A STUDY OF SOIL AMMONIUM NITROGEN
IN SOME SOILS OF MANITOBA

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ABSTRACT

A study was made of soil ammonium nitrogen of different types of soils of Manitoba. Methods used were: 1. Potentially available Nitrogen (PAN) determined according to the method suggested by Purvis and Leo (73); 2. Exchangeable ammonium determined according to the method described by Jackson (54). The PAN and exchangeable ammonium nitrogen were evaluated by statistical comparison with two weeks incubation nitrate nitrogen.

In general PAN values, in forty-five surface soils of Manitoba Province, correlated highly significantly with two weeks incubation nitrate nitrogen. The correlation coefficient was 0.707**, which was significant at the 1 per cent level. However the good correlations were obtained particularly in slightly calcareous and non-calcareous Black and Dark Grey soils. The correlation coefficient existing between PAN and two weeks incubation nitrate nitrogen, in the slightly calcareous Black and Dark Grey soil group was 0.971** , and the correlation coefficient in non-calcareous Black and Dark Grey soil group was 0.940**. But there was no significant correlation between PAN and two weeks incubation nitrate nitrogen in the Grey Wooded soil group as the correlation obtained was -0.127.

Exchangeable ammonium nitrogen values of thirty-five Manitoba soils studied correlated highly significantly with their two weeks incubation nitrate nitrogen. The correlation coefficient was 0.926** and is higher than the correlation coefficient that was obtained between PAN and two weeks incubation nitrate nitrogen.

The highly calcareous soils were conspicuous by their low PAN and low exchangeable ammonium values. These soils have also slow rates of nitrification as evidenced by the low two weeks incubation nitrate nitrogen values.

Nitrogen uptake and "N" values, obtained in a green house experiment conducted, with different genetic types of soils, did not correlate significantly with PAN and exchangeable ammonium of the soils.

The mode of transformation of PAN with respect to the formation of nitrates during four weeks incubation of soils at 30°C, the existance of a highly significant correlation between PAN values

and exchangeable ammonium nitrogen values (r is 0.877**) suggest that PAN of soil is mainly constituted of easily mineralizable ammonium and amino nitrogen. This is also supported by the fact that Purvis and Leo's method of PAN determination extracted little or no nitrogen that is immobilized during incubation of soil with plant material of 1.18 per cent of nitrogen, suggesting that this method does not involve degradation of soil organic nitrogen complex to any great extent.

The recoveries of the added ammonium nitrogen as exchangeable ammonium by extracting with 10 per cent NaCl solution of pH 2.5, and as nitrate after four weeks of incubation of soils at 30°C reveal that considerable amounts of added ammonium nitrogen is lost in calcareous soils. This loss is attributed mainly to gaseous loss of ammonia as these calcareous soils have alkaline pHs. Another possible reason is that larger amounts of calcium present in these soils might be inhibiting nitrification as addition of 20 per cent of calcium carbonate to a highly fertile soil has reduced its nitrification about 74 per cent. Nitrogen uptake percentages of ammonium nitrogen added to calcareous soils are also lower than those for non-calcareous soils. The nitrogen uptake percentages in general are comparable to the recoveries of added ammonium nitrogen to soils as exchangeable ammonium by extracting soils with 10 per cent sodium chloride solution of pH 2.5.

CHAPTER I

INTRODUCTION

Nitrogen is a macronutrient element and is required in substantial amounts for plant growth. Soil nitrogen and atmospheric nitrogen are two important natural sources of nitrogen for plants. Most plants cannot fix elemental nitrogen of the atmosphere, and hence its direct utility is limited. This leaves soil nitrogen as the main natural source of nitrogen for plants. Nitrogen is returned to the soil as organic nitrogen bound in plant and animal residues and is in due course converted into the humic fraction of the soil organic matter. The large part of the nitrogen locked in this humic fraction is not immediately mineralized and is not immediately available to plants because the humic fraction is relatively stable. However, a small fraction of the soil humus is active and undergoes microbial decomposition releasing nitrogen in mineral form which is directly taken up by plants. The mineralized nitrogen often is lost due to leaching and volatilisation if it is not immediately utilized by plants. Therefore, nitrogen often forms the limiting factor for plant growth in the field. This necessitates a supply of fertilizer nitrogen to soil to meet the needs of plants. For economically profitable application of fertilizer nitrogen, one should have a reasonably good idea about how much nitrogen the soil can supply for a growing crop.

In view of the importance of nitrogen in plant growth and in soil fertility, it is no wonder that extensive studies of the soil nitrogen fraction and its transformation have been made. Different soil nitrogen fractions, such as total soil nitrogen intermediate ammino and ammonical nitrogen, and mineral nitrogen, have been investigated for their utility as measures of nitrogen supplying capacity of the soil. The determination of total nitrogen and organic matter gives some idea about the fertility of the soil as they measure the substrate that is undergoing decomposition during microbial transformations. However, a large part of the total soil nitrogen and organic matter represent relatively stable matter as it is only the small fraction of the total soil nitrogen that is mineralized and made available to a growing crop. Moreover, the actual nitrogen fraction that is mineralized during the cropping season is dependent on many other variables such as soil pH, moisture content, microbial population and temperature etc. Soils having similar organic matter contents or total soil nitrogen may have different nitrogen supplying capacities due to their different rates of mineralization. The mineral nitrogen fraction of soil: nitrate nitrogen and ammonium nitrogen, represent immediately available forms of nitrogen as nitrogen in this form is readily taken up by plants. This fraction is susceptible for ready losses due to leaching, and volatilisation. Attempts have been made to determine the active fraction of the soil organic nitrogen that is labile and undergoes decomposition and is made available to plants. This fraction is referred to as potentially available nitrogen. Commonly employed incubation tests involve microbial decomposition of such fractions or parts of it and the measurement of the mineral nitrogen that is formed gives useful information regarding the nitrogen supplying capacity of the soil. The determination of potentially available nitrogen of soils is also attempted by carrying out chemical decomposition of organic matter. Truog's (92) alkali permanganate oxidisable nitrogen determination and Purvis and Leo's (73) potentially available nitrogen determinations are two important attempts in this regard. The success of such chemical methods largely depends on their ability to extract the right amount of soil nitrogen that will correlate with the actual amount of nitrogen taken up by the crop.

In Manitoba, information regarding the amounts of nitrate nitrogen accumulated in the top two feet of the soil profile is used for nitrogen fertilizer recommendations.

This investigation was initiated to study the amounts of ammonium nitrogen present in the surface soils of Manitoba and their importance as a source of nitrogen for plants. In this following are the topics that are studied:

1. The evaluation of Potential Available Nitrogen (PAN) fraction of soils, determined according to the procedure suggested by Purvis and Leo (73), and the investigation regarding the nature and ease of transformation of PAN fraction and its importance as available nitrogen.

2. A similar study of the exchangeable ammonium nitrogen status of soils.

3. A study of the influence of calcium carbonate content of soil on the accumulation of ammonium nitrogen and on its uptake by the plants.

CHAPTER 2

LITERATURE REVIEW

The mineral form of nitrogen present in the soil root zone and the capacity of the soil to mineralize organic nitrogen present in the soil are two important factors that govern the nitrogen supply to a growing crop. Many methods have been developed to estimate the availability of soil nitrogen and these are discussed under headings of the soil nitrogen fraction which they estimate.

A. Total Soil Nitrogen and Organic Matter

Total nitrogen and organic matter of soils have for a long time been used as fertility indices of soils. They are important because they provide a measure of the substrate that undergoes decomposition during soil nitrogen mineralization. Fraps (42) found that the release of mineral nitrogen during incubation studies and in the field experiments was proportional to the total nitrogen content of soils, but these soils were of uniform type. Carpenter *et al.* (26) found a close significant relationship between the yield of wheat and total nitrogen content of the upper 12 inch layer of soil. In Missouri (50) total nitrogen data is being used in predicting fertilizer needs of soils. It is assumed that 1.25 per cent of the total nitrogen in clay and clay loam soils, 1.5 to 3.0 per cent of total nitrogen in silt loams, and 4 to 6 per cent of total nitrogen in sandy loams are mineralized during a cropping season. In Kansas (50) organic matter values are being used to predict nitrogen fertilizer needs of soils. Two per cent and less of organic matter is supposed to be an indication of low nitrogen availability. The use of total nitrogen and organic matter values for nitrogen fertilizer recommendations is limited. This is because total nitrogen and organic matter values represent inert and stable nitrogen substrates only a small fraction of which undergoes decomposition annually. Black (13) estimates it to be only 1 per cent to 2 per cent. The fraction that is mineralized may not be proportional to the total nitrogen content of soils. The mineralization is governed by factors such as temperature, moisture content, soil structure, aeration, pH, kind of organic matter, nutrient status of soil and microbial population etc., and so different soils having similar total nitrogen contents may have different rates of mineralization. Fraps and Sterges (43), working on different types of soils, came to similar conclusions but they attributed the mineralization differences to different soil physical conditions and soil reactions and maintained that mineralization of nitrogen primarily depends upon the amount of total nitrogen content of soils. Allison and Sterline (3) reinvestigated this problem and found that a close relationship exists between nitrogen mineralized during incubation under optimal conditions and total nitrogen. The correlation coefficient was found to be 0.7** to 0.8** which was significant at the 1 per cent level. This conclusion, as they pointed out, is true only for those soils which are of the same type with uniform climatic conditions and topography. Many workers have shown beyond doubt that this relation breaks down when different types of soils are considered, as they found that correlations existing between total nitrogen and nitrogen uptake by plants is very low and non-significant (3, 48, 59, 69, 89). Therefore, in spite of the general positive relationship existing between total nitrogen and organic matter values and availability of soil nitrogen, total nitrogen and organic matter by themselves, do not give a reliable indication of available nitrogen.

B. Mineral Nitrogen

Soil mineral nitrogen (nitrate nitrogen and ammonium nitrogen) constitutes the bulk of nitrogen that is present in the available form at a given moment, but they usually sum up to only a fraction of the nitrogen that will be at the disposal of the growing crop. Moreover, the mineral nitrogen content of the soil at any given moment does not reflect the mineralizing power of the soil, because the latter is influenced by factors such as drainage, aeration, pH, climatic conditions, and cultivation practices. Nitrate nitrogen, in well drained soils, may get lost due to leaching, or may get refixed in the form of organic matter due to the presence of fresh plant residues. In those soils wherein conditions are favourable for denitrification, nitrate nitrogen may get lost in gaseous form as denitrifiers use nitrate ion as a hydrogen acceptor. Ammonium nitrogen is an intermediate product during mineralization, and is usually nitrified immediately. However, ammonium nitrogen accumulates in those soils in which conditions are not favourable for nitrification. Ammonium nitrogen in soils is present mainly as the exchangeable ammonium cation on the soil exchange complex. Hence, it may not suffer leaching loss as much as nitrate nitrogen does, but it may get fixed in a difficultly exchangeable position in the crystal lattices of clay minerals such as illite, vermiculite, and chlorite, in the same way as potassium ions are fixed (3, 4, 5, 6, 9, 17, 97, 100). Only a fraction of such fixed ammonium is available for nitrification and plant uptake. It may also get fixed by reaction with lignin during humification (11). In alkaline and neutral soils, it may get lost due to volatilization; drying accelerates such gaseous loss (56, 58, 63, 95). Thus, the accumulation of mineral nitrogen in soils is low and variable, and it is generally regarded that mineral nitrogen values do not reflect nitrogen supplying capacity of soils.

Nitrate Nitrogen

As nitrate nitrogen is the form of nitrogen that is readily absorbed by plants, earlier agriculturists tried to determine needs for fertilization by analysis of the soils for nitrate nitrogen content. In case of nitrate rich soils in which nitrate nitrogen is not lost due to leaching or any other means, it may provide useful information for making fertilizer recommendations. Peterson *et al.* (69), working on Wisconsin soils, obtained good correlation between soil nitrate nitrogen content and nitrogen uptake by the first crop of tobacco in a greenhouse experiment. The correlation coefficient obtained was 0.97^{**} and was significant at 1 per cent level of probability. A lower correlation was obtained when nitrate nitrogen was compared to the nitrogen uptake by the second crop. Soper and Huang (80), working on Red River and Lakeland soils, found that in these imperfectly to poorly drained soils, considerable amounts of nitrate nitrogen, ranging from 15 pounds to 105 pounds per acre, accumulate in the soil profile to the 4 foot depth and this can be utilized by a growing crop. They found a highly significant correlation between percentage yield of barley and nitrate nitrogen content in the soil profile to the 4 foot depth. The correlation coefficient obtained was 0.95^{**}, and was significant at 1 per cent level of probability. At present, the soil testing programme of Manitoba uses the nitrate nitrogen content of the 2 foot depth for making nitrogen fertilizer recommendations.

Ammonium Nitrogen

Ammonium content of the soil is neglected and is rarely considered as a source of nitrogen for plants. However the ready absorption of ammonium nitrogen and utilization by plants has been shown by many workers. Hutchinson and Miller (49) showed that agricultural plants can take up ammonia with ease and produce normal growth when ammonium salts were the only nitrogen source, and under conditions wherein the possibility of nitrification of them was excluded. Clark and Shive (28), and Davidson and Shive (34) reported that tomato plants and peach trees, in culture experiments, absorb ammonia preferentially at pH 6 and 7, and the rate of absorbtion of ammonia by these plants was higher than the rate at which nitrates were absorbed. Schreven (79) has recently reported that the pioneer vegetation of the soil polders recently reclaimed from Lake Ijssel in The Netherlands was found to absorb all exchangeable ammonia that is present in the soil profile up to the depth of 80 cm. within two years. Swezey and Turner (89) report that the addition of 2-chloro-6 (Trichloromethyl)-pyridine, which inhibits (44) the conversion of ammonia to nitrate, to ammonium fertilizers (0.5 to 2 per cent of N fertilizers), increased the efficiency of these fertilizers, producing improved growth of cotton and sugar beets. Thus, there is little doubt regarding the utilization of ammonia by plants. Moreover, ammonia in the soil is readily converted to nitrates and made available to plants. Lees and Quastel (60) have shown that the absorption of ammonium on the soil exchange complex facilitates nitrification rather than hindering it. The main discouraging fact about the study of ammonium nitrogen in the soil as a source of nitrogen for plants is that its accumulation in the soil is very small as it may readily get nitrified, or it may get fixed in clay mineral crystal lattices, and in the humus fraction of the organic matter by reacting with lignin. However, ammonium nitrogen may accumulate in those soils where conditions are favourable for ammonification, but do not permit vigorous nitrification. Grassland soils, due to their high organic matter content and poor aeration, may have conditions more favourable for ammonification, resulting in an accumulation of ammonia. Soulides and Clark (81) reported that acidic grassland soils retained ammonia as much as 27.7 to 80.9 P.P.M., and they attributed this retention capacity of these grassland soils to their poor aeration and to the secretion of bacteriostatic substances by the grass roots. MacLean and Robinson (61) found North Wales soils to contain 10 to 40 P.P.M. of exchangeable ammonia and some fertile soils, they reported, contained as high as 142 to 229 P.P.M. In forest soils, like grey wooded and podzols, ammonification is the predominant process of nitrogen mineralization , because these soils usually have acidic pH's and mor type of organic matter with a lesser degree of humification. Cork (32,33) working on Ontario podzols found that in these forest soils mineralization of nitrogen is slow because these soils have poor microbial populations. They have also noticed that ammonification is the more predominant process of nitrogen mineralization in these soils. Stojanovic and Broadbent (87) have shown that at low temperatures ammonification is permitted but nitrification is inhibited. They noticed that ammonification is significantly prevalent at as low a temperature as 5°C, and the rate of formation of ammonia during incubation at 10°C is almost two times that of 5°C. Such low temperatures prevail in soils at the beginning of spring, hence ammonia may form and accumulate in soils at the beginning of spring.

It was MacLean and Robinson (61) who recognized that ammonia in soils exists mainly as an exchangeable cation on the soil exchange complex, and they determined it by displacing it with ammonium ions by leaching soil with 15 per cent sodium chloride solution. Many modifications of this method have been adopted. Bremner and Shaw (18) extracted soils with potassium sulphate solution acidified to pH's of 1.0 to 1.5 with sulphuric acid. Later they determined exchangeable ammonia by using 2N KCl solution as the extractant. Stojanvoic and Broadbent (86) used sodium acetate solution acidified with acetic acid to pH 4.8 and 1 N KCl acidified with HCl to a pH of 1 as extracting solutions, for extracting ammonia added to the soils. Ammonia may also exist in soils as fixed ammonia, being held in difficulty exchangeable positions within the clay mineral lattices in a position similar to K . Only a fraction of such fixed ammonia is immediately available for nitrification or direct uptake by plants. This is evident from works of Allison and coworkers (4,5,6), Bower (17), and Auxley and Legg (9) and many others. But very little work has been done to evaluate soil ammonia as a source of nitrogen for a growing crop.

C. Potentially Available Nitrogen

Only a very small fraction of the soil organic nitrogen complex which is otherwise stable and resistant to microbial decomposition, undergoes mineralization and will be made available to a growing crop. This fraction is referred to as potentially available nitrogen. Tyurin and Konova (92) recognized the existance of such an active fraction of organic matter that is susceptible for microbial decomposition and they tried to extract it by hydrolysing the organic matter with dilute H_2SO_4. Recently Stewart et al. (85) noted such a fraction in their acid soluble nondistillable hydrolysate of the organic matter. Few chemical and microbiological methods have been evolved to estimate such a fraction. These methods are supposed to estimate nitrogen supplying power of soils to growing crops, hence the success of such methods depends on whether or not their values correlate well with nitrogen uptake by crops.

The incubation method is an important microbiological method which involves, essentially, the mineralization of soil nitrogen under controlled optimal conditions. During incubation, the active fraction of the organic matter is mineralized and the mineral form of nitrogen that is accumulated during a certain interval of time, gives a measure of nitrogen supplying power of soils. Different workers have handled this method in different ways and so there is a lot of variation in detail. Varying amounts of soil from 10 gms. to 300 gms. have been employed for incubation. Fitts et al. (41) have shown that 10 to 25 gms. of soils give nitrification results comparable to those obtained by using 100 gms. of soils.

Generally, soils are taken immediately after air drying for incubation. However air drying and storing was found to increase nitrifying rate due to the partial sterilization effect. Birch (12) found that for a given soil, mineralization of carbon and nitrogen is a function of the logarithm of time over which soils were stored in the air dry state prior to incubation. Therefore, Clement and Williams (30) preferred to store soil samples in a frozen condition at -15°C. Eagle et al. (35) stored samples in a moist state at 10°C to reduce fluctuations due to air drying and storing. They also hold the opinion that this also minimizes the variation due to different dates of sampling.

To improve aeration, Kresge and Markle (59) mixed the soil with an equal quantity of quartz sand. Stanford and Hanway (83) and Kresge and Markle (59) added lime to bring the soil pH to neutrality and potassium and phosphate salts so that their deficiencies may not form limiting factors for mineralization. Allison and Sterline (3) innoculated the soil with the infusion of a fertile soil so that there will be the necessary microbial population to carry out mineralization. The main idea behind these various pretreatments of soils before incubation, is to remove limiting factors and to create uniform optimal conditions during incubation so that results can be compared. Harmsen and Van Schreven (48) feel that these treatments mask true characteristics of soil and results sometimes are misleading. Earlier workers got as much as 2 per cent to 25 per cent of the total organic nitrogen being mineralized during a few weeks incubation, whereas in fields only 1 or 2 per cent gets mineralized annually. Now the tendency is to control only those factors such as aeration, moisture and temperature at optimal levels so that the incubation method will be uniform for all soils and characteristics of soils are not much altered. Different workers have employed different periods of incubation. Bogdonov (14) used 24 hours incubation period. Fitts et al.(40) preferred 3 weeks incubation period. Kresge and Markle (59) employed 12 weeks incubation. Stanford and Hanway (83), Hanway and Dumenil (47), Synghal et al. (89), Eagle and Mathews (35) and Cook et al. (31) have shown that nitrates accumulated for two weeks incubation at temperature of 30 to 35°C correlated more closely with nitrogen uptake by plants than 4 to 6 weeks incubation results do. The commonly employed method of incubation is that of Stanford and Hanway (83).

The popularity of the incubation is due to its being the only reliable method to determine availability of the soil nitrogen. It has the advantage of being less artificial and simulates the natural process of mineralization. As far back as 1900, Bogdonov (14) used this method successfully and found that the mineral nitrogen that is accumulated after 24 hours of incubation at 30°C correlated highly with the yields of crops. Pritchet et al. (79) showed that the yields of wheat and oats, grown in unfertilized plots were directly related to the quantity of nitrogen mineralized during three weeks incubation at 30°C, and they concluded that a regression equation relating response of oats to nitrogen fertilization, representing several years data, can be used for nitrogen fertilizer recommendations. Fitts et al. (40) found that a highly significant correlation exists between nitrification rate and nitrogen uptake by the crop and concluded that profitable yields of corn can be obtained by applying 40 to 60 pounds of N per acre only on those soils which accumulate less than 40 P.P.M. of nitrate nitrogen after three weeks incubation at 30°C. Hanway and Dumenil (47), by analyzing data of large numbers of field experiments, came to the conclusion that the increase in yield due to the application of nitrogen fertilizer is directly related to the amount of nitrate nitrogen accumulated during two weeks incubation at 30°C, and they formulated as follows.

$$\text{Log. } Y = \text{Log. } 104\ (1-10^{-0.003525X}) - 0.0098B_1$$

where Y is bushels per acre increase in yield to be expected with an application of X pounds of nitrogen fertilizer per acre if B_1 is the amount of the nitrate nitrogen accumulated during two weeks incubation of the soil at 30°C. Munson and Stanford (54) obtained 'N' value by extrapolating a linear relationship that was found to exist between the amount of nitrogen fertilizer added and nitrogen uptake by the crop grown. The 'N' values for soils reflect the amount of nitrogen the soil supplied to the crop because these values correlated highly significantly with the nitrogen uptake by the crop in check treatments. The correlation coefficient was 0.993** and was significant at the 1 per cent of probability. They noticed that these 'N' values correlated, among soil tests they employed, best with nitrate nitrogen accumulated during two weeks incubation of soils at 30°C. Cook et al. (31) working on some soils of Saskatchewan obtained a high positive correlation between nitrogen uptake and two weeks incubation nitrate nitrogen. In stubble fields yield ratios, which are measures of response of a crop to fertilization, were correlated highly with incubation nitrate nitrogen values of these soils, the correlation coefficient being 0.846.** Works of Eagle and Matthews (35), Synghal et al. (89) and Soper and Huang (73) reveal the usefulness of the two weeks incubation nitrate nitrogen values for predicting nitrogen fertilizer needs of soils.

In spite of the superiority of this method it is not infallible. The serious draw back of this method is that it is a microbiological method and hence is quite sensitive to variables such as moisture content, pH, and other nutrient levels in soils, etc. Incubation nitrate nitrogen values of soils may vary depending upon their date of sampling, handling of samples, pretreatments of samples, and cultivation practices. And so, as Harmsen and Van Shreven (48) point out, one should consider all these factors while interpreting incubation mineral nitrogen results. Incubation results, generally, are at best comparable, in case of soils of the same types and they suffer limitations when different types of soils are compared as different types of soils need different conditions and treatments for the necessary mineralization to take place. It is also difficult to maintain the variables of soils such as moisture and nutrient levels and pH, at particular constant values throughout the incubation experiment as they will progressively change with the time. Moreover this method, despite the recent simplification by Fitts et al. (41) remains time consuming and is not easily adaptable for routine soil testing. In spite of these short-comings this method seems to be most reliable for determining the nitrogen supplying power of soils.

There are other indirect microbiological methods for evaluating available and availability of nitrogen. These methods measure the increase in activity or in population of the test organism in response to the available nitrogen in the soil during incubation. In these methods test micro-organisms are supplied all the required nutrients except nitrogen so that their growth is limited by nitrogen, and growth response will be a measure of available nitrogen. Richer and Holben (74) found a highly significant correlation between nitrifying capacities of soils and the amount of carbon dioxide produced during 24 hours incubation of soil with yeast. Peterson et al. (69) incubated soils with Aspergillus niger with all the required nutrients supplied except nitrogen and an increase in the weight of this fungus after incubation was taken as an index of available nitrogen. These values, they found, correlated significantly with nitrogen uptake by the first and second crops of tobacco, whereas nitrate nitrogen values failed to correlate with nitrogen uptake by the second crop. Boswel et al. (16) used Pseudomonas Aeruginosa as a test organism and the production of pigment pyocyanin was used as a measure of available nitrogen and they found highly significant negative correlation between the amount of pycocynin produced and the nitrifying power of soils.

Chemical Methods

Chemical methods usually involve partial oxidation or hydrolytic degradation of soil organic matter whereby the less stable nitrogen fraction of the soil organic matter is liberated. This chemically less stable fraction is likely to be more susceptible to microbial degradation. Tyurin and Kononova (92) determined such a nitrogen fraction by subjecting soil organic matter to dilute sulphuric acid hydrolysis. These values were successfully used to predict nitrogen needs of soils. Truog (93) developed a method of determining available nitrogen. In this method soil organic matter was subjected to partial oxidative degradation by treating soil with 5 per cent $KMnO_4$ and 3 per cent NaOH solution. Kresge and Markle (59) evaluated this fraction and found it to represent a stable fraction. It took 12 weeks of incubation under optimal conditions for the amount of soil nitrogen equivalent to this available nitrogen, to mineralize. They also obtained a very low correlation between response of crop to nitrogen fertilizer and these alkali permanganate available nitrogen values. Munson and Stanford (64) reported a very low correlation between 'N' values and these available nitrogen values. Soper and Huang (80) obtained a low correlation coefficient of 0.69**, significant at 5 per cent level of probability, between per cent yield and these alkaline permanganate available nitrogen values. Peterson _et al._ (69) tried to correlate nitrogen uptake by a tobacco crop with the amounts of ammonium nitrogen extracted from the soil by 0.1N,4N,5N, and 18 N sulphuric acid solutions, and had some success with those nitrogen values, obtained using 0.1N sulphuric acid as an extractant. Purvis and Leo (73) developed a method for the estimation of what they call potentially available nitrogen in soil. They treated the soil with very dilute sulphuric acid, hydrolysis was immediately stopped by drying on a steam bath. The liberated ammonium nitrogen was extracted with water and was determined colorimetrically after Nesslerisation. They obtained a highly significant correlation (r.0978**) between nitrogen uptake and potentially available nitrogen. Boswel et al. (16) obtained a highly significant correlation between PAN values and nitrifying capacities of 30 soils, with samples selected from Georgia, Iowa, New Jersey and Pennsylvania. Soper and Huang (80) working with Manitoba soils obtained a highly significant correlation coefficient 0.84** between PAN values and per cent yields in a field experiment. Huang (51) also noticed that PAN values are comparable with values of nitrate nitrogen accumulated during two weeks incubation at 30°C. Hence PAN values seem to be meaningful.

