COMPARATIVE EFFECT OF VARIOUS NITROGENOUS FERTILIZERS ON SOIL REACTION AND SOIL AGGREGATION OF DIFFERENT SIMCOE SOILS

COMPARATIVE EFFECT OF VARIOUS NITROGENOUS FERTILIZERS ON SOIL REACTION AND SOIL AGGREGATION OF DIFFERENT SIMCOE SOILS

by

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SCOPE AND CONTENT:

During 1967-68 experiments to determine the comparative effect of various nitrogenous fertilizers on soil reaction and soil aggregation of the Fox sandy loam, the Lincoln loam and the Lincoln clay loam were carried out in the pedology Laboratory of the Department of Geography, McMaster University. The soil samples were taken from the Horticultural Experiment Station, Simcoe, Ontario. A review of literature is presented in Chapter II. Chapter III discusses experimental techniques, results and a discussion of problems encountered. Chapter IV summarizes the results of the survey and analyses.

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CHAPTER I

INTRODUCTION

Good soil structure is said to be that condition of the soil which will provide the crop with optimum physical growing conditions especially rooting and support during the whole growing season. The physical properties of soil influence plant growth through their effects on soil moisture, soil air, soil temperature and mechanical impedance of root and of shoot emergence. If the physical condition of a soil is of such a nature that plant roots or water do not readily penetrate it, or that germinating seeds cannot break through a soil crust, the final crop yields will be reduced, even though the soil may be adequately supplied with plant nutrients.

It is also widely recognized that different soils under the same environmental conditions vary in erodibility because of physical, chemical and biological characteristics. The kind of macroflora and microflora, the kind of fertilizers used, and cultural practices produce changes in soil properties which influence soil erosion. In addition to this, continuous cropping on a soil seems to lower the water stability of the soil aggregates and this reduces the soil's productivity.

Optimum availability of plant nutrients to the crop plants is experienced within the range of pH 6.0 - 7.3. When nitrogenous fertilizers are applied to the soil a change in pH takes place (Chapter II) so the ability of the soil to supply nutrients and moisture to the physiological needs of the plants is affected. Soil pH seems to have considerable influence not only upon (1) the solubility but also upon (2) the facility with which nutrients, even when readily soluble, are absorbed and used by the plants. Iron and manganese are excellent examples of the first relationship, as they tend to become less and less soluble as the pH rises towards 8. Almost all nutrients appear in the second category, their absorption and utilization, after they become soluble, being in some degree conditioned by the H-ion concentration of the soil solution. At a pH above 6, ammonium salts are thought to be utilized more readily. But in moderately to strongly acid soils, nitrates apparently are absorbed with greater ease.

Work on the effect of fertilizers on soil properties is in progress at the Simcoe Horticultural Experiment Station, but no relevant data is available regarding the comparative effect of nitrogenous fertilizers on soil reaction and soil aggregation of different soils. The Fox sandy loam, Lincoln loam and Lincoln clay loam which comprise the major portion of the farm, were taken for this study. Consequently, this study aims firstly to see whether various nitrogenous fertilizers might differ in their influence on soil reaction with some possibility of one being more effective than the other in reducing or increasing the pH of different soils and secondly to see their comparative effect on soil aggregation of different Simcoe soils.

CHAPTER II

REVIEW OF LITERATURE

HISTORICAL:- Theories regarding effect of nitrogenous fertilizers on soil reaction:-

The effect of nitrogenous fertilizers on soil reaction has been variously explained. Mayer, as is explained in detail by Kappen (1927) was probably the first to advance a theory regarding their action. He classified fertilizers as being physiologically acid, physiologically alkaline and physiologically neutral, depending on whether the plant absorbed the basic part, the acid part, or both parts of the salt.

Field work with $NaNO_3$ and $(NH_4)_2SO_4$ tended to substantiate this view point of Mayer, because these salts were found to decrease and increase the acidity of the soil, respectively. Hall (1920) explained the effect of $(NH_4)_2SO_4$ as follows, "The acidity of the soil where the NH_4^+ salts have been used is due to the attack of various molds and other micro-fungi; they seize upon the nitrogen for their own nutrition and set free the acids with which the ammonia was combined. Frear (1915) states as follows in regard to $(NH_4)_2So_4$, " Its continuous use inevitably tends to produce pronounced acidity in the soil."

As a result of the work at Rothamstead Experimental

Station, Harpenden, England which showed that the addition of $(NH_4)_2SO_4$ to a soil resulted in an almost immediate formation of sulphates combined with calcium and magnesium in the drainage water. Wheeler (1920) asserted that double decomposition occurs in this reaction, that ammonia is absorbed by the soil, that the sulphate unites with the calcium and magnesium to be lost from the soil as such, thereby causing a loss of bases, and a further loss of bases occurs as a result of nitrification of the ammonia, by which process the nitric acid formed unites with bases in the soil to be used up by the plants, or else lost through leaching as calcium or magnesium nitrates.

Ames and Schollenberger (1916) first emphasized that it is because of the nitrification process alone that $(NH_4)_2So_4$ causes soil to become acid. This view has been expanded more fully by Page (1927) who explained it according to the modern ideas of base exchange. He emphasized the fact that nitrification is the cause of the acidity developed by $(NH_4)_2So_4$ and, furthermore, that it makes no difference in the acidity formed whether or not the calcium sulphate resulting from the base exchange reaction between the $(NH_4)_2So_4$ and the calcium complex leached out of or remained in the soil. This view, that nitrification rather than selective absorption of the fertilizer salt by the plant is the cause for the acidity developed by $(NH_4)_2So_4$ is further substantiated by experiments (1927) showing that approximately the same amount of acidity is developed whether or not plants are growing on the soil fertilized with $(NH_4)_2So_4$. Finally, Page (1927) believes that the term physiological acidity, therefore, is not strictly correct, since the action is not caused by the plant but is strictly a chemical or biological process.

MECHANISM:

The effect of $(NH_4)_2So_4$ on soil reaction can be explained by assuming that ammonium salt added undergoes a base exchange reaction with the absorbing complex. The absorbing complex of the soil can be represented by the formula CaX, in which calcium represents the various exchangeable bases with which the insoluble anions X are combined in an exchangeable form. Let it now be assumed for ease of dicussion that X can only be combined with one calcium. When $(NH_4)_2So_4$ is added to a soil the following reactions take place.

1. $(NH_4)_2So_4 + CaX \rightarrow CaSo_4 + (NH_4)_2X$

2. $2(NH_4)_2X + 4O_2 \text{ Nitrification} \rightarrow 2HNO_3 + H_2X + 2H_2O$

3. $2HNO_3 + CaX \rightarrow Ca(NO_3)_2 + H_2X$

As a result of the reaction represented in Equation 1, it is evident that no acidity is developed. Moreover, it makes little difference whether or not $CaSO_4$ is leached out of the soil, for the calcium it contains has been replaced in the exchange complex by another base, ammonium. Until nitrification, represented in equation 2 goes on, no acidity is developed. The nitric acid in equation 2 may further react with another molecule of CaX forming $Ca(NO_3)_2$ in which form the nitrate may be taken up by the plant, and another molecule of H_2X formed. Thus from one molecule of $(NH_4)_2SO_4$ two molecules of a diabasic soil acid are eventually formed. These reactions are believed to represent quite accurately what takes place when $(NH_4)_2SO_4$ is added to a soil, for it is well known that absorption by the soil of the ammonia from $(NH_4)_2SO_4$ is very rapid .

With $Co(NH_2)_2$ the reaction can be represented as follows.

$$1.\ Co(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2Co_3$$

$$2.\ (NH_4)Co_3 + CaX \rightarrow CaCo_3 + (NH_4)_2X$$

$Co(NH_2)_2$ after being converted into $(NH_4)_2Co_3$ undergoes a base exchange reaction with the soil as does $(NH_4)_2SO_4$.

