement}} - \underset{\text{(present)}}{\text{carbonate}}}$$

gives the per cent of the total lime requirement which has been satisfied. The figures thus obtained he compared with the effect of liming upon the growth of clover. The results show that liming has been beneficial wherever the percentage of the total lime requirement satisfied has been 85 or below; at 90 per cent no benefit from liming was observed.

THEORIES OF THE NATURE OF SOIL ACIDITY.

One of the oldest and most generally accepted theories regarding the nature of soil acidity is that it is produced by organic acids resulting from the natural decomposition of organic matter in the soil, that these organic acids, generally referred to as humus acids, in the absence of sufficient amounts of bases in the soil to neutralize them, produce a toxic effect on plant growth. Thus Hilgard, speaking of the functions of lime in the soil, states: "The current neutralization of humus acids is unquestionably one of the cardinal advantages of calcareous lands". Since a water extract of an acid soil very seldom gives an acid reaction, it was assumed that these organic acids must be insoluble or only very slightly soluble in water. The first method for the estimation of the lime requirement of soils, the Müntz method described above, was based upon this theory of free organic acids. The later methods also emphasize the importance of organic acids in the soil. Methods like those of Hopkins, Daikuhara and Jones, which use a neutral salt solution as the reagent, are based upon the supposition that when a neutral salt is added to an acid soil a double decomposition takes place, whereby a soluble mineral acid is set free

$$R\ COOH + KNO_3 \longrightarrow R\ COOK + HNO_3$$

Veitch (51) has made a great number of analyses on the soil extracts by the Hopkins method, but in no case was he able to find any appreciable amounts of hydrochloric acid in solution. He states: "that there is practically no reaction between the organic matter and the salt solution, whereby difficultly soluble organic acids are dissolved, but that the acidity of the filtrate (or that acidity which is greater than would be given by water under the same conditions) is due to the solution of alumina or some other acid-salt yielding bases. These observations have been fully corroborated by the extensive studies of Daikuhara (11) on the reaction between a soil and a neutral salt solution, which shows that there exists an almost quantitative relation between the acidity of a neutral salt extract of a soil and the amount of alumina and iron salts dissolved in that extract. On the other hand, it appears from more recent observations that free acids, presumably of organic nature, do exist in the soil. Thus Shorey, Fry and Hazen (44, p. 76) state: "It is the experience of the authors that when a good grade of litmus paper is pressed in contact with a moist soil and gives a color change indicating an acid condition, a filtered water extract of that soil on concentrating in platinum will very frequently give a consentrated extract acid to litmus, or will lose volatile acids which, by proper means can be recovered and the acid nature demonstrated".

The United States Bureau of Soils (39,40,41) has done considerable work on the isolation and the identification of organic compounds of the soil. Plant cultures with nutrient solutions containing the various organic compounds under various conditions have shown several of them to have an harmful effect on plant growth. Among the toxic organic substances the best known is Dihydroxystearic acid and Picoline carboxylic acid and aldehydes. Very little work has been done in the study of the effect of these substances upon soil media. The only work of this nature was done by Plummer (35) who has shown dihydroxystearic acid had a distinctly toxic effect upon wheat plants when added to an acid soil, but, when the same soil was previously treated with lime, there was no toxic effect, which goes to show that this substance retained its acid properties only in a lime-deficient soil. However, the isolation of such acids is not deemed to be a definite proof of their existence in free state or in a condition to produce a harmful effect on plant growth. Shorey (43, p. 7) makes this statement to that effect - "Although several acids have been isolated from soils, there is as yet no conclusive evidence as to the identity of free acids, if such exist, in acid soils".

The effect of decaying vegetable matter on the acidity of a soil has been the subject of some experimental work. Coville (9) has determined the amount of acidity added to a soil by various green manures. He determined the lime content of these green crops, deducted the neutralizing effect of this and expressed the residual acidity in terms of lime requirement as $CaCO_3$. The results are shown in the table below:

Table XII - Showing the acidity produced by green manures per acre.

Crop	Weight Tons	Lime content Pounds	Acidity, expressed as lime requirement Pounds
Alfalfa	2½	139	267
Red clover	2	131	142
Cow peas	2½	92	200
Rye	2	11	178
Brown sedge	1	4	89

These figures substantiate the popular belief that green manures produce an acid condition in the soil. On the other hand, Temple (48) reports experiments on the effect of organic acids added to soils and also the effect of green manures. He found that soil micro-organisms were able to destroy such organic acids as acetic, lactic, citric and tartaric when these were added to a soil. The results from adding pea vines at a rate of 50 tons per acre indicate that the soil bacteria do not ferment the green legumes in such a way as to produce acid, but, on the contrary, their action is such as to partly neutralize any acid that might be present in the soil.

Whatever the effect of organic matter and humus may be upon the reaction of soils rich in vegetable matter, it could not explain the phenomen of acidity of a great number of surface soils and subsoils practically devoid of organic matter. Loew (27), working with red clay soils of Porto Rico has found that these owe their acid reaction not to humus or any organic substance but to the acid clay which he calls argillic acid. From a consideration of its behavior he assigned to it the formula

```
                    O
        HO - Si  -  O  -  Al - OH
 (A)            O                          (b)
        HO - Si  -  O  -  Al - OH
                    O
```

According to Loew, the application of basic materials, such as $Ca(OH)_2$ would result in the neutralization of the acid hydrogens at (a), while the adsorption of phosphoric acid can be explained by the basic hydroxyls at (b). Loew attributes the formation of such acid clays to heavy rains charged with carbonic acid which by the loss of mass action decompose the neutral salts which, upon removal of the bases in drainage water, become acid. The theory of argillic acids finds support in the experiments of Harris (17) who observed that Kaolin in its native state has no power to withdraw bases from a neutral salt solution, but when some of its own basic materials have been removed by an acid extraction, the residue behaves in like manner with the acid sandy loam, by withdrawing basic materials from neutral solutions of such salts as potassium nitrate, sodium acetate and sodium chloride. The above theory also explains the effect of applications of ammonium sulphate to an acid soil. The common occurrence of acidity upon plots heavily fertilized with ammonium sulphate is explained by the decomposition of the neutral salt by the acid hydrogens of the acid clay, the base being absorbed and the acid set free.

Another theory advanced in connection with the behavior of an acid soil in setting free acid substances from a neutral salt solution has been the colloidal adsorbtion theory. This theory ascribes the apparent soil acidity, i.e., the acidity produced by a soil when treated with a neutral salt solution, to the adsorbing power of the gelatinous (colloidal) portion of the soil mass which, at normal moisture conditions, may include gelatinous silica, hydrated silicates, humates, iron and aluminum hydrates. The adsorption is considered a physical action due to the fact that part of the bases adsorbed can be washed out again immediately after the soil treatment. However, the purely physical nature of the action of a soil upon a neutral salt solution has never been demonstrated.

Another theory is that the acidity is caused by the root action of growing plants, what is known as physiological acidity. This theory is based upon the general assumption that soils that have been long under cultivation are more apt to be acid than those which have only recently been brought under the plow.

Hilgard (18, p. 123) states: "It has been long known that after long continued cultivation, soils originally of neutral or slightly basic reaction become acid".

The evidences in favor of this theory consist of observations made on plant nutrition in water cultures. There is has been observed that a given plant did not consume at equal rates the basic and acid constituents of the several salts used. Breazeale and LeClerc (8), working with wheat seedlings in water cultures, found that these have given a distinctly acid reaction to an originally neutral media of potassium chloride and potassium sulphate.

Field records bearing upon this question are very few and not altogether complete. Veitch (52), reporting the results obtained from various experiments of the Bureau of Chemistry, notes that "different plants affect the reaction of the soil in different degrees" He further calls attention to the fact that: "In six years oats followed by buckwheat had decreased the total apparent acidity of nearly all the soils, making some of them alkaline in reaction. On the other hand, beans followed by buckwheat in the same time increased the total apparent acidity, rendering some originally alkaline soils acid". The conclusion drawn is that beans are more acid producing plants than oats. Gardner and Brown (14) furnish some records on the changes of the soil reaction at monthly intervals during the growing season of a number of crops upon the general fertilizer plots of the Pennsylvania station. The figures below give the lime requirement by the Veitch method in pounds of CaO per acre 7 inches, and represent an average of 36 analyses from as many plots:

Table XIII -

	Wheat	Oats	Corn	Clover & timothy
1st period	404	178	656	308
2nd "	331	99	481	458
3rd "	418	95	546	633
Average	384	124	561	465

Taking the above averages as the basis the authors have ranked the crops in order of the acid producing effect on the soil - corn first; clover and timothy, second; wheat, third and oats last. However, a critical inspection of the above data will show that the variations attending the results obtained on the same crop frequently exceed the average difference between the different crops. For instance, in the column of clover and timothy there is a difference of 328 pounds CaO between the first and the third period determinations as against an original lime requirement of 308 pounds CaO. That is, the acidity accumulated during the last two months exceeded the total acidity formed during the several years of the same treatment. Since the lime requirement of each plot previous to the experiment is not known there is no way of arriving at the actual increase or decrease in the acidity of those plots for any certain length of time. The conclusions drawn from the above figures by Gardner and Brown seem to be unwarranted.

Of the various theories suggested, Loew's explanation of the origin of acid clays probably comes the nearest to explaining the acid condition of the greatest number of upland acid soils. Although the formula of the acid substance and its reaction may not be quite as simple and clear cut as suggested by Loew, the main features of his theory, however, are well supported by general facts on rock weathering and by extensive investigations of drainage waters. The chief cause of acidity must be recognized in the constant removal of basic material by drainage waters from the soil and the effect of the residual acid silicates, aluminum and ferric hydrate on plant growth.

The humus acid theory, although quite frequently quoted, finds very little application since it is only borne out on soils rich in organic matter, and at the same time deficient in basic materials, that is, soils already subjected to the action described in the previous paragraph. The humus acid theory seems to hold only as an incidental cause of soil acidity.

The colloidal adsorption theory of soil acidity and that of physiological acidity produced by plant growth as yet have received little experimental support.

EXPERIMENTAL.

A COMPARISON OF LABORATORY METHODS FOR THE LIME REQUIREMENT OF SOILS.

For the purpose of this comparison six soils were selected. These included three from the University Famat St. Paul, two from the southeastern part of the state, and one from Duluth. The University Farm soils are all of Hempstead silt loam, No. 1 representing a composite from the surface 6 inches of a number of unlimed areas adjacent to the limed alfalfa plots, No. 2, a composite of the subsoils of the same plots and No. 3 a composite from the surface soils of Field C. Nos. 4 and 5 represent two soils from the southeastern part of the state where liming and alfalfa experiments had been carried out, No. 6 is a gray surface soil from the Duluth Experimental Farm, somewhat recently cleared from forest.

