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Fate of Added Nitrogen in Soils

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Abstract

The transformation of added N in some Manitoba soils was studied in the laboratory. Addition of urea-N to acid soils led to accumulation of nitrite ions and some of this nitrogen was chemically dentrified. The initial rate of molecular N production was 3.2% of added NO_2 per day in acid Wellwood soil and 1.4% for acid Pine Ridge soil. Nitrite ions also accumulated in the calcareous Almasippi soil (pH 7.7) for a short period, but was dentrified. Oxidation of ammonium ions was very slow in the acid soil.

Soil fixation of added N was greater at low than at high soil pH, and soil organic matter fixed approximately 5 to 10 times as much N per unit weight as did clay. Liming the acid soils considerably reduced the amount of added N fixed.

Introduction

Plant uptake of added fertilizer nitrogen is of prime concern in agriculture. Adequate knowledge of the reaction of various carriers in soils is important in determining efficiency of utilization of added N. In a previous study (Obi et al. 1986) it was shown that plant availability of N from urea was less than from calcium nitrate especially in soils with pH values below 6.0. However, soil fixation (i.e. the portion of added N which could not be extracted from the soil with 2 Mol L^{-1} KCl after series of leaching with this solution) was greater with urea than with calcium nitrate (Obi et al. 1986). Fixation of added N by both organic and inorganic fractions in some soils has been reported by other workers (Bunyakina 1976, Burge and Broadbent 1961, Nommik 1965). It has also been reported by Sowden (1975), that fixation of nitrogen added as manure and ammonium sulphate to a Brunisolic soil containing 20% clay was largely in the vermiculite portion of the clay fraction. Fixation amounted to 50 mg kg^{-1} from manure and 80 mg kg^{-1} from ammonium sulfate.

Added N fixed by soil is directly related to the organic matter and inversely related to soil pH (Nommick and Nilsson 1963b, Porter and Stewart 1970, Smith and Chalk 1980). It has also been observed (Sohn and Peech 1958) that acid soil containing a substantial amount of organic matter has the greatest capacity for ammonia fixation. The purpose of this study was to investigate the fate of added N in some Manitoba soils and to evaluate quantitatively the reactions that lead to temporary or permanent loss of added N.

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Materials and methods

The studies reported were conducted using four Manitoba soils ranging in pH from 5.8 to 7.7. The properties of these soils are summarised in Table 1.

Table 1: SUBGROUP DESIGNATION, LEGAL LOCATION, AND SOME PHYSICAL CHEMICAL PROPERTIES OF THE SOILS STUDIED

Soil Name **Subgroup***	**Pine Ridge** **Eluviated Eutric Brunisol**	**Wellwood** **Orthic Black Chernozem**	**Newdale** **Orthic Black Chernozem**	**Almasippi** **Gleyed Rego Black Carbonated phase**
Texture	FS	FSL	CL	VFSL
pH (1:1 Soil: H_20)	5.8	6.0	7.4	7.7
C.E.C. (cmolkg1)	8.2	21.7	41.2	20.8
Conductivity (Sm^{-1})	0.1	0.2	0.5	1.6
Organic matter (%)	2.4	4.1	9.1	4.6
$CaCO_3$ (%)	0.4	2.2	2.4	6.6
$NaHCO_3$ extr. P (mg kg^{-1})	7.9	11.4	14.8	14.7
H_20 at -0.03 M Pa (%)	17.9	27.0	34.0	27.0
Total N by Kjeldahl (%)	0.10	0.19	0.48	0.24
Exchangeable K (mg kg^{-1})	37.4	307.0	227.0	168.0

FS - Fine Sand FSL - Fine Sandy Loam CL - Clay Loam VFSL - Very Fine Sandy Loam

*Canada Soil Survey Committee, Subcommittee on Soil Classification, 1978. The Canadian System of Soil Classification. Can. Dept. Agric. Pub. 1646. Supply & and Services Canada, Ottawa, Ont. 164 pp.