CHAPTER 3

METHODS AND MATERIALS

A. Determination of pH of Soils

Determination of pH of soils was carried out using a saturated paste. The method described by Atkinson et al. (8) was used.

B. Determination of $CaCO_3$ in Soils

The method used is the modification of the one given by Adams (1). One gm. of oven dried soil (1 mm.) was digested with 60 ml. of 1:10 HCl for 15 minutes. The carbon dioxide evolved was drawn through traps of concentrated Sulphuric Acid and anhydrous $CaCl_2$. Thus dried carbon dioxide was finally absorbed by ascarite in a pre-weighed Nesbitt tube.

C. Determination of Organic Matter in Soils

The method described by Peech et al. (62) was used.

D. Determination of Potentially Available Nitrogen (PAN)

The method adopted is a modification of the one suggested by Purvis and Leo (73). One gm. of air dried soil (1 mm.) was treated with 2 ml. of dilute sulphuric acid (2:1000) and was then dried on a steem bath for 45 minutes. Then the soil was extracted with distill water and was filtered into a 100 ml. volumetric flask, then 2 ml. of 10 per cent sodium potassium tartarate solution was added to prevent interference of ions such as

Ca^{++} and Mg^{++}. Ammonium nitrogen extracted was colorimetrically determined after Nesslerisation.

E. Incubation of Soils

The method used for incubation of soils is as follows: 30 gms. of air dried soil (2 mm.), in triplicate were placed in 50 ml. beakers and were wetted to their field capacities and then were incubated at 30°C for the period required.[1] During incubation soils were wetted to their field capacities twice a week. After incubation soils were dried at 80°C for about three hours or more and were ground to mix thoroughly and nitrate nitrogen in these soils were determined by the colorimetric Phenol disulphonic acid method as modified by Harper (52).

This method of incubation has two advantages. The soil characteristics are least disturbed as pretreatments of soils that were used to create optimal conditions for nitrifications are avoided. Another advantage is that, as soils are not treated, the changes in PAN values due to incubation of soil can be followed by determining PAN values in the air dried incubated soils.

F. Determination of Exchangeable Ammonium Nitrogen in Soils

Exchangeable ammonium nitrogen of soils were determined according to the method described by Jackson (54).

Fifty gms. of air dried soil (2 mm.) was shaken with acidified 10 per cent NaCl solution (pH 2.5) for an hour, and was filtered in Buckner funnel using suction. The soil was further washed with sodium chloride solution and the washings are made up to 250 ml. From this an aliquot of 15 ml. was put in a 100 ml. flask and was then diluted

1 "Incubation nitrate nitrogen" in this thesis usually refers to the the amount of nitrate nitrogen accumulated during two weeks of incubation of the soil.

to 90 ml. with distilled water. To this, 2 ml. of sodium potassium tartarate solution (10 per cent) was added and ammonium nitrogen was determined colorimetrically after Nesslerization.

G. Determination of Nitrite Nitrogen in Soils

The adopted method for the determination of nitrite nitrogen in soils is essentially the same as the one described by Prince (71), the only modification being made was that ethylene diamine hydrochloride was used as an indicator instead of α-naphthylamine.

CHAPTER 4

AN EVALUATION OF PURVIS AND LEO'S METHOD OF DETERMINING POTENTIALLY AVAILABLE NITROGEN (PAN)

Purvis and Leo (73) have developed a rapid method for determining what they call potentially available nitrogen (PAN). This method involves partial hydrolysis of the soil organic nitrogen fraction by treating a soil with very dilute sulphuric acid and then stopping hydrolysis by drying the soil on a steam bath. The liberated ammonium nitrogen is then extracted with distilled water and is quantitatively determined colorimetrically after Nesslerization. In a green house experiment, they showed that PAN values of soils correlate highly significantly with the nitrogen uptake by plants and they found a correlation coefficient of 0.98^{**} between PAN values and yields of wheat grown in the green house experiment. Boswel et al. (16) also obtained a significant correlation between PAN values and nitrification values for two weeks incubation at 30°C, of thirty different soils of Iowa, New Jersey, Pennsylvania and Georgia states. Soper and Huang (80), working with some Manitoba soils obtained a highly significant correlation ($r = 0.84^{**}$) between yield ratio and PAN values. Huang (51) also noticed that PAN values are generally comparable with nitrate nitrogen, accumulated during incubation of the soils at 30°C for two weeks. This is interesting because, in past, many workers such as Stanford and Hanway (83), Hanway and

Dumenil (47), Synghal et al.(89), Eagle and Matthews (35) and Cook et al. (31) have shown that soil nitrogen availability indices such as nitrogen uptake by plants, "N" values, and response of crop to nitrogen fertilization, correlate highly with nitrate nitrogen accumulated during a two week incubation of soils at 30°C. The PAN determination method is a simple and rapid chemical method, hence has an advantage over incubation tests. Therefore, the method of PAN determination showed the immense possibility of developing into a soil test for available nitrogen. An attempt was made to test the utility of this method for determining the nitrogen supplying capacities of different types of Manitoba soils.

A. PRELIMINARY STUDY OF THE METHOD OF PAN DETERMINATION

After a few attempts to determine PAN according to the method suggested by Purvis and Leo (73), it became evident that this method had to be modified to prevent interference of ions such as Ca^{++} and Mg^{++}, which are present in most of the soils. These ions, in excess, cause cloudiness by reacting with Nessler's reagent and upset the colorimetric readings. The method adopted is given on page 18.

In this procedure, extraction of ammonium nitrogen seems to be affected in two ways. One is by the effect of the dilute sulphuric acid used and the other one is by the effect of heat of the steam drying of the acid treated soil. It is quite possible that the effect of these two agents, may not be the same on different types of soils. The degree and extent of the probable hydrolytic action of the acid in calcareous and noncalcareous soils may be different, because free carbonate of calcareous soils may neutralize the acid and render it ineffective. In Grey Wooded soils, because of the lesser degree of humification and of acid nature of their organic matter the hydrolytic action of the dilute acid used in these soils may be much more pronounced than that in Black soils. The following experiment was conducted to examine the above points.

(1) Material and Method

Ten soils of different genetic type with varying calcium carbonate contents were selected for the study. The locations and genetic types of the soils and some characteristics such as pH, organic matter content and calcium carbonate content, are given in Table 1, on page 26.

These soils were subjected to extraction by the following procedures:

1. The same as in the method of PAN determination given on page 18.

2. Two ml. of distilled water was added to 1 gm. of the soil and was dried on steam bath for 45 minutes. The rest of the procedure is the same as that of PAN determination.

3. Two ml. of dilute H_2SO_4 was added to 1 gm. of soil and was allowed to stand for 45 minutes on the bench instead of steam drying. The rest of the procedure is same as that of PAN determination.

4. Two ml. of distilled water was added and was allowed to stand for 45 minutes. The rest of the procedure is the same as that of PAN determination.

The second and third procedures were devised to ascertain the contribution of the action of dilute acid alone, and of the heat alone respectively, to the amount of ammonium nitrogen extracted in the determination of PAN. The fourth procedure determines the water soluble ammonium nitrogen in the soils.

2. Results and Discussion

The results of this experiment are given in Table 1 on page 26.

There is little or no water soluble ammonium nitrogen in these soils as the fourth method extracts no ammonium nitrogen in these soils. A substantial amount of ammonium nitrogen is extracted in the third procedure. In this procedure the main mechanism of release of ammonium is through the action of heat of steam drying as water by itself did not extract much ammonium nitrogen in these soils. Therefore, the drying of the acid treated soils on the steam bath, during the PAN determination, does not just accomplish the stopping of acid hydrolysis of organic nitrogen fraction, but by itself releases a substantial amount of ammonium nitrogen from the soil. The second procedure, which uses dilute acid alone for extraction, resulted in the extraction of substantial amounts of ammonium nitrogen from all the soils tested. Hence in the determination of PAN of soils, the dilute acid and heat of steam drying, are both responsible for the amount of ammonium nitrogen extracted. The action of heat of steam drying may be that of release of exchangeable ammonium from the exchange complex of the soils and also release of ammonium nitrogen through oxidative decomposition of the organic nitrogen fraction of soils. The action of dilute acid may be that of releasing exchangeable ammonium through exchange reaction and that of releasing ammonium nitrogen by the hydrolysis of organic nitrogen fraction is the soils. However the acid hydrolysis may not be the main factor in calcareous soils as the acid used is very dilute and may be neutralized by free carbonates. A study of results of non-calcareous soils reveal that the PAN of these soils are almost equal to the sum of the ammonium nitrogen extracted in second and third procedures. This suggests that the PAN of these non-calcareous soils is mostly exchangeable ammonium and ammonium nitrogen released due to acid hydrolysis and/or oxidative decomposition of organic nitrogen fraction of soils. In calcareous soils, the amounts of ammonium nitrogen extracted in the second and third procedures are similar and are comparable with the PAN values of these soils. It suggests that all three procedures may be estimating mainly the same fraction of ammonium nitrogen of soils. This fraction is possibly exchangeable ammonium as acid hydrolysis of orgnic nitrogen complex may not be of much consequence in the calcareous soils. However, the release of ammonium nitrogen due to oxidative decomposition of organic nitrogen fraction due to heat of steam drying may also be included in the PAN of these soils.

In general terms, the PAN of non-calcareous soils included both exchangeable ammonium of soils and ammonium nitrogen released due to the acid hydrolysis of organic nitrogen, whereas the PAN of the calcareous soils includes mainly the exchangeable ammonium of the soils. The PAN may also include ammonium nitrogen released due to oxidative decomposition of organic nitrogen by the heat of steam drying. These points have to be considered when interpreting the PAN values of different types of soils.

TABLE NO. 1

AMMONIUM NITROGEN EXTRACTED BY DIFFERENT MODIFIED PAN METHODS

Soils	Genetic Types	pH	O.M%	$CaCO_3$%	I NH_4-N P.P.M.	II NH_4-N P.P.M.	III NH_4-N P.P.M.	IV NH_4-N P.P.M.
Waitville II	Grey Wooded	6.9	3.2	0.0	45.24	23.78	20.88	0.0
Waitville I	Grey Wooded	6.8	4.1	0.1	61.48	20.88	27.26	0.0
Waitville V	Grey Wooded	7.0	2.9	0.5	51.62	22.66	19.72	0.0
Wellwood III	Black	5.9	8.6	0.0	42.34	29.14	15.66	0.0
Wellwood I	Black	6.0	5.1	0.6	27.12	19.72	10.44	0.0
Portage III	Orthic Black	7.6	10.6	1.3	40.50	40.30	40.50	-
Altona III	Rego Black	8.0	5.6	4.7	20.40	18.56	14.50	0.0
Lakeland II	Cal. Rego. Black	7.9	8.4	13.55	29.58	27.26	24.94	4.06
Lakeland I	Cal. Rego. Black	7.8	8.7	17.76	29.58	33.64	26.68	0.0
Balmoral I	Cal. Meadow	7.8	12.4	33.9	40.26	38.72	39.88	0.0
Average of Non-careous soils		6.4	4.8	0.2	45.50	23.20	18.70	-
Average of Calcareous soils		7.8	9.1	14.2	32.10	31.70	29.30	-

I NH_4-N extracted by PAN method.

II NH_4-N extracted by a modified PAN method in which 2 ml. of distilled water is used in place of dilute acid and the rest of the procedure is the same as that of PAN.

III NH_4-N extracted by a modified PAN method in which the drying of acid treated soil on steam bath is omitted, instead it is allowed to stand for 45 minutes.

IV Water soluble ammonium nitrogen.

B. AN EVALUATION OF THE PAN STATUS OF SOILS OF MANITOBA

Forty-five Manitoba soils, representing agriculturally important soil associations, belonging to major soil zones namely:

1. Black soil zone.
2. Degraded Black or Dark Grey soil zone.
3. High Lime Dark grey and Black soil zone.
4. Grey wooded soil zone.

were selected for the study. The approximate locations at which they were sampled are shown in the map in Figure 1 on page 32.

The Black soil zone is the most important soil zone in the province, being the major and agriculturally important zone. These soils were developed mainly under the lush growth of tall prairie grasses. The Description of a typical profile is given below:

Horizons

A. Thick, very dark gray to black A_h horizon, high in organic matter, granular, friable, slightly acid to alkaline.

B. May be absent or weakly to moderately well developed, with little or no illuvial clay, brownish in colour, granular to sub-angular blocky aggregates may cohere into column-like structure, neutral to mildly alkaline.

C. Whiteish lime carbonate layer that grades into a relatively unaltered parent material.

These soils mainly occur in the south-western part of Manitoba, and were developed on mixed, sorted, and transported material of glacial origin. Those in the Red River Valley (2a and 2b of Fig. 1) are developed on fine textured lacustrine and medium to coarse textured deltaic deposits, while those in the western uplands (1 and 2c of Fig. 1) are developed mainly on medium textured glacial till of mixed shale, limestone and granitic rocks. The drainage in the profiles varies from well to poor depending upon local relief and texture of the soils. In the south-western part of the zone (1 of Fig. 1), the soils tend to be shallower. The Black soils are generally fertile soils, and are agriculturally the most important soils in Manitoba.

The Degraded Black or Dark Grey soils were first developed as Black soils under grass vegetation, but with the invasion of trees, soil forming processes have been modified, and have resulted in Dark Grey soils. A brief description of the typical profile is as follows:

Horizons

L-H. Thin leaf and humus layers, neutral in reaction.

A. Grey to dark grey horizon Ahe, moderately high in organic matter, granular, friable, slightly acid to neutral in reaction.

B. Moderately well developed, brownish horizon, blocky to subangular blocky structure (Bt), slightly acid in AB horizon and mildly alkaline in the BC.

C. Whiteish lime carbonate layer grading into a relatively unaltered parent material.

The Dark Grey soils are transitional soils between Black and Grey Wooded soils. These are fairly fertile soils as they have not been degraded to impoverishment due to leaching. These soils occur in the Western Uplands and Manitoba Lowlands (3 and 4 in Fig. 1) in the area of better precipitation effectivity than Black soils. These soils are also agriculturally important soils.

The Grey Wooded soils in Manitoba are found chiefly at higher altitudes in the Western Uplands (5 of Fig. 1), and in the wooded local subhumid region of the Manitoba Lowlands (6b and 7 in Fig. 1). These soils have developed under dominantly mixed deciduous and coniferous forest, and under cooler and more humid conditions than Black and Dark Grey soils. A brief description of the typical soil profile is given below.

Horizons

L-H. Leaf and humus layers, slightly acid.

A. Grey to dark grey layer Ah or Ahe, moderately to slightly acid, underlain by light coloured leached Ae horizon, granular or platy, structureless, friable, moderately to slightly acid.

B. Well developed brownish, subangular to blocky, Bt; slightly acid in AB and Bt to mildly alkaline in BC horizon.

C. Whiteish lime carbonate layer grades into relatively unaltered parent material.

These soils are dominantly well drained. These are naturally poor soils with low organic matter and other plant nutrients being leached out of the profile. However, they can be built up into good agricultural soils, especially for mixed farming, by good management and cultivation practices.

The high lime Dark Grey and Black soils are found in the West-Lake, and in the Interlake areas (6a and 6b in Fig. 1). These are predominantly developed under woods, but on highly calcareous very stony glacial till. If not for the highly calcareous nature of their parent materials, these soils would have been developed mainly as Grey Wooded soils. These soils have a shallow black surface (Ah) horizons. As we go towards the north, where conditions are more humid, soils show evidence of degradation as a whitish-grey leached horizon appears below the leaf mat. This leached horizon may be only one or two inches in thickness, and is underlain by a more compact B horizon. Surface horizons may develop a slightly acidic reaction, but lower horizons are neutral to alkaline in reaction. These soils are shallow; the A and B horizons together are often less than 12 inches in thickness. These soils can be, with good agricultural practices and management, developed into good farming soils for growing clover, alfalfa and barley.

In the present study, the Black soil zone is represented by the Portage, Red River, Altona, Wellwood, and Stockton associations. The degraded black or dark grey soil zone is represented by the Newdale and Erickson associations. The High Lime Dark Grey and Black soil zone is represented by the Lakeland Garson, and Balmoral associations. The associations of Waitville and Erickson are of the Grey Wooded soil zone. A brief description of these soil associations is given below, as it will be helpful in understanding the behaviour of the soils. A detailed description of these soil associations is given by Ehrlich et al. in soil reports (36, 37, 38, 39) and Pratt et al.(70).

A. Almasippi Association:

These soils are predominently black soils and are developed on sandy deltaic and lacustrine deposits, underlain by a fine structured substrate, at about 10' below the surface. They are generally fine sandy loams, but, because of their fine textured substrate their drainage is

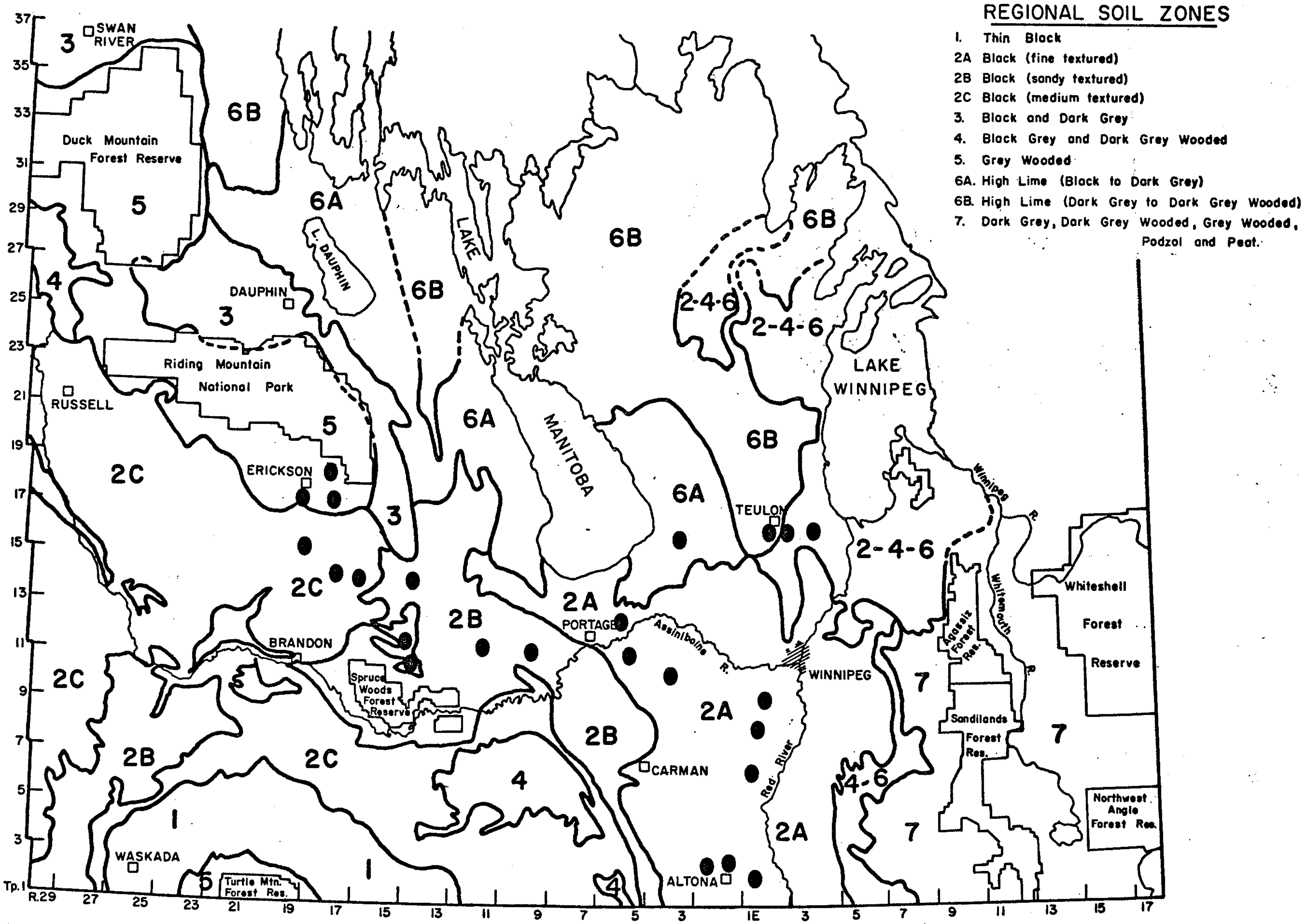

Fig.1 Distribution of Regional Soils in Southern Manitoba and Approximate Location of Sampling Sites

imperfect to poor. These soils are naturally low in fertility and have low moisture retention capacities.

B. Altona Association:

These are black soils developed on sandy to silty deltaic and lacustrine sediments. Surface soils have textures ranging from fine sandy loams to fine sandy clay loams. The topography is generally smooth or level. The drainage is good. These are highly fertile soils.

C. Balmoral Association:

This soil association consists of poorly drained Peaty carbonated Rego Humic Gleysols, developed on strongly calcareous, moderately fine textured deltaic sediments. The surface soil texture varies from clay to silty clay. Under virgin conditions these soils are covered by a thin peaty layer underlain by a dark Ah horizon. The cultivation has resulted in the mixing of the surface horizon with the calcareous parent material, hence the surface soils may contain large quantities of lime carbonate. These are poorly drained soils and may show saline characteristics.

D. Erickson Association:

The soils in this association are dominantly well drained, orthic dark grey types and are developed on boulder till of mixed composition, derived from shale, grantic and dolomitic rocky materials.

These soils are subjected to stronger leaching than the Newdale soils and are characterized by thin moderately well developed Ahe horizons. These are medium textured soils. The topography is irregular to moderately sloping. These soils have a relatively low organic matter content but have a good supply of plant nutrients.

E. Garson Association:

These soils are mainly miniature grey wooded soils, developed on strongly calcareous glacial till under forest vegetation. The soil profile is very shallow, seldom exceeding 8" in thickness. The surface texture varies from sandy loam to clay loam, but generally is clay loam. The cultivated soils have neutral to alkaline reactions and surface soils can contain considerable quantities of free carbonates. The topography is gently to greatly sloping. These soils are low in natural fertility because of their low organic matter content and shallow profile character.

F. Lakeland Association:

These are imperfectly drained, Gleyed carbonated Rego black soils developed on strongly calcareous deltaic deposits. The texture of surface soil ranges from clay loam to silty loam. The Topography is nearly level. The drainage is imperfect. The surface Ah horizon is alkaline in reaction and is calcareous. These soils are moderately good agricultural soils and have no major management problems, but are low in native available phosphorus.

G. Newdale Association:

These soils vary from orthic black to dark grey or degraded black soils. These are medium textured soils developed on boulder till of mixtured materials. The Topography is irregular and varies from gently sloping and nearly level to rough undulating. The internal drainage of the profile varies from poor to good. These soils are highly fertile having high organic matter contents, favourable medium texture and good moisture retention capacities.

H. Portage Association:

These soils are deep black soils developed on moderately calcareous, medium to fine textured, alluvial fan. This alluvial deposit is underlain by lacustrine sand which in turn is underlain by lacustrine clay. The texture of the surface varies from very sandy loam to silty clay. The Topography is generally smooth and gently sloping; but appears to be undulating in areas containing well developed level channels. The soil drainage is good. These are fertile and agriculturally important soils.

I. Red River Association:

These soils are dominantly Rego Humic Gleysols and Gleyed Rego black soils. These soilswere developed on weakly to moderately calcareous lacustrine clay sediments of the Lake Agassiz basin. The texture of the surface is clay. The Topography is level. The soil drainage is moderate to poor. These soils have favourable pHs, good reserve of organic matter and excellent water retention capacities. These soils are good agricultural soils with some management problems due to their heavy texture and poor drainage. Soils of this association have been developed under wet to very moist conditions and are slowly passing through conditions of poorly drained to better drained conditions, because of the installation of ditches since settlement.

J. Stockton Association:

These black soils are developed on deep sandy deltaic deposits. The surface texture of these soils varies from sand to fine sandy loam. The Topography is gently undulating. These are well drained soils. However, these soils have low organic matter content and are not very fertile. Their agricultural value is further limited by their susceptibility to wind erosion.

K. Waitville Association:

These are medium textured dark grey wooded to grey wooded soils, developed on boulder till. These soils have been strongly leached. The Topography is moderately sloping to hilly. These soils are slightly acidic to acidic in reaction and are low in organic matter content and other plant nutrients.

L. Wellwood Association:

These are black soils developed in medium textured lacustrine deposits, which normally overlie stratified sand. The texture of surface soils varies from sandy loam to clay loam. The Topography is generally level. Due to the high permiability of the soils, drainage is dominantly good.

Most of these soils were sampled during August and September, however, some were sampled in the spring. Surface soils up to the depth of 6" were transported in polyethelene bags and were air dried immediately in greenhouse and stored. Soils and their locations and associations to which they belong, are given in Table 2 on page 40.

METHOD OF INVESTIGATION

Many workers such as Stanford and Hanway (83), Hanway and Dumenil (47), Cook et al. (31) and Boswel et al. (16), have used nitrate nitrogen accumulated during two weeks incubation at 30°C as a reference test for nitrogen availability in soils and the results of different soil tests for nitrogen were compared with the incubation test values. In this study also, two weeks incubation nitrate nitrogen was used as a standard soil test for the determination of the nitrogen supplying capacity of the soil. The PAN values were statistically compared with incubation test values.