And with $Ca(No_3)_2$, $NaNo_3$ and KNO_3 the following reactions take place.

$$1.\ Ca(NO_3)_2 + KX \rightarrow KNO_3 + CaX$$

$$2.\ NaNO_3 + CaX \rightarrow Ca(NO_3)_2 + NaX$$

$$3.\ KNO_3 + CaX \rightarrow Ca(NO_3)_2 + KX$$

SOIL REACTION:

Plummer (1918) probably was the first who studied the effect of various fertilizers on hydrogen ion concentration and found that $(NH_4)_2SO_4$ materially increased the hydrogen ion concentration of all plots which had received application of this material. The acidity thus developed often extended into sub-soil. Pierrie (1928) explored the effect of various nitrogenous fertilizers on the reaction of Norfolk sandy loam and Cecil clay loam concluding that $(NH_4)_2SO4$ caused the greatest increase in H-ion concentration, followed by $Co(NH2)_2$.

The results of field experiment conducted by White (1931) indicated that $(NH_4)_2SO_4$ increased soil acidity.

Brown (1934 and Volk and Tidmore (1946) confirmed the results of White (1931) working with $(NH_4)_2SO_4$.

Hubbell and Stubblefield (1948) concluded that application of $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ at the rate of 15 tons/acre and 19 tons/acre caused an increase in total soluble salts but pH values were unaffected on Gila clay and Gila loam soal. No reason for this is mentioned.

Trogdon and Volk (1949) suggested that banding $(NH_4)_2So_4$ on the furrow bottom of Canfield silt loam resulted in an increase in the soil acidity in that portion immediately around the fertilizer band. Broadcasting the nitrogen sources caused soil reaction changes similar to those caused by banding the nitrogen but to a lesser extent. Dunton, *et al* (1954) working on $(NH_4)_2SO_4$ at the rate of 2000 lbs/acre on sandy loam soil find results similar to Trogdon and Volk (1949).

Broadbent,*et al* (1958) added $Co(NH_2)_2$ at 200, 400 and 800 ppm to clay, loam and sandy loam soils concluding that $Co(NH_2)_2$ in the beginning increases pH but later on it produces acidity. Harding, *et al* (1958) discovered that application of $(NH_4)_2SO_4$ resulted in marked acidification through the surface 2 feet of soil. They further emphasized that soil organisms are not efficient in converting NH_4^+ to NO_3' in soil having a reaction in the neighbourhood of pH 4 and finally this has resulted in an accumulation of NH_4^+.

Leo, *et al* (1959) applied $(NH_4)_2SO_4$ and $NaNO_3$ to silt loam soil and concluded that continued use of $(NH_4)SO_4$ increased soil acidity while use of $NaNO_3$ maintained a steady pH. Samuels and Gonzalez (1962) suggested that increasing rates of $(NH_4)_2SO_4$ lowered soil pH values for horizons between 0-6 and 12-18 inches in a clay loam soil.

Brioux (1924) treated a slightly acid soil (pH 6.45) with a solution of $Co(NH_2)_2$ to concentration of 0.1% and a moisture content 18%, and kept at room temperature. The pH increased progressively to 7.1 after 7 hours and to 8.0 for 48 hours where it remained for 15 days. In another experiment samples of the same soil were treated with amounts of $Co(NH_2)_2$ and $(NH_4)_2SO_4$ equivalent to 0.1 g.N per 500 g. of soil. With

$Co(NH_2)_2$ the pH increased to 7.6 after 48 hours and gradually dropped to 5.35 after 35 days, where it remained for 14 days more; with $(NH_4)_2SO_4$ the pH increased slightly 6.9 after 48 hours and dropped to 5.1 after 76 days. Finally, he concluded that $Co(NH_2)_2$ acts first as an alkali, owing to its rapid convertion to $(NH_4)Co_3$; but as nitrification takes place, its action becomes distinctly acidifying like that of other commercial fertilizers.

Pierrie (1928) saw the effect of various nitrogen fertilizers on pH of Norfolk sandy loam and Cecil clay loam and found that $Ca(NO_3)_2$ and $NaNO_3$ decreased the H-ion concentration.

Clevenger and Willis (1935) studying the immediate effect of fertilization on soil reaction found that there was an extremely rapid increase in pH by the application of $Co(NH_2)_2$. In Cecil clay loam the maximum values were reached in 1-6 days with $Co(NH_2)_2$ application.

Colk and Tidmore (1946) also concluded that addition of $Ca(NO_3)_2$ on Norfolk sandy loam and Cecil clay increased the pH and decreased the amount of exchangeable hydrogen in proportion to the basicity of the fertilizer after 11 years.

Overrein and Moe (1967) pointed out that maximum pH of 8.8 was attained with both 224 and 896 Kg/ha (2.5 acres) of $Co(NH_2)_2$ application rates when applied on the soil surface of Chalmers silt loam and plainfield sand.

SOIL AGGREGATION:-

Quite a few studies have shown the effect of various nitrogenous fertilizers on soil aggregation. Elson (1940) applied $(NH_4)_2SO_4$ at the rate of 308 lbs/acre concluding that fertilizing of crops with $(NH_4)_2SO_4$ hastened the formation of large aggregates.

Aldrich, et al (1945) experimenting with $(NH_4)_2SO_4$ on silt loam showed that poor physical condition of $(NH_4)_2SO_4$ plots is apparently due to the dispersing action of the NH_4^+ ion, which builds up in the exchange complex as a result of the reduced ability of soil micro-organisms to nitrify the NH_4^+ at low pH produced by the continued application of $(NH_4)_2SO_4$. He further suggested that water stable aggregates > 0.1 mm were 15.6%, 3.2%, 10.4% and 6.0% in $Ca(NO_3)_2$, $(NH_4)_2SO_4$, $Co(NH_2)_2$ and $NaNO_3$, respectively.

While studying the effect of various nitrogenous fertilizers on Sunmore silt loam Elson (1943) found that completely fertilized plots had 8% by number more aggregates than the untreated ones. Hubbell and Stubblefield (1948) showed that addition of fertilizers had no significant effect on the formation of water stable aggregates in either the field or the laboratory soils.

Cecconi, et al (1963) determined water stability of six soils of different texture, after application of one normal solution of different fertilizers and found that stability was unaffected by NH_4^+ and SO_4 ions.

Schachtschabel (1967) suggested that stability of aggregates depends mainly on the cementing power of divalent (Ca^{++}) ions on the exchange complex towards organo-matter particles.

Lastly, Vlasyuk (1967) said that K fertilizers increased aggregation in Chernozemic soils.

It is clear from the above discussion that there is a contradiction regarding the effect of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ on soil reaction and soil aggregation. It was firstly, decided to clarify the effects of these two fertilizers statistically on soil reaction and soil aggregation of different soils.

Similarly, there is contradiction regarding the effect of various nitrogenous fertilizers on these soil properties. Secondly, this study aims to see whether $(NH_4)_2SO_4$, $Co(NH_2)_2$, $Ca(NO_3)_2$, $NaNO_3$ and KNO_3 might differ in their influence with some possibility of one being more effective than the other in reducing or increasing the pH and soil aggregation of Lincoln clay loam after different time intervals.

CHAPTER III

EXPERIMENTAL TECHNIQUES
RESULTS AND DISCUSSION

Part I

Comparative effect of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ on soil reaction and soil aggregation of different soils

Three different textured soils were selected from different positions on the farm. Each of the samples were taken with a spade from the upper 9 inches of soil from two different places and thoroughly mixed to form a composite soil sample.

(1) Laboratory preparation of samples:- Field samples were brought to the laboratory and sieved through 2.0 mm sieve in the suitable moist condition (when aggregates were easily breakable). Soil samples were dried on polyethylene sheets for four days and subsequently a portion of each soil was stored in glass bottles for analysis. The remaining samples were stored in cloth bags for further experiment. The soils were analyzed mechanically by hydrometer method and results are given in Table 1. In addition to this, moisture content, saturation percentage, calcium carbonate content and organic matter content were determined and results are presented in Table 2.

