A STUDY OF SOIL AMMONIUM NITROGEN
IN SOME SOILS OF MANITOBA

A Thesis
Submitted to the Faculty of Graduate Studies and Research
of The University of Manitoba

by

Bheemanagouda N. Patil

In partial fulfillment of the
requirements for the Degree of

Master of Science

June, 1965

ACKNOWLEDGEMENTS

The writer wishes to express his indebtedness to Dr. R. J. Soper of the Department of Soil Science, The University of Manitoba, who suggested the problem and under whose supervision the investigation was conducted.

Acknowledgement is also made to Dr. R. A. Hedlin, Dr. M. A. Zwarich and Mr. R. E. Smith for helpful suggestions and criticism of the manuscript.

The financial assistance afforded to the author by the Consolidated Mining and Smelting Company of Canada, Ltd., during the investigation is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE		PAGE

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