However, the incubation test was modified. The treatments used to improve conditions of soils for nitrification, such as pH, aeration, and nutrition status etc. were omitted, as these as Harmsen and Van Schreven (48) point out, mask the characteristics of soils. The incubations were carried out under optimal conditions of moisture and temperature. The details of this method are given on the page 19.

Other characteristics of soils such as pH, calcium carbonate content and organic matter contents were also determined according to the procedures on page 18 and their influence on PAN values of soils and incubation nitrate nitrogen were statistically assessed. The nitrate nitrogen accumulated during the two weeks incubation, is taken as the dependent variable and the other soil characteristics such as pH, $CaCO_3$ per cent, O.M per cent; and PAN as independent variable and inter-relationships between these variables were determined by running multiple correlations on these data. As definite trends were perceived in certain groups of soils, multiple correlation analysis was carried out on the data of these groups separately. The multiple regression analysis was carried out, taking incubation test nitrate nitrogen values as a dependent variable, and also taking PAN as a dependent variable and regression equations were obtained. These statistical analysis were carried out by using an IBM computer 1620.

RESULTS AND DISCUSSION

Results are presented in the Table No. 2 on page 40. A preliminary study of the PAN method suggested that free carbonates and kind of organic matter are two main factors that influence PAN values determined according to the procedure of Purvis and Leo. The soils were arranged in groups based on these two characteristics. Groups made are:

1. (Non-Calcareous) Grey Wooded Soils - mostly Grey Wooded soils have calcium carbonate contents less than 2 per cent.
2. Non-Calcareous Soils - Black and Dark Grey soils with less than 2 per cent of calcium carbonate.
3. Slightly Calcareous Soils - mostly Black and Dark Grey soils with calcium carbonate contents between 2 to 5 per cent.
4. Highly Calcareous Soils - these soils have calcium carbonate contents greater than 5 per cent.

Though such arbitrary groupings are not desirable and are of little value for drawing general conclusions because of the small population they involve, still certain characteristic trends can be perceived in these groups and they help to explain the results. The results of the multiple correlation run on the data is given on the pages 43 and 44. The results of the multiple correlation analysis, run on the data of soils arranged in above groups, are summarized on the same page so as to show how correlation coefficients vary in different groups of soils.

TABLE NO. 2

PAN AND OTHER CHARACTERISTICS OF SOILS OF DIFFERENT SOIL ZONES OF MANITOBA PROVINCE

Sl. No.	Soil Location and Genetic Class		pH	$CaCO_3$%	O.M.%	PAN PPM	Incubation NO_3-N PPM
Grey wooded soils (non-calcareous)							
1	Waitville I	Grey wooded	6.9	0.1	4.1	61.5	14.7
2	" II	" "	6.9	0.0	3.2	44.1	14.9
3	" III	" "	6.0	0.4	1.9	41.2	5.5
4	" IV	" "	6.4	0.1	3.7	61.3	24.7
5	" V	" "	7.0	0.5	2.9	49.9	11.4
6	" VI	Dark Grey wooded	6.5	0.7	7.3	37.1	26.8
7	Erickson I	Dark Grey	7.1	0.6	3.1	41.2	19.1
8	" II	" "	6.1	0.6	5.2	33.6	26.5
Non-calcareous Soils							
9	Portage I	Orth. Black	7.7	0.9	7.5	25.6	25.3
10	" II	" "	7.4	0.1	8.3	24.5	18.8
11	" III	" "	7.6	1.3	10.6	39.7	32.2
12	" IV	" "	7.5	0.1	8.6	112.0	91.6
13	" V	" "	7.3	0.6	7.3	78.8	83.9
14	Wellwood I	Orthic Black	6.0	0.6	5.1	26.68	18.7
15	" II	" "	6.5	0.4	5.6	23.8	23.8
16	" III	" "	5.9	0.0	8.6	41.28	43.3
17	" IV	" "	6.4	0.2	5.8	18.6	14.9
18	Redriver I	Rego Black	7.3	0.1	6.8	18.8	25.7
19	" II	" "	7.5	0.3	6.6	18.8	37.3

(continued)

Table No. 2 (continued)

Sl. No.		Soil Location and Genetic Class	pH	$CaCO_3$%	O.M.%	PAN PPM	Incubation NO_3-N PPM.
20 Redriver	III	Rego Black	6.6	0.0	6.4	100.8	108.6
21 Altona	I	" "	7.2	0.7	5.7	22.6	20.6
22 Almasippi	I	Black	7.7	1.7	3.5	10.4	12.7
23 "	II	"	7.1	0.3	3.7	35.1	21.3
24 Stockton	I	"	7.4	0.2	3.5	22.6	12.5
25 Newdale	I	Dark Grey	7.2	0.9	6.3	27.3	28.0
26 "	II	" "	7.2	0.6	10.0	37.8	22.3
27 "	III	" "	7.4	1.5	9.2	12.8	27.5
Slightly calcareous Soils							
28 Portage	VI	Orth. Black	7.8	2.3	4.3	47.0	63.7
29 Redriver	IV	Rego Black	7.3	3.9	7.5	72.4	115.5
30 Altona	II	Orth. Black	8.1	4.5	4.5	25.6	21.8
31 Altona	III	" "	8.0	4.7	5.6	20.2	25.8
32 Altona	IV	" "	7.8	3.3	3.9	2.3	20.3
33 Altona	V	" "	7.6	2.1	6.9	15.7	23.8
34 Altona	VI	" "	7.7	2.1	3.7	9.3	19.3
35 Garson	I	Orthic Greywood	7.4	3.5	1.9	10.4	14.8
36 Newdale	II	Dark Grey	7.7	2.2	7.1	11.0	25.1
Highly calcareous Soils							
37 Lakeland	I	Cal Rego Black	7.9	17.7	8.7	25.6	25.0
38 "	II	" " "	7.9	13.6	8.4	18.8	25.8
39 "	III	" " "	7.8	22.9	6.4	0.0	6.3
40 "	IV	" " "	7.8	29.2	3.8	0.0	6.2

(continued)

Table No. 2 (continued)

Sl. No.		Soil Location and Genetic Class	pH	$CaCO_3$%	O.M.%	PAN PPM.	Incubation NO_3-N PPM.
41 Lakeland	V	Cal. Rego Black	7.8	32.0	4.1	2.3	21.1
42 Lakeland	VI	" " "	7.8	15.4	4.7	4.1	28.3
43 Balmoral	I	Cal. Meadow	7.9	33.9	12.4	38.3	44.8
44 Plumridge	I	Orthic grey wooded	7.8	5.1	4.7	0.0	12.6
45 Garson	II	" " "	7.4	5.8	3.2	0.0	9.3

TABLE 3

CORRELATION
COEFFICIENTS BETWEEN pH, O.M%, $CaCO_3$%, PAN
AND INCUBATION NITRATE NITROGEN
OF FORTY-FIVE SOILS

	pH	$CaCO_3$%	O.M%	PAN	Incubation NO_3-N
pH	1	0.472**	0.141	-0.363*	0.029
$CaCO_3$%	0.472**	1	0.161	-0.357	-0.095
O.M%	0.141	0.161	1	0.205	0.379*
PAN	-0.363*	-0.357	0.205	1	0.707**
Incubation NO_3-N	0.029	0.095	0.379*	0.707**	1

Note: * significant at 5% level of probability
** significant at 1% level of probability

TABLE 4

CORRELATION COEFFICIENTS OF INCUBATION NO_3-N with pH, O.M%, PAN and $CaCO_3$% IN DIFFERENT GROUPS OF SOILS

Soil Groups	pH	$CaCO_3$%	O.M%	PAN
Grey wooded	-0.241	0.320	0.794**	-0.127
Non-calcareous Black and Dark Grey	-0.043	-0.361	0.214	0.940**
Slightly calcareous Black and Dark Grey	-0.471	0.116	0.483	0.971**
Highly Calcareous Black and Dark Grey	0.502	0.331	0.734*	0.852**

TABLE 5

CORRELATION COEFFICIENTS OF PAN WITH pH, O.M%, $CaCO_3$%, AND INCUBATION NO_3-N IN DIFFERENT GROUPS OF SOILS

Soil Groups	pH	$CaCO_3$%	O.M%	Incubation NO_3-N
Grey Wooded	0.143	-0.381	0.402	-0.127
Non-calcareous Black and Dark Grey	-0.087	-0.409	0.236	0.940**
Slightly Calcareous Black and Dark Grey	-0.317	0.236	0.399	0.972**
Highly calcareous Black and Dark Grey	0.532	0.328	0.947**	0.852**

Note:
* significant at 5% level of probability
** significant at 1% level of probability

In general, results show that a wide range of soils are represented in this investigation. pH values range from 6 to 8 whereas $CaCO_3$ per cent in these soils vary from nil to 34 per cent, and organic matter contents range from 2 per cent to 12 per cent. These soils also show a wide range of PAN values, varying from nil to 112 P.P.M. Most of the soils have PAN values within the range of 20 P.P.M. to 40 P.P.M. The two weeks incubation nitrate nitrogen of these soils varies from 6 P.P.M. to 115 P.P.M. In general, grey wooded soils have PAN values which are higher than their corresponding two weeks incubation nitrate nitrogen values, while in slightly calcareous and non-calcareous soils the difference between these values are less. The highly calcareous soils are conspicuous by their low PAN values and low incubation nitrate nitrogen values.

The statistical analysis of these results reveal that PAN values of these soils are significantly correlated with two weeks incubation nitrate nitrogen values. The correlation coefficient between them is 0.707** and is highly significant at the 1 per cent level. Purvis and Leo (73) obtained a higher correlation between PAN values and incubation nitrate nitrogen. Huang (50) obtained a higher correlation of 0.94** between PAN value and nitrifying powers of six soils he used in his field experiment. These higher correlation coefficient may be attributed to the fact that similar types of soils were used. Boswel et al. (16), working on 30 soils selected from Georgia, Iowa, New Jersey and Pennsylvania, obtained a correlation coefficient of 0.524** between PAN values and two weeks incubation nitrate nitrogen values.

A positive correlation exists between incubation two weeks nitrate nitrogen and organic matter contents of soils. The correlation coefficient between them is 0.379* and is significant at the 5 per cent level. But there is no significant correlation between organic matter contents of soils and their PAN values. The correlation coefficient is 0.205 and is not significant. Another fact to be noted is that PAN is significantly negatively correlated with calcium carbonate contents of the soils. The correlation coefficient is -0.357* and is significant at 5 per cent level. This reveals that PAN determinations are influenced by the calcium carbonate contents of the soils, as was suspected in the preliminary study of the PAN method.

The multiple regression analysis was carried out on this data, taking two weeks incubation nitrate nitrogen as the dependent variable and the other characteristics of soils such as pH, o.M per cent, $CaCO_3$ per cent, and PAN as independent variables. The following regression equation was obtained:

$$\text{Incubation } NO_3 - N = 11.47 \text{ pH} + 0.087 \; CaCO_3\% + 1.78 \; \text{O.M}\% + 0.79 \text{ PAN} - 88.45.$$

The multiple regression coefficient is 0.78** and is significant at the 1 per cent level of probability. A comparison of "t" values for the regression coefficients reveals that PAN is the most significant factor contributing to the relationship. This equation expresses the relationship between PAN and two weeks incubation nitrate nitrogen and also reveals the influence of pH, calcium carbonate content and organic matter content of the soils on this relationship. The multiple regression analysis carried out taking PAN as the dependent variable and pH, $CaCO_3$% and organic matter as independent variables yielded the following regression equation:

$$PAN = 3.1 \ O.M\% - 12.6 \ pH - 0.758 \ CaCO_3\% + 107.86$$

The multiple regression coefficient of the equation is 0.52** and is significant at 1 per cent level of probability. The comparison of the 't' values for the regression coefficients reveals that pH, organic matter per cent and $CaCO_3$% are all significant factors contributing to this relationship. This equation reveals how PAN is dependent on the other soil characteristics such as pH, and calcium carbonate content and organic matter content.

If we examine this data group wise in which they are divided, we notice some interesting features and characteristics trends of these groups.

The soils of the grey wooded soils group are non-calcareous, slightly acid to neutral in reaction and have low organic matter contents with a mean value of 3.8 per cent. These soils have PAN values ranging from 22 P.P.M. to 61 P.P.M. and incubation nitrate nitrogen varies from 11 P.P.M. to 26 P.P.M. The noteable feature of these soils is that PAN values are much higher than their two weeks incubation nitrate nitrogen. In these soils PAN values are not significantly correlated with their two weeks incubation nitrate nitrogen, as the correlation coefficient between them is -0.127 and is non-significant. The existence of negative correlation between PAN values and two weeks incubation nitrate nitrogen values in these grey wooded soils may be attributed to two reasons. The first possible reason is that in these soils, existing conditions, such as acid reaction and less humified organic matter and very low lime carbonate contents may be unfavourable for nitrification but may permit ammonification. This may cause an accumulation of ammonia in these soils giving high PAN values. Cork et al. (72, 36) have noticed that ammonification is prominent in forest soils. Another possible reason is that the method of PAN determination, may be extracting organic nitrogen which may not be immediately nitrifiable, as these soils contain less humified and easily hydrolysable organic matter. Thus, in grey wooded soils there is not positive relationship between PAN values and their two weeks incubation nitrate nitrogen values.

Non-calcareous black and dark soils are neutral in reaction and have high organic matter contents with a mean value of 7.0 per cent. The PAN values of soils of this group range from 12.8 P.P.M. to 112 P.P.M. with a mean value of 37.5 P.P.M. Incubation nitrate nitrogen of these soils vary from 14 P.P.M. to 108 P.P.M., the mean value being 36 P.P.M.

In this group of soils there is a highly significant correlation between PAN values and incubation nitrate nitrogen values. The correlation coefficient is 0.940**, and is significant at the 1 per cent level of probability.

Soils of the slightly calcareous group have a slightly alkaline reaction and have free carbonates. The mean values of $CaCO_3$% in these soils is 3.2 per cent. In these soils PAN values range from 2.3 P.P.M. to 79 P.P.M. the mean being 25 P.P.M. whereas incubation nitrate nitrogen values vary from 21 P.P.M. to 115 P.P.M., the mean being 37 P.P.M. Thus, these soils show higher nitrification than their corresponding PAN values. This may be due to the fact that they have a favourable pH for nitrification and enough lime carbonate to meet nutrient requirement of the microbial population of the soil and to act as a buffer to prevent the changing of pH towards the acid side during nitification. The statistical analysis of the data of this group shows the existence of a highly significant correlation between PAN values and incubation nitrate nitrogen values, the correlation coefficient being 0.972** significant at the 1 per cent level of probability.

The soils of the highly calcareous soils group are alkaline in reaction and have calcium carbonate contents ranging from 5 per cent to 34 per cent, the mean value being 19.6 per cent. These soils are fairly rich in organic matter, as the mean value of their organic matter content is 6.2 per cent. The striking feature of this group of soils is that these soils have low PAN values and low two weeks incubation nitrate nitrogen values, with the exception of those soils which are very high in organic matter. Greaves et al. (45) have shown the nitrification is inhibited by the presence of large amounts of calcium carbonate. Halverson and Caldwell (46) have reported that the rate of nitrification of the added ammonium nitrogen is low in highly calcareous soils and they attributed it to the inhibition of nitrification by the large amount of calcium carbonate present. Bain and Chapman (10), and Justice and Smith (57) have put forward a evidence to show that in calcareous soils nitrification may stop at the nitrite stage. The low PAN values of these calcareous soils may be attributed to the fact that these soils have conditions which are unfavourable for ammonium accumulation. Workers such as Jewitt (56), Meyer et al. (63), and Kresge and Markler (58) have shown that alkaline pH, favours gaseous loss of ammonia. However, the statistical analysis of the data of this group of soils reveals that PAN values of these soils are highly correlated with incubation nitrate nitrogen. The correlation coefficient is 0.852** and is significant at 1 per cent level of probability.

Conclusion

Analysis of forty-five surface soils belonging to four major soil zones of Manitoba, for their pH, $CaCO_3$ per cent, organic matter contents, PAN and two weeks incubation nitrate nitrogen, and subsequent analysis of the data statistically revealed some interesting facts.

In general, there is highly significant correlation between PAN values and their two weeks incubation nitrate nitrogen values, of the forty-five soils studied. The correlation coefficient is 0.707** and is significant at the 1 per cent level. Therefore, PAN values are useful as a measure of the nitrogen supplying capacities of these soils. The PAN values are most reliable in non-calcareous and slightly calcareous (less than 5 per cent of $CaCO_3$ per cent) soils, because correlation coefficients for non-calcareous and slightly calcareous soils are 0.940** and 0.972** respectively. However, the analysis of the data of grey wooded soils revealed that there is no positive relationship between their PAN values and incubation nitrate nitrogen values, as the correlation coefficient between them is -0.127 and is not significant. The highly calcareous soils are conspicuous by their low PAN and incubation nitrate nitrogen values. However, the correlation existing between their PAN and incubation nitrate nitrogen values is 0.852** and is significant at 1 per cent level. The results also indicate that PAN of the soils are affected by the kind of organic matter they contain and by their calcium carbonate contents.

CHAPTER 5

THE TRANSFORMATION OF PAN OF SOILS DURING INCUBATION

The earlier experiment suggested that PAN values of non-calcareous and slightly calcareous Black soils, are useful as a measure of the availability of soil nitrogen in these soils. The existance of a highly significant correlation between PAN values of these soils and their two weeks incubation nitrate nitrogen values suggests that the method of PAN determination may be extracting intermediate products of soil nitrogen decomposition. The intermediate products of soil nitrogen decomposition range from complex degraded proteins and polypeptides to simple amino acids and ammonia. The mode of transformation of PAN fraction during incubation with respect to the nitrate formation, may throw some light on the nature of the PAN fraction. This may also reveal if the PAN fraction of soils exerts any controlling influence on nitrification. In addition, this will also ascertain the ease of mineralisability of PAN fraction and its availability to a growing crop.

A. Material and Methods

Five soils of varying PAN values were selected for the study. PAN values of the selected soils range from 72.4 P.P.M. as in Red River IV soil, to 5.1 P.P.M. as in the Altona B soil sampled after growing an oat crop. The Red River IV and Portage VI are slightly calcareous Black soils and are highly fertile having a high rate of nitrification. The Portage III and Altona soils are non-calcareous Black soils and they have moderately good rates of nitrification. The Altona B soil that was sampled after growing an oat crop is naturally depleted of available nitrogen and therefore it had a low PAN value and low incubation nitrate nitrogen value.

Four sets of each soil were prepared and kept for incubation for varying periods. The first set was incubated for the period of 1 week, the second set was incubated for 2 weeks, the third set for 3 weeks, and the fourth set was incubated for 4 weeks. The details of the procedure of incubation of the soils are given on page 19. Each set was removed after its incubation period and the soils were thoroughly mixed. A part of each soil was air dried and the rest was oven dried at 80°C. PAN was determined on the air dried portion of the incubated soils and nitrate nitrogen was determined on the oven dried portion of the soils.

B. Results and Discussion

Nitrate nitrogen and PAN present in the soils at the beginning of incubation and after different periods of incubation are given in Table 6, on page 57. The transformation of PAN and formation of nitrates with time of incubation in these soils are depicted in graphs on pages 58-60, on the basis of these results.

In general, in all these soils the formation of nitrates is accompanied by decreases of PAN values. This negative relationship existing between PAN transformation and nitrate formation is clearly revealed in the graphs (Figs. 2, 3, 4). The increase of nitrification is followed by a decrease in PAN and the decrease of nitrification resulted in an accumulation of PAN.

The curves of nitrification against time of incubation resembles microbial growth curves with their lag, logarithmic and stationary phases. In the lag phase of the nitrification curve, the decrease of PAN is slow corresponding to the slow increase of nitrification. When the nitrification curve enters the logarithmic phase, wherein nitrification increases logarithmically with time of incubation, PAN also decreases almost logarithmically. In the stationary phase PAN begins to accumulate as nitrification slows down. Such behaviour of PAN curves with respect to nitrification curves clearly indicate that PAN of soils acts as an immediate substrate for nitrification organisms. This suggests that the PAN fraction of soils, may be mainly constituted of ammonium nitrogen. The curves of Red River IV, Portage VI, and Portage III soils are well defined. In these soils, their high PAN, may be favouring nitrification. In the Altona B soil, low PAN seems to act as limiting factor in nitrification and appreciable nitrification takes place, only after the accumulation of PAN. These results indicate that the

PAN status of soils has an influence on the rate of nitrification.

During incubation ammonification also takes place with the formation of ammonia and, as conditions will be normally favourably for nitrification, this ammonia will be immediately transformed into nitrates. But ammonia may accumulate following the decrease in the rate of nitrification. In the stationary phase of nitrification of the soils studied, it will be noticed that the rate of nitrification is reduced. Hence ammonia may accumulate in this stage. The increase of PAN in the stationary phase of nitrification, following the decrease of the rate of nitrification, suggests that products of ammonification appear as a PAN fraction of the soil.

The formation of nitrates is accompanied by a decrease in the PAN fraction of the soil. In other words, during incubation, PAN transforms into nitrates. But, in most of these soils, the amount of PAN decreased is not equivalent to the nitrate nitrogen formed. In these soils, the amount of nitrate nitrogen formed is almost equivalent to the twice the amount of PAN decreased. This is not surprising because, during incubation, not only is PAN transformed into nitrates but also the decomposition of soil nitrogen occurs with the formation of products that may constitute a PAN fraction, and transform into nitrates.

Therefore, the PAN fraction as determined by Purvis and Leo's method is mainly constituted of products of ammonification. In soils ammonia, if it is not immediately converted into nitrates, will be held mainly as exchangeable ammonium and/or will be fixed in humus (11) or in the crystal lattices of clay minerals (4, 5, 9, 17). The Purvis and Leo's method of PAN determination may extract exchangeable ammonium and part of the fixed ammonium as it was concluded from the results of the preliminary study of this method. Paul _et al_. (67) report the presence of free amino acids in amounts of 5 to 50 P.P.M. Easy mineralizability of free amino acids is shown by workers such as Schmidt _et al_. (77). The easy mineralizability of the PAN fraction suggests that PAN may also include amino nitrogen.

C. Conclusion

The examination of curves of nitrate formation and PAN transformation, during four weeks of incubation, reveal that PAN acts as substrate for nitrification. The mode of transformation of PAN with respect to the formation of nitrates during incubation suggests that PAN may be mainly constituted of easily mineralizable intermediate products of soil nitrogen transformation such as ammonium nitrogen and amino nitrogen.

TABLE NO. 6

A. CHANGES IN PAN VALUES DURING FOUR WEEKS INCUBATION

Soils		Initial PAN P.P.M.	PAN after 1 Week P.P.M.	PAN after 2 Weeks P.P.M.	PAN after 3 Weeks P.P.M.	PAN after 4 Weeks P.P.M.
Red River	IV	72.4	69.5	35.6	9.4	20.1
Portage	VI	52.2	34.9	28.4	11.3	16.1
Portage	III	39.7	31.1	33.9	16.1	21.7
Altona	A	30.0	35.6	39.7	18.3	28.4
Altona (after oats)	B	5.1	10.0	21.7	7.2	5.0

B. CORRESPONDING CHANGE IN NITRATE NITROGEN VALUES DURING FOUR WEEKS INCUBATION

Soils		Initial NO_3-N P.P.M.	NO_3-N After 1 Week P.P.M.	NO_3-N After 2 Weeks P.P.M.	NO_3-N After 3 Weeks P.P.M.	NO_3-N After 4 Weeks P.P.M.
Red River	IV	7.2	33.3	127.2	150.5	144.2
Portage	VI	18.4	47.1	79.8	102.6	80.8
Portage	III	13.8	39.9	54.1	57.7	59.9
Altona	A	7.1	35.7	46.9	47.1	19.3
Altona (after oats)	B	0.9	9.7	9.1	18.0	12.3

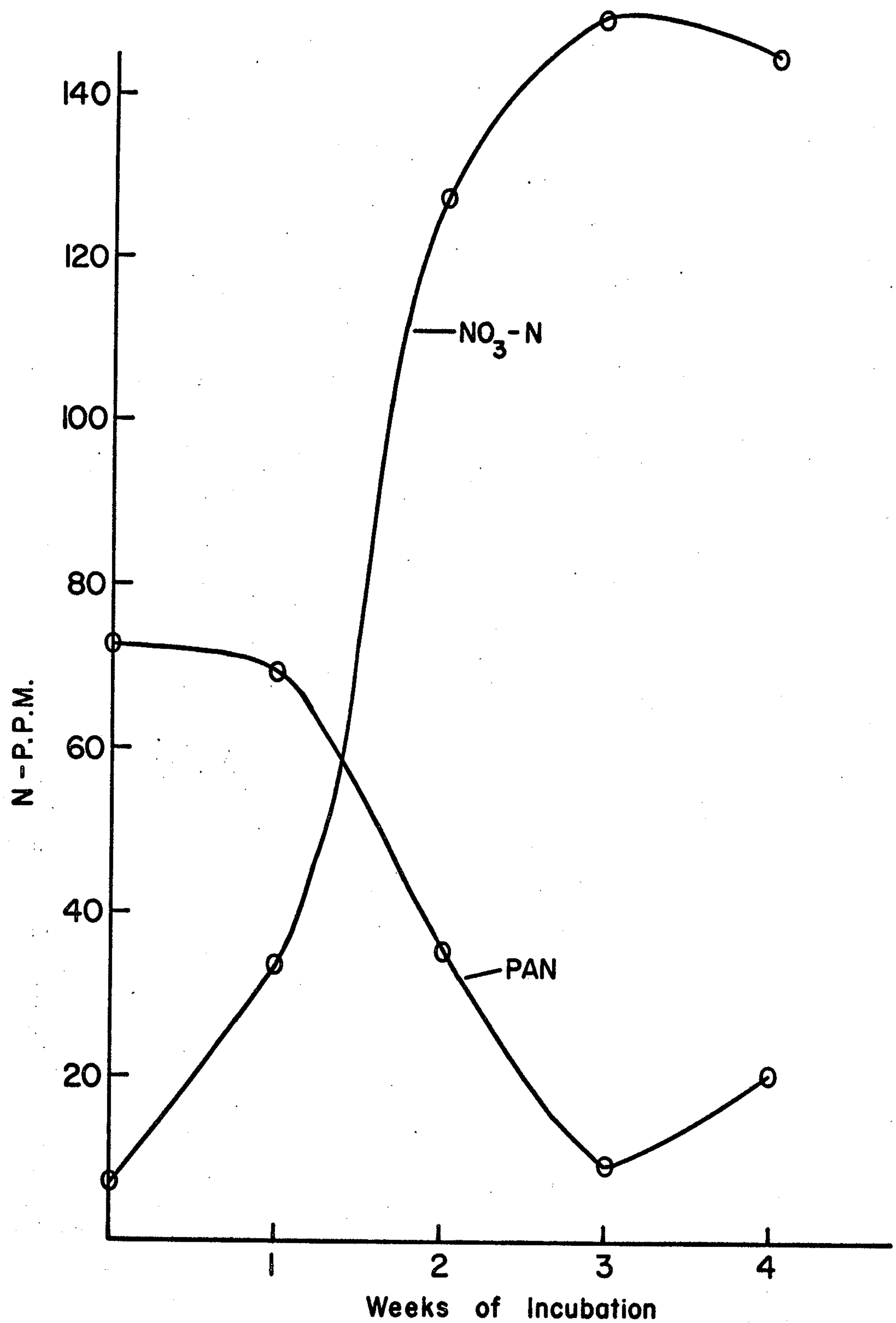

FIGURE 2

Transformation of PAN and Formation of Nitrate Nitrogen During Four Weeks of Incubation of Red River IV Soil.