Table 1 showing mechanical analysis of the experimental soils

% oven-dry soil

Sites	Sand	Silt	Clay	Soil series and Textural Class
	(2-0.05 mm)	(0.05-0.002 mm)	(<0.002 mm)	Atherley
A	70.8	17.6	11.6	Fox sandy loam
B	56.4	22.4	21.2	Lincoln loam
C	52.8	15.2	32.0	Lincoln clay loam

Table 2 showing some characteristics of the experimental soils

Depth	Textural Class	% moisture content of air-dry soil	Saturation Percentage	•CaCo$_3$ %	•Organic matter %
0 - 9"	Fox sandy loam	0.31	31.0	0.05	1.0
0 - 9"	Lincoln loam	0.34	34.0	0.00	1.3
0 - 9"	Lincoln clay loam	0.46	44.0	0.34	1.5

•oven dry basis

(2) Experimental technique:- Air-dry soil was sieved through a 0.25 mm sieve. Soil < 0.25 mm was used for the experiment. The experiment was conducted in glass dishes, measuring 100 x 50 cm. 300 g. of soil was used in each dish. For the experiment with $(NH_4)_2SO_4$ and $Co(NH_2)_2$ there were three treatments replicated three times (In split plot design experiments minumum three replications are allowed to reduce error) on three different soils. Treatments were placed at random with each replication of 9 dishes. Lay out of the experiment in given in Fig. 1. The treatments were:-

F_o = control
$F_1 = (NH_4)_2SO_4$
$F_2 = Co(NH_2)_2$.

Both fertilizers were applied at the rate of 200 lbs N/acre. 0.142 g. of $(NH_4)_2SO_4$ and 0.065 g. of $Co(NH_2)_2$ were weighed and spread evenly on the surface of the soil in the specified dishes on 19th March, 1968. The soil in each dish was saturated with water initially and then was allowed to dry out and to be rewetted periodically throughout the whole period of study until the samples were finally taken from the dishes on 5th April , 1968, for analysis after 17 days. The dishes were kept at room temperature. Soil samples were analyzed for soil reaction and soil aggregation as follows.

(a) Soil Reaction:- 50 g. of soil was taken in a 200 c.c. beaker and distilled water was added while stirring with a spatula. At saturation the soil paste glistened as it re-

reflected the light, it flowed slightly when the beaker was tipped, and the paste slides freely and cleanly off the spatula. After mixing, the soil sample was allowed to stand for an hour to recheck the criteria of water saturation. The soil reaction was measured with a battery pH meter E280A, Fisher Scientific. The pH meter was standardized with buffer 7.0 and the electrode was washed with distilled water and cleaned with filter paper. The electrode was inserted into the saturated soil paste and raised up and down repeatedly until constant pH was recorded.

(b) Soil Aggregation:- Dry-sieve analysis of the sample was carried out in a nest of sieves of 2.0 mm; 1.0 mm; 0.5 mm and 0.25 mm. On the top sieve 50 g. of soil sample was evenly spread with a soft hair brush. The sieving was done, by shaking for 5 minutes on a Cenco Meizer sieve shaker. The sieves were dipped several times into a bucket of water until the outflowing water was clear. The water stable aggregates remaining on the sieves were combined, oven dried at 105°C and weighed. The method was followed as described by Gupta (1965) and Leeper (1964). The degree of aggregation of each treatment has been calculated, taking 0.25 mm (p. 21) as the lower limit of effective aggregates and the results have been interpreted on this basis.

(3) Analytical methods Employed: Soil moisture content, saturated soil paste were determined by procedures outlined in U.S.D.A. Handbook No. 60 (1954). Mechanical analysis and

Fig. 1 showing lay out of the experiment

	S_1			S_3			S_2		
R_1	F_2	F_o	F_1	F_o	F_2	F_1	F_1	F_o	F_2
R_2	F_1	F_2	F_o	F_1	F_o	F_2	F_o	F_2	F_1
R_3	F_o	F_1	F_2	F_2	F_1	F_o	F_2	F_1	F_o

S_1 = Fox sandy loam

S_2 = Lincoln loam

S_3 = Lincoln clay loam

System of lay out = split plot design

Replication = 3

Treatments = F_o = control
F_1 = $(NH_4)_2SO_4$
F_2 = $Co(NH2)_2$

organic matter content were determined by methods given in "Laboratory Manual for Soil Fertility" 1968. Calcium carbonate contents were determined with Collin's calcimeter.

(4) Comparative effect of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ on pH of different soils at 5% level

The results obtained due to the action of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ on pH of different soils were statistically analyzed. Table 3 showing analysis of variance is given on page 20. The mean values of pH after various treatments (F_o, F_1, F_2; replications against fertilizers have been averaged) for Fox sandy loam, Lincoln loam and Lincoln clay loam are 5.2, 6.1 and 5.9, respectively. These figures show that various treatments have no significant difference on any of the soils. From the analysis of Variance table it is clear that texture does not influence pH of different soils.

Further, an analysis of Table 3 shows that $(NH_4)_2SO_4$ and $Co(NH_2)_2$ reduced pH to 5.5 and 5.8, respectively. However, this is not statistically significant at 5% level as compared with control. $(NH_4)_2SO_4$ and $Co(NH_2)_2$ while undergoing the process of nitrification may not produce H ions (p.6 and 7) to such an extent which can influence the soil reaction to an appreciable extent as compared with control. This would confirm the findings of Hubbell and Stubblefield (1948) who concluded that pH values were unaffected with $(NH_4)_2SO_4$ application

Table 3 showing analysis of variance of pH values

Due to	degree of freedom	Sum of squares	Mean sum of squares	F value	Critical F values (as derived from Tables)	
Replication	2	0.07	-	-	5%	1%
Soil	2	3.71	1.85	3.24 N.S.	6.94	18.0
Error (i)	4	0.23	0.57	-	-	-
Fertilizers	2	1.20	0.60	1.2 N.S.	4.46	8.65
Soils x Fertilizers	4	0.36	0.9	1.8 N.S.	3.84	7.01
Error (ii)	8	0.45	0.5	-	-	-

Soils =	S_1	S_2	S_3
Mean values=	5.2	6.1	5.9
Treatments =	F_o	F_1	F_2
Mean values =	6.0	5.5	5.8

N.S. = Non Significant

on Gila clay and Gila loam soils.

(5) Comparative effect of $(NH_4)_2SO_4$ and $CO(NH_2)_2$ on soil aggregation of different soils at 5% level

The best way of expressing aggregate analysis results is by taking into account the percentage of the total weight of the sample above a certain size limit. The aggregates below that limit should not appreciably influence the over all aggregation status of soil and its related physical properties. A search of relevant literature shows that aggregates below the size limit of 0.25 mm diameter does not materially contribute towards the physical condition of the soil regulating the soil water and air movement. Some workers are of the view that aggregates greater than 0.5 mm. or even 1.0 mm. should be taken into account. Browning and Milam (1944) showed that there was a high correlation coefficient (-.93) between percentage aggregates > 0.25 mm and the dispersion ratio which was calculated as follows.

$$\frac{\text{\% aggregate greater than 0.05 mm. before dispersion}}{\text{\% aggregate greater than 0.05 mm. after dispersion}}$$

The correlation coefficient between percent aggregates > 1.0 mm. and dispersion ratio were not so high (-.71). From the above consideration, 0.25 mm has been taken as the lower size limit in this work in expressing the aggregation as a single value.