The liming experiments at the University Farm were begun four years ago, and the yields show that on the soils in question alfalfa has yielded no better after liming. The liming experiments in the southeastern counties were initiated in 1915, and, as shown by the yields, lime has a markedly beneficial effect upon the growth of alfalfa on these soils. The Duluth soil had been seeded to grass and clover for the first time, the clover failing completely and the grass making a very scanty growth.

The methods included in this comparison were the Hopkins, Veitch, Litmus, Daikuhara and Truog.

The Hopkins method was carried out according to the procedure outlined in Bulletin 73 of the United States Bureau of Chemistry. The Veitch method was applied according to the procedure outlined by its author in Jour. of Industrial & Engineering Chemistry Vol.XXVI, with only a few modifications. The mixture, after standing over night, instead of being decanted, was well shaken up and immediately filtered, 15 to 20 cc. of the first of the filtrate discarded and 50 cc. of the clear filtrate then collected in a Jena beaker, boiled down to about 15 to 20 cc., and phenolphthalein added at that point instead of at the beginning. The liquid, if not alkaline already, was further boiled down until only between 5 and 10 cc. remained, or until it turned alkaline.

The litmus test was applied in the usual way and also with the modification suggested by Barlow, only one side of the litmus paper being brought into contact with the soil, the other side resting upon a glass plate through which the color change may be observed at any time without disturbing the test. The advantage of this modification lies in the point last mentioned. In applying it to the same soils to which the ordinary litmus test was used it was found that the corresponding color changes have appeared at the end of 1 to 2 hours, instead of from 5 to 15 as is the case where both sides of the litmus paper are brought into contact with the soil. Furthermore, it has been observed that in the case of soils not strongly acid, the change in color of the litmus paper is more distinct on the side next the soil than on the side next the glass plate. For the above reasons the usual procedure was considered preferable to the modification, and all tests were read after 15 minutes of contact with the soil.

The Daikuhara, or sodium nitrite test, has been used quite extensively in connection with other tests. The procedure followed in this laboratory is quite simple. About five grams of soil is placed in a 20 cc. crucible, the soil is slightly moistened, two cc. of a 30 per cent sodium nitrate solution added, a strip of moist starch potassium iodide paper suspended and the crucible immediately covered up with a watch glass. When conditions are properly controlled this test is found very simple and reliable. The greatest difficulty encountered in the employment of the test is the adjustment of the moisture content of the soil tested. Thus when the soil is in an air-dry or slightly moist condition the results will be found quite concordant with those of other methods, but, when the moisture content is too high, acid soils may show negative results with this test, even after prolonged standing. Again, when a moist soil, neutral by the Veitch test, had been evaporated to dryness on a steam bath, and the test directly applied without the addition of water, the soil may show a very strongly acid reaction. Since the right moisture conditions are rather difficult to obtain just at the time of testing, especially if that should occur in the field, this test is considered not so reliable as some of the other tests used.

The Truog test has been quite extensively employed by the Division of Soils of the Minnesota Experiment Station for the last two years. During the summer of 1916 the author had occasion to test several hundred soil samples sent in to the Division of Soils from various parts of the state. The Truog method was largely used and occasionally the same samples were tested also with litmus paper, and sodium nitrite. The reactions obtained by the Truog nearly always agreed with these obtained by the litmus test, but the degrees of acidity could not be so definitely determined with the litmus.

A point of interest that occurred to the author, while working with the Truog methos, is one concerning the time allowed by Truog for expelling the carbon dioxide from the soil before applying the test. While one minute recommended by Truog was found sufficient for subsoils and soils poor in organic matter, with soils rich in organic matter, better results were obtained when 2 minutes of boiling were allowed for the expulsion of the carbon dioxide before applying the lead acetate paper. This was learned from the observation that when the ordinary procedure was followed an acid reaction was sometimes obtained by the Truog method with soils which were alkaline to the Veitch test. When these soils were boiled two or three minutes before applying the lead acetate paper the result was more concordant with the Veitch test. It has been further observed that the evolution of hydrogen sulphide from the treated soil is quite constant several minutes after the test has been performed. Over two hundred soils were tested, obtaining with each a second test by applying a second strip of lead acetate paper for two minutes immediately following the first test. The test papers were placed side by side, and with none of the soils was there found any perceptible difference in color between the first and second test papers. In view of the above it is not improbable that the boiling of the soil for 2 or 3 minutes before applying the lead acetate paper would be preferable for all soils.

The results obtained by the above methods on the six soils tested are given in Table XIV.

Table XIV Comparison of different methods for determination of soil acidity.

Soil No.	$CaCO_3$ required: Hopkins	$CaCO_3$ required: Veitch	Truog Test	Litmus Test	Field Results
1	63	2200	Medium	Slightly acid	Not benefited by lime
2	3750	1760	Medium	Distinctly acid	No treatment
3	63	2600	Medium	Distinctly acid	No treatment
4	63	440	Slightly acid	Neutral	Benefitted by lime
5	438	4400	Strongly acid	Medium acidity	Benefitted by lime
6	9250	14080	Very strongly acid	Strongly acid	No treatment

From the above data it appears that the Veitch method generally gives higher results than the Hopkins method. In the case of Soil No. 2 the Hopkins method shows a higher lime requirement than the Veitch. This exception is in accord with the observations of Veitch who states that the Hopkins method falls short only when applied to surface soils or soils containing large amounts of organic matter. The Truog test shows uniformly concordant results with the Veitch. It appears that a slightly acid reaction by the Truog test expressed a lime requirement of about half a ton by the Veitch method. A lime requirement of one ton by the Veitch corresponds to a medium reaction by the Truog and a lime requirement of about two tons is equivalent to strongly acid by the Truog. For very strongly acid soils the Truog method does not allow any differentiation, by the present procedure. It seems that a very strong reaction by the Truog is obtained when the lime requirement by the Veitch is over two tons, and the same will be obtained when the requirement is 4 tons or more. A feasible method for differentiating the very strongly acid soils by the Truog test would seem to be the cutting down of the time. Thus, if one soil gives a strongly acid reaction by one minute boiling it may be assumed that this soil is twice as acid as another which gave the same coloration after two minutes boiling. Such tests have been obtained by the author with various acid soils, but no quantitative correlation has as yet been attempted.

The litmus test agrees with the Veitch indication but not quite so regularly as does the Truog.

Comparing the above indicators with the field results obtained from liming those soils, it will be seen none of the methods affords a perfect concordance when applied to all the soils. The Hopkins appears to give true indications as to the lime requirement of Nos. 1, 3, and probably 6, but fails to show any appreciable lime requirement for Nos. 4 and 5, and gives too high indication for No. 2. The Veitch method appears to give a true indication for Nos. 4, 5 and 6, but falls short on Nos. 1, 2 and 3.

Soils 3, 4, 5 and 6 have also been tested by the Hutchinson and MacLennan method. The lime requirements for the respective soils were 3200, 2400, 5200 and 10200 lbs of calcium carbonate per acre. From these data it appears that the Hutchinson and MacLennan method gives somewhat higher results than the Veitch method with the exception of Soil 6, but it does in no way add anything to the other methods in distinguishing between the University Farm soils (No.3) and the southeastern acid soils (Nos. 4 and 5).

RELATION OF ACIDITY TO CARBONATE CONTENT

An extensive set of soil samples from the southern tier of counties in Minnesota, which had been collected by Mr. P. R. McMiller, who made determinations of the moisture equivalent and content of carbon dioxide, offered an opportunity to determine the relation of the acidity as indicated by the Truog method to both the texture and the carbonate content. I have made use of these data from the thesis of Mr. McMiller (30-a).

The samples represent ten localities, each represented by five virgin fields, from which two sets of composite samples were taken, each composite sample being secured from 10 individual borings. The first three one-foot sections are represented, thus giving a total of 294 samples. The degree of acidity of each sample is reported in Table XV. The numerals - 0 to 5 have the following significance:

0 - Neutral or alkaline
1 -- Very slightly acid
2 - Slightly acid
3 - Medium
4 - Strongly acid
5 - Very strongly acid

Intermediate degrees of intensity have been estimated. The average acidity for each section from the two sets has been calculated for comparison with the carbon dioxide content, this having been determined in only the field composites.

The relation of acidity to the carbon dioxide content can be seen in detail from Table III. In order to show this relation in a more concise manner a summary table (XVI) has been constructed. All samples were grouped according to reaction, the first for non-acid soils, the second for those with acidity from .25 to 1.0

the third those with an acidity of 1.25 to 2.0, the fourth those with acidity from 2.25 to 3.0, the fifth those with acidity from 3.25 to 4.0, and the sixth and last, those with acidity from 4.25 to 5.0. Then each of the groups was subdivided according to the depths. The carbon dioxide percentages for each such subdivision were added, the sum divided by the number of samples to secure the average carbon dioxide content. The range of the carbon dioxide content also is shown. From the Table it will be seen that the carbon dioxide content of the neutral soils has shown very wide range, namely: from 0 to 7.63 per cent. Thus the absence of carbonate from any soil does not necessarily render the soil acid in reaction, a fact which has been observed on numerous occasions, as mentioned elsewhere in this thesis. The carbon dioxide content of the samples showing the various degrees of acidity above 1 seems to be about the same, fluctuating around 0.1 per cent, and this is negligible, it being within the limits of experimental error. The first foot from Jackson, II, containing a large amount, .45 per cent of carbon dioxide, while still showing an acid reaction is an interesting exception. From the above data we may conclude that soils shown acid by the Truog test have at most only a negligible carbonate content.