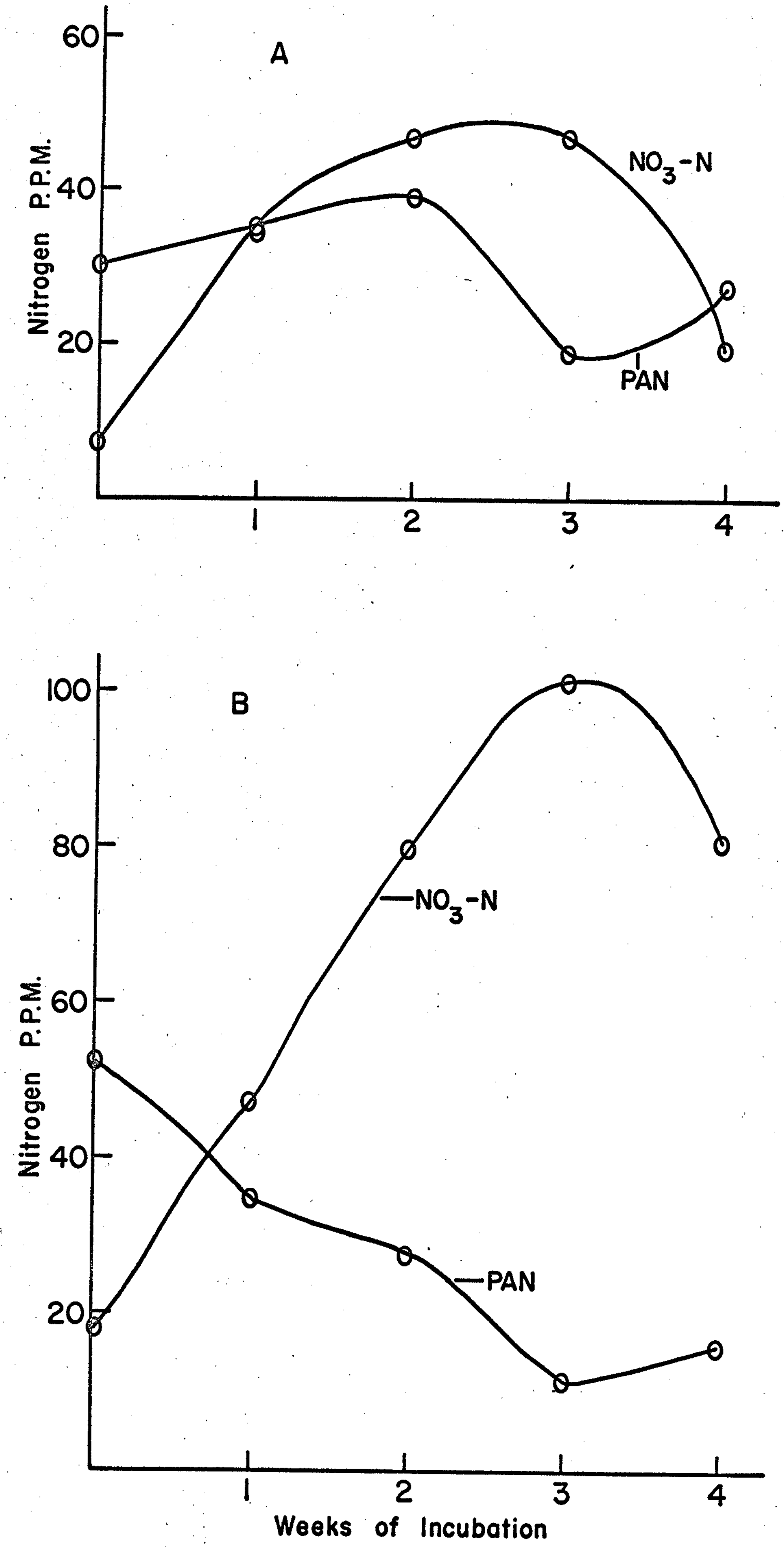

FIGURE 3

Transformation of PAN and Formation of Nitrate Nitrogen During

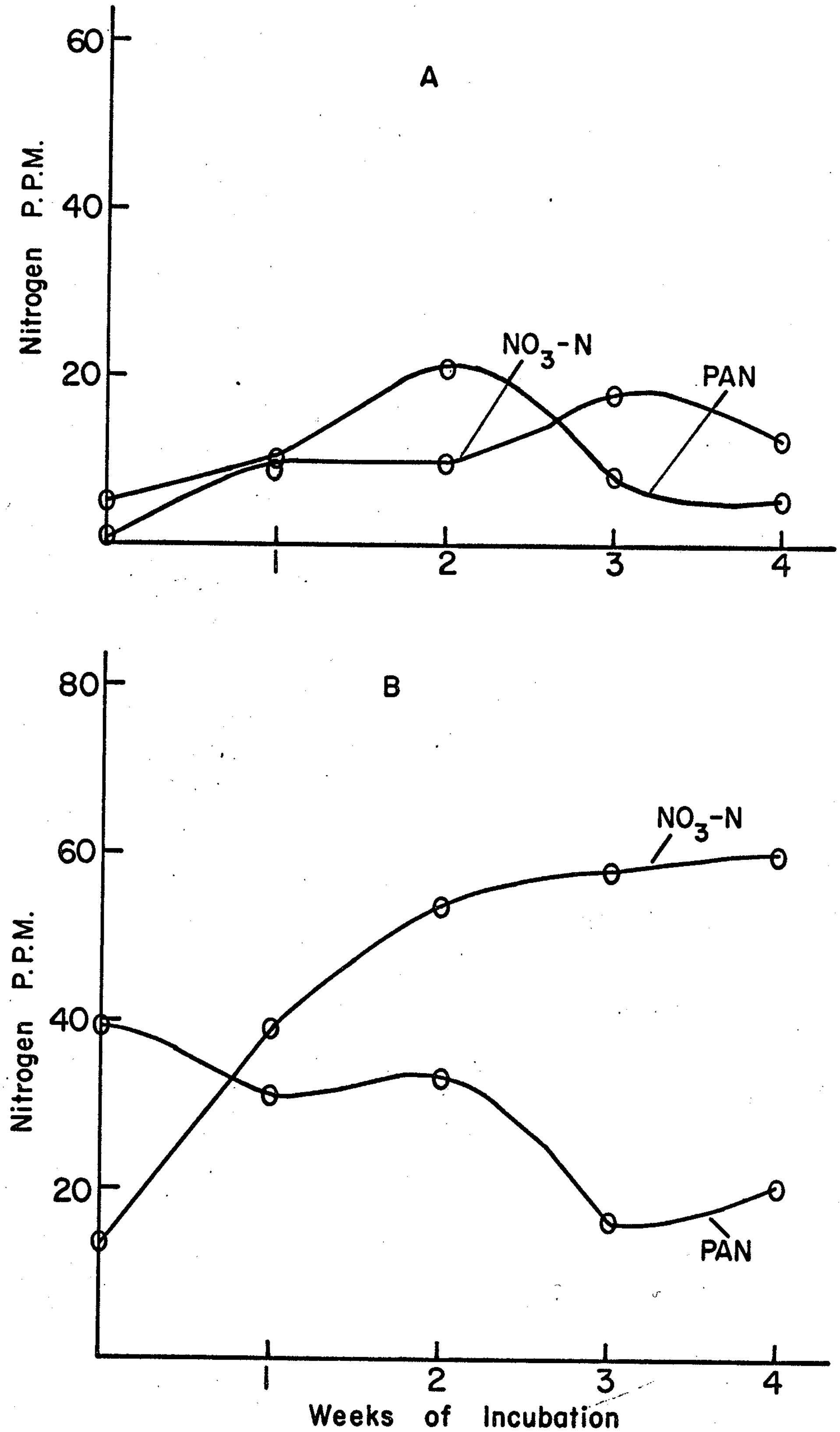

FIGURE 4

Transformation of PAN and Formation of Nitrate Nitrogen During Four Weeks of Incubation of A) Altona B and B) Portage III Soils.

CHAPTER 6

CHANGES OF PAN DURING DECOMPOSITION OF RAPE PLANT MATERIAL OF DIFFERENT NITROGEN CONTENTS IN SOILS

The immobilization or mineralization of nitrogen takes place during decomposition of plant material when it is incubated with soil. This depends upon the nitrogen content of plant material. Jensen (55) in an experiment in which organic materials of different C:N ratios were allowed to decompose in soils found that organic nitrogen is mineralized only in case of those organic materials which have C:N ratios less than 25. Recently Irtani and Arnold (53) have shown that when C:N ratios of plant materials were plotted against the amounts of nitrogen mobilized or immobilized, a curvilinear regression was obtained. They have also found that positive mineralization occurs only in case of those plant materials which have C:N ratios less than 20, or they must contain a minimum amount of nitrogen of 1.7 to 1.9 per cent. In general soil nitrogen is immobilized if the carbon to nitrogen ratios of plant materials added are greater than 33 or the nitrogen content of the plant material is less than 1.2 per cent. On the other hand plant nitrogen will be mineralized if the C:N is less than 15, or nitrogen content of the plant material is more than 2.6 per cent.

Bremner (21) reported that immobilization of nitrogen during oat straw decomposition in soil is accompanied by a synthesis of organic nitrogen. Chang and Kurtz (25), using the radio active isotope N^{15}, found that 90 per cent of the added nitrogen immobilized, appeared in the acid hydrosylate products of the soil organic matter, mainly as amino acids and amino sugars. Stewart et al. (84) also report that most of the nitrogen, immobilized during incubation of oat straw with soil, appeared in "non distillable acid soluble" fraction of the soil organic matter hydrosylate.

Thus the interesting feature about the nitrogen immobilized is that, it has been shown to appear in the acid hydrosylate of organic matter of soils, mainly as amino acids and amino sugars (21, 25, 84). As the method of PAN determination is also supposed to involve acid hydrolysis it is logical to think that the PAN determination may also estimate at least part of the nitrogen immobilized. Therefore the following experiment was devised to follow the PAN and nitrate nitrogen changes during incubation of soils with added plant materials of different nitrogen contents.

A. Materials and Methods:

Six soils belonging to different genetic classes were chosen for the study. The Portage III and Portage V are Orthic Black soils. The Balmoral I and Lakeland soils are Calcareous Meadow and Calcareous Black soils respectively. The Waitville soil is a Grey Wooded soil, and the Newdale is a Dark Grey soil.

The plant material used was rape taken at different stages of growth. The plant material, designated as low in nitrogen content, contained 1.18 per cent nitrogen and the one which is designated as high in nitrogen content contained 5.69 per cent nitrogen.

Three sets of soils were prepared for incubation as described on page 19. The first set was kept as a check. To the second set rape plant material with low nitrogen content was added at the rate of 1 per cent of the soil. Similarly, to the third set plant material with a high nitrogen content was added. In both cases finely ground, oven dried plant material was used. Plant material and soils were thoroughly mixed and wetted to their field capacities and kept for incubation at 30°C for three weeks. Details of the method of incubation of soils are given on page 19. After incubation the soils were thoroughly mixed and part of each of them was air dried and rest was oven dried at 80°C. PAN was determined on the air dried soil before and after incubation. Nitrate nitrogen was determined on oven dried samples after incubation.

B. Results and Discussion:

The results of this experiment are presented in Table 7 on page 68 These are also depicted in bar graphs on pages 69, 70, 71.

The results of nitrate nitrogen accumulation and immobilization have followed the same trends reported by workers such as Jensen (55), Stojanvoic and Broadbent (88), Bremner (19), and Iritani and Arnold (53), in that, incubating soils with plant material low in nitrogen content has resulted in immobilization of soil nitrogen and incubation of soils with plant material of high nitrogen content has resulted in mineralization of plant nitrogen. The comparison of nitrate nitrogen accumulation results of soils incubated without plant material, with those results of the same soils incubated with plant material of low nitrogen content, reveals that substantial amounts of nitrate nitrogen are immobilized. On the other hand incubation of soils with plant material high in nitrogen content has resulted in mineralization of plant nitrogen. In Black and Dark Grey soils, Portage III, Portage V and Newdale soils, as much as 56 per cent to 60 per cent of the plant nitrogen added was mineralized, whereas in the highly calcareous soils, Balmoral I and Lakeland soils, it is about 30 to 42 per cent. The high lime content of these soils seems to inhibit mineralization or the high pH (7.8 and 7.9) of these soils may not be very favourable for those hetrotrophic organisms that are involved in the decomposition of plant material added to these soils. The Grey Wooded Waitville soil, shows very low mineralization of plant nitrogen. This may be possibly due to the poor nutrient status of this Grey Wooded soil that may not be able to support a rich vigorous microbial population required to decompose plant material and to mineralize nitrogen. This is in accordance with the conclusion of Cork _et al._ (32, 33) that microbial population in forest soils is poor.

All soils in this experiment except the Waitville soil, show little change in their PAN values that can be attributed to the decomposition of plant material either of low or high nitrogen content. The expected lowering of PAN values, that is associated with nitrification is evidenced in Portage III, Portage V, and Balmoral soils when they were incubated without plant material. The incubation with plant material of low nitrogen content has caused no further change in case of the Portage V soil, while in case Portage III and Balmoral soils it has caused some lowering in their PAN values. It is interesting to note that immobilization of nitrate nitrogen of these soils, on incubation with plant material of low nitrogen content, has not caused any increase of PAN in these soils. Bremner (21), Chang and Kurtz (25) and Stewart et al. (84), have shown that immobilization of nitrogen is accompanied by a synthesis of organic nitrogen and that it is extracted mainly as amino acids and amino sugars in the acid hydrosylate of the organic matter of the soils. The results of this experiment suggest that the Purvis and Leo's method of PAN determination does not much involve hydrolysis or oxidative decomposition of the organic nitrogen complex of these soils. If it had involved partial hydrolysis or decomposition of organic nitrogen, part of the immobilized nitrogen might have appeared in the PAN fraction of these soils. On the contrary, the lowering of PAN of Portage III and Balmoral soils, on incubation with the plant material of low nitrogen content, suggests the mineral nitrogen character of the PAN fraction.

The incubation of these soils with plant material of high nitrogen content has resulted in only small increases of PAN values in the case of Portage III and Balmoral soils, whereas in the case of Portage V it has not produced any further change. This may be attributed to the fact that these soils have good rates of nitrification. In the Lakeland soil, on the other hand, incubation has resulted in the substantial increases of PAN value on incubation with plant material of both high and low nitrogen content. This lends support to the fact in these calcareous soils conditions are not favourable for nitrification. In the Waitville Grey Wooded soil, the incubation of soil alone, and with plant material of low nitrogen content, and with the plant material high in nitrogen content, have all resulted in a progressive increase of PAN value of this soil. This suggests that ammonification is the predominant process of nitrogen mineralization in this soil. This agrees with the conclusion of Cork et al. (32, 33), regarding the microbial activity in forest soils that the predominant process of nitrogen mineralization in these soils is ammonification.

C. Conclusions:

1. The incubation of soils with plant material low in nitrogen content (1.18 per cent) has resulted in the immobilization of nitrogen. The incubation of soils with plant material, high in nitrogen content (5.68 per cent), has resulted in the mineralization of large amounts of plant nitrogen. This mineralization is higher in non-calcareous Black and Dark Grey soils than that in calcareous Black and Meadow soils and it is very low in the Grey Wooded soil.

2. In the Grey Wooded soils the microbial activity is low and the predominant process of nitrogen mineralization in these soils seem to be ammonification.

3. The increase of PAN values in the Grey Wooded and calcareous soils, on incubation with plant material of both high and low nitrogen content, suggests that conditions are not highly favourable for nitrification in these soils. This also confirms the earlier conclusion that PAN is mainly constituted of ammonium nitrogen.

4. The immobilization of nitrogen, on incubation of soils with plant material of low nitrogen content, has not caused any increase in the PAN contents. This suggests that the Purvis and Leo's method of PAN determination does not seem to attack the organic nitrogen complex that is synthesized during nitrogen immobilization.

TABLE NO. 7

A. CHANGES OF PAN VALUES AFTER THREE WEEKS OF INCUBATION OF SOILS WITHOUT AND WITH 1 PER CENT PLANT MATERIAL OF LOW* AND HIGH** NITROGEN CONTENT

Soils and their Genetic Classes	Initial PAN P.P.M.	PAN After Incubation Without Plant Material P.P.M.	PAN After Incubation With Low Nitrogen Plant Material P.P.M.	PAN After Incubation With High Nitrogen Plant Material P.P.M.
Portage III Orthic Black	39.7	18.7	15.7	20.9
Portage V Orthic Black	78.8	29.6	29.6	29.6
Balmoral I Calcareous Meadow	38.3	20.9	12.8	19.7
Lake land Calcareous Black	5.2	5.2	15.7	49.8
Newdale Dark Grey	15.7	27.3	32.4	31.6
Waitville Grey Wooded	41.2	61.5	93.4	124.7

B. CHANGES IN NITRATE NITROGEN AFTER THREE WEEKS INCUBATION OF SOILS WITHOUT AND WITH LOW * AND HIGH** NITROGEN PLANT MATERIAL

Soils and their Genetic Classes	Initial NO_3-N P.P.M.	NO_3-N After Incubation Without Plant Material P.P.M.	NO_3-N After Incubation With Low Nitrogen Plant Material P.P.M.	NO_3-N After Incubation With High Nitrogen Plant Material P.P.M.
Portage III Orthic Black	10.8	41.3	7.8	327.9
Portage V Orthic Black	15.1	96.1	58.1	365.0
Balmoral I Calcareous Meadow	26.7	59.8	3.5	244.0
Lakeland Calcareous Black	13.7	20.8	0.5	166.9
Newdale Dark Grey	4.3	27.6	19.3	324.0
Waitville Grey wooded	0.4	9.3	1.3	20.9

* rape plant material with 1.18 per cent of nitrogen
**rape plant material with 5.68 per cent of nitrogen

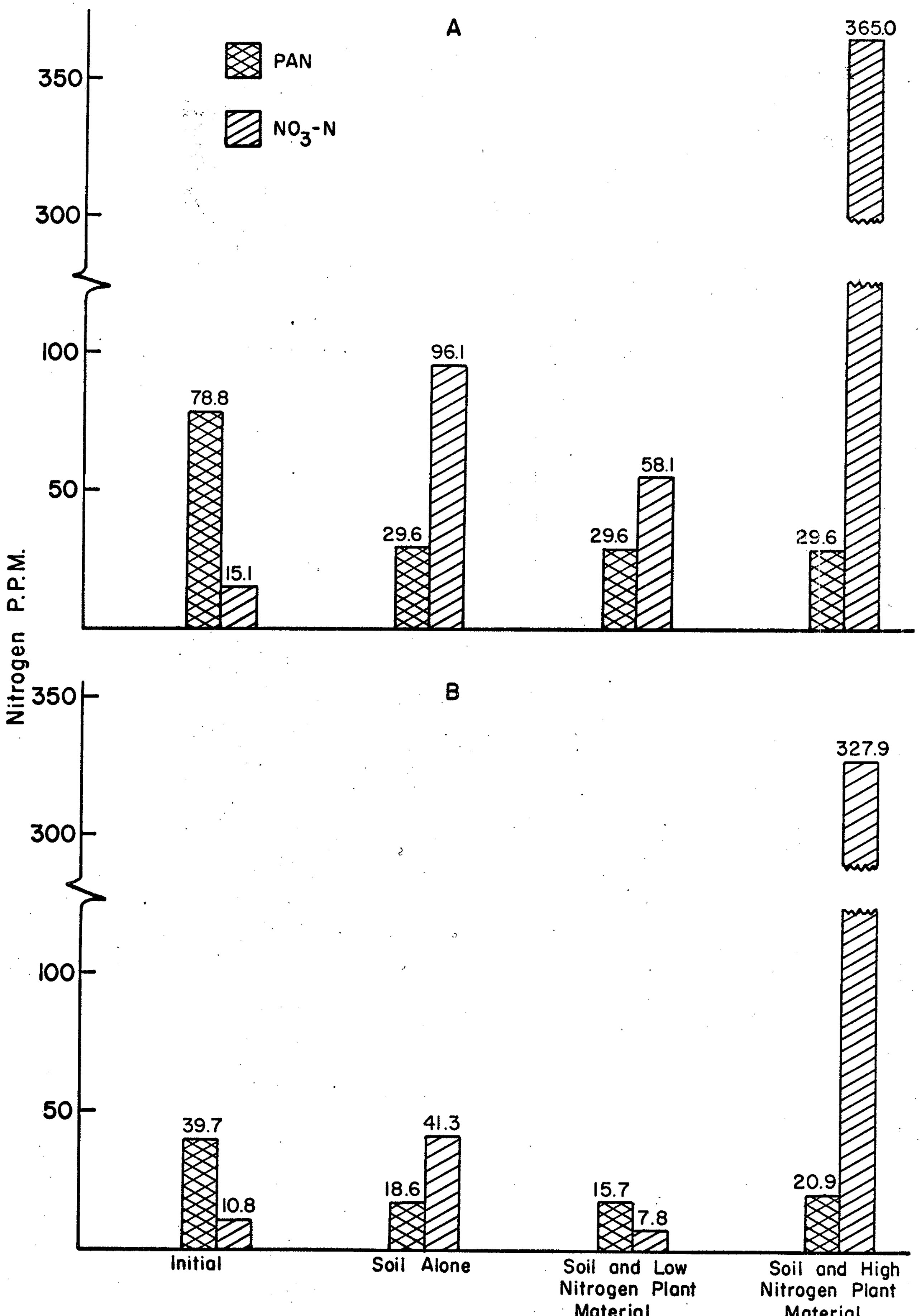

FIGURE 5

Changes of PAN and Nitrate Nitrogen After Three Weeks of Incubation Without and With 1 Per Cent Rape Plant Material With Low and High Nitrogen Content in - A) Portage V and B) Portage III Soils.

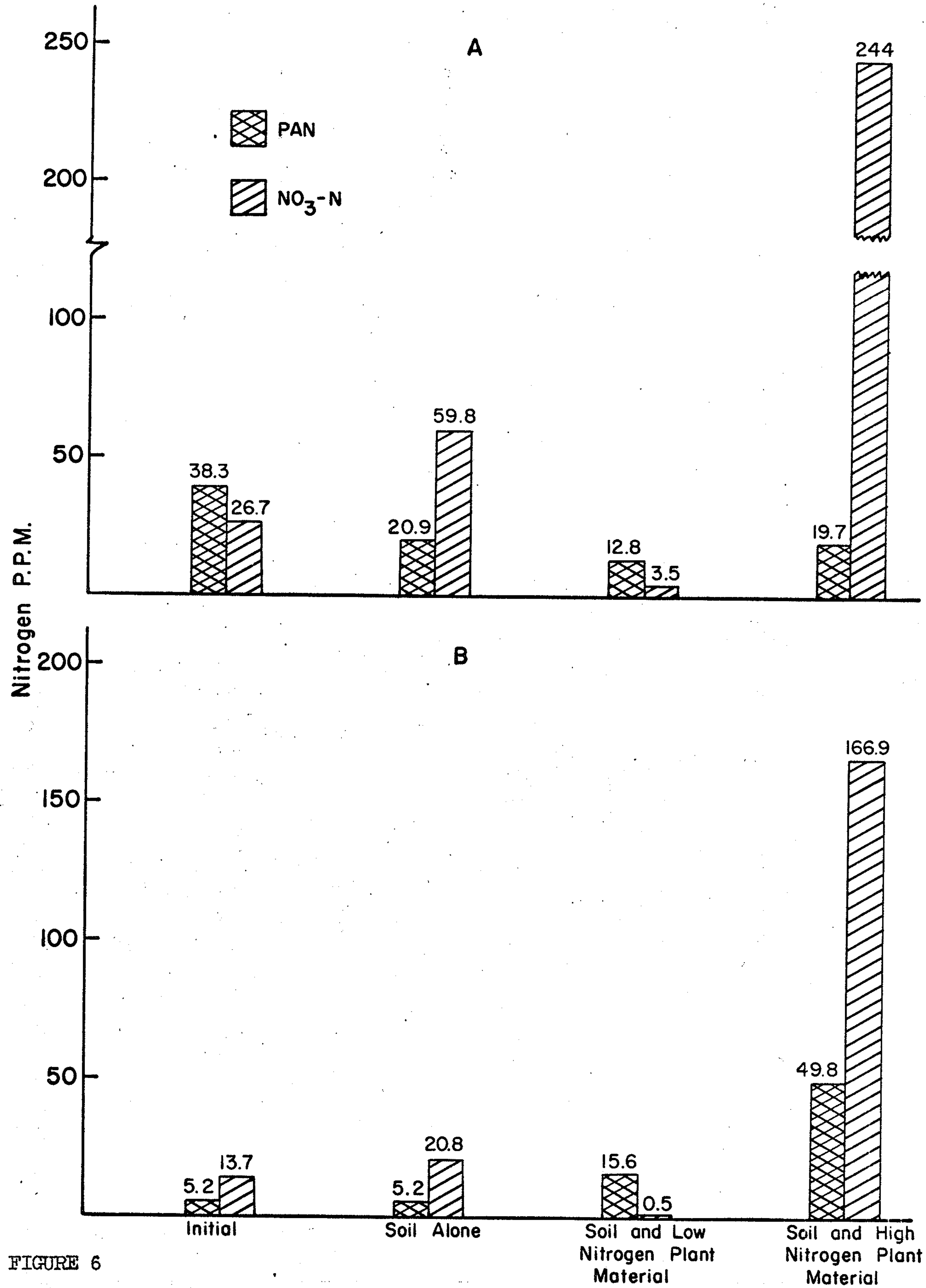

FIGURE 6

Changes of PAN and Nitrate Nitrogen After Three Weeks of Incubation Without and With 1 Per Cent Rape Plant Material With Low and High Nitrogen Content in - A) Balmoral I and B) Lakeland Soils.

