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SOIL REACTIONS OF
ANIMAL WASTE NITROGEN

by

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INTRODUCTION

In the United States disposal of animal wastes has become a major problem in recent years. It is estimated that domestic animals in this country produce over one billion tons of fecal wastes and over 400 million tons of liquid wastes annually.

The problem of animal waste disposal results from the highly concentrated nature of many modern large cattle and poultry operations where production units containing 10,000 cattle or 1,000,000 birds are common. A unit of 10,000 cattle often produces more than 300 tons of manure daily.

Soil provides perhaps the best facility we have for the disposal of animal wastes. On the other hand, animal wastes provide various nutrients which are essential for crop production. Quantities of manure applied to the soil have normally been limited fairly closely to plant requirements for nutrients. A rate of application of ten tons per acre per year presents no particular problem; decomposition proceeds smoothly and the nutrients released to soil are easily absorbed by the plants (Loehr, 1969).

Due to large tonnage production of animal wastes, the application rate of manure to the soil is increasing. The rate of application is high, sometimes from 50 to 100 tons per acre per year or more. Nitrate accumulation in the soil may result at such high rates of manure application. The accumulated nitrate may pollute ground water by leaching or result in high concentrations of nitrate in crops. Crops grown for silage could contain enough

nitrate to be a health hazard for livestock (Mathers and Stewart, 1971).

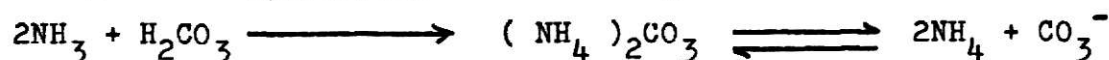
Witzel et al. (1969) reported the results of a study concerning the effect of farm wastes on the pollution of water and they concluded that heavy manure applications can result in dangerously high nitrate concentrations in farm wells.

Another danger that can arise from the use of large amounts of manure on land is salt accumulation. Depressed corn yields were observed due to accumulations of soluble salts in the soil from large continued applications of solid animal wastes (Murphy et al. 1972).

MINERALIZATION OF ANIMAL WASTE NITROGEN

Mineralization

The conversion of organic nitrogen to the more mobile, inorganic state is known as nitrogen mineralization.



This process consists of three steps (1) aminization, (2) ammonification, and (3) nitrification, so named to indicate the form of N each produces. The mineralization of animal waste (N) or organic (N) is predominantly brought about in the soil by microorganisms.

Aminization

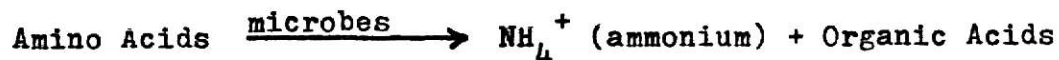
The first step of mineralization results in the formation of amino compounds by enzymatic hydrolysis of protein.



This reaction provides (N) in a form that is readily metabolized by heterotrophic microorganisms responsible for organic matter decay. Since amino compounds are either utilized by microorganisms or rapidly transformed by the process of ammonification, thus they tend not to accumulate in the soil.

Ammonification

In this step of mineralization, amino acids are transformed to ammonium ions and organic acids.

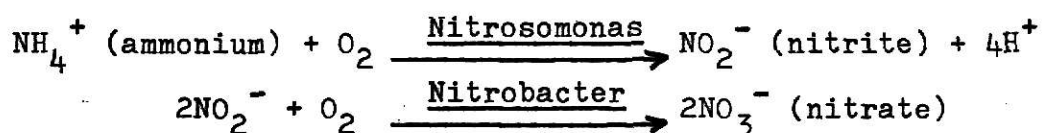


Those heterotrophic microorganisms responsible for aminization are also active in ammonification.