The data due to the effect of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ was statistically analysed. Table 4 showing analysis of variance is given on page 23 and 24. Mean percentage of water stable aggregates (expressed in terms of oven dry weight basis) after various treatments; (F_o, F_1, F_2; replications against fertilizers have been averaged) are 7.3%, 11.1% and 15.1% at 5% level. Martin, et al (1955) proposed that clay is the dominant binding agent in soil aggregation and that organic materials do not act primarily to hold clay, silt and sand grains together, but their chief role may be to modify the forces by which clay particles are attached to one another. Russell (1950) found that in most soils, clay forms a continuous network that emeshes and binds silt and sand particles. If this is the case then it may be concluded that these soils with different textural characteristics are statistically significant from one another in percentage water stable aggregates. The effect of various textural treatments increased as the percentage of clay increased in different soils.

Further, an analysis of Table 4 shows that mean values of percentage water stable aggregates due to various treatments (F_o, F_1, F_2) are 4.7%, 15.4% and 13.9%, respectively. The values against $(NH_4)_2SO_4$ and $Co(NH_2)_2$ are statistically insignificant, probably because both fertilizers undergo the same process of nitrification. Nitrification is the formation of nitrates from ammonium compounds, through the action of bacteria. Two forms of bacteria are known as nitrite bacteria,

Table 4 showing analysis of variance of percentage of water stable aggregates

Due to	Degree of freedom	Sum of Squares	Mean sum of squares	F.value	Critical value (as derived from tables)	
					5%	1%
I						
Replication	2	0.09	-	-		
Soils	2	315.74	157.87	1578.7**	6.94	18.0
Error(i)	4	0.42	0.10	-	-	-
II						
Fertilizer	2	602.30	301.15	120.9**	4.46	8.65
Soils x Fertilizers	4	39.02	9.75	3.9*	3.84	7.01
Error(ii)	8	2.65	2.49	-	-	-

I. S.E. D.M. $= \sqrt{\frac{0.10 \times 2}{9}} = \sqrt{\frac{2}{9}} = 0.14$

Difference between = S.E.D.M. x t value

% mean 0.14 x 2.776 = 0.38864

Difference between = S.E.D.M. x t value

1% mean 0.14 x 4.604 = 0.64456

Soils = S_1 S_2 S_3

Mean Value = 7.3% 11.1% 15.1%

II S.E.D.M. $= \sqrt{\frac{2.49 \times 2}{9}} = 0.74$

Difference between % = S.E.D.M. x t value

means 0.74 x 2.306 = 1.70644

Difference between 1% = S.E.D.M. x t value

means 0.74 x 3.355 = 2.48270

Fertilizers =	F_o	F_1	F_2
Mean values =	4.7%	15.4%	13.9%

$*$ = significant

$**$ = Highly significant.

viz. nitrosomonas and nitrosococcus, convert ammonium compounds to nitrous acid. The nitrous acid is then neutralized to nitrify by the bases of the soil. In the second bio-chemical change the nitrates are converted to nitrates by the genus nitrobacter. Harris, et al (1966) showed that most bacteria including nitrifying bacteria appear somewhat slimy and gelatinous. Alexander (1961) showed that these bacteria also secrete gelatinous substances during their activity. Therefore, soil aggregation has probably been due to the fact that these bacteria are slimy and gelatinous or may be due to the gelatinous substances secreted by these micro-organisms. Similarly, Elson (1943) studied the effect of nitrogenous fertilizers on Sunmore silt loam and found that completely fertilized plots had 8% more aggregates as compared with control.

PART II

Effect of various nitrogenous fertilizers after different time interval on soil reaction and soil aggregation of Lincoln clay loam

(1) Experimental Technique:- In this part, studies were made on the effect of different nitrogenous fertilizers on soil reaction and soil aggregation of Lincoln clay loam soil. The soil was passed through 2.0 mm. sieve and air-dried for two days on polyethylene sheets. It was then placed in 24 dishes, each containing 300 g. of soil. The fertilizing materials were added at the rate of 80 lbs N/acre. $(NH_4)_2SO_4$, $Co(NH_2)_2$, $Ca(NO_3$, $NaNO_3$ and KNO_3 were added as 60 mg; 27 mg; 77 mg; 75 mg and 89 mg. respectively to each dish and evenly spread on the surface of the soil on 5th May, 1968. There were six treatments in all including the control. Each treatment and check was repeated four times to study the effect of time after 1, 2, 3 and 4 weeks. Initially, the soil in each dish was saturated with water and then it was allowed alternately to dry and to wet, at regular intervals, throughout the whole period until samples were taken for final analysis. The dishes were kept at room temperature. Lay out of the experiment is given in fig. 2 on page 27. Soil reaction and soil aggregation determinations were made after 1, 2, 3 and 4 weeks as described on pages 16 and 17.

Fig. 2 showing lay out of the second part of experiment

Treatments

1 week	F_o	F_3	F_5	F_2	F_4	F_1
2 week	F_2	F_5	F_1	F_3	F_o	F_4
3 week	F_4	F_o	F_2	F_5	F_1	F_3
4 week	F_1	F_4	F_o	F_2	F_3	F_5

Treatments:- F_o = check
F_1 = $(NH_4)_2SO_4$
F_2 = $Co(NH_2)_2$
F_3 = $Ca(NO_3)_2$
F_4 = $NaNO_3$
F_5 = KNO_3

Soil: Lincoln clay loam

(2) Effect of Various Nitrogen Fertilizers After Different Time Intervals on Soil Reaction

The pH values due to various treatments are presented in Table 5. Each figure corresponds to a particular treatment and time. The results due to the effect of $(NH_4)_2SO_4$ indicate that pHvalues dropped to 6.9 and 6.6 after one week and two weeks respectively, but later on the values became constant. Plummer (1918) first studied the effect of various fertilizers on hydrogen ion concentration and found that $(NH_4)_2SO_4$ materially increased the hydrogen ion concentration of all plots. Pierrie (1928) explored the effect of $(NH_4)_2SO_4$ on Norfolk sandy loam and Cecil clay loam concluding that $(NH_4)_2SO_4$ caused the greatest increase in H-ion concentration. White (1931) experimenting with $(NH_4)_2SO_4$ showed that this fertilizer produced acidity in the soil. Dunton, _et_ _al_ (1954) and Leo, _et_ _al_ (1959) also concluded that $(NH_4)_2SO_4$ decreased soil pH. Therefore, it may be assumed that the greatest nitrification, carried out by nitrifying bacteria takes place during the first two weeks. Later on this process probably occurs at a more constant rate and does not affect the pH of the soil.

Application of $Co(NH_2)_2$ also decreased the pH values to 7.1, 6.9, 6.7 and 6.5 after each week, respectively. There is a constant decrease in pH values. $Co(NH_2)_2$ in the beginning is converted to $(NH_4)_2CO_3$ and then undergoes a base exchange reaction and ultimately nitrifies into NO_3' by nitrifying bacteria

Table 5 showing pH values in various treatments at intervals of 1, 2, 3 and 4 weeks•

Treatments	1 week	2 weeks	3 weeks	4 week
(1) Control	7.4	7.3	7.5	7.5
(2) $(NH_4)_2SO_4$	6.9	6.6	6.6	6.6
(3) $Co(NH_2)_2$	7.1	6.9	6.7	6.5
(4) $Ca(NO_3)_2$	7.3	6.7	7.3	7.2
(5) $NaNO_3$	7.2	7.1	7.1	7.2
(6) KNO_3	7.2	7.1	7.1	7.0

• Average values of two determinations

producing acidity in the soil. Pierrie (1928) explored the effect of $Co(NH_2)_2$ on the reaction of Norfolk sandy loam and Cecil clay loam concluding that $Co(NH_2)_2$ produces acidity in the soil. Broadbent, et al (1958) added $Co(NH_2)_2$ at 200, 400, 800 ppm to clay, loam and sandy loam soils concluding that $Co(NH_2)_2$ in the beginning increase pH but later on produces acidity.