Nitrogen transformation

Duplicate 100 g samples of air-dried soil were weighed into 250 ml beakers. Ten ml of a urea solution containing 50 mg N was added to each beaker resulting in a urea N content of 500mg kg $^{-1}$. The soil and fertilizer were thoroughly mixed, the soil was moistened to achieve water potential of -0.03 M Pa and the beakers were covered with a polyethylene sheet to minimize loss of water. The beakers were placed in a humidified desiccator and incubated at 20°C for 33 days. A 10 g sample was taken from each beaker every three days, and the remaining soil was kept at a moisture content of -0.03 M Pa suction. The soils were analysed for NH^+_4-N, NO^-_3-N and NO^-_2-N as described by Obi et al. (1986). Moisture content of the soil at the time of sampling was determined.

Chemical denitrification studies

Chemical denitrification has been shown to occur by a van Slyke type of reaction in which one atom of N comes from nitrite and one from soil organic matter (Christianson et al. 1979). The extent to which chemical denitrification occur in the soils used in this study was determined using 25 g soil samples to which $NaNO_2$ containing 50.0% excess ^{15}N was added at a rate of 100 mg N kg^{-1}. The evolved N_2 gas was determined mass spectrometrically as described by Christianson et al. (1979).

Soil and nitrogen fertilizer interactions

Soil and nitrogen fertilizer interactions were studied using ^{15}N labelled urea, $Ca(NO_3)_2$ and $(NH_4)_2SO_4$. The ^{15}N enrichments were 52.7, 52.3 and 54.4 percent excess respectively. The nitrogen carriers were added to 50 g soil samples in 100 ml beakers at a rate of 500 mg kg^{-1}N on a dry soil weight basis. The soils were moistened to achieve a water potential of -0.03 M Pa and incubated in humidified desiccators at 20°C. Incubation times were 14, 28 and 56 days at which times NH^+_4N, NO^-_2N were determined. The desiccators were opened daily to permit air exchange.

Effect of liming acid soils on the amount of N fixation was studied using two acid soils only (Pine Ridge and Wellwood) with and without the addition of lime. The acidity of both soils (Pine Ridge and Wellwood) was adjusted to pH of 7.5 in water by $CaCO_3$ additions of 0.628 and 2.634 g, respectively, per 50 g of soil. Both soils were moistened to achieve a water potential of -0.03 M Pa and incubated for one week before urea and ammonium sulphate additions. Following incubation times of 14, 28 and 56 days the soils were analyzed for NH^+_4-N, NO^-_2N and NO^-_3-N ions. The N not recovered (Fixed N) by KCl extraction was calculated.

Immobilization of N by the soils

An assessment of the amount of organically bound nitrogen was undertaken using the following procedure. To the four soils, labelled urea containing 52.96% excess ^{15}N was added at a rate calculated to give 500 mg N kg^{-1} on a dry soil basis. Fifty-gram samples of each soil were used and each was replicated four times. Soils were moistened to field capacity and incubated at 20°C for four weeks. At the end of the incubation period, the inorganic N was extracted with 2 mol L^{-1} KCl from all the soil samples. Two replicates of each of the extracted soil sample was analyzed for total N by the Kjeldahl procedure. The N content of each soil sample together with the degree of ^{15}N enrichment of the Kjeldahl N was used to calculate the amount of added N fixed against KCl extraction. The other two replicates from each soil sample were treated with 1 mol L^{-1} H_2SO_4 and 30 percent H_2O_2 to destroy the organic matter only without affecting the inorganically fixed NH_4-ions. The soil was then analyzed for total organically bound N. The inorganically fixed N was calculated as the difference between the total N fixed and the N fixed organically. Nitrogen that cannot be extracted with 2 mol L^{-1} KCl is the fixed N, which is determined by Kjeldahl procedure. Organically bound N is determined after treatment with 1 mol L^{-1} H_2SO_4 and 30% H_2O_2. The difference between the two (Total fixed N and organically fixed N) constitute the inorganically fixed N.