Table XV Relation of acidity as indicated by the Truog method to the carbonate content, expressed as carbon dioxide

Depth	Field I		Field II		Field III		Field IV		Field V	
	CO_2	Acidity	CO_2	Acidity	CO_2	Acidity	CO_2	Acidity	CO_2	Acidity
Foot	P.ct.		P.ct.		P.ct.		P.ct.		P.ct.	
					CALEDONIA					
1	.07	1.75	.11	3.25	.12	2.0	.10	2.25	.10	2.5
2	.05	2.25	.15	2.5	.06	3.0	.06	2.75	.06	2.75
3	.04	1.5	.07	2.5	.05	3.0	.05	2.5	.07	3.25
					PRESTON					
1	.07	2.0	.11	2.25	.08	2.0	.11	1.0	.06	2.0
2	.05	2.0	.08	2.25	.06	2.0	.10	2.5	.05	4.0
3	.04	2.0	.12	2.25	.04	2.0	.13	2.5	.02	4.0
					SPRING VALLEY					
1	.13	3.5	.09	4.0	.10	2.5	.09	2.75	.08	2.0
2	.12	4.0	.09	4.5	.04	2.5	.08	2.75	.05	2.5
3	.08	4.5	.05	3.0	.03	2.5	.06	2.0	.03	2.5
					ALBERT LEA					
1	.11	2.0	.06	1.5	.08	2.0	.11	1.5		
2	.11	1.5	.18	.75	.11	2.0	.08	1.5		
3	.13	1.0	1.88	0	.09	1.0	.07	1.0		
					WELLS					
1	.03	0	.45	0	6.15	0	3.58	.0	.91	0
2	.05	0	3.09	0	5.19	0	5.38	0	1.37	0
3	.0	0	5.71	0	4.49	0	5.75	0	2.26	0
					FAIRMONT					
1	.09	1.5	3.35	0	.11	1.0	.09	.5	.08	1.75
2	.09	1.75	5.37	0	.64	0	.17	.0	.08	1.75
3	.04	0.5	7.43	0	6.98	0	2.45	0	2.20	0
					JACKSON					
1	2.42	0	.31	0	.14	0.5	1.45	0	.08	.25
2	4.60	0	.85	0	.48	0	2.67	0	.54	.0
3	7.27	0	3.47	0	3.41	0	7.63	0	5.72	.0
					WASHINGTON					
1	.16	0.5	.15	1.0	.70	0	.08	1.5	.13	.75
2	.22	0	.16	0.5	.75	0	.13	0	.25	.0
3	4.34	0	1.94	0	2.45	0	3.97	0	6.04	.0

Table XV (Continued)

Depth	Field I		Field II		Field III		Field IV		Field V	
	CO_2	Acid-ity	CO_2	Acid-ity	CO_2	Acid-ity	CO_2	Acid-ity	CO_2	Acid-ity
Foot	P.ct.		P.ct.		P.ct.		P.ct.		P.ct.	
					ADRIAN					
1	.03	1.25	.09	1.25	.07	1.25	.07	2.0	.10	0.5
2	.10	1.25	.17	0	.13	.5	.12	2.0	1.46	0
3	4.04	0	1.54	0	.10	0	.85	0	4.39	0
					LUVERNE					
1	.22	1.75	.08	0	.10	1.5	.09	2.0	.08	2.0
2	1.61	0	1.02	0	.09	1.25	.07	0	.38	0
3	2.87	0	4.17	0	.08	0	1.31	0	3.70	0

Table XVI Showing the relation of the carbon dioxide content to the degree of acidity.

Degree of acidity	Section: Foot	No. of samples	Carbon dioxide content: Extremes	Carbon dioxide content: Average
			Per cent	Per cent
0	1	10	.03 - 6.15	.22
0	2	22	.07 - 4.60	.97
0	3	29	0 - 7.63	3.37
1	1	10	.08 - 1.45	.26
1	2	4	.13 - 1.61	.52
1	3	5	.04 - .85	.23
2	1	21	.03 - .22	.09
2	2	13	.06 - 1.10	.19
2	3	5	.04 - .06	.05
3	1	5	.10 - .11	.10
3	2	7	.04 - .15	.07
3	3	8	.03 - .13	.07
4	1	3	.09 - .13	.11
4	2	2	.06 - .12	.09
4	3	2	.02 - .07	.05
5	1	0	-	-
5	2	1	.09	.09
5	3	1	.08	.08

Table XVII Showing the relation of acidity to depth of soil section.

Part A - According to the number of samples

Section Foot	No. tested	0	1	2	3	4	5
1	49	10	10	21	5	3	0
2	49	22	04	13	7	2	1
3	49	29	5	4	8	2	1

Part B - According to the percentages

Section Foot	Total number	Degree of acidity 0	1	2	3	4	5	Average acidity
1	99	20	20	43	10	6	0	1.6
2	100	45	8	27	14	4	2	1.3
3	100	60	10	8	16	4	2	1.0

SIMILARITY IN DEGREE OF ACIDITY OF DUPLICATE SAMPLES FROM THE SAME FIELD.

The soils used for these comparisons have already been described above (p. 49 and p.81). The difference in reaction with composites from two parallel sets of borings in the same field of the southern counties of Minnesota is shown in Table XVIII . The results with soils from 12 plots on the University Farm soils are shown on Plate VI, p. 85-a. Separate tests were made with the samples from the two halves, south and north, of each of these plots, and these papers have been mounted on the plate according to their respective positions on the plots. Accordingly the test papers show the differences between the north and south halves of each of these plots as well as between the 12 different plots.

From the above mentioned data it will be seen that the lack of concordance of the duplicate samples is greater in the case of the southern Minnesota soils than with the University Farm soils. From Plate VI it will be seen that on only one of the 12 plots is there a marked lack of concordance (series I, plot 11), while Table XVIII shows that out of 146 pairs of duplicate samples from the southern counties there are 49 showing a difference in acidity, i.e. four times as great a proportion as found with the soils from the University Farm. In the matter of the distribution of the lack of concordance by separate fields, it will be seen that this is most frequent and most marked in the fields of the southeastern counties, especially at Caledonia and Spring Valley.

Table XVIII - Similarity in degree of acidity* of duplicate samples from the same field. In the case of all fields where the duplicate samples are not concordant the degree of acidity of both samples is reported.

Depth foot	Field I	Field II	Field III	Field IV	Field V	Field I	Field II	Field III	Field IV	Field V
	LUVERNE					ADRIAN				
1-a	1.5	-	-	-	-	1.5	1.0	1.5	-	0
b	2.0					1.0	1.5	1.0		1.0
2-a	1.0	-	1.5	-	-	1.5	-	1.0	-	-
b	0		1.0			1.0		0		
3-a	-	-	-	-	-	-	-	-	1.0	-
b									0	
	WORTHINGTON					JACKSON				
1-a	0	0	+	-	1.5	-	-	0	1.0	0
b	1.0	2.0			0			1.0	0	0.5
2-a	-	0	-	-	-	-	-	-	-	-
b		1.0								
3	-	-	-	-	-	-	-	-	-	-
	FAIRMONT					WELLS				
1-a	-	-	-	-	2.0	-	-	-	-	-
b	-	-	-	-	1.5					
2-a	2.0	-	-	-	2.0	-	-	-	-	-
b	1.5				1.5					
3-a	1.0	-	-	-	-	-	-	-	-	-
b	0									
	ALBERT LEA					SPRING VALLEY				
1-a	-	-	1.0	1.0		4.0	-	2.0	2.5	-
b			3.0	2.0		3.0		3.0	3.0	
2-a	-	1.5	1.0	-		-	4.0	3.0	2.5	2.0
b		0	3.0				5.0	2.0	3.0	3.0
3-a	-	-	-	-		5.0	4.0	3.0	-	3.0
b						4.0	2.0	2.0		2.0
	PRESTON					CALEDONIA				
1-a	-	2.5	-	-	-	2.0	2.5	-	2.0	-
b		2.0				1.5	4.0		2.5	
2-a	-	2.5	-	-	-	2.5	-	-	2.5	2.5
b		2.0				2.0			3.0	3.0
3-a	-	2.5	-	2.0	-	3.0	3.0	-	-	3.0
b		2.0		3.0		2.0	2.0			3.5

*1 = Very slightly acid
2 = Slightly acid
3 = Medium acid
4 = Strongly acid
5 = Very strongly acid

RELATION OF ACIDITY TO TOTAL CaO CONTENT.

For this experiment six soils were used, one - a composite from Field C on the University Farm, a second a composite from many fields in southeastern Minnesota, and the other four composites from Caledonia, Spring Valley, Preston and Luverne, respectively. The reaction of the soils were, in order, medium acid, medium acid, strongly acid, strongly acid, slight to medium and slightly acid. In all the soils the total CaO was determined by fusion with anhydrous sodium and potassium carbonates, followed by a double precipitation with ammonium oxalate. The determinations were made volumetrically. The results are reported in Table XIX.

Table XIX - Relation of acidity as shown by Truog test to the total CaO content.

Source of soil	Reaction	CaO present
Caledonia	Strong	.61
Spring Valley	Strong	.61
Southeastern composite	Medium	.65
University Farm "	Medium	.97
Preston	Slight to medium	.77
Luverne	Slight	.85

From the above data it would appear that the soils having the least amount of CaO are the most strongly acid, those having the highest amount are the most slightly acid, and, in general, the degree of acidity seems to be in proportion to the total CaO content. The only exception to this rule is the University Farm soil.

RELATION OF THE GROWTH AND COMPOSITION OF ALFALFA TO THE ADEQUACY OF THE LIME SUPPLY.

The data reported on this subject have been obtained from alfalfa samples gathered in the southeastern Minnesota cooperative liming experiments by Mr. Forbell during the season of 1916. The samples were taken from the first crop in that season. In the case of each field 50 plants were selected from the unlimed portion of the field and the same number from the limed portion, tied together to prevent loss of leaves, etc. in further handling, wrapped in paper in separate packages, sent by express to the laboratory, dried for 3 days in a water-oven and weighed. Then the leaves were carefully stripped from the stems, the latter weighed and the weight of the leaves determined by difference.

The total nitrogen was determined in the leaves and stems, each separately. Additional moisture determinations were made on the dry samples to allow for the moisture absorbed during the preparation (grinding, etc.) of these samples. The moisture thus absorbed was found to be about 3 per cent and corrections were made in the percentages of nitrogen. The data given below represent the average of closely concordant duplicate determinations.

For the determination of the ash and lime content composites were made from equal weights from the different fields. In the determination of the ash 2.5 gram samples were placed in platinum dishes, ignited over a low flame, so the contents of the dish became completely charred, the alkali salts washed and the residue dried and ignited in a muffle; the filtrate was evaporated at 100° C and the weight of the residue added to that of the ash. The averages of two or more closely concordant determinations are given below.

To determine the total CaO content the ash was treated with concentrated hydrochloric acid and twice evaporated to dryness, taken up with dilute hydrochloric acid and filtered. The filtrate was made up to 250 cc. and 100 cc. portions used for each determination, carried out by the usual procedure, (p. 57).

From Table XX it will be seen that there is a marked and consistent excess of dry matter in the plants from the limed areas compared with those from the unlimed. Attention should be called to the fact, shown by this table, that this increase is notequally distributed between the leaves and stems of these plants, but generally is greater in the stems. So that the data obtained from the average of 12 samples (Table XXIII) show that the total increase of dry matter due to liming is 70 per cent, the increase of that in the leaves is 56 per cent and that in the stems 81. From the above it appears that the addition of lime to a lime-deficient soil causes a proportionately greater growth of stem than of leaf in the case of alfalfa.

The ash and lime content were not determined in the individual samples. The results obtained on the composites from those samples are reported in Table XXIII.

The proportion of ash seems to be but slightly affected by the addition of lime, there being only 0.1 per cent more ash in the plants from the limed than in those from unlimed portions. This slight difference is due entirely to the higher ash content of the leaves, as the stems from the limed portions show even sligntly less ash than do those from the unlimed. This relation holds also as regards the effect of liming upon the lime content, the difference being only 0.1 per cent in favor of the limed areas, this being caused by a difference of 0.26 per cent in the leaves, while in the stems little difference is shown.