It is interesting to note that pH values dropped to 6.7 in the second week due to $Ca(NO_3)_2$ and later on again rose to 7.3 and remained almost constant. Ca^{++} from $Ca(NO_3)$ was presumably adsorbed on the exchange complex and H ions combined with NO_3' to form HNO_3 which may be responsible for decrease in pH of soil. Rise in pH may be due to the leaching of HNO_3 in the soil. Hubbell and Stubblefield (1948) concluded that application of $Ca(NO_3)_2$ to Gila clay and Gila loam had no effect on pH values.

pH values due to $NaNO_3$ treatment dropped to 7.2, 7.1 and 7.1 after 1, 2 and 3 weeks respectively and later on again rose to 7.2 and remained constant. Na from $NaNO_3$ was probably adsorbed on the exchange complex and may exchange with H ions which decreased pH values. Here, too, rise in pH may be due to leaching of HNO_3 in the soil. In this case, the effect is less as compared with $Ca(NO_3)$. This may be due to less adsorption of Na on exchange complex which depends upon:

(i) Valency of the ion

(ii) Size of the hydrated ion.

Leo, et al (1959) applied $NaNO_3$ to silt loam soil concluding that use of $NaNO_3$ maintained a steady pH.

Similarly, application of KNO_3 also reduced pH to 7.2, 7.1, 7.1 and 7.0 after 1, 2, 3 and 4 weeks, respectively. K from KNO_3 was presumably adsorbed on the exchange complex and may exchange with H ions. These H ions are probably responsible for decrease in pH value.

(3) Effect of Various Nitrogenous Fertilizers After Different Time Intervals on Soil Aggregation:-

The results of aggregate analysis expressed as degree of aggregation taking 0.25 mm. diameter as the lower size limit are presented in Table 6. Each figure corresponds to a particular treatment and time. The degree of aggregation of untreated samples corresponding to four time intervals are 15.2%, 17.7%, 17.8% and 17.7%. These values indicate that under conditions of alternate wetting and drying, changes take place in aggregation of soil even if it is otherwise left untreated. In this case aggregation takes place in the initial stages and the soil ultimately reaches a state which is more or less in equilibrium. Russell (1934) noted that drying tends to increase the inherent stability of aggregates by dehydration of aggregating cements. While Baver (1956) indicated that clay particles in most soils are surrounded by a film of water. As dehydration takes place, these films become thinner and thinner until adjacent particles are held together by cohesive forces.

Table 6 showing percentage of water stable aggregates in various treatments at intervals of 1, 2, 3 and 4 weeks•

Treatments	1 week	2 week	3 week	4 week
(1) Control	15.2	17.7	17.8	17.7
(2) $(NH_4)_2SO_4$	17.2	21.1	21.2	21.0
(3) $Co(N_2H_2)$	19.5	20.9	21.0	21.1
(4) $Ca(NO_3)_2$	18.0	19.8	22.8	23.0
(5) $NaNO_3$	15.1	14.4	14.4	14.5
(6) KNO_3	15.2	15.8	16.0	17.0

• Average values of duplicate determinations.

Therefore, dehydrated clay colloids, can exert a vigorous cementing action in soil aggregates. Harris, et al (1966) showed that the exact mechanisms involved in increased aggregate stability with drying are not completely understood. Irreversible or slowly reversible dehydration of organic or inorganic colloidal substance is probably a major feature of this mechanism.

The corresponding values of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ treated samples show that these fertilizers increase the percentage of aggregates up to the second week while later on the values become almost constant. This may be due to the fact that nitrifying bacteria are more active in the initial stages of the process of nitrification. Since most bacteria including nitrifying bacteria appear somewhat slimy and gelatinous (p. 25) so it may be deduced that bacteria in the soil may serve to bind soil particles together.

Degree of aggregation of the soil treated with $Ca(NO_3)_2$ constantly increased from 18.0% to 23.0% after 4 weeks interval. Baver (1956) showed that adsorption of Ca^{++} ion decreases the zeta potential (total extent of negative charges on the exchange complex) due to which there will be a tendency for attraction and the particles will coalesce as a result of a collision and settle out as a floccule. He further showed that, in general, the amount of electrolyte required to produce flocculation decreases as the valency of the added cation increases or as stated in terms of Schulze's rule (Weiser,1938), the flocculating power of ions increases with their valence. Gedroits (1955) suggested two distinct stages in soil aggregation. (a) Coagulation of soil colloids under the influence of calcium ions to form primary micro-aggregate .(b) Cementation of micro-aggregates into macro-aggregates by highly dispersed organic substances. Alexander (1961) suggested that Ca^{++} ions increase the activity of micro-organisms in the soil. Therefore, soil aggregation may be due to the fact that Ca^{++} adsorbed on the exchange complex has a flocculating effect or may be due to increased activity of micro-organisms in the soil. These results agree with Schachtschabel (1967) who pointed out that stability of aggregate depends mainly on the cementing power of divalent (Ca^{++}) ions on the exchange complex towards organo-matter particles.

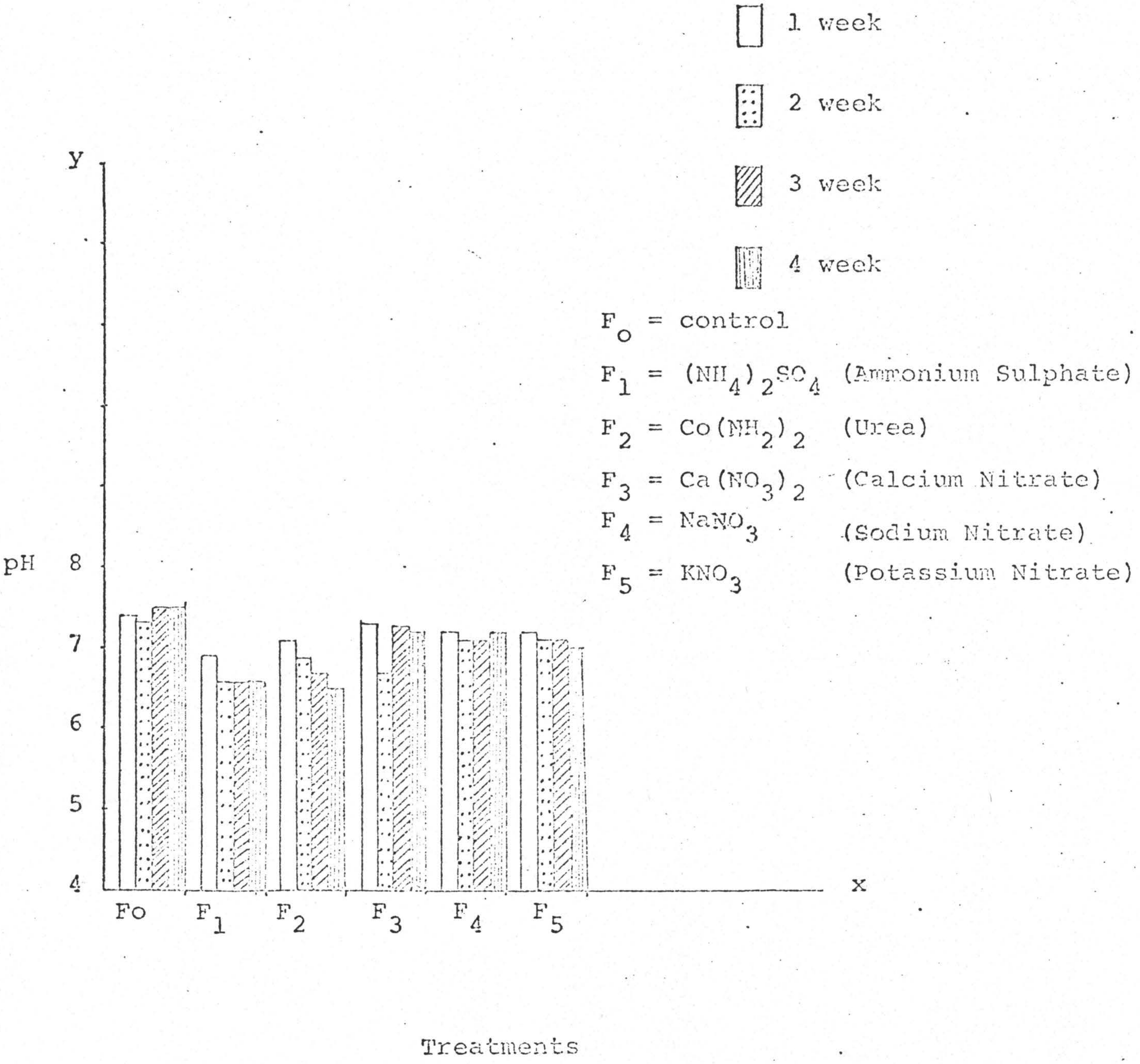
Further, an analysis of Table 6 reveals that $NaNO_3$ decreased the percentage of water stable aggregates. Baver (1958) showed that efficiency of various monovalent cations lies in their ability to increase the negative potential of the clay particles. Since this effect increases with the hydration of the ion, thus it should be expected that the dispersive power of the common monovalent cation would vary as follows.