Nitrification

The conversion of ammonium to nitrite and nitrate is called nitrification. Nitrogen that has been released as ammonium from organic forms in soil may be utilized by heterotrophic organisms in further decomposing organic carbon residues. It may also be fixed in a biologically unavailable form in the lattice of certain expanding type clay minerals or converted to nitrite and nitrate by the process of nitrification. As far as plant utilization is concerned no further change in the form of ammonium is required. However, in the soil, the NH_4^+ ion is usually less stable than NO_3^- , due to its rapid conversion to nitrate by nitrification.

Irrespective of the original source of the ammonium ions which are present in the soil, nitrification begins as soon as soil conditions are conducive for bacterial activity. Two steps mediated by different types of organisms are involved in the transformation:



Some of the nitrogen-oxidizing species are listed in Table 1. The organisms active in this process are all special purpose autotrophs. They obtain most of their energy by the oxidation of inorganic compounds (nitrogen) and carbon for cell synthesis is derived from CO_2 , carbonates, or bicarbonates. Under ideal temperature, and moisture conditions, nitrification occurs at a very rapid rate. Daily rates of 6 to 22 pounds of nitrogen per 2 million pounds of soil have been found when 100 pounds of nitrogen in the ammonium form were added (Broadbent, 1957).

Table 1. Nitrifying autotrophic microorganisms (Alexander, 1964).

Ammonium oxidizers	Nitrite oxidizers
<u>Nitrosomonas</u>	<u>Nitrobacter</u>
<u>Nitrosococcus</u>	<u>Nitrocystis</u>
<u>Nitrospira</u>	
<u>Nitrosocystis</u>	
<u>Nitrosogloea</u>	

The rate of mineralization of manure N depends on its type and composition. It was unanimously recognized in the older papers that the organic N of farm manure slowly become available to the crop and no more than 25 per cent of the total N of manure could be used by the crop during the first year of application. Liberation of about 40 per cent of the total N in farm manure within 150 days was reported by Lindhard (1944). Manures function much like soil organic matter in that the organic nitrogen is released or mineralized very slowly (Bremner and Shaw, 1957., Barrow, 1961).

Factors affecting mineralization

a. Substrate composition

Animal wastes added to soil are attacked enzymatically by microorganisms and are split into small molecular or ionic units, which, together with the organic and mineral constituents already present, constitute the nutrient medium from which microorganisms derive energy for metabolism and components for building cellular tissue. Mineralization and immobilization of nitrogen occur continuously in microbial metabolism, and the magnitude and direction of the net effect is greatly influenced by the nature and quantity of manure added.

Manure from animals varies widely in composition, depending upon the type of animal, kind of feed consumed, climatic conditions, management of manure in holding structures, systems of handling upon removal from holding structures, and methods used to return the manure to the soil. Manure contains all the inorganic nutrients needed by plants (Tables 2, 3, and 4). Nearly 90 per cent of the dry matter in manure (beef cattle) is organic waste material from animal digestion of feeds. Animal rations consist largely of

Table 2. Characteristics of Animal manure (Loehr, 1968)

Animal	Moisture	N	P	K	S	Ca	Fe	Mg	Volatile solids	Fat
	%	Kg/metric ton								
Dairy cattle	79	5.6	1.2	5.0	0.5	2.8	0.04	1.1	161	3.5
Fattening cattle	80	7.0	2.0	4.5	0.85	1.2	0.04	1.0	197.5	3.5
Hogs	75	5.0	1.4	3.8	1.35	5.7	0.28	0.8	199.5	4.5
Horse	60	6.9	1.0	6.0	0.7	7.85	0.135	1.4	193.0	3.0
Sheep	65	14.0	2.1	10.0	0.9	5.85	0.16	1.85	283.5	7.0
Broiler	25	17.0	8.1	12.5	From Perkins, Parker, and Walker (1964)					
Hen	37	13.0	12.0	11.4						

Table 3. Trace element concentration of fresh manures
(Atkinson, Giles, and Desjardins, 1954)

Element	Minimum	Maximum	Average
—— ppm, dry-matter basis ——			
Boron	4.5	52.2	20.0
Manganese	75.0	549.0	201.1
Cobalt	0.25	4.70	1.04
Copper	7.6	40.8	15.6
Zinc	43.0	247.0	96.2
Molybdenum	0.84	15.83	2.37

Data from 44 samples of farmyard manure, representing fresh cow, horse, swine, sheep, poultry, and mixed manures and composted cow and mixed manures.