The nitrogen content for each sample will be found in Table XXI. Although the average nitrogen content from the limed portions is slightly (0.08 per cent) higher, in five instances this relation does not hold. Examining the component parts, the leaves and the stems, we find that the lack of regularity is due to the variations shown by the stems in every instance, except one, Field I, the leaves from the limed area show a decidedly higher nitrogen content. The averages are given in Table XXIII. The increase of nitrogen in the dry-matter due to liming is 0.27 per cent for the leaves, nothing for the stems and 0.08 for the whole aerial portion of the plant.

In the past few years several experiments dealing with the effect of lime upon the growth as well as upon the composition of certain plants have been reported. White (55) of the Pennsylvania Experiment Station has studied the effect of various amounts of lime upon the growth and composition of clover and sorrel. According to him the addition of increasing quantities of lime to an acid soil causes a gradual increase of the nitrogen and lime content in the dry matter of clover. The ash content is similarly affected, but is subject to considerable variation. The above results were obtained from pot experiments, using only a single soil and making the analyses of only the whole plant.

The largest amount of work on the subject has been carried out at the New Jersey Experiment Station in connection with field and pot tests on the availability of nitrogen under various treatments, Lipman (26-b) finding in pot experiments that the effect of lime added to variously treated soils is to increase the percentage of nit-

Table XX - Dry matter in 50 alfalfa plants from the limed and unlimed portions of the same field.

Field No.	Leaves		Stems		Tops	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	Grams	Grams	Grams	Grams	Grams	Grams
1	22	33	30	44	52	77
2	16	24	18	40	34	64
3	22	22	30	44	52	66
4	10	20	22	32	32	52
5	15	37	17	52	32	89
6	16	32	20	57	36	89
7	20	17	25	25	45	42
8	9	21	13	29	22	50
9	19	33	21	43	40	76
10	11	20	16	30	27	50
11	18	19	26	31	44	50
12	13	21	15	34	28	55
Average	16	25	21	38	37	63

Table XXI - Nitrogen content of alfalfa plants from the limed and unlimed portions of the same field.

Field No.	Leaves		Stems		Tops	
	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.	P.ct.
1	4.35	4.33	2.32	1.94	3.18	2.96
2	4.21	4.97	1.80	2.11	2.94	3.18
3	4.10	4.57	2.94	2.60	3.43	3.26
4	3.55	4.13	2.59	2.62	2.89	3.30
5	4.40	4.56	2.41	2.16	3.38	3.11
6	3.99	4.14	2.80	2.30	3.35	2.96
7	3.38	4.45	1.80	2.29	2.55	3.13
8	4.17	4.36	2.89	2.63	3.50	3.36
9	4.14	4.41	1.76	2.07	2.90	3.09
10	3.88	4.73	1.89	2.32	2.89	[illegible].20
11	4.38	4.60	2.35	2.52	3.18	3.27
12	3.81	4.53	2.34	2.49	3.02	3.27
Average	4.06	4.33	2.34	2.31	3.08	3.16

Table XXII - Weight of nitrogen in 50 alfalfa plants from the limed and unlimed portions of the same field.

Field No.	Leaves Unlimed Grams	Leaves Limed Grams	Stems Unlimed Grams	Stems Limed Grams	Tops Unlimed Grams	Tops Limed Grams
1	.957	1.429	.696	0.854	1.653	2.283
2	.674	1.193	.324	.844	.998	2.037
3	.902	1.005	.882	1.145	1.784	2.150
4	.355	.826	.570	.839	.925	1.665
5	.660	1.687	.410	1.122	1.070	2.809
6	.638	1.325	.560	1.311	1.198	2.636
7	.676	.757	.470	.558	1.146	1.315
8	.394	.916	.376	.763	.770	1.676
9	.787	1.455	.370	.890	1.157	2.345
10	.427	.946	.302	.696	.729	1.642
11	.788	.855	.611	.781	1.399	1.636
12	.495	.951	.351	.847	.846	1.798
Average	.646	1.080	.494	.888	1.140	2.000

Table XXIII - Dry matter, ash, lime and nitrogen content in alfalfa plants from the limed and unlimed portions of the same fields.

	In 100 plants		Proportion		Increase in weight due to liming	
	Unlimed	Limed	Unlimed	Limed		
Leaves	Grams	Grams	P.ct.	P.ct.	Grams	P.ct.
Dry matter	32.0	50.0	-	-	18.0	56
Ash	3.136	5.500	9.80	11.00	2.364	75
Lime (CaO)	1.120	1.880	3.50	3.76	.760	68
Nitrogen	1.292	2.160	4.06	4.33	.868	67
Stems						
Dry matter	42.0	76.0	-	-	34.0	81
Ash	3.094	5.244	7.20	6.90	2.220	73
Lime (CaO)	.525	.942	1.25	1.24	.417	79
Nitrogen	.989	1.776	2.34	2.31	.787	80
Total (Tops)						
Dry matter	74.0	126.0	-	-	52.0	70
Ash	6.034	10.972	8.40	8.50	4.938	82
Lime (CaO)	1.645	2.822	2.24	2.35	1.177	72
Nitrogen	2.281	4.000	3.08	3.16	1.719	75

rogen in the dry matter of crimson clover and soy beans. The average increase of the nitrogen percentage was a little over 0.25 for the clover and about 0.50 for the soy beans. Experiments with non-legumes consisted in adding lime in increasing quantities (0.12, 1.0, 2.0, 5.0 and 10.0 per cent) to soils planted to barley. Here again the results indicated an increase of the nitrogen content in the limed pots, with the exception of the 10 per cent treatment. These data, however, when subjected to detailed scrutiny do not show concordant results. For example, where the yield of dry matter was the largest (1.0 per cent lime treatment) the average increase in nitrogen content above the check was 0.087, while the variation in duplicates of the above treatment was found to be 0.118 per cent. The conclusions drawn by the New Jersey authors seem to be based entirely upon the averages of the series of determinations, and no explanation is offered for the lack of concordance among the individual determinations.

Experiments on the influence of lime upon the yields and nitrogen content of corn have recently been reported by Blair and McLean (6-a). The corn was grown on 20 differently fertilized plots in the regular 5-year rotation of the New Jersey Experiment Station. One-half of each plot (Section B) had been limed in 1908 and again in 1913 at the rate of 1 and 2 tons of ground limestone, respectively. The data published by the above authors is based upon the analyses of the grain, stalks and cobs of the 1913 corn crop from each of the limed and unlimed sections. The averages from all the limed and unlimed sections show an increase in the percentage of nitrogen amounting to 0.028 per cent in the case of the grain, 0.085 in the stalks and a decrease of 0.070 in the cobs. They conclude from the above results that the application of lime causes a slight increase in the nitrogen content of the grain and stalks of corn.

Similar analyses were reported on the 1908 corn crop by Lipman and Blair. Their results (26-a, p. 24) show that the average percentage of nitrogen in the dry matter is practically the same on the limed as on the unlimed plots.

The only previous experiment of a similar nature with alfalfa is reported by Arny and Thatcher (3-a and 3-b), who found on the fields of the University Farm that the effect of lime upon the protein content of alfalfa was negligible. It should, however, be pointed out that alfalfa on this farm is not benefited by liming, as pointed out elsewhere in this thesis. Their results, accordingly, do not bear upon the question of the effect on the nitrogen content when lime is added to a lime-deficient soil.

All of the experiments referred to have been limited to furnishing data on the composition of the total plants (stalk and leaves), while my data take into consideration the distribution of stalk and leaves in the dry matter of the plant and the effect upon the composition of the entire plant. My results with alfalfa confirm, in a general way, those of previous experiments with other leguminous crops. My data further emphasize the importance of the lack of concordance occurring between individual determinations in my own as well as in previous experiments, and they show that, so far as the nitrogen and lime content is concerned the composition of the leaves of the plant furnishes a much more reliable index of the effect of lime than the composition of the whole plant. This can be seen from the facts already mentioned that the average increase in the nitrogen in the leaves due to liming, was 0.27 per cent, while the corresponding amount for the entire plant was only 0.08. Further, in the case of the samples from the 12 individual fields there was no definite exception to the rule in the case of the leaves, while in the case of the entire plant the exceptions are about as frequent as the concordance. The similarity in the relations of the nitrogen and the lime content in the various parts of the alfalfa due to liming is almost striking. This becomes apparent from comparing the percentage increase of these two ingredients. The effect of the lime on relative proportion of leaves to stems is to encourage the growth of the stem rather than that of the leaves.

THE GROWTH OF ALFALFA ON MIXTURES OF ACID PEAT AND A MINERAL SOIL.

Of the two soils used in this experiment one was a very acid peat from Grand Rapids and the other the surface 6 inches of Thurston loam from University Farm, showing a slight acidity with the Truog test. These two soils were used both singly and as mixtures, viz. A, peat only; B, mineral soil only; C, a mixture of two parts of B to one of A; D, a mixture of equal weights of A and B, and E, a mixture of one of B to two of A. Two wooden boxes 12 inches square and 8 inches deep were filled with each preparation, making 10 boxes in all. On December 14, 1916, all were seeded to alfalfa and kept in the green-house until April 19, 1917. On January 30, 1917 the plants were thinned to about 20 in each box. For watering the plants distilled water was used. Striking differences in the growth of the plants were to be observed while they were still young and these persisted through the 17 weeks of the experiment, as may be seen from Table XXIV and photographs, Plates I, II, III, IV and V. 130 days after sowing the seed the roots were removed from the soil as carefully as possible, washing the soil away by a strong jet of water. The plants from each box were kept separately and one of each pair of boxes representative plants were photographed. Then all the plants from each box were separated into roots and tops and these parts dried at 100° C and weighed.