Results and discussion

In the acid Pine Ridge and Wellwood soils, most of the added urea was hydrolyzed after six days incubation (Fig. 1a and 1b). As the incubation was continued the level of NH_4-ions decreased. After 33 days it had dropped to 200 mg kg^{-1} and 50 mg kg^{-1} for the Pine Ridge and Wellwood soils, Respectively. Nitrite began to accumulate early in the incubation period and in both soils it reached a maximum after 12 days of incubation (Fig. 1a and 1b). Disappearance of the nitrite took place slowly in the Pine Ridge soil but little remained after 33 days incubation. Small amount of NO_2 accumulated in the Wellwood soil during the incubation period. The total inorganic N was calculated by a summation of the amounts of NH^+_4-N, NO^-_2-N and NO^-_3-N. In the Pine Ridge soil NH^+_4-N amounted to more than 50 percent of the total inorganic N at the end of the incubation period whereas in the Wellwood soil the NO^-_3-N (over 80% total inorganic N) was the dominant soil inorganic form after 33 days incubation. In both soils incomplete nitrification of the urea was probably due to the low pH, which inhibited the activity of Nitrobacter species. There was a gradual decrease in the total amount of inorganic N in both soils during incubation.

In the alkaline Newdale and Almasippi soils hydrolysis of urea was rapid as indicated by the high NH^+_4-N content after six days (Fig. 2a and 2b). Disappearance of the NH^+_4-N was complete after 12 days in the Newdale soil and 15 days in the Almasippi soil. There was a small accumulation of NO^-_2-N in the Newdale soil but this had dissappeared within 12 days of incubation by which time essentially all the inorganic N was present as nitrate. In the Almasippi soil NO_2-ions comprised about 50 percent of the inorganic N in the soil after 12 days of incubation. In 21 days about 90% of the inorganic N was converted to nitrate. The rapid and complete conversion of the added N to nitrate in these soils was probably enhanced by their favourable pH for the nitrification process.

Denitrification study

Accumulation of nitrite may lead to gaseous loss of N via chemical denitrification by a Van Slyke type reaction (Christianson et al. 1979). When nitrite was added at

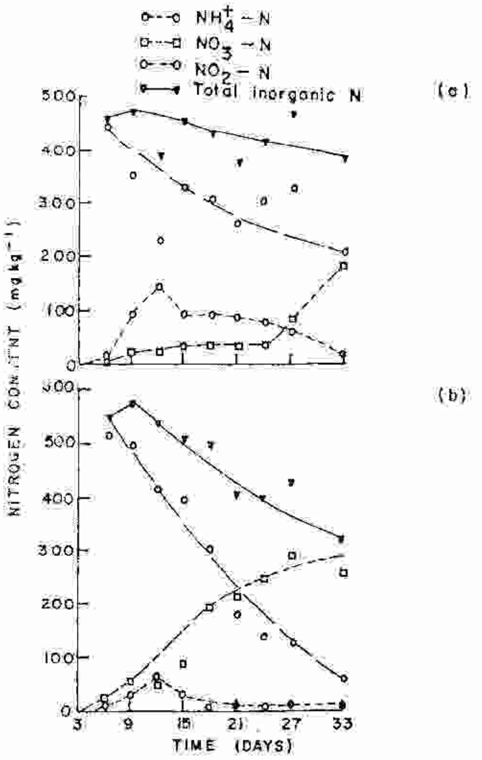

Fig. 1a & 1b : Ammonium, nitrite, nitrate and total inorganic nitrogen in (a) Pine Ridge and (b) Wellwood soils treated with urea – N at 500 mg N kg^{-1}.