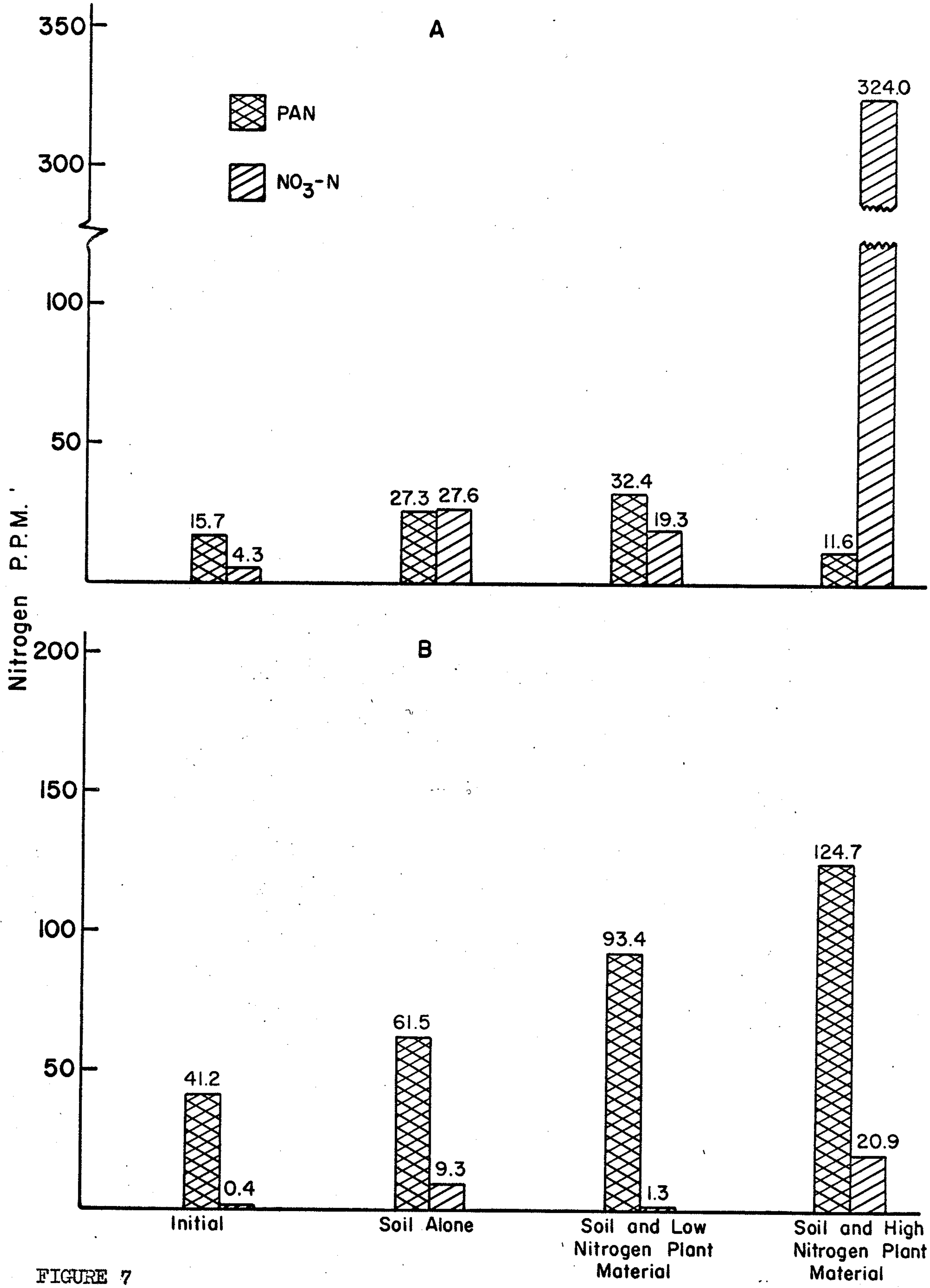

FIGURE 7

Changes of PAN and Nitrate Nitrogen After Three Weeks of Incubation Without and With 1 Per Cent Rape Plant Material With Low and High Nitrogen Content in - A) Newdale and B) Waitville Soils.

CHAPTER 7

A STUDY OF EXCHANGEABLE AMMONIUM IN MANITOBA SOILS

The earlier experiments suggest that the PAN fraction is mainly constituted of soil ammonia. Soil ammonia is an intermediate product of organic nitrogen mineralization, and is normally converted immediately to nitrates. As conditions in normal soils are favourable for nitrification, ammonia accumulates in soil in very small quantities. Russel (76) held that ammonium nitrogen in soils tend to be at a minimum constant and its magnitude depends upon the organic matter content of soils. However ammonia may accumulate in those soils in which conditions are favourable for ammonification, but are not optimum for nitrification. McLean and Robinson (61), Soulides and Clark (81), Schreven (78) and others have reported existence of substantial amounts of exchangeable ammonium in soils. It is possible that in the heavy textured, high organic matter soils of the Black soil zone and in Grey Wooded soils of Manitoba, conditions may prevail that are not highly optimum for nitrification. Stojanvoic and Broadbent (87) have, in an incubation experiment, shown that at low temperatures of 5^{o} to $10^{o}C$, nitrification is retarded but ammonification prevails. In the early spring, it is not unusual to have soil temperature in the range of 5^{o} to $10^{o}C$. So ammonia may accumulate in appreciable quantities in some Manitoba soils. The high PAN values obtained in case of some Black and Grey Wooded soils lend support to this fact. Therefore a study was undertaken to evaluate exchangeable ammonium in different types of soils of Manitoba. The emphasis has been placed on the exchangeable form of soil ammonia because it is the major form of ammonia in soils and its immediate availability to plant and microorganisms is not in doubt.

A. Materials and Methods:

Thirty-four soils were selected for this study and they represent all Associations and series chosen for the PAN evaluation. The list of soils that were studied for their exchangeable ammonium are given in Table 8, on page 77. The description of soil zones and associations to which they belong is given on pages 27 and 37.

Soils were sampled in the fall and late spring and were air dried and stored as in the case of PAN study.

Exchangeable ammonium was determined on these soils by the procedure given on page 19. The exchangeable ammonium values of the soils were compared with their PAN and two weeks incubation nitrate nitrogen by running multiple correlation analysis on the data. The influence of other soil characteristics; pH, $CaCO_3$ per cent, organic matter content, on exchangeable ammonium was also statistically assessed. These statistical analysis were carried out, by running multiple correlations on an IBM computer 1620.

B. Results and Discussion:

Results of this investigation are given in Table 8, on pages 77 and 78. The correlation coefficients between various characteristics of soils, obtained from results of multiple correlation run on these data are given in the Table 9 on page 79. As exchangeable ammonium nitrogen values seemed to be not much influenced by the kind of organic matter or calcium carbonate content of soils, no attempt has been made to arrange the data in the groups as was done in the PAN studies of soils.

In general the results reveal that considerable amounts of exchangeable ammonia are present in surface soils of Manitoba. In most of these soils, exchangeable ammonium nitrogen ranged from 5 P.P.M. to 35 P.P.M. In some fertile Black soils these values are as high as 80 P.P.M. to 140 P.P.M., whereas in some highly calcareous they are as low as 1 to 3 P.P.M. In non-calcareous and slightly calcareous Black or Dark Grey soils exchangeable ammonium nitrogen values are comparable with those of PAN and two weeks incubation nitrate nitrogen values. However, in Grey Wooded soils exchangeable ammonium values are much less than PAN values but they are comparable with those of two weeks incubation nitrate nitrogen. This may suggest that Purvis and Leo's method of PAN determination may be extracting, in Grey Wooded soils, nitrogen all of which is not immediately nitrifiable. The highly calcareous soils are conspicuous by their low PAN values and exchangeable ammonium nitrogen values. This may be attributed to the fact that these soils have condition of high pH, which may favour gaseous loss of ammonia resulting in little accumulation of ammonium nitrogen in these soils (56, 58, 63). However these soils also show lower rates of nitrification.

The results of multiple correlations run on these data reveal interesting features. Exchangeable ammonium nitrogen values correlates significantly with PAN values. The correlation coefficient between them is 0.877** significant at 1 per cent level of probability. This substantiates the fact that PAN determined according to the method of Purvis and Leo, is mainly constituted of soil ammonia. The important fact is that exchangeable ammonium values correlate significantly with two weeks incubation nitrate nitrogen values and the correlation coefficient between them is 0.926** and is significant at 1 per cent level, whereas correlation coefficient between PAN and two weeks incubation nitrate nitrogen is only 0.81** . The calcium carbonate content of soils seem to affect PAN determination significantly, as there is a highly significant negative correlation between calcium carbonate content of soils and their PAN values, the correlation being -0.349* significant at 5 per cent level. Thus exchangeable ammonium values have advantages over PAN values. The exchangeable ammonium represents a definite fraction of the soil nitrogen whose nature and availability is not as obscure as that of the PAN fraction. However, the PAN method has the advantage of being a simple and rapid method that can be adopted for routine soil testing analysis.

C. Conclusions:

The exchangeable ammonium studies carried out on thirty-four soils of Manitoba reveal the following facts:

1. Considerable amounts of exchangeable ammonium is present in the surface soils of the Black, Dark Grey and Grey Wooded zones.

2. The exchangeable ammonium values correlate both with PAN values and incubation nitrate nitrogen significantly, the correlation coefficients being 0.877** and 0.926** respectively.

3. Exchangeable ammonium values seemed to have an advantage over PAN values because they correlate more highly with incubation nitrate nitrogen than PAN values do. The correlation coefficient between exchangeable ammonium and incubation nitrate nitrogen is 0.926** and that between PAN and incubation nitrate nitrogen is 0.810**. Incubation nitrate nitrogen of Grey Wooded soils are more comparable to exchangeable ammonium values than they are to PAN values.

TABLE NO. 8

EXCHANGEABLE
AMMONIUM NITROGEN AND OTHER CHARACTERISTICS OF 34 SOILS OF DIFFERENT SOIL ZONES OF THE PROVINCE OF MANITOBA

Sl. No.	Soils, Location, Genetic Class			pH	$CaCO_3$ %	O:M %	PAN P.P.M.	Ex. NH_4^+ P.P.M.	Incubation NO_3-N P.P.M.
1	Waitville	IV	Grey Wooded	6.9	0.1	3.7	61.3	23.8	24.7
2	"	V	"	7.0	0.5	2.9	49.9	9.5	11.4
3	"	VI	"	6.5	0.7	7.3	37.1	23.3	26.8
4	Erickson	I	Dark Grey	7.1	0.6	3.1	41.2	12.4	19.1
5	Newdale	I	"	7.2	0.9	6.3	27.3	8.0	28.0
6	"	IV	"	7.7	2.2	7.1	11.6	6.8	25.1
7	Portage	I	Orth. Black	7.7	0.9	7.5	25.6	23.8	25.3
8	"	II	"	7.4	0.1	8.3	24.5	20.3	18.8
9	"	III	"	7.6	1.3	10.6	39.7	40.7	32.2
10	"	IV	"	7.5	0.1	8.6	112.0	140.1	91.6
11	"	VI	"	7.8	2.3	4.3	47.0	82.6	63.7
12	Almassipi	I	"	7.7	1.7	3.5	10.4	5.0	12.7
13	"	II	"	7.1	0.3	3.7	35.1	7.5	21.3
14	Wellwood	I	"	6.0	0.6	5.1	26.68	10.8	18.1
15	"	II	"	6.5	0.4	5.6	23.8	12.4	23.8
16	"	IV	"	6.4	0.2	5.8	18.6	15.6	14.9
17	Stockton	I	"	7.4	0.2	3.5	22.6	9.4	12.5

(Table No. 8 continued)

Sl. No.	Soils, Location, Genetic Class			pH	$CaCO_3$ %	O:M %	PAN P.P.M.	Ex. NH_4^+ P.P.M.	Incubation NO_3-N P.P.M.
18	Altona	II	Orth. Black	8.1	4.5	4.5	25.6	18.5	21.8
19	"	III	"	8.0	4.7	5.6	20.2	13.5	25.8
20	"	IV	"	7.8	3.3	3.9	2.3	9.0	20.3
21	Redriver	I	Rego Black	7.3	0.1	6.8	18.8	10.5	25.7
22	"	II	"	7.5	0.3	6.6	18.8	10.0	37.3
23	"	III	"	6.6	0.0	6.4	100.8	117.4	108.6
24	"	IV	"	7.3	3.9	7.5	72.4	102.4	115.1
25	Altona	I	"	7.2	0.7	5.7	22.6	10.0	20.6
26	Lakeland	I	Cal. **Rego Black**	7.9	17.7	8.7	25.6	15.3	25.0
27	"	II	" "	7.9	13.6	8.4	18.8	13.5	25.8
28	"	III	" "	7.8	22.9	6.4	0.0	1.3	6.3
29	"	IV	" "	7.8	29.2	3.8	0.0	2.7	6.2
30	"	V	" "	7.8	32.0	4.1	2.3	4.6	21.1
31	"	VI	" "	7.8	15.4	4.7	4.1	5.8	28.3
32	Balmoral	I	Cal. **Meadow**	7.9	33.9	12.4	38.3	17.1	44.8
33	Plumridge	I	" Orth Grey wooded	7.8	5.1	4.7	0.0	9.4	12.6
34	Garson	II	"	7.4	5.8	3.2	10.0	6.1	14.8

TABLE 9

CORRELATION COEFFICIENTS BETWEEN pH, O.M PER CENT, $CaCO_3$ PER CENT, PAN, NITRATE NITROGEN AND EXCHANGEABLE AMMONIUM IN THIRTY-FOUR SOILS OF MANITOBA

	pH	$CaCO_3$%	O.M%	PAN	Ex. NH_4	Incubation NO_3-N
pH	1	0.485**	0.168	-0.349*	-0.106	-0.079
$CaCO_3$%	0.485**	1	0.237	-0.349*	-0.223	-0.100
O.M%	0.169	0.237	1	0.250	0.289	0.358*
PAN	-0.349*	-0.349*	0.250	1	0.877**	0.810**
Ex. NH_4	-0.106	-0.223	0.289	0.877**	1	0.926**
Incubation NO_3-N	-0.079	-0.100	0.358*	0.810**	0.926**	1

** Significant at 1 per cent level.

* Significant at 5 per cent level.

CHAPTER 8

THE EFFECT OF ADDED CALCIUM CARBONATE ON PAN, EXCHANGEABLE AMMONIUM VALUES AND ON THE NITRIFICATION IN NON-CALCAREOUS SOILS

In earlier experiments it was noted that highly calcareous soils were conspicuous by their low PAN values, low exchangeable ammonium contents and low rate of nitrification; the exception being soils rich in organic matter. The low PAN values could be partly explained on the basis of the ineffectiveness of acid hydrolytic degradation that is involved in the Purvis and Leo's method of PAN determination, because of the neutralization of the dilute acid employed, by the free carbonates present in these soils. But results of earlier experiments also suggest that the PAN fraction of a soil is mainly constituted of exchangeable ammonium. This influence of calcium carbonate on the accumulation of ammonium and on nitrification in these soils and their nitrification is not altogether surprising. Many workers such as Jewitt (56) Meyer et al. (63) and Kresge and Stachell (58) have shown that the alkaline pH of calcareous soils and drying of soils favour gaseous loss of ammonia. Bain and Chapman (10) report that pH's higher than 7.7 favours accumulation of nitrites in such soils, indicating that vigorous nitrification in these soils may stop at the nitrite stage. Greaves et al. (45) have found that when

Ca is added as $CaCO_3$ to a soil containing 12 per cent of calcium carbonate, it inhibited nitrification and the addition of 1191 P.P.M. of Ca as $CaCO_3$, reduced nitrification to 59 per cent of the normal. Recently Halverson and Caldwell (46) have also noted the inhibition of nitrification in two highly calcareous soils due to the presence of large amounts of calcium carbonate. Thus, in highly calcareous soils conditions are not favourable for the accumulation of ammonia and for vigorous nitrification. So it was decided to investigate the role played by calcium carbonate in inhibition of nitrification and how it influences the PAN and exchangeable ammonium nitrogen contents by adding calcium carbonates to non-calcareous soils.

A. Materials and Methods:

Two non-calcareous soils were chosen for this study. One is a highly fertile Black soils with high organic matter and high rate of nitrification and the other one is a Grey Wooded soil with a low rate of nitrification. The Black soil contains 0.6 per cent of calcium carbonate equivalent and 11.2 per cent organic matter content. The Grey Wooded soil contains 0.1 per cent of calcium carbonate equivalent and 1.9 per cent organic matter.

The calcium carbonate used in this experiment is of reagent grade.

To each of the air dry soils calcium carbonate was added in the following percentages of the weight of the soil taken:

Treatment	1.	Check	$CaCO_3$ - nil
"	2.	1 per cent	"
"	3.	5 " "	"
"	4.	10 " "	"
"	5.	20 " "	"

The soils and added calcium carbonates were thoroughly mixed. On these treated soils PAN and exchangeable ammonium were determined according to the procedures given on pages 18-19. These treated soils were also incubated at 30°C, for two weeks according to the procedure given on page 19, and nitrate nitrogen accumulated for two weeks were determined. All results were calculated on the basis of actual weight of soil taken so that these results can be compared with those of the soils in the check treatment.

B. <u>Results and Discussion:</u>

Results of this experiment are presented in Table 10 on page 87.

The Black and Grey Wooded soils, both have slightly acidic reactions, their pHs being 5.9 and 6.4 respectively. The Black soil is a fertile soil with high two weeks incubation nitrate nitrogen and exchangeable values of 66.0 P.P.M. and 64.1 P.P.M. respectively, whereas the Grey Wooded soil has an exchangeable ammonium nitrogen and two weeks incubation nitrate nitrogen values of 23.8 P.P.M. and 24.6 P.P.M. respectively. The Grey

Wooded soil has a high PAN value of 61.3 P.P.M. and the Black soil has a PAN of 39.7 P.P.M. The closeness between exchangeable ammonium nitrogen values of soils and their two weeks incubation nitrate nitrogen values is evident.

In the Black soil and in the Grey Wooded soil, the increase in calcium carbonate content of these soils has resulted in a progressive decrease of PAN values. This indicates that the calcium carbonate content of soils do affect PAN results. In the case of the Black soil, an increase of calcium carbonate of 20 per cent has caused a decrease in its PAN by only 4 P.P.M., but in the case of the Grey Wooded soils, a similar increase of calcium carbonate has resulted in a decrease of PAN values by about 50 P.P.M. This may be attributed to the different kinds of organic matter these Black and Grey Wooded soils contain. The Grey Wooded soils contain acidic mor type of organic matter that is humified to a lesser degree than the organic matter in Black soils. Therefore organic matter of Grey Wooded soils is susceptible to the acid hydrolytic degradation, and the PAN of these soils may be mainly constituted of ammonium nitrogen that is derived from such acid hydrolytic degradation and some exchangeable ammonia. The addition of calcium carbonate neutralize the acid used in the PAN extraction, and may curtail the acid hydrolytic degradation of organic matter of these soils, causing the greater decrease of PAN values of these soils. On the other hand Black soils have highly humified organic matter that is less susceptible to the hydrolytic degradation. The PAN fraction of these Black soils, as was concluded from the preliminary study of the PAN method, is mainly constituted of exchangeable ammonium and some ammonium nitrogen of acid hydrolytic degradation. Therefore addition of calcium carbonate to the Black has caused only a small decrease in its PAN value.

The exchangeable ammonium nitrogen results, reveal that they, in both soils, are relatively less affected by the increase of calcium carbonate content. In the Black soil, an increase of calcium carbonate content of 5 per cent has resulted in a decrease of exchangeable ammonium cation from 64.1 P.P.M. to 49.0 P.P.M. The further increase in calcium carbonate has caused an increase in exchangeable ammonium values and the addition of 20 per cent calcium carbonate has almost restored its original exchangeable ammonium nitrogen values. The same can be said in the case of the Grey Wooded soil, though the magnitude of the changes in this soil are less.

The changes in two weeks incubation nitrate nitrogen values with the increases in the calcium carbonate content of the soils are interesting. In the Black soil, whose pH is 5.9, the addition of 1 per cent and 5 per cent of calcium carbonate has caused a large increase in the rate of nitrification. With 5 per cent of calcium carbonate addition, incubation nitrate nitrogen has almost doubled. This agrees with the beneficial effect of liming a soil with respect to the nitrification and yield increase observed by earlier workers. This is attributed to the change of pH of soil into a neutral and slightly alkaline range which is optimum for nitrification. The calcium carbonate also acts as a buffer and prevents the shifting of pH in to an acidic range during incubation. But the further increase of calcium carbonate has caused inhibition of the nitrification. The addition of 20 per cent of calcium carbonate has lowered the incubation nitrate nitrogen from 125.2 P.P.M. (with 5 per cent $CaCO_3$) to 17.4 P.P.M. However the addition of 20 per cent of calcium carbonate has not caused much change of the soil's pH. Therefore this lowering of nitrification cannot be attributed to the reaction of the soil. The possible cause might be attributed to the inhibition of nitrification by the presence of the large amount of calcium carbonate. Greaves et al. (45) have demonstrated the toxic effect of Ca^{++} on nitrification in calcareous soils. Halverson and Caldwell (46) have also noted such inhibitory action in the highly calcareous soils they studied. The results from the Grey Wooded soils also follow the same trend. The nitrification is almost completely inhibited with the addition of 10 per cent of calcium carbonate, and with the addition of 20 per cent calcium carbonate nitrification it hardly proceeds. It is also to be noted that the addition of 1 per cent of calcium carbonate to this Grey Wooded soils has brought about only a slight increase in nitrification. Therefore a low rate of nitrification in Grey Wooded soils may not be just due to lack of calcium carbonates and acidic reaction of these soils. The fundamental reason for the poor nitrification may be due to the poor microbial population of these soils.

C. Conclusions:

1. PAN values are affected by the addition of calcium carbonate

to the soil. This effect is more pronounced in Grey Wooded soils confirming that organic matter of the soils is highly susceptible to acid hydrolysis.

2. The exchangeable ammonium values are relatively less affected by the addition of calcium carbonate content to the soil.

3. The nitrification in acidic soils is stimulated by the addition of calcium carbonate up to 5 per cent of their weight and a further increase brings about inhibition of nitrification. The addition of 20 per cent of calcium carbonate has resulted in a large reductions of nitrification.

TABLE 10

EFFECT OF ADDITION OF CALCIUM CARBONATE ON PAN AND EXCHANGEABLE AMMONIUM VALUES AND NITRIFICATION IN TWO NON-CALCAREOUS SOILS

Soils and Treatment	pH	PAN P.P.M.	Ex. NH_4-N P.P.M.	Incubation NO_3-N P.P.M.
Black Soil (0.6% $CaCO_3$)	5.9	39.7	64.1	66.0
" " + 1 % "	6.9	37.6	49.0	110.3
" " + 5 % "	7.0	36.6	47.5	125.2
" " + 10 % "	7.0	33.2	54.6	112.7
" " + 20 % "	6.9	35.6	63.3	17.4
Grey Wooded Soil (6.1% $CaCO_3$)	6.4	61.3	23.8	24.8
" " + 1 % "	6.6	21.3	21.1	32.1
" " + 5 % "	6.8	12.9	21.1	20.8
" " + 10 % "	6.8	10.9	22.4	1.2
" " + 20 % "	6.8	10.9	22.4	0.0

CHAPTER 9

THE RECOVERY OF AMMONIUM NITROGEN ADDED TO SOILS

The availability of ammonium nitrogen in soils to plants and for nitrification depends mainly upon the kind of reaction ammonia undergoes in the soils, and on the prevailing conditions of the soils that affect nitrification. Ammonia is held with a different tenacity in soils depending upon the kind of reaction between ammonia and soil. Ammonia is usually held as an exchangeable cation on the exchange complex of the soils. Ammonia may also get sorbed and held by hydrogen bonding on the soil particles. The availability of such sorbed ammonia and exchangeable ammonium to plants and microorganisms is not doubted. The ammonium may also replace cations in interlayers in the expanded lattice of clay minerals such as vermiculite and montmorillonite and will be trapped and fixed when the lattices contract due to drying. (4,6). The ammonium ion may also get fixed in the crystal lattice of the clay mineral, in a manner similar to the fixation of potassium in clay minerals such as illite (9, 17, 82). Though the ammonium fixed in vermiculite was reported to be available for nitrification (99) the availability of fixed ammonium in other clay minerals for immediate nitrification is still doubtful (4, 5, 9, 20).

The ammonia may also get fixed in humus by reacting with lignin (11, 24). The availability of fixed organic nitrogen depends upon the presence of energy supplying materials for microbial decomposition in soils. The ammonia may also get lost from soils due to gaseous diffusion, volatilization, and due to microbial activity. Jewitt (56) has suggested the following mechanism for the gaseous loss of ammonia in alkaline soils:

$$NH_4^+ + OH^- \longrightarrow NH_3\uparrow + H_2O$$

The high pH of calcareous soils and drying facilitates such gaseous loss of ammonia (56, 63, 58). Aleem et al. (1), Clark et al. (29) and Webber and Gainey (98) have found that vigorous nitrification in these calcareous soils may stop at the nitrite stage and they have attributed it to the highly alkaline reaction of these soils and to the inhibition of the process of conversion of nitrite to nitrate by the added ammonia. Clark et al. (29) have reported the loss of accumulated nitrites, in a poorly buffered soil, as N_2O because of the instability of nitrous acid in acidic conditions, developed due to nitrification.