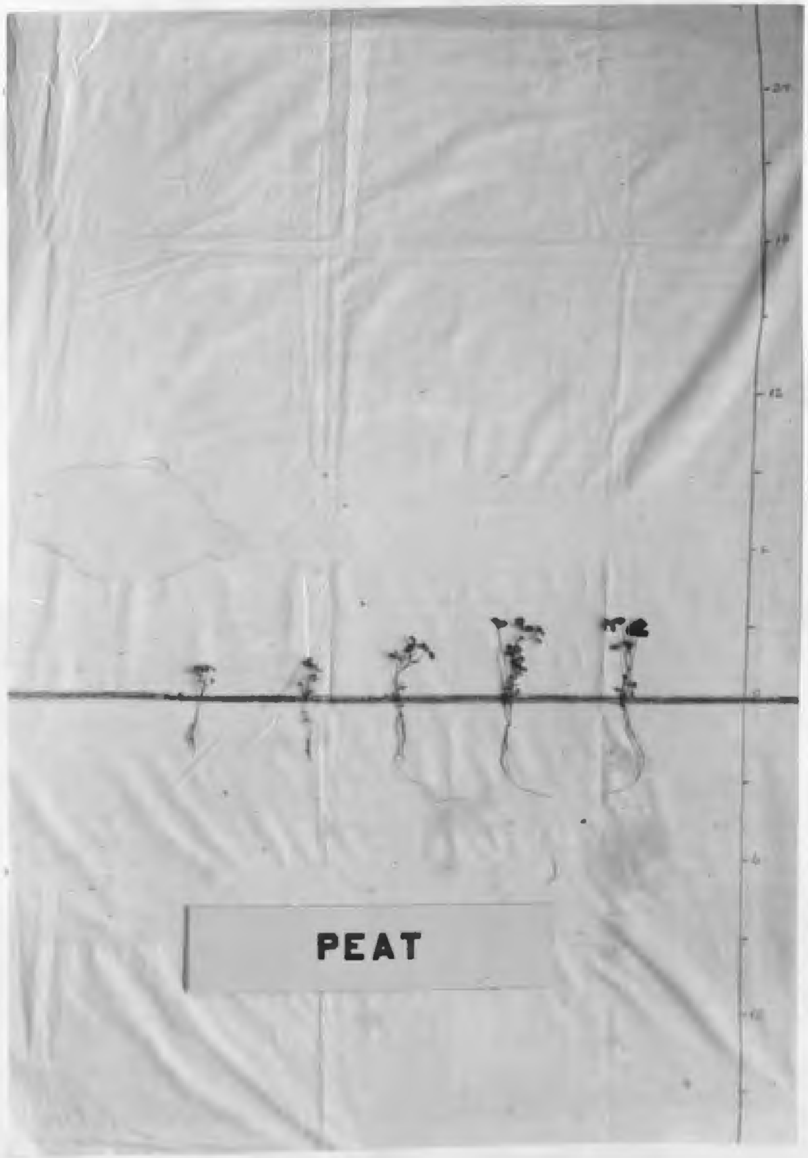
Table XXIV Yields of alfalfa grown on a mineral soil, acid peat and mixtures of these.

Soil	Box No.	No. of plants per box	Total weight: roots	Total weight: tops	Weight per plant: roots	Weight per plant: tops
			Grams	Grams	Grams	Grams
Peat	1	17	0.2	0.4	.012	.024
	2	17	0.3	0.7	.018	.041
	Av.	17	0.2	0.5	.015	.032
Soil	1	22	10.5	18.7	.52	.87
	2	22	14.3	18.3	.65	.85
	Av.	22	12.4	18.5	.58	.86
Peat 1 Soil 2	1	22	8.9	15.8	.40	.72
	2	24	16.4	20.5	.70	.86
	Av.	23	12.6	18.1	.55	.80
Peat 1 Soil 1	1	19	14.0	19.0	.74	1.00
	2	22	17.3	19.6	.80	.89
	Av.	20.5	15.6	19.3	.76	.94
Peat 2 Soil 1	1	13	12.7	23.7	.98	1.82
	2	22	16.9	25.0	.77	1.14
	Av.	17.5	14.8	24.3	.85	1.48

PLATE I.

Alfalfa, 130 days old, grown on a slightly acid mineral soil.

PLATE II.



Alfalfa, 130 days old, grown on a very strongly acid peat.

PLATE III.

Alfalfa, 130 days old, grown on a mixture of soils mentioned on Plates I and II, in the proportions of 2 of mineral soil and 1 of peat.

PLATE IV

Alfalfa, 130 days old, grown on a mixture of the soils mentioned on Plates I and II, in the proportions of 1 of mineral soil and 1 of peat.

PLATE V.

Alfalfa, 150 days old, grown on a mixture of soils mentioned in Plates I and II in the proportions of 1 mineral soil and 2 of peat.

From the data in the above table it will be seen that by far the lowest yield was obtained from the boxes with peat alone. Those with soil alone, and those with soil mixed with half as much, or an equal weight of peat, gave good yields, all being similar, and yield over 30 times as much as the peat alone. The boxes containing twice as much peat as mineral soil gave the highest yields of all, about 30 per cent more than those with only mineral soil. It is surprising that such a very strongly acid peat, added in such large amounts to a soil, itself slightly acid, should not in the slightest degree less the productivity of the soil for alfalfa, and especially that in a series of mixtures in various proportions the most luxuriant growth should occur where the peat is in the largest proportion. It should be remembered that the mineral soil alone gave an excellent growth of alfalfa.

Table XXV - A comparison of the average weight per plant from each soil mixture with the respective averages of the 5 plants shown in the photos.

Soil	Weight of plants photographed: Roots	Tops	Total	Ave. wt. of plants xx photo	Ave. wt. of plants	Relative wt. of plants inx on photo	Relative wt. of all plants
Peat	.1	.2	.3	.06	.047	.024	.033
Soil	6.0	6.7	12.7	2.54	1.43	100	1.00
Peat 1-Soil 2	4.7	6.0	10.7	2.14	1.34	84	.94
Peat 1 Soil 1	7.3	.09	18.2	2.64	1.70	.104	1.19
Peat 2 Soil 1	8.0	11.2	19.2	3.84	2.25	1.51	1.57

Table XXV shows how closely the plants photographed really represent the growth on the various soil mixtures. It will be seen that while the average weight of those photographed is in every instance higher than the average of all the plants grown in that soil, or soil mixture, the relative order of plant growth is, in every case, strictly concordant. That is, while the photographs do not accurately represent averages from each soil, they represent the range and the relative productivity.

The acidity of both soils and of each mixture was determined by the Truog test, at the time the plants were photographed. Plants in each soil as well as the relative weights have been calculated. The results are shown in Table XXVI.

Table XXVI - Comparison of reaction of soil with the growth of alfalfa.

Soils	Degree of Acidity	Average weight per plant			Relative weight		
		Roots	Tops	Total	Roots	Tops	Total
Soil 1	Very slight	.58	.86	1.45	1.00	1.00	1.00
Peat 1 Soil 1	Slight	.55	.80	1.34	.95	.93	.94
Peat 1 Soil 1	Medium	.76	.94	1.70	1.31	1.10	1.19
Peat 2 Soil 1	Strong	.85	1.40	2.25	1.47	1.63	1.57
Peat 1	Very strong	.015	.032	.047	.026	.037	.033

The mineral soil was the least acid, the peat is the most strongly acid, so, while in the mixture the degree of acidity was in direct proportion to the amount of peat in the mixture Table XXVI shows no relation between the acidity of the mixture and the growth of the alfalfa. In other words, the acidity, as determined by laboratory methods, does not correspond to any degree of toxicity in the soils studied. Additional evidence bearing upon this point is found in the fact that the most abundant development of bacteria nodules was observed on the roots of the plants from the mixture D, that with the largest proportion of peat, and having the most strongly acid reaction of the series, except the peat alone.

COMPARISON OF FIELD WITH GREENHOUSE RESULTS

The soils for this experiment were composites from the various lime-deficient fields in the southeastern portion of the state. The most strongly acid samples from each locality were mixed together to make up the separate composites. Three series of treatments were planted to alfalfa on February 10, 1916 - 1, no lime added; 2, 2 tons of ground limestone per acre; 3, 4 tons of ground limestone per acre. Distilled water was used in watering the plants. Five cuttings had been made up to April 14, 1917, and the experiment is being continued. The yields of the successive cuttings are given in Table XXVII. The reaction of the soils at the present time is shown in Plate VII.

The results of liming the fields from which the above composite samples were secured have been reported in Table XX, p. 61. It will be seen that in the case of the field experiments the increase due to liming was very marked (over 70 per cent), while the average of the five cuttings from the pots showed no effect at all. This seems to indicate that the data obtained with pot experiments alone are likely to be entirely misleading.

Table XXVII - Yields of 5 crops of alfalfa from limed and unlimed soils.

	GREENHOUSE YIELDS				
	1st	2nd	3rd	4th	Total
	Grams	Grams	Grams	Grams	Grams
Adams					
Unlimed	14.0	14.0	11.0	21.0	60.0
Limed, 2 tons	12.0	17.0	12.0	23.0	64.0
Caledonia					
Unlimed	12.0	18.0	12.0	20.0	62.0
Limed, 2 tons	16.0	16.0	9.0	21.0	62.0
Spring Grove					
Unlimed	13.0	16.0	7.0	10.0	46.0
Limed, 2 tons	15.0	13.0	8.0	16.0	52.0
Austin					
Unlimed	10.0	13.0	9.0	14.0	46.0
Limed, 2 tons	12.0	18.0	7.0	16.0	53.0
Rushford					
Unlimed	14.0	14.0	7.0	12.0	47.0
Limed, 2 tons	11.0	14.0	10.0	17.0	52.0
" 4 tons	14.0	15.0	8.0	14.0	51.0
Spring Valley					
Unlimed	12.0	18.0	6.0	13.0	49.0
Limed, 2 tons	11.0	14.0	7.0	15.0	47.0
" 4 tons	12.0	16.0	7.0	15.0	50.0

Plate X - Reaction of southeastern soils used in greenhouse experiments.

A

B

C

LEGEND

1 - Spring Valley
2 - Rushford
3 - Austin
4 - Spring Grove and Harmony
5 - Caledonia
6 - Adams

A - No lime
B - 2 tons of lime
C - 4 tons of lime

EFFECT UPON THE GROWTH OF ALFALFA OF LIMING THE SUBSOIL.

For this experiment University Farm surface soil and subsoil were used. The surface soil was slightly acid and the subsoil was from medium to strongly acid, as shown by the Truog test. In 4 cylinders 3 feet deep and 12 inches in diameter 2 feet 4 inches of the subsoil were first placed and this covered with 8 inches of the surface soil. The subsoils in the case of two of these cylinders had been mixed with 2.0 per cent of finely ground limestone, while that in the other two remained untreated. All were seeded to alfalfa on December 14, 1916. On February 15, 1917 the plants were thinned out to about 20 in each cylinder. Distilled water was used for watering the plants throughout the experiments. No appreciable differences could be observed in the growth of alfalfa at any time during the course of the experiment. On May 3 the alfalfa was harvested. The dry weights are recorded in Table XXVIII.

Table XXVIII - Yields of alfalfa from a limed and unlimed subsoil underlying the same acid surface soil.

Cylinder No.	Treatment	Dry Weight Grams
1	Unlimed	40.0
2	"	36.0
3	Limed, 2 %	38.0
4	"	36.0

From the above it appears that the addition of lime to the acid subsoil did not have any effect upon the yields of alfalfa. This experiment, however, does not justify any general conclusions as to the effect of liming a subsoil upon the growth of alfalfa, because of the peculiar behavior of this particular soil (University Farm), as mentioned in an early part of this thesis.

THE EFFECTS OF VARIOUS CROPPING SYSTEMS UPON THE SOIL REACTION.

In the historical review given in the first part of this thesis specific reference has been made to the so-called physiological acidity of soils, i.e. the acidity produced by living plants through the selective absorption of basic materials from the soils. Views have been advanced that the acidity thus produced varies according to the plants grown, but field studies supporting the above views are very few, and even these, pointed out above, do not permit of any definite conclusions. In order to obtain some definite data which would justify generalizations on this phase of the subject a study was made of the soils of the rotation plots in Field C on the Minnesota Experiment Station farm, and the reaction of the soils correlated with the various systems of cropping carried out on the above plots.