$$Li > Na > K > NH_4 .$$

Therefore, Na^+ from $NaNO_3$ adsorbed on the exchange complex and disperse the soil particles thereby, decreasing the percentage of water stable aggregates.

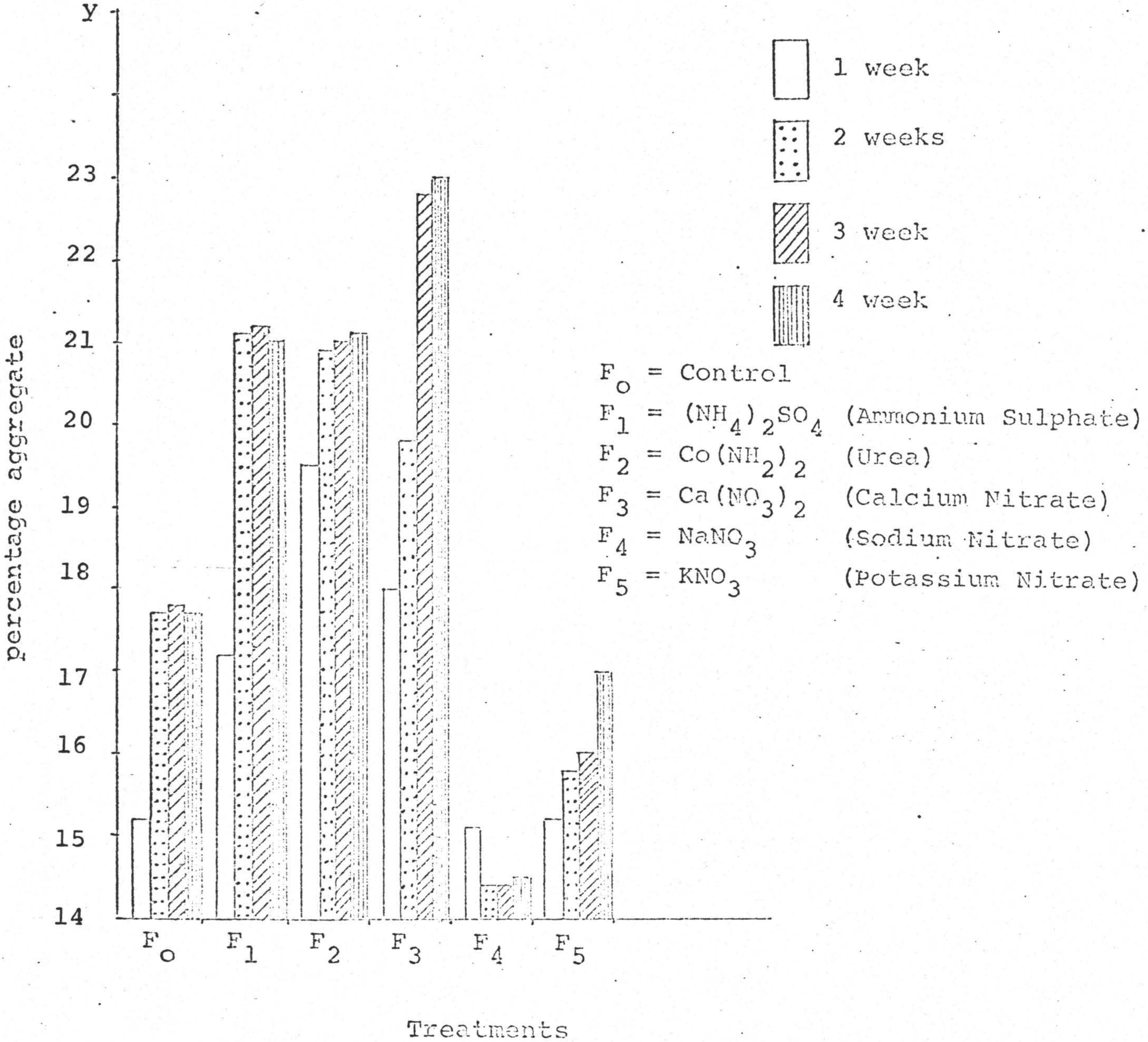
The relevant data also shows that application of KNO_3 constantly increased the percentage of water stable aggregates but rate of increase is much less as compared with $Ca(NO_3)_2$. This may be due to the lesser ability of K^+ to decrease the zeta potential of the clay particle . These results agree with Vlasyuk (1967) who said that K fertilizers increased aggregation in Chernozemic soils.

Taking all treatments into consideration, it may be deduced that order of effectiveness of the treatments under study is $Ca(NO_3)_2$, $(NH_4)_2SO_4 = Co(NH_2)_2$, KNO_3 while $NaNO_3$ has an opposite effect on percentage of water stable aggregates.



Histograms showing pH values of different treatments after 1, 2, 3 and 4 weeks time interval

Figure 3



stograms showing percentage water stable aggregates of different treatments after 1, 2, 3 and 4 weeks time interval

Figure 4

CHAPTER IV

SUMMARY AND CONCLUSIONS

Studies were made in the laboratory at first to compare the effect of $(NH_4)_2SO_4$ and $Co(NH_2)_2$ on soil reaction and soil aggregation of Fox sandy loam, Lincoln loam and Lincoln clay loam and secondly to see the effect of different nitrogenous fertilizers after 1, 2, 3 and 4 weeks intervals on soil reaction and soil aggregation of Lincoln clay loam. In the first case $(NH_4)_2SO_4$ and $Co(NH_2)_2$ were added 200 lbs N/acre and in the second case $(NH_4)_2SO_4$, $Co(NH_2)_2$, $Ca(NO_3)_2$, $NaNO_3$ and KNO_3 at 80 lbs N/acre. Soil reaction and soil aggregation determinations were made at the end of experiment. The soil was kept alternately moist and dry to approximate local field conditions. Various conclusions are given below.

(1) In the beginning, under conditions of alternate wetting and drying, changes took place in soil aggregation but afterwards aggregates become more or less stable.

(2) $(NH_4)_2SO_4$ and $Co(NH_2)_2$ have no significant (5% level) effect on pH values of Fox sandy loam, Lincoln loam and Lincoln clay loam and both have an acidic effect on these soils.

(3) $(NH_4)_2SO_4$ and $Co(NH_2)_2$ have significant (5% level) effect on soil aggregation of the various soils studied.

(4) There is no significant (5% level) difference between $(NH_4)_2SO_4$ and $Co(NH_2)_2$ on soil aggregation but both fertilizers gave significant results as compared with control.