Table 4.

Solid Manure Analysis- Pratt Feedlot

(Murphy, Wallingford, Powers and Manges, 1972)

(dry weight basis)

	N	K	Ca	Mg	P	Zn	Fe	Na
	%	%	ppm	ppm	ppm	ppm	ppm	ppm
Mean	1.04	1.09	7757	3934	4166	66	8825	2280
High	1.59	1.40	10334	5007	5410	102	10250	3174
Low	0.64	0.85	6222	2989	3090	53	7171	1523

Table 5. The total-N content and the rate of production of NO_3^- from several organic materials (Rubins and Bear, 1942).

Organic Material	Total N	Water-soluble N	Conversion to NO_3^-	
			in 20 days	in 40 days
	(%)	(% of total-N)	(% of total-N)	(% of total-N)
Cottonseed meal	7.2	7	49	54
Dried blood	13.8	2	60	66
Horse manure	1.5	20	-19	-16
Chicken manure	2.3	67	22	30
Wheat straw	0.3	38	-16	-15

absence of a marked pH effect on conversion of organic nitrogen to ammonium after dissipation of the temporary effect of liming acid soils may be accounted for on the basis that this transformation is brought about by many different organisms. Hence the change in nature of the soil population with change of soil pH merely substitutes one group of organisms for a somewhat different group that does the same thing.

Organic nitrogen mineralizes more rapidly in neutral soils than in acid soils. At pH values below 5.5, fungi are most active but at pH values of 6.0 and above, actinomycetes and bacteria are more prominently involved. In strongly acid soils Al toxicity, as well as H ion toxicity, may limit microbial breakdown of organic matter. However, Densison (1922) reported that Al actually stimulated ammonifying organisms but adversely affected the nitrifying bacteria.

carbohydrates, some proteins, fats, small amounts of lignin, and numerous inorganic nutrients, such as N, P, K, and a number of micronutrients.

Speed of mineralization varies with the relative availability of carbonaceous and nitrogenous material for the microorganisms. If the nitrogenous material is in excess, nitrogen is mineralized; if the carbonaceous material is in excess, nitrogen is immobilized. Nitrogen is a key nutrient for microbial growth and hence for mineralization of manure. If the nitrogen content of animal waste material is high, the element is readily utilized by the microorganisms. Due to the increased growth of microorganisms, mineralization is rapid and so is release of nitrogen.

In general, in relation to mineralization, a carbon-to-nitrogen ratio of about 22 or a nitrogen percentage of about 2 are critical values. In other words, materials with carbon-to-nitrogen ratios below the critical value and with nitrogen percentages above the critical value may be expected to result in net mineralization of nitrogen in the soil and a release of nitrogen into soil solution.

The experimental results presented in Table 5 indicate determined rates of release of nitrogen from several organic materials.

Negative values indicate that nitrogen was consumed in the biological degradation of organic materials containing less than 1.5 to 2.0 percent of total N. Those with a higher content of N normally result in an early increase in the NO_3^- concentration in the soil solution.

b. Soil pH

Allison and Sterling (1949) noted that nitrogen mineralization usually increased when acid soils were limed.

The rate of nitrification is closely related to pH, and the optimum reaction in soil for many and possibly most of the ammonium oxidizers is above neutrality, while that for the nitrite oxidizers is close to the neutral point (Morrill and Dawson, 1962). Optimum pH beyond 7.5 leads to accumulation of ammonium nitrogen and affects nitrification rate particularly the conversion of nitrite to nitrate. As the alkalinity increases, the nitrite oxidizers (Nitrobacter) are inhibited more readily, with ammonia being especially toxic. Nitrite formation frequently exceeds