The recovery of added ammonium nitrogen to soils, as exchangeable ammonium by extracting the soil or as nitrates after incubating the soils, gives some idea about the behaviour of ammonia in soils and about its availability. Stojanvoic and Broadbent (86), Young and Cattani (100) have all experienced difficulty in achieving full recovery of the added ammonium nitrogen in soils, by their different extracting procedures. Stojanvoic and Broadbent (80) used a sodium acetate solution of pH 4.8 and potassium chloride solution of pH 1.0 as the extracting solution. They noted that an alkaline calcareous soil fixed considerable amounts of nitrogen and the fixation was enhanced by air drying. Using a sodium acetate solution for extraction, they could recover 69 per cent of the added ammonium nitrogen by extracting in wet . Air drying of the soil reduced the recovery to 47 per cent. Allison and co-workers (4, 5, 6), Stanford and Pierre (82), Young and Cattani (100) and Auxley and Leg (9) have experienced difficulty in getting full recovery of the added ammonium, as nitrates after incubation. Auxley and Leg (9) reports nitrification of 57 per cent to 96 per cent of the added ammonium. Allison et al. (4, 5) have noted that recoveries are lower in calcareous soils and they obtained only 60 to 80 per cent of the added ammonium nitrogen. They attributed these deficits to the fixation of ammonium nitrogen in the crystal lattices of clay minerals such as montmorillonite, vermiculite and illite etc. Clark et al. (29) have reported the loss of 27 per cent of the mineral nitrogen during incubation and they attributed it to the loss of accumulated nitrites as N_2O in their poorly buffered soil.

In the following experiment an attempt has been made to recover added ammonium nitrogen as exchangeable ammonium by extracting soils with 10 per cent NaCl solution of pH 2.5 and also as nitrate nitrogen by incubating these soils for four weeks. The possibility of nitrification being stopped at the nitrite level was also investigated. In this experiment nitrification and recoveries of the added ammonium in calcareous soil were compared with those in non-calcareous soils with an object to investigate into the possible reasons for the low rate of nitrification in calcareous soils.

A. Material and Methods:

Three calcareous and three non-calcareous soils were selected for this study. Of the three non-calcareous soils, Waitville A and Waitville B are Grey Wooded soils and the Wellwood is a Black soil.

Ammonium sulphate was added to the air dried soil in the following manner. Two hundred grams of air dried soil ground to pass a 2 mm. sieve was spread out thinly. From a pipette 20 ml of ammonium sulphate solution containing 500 P.P.M. of nitrogen was added uniformly over the soil. The soil was immediately mixed thoroughly and again air dried.

Two methods were employed to recover the added ammonium. In the first method exchangeable ammonium was extracted with 10 per cent NaCL solution of pH 2.5. Details of this procedure of determining exchangeable ammonium are given on page 19. In another method added ammonium nitrogen was recovered as nitrate by incubating these treated soils at 30°C for four weeks. The longer period of incubation was used because earlier results have suggests that rates of nitrification, in calcareous and Grey Wooded soils, are slow. Details of the procedure of incubation are given on page 19. Along with these treated soils, untreated soils were also incubated for the same period. The difference between nitrate nitrogen formed in treated soils and in untreated soils during incubation, is taken as the amount of added ammonium nitrogen, that is nitrified. Nitrite nitrogen was determined to see if nitrite nitrogen accumulates in these soils. The method followed for the nitrite nitrogen determination is given on page 20.

B. Results and Discussion:

The results of this experiment are presented in Table 11 on page 96, along with some characteristics of the soils.

The percentage recoveries of the added ammonium nitrogen, as exchangeable ammonium, ranged from 67.4 per cent to 84.8 per cent. The percentage recoveries for non-calcareous soils are higher than those for calcareous soils. The percentage recoveries in non-calcareous soils ranged from 80.0 per cent to 84.8 per cent whereas for calcareous soils they ranged from 67.4 per cent to 76.2 per cent. Thus these soils retained considerable amounts of ammonium nitrogen added to these soils, against 10 per cent sodium chloride extraction. These results are comparable with those obtained by Stojanovic and Broadbent (86). Part of such retained ammonium nitrogen might have been fixed in difficultly exchangeable positions in the clay minerals, such as montmorillonite, vermiculite and illite. It is not unusual for Manitoba soils to contain these clay minerals. The lesser recoveries of ammonium nitrogen in calcareous soils may be attributed to the loss of ammonia as per reaction; $NH_4 + OH \longrightarrow NH_3 + H_2O$, suggested by Jewitt et al. (56). Because these calcareous soils have alkaline pH's and have been air dried before extraction. Stojanovic and Broadbent (86) also attributed the lower recoveries of the added ammonium they obtained in an air dried alkaline calcareous soils for the gaseous loss of ammonia.

The percentage recoveries of the added ammonium nitrogen, as nitrate nitrogen accumulated after four weeks incubation, ranged from 46 per cent to 100 per cent. It is interesting to note that in non-calcareous soils, all the added ammonium was fully recovered. The ammonium nitrogen that is not recovered as exchangeable ammonium, is not lost and it is eventually made available for nitrification. This availability of the fixed ammonium for nitrification suggests this ammonium might have been fixed in inter layer spaces of expandable lattice of clay minerals such as montmorillonite and vermiculite which on wetting expand their lattices and release the fixed ammonium. In these non-calcareous soils there seemed to be little or no gaseous loss of ammonia. This agrees with the conclusion drawn by Kresge and Satchel (58), that no ammonium is lost due to volatilization as long as the pH is not above 7.0. Another important point to be noted is that all the added ammonium nitrogen added to Grey Wooded soil is nitrified. This suggests that nitrification in these soils, may be slow but is not inhibited and with the longer period of incubation, all ammonium ions will be nitrified. The percentage recoveries as nitrate, in calcareous soils, are in the range of 46.2 per cent to 52.4 per cent. These are lower than percentage recoveries obtained for these soil as exchangeable ammonium with 10 per cent NaCl solution extraction. It seems that gaseous loss of ammonia has continued during incubation. It is also possible that some of this ammonia might have been fixed in the manner similar to the fixation of potassium in illite type of clay minerals, thus becoming unavailable for immediate nitrification. In calcareous soil conditions seem to be favourable for loss of ammonia.

Nitrite nitrogen in these soils varies from 0.14 P.P.M. to 0.96 P.P.M. and the incubation of these soils with 50 P.P.M. of NH_4-N has resulted in only small increases in their nitrite nitrogen contents. The increase in nitrite nitrogen in calcareous soils are higher than those for non-calcareous soils. However there is no evidence for the inhibition of the process of conversion of nitrite to nitrate.

C. Conclusions:

1. Non-calcareous soils retain 15 to 20 per cent of the added nitrogen against 10 per cent sodium chloride solution extraction. But this retained ammonium nitrogen is made available for nitrification as incubation of treated soils for four weeks of 30°C has recovered all of the added ammonium nitrogen, as nitrates. Some of this retained non-exchangeable ammonium might have been held in interlayer space in expanded lattices of clay minerals such as Montmorillionite and vermicu-

lite due to their contraction during air drying. This may be released on wetting and made available for nitrification.

2. In calcareous soils as much as 25 to 35 per cent of the added ammonium nitrogen is retained against 10 per cent NaCl solution extraction. The recoveries of the added ammonium nitrogen as nitrate after incubation of soils, are still lower being only 46.2 to 52.4 per cent. As these soils have alkaline pHs, drying of the soils after addition of ammonium nitrogen might have induced a gaseous loss of ammonia.

3. Nitrite nitrogen was not found to accumulate in appreciable quantity during incubation, in the soils studied.

TABLE 11

A. RECOVERIES OF AMMONIUM NITROGEN ADDED TO SOILS

Soils	pH	$CaCO_3$%	NO_3^--N Accumulated in Four Weeks Incubation of Untreated Soils P.P.M.	NO_3-N Accumulated in Four Weeks Incubation of the Soils, 50 P.P.M. NH_4-N added P.P.M.	% Recovery of Added NH_4-N as Nitrates	% Recovery of Added NH_4-N as Ex.NH_4-N
Wellwood	6.4	0.2	40.6	92.5	102.8	80.0
Waitville A	6.9	0.1	5.3	57.1	102.6	84.8
" B	7.0	0.5	45.9	97.1	102.4	80.0
Lake land A	7.9	17.7	85.2	111.4	52.4	76.2
" B	7.8	29.2	41.8	67.6	51.6	70.4
" C	7.8	32.0	54.1	77.2	46.2	67.4

B. ACCUMULATION OF NITRITE NITROGEN DURING FOUR WEEKS INCUBATION OF SOILS TO WHICH 50 P.P.M. NH_4-N WAS ADDED

Soils	NO_2-N Before Incubation P.P.M.	NO_2-N After Incubation P.P.M.
Wellwood	0.14	0.36
Waitville A	0.03	0.20
" B	0.45	0.13
Lake land A	0.25	1.00
" B	0.96	0.74
" C	0.27	0.56

CHAPTER 10

GREEN HOUSE EXPERIMENT

In earlier experiments, it was noted that PAN values and exchangeable ammonium values of soils are useful as indicators of soil nitrogen availability, but these values may be misleading in case of Grey Wooded and calcareous soils. Do the high PAN values of Grey Wooded soils and low PAN values of calcareous soils, truly represent the availability of soil nitrogen in these soils? Such questions can be answered with some certainty, only after comparing these values with nitrogen uptake by plants grown in these soils. A green house experiment was conducted in the fall of 1964. In this experiment it was sought to compare PAN and exchangeable ammonium values with actual nitrogen uptake by plants. These values were also compared with "N" values of soils obtained according to the method suggested by Munsen and Stanford (64). Munson and Stanford (64) found "N" values to reflect the amount of nitrogen supplied by soils to crops grown in them. The influence of calcium carbonate contents of soils on the nitrogen uptake from added ammonium nitrogen was also investigated.

Experimental Procedure:

Nine soils were selected for this green house experiment.

Waitville A and Waitville B are Grey Wooded soils whereas Waitville C is a Dark Grey Wooded soil. The Newdale is a Dark Grey soil and the Almassipi and Wellwood soils are Black soils. Lakeland A and Lakeland B are highly calcareous Black soils, whereas Garson is an Orthic Grey Wooded soil developed on highly calcareous parent material.

These soils were taken from 0-6 inch depth in the fall and were air dried in the green house.

A randomized block design with four replications of each treatment was used in this experiment. In order to find the "N" values of the soils the following treatments were employed:

1. Check.
2. 40 pounds N/acre.
3. 80 pounds N/acre.

For each treatment of a soil, four replicate pots, each containing 2000 grams of air dried soil, were prepared. Nitrogen was added in the form of an ammonium sulphate solution at about the six inch depth, at the rate indicated in the treatments above. To each pot potassium biphosphate solution was applied at the rate of 20 pounds P/acre, at about two inch depth. A sodium sulphate solution was also added, to the check and the 40 pounds N/acre treatments, in the necessary amounts so that sulphates added to soils in all treatments would be same. This precaution was taken because some Manitoba soils have been found to respond to sulphur application. In each pot 12 to 14 oat seeds were planted at about the two inch depth. Then they were wetted to their field capacities.

Along with these pots four replicates of each soil were also wetted to their field capacities and were kept for incubation in the green house. These soils were incubated for 86 days which was the period of this green house experiment.

The temperature in the green house fluctuated between 70°F and 80°F.

There seemed to be some difficulties with germination in the Grey Wooded soils, and the emergence of the oat plant was delayed one to two days. Five days after complete germination, the seedlings in each pots were thinned and six good plants were allowed to grow. During this experiment, pots were watered alternate days, each time bringing the moisture levels of soils about to their field capacities.

After 80 days of growth the crop was harvested at ground level. The crop was cut into small pieces and were oven dried at 80°C for overnight and were weighed. Plant materials were analyzed for nitrogen using the improved Kjeldahl 's method.

Nitrogen uptake by plants (average of the four replicates of a treatment) was plotted against the amount of fertilizer nitrogen added. For all soils studied, linear relationships were found to exist between nitrogen uptake and nitrogen applied. The linear regression thus obtained were extrapolated so as to cut the X axises. This gave the "N" values. The graphs are given in the appendix.

Some characteristics of the soils such as PAN, Ex. NH_4^+, organic matter and calcium carbonate contents and two weeks incubation nitrate nitrogen were determined according to the procedures previously given.

After 86 days of incubation, the soils incubated in the green house, were taken out and mixed thoroughly. A representative sample was oven dried at 80°C and the amount of nitrate nitrogen accumulated during the incubation was determined. The average of the four replicates is presented as green house incubation nitrate nitrogen.

The soil tests for nitrogen availability were evaluated by comparing them statistically with nitrogen uptake values. The multiple correlation was carried out in the IBM computer 1620.

Results and Discussion:

The data of this experiment is presented in Table 12 on page 109 The results of the multiple correlation run on this data are given in Table 13 on page 110.

For all soils studied, the relationship existing between nitrogen uptake and the fertilizer nitrogen applied is linear. The "N" values of the soils studied in this experiment ranged from 35 pounds/acre to 93 pounds N/acre. These "N" values of the soils seem to be giving a true picture of the availability of soil nitrogen, because they correlate highly significantly with nitrogen uptake in check soils. The correlation coefficient between "N" values of soils and nitrogen uptake values is 0.952** , significant at the 1 per cent level. This compares well with the correlation coefficient 0.993**, obtained by Munson and Stanford (64), in spite of the fact that different genetic types of soils are used. Thus these results confirm the contention of Munson and Stanford, that "N" values are measures of the relative availability of soil nitrogen.

The PAN values of the Black and Dark Grey soils, compare well with the nitrogen uptake values for these soils. But the PAN values of the Grey Wooded soils are higher than their corresponding "N" values and nitrogen uptake values. This suggests that only a fraction of the PAN of these soils is actually made available to the growing crop. Therefore, in Grey Wooded soils, Purvis and Leo's method of PAN determination may be extracting nitrogen all of which may not be available for the growing crop. On the other hand PAN values of Calcareous Black soils are lower than their "N" values and nitrogen uptake values. Therefore, PAN values of calcareous soils may not adequately represent the amount of nitrogen that will be made available to the growing crop by the soil. It may be concluded that PAN values failed to represent the available nitrogen of Grey Wooded and Calcareous soils. This is reflected in the low correlation coefficients that were found to exist between PAN values and "N" values and nitrogen uptake values. The correlation coefficient between PAN values and "N" values is 0.086 and is not significant, whereas the correlation coefficient between PAN and nitrogen uptake value is 0.179 and is non-significant. Therefore the usefulness of the PAN values, as determined by Purvis and Leo's method is limited when genetically different types of soils are considered.

Exchangeable ammonium nitrogen values correlate highly significantly with incubation nitrate nitrogen values. The correlation coefficient is 0.903** and is significant at 1 per cent level. However when exchangeable ammonium nitrogen values were compared with "N" values and nitrogen uptake values it is evident that they are very low and represent only a fraction of the soil nitrogen that is made available to plants. The correlation between exchangeable ammonium nitrogen and nitrogen uptake values is low and non-significant. The correlation coefficient is 0.524. The same can be said of the relationship between exchangeable ammonium nitrogen and "N" values, because the correlation coefficient between them is 0.351 and is not significant. Thus exchangeable ammonium nitrogen of a surface soil represents only part of the soil nitrogen thst is made available to the growing crop, hence they may not give the complete picture of soil nitrogen availability, under green house conditions.

Incubation nitrate nitrogen values are also generally lower than "N" values and nitrogen uptake values. This is striking in the case of the calcareous soils. The low incubation nitrogen values may be attributed to the fact that the incubation of these soils were carried out in a nearly natural state, without making any attempt to create optimal conditions such as good aeration, neutral pH, presence of nutrients for vigorous microbial activity, etc. Another possible reason is that nitrification in calcareous and Grey Wooded soils was observed to be slow, hence the period of two weeks of incubation, in these different types of soils may not be long enough for an accumulation of enough nitrate nitrogen to indicate adequately the nitrogen supplying capacities of these soils. The incubation nitrate nitrogen values correlate poorly with "N" values and nitrogen uptake values. The correlation coefficients between incubation nitrate nitrogen and nitrogen uptake values is 0.770* and is significant at the 5 per cent level. The correlation between incubation nitrate nitrogen and "N" values is not significant, the correlation coefficient being 0.640. These poor correlations may be attributed to the fact that the soils considered here are of different genetic types. Harmsen and Van Schreven (48) drew attention to this fact while they discussed the limitations of the incubation method. They concluded that reliable results, sufficiently correlated with nitrogen requirement of field can be expected only when the incubation technique is restricted to one soil type, and one climatic zone.

Comparatively green house incubation nitrate nitrogen values are much better than two weeks incubation nitrate nitrogen values. The green house incubation nitrate nitrogen values correlate highly significantly with "N" values and nitrogen uptake values. The correlation coefficient between the green house incubation nitrate nitrogen values and "N" values is 0.917** which is significant at 1 per cent level. The correlation coefficient between incubation nitrate nitrogen and nitrogen uptake values is 0.979**, significant at the 1 per cent level. This is not surprising because the period of the green house incubation is the same as the growth period of the crop and the condition under which soils were incubated are similar to those in which the crop was grown in the green house. In other words, the nitrate nitrogen formed has been accumulated in these green house incubated soils because no crop was grown on them. These high correlations may also be attributed to the fact that, in the green house incubation, the soils were incubated for a long period (86 days) and as a result, even in Grey Wooded and calcareous soils enough nitrate nitrogen has accumulated to indicate nitrogen supplying capacities of these soils. Therefore it is advisable to use longer periods of incubation in the case of Grey Wooded and calcareous soils.

The results of this green house experiment bring out that PAN values, determined according to the Purvis and Leo's method, do not truly reflect the soil nitrogen availability of Grey Wooded and calcareous soils. Though exchangeable ammonium nitrogen values are better than PAN values, they do not show a significant correlation with "N" values and nitrogen uptake values. This may be attributed to the fact that different genetic types of soils were used in this experiment. The reason for the poor correlation that was obtained between two weeks incubation nitrate nitrogen and "N" values and nitrogen uptake values may also be traced to the same fact. In calcareous soils and in Grey Wooded soils the rate of nitrification is found to be slow and no attempt was made to create optimum conditions for nitrification in these soils during incubation test, therefore adequate amounts of nitrate nitrogen may not have accumulated during two weeks incubation, in case of these soils. However nitrification proceeds in these soils and adequate amounts of nitrates are formed but require long periods. This is suggested in the fact that the green house incubation nitrate nitrogen values, which are the amounts of nitrates accumulated during 86 days incubation in the green house, correlate highly significantly with "N" values and nitrogen uptake values. So a longer period of incubation is advisable in the case of calcareous and Grey Wooded soils. The results of this green house experiment also confirms that "N" values are a good measure of the relative availability of the soil nitrogen.

THE EFFECT OF CALCIUM CARBONATE CONTENT OF SOIL ON THE NITROGEN UPTAKE BY PLANTS FROM ADDED AMMONIUM NITROGEN

In Table 14, on page 111, data regarding the nitrogen uptake by oat plants, in different treatments of green house experiment are presented. The percentage uptake of nitrogen of the added ammonium nitrogen was calculated for 40 pounds/acre and 80 pounds/acre treatments.

The percentage uptake of the added ammonium nitrogen by the plants from these different soils ranged from 56.8 per cent to 83.9 per cent in the 40 pounds N/acre treatment and 65.6 to 85.9 per cent in the 80 pounds N/acre treatment. The average uptake of added ammonium nitrogen of both 40 pounds N/acre and 80 pounds N/acre treatments are taken as the indices of the availability of added ammonium nitrogen. The average nitrogen uptake values for these soils ranged from 63.4 per cent to 84.9 per cent of the ammonium nitrogen added. It is interesting to note that there is a curvilinear relationship between nitrogen uptake and calcium carbonate contents of the soils. This is shown to be in the graph obtained by plotting nitrogen uptake against calcium carbonate contents of the soils (fig. no. 9). The nitrogen uptake seems to be affected in only those soils in which calcium carbonate content is more than about 5 per cent. The per cent uptake of nitrogen of the ammonium nitrogen added, in calcareous soils are lower than those for non-calcareous soils. Previously it was noted that the nitrogen uptake in the check treatment, was negatively correlated with calcium carbonate contents of the soils and the relationship was not significant. The correlation existing between nitrogen uptake of the added ammonium nitrogen and calcium carbonate contents of soils, is also negative and is non-significant. The correlation coefficient that was found to exist between them was -0.514. Another interesting feature to be noted is that nitrogen uptake of the ammonium nitrogen added, in

Grey Wooded soils, compare well with those of non-calcareous soils. In a previous experiment it was also noted that, in Grey Wooded soils, recoveries of the added ammonium nitrogen as nitrates after four weeks incubation were 100 per cent. Therefore it may be concluded that there is little or no difficulty in the full utilization of the ammonium nitrogen added in Grey Wooded soils.

These results suggest that in soils calcium carbonates less than 5 per cent do not seem to depress the nitrogen uptake of the ammonium nitrogen added whereas calcium carbonates more than 5 per cent do depress the nitrogen uptake of the ammonium nitrogen added. This is not surprising because calcium carbonate in small quantities stimulates nitrification by maintaining a favourable pH and meeting nutritional requirements of the microbial population (76, 96) whereas in large quantities, calcium carbonates inhibit nitrification and favour loss of ammonia by volatilization (45, 46, 56, 86).

When percentage of nitrogen uptake of added ammonium nitrogen were compared with percentage recoveries of added ammonium nitrogen by different procedures, it is evident that the percentage nitrogen uptake by oat plants compare well with percentage recoveries of ammonium nitrogen as exchangeable ammonium (by extracting with 10 per cent sodium chloride solution of pH 2.5). Therefore it may be concluded that added ammonium nitrogen that is held in the soil as exchangeable ammonium, is efficiently utilized by plants.

TABLE 12

GREEN HOUSE EXPERIMENT RESULTS

SOME CHARACTERISTICS OF SOILS USED IN THE GREEN HOUSE EXPERIMENT

Soils	pH	O.M%	Ca-CO_3%	PAN lb/ac	Ex. NH_4-N lb/ac	Incub. NO_3-N lb/ac	Green House Incub. NO_3-N lb/ac	"N" Value lb/ac	Nitrogen Uptake In Check Soils lb/ac
Lakeland A	7.8	4.1	15.4	4.6	9.2	12.6	37.4	36.0	25.8
Lakeland B	7.8	4.7	32.0	8.2	11.6	10.2	27.4	40.0	26.0
Carson	7.4	1.9	3.5	20.8	12.2	29.6	55.2	63.0	44.0
Newdale	7.6	6.8	6.6	67.0	33.0	51.2	49.6	93.0	69.0
Almissipi	7.2	4.2	0.3	37.2	20.8	26.8	44.4	36.0	35.0
Wellwood	6.4	5.8	0.2	37.2	31.2	29.8	45.2	42.0	39.7
Waitville A	6.4	3.7	0.1	122.6	47.6	49.4	37.4	35.0	30.8
Waitville B	7.0	2.9	0.5	99.8	19.0	23.2	36.8	39.0	27.8
Waitville C	6.5	7.3	0.7	74.2	46.6	53.6	100.4	80.0	62.6

TABLE 13

CORRELATION COEFFICIENTS AMONG pH, O.M%, $CaCO_3$%, PAN EX. NH_4-N, INCUBATION NO_3-N, GREEN HOUSE INCUBATION NO_3-N, 'N' VALUES, AND NITROGEN UPTAKE IN CHECK SOILS, IN THE GREEN HOUSE EXPERIMENT

	pH	O.M%	$CaCO_3$%	PAN	Ex. NH_4-N	Incub. NO_3-N	Green House Incub. NO_3-N	"N" Value	Nitrogen Uptake In Check Soils
pH	1	-0.209	0.714*	-0.653	0.789*	0.575	-0.183	0.081	0.139
O.M%	-0.209	1	0.008	0.075	0.547	0.494	0.710*	0.573	0.667
$CaCO_3$%	0.714*	0.008	1	0.599	-0.555	-0.613	-0.368	-0.115	-0.336
PAN	-0.653	0.075	-0.599	1	0.745*	0.680	0.198	0.086	0.179
Ex. NH_4-N	-0.789*	0.547	-0.555	0.745*	1	0.903**	0.550	0.351	0.524
Incub. NO_3-N	-0.575	0.494	-0.613	0.680	0.903**	1	0.766*	0.640	0.770*
Gr.House Incub. NO_3-N	-0.183	0.710*	-0.368	0.198	0.550	0.765*	1	0.917**	0.979**
"N" Values	0.081	0.573	-0.115	0.086	0.351	0.640	0.917**	1	0.952**
Nitrogen Uptake In Check Soils	-0.139	0.667	-0.336	0.179	0.524	0.770*	0.970**	0.952**	1

* significant at 5 per cent level of probability

** significant at 1 per cent level of probability

TABLE 14

NITROGEN UPTAKE BY OAT PLANTS FROM ADDED AMMONIUM NITROGEN IN THE GREEN HOUSE EXPERIMENT

Soils	pH	$CaCO_3$%	Lb N/acre Taken By By Oat Plants, In Different Treatments			% Uptake of Added Ammonium Nitrogen		
			Check	40 lb N/acr	80 lb N/acr	40 lb N/acr	80 lb N/acr	Average
Waitville A	6.4	0.1	30.8	64.4	99.6	83.9	85.9	84.9
Waitville B	7.0	0.5	27.6	56.7	83.9	72.9	70.4	71.6
Waitville B	6.5	0.7	62.5	92.5	124.9	74.9	77.9	76.4
Wellwood	6.4	0.2	39.7	72.1	108.6	81.2	85.8	83.5
Almissipi	7.2	0.3	35.1	62.3	102.1	68.0	83.8	75.9
Garson	7.4	3.5	44.1	71.4	99.8	68.0	70.0	69.0
Newdale	7.6	6.6	69.0	91.7	124.1	56.8	69.9	63.4
Lakeland A	7.8	15.4	26.0	53.0	78.5	67.9	65.6	66.8
Lakeland B	7.8	32.0	25.8	53.3	80.5	68.8	68.4	68.6