(5) $Ca(NO_3)_2$ and $NaNO_3$ decreased pH values but later on again rose and remained constant on Lincoln clay loam.

(6) pH values decreased slightly with KNO_3 application on Lincoln clay loam.

(7) $Ca(NO_3)_2$ and KNO_3 consistently increased soil aggregation of Lincoln clay loam but effect was more pronounced in $Ca(NO_3)_2$.

(8) $NaNO_3$ decreased the percentage of water stable aggregates.

Note:- For short duration crops $(NH_4)_2SO_4$ can be used while $Ca(NO_3)_2$ is a good fertilizer for long duration crops.

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APPENDICES

Statistical analysis of pH values

	S_1			S_3			S_2			Total
R_1	4.8 F_2	5.4 F_o	5.0 F_1	6.2 F_o	6.0 F_2	5.4 F_1	6.2 F_1	6.4 F_o	6.0 F_2	51.4
R_2	5.0 F_1	5.6 F_2	5.4 F_o	5.5 F_1	6.3 F_o	6.5 F_2	6.4 F_o	5.9 F_2	5.9 F_1	52.5
R_3	5.5 F_o	5.2 F_1	5.4 F_2	5.9 F_2	5.5 F_1	6.4 F_o	6.2 F_2	5.8 F_1	6.1 F_o	52.0
Total	15.3	16.2	15.8	17.6	17.8	18.3	18.8	18.1	18.0	155.9 Grand Total

(1) Correction factor $= \frac{(155.9)^2}{27} = 900.17$

(2) Total sum of squares $= (4.8)^2 + (5.4)^2 + (5.0)^2 + (6.2)^2 +$
$(6.0)^2 + (5.4)^2 + (6.2)^2 + (6.4)^2 +$
$(6.0)^2 + (5.0)^2 + (5.6)^2 + (5.4)^2 +$
$(5.5)^2 + (6.3)^2 + (6.5)^2 + (6.4)^2 +$
$(5.9)^2 + (5.9)^2 + (5.5)^2 + (5.2)^2 +$
$(5.4)^2 + (5.9)^2 + (5.5)^2 + (6.4)^2 +$
$(6.2)^2 + (5.8)^2 + (6.1)^2 - 900.17$

$906.19 - 9.00\ 17 = 6.02$

(3) Replication sum of squares $= \frac{(15.4)^2 + (52.5)^2 + (52.0)^2}{9} - 900.17 = 0.07$

(4) Soil sum of squares $= \frac{(47.3)^2 + (54.9)^2 + (53.7)^2}{9} - 900.17 = 3.71$

(5) Total sum of squares for SxR sub-table = $(15.2)^2+(18.6)^2 + (17.6)^2 + (16.0)^2 + (18.2)^2 + (18.3)^2 + (16.1)^2 + (18.1)^2 + \frac{(17.8)^2}{3} - 900.17$

$904.18 - 900.17 = 4.01$

	S_1	S_2	S_3
R_1	15.2	18.6	17.6
R_2	16.0	18.2	18.3
R_3	16.1	18.1	17.8
Total	47.3	54.9	53.7
Mean	5.2	6.1	5.9

(6) Error (i) = Total SxR - soils sum of squares - replication

4.01 - 3.71 - 0.07 =

Sum of squares

0.23

(7) Fertilizer sum of squares =

$$\frac{(54.1)^2 + (49.5)^2 + (52.3)^2}{9} - 900.17 = 1.20$$

Soils Fertilizers	S_1	S_2	S_3	Total	Mean
F_o	16.3	18.9	18.9	54.1	6.0
F_1	15.2	17.9	16.4	49.5	5.5
F_2	15.8	18.1	18.4	52.3	5.8

(8) Total sum of square of soils x fertilizers sub table = $(16.3)^2 + (15.2)^2 + (15.8)^2 + (18.9)^2 + (17.9)^2 + (18.1)^2 + (18.9)^2 + (16.4)^2 + \frac{(18.4)^2}{3} - \text{c.f.} = 5.27$

(9) Soil x fertilizer sum of squares = 5.27-3.71-1.20 = 0.36

(10) Error(ii) = 6.02-0.07-3.71-0.23-1.20-0.36 = 0.45

Statistical analysis of percentage water stable aggregates

	S_1			S_2			S_3			Total	
R_1	F_2 8.5	F_o 3.0	F_1 10.5	F_o 4.1	F_2 13.8	F_1 15.3	F_1 20.9	F_o 7.6	F_2 19.3	103.00	
R_2	F_1 9.9	F_2 9.1	F_o 2.5	F_1 15.9	F_o 4.5	F_2 13.4	F_o 7.0	F_2 18.9	F_1 20.5	101.7	
R_3	F_o 3.2	F_1 10.8	F_2 8.2	F_2 14.2	F_1 15.1	F_o 3.9	F_2 19.9	F_1 20.0	F_o 6.9	102.2	
Total	21.6	22.9	21.2	34.2	33.4	32.6	47.8	46.5	46.7	306.9	Grand Total

(1) Correction factor $= \frac{(306)^2}{27} = 3488.43$

(2) Total sum of squares $= (8.5)^2 + (3.0)^2 + (10.5)^2 + (4.1)^2 + (13.8)^2 + (15.3)^2 + (20.9)^2 + (7.6)^2 + (19.3)^2 + (19.3)^2 + (9.9)^2 + (9.1)^2 + (2.5)^2 + (15.9)^2 + (4.5)^2 + (13.4)^2 + (7.0)^2 + (18.9)^2 + (20.5)^2 + (3.2)^2 + (10.8)^2 + (8.2)^2 + (14.2)^2 + (15.1)^2 + (3.9)^2 + (19.9)^2 + (20.0)^2 + (6.9)^2 - 3488.33$

$$4448.65 - 3488.33 = 960.22$$

(3) Replication sum of squares =

$$\frac{(103.00)^2 + (101.7)^2 + (102.2)^2}{9} - 3488.43 = 0.09$$

(4) Soils sum of squares =

$$\frac{(65.7)^2 + (100.2)^2 + (141.0)^2}{9} - 3488.43 = 315.74$$

(5) Total sum of squares for SxR sub table =

$$\begin{aligned}&(22.0)^2 + (33.2)^2 + (47.8)^2 + (21.5)^2\\&+ (33.8)^2 + (46.4)^2 + (22.2)^2 + (33.2)^2 +\\&\frac{(46.8)^2}{3} - 3488.43 = 316.25\end{aligned}$$

	S_1	S_2	S_3
R_1	22.0	33.2	47.8
R_2	21.5	33.8	46.4
R_3	22.2	33.2	46.8
Total	65.7	100.2	141.0
Mean	7.3	11.1	15.6

(6) Error(i) = 316.25 - 315.74 - 0.09 = 0.42

Soils / Fertilizers	S_1	S_2	S_3	Total	Mean
F_o	8.7	12.5	21.5	42.7	4.7
F_1	31.2	46.3	61.4	138.9	15.4
F_2	25.8	41.4	58.1	125.3	13.9

(7) Fertilizer sum of squares $= \dfrac{(42.7)^2 + (138.9)^2 + (125.3)^2}{9}$

$$- 3488.43 = 602.30$$

(8) Total sum of squares for soils x fertilizers

$$\begin{aligned}\text{sub table} \quad = \quad &(8.7)^2 + (12.5)^2 + (21.5)^2 + (31.2)^2 =\\&(46.3)^2 + (61.4)^2 + (25.8)^2 + (41.4)^2\\&+ \frac{(58.1)^2}{3} - \text{c.f.} = 957.06\end{aligned}$$