Field C, located on the northeast corner of the University Farm, has 4 series of 11 plots each. Each plot is 2 by 8 rods. The system of cropping which was started in 1894 and since used is shown in Table XXIX.

Samples were collected in the autumn of 1915, using a tube sampler devised at this station. This consists of a brass tube with a steel cutting edge, with the internal diameter of 1.5 inches. The cutting edge is 0.25 less in diameter, thus cutting a core small enough to pass upward into the tube without being compacted. The tube is 18 inches long and graduated into 3 inch sections. There are openings on one side near the mark for each section to permit of the intrudustion of a spatula by which the core may be cut into the desired sections. These openings, also, by providing a full view of the natural soil column, permit any peculiarities, such as sharp color changes, differences in structure, etc. to be readily detected, while the samples are being collected. Samples were taken to a depth of 9 inches, 20 borings being made for each composite sample, at places marked by stakes at points spaced uniformly in each direction with reference to each other and to the edges of the plots. Each core was divided into two sections, viz. 0"-6" and 7"-9" inch. The composites from the 2-9 cores were placed in numbered cotton sacks and the description at once recorded in the field book. After being air dried the samples were ground up, and placed in jars. On the check plots and certain others samples were taken separately from the north half and south half. The others were sampled only on the north half. It will be shown later that in so far as acidity is concerned differences between the two halves of a plot are in most cases negligent.

All the samples were tested in the laboratory by the four methods, viz. litmus, Truog, Daikuhara and Hopkins. The results of each test are shown both on a separate diagram, indicating the actual arrangement of the plots in the field and in a tabular form. From an examination of these results it appears that the soil on all the plots is distinctly acid, the difference in lime requirement between the most strongly acid and the least acid plot, as determined by the Hopkins method, being only 600 pounds of $CaCO_3$ per acre foot of 2 million pounds. Since the study of the effect of cropping systems upon the soil reaction is only a comparative study so any qualitative test which possesses the highest sensitiveness would be the best suited to the purpose. For this reason and for considerations that will be discussed under the heading of

"Methods" the Truog test was selected for this study.

The most direct and probably the most correct method of interpretation of the results presented by the Truog chart would be the comparison of the present reaction of the soil of each plot with that just previous to starting the rotations in 1894. Unfortunately samples taken at the time the field experiment was begun are not available for this purpose. For this reason comparison has to be confined to the samples taken in 1915. A mere glance at the diagrams will show that among the 12 check plots as great differences are to be found as between any others. Since during the last 22 years the check plots had received identically the same treatment this precludes much hope of finding any distinct effect upon the soil reaction of these plots, due to the difference in the cropping systems. We must infer that 20 years ago the soil of the check plots must have varied much in reaction, and also that in the whole field the acidity varied much from place to place. For this reason it appears better to compare the acidity of each plot not with the average acidity of the check plots, but with the average of the two nearest check plots to record the resulting effect on each plot as an increase or decrease of acidity as compared with this average. To permit of a correlation of these results with the cropping systems Table XXI has been made.

In addition to the above samples were secured from 2 plots which had received heavy applications of manure. The results were as follows: - 1 - with no manure; medium acidity. 2 - with a yearly application of 2 tons of manure; medium acidity. 3 - with a yearly application of 6 tons of manure; slight to medium acidity. 4 - with a yearly application of 12 tons of manure; slight acidity.

I shall consider first the effect of various modifications of the standard 5 year rotation. The substitution of potatoes or sunflowers in the place of corn in the 5 year rotation causes a decrease of 0.5 degrees of acidity; of mangles or rape a decrease of 1 degree; of bromus or timothy in place of timothy and clover, a decrease of 1 degree; of millet in place of corn, a decrease of 1.5 degree. When tankage was used in place of barnyard manure, a green manure in place of corn and manure, or flax in place of wheat no change in the acidity was caused.

Of the 6 plots in a four year rotation 3 show no change, the other 3 an increase in acidity of 0.5 of a degree. Two of the latter three received an application of manure every four years.

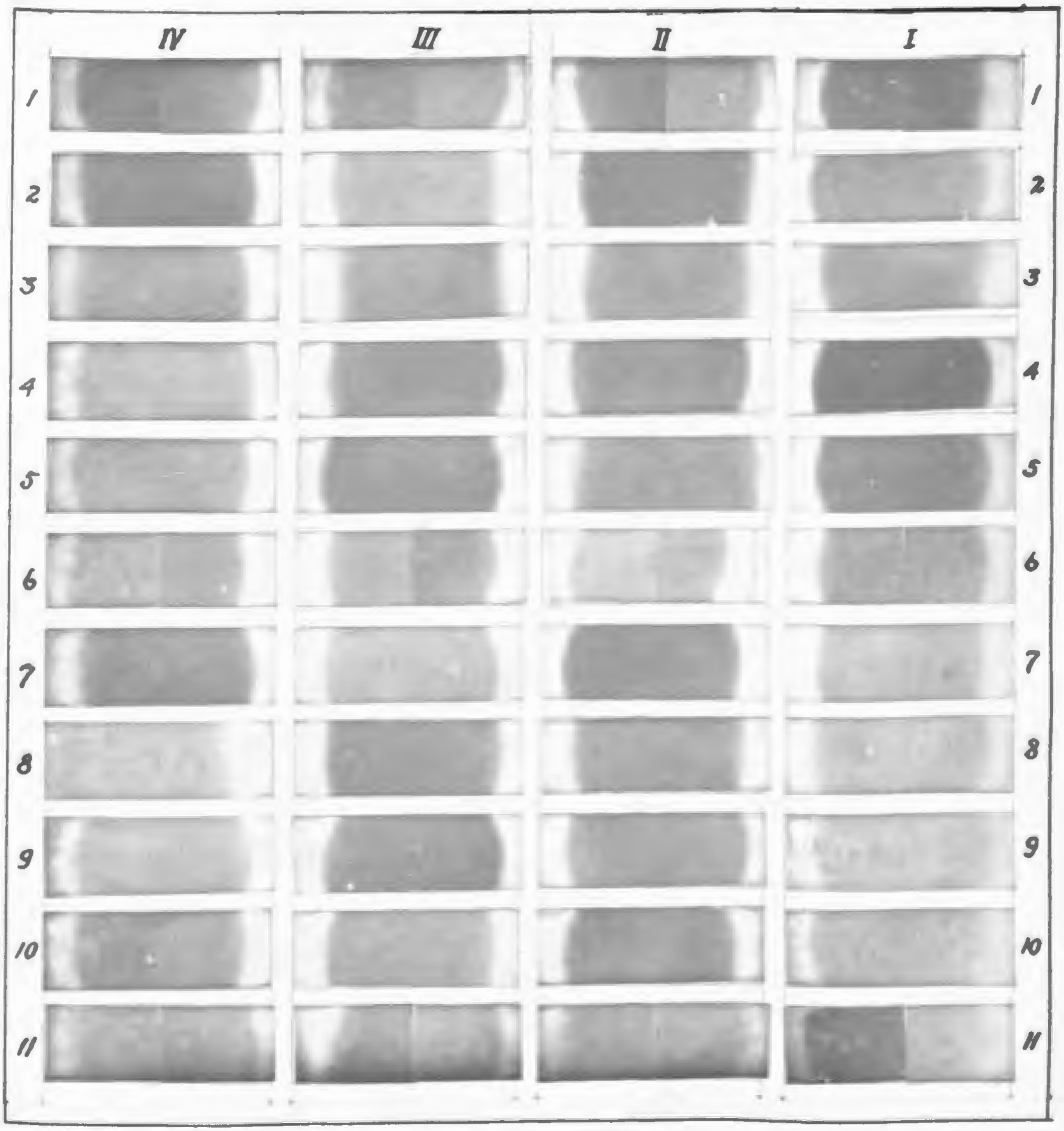
In the case of single crops grown continuously, corn, potatoes, mangles or peas, show an increase of 1 degree of acidity; wheat and meadow, an increase of 1/2 degree, but grass pasture and rape no change.

In summarizing the results obtained on the 44 plots of Field C we may state that there is a tendency for the increase of acidity where a single crop, other than pasture, is grown for a long period, that clover causes a greater increase in acidity than grasses, and that green manures and stable manure cause no increase.

Table XXX Present reaction and gain or loss of acidity due to different cropping systems, as compared with the standard five-year rotation.

Cropping System	Series	Plot	Present Reaction: Lime ($CaCO_3$) requirement by Hopkins Pounds	Litmus	Nitrite	Truog	Gain or loss of acidity
Standard Rotation	I	1	781	Acid	4	3+	
	I	6	250	"	4	3+	
(1st year - corn;	I	11	531	"	4	2	
2nd year- wheat;	II	1	344	"	4	3	
3rd and 4th years	II	6	313	"	3	2	
clover and tim-	II	11	469	"	4	2	
othy; 5th year -	III	1	406	"	3	3	
oats + 8 tons of	III	6	250	"	4	2+	
manure with each	III	11	281	"	3	2+	
corn crop)	IV	1	750	"	4	3	
	IV	6	250	"	3	2+	
	IV	11	250	"	3	2	
Modified 5-year rotation:							
Millet (in	I	5	406	"	4	2	-1.5
Mangles (place	I	7	438	"	3	2	-1.0
Rape (of	I	8	563	"	3	2	-1.0
Potatoes (corn)	I	9	469	"	3	2	- .5
Sunflowers "	I	10	-	"	3	2	- .5
Green manure "	IV	2	281	"	4	3	0
Flax in place of wheat	IV	3	281	"	4	2+	0
Four-year rotation:							
Wheat, clover, oats corn	I	4	656	"	4	4	.5
Corn, peas, barley clover	II	2	844	"	4	3	0
Barley, oats, timothy	II	3	594	"	4	2+	0
Millet, barley, corn oats	II	5	438	"	4	3	.5
Corn, rye, barley Pasture	IV	5	281	"	4	2+	.0
Single crop							
Corn	II	7	281	"	4	3	1
Potatoes	II	8	750	"	4	3	1
Mangles	II	9	594	"	3	3	1
Peas	II	10	281	"	3	3	1
Wheat	III	2	250	"	3	2+	.5
Pasture	III	7	344	"	3	2+	0
Meadow	III	8	500	"	4	3	.5
Rape pasture	III	10	438	"	3	2+	0

Plate VI - Acidity of rotation plots of Field C of the University Farm at St. Paul.



FIELD C. 0-6 INCHES TRUOG TEST.

Plate VII - Acidity, by the litmus test, of rotation plots on Field G, University Farm, St. Paul.