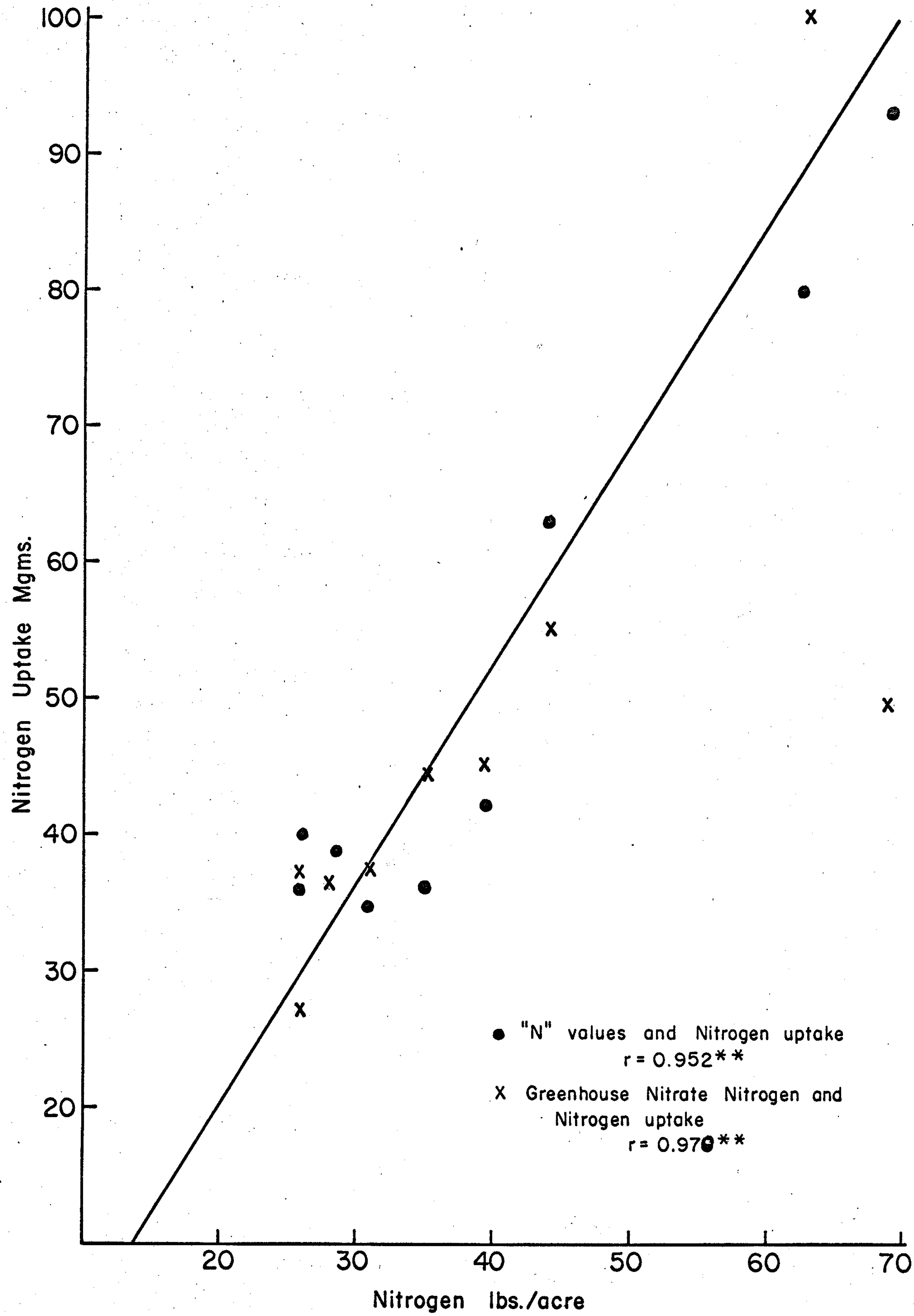

FIGURE 8

Relationship of Nitrogen Uptake With Greenhouse Incubation Nitrate Nitrogen and With "N" Values

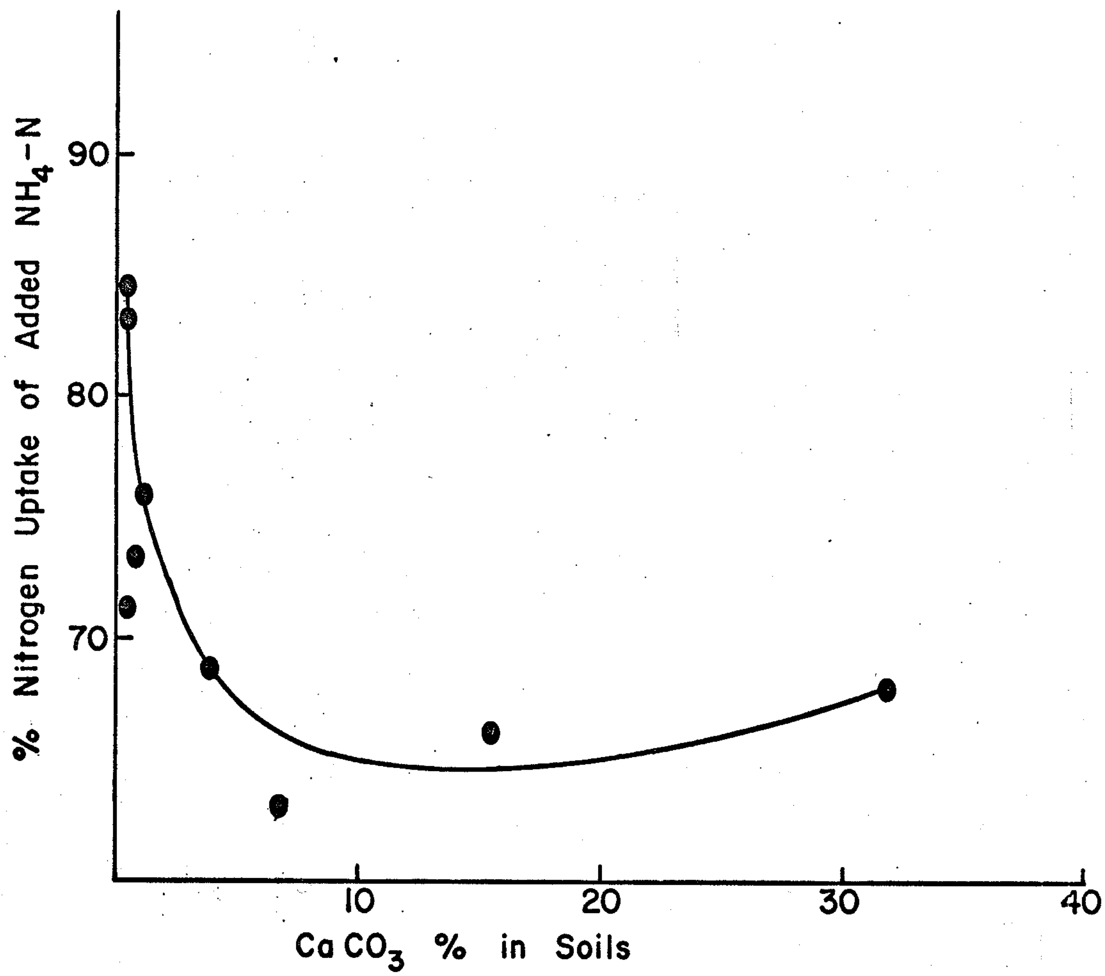

FIGURE 9

Relationship Between Per Cent Uptake of Added Ammonium Nitrogen and Calcium Carbonate Contents of Soils.

CHAPTER 11

SUMMARY AND CONCLUSIONS

Potentially available nitrogen (PAN) of soils determined according to the method suggested by Purvis and Leo (73) was evaluated as a possible test for nitrogen availability in soils of Manitoba. The PAN values of forty-five surface soils were statistically compared with their two weeks incubation nitrate nitrogen values. In general PAN values were found to be useful, because a highly significant correlation was found to exist between them and two weeks incubation nitrate nitrogen. The correlation coefficient was 0.707**which was significant at the 1 per cent level. This study also revealed the limitations of this method of PAN determination. The PAN values found to be influenced by the calcium carbonate content of soils and the kind of organic matter they contain. Therefore the data were grouped on the basis of the amounts of calcium carbonate and the kind of organic matter the soils contain. The examination of such groups revealed interesting features. The PAN values were shown to be **very** good indicators of nitrogen supplying powers of soils, in non-calcareous and slightly calcareous (less than 5 per cent of calcium carbonates) Black and Dark Grey soils. In these groups of soils, the highly significant correlation was found to exist between PAN values and two weeks incubation nitrate nitrogen values. The correlation coefficient for non-calcareous Black and Grey soils was 0.940** and the correlation coefficient for slightly calcareous Black and Dark Grey soils was 0.972** and both were significant at 1 per cent level. However in the case of Grey Wooded soils there was no correlation between PAN values and their two weeks incubation nitrate nitrogen. The correlation coefficient between them, in this non-calcareous Grey Wooded soils group, was -0.127. This may be attributed to the acidic and mor type of organic matter (with a lesser degree of humification) they contain. The method of PAN determination, as it involves acid hydrolysis, might be extracting organic nitrogen of the Grey Wooded soils that may not be immediately nitrified. In the case of calcareous soils, there was a highly significant correlation between PAN values and two weeks incubation nitrate nitrogen values. The correlation coefficient that was found to exist between them was 0.852**. But these calcareous soils have low PAN values. Therefore it was concluded that the determination of PAN is useful mostly on non-calcareous and slightly calcareous Black and Dark Grey soils.

Exchangeable ammonium nitrogen in the surface soils was similarly investigated. The exchangeable ammonium nitrogen contents of thirty-six surface soils of Manitoba were determined according to the method described by Jackson (54) and were statistically compared with two weeks incubation nitrate nitrogen. This study revealed that substantial amounts of exchangeable ammonia accumulate in the surface soils of Manitoba. In these soils, exchangeable ammonium nitrogen values ranged from 5 P.P.M. to 40 P.P.M. But in some highly fertile Black soils they were as high as 60 P.P.M. and above, whereas in calcareous soils they were as low as 1 to 3 P.P.M. The important fact is that these exchangeable ammonium nitrogen values correlated highly significantly with two weeks incubation nitrate nitrogen values. The correlation coefficient between them is higher than that between PAN values and two weeks incubation nitrate nitrogen. For the thirty-six soils studied the correlation coefficient between exchangeable ammonium nitrogen values and two weeks incubation nitrate nitrogen was 0.926** whereas the correlation coefficient between PAN values and two weeks incubation nitrate nitrogen values was only 0.81**. This may be attributed to the fact that exchangeable ammonium nitrogen values of Grey Wooded soils are more comparable to two weeks incubation nitrate nitrogen than the PAN values are. These results suggest that the exchangeable ammonium nitrogen is an important form of available nitrogen in Manitoba soils and deserves consideration.

An attempt was made to know the nature and mineralisability of the PAN fraction of soils. The transformation of PAN of soils with respect to the nitrate formation, during an four weeks incubation was studied. It was noticed that the soils having high PAN values have good rates of nitrification whereas in soils having low PAN, substantial nitrification took place only after sufficient PAN accumulated. There was a negative relationship between PAN transformation and nitrate formation. The comparison of the curves of nitrate formation and of PAN transformation, suggests that PAN acts like an immediate substrate for nitrifiers. This reveals the ammonium nature of the PAN fraction. In another experiment soils were incubated with rape plant material of low and high nitrogent contents (1.18 per cent and 5.69 per cent of nitrogen respectively), and the change of PAN of soils with respect to nitrogen mineralisation and nitrogen immobilisation was studied. In all soils studied, except the Grey Wooded soils, the immobilisation of soil mineral nitrogen during incubation of the soils with rape plant material of low nitrogen content did not increase the PAN values. In view of the fact that, during immobilisation of mineral nitrogen organic nitrogen was found to be synthesized in soils (21) and that the synthesized organic nitrogen appears mainly as amino acid and amino sugars in the acid hydrosylate of organic matter (25, 84), these results suggest that the Purvis and Leo method of PAN determination does not involve an hydroysis of organic nitrogen complex of soils to any great extent. In other words, the method of PAN determination may not involve much degradation and extraction of complex organic nitrogen compounds of soils. In the Grey Wooded soil studied, the incubation of the soils alone, the incubation of the soil with plant material of high and low nitrogen contents have all resulted in progressive increase of its PAN values. In Grey Wooded soils, ammonification is the predominant process of nitrogen mineralisation because of the acidic pH, and mor type of organic matter they contain (32). In the highly calcareous soils, wherein conditions are not that favourable for nitrification (45, 46), results show a tendency for accumulation of PAN during incubation. These results suggest that the end products of ammonification appear in the PAN fraction. The comparison of exchangeable ammonium nitrogen values of thirty-six surface soils of Manitoba with their PAN values, revealed that though exchangeable ammonium nitrogen values are generally lower than their corresponding PAN values there is significant correlation between them. The correlation coefficient between exchangeable ammonium nitrogen values and PAN values of the thirty-six soils studied was 0.877** and was significant at 1 per cent level. This suggests that one of the main constituents of the PAN fraction of these soils is exchangeable ammonium. Thus there is evidence to suggest that PAN is mainly constituted of easily mineralisable ammonium and possibly amino nitrogen of soils.

A green house experiment, employing different genetic types of soils, was conducted to see if the exchangeable ammonium nitrogen and PAN of these soils truly represent the availability of soil nitrogen in these soils. The PAN and exchangeable ammonium nitrogen of these soils were compared to the green house incubation nitrate nitrogen, 'N' values and nitrogen uptake in check soils. The 'N' values of these soils were determined according to the method suggested by Munson and Stanford (64). These 'N' values correlate significantly with nitrogen uptake in check soils. The correlation coefficient obtained was 0.952** and was significant at 1 per cent level. Thus these 'N' values give relative amounts of available nitrogen present in the soils. The green house incubation nitrate nitrogen values are the amounts of nitrate nitrogen accumulated in the soils due to 86 days incubation of soils in the green house under conditions similar to those in which crop was grown. These green house incubation nitrate nitrogen values represent the amount of nitrogen mineralised and made available to plants grown in check soils, because there is highly significant correlation exists between the green house incubation nitrate nitrogen values and nitrogen uptake in check soils. The correlation coefficient between them is 0.979** and is significant at 1 per cent level. Therefore 'N' values and green house incubation nitrate nitrogen are good indicators of nitrogen availability in soils. When PAN values and exchangeable ammonium nitrogen values of these soils were compared with 'N' values, green house incubation nitrate nitrogen and nitrogen uptake in check soils, it became evident that they are not adequate to give a true picture of the nitrogen availability in soils. The correlation coefficients of PAN values with the green house incubation nitrate nitrogen and 'N' values and nitrogen uptake in check soils were 0.198, 0.086 and 0.179 respectively and none of them was significant. The correlation coefficients of exchangeable ammonium nitrogen values with green house incubation nitrate nitrogen values, 'N' values and nitrogen uptake in check soils were 0.550, 0.351, 0.524 respectively and all of them are not significant. These poor correlations of PAN and exchangeable ammonium nitrogen values with nitrogen uptake "N" values may be attributed to the fact different genetic types of soils were used in this green house experiment. The green house experiment results also reveal that even the two weeks incubation nitrate nitrogen values have limited application when genetically different types of soils were considered. The correlation of two weeks incubation nitrate nitrogen values of these soils with their green house incubation nitrate nitrogen, and with 'N' values and with nitrogen uptake in check soils are low and the respective correlation coefficients were 0.766* , 0.640 , 0.770* (* significant at 5 per cent level). These low correlations may be due to the fact the two weeks of incubation was carried out under natural conditions without making any attempt to create optimum conditions such as good aeration, neutral pH, etc. This may also be due to the fact that in the green house experiment genetically different types of soils are considered and incubation results are best applicable for soils of the same type (48). Another possible reason is that two weeks incubation may not be long enough for Grey Wooded and calcareous soils because it was noticed that in these soils nitrification is slow. This is supported by the fact that, the green house incubation nitrate nitrogen values, (nitrate nitrogen accumulated during 86 days incubation in green house), correlate significantly with 'N' values and nitrogen uptake in check soils.

An attempt was made to investigate the causes of the low ammonium nitrogen status and low nitrifications rates of highly calcareous soils. The recoveries of added ammonium nitrogen by extraction with 10 per cent sodium chloride solution of pH 2.5, and as nitrate after four weeks of incubation at 30°C, are low in the case of calcareous soils. The alkaline reactions of these calcareous soils may favour a volatilization loss of ammonia (56, 58, 95). It is interesting to note that, in the case of Grey Wooded soils in which nitrification was found to be slow, all the added ammonium nitrogen was nitrified during four weeks incubation at 30°C. Evidence was also obtained to show that the presence of high amounts of calcium carbonate in soils causes inhibition of nitrification. The addition of 20 per cent of calcium carbonate to a highly fertile Black soil reduced the nitrification from 66.0 P.P.M. of nitrate nitrogen, for two weeks of incubation at 30°C, to only 17.4 P.P.M. However there is no evidence to suggest that nitrification may stop at nitrite stage in the calcareous soils. This is because there was little or no nitrite accumulated at the end of three weeks incubation of calcareous soils with 50 P.P.M. of ammonium nitrogen added. The nitrogen uptake of the added ammonium nitrogen from the calcareous soils, as green house experiment results show, are also lower than those in non-calcareous soils.

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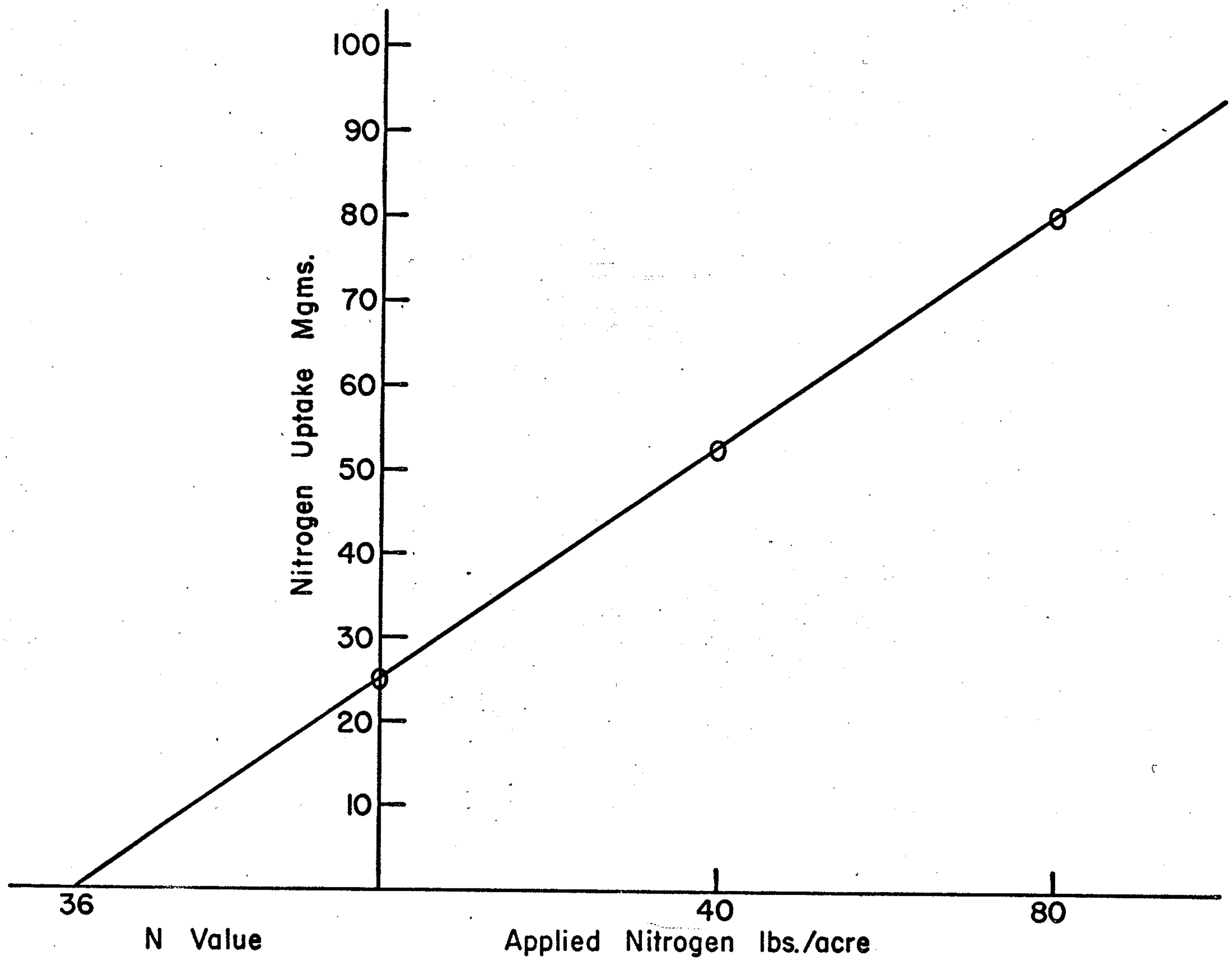
APPENDIX

'N' VALUE GRAPHS OF SOILS OF GREENHOUSE EXPERIMENT

FIGURE 10

'N' Value Graph of Lakeland A Soil.



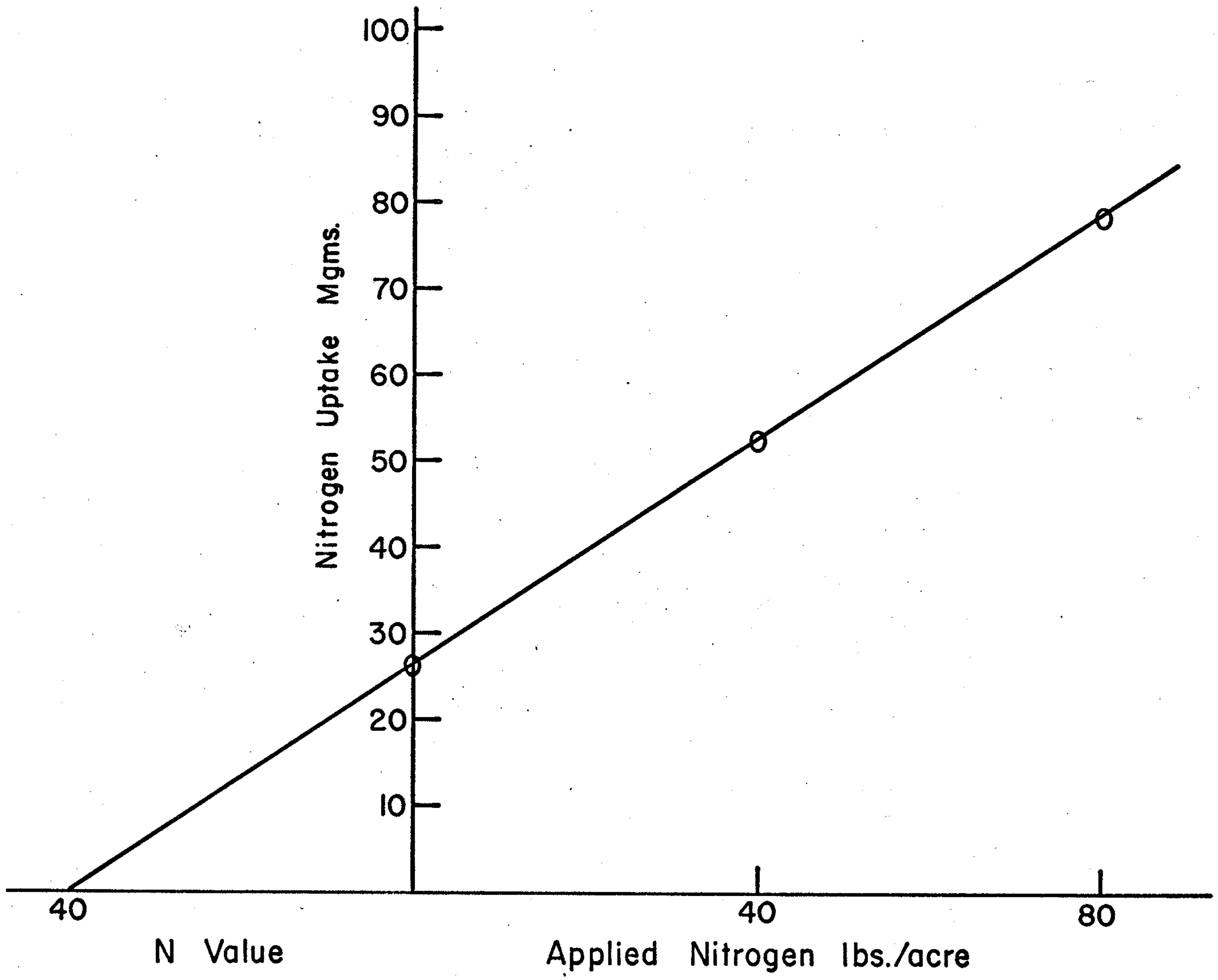
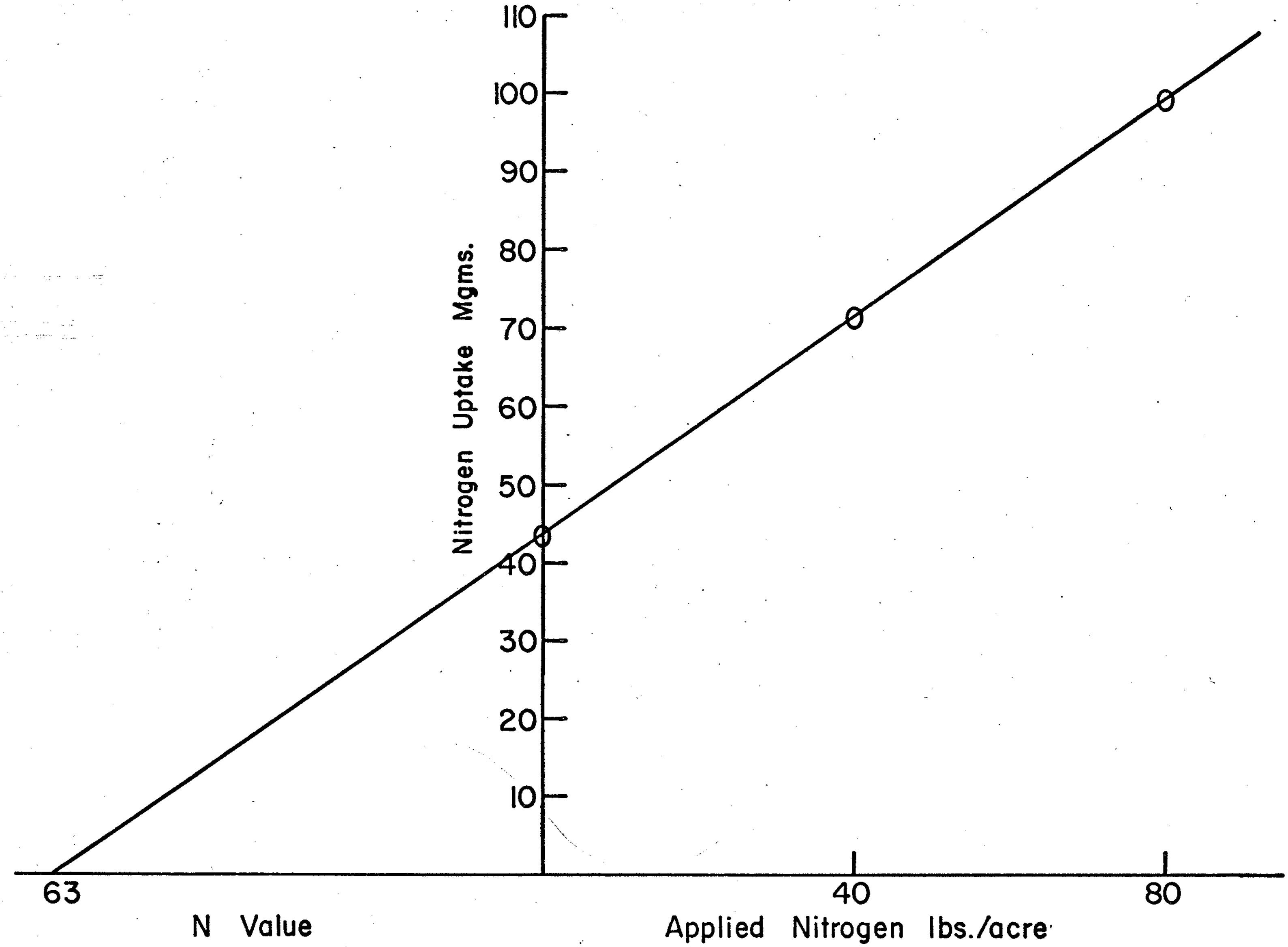


FIGURE 11

'N' Value Graph of Lakeland B Soil.