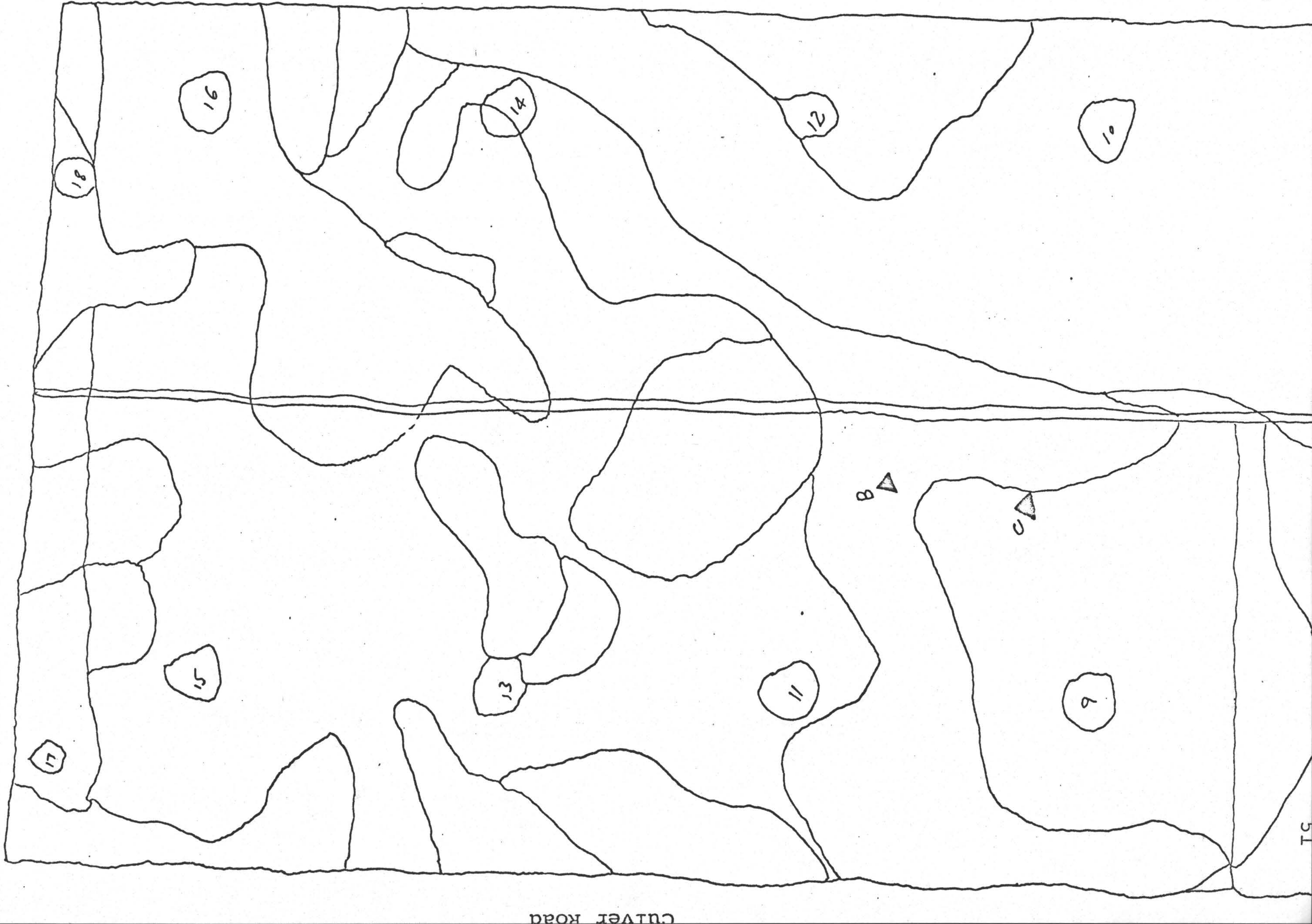
(9) Soils x fertilizers sum of squares =

957.06 - 602.30 - 315.74 = 39.02

(10) Error (ii) 960.22 - 0.09 - 315.74 - 0.42 - 602.30 - 39.02 =

960.22 - 957.57 = 2.65

Horticultural Experiment Station, Simcoe
North farm
Figure 5



Horticultural experiment station, Simcoe

South farm

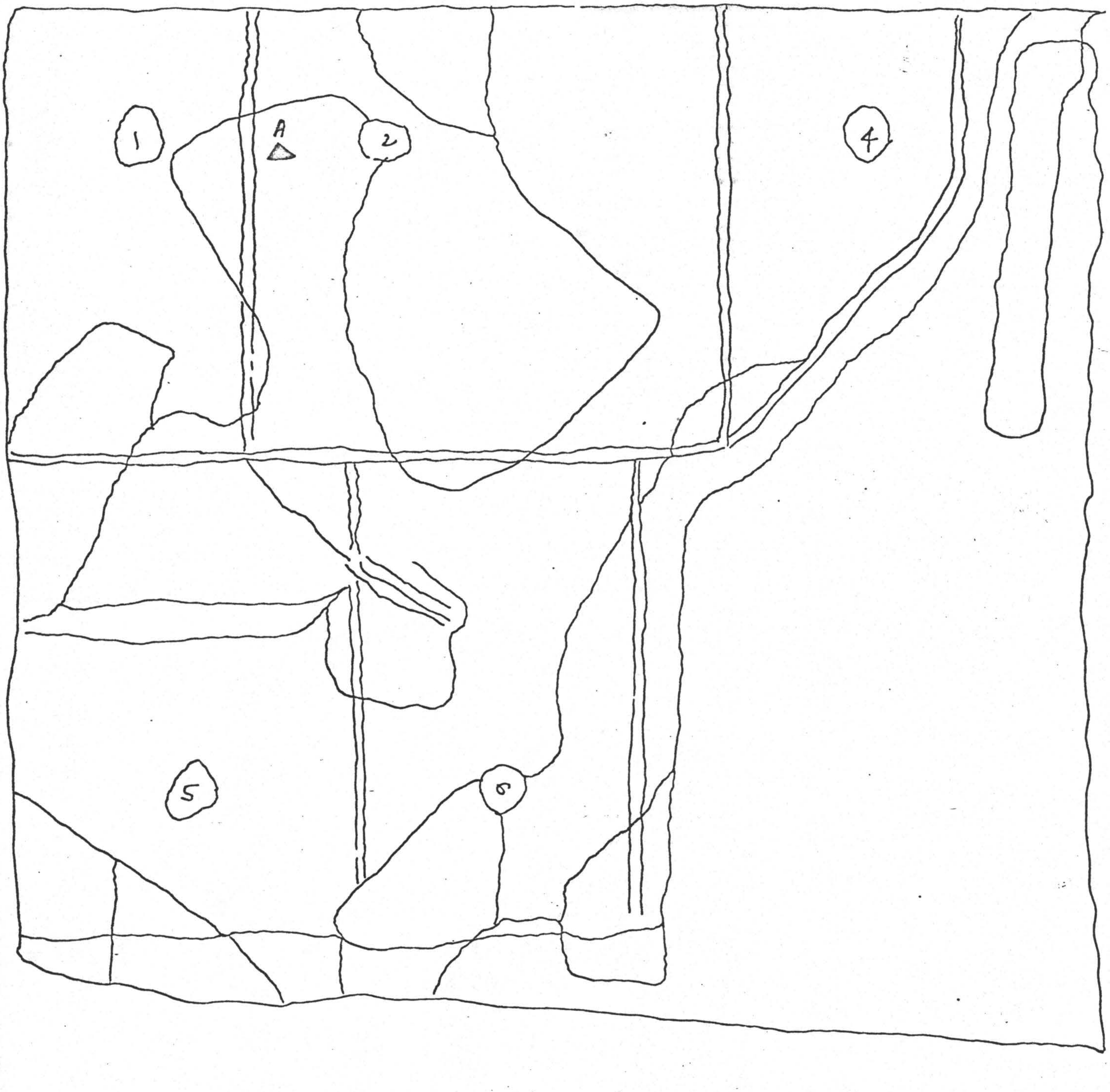


Figure 6