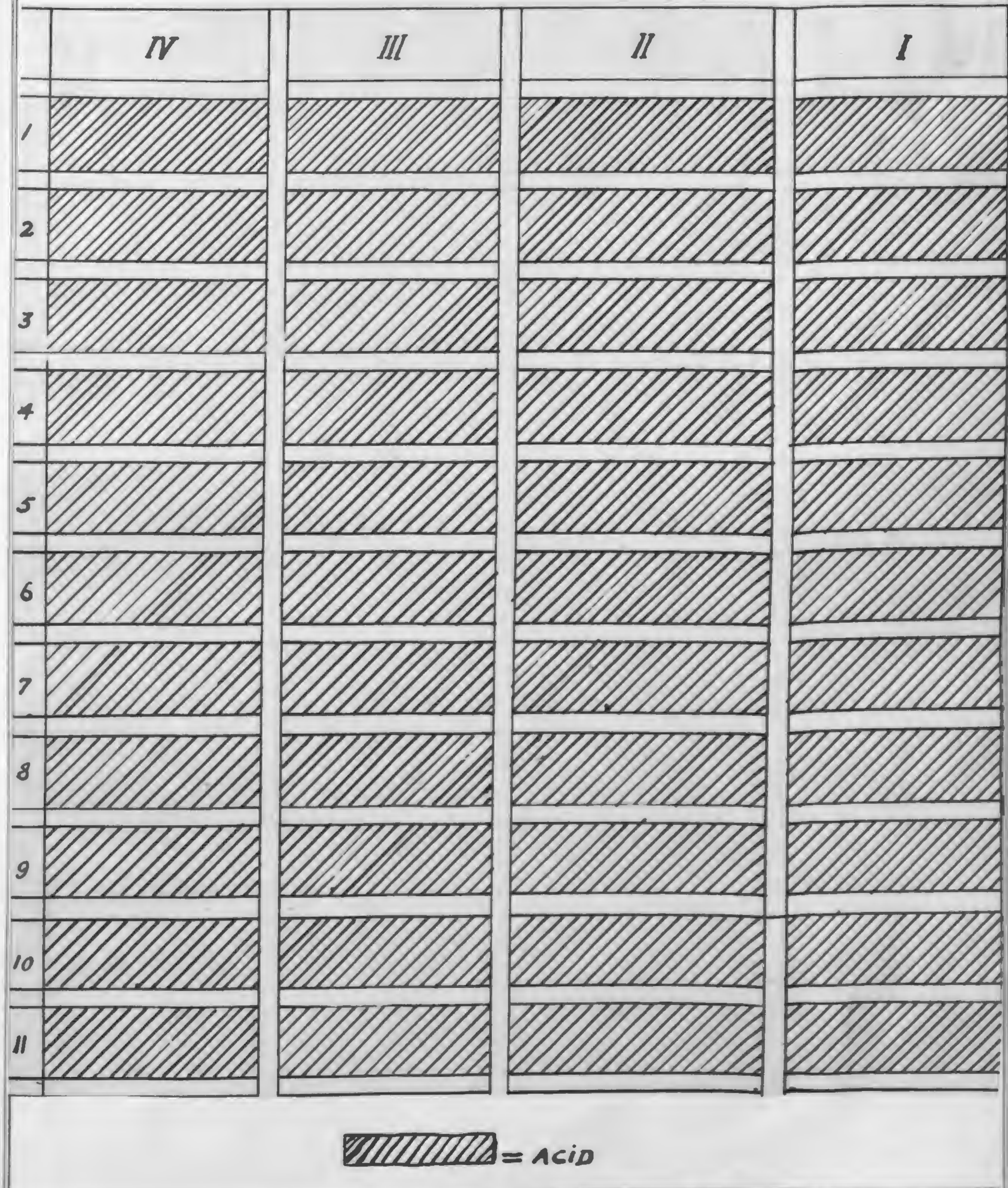


Plate VIII - Acidity by the Nitrite test of rotation plots on Field G of the University Farm.

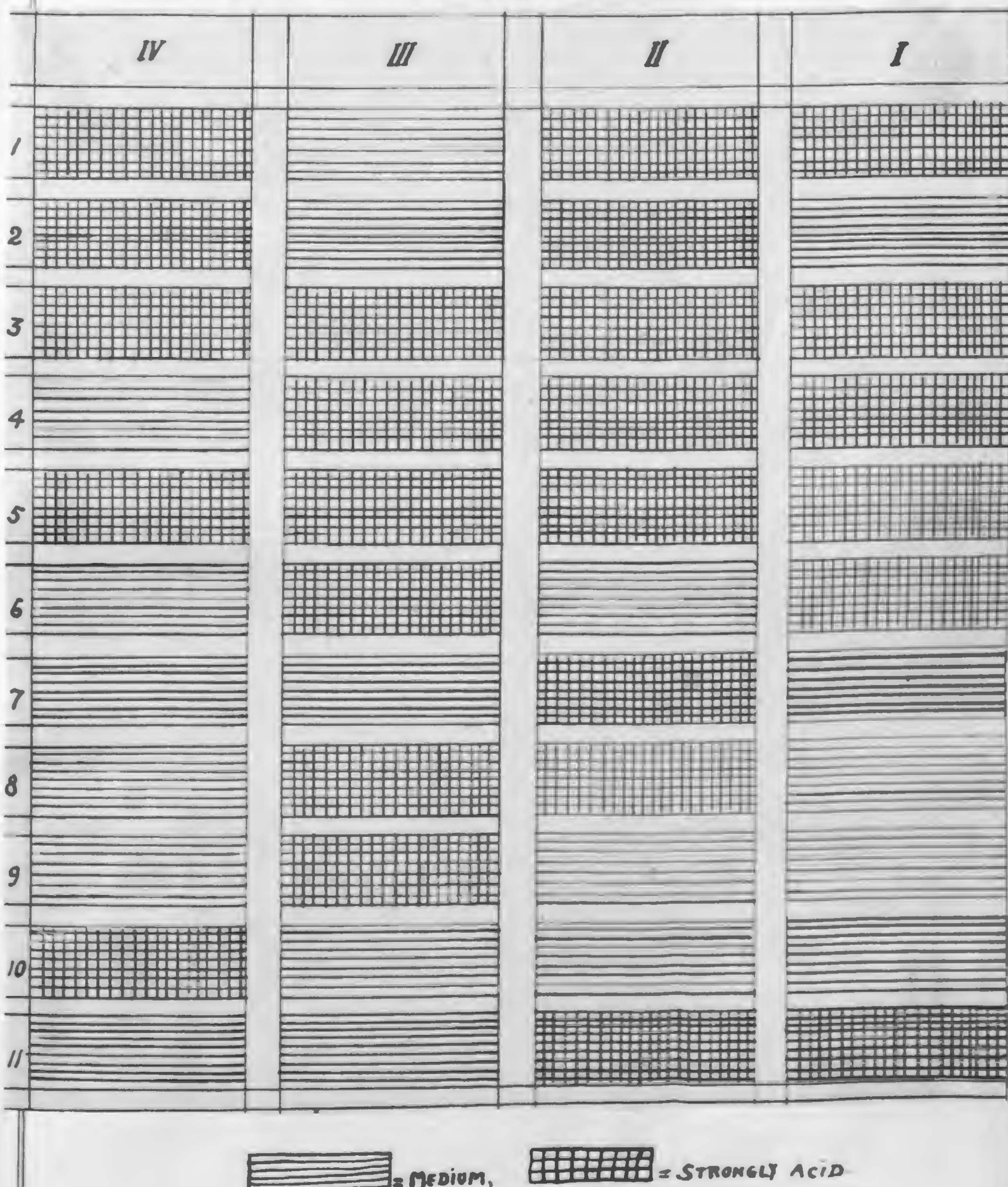
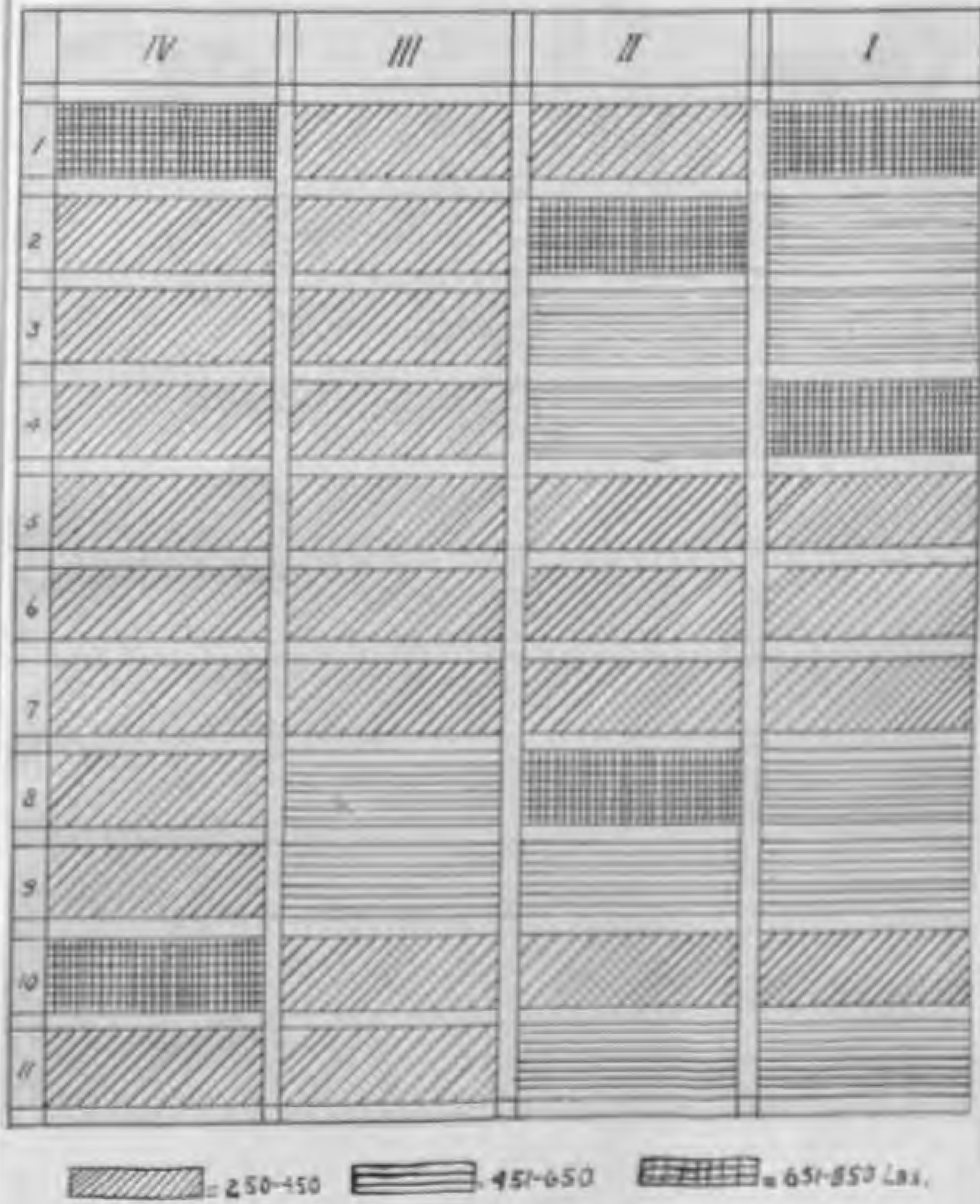


Plate IX - Lime requirement by the Hopkins method of each plot, Field G, University Farm.