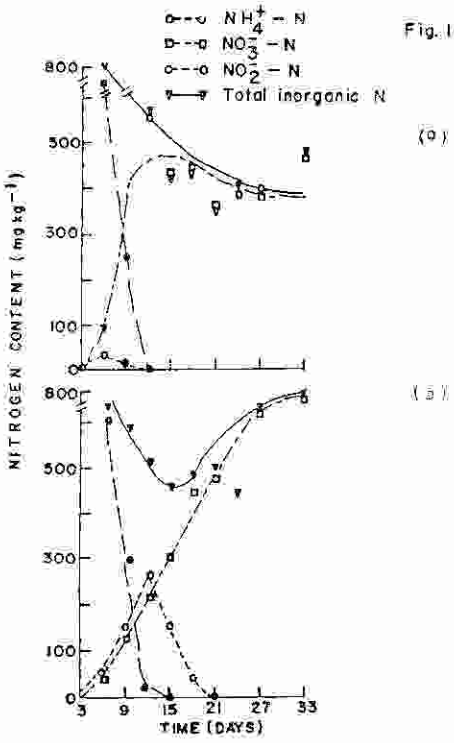

Fig. 2a & 2b : Ammonium, nitrite, nitrate and total inorganic nitrogen in (a) Newdale and (b) Almasippi soils to which 500 mg N kg^{-1} urea was added.

a rate of 100 mg N kg^{-1} as $NaNO_2$ to the Pine Ridge and Wellwood soils a considerable amount of molecular nitrogen was produced (Fig. 3). The initial rate of production of molecular N from added nitrite in Wellwood soil was 3.2 percent of the added N per day and 1.4 percent per day from the Pine Ridge soil. The difference in the rate of cnemically produced N between the two soils may be due to the higher organic matter content (4.1%) in the Wellwood than in the Pine Ridge soil (2.4%). The Almasippi soil which temporarily accumulated NO_2-ions from added urea did not show any appreciable producuon of molecular N in this study. This may be due to the rapid oxidation of NO_2-ions to NO_3-ions which occurred in this soil.

Soil fixed N in organic and inorganic soil fractions

Soil fixed N can be defined as N remaining in the soil after prolong extraction with 2 mol L^{-1} KCl. This may include N fixed chemically by both organic matter and the clay fraction, and also biologically immobilized N. Since biologically immobilized N cannot be distinguished by chemical means, it is here defined as fixed N. The low quantity of N fixed from $Ca(NO_3)_2$ indicates that NH^+_4-N was immobilized preferentially to NO^-_3-N, a fact which has been documented in many immobilization studies (Hargrove and Kissel, 1977; Crasswell, 1979; Dev and Rennie, 1979).

The nature of the soil fixed N and the amount that was bound by the inorganic soil fractions were evaluated. The percentages of the added urea N fixed ranged from 7.0 to 12.6 percent (Table 2). In each soil 60 percent or more of the nitrogen that was fixed was by the organic fraction of the soil. The difference between the total fixed N and that fixed by organic matter was designated as clay fixed N. On the basis of organic matter and clay contents, specific fixation by each of these constituents was calculated. In the more acid soils (Pine Ridge and Wellwood) the specific fixation by both clay and organic matter was greater than in those of alkaline pH. Fixation of added Nitrogen by organic matter ranged from 460 to 1890 mg kg^{-1} and for clay from 50 to 350 mg kg^{-1}.

Table 2: FIXATION OF NITROGEN ADDED AS UREA BY FOUR MANITOBA SOILS (N rate = 500mg kg^{-1}).

	Add N Fixed			**Specific N Fixation**	
Soil	**O.M.**	**Clay**	**Total**	**O.M**	**Clay**
	(%)			(mgkg-1)	
Pine Ridge	9.1	3.5	12.6	1890	350
Wellwood	7.5	5.1	12.6	920	150
Newdale	8.4	3.1	11.5	460	50
Almasippi	5.4	1.6	7.0	580	50

Effect of increasing the pH of Pine Ridge and Wellwood soils on fixation of nitrogen is shown (Fig. 4). Fixation of N from urea added to the Pine Ridge soil at pH 5.8