FIGURE 12

'N' Value Graph of Garson Soil.



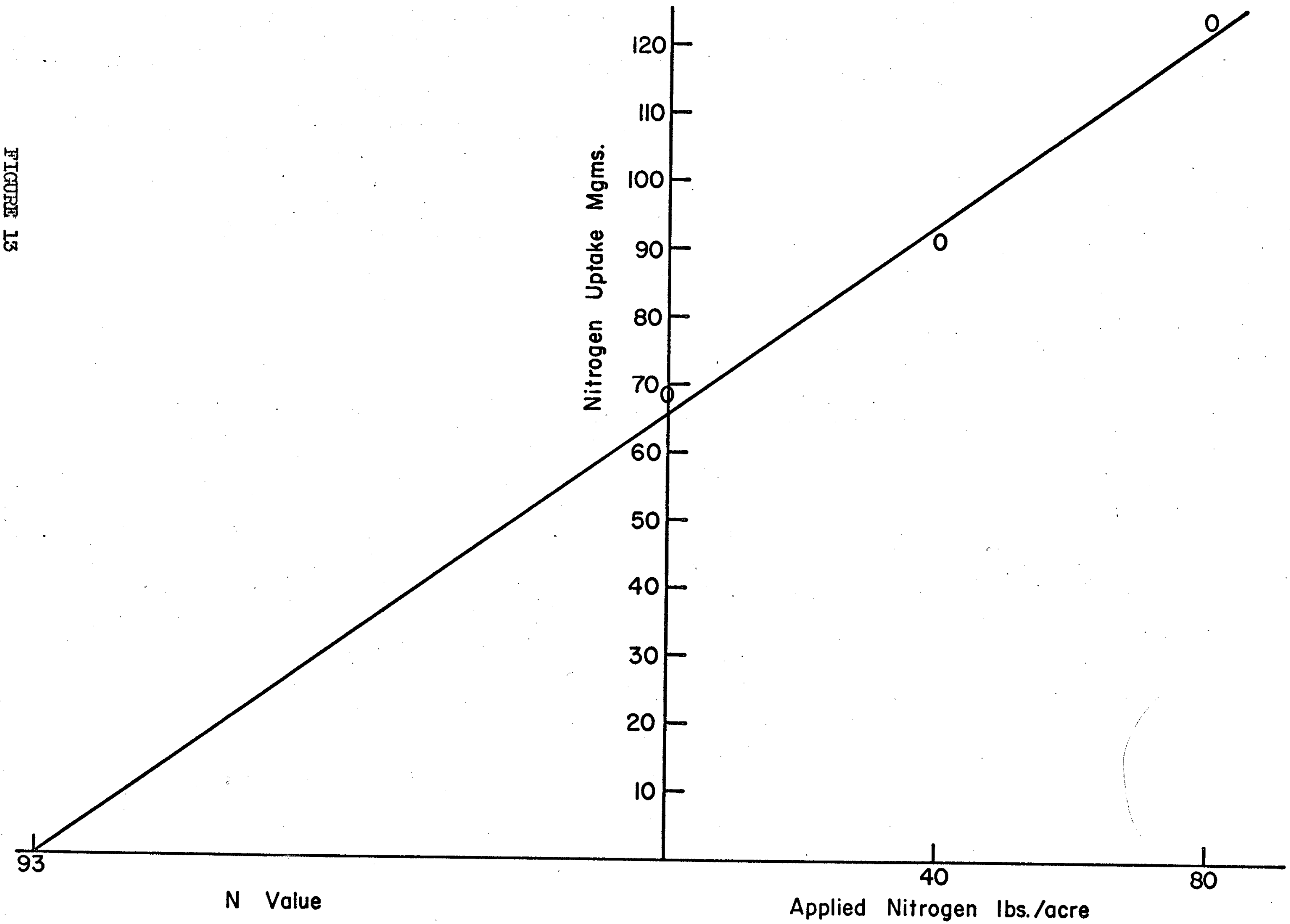


FIGURE 13

'N' Value Graph of Newdale Soil.

FIGURE 14

'N' Value Graph of Almassipi Soil.

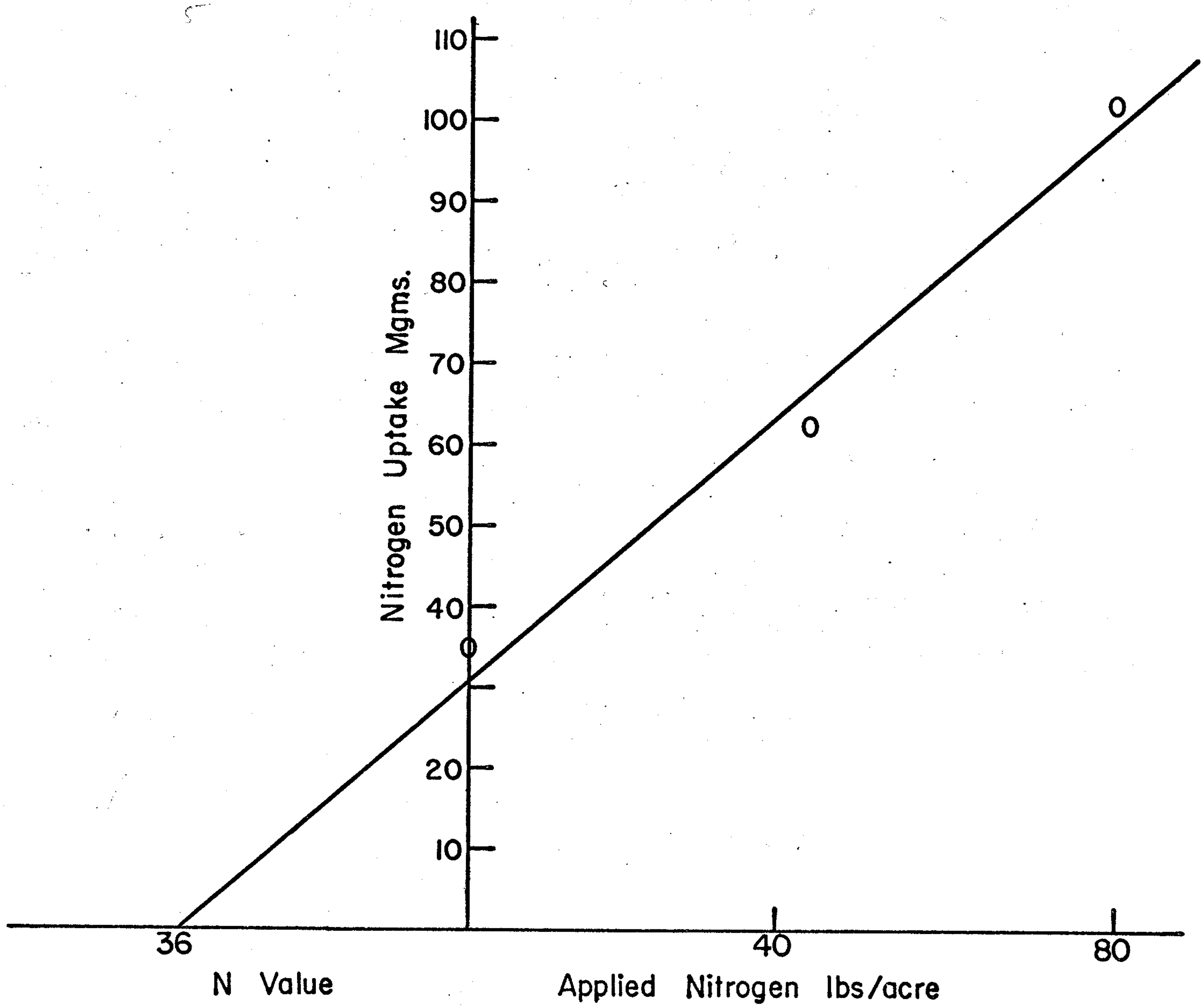


FIGURE 15

'N' Value Graph of Wellwood Soil.

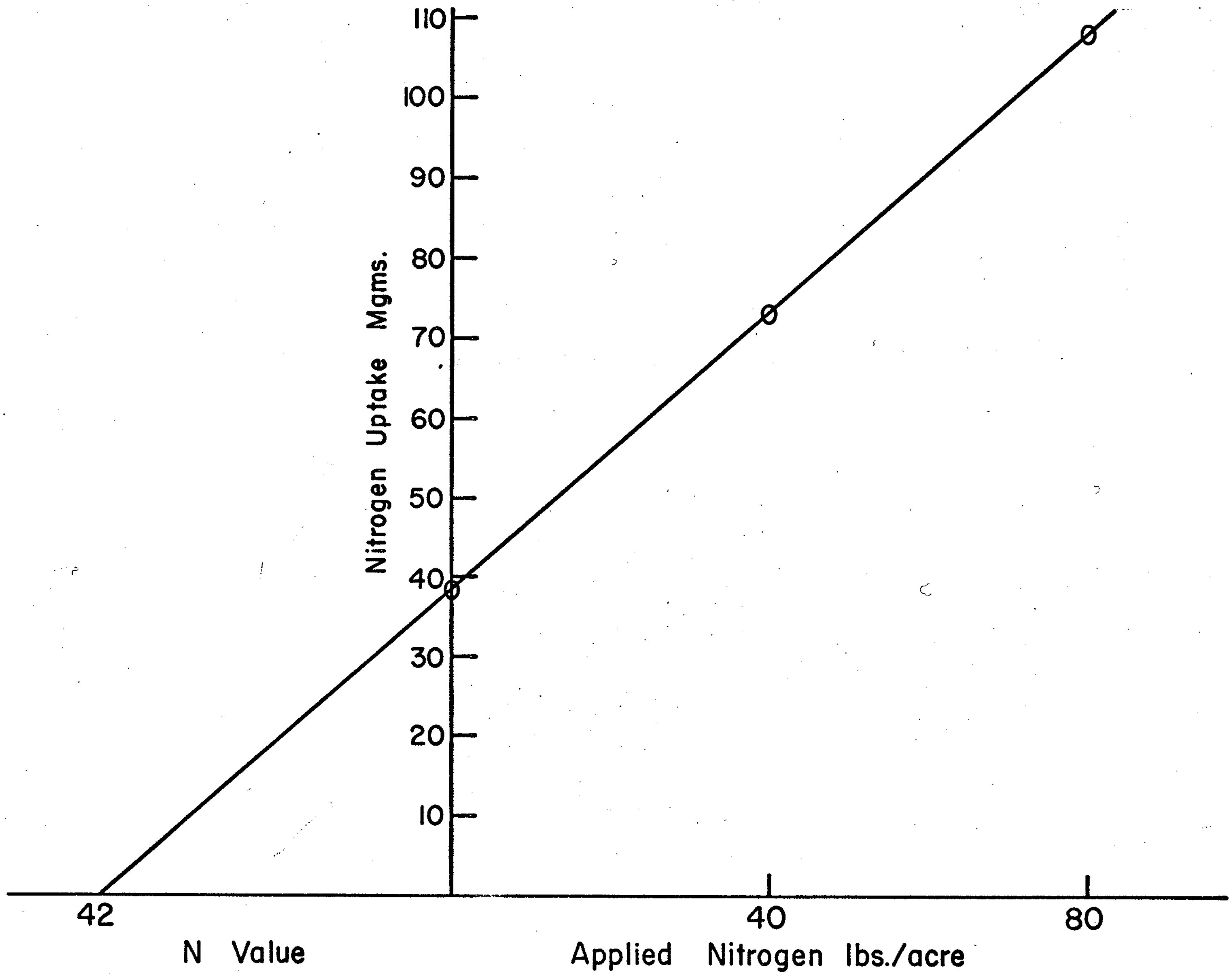


FIGURE 16

'N' Value Graph of Waitville A Soil.

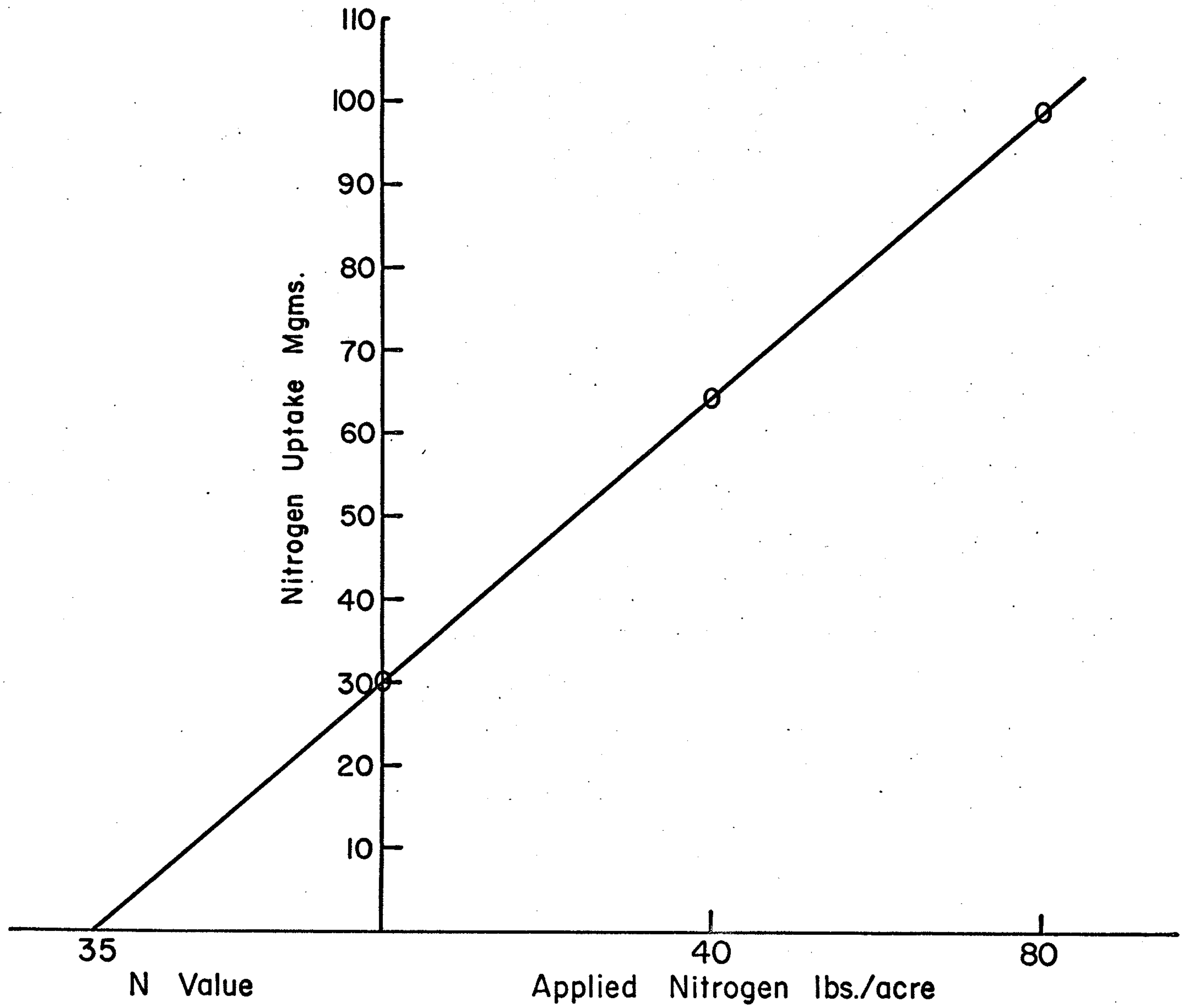
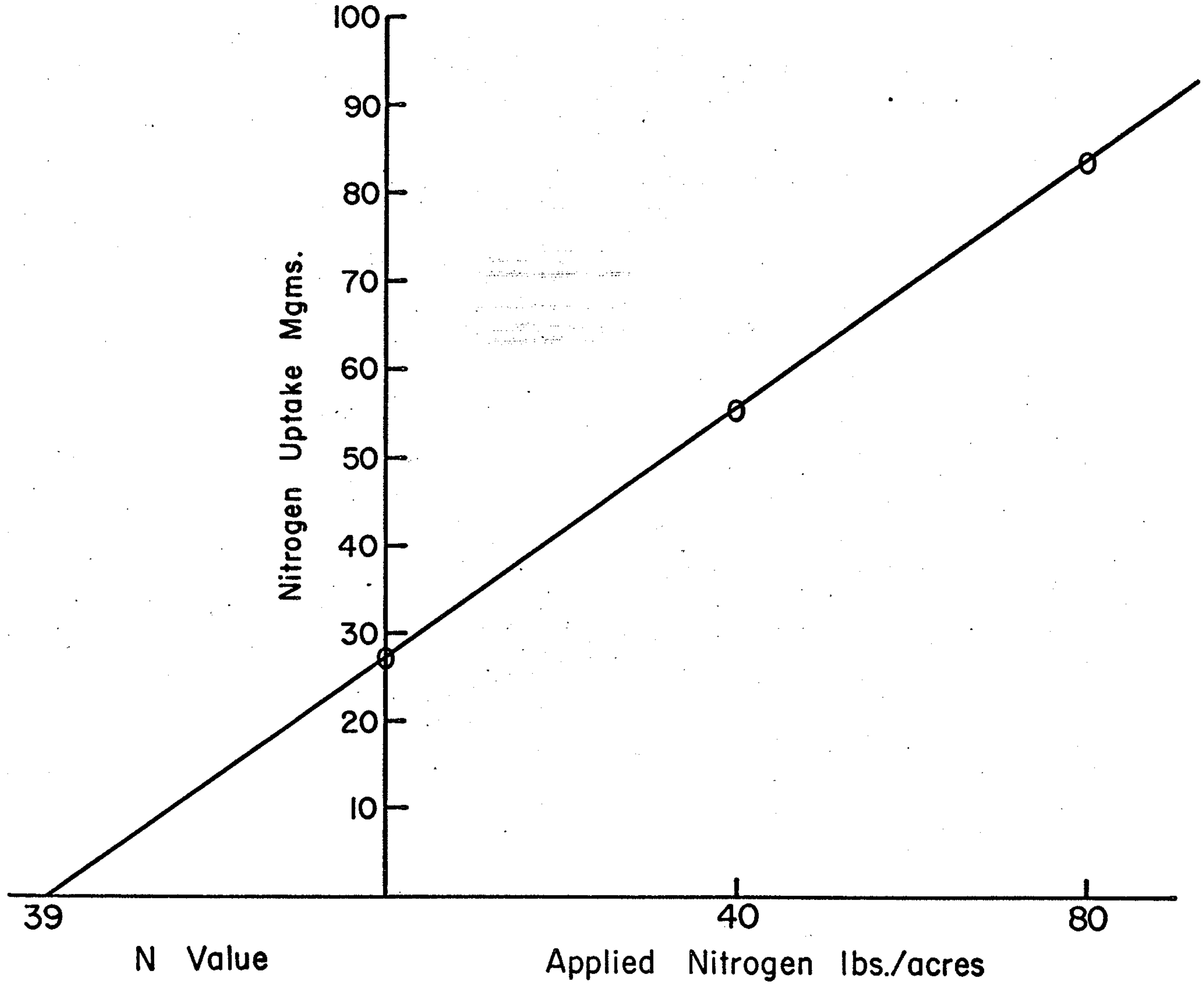


FIGURE 17

'N' Value Graph of Waitville B Soil.



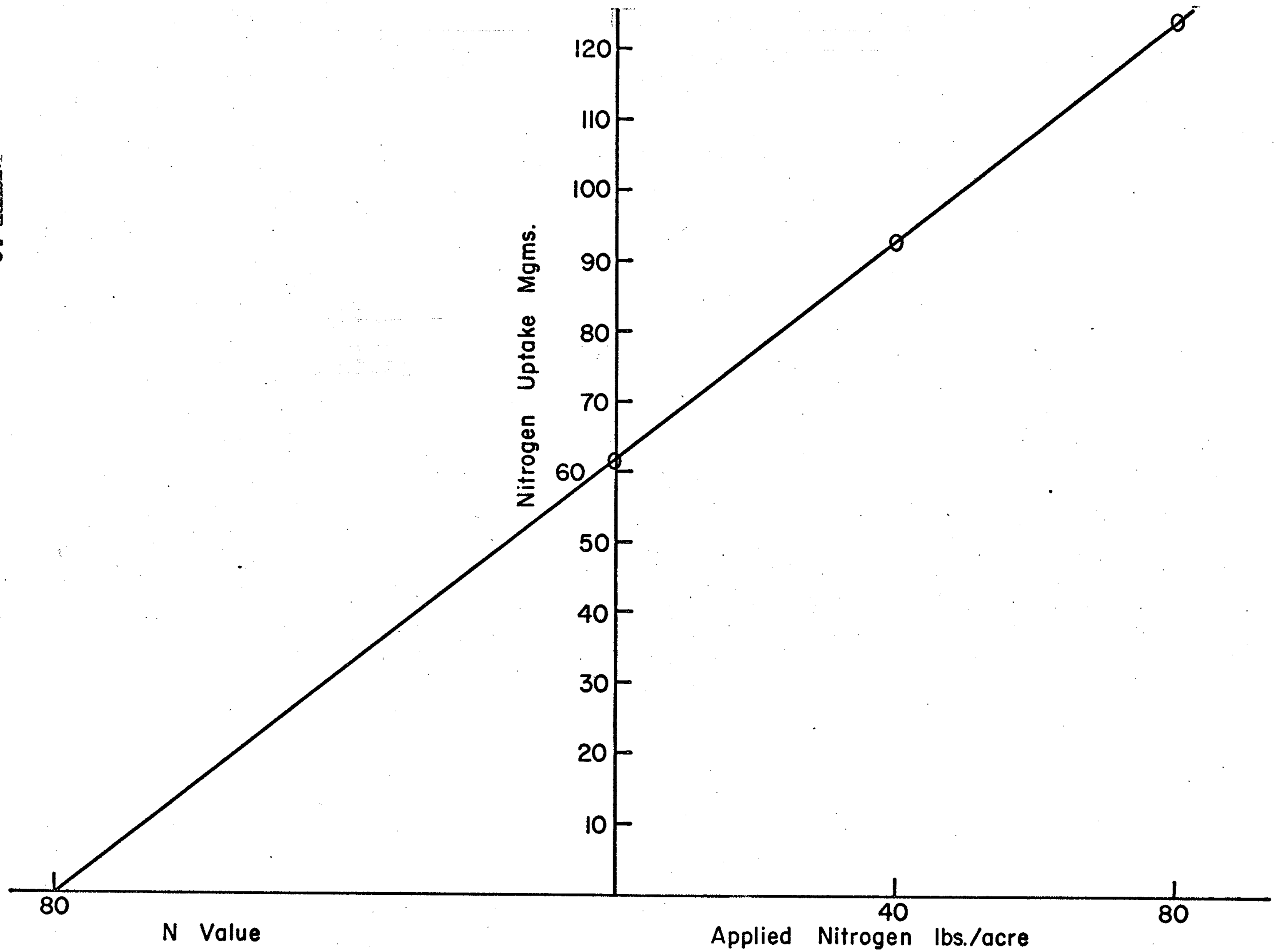


FIGURE 18

'N' Value Graph of Waitville C Soil.