RELATIVE ACIDITY OF DIFFERENT SOIL TYPES AND SOIL SERIES.

Mr. I. Husby of Cannon Falls, during the summer and autumn of 1916 collected 273 samples from northeastern portion of Goodhue County, all being composites from the surface 6 inches and each representing only a single field on one type. The coincidence of three facts accounts for the work in Goodhue County. This is the only county in the low-lime part of the state of which a soil survey has been made, Mr. Husby was much interested in the relative acidity of the different types, and volunteered to collect the samples without remuneration, and the Cannon Falls school Board was willing to provide the necessary transportation.

The exact location of the field from which each sample was secured is indicated by a number on the soil survey map, each number corresponding to a numbered tag which was attached to the sack containing the sample.

Tests by the Truog method were made of all the samples and the test papers preserved for comparison. The soils showed a considerable range in acidity. Since the exact location of the samples is known and the soil type indicated on the survey map, the data presented an opportunity for the study of the relation of soil acidity to soil type as represented in the county. For this purpose the test papers representing a single type were grouped together and each compared with the Truog "Standard Color Chart" and all classified according to their degree of acidity. The different degrees on the Truog chart I have, for convenience, assigned the successive numbers - 1, 2, 3, 4, 5 and 0, the last being assigned to tests which gave a neutral or alkaline reaction.

The data are summarized in Table XXXI in which which are reported the soil represented, the number of samples from each type, and the number of samples corresponding to the various degrees of acidity. The average degree of acidity for any one type has been computed by multiplying the number of samples by their rank in acidity, adding these products and dividing the sum by the total number of samples tested. So Table XXXI shows the range as well as the average degree of acidity of all the samples from each type. Table XXXII shows the influences of the texture upon the acidity.

From Table XXXI it may be seen that the different types within a given series are fairly concordant, the greatest difference within a single series being one degree of acidity and such difference occurs only between types differing widely in texture. The difference between successive grades of texture is, as a rule, from 0.2 to 0.4. As the different series are not represented by a sufficient number of types the relation of acidity to texture within a single series is not satisfactorily demonstrated. In the majority of cases any difference in acidity which might be attributed to difference in texture is very slight. When the soils are arranged in order of their increasing acidity, as in Table XXXI the most persistent relation of acidity to type appears. In this Table 14 different types of soils, representing 3 classes, are arranged in the order mentioned. It is of interest to note that the respective positions of a soil series within any one class is very similar to its position in both the other two classes. Thus, with the loams the Wabash loam is the least acid, Waukesha the most and Carrington occupies an intermediate position. The same respective positions are maintained by these series in both the fine sandy loam and the silt loam classes. The only exception to the general order of arrangement is the position of the Carrington silt loam which would properly precede the Waukesha silt loam, but it will be seen that the departure is very small. Thus, leaving out the slight difference due to texture variation, the soil series becomes the basis of comparison. According to results obtained from these Goodhue soils the order of increasing acidity is as follows:1-Wabash Series, 2- Marshall Series, 3 - Knox Series, 4 - Miami Series, 5 - Carrington Series, 6 - Waukesha Series. Incidently this arrangement also shows the relation of the degree of acidity to the origin of the soil, the acidity being in order of increasing acidity - 1 - Alluvial, 2 - loessial, 3 - glacial, 4 - fluvioglacial.

Table XXXI Acidity of 250 Goodhue County soils, as shown by the Truog test.

Soil Type	Samples tested	Degree of Acidity 0 P.ct.	1 P.ct.	2 P.ct.	3 P.ct.	4 P.ct.	5 P.ct.	Average of all
Miami loamy sand	12	33	50	17	0	0	0	0.8
" fine sandy loam	13	8	23	46	23	0	0	1.8
" " silt loam	11	9	55	27	0	9	0	1.4
Marshall silt loam	23	0	22	35	43	0	0	2.4
Knox silt loam	66	19	41	30	8	3	2	1.4
" fine sandy loam	9	33	33	11	23	0	0	1.2
Carrington loam	15	7	20	20	46	0	7	2.3
" silt loam	16	13	19	25	31	13	0	2.1
" fine sandy loam	14	0	36	14	21	21	8	2.5
Wabash loam	3	0	33	66	0	0	0	1.7
" silt loam	25	24	40	16	16	4	0	1.3
" fine sandy loam	3	66	0	33	0	0	0	0.7
" gravelly loam	2		50		50			2.0
Waukesha loam	8	0	50	0	50	0	0	2.0
" fine sandy loam	12	8	25	16	42	8	0	2.8
" silty clay loam	9	0	22	11	34	34	0	2.8
Sogn clay loam	5	40	20	40	0	0	0	1.0
Red Wing clay loam	4	0	25	50	25	0	0	3.0
	250							

Table XXXII-Relation of acidity of different types to the texture.

Class	Series	Description of Series: Derivation	Topography	Natural drainage	Organic matter content	Number of soils tested	Average acidity
Fine sandy loam	Wabash	Alluvial	Level	Poor	High	3	0.7
Fine sandy loam	Knox	Loessial	Undulating	Good	Liberal	9	1.2
Fine sandy loam	Miami	Glacial	"	"	Medium	13	1.8
Fine sandy loam	Carrington	"	"	"	High	14	2.5
Fine sandy loam	Waukesha	Fluvioglacial	"	Excessive	Low	12	2.5
Loam	Wabash	Alluvial	Level	Poor	High	3	1.7
"	Carrington	Glacial	Undulating	Good	"	15	2.3
"	Waukesha	Fluvioglacial	"	Excessive	Low	8	2.5
Silt loam	Wabash	Alluvial	Level	Poor	High	25	1.3
" "	Marshall	Loessial	Undulating	Good	Medium+	23	1.4
" "	Carrington	Glacial	"	Good	High	16	2.1
" "	Knox	Loessial	"	"	Liberal	66	2.3
" "	Miami	Glacial	"	"	Medium	11	2.4
" "	Waukesha	Fluvioglacial	"	Excessive	Low	9	2.8

SUMMARY AND CONCLUSIONS

Using 6 different mineral soils (5 surface and 1 subsoil) part of which had been found by field tests with alfalfa to respond markedly to lime and part of which showed no response, the lime requirement was determined qualitatively by three methods, viz. the litmus paper, the Daikuhara and the Truog, and quantitatively by two others, viz. the Hopkins and the Veitch. Four were subjected also to the Hutchinson and MacLennan quantitative method. Compared with the Veitch method the Hopkins indicated a lower lime requirement in the case of all the surface soils and a higher one with the subsoil. The Hutchinson and MacLennan gave results in general parallel with, but slightly higher than, the Veitch. The litmus gave results in general concordant with the Veitch, but failed to show satisfactory quantitative differences. Both the Daikuhara and the Truog methods gave results closely concordant with the Veitch, the first, however, being subject to great variation on account of the variable moisture condition of the soil. The Truog test was found much the superior of the above mentioned qualitative methods on account of its ease of manipulation, its perfectly concordance results and the permanent record of the tests which it affords. Of quantitative methods both the Veitch and the Hutchinson-MacLennan are superior to the Hopkins. The Hutchinson-MacLennan method is preferable to the Veitch because it gives equally good results while doing away with the time-consuming and tedious procedure of the latter. Everyone of the methods used failed to distinguish between the University Farm soil, which does not respond to liming and the other acid soils on which alfalfa had proved a failure except where limed.

117 samples from southeastern Minnesota, of which the carbon dioxide had been previously determined, were tested for acidity by the Truog method and the degree of acidity correlated with the carbonate content. The results show that the lack of carbonates does not preclude a neutral or alkaline reaction of the soil and that soils showing an acid reaction to the Truog test may still have a slight carbonate content.

The acidity of duplicate samples from a large number of fields was determined to establish their degree of concordance. The results show that in the regions where the acidity is the greatest the difference in the reaction of the duplicates is quite frequent and of considerable extent.

Six composite samples, representing various localities, were analyzed for total CaO content and correlated with the degree of acidity indicated by the Truog method. The degree of acidity varies in inverse proportion as the total CaO content of the soils, the only exception to this being formed by the University Farm soil which shows an acid reaction and also a high lime content.

Alfalfa grown on limed and unlimed areas of lime-deficient soil was analyzed for dry matter, ash, nitrogen and CaO, treating the leaves and stems separately. The average increase in dry matter, due to liming, amounted to 70 per cent, the effect of the lime being to stimulate a greater proportion of stems to leaves. The application of lime to the soil had only a slight effect upon the average ash, nitrogen and lime content of the whole alfalfa plant. However, when the leaves only were taken into consideration the effect of the lime upon the nitrogen and CaO content was quite apparent and consistent from field to field, but this effect is not sufficient to permit of a distinct line of demarcation being drawn between the composition of plants from all limed areas and those from all unlimed grown on lime-deficient soils, and that of those from soils with an adequate supply, in other words that the lime content of alfalfa plants cannot serve as a general index of the adequacy of the lime supply.

Alfalfa was grown 130 days on a slightly acid mineral soil, on a strongly acid peat and on mixtures of the two in various proportions. The growth and yield of the plants showed that the acid peat, when mixed with the mineral soil in equal proportion or less, did not in any way lessen the productive capacity of that soil for alfalfa, and that when mixed in larger proportions it increased the growth, not only above that on the acid peat, but also above that on the highly productive mineral soil. Further, in the mixtures in which the peat was in the largest proportion nodules on the roots of the alfalfa developed, in spite of the fact that the reaction of this mixture was most strongly acid, almost as strong as that of the peat alone.

Composites from lime deficient soils were used in greenhouse tests with alfalfa, both without liming and with applications of ground limestone at the rate of 2 and 4 tons per acre. In the 5 crops harvested no distinct benefit was shown by the liming, although the field trials showed a very marked benefit.

Alfalfa was grown in cylinders on a slightly acid surface soil with a decidedly acid subsoil both without an addition of lime and with 2 per cent of ground limestone mixed with the subsoil. The yields showed no effect from the liming.

In the case of 44 plots in one field on the University Farm, which, for the past 20 years, have been under diverse cropping systems, including also varying applications of manure a detailed study of the soil reaction was made. It was found that the reaction of the soil was very little affected by the kind of rotation practiced, except that when a single crop other than pasture is grown for a long time there appears a tendency for the acidity to increase, while frequent applications of manure counteracted this tendency.

250 samples from various soil types in Goodhue County were tested by the Truog method. The degree of acidity was more determined by the series than by the class divisions.

In the conclusions it should be emphasized that the acidity, as indicated by any one test so far proposed, does not in all cases truly indicate the field lime requirement.

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