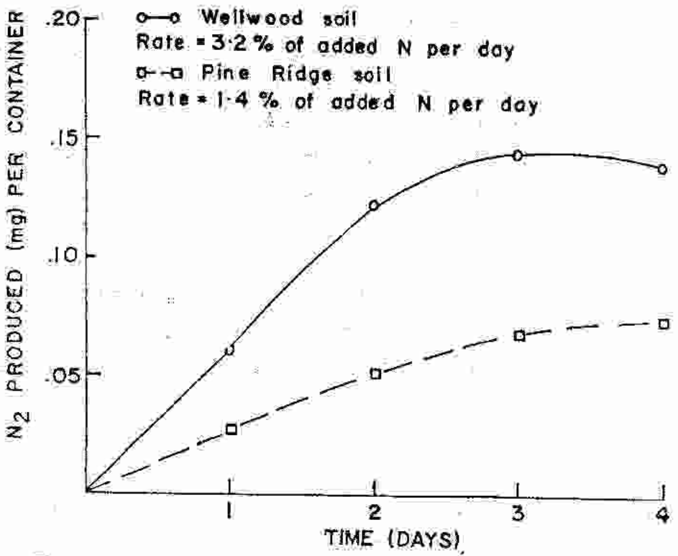

Fig.3 : Chemical Denitrification in Wellwood and Pine Ridge soils Following addition of 2 mg N as $NaNO_2$ containing 50·0 % excess ^{15}N to 20g. soil.

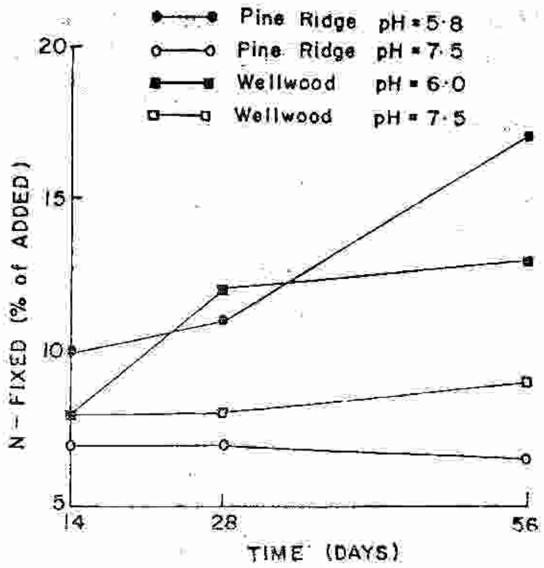

Fig.4 : Fixation of urea N added at 500 mg kg^{-1} by Pine Ridge and Wellwood soils at two pH levels.

amounted to 10 percent after 14 days and increased to 17 percent by 56 days. When pH of this soil was adjusted by liming the quantity of nitrogen fixed amounted to only 8 percent at 14 days and showed very little decrease over time. A similar result was obtained with the Wellwood soil. With this soil fixation reached 13 percent of the nitrogen added at pH 6.0 but when the soil was limed to pH 7.5 fixation of nitrogen amounted to only 6 to 7 percent of that added.

Summary and conclusion

An incubation study indicated that oxidation of NH_4-ions was considerably slower in acid than calcareous soils. Some of the NH_4-ions from added urea remained in acid Pine Ridge soil after 33 days of incubation at 20°C. Nitrite ions accumulated and persisted in Pine Ridge and Wellwood soils following treatment with urea. Accumulation of nitrite was also observed in calcareous Almasippi soil, but only for a short time since it was rapidly oxidised to nitrate.

A tendency for chemical denitrification, with the production of molecular nitrogen, in acid Pine Ridge and Wellwood soils was demonstrated using ^{15}N-labelled $NaNO_2$. The initial rate of production of molecular N in Wellwood soil was 3.2% of added N per day and 1.4% per day for Pine Ridge. Neither of the two calcareous soils, Newdale and Almasippi, produced molecular N from nitrite.

Laboratory study of the interaction between soil and N-carriers in pH amended soils showed that liming acid Pine Ridge and Wellwood soils decreased considerably the amount of added N fixed from ammonium yielding carriers. This was attributed to the reduction in the residence time of NH^+_4-N, Calcium blockage, and a probable increase in microbial population and activity which hastens NO^-_3-N formation from NH^+_4-N yielding carriers.

Assessment of the amount of added urea N fixed per unit weight of organic matter indicated that soil fixation of added N was inversely related to soil pH. The organic matter fixed five to ten times as much nitrogen per unit weight as clay. Also, clay had a greater capacity to fix added N from NH^+_4-yielding carriers at low rather than high soil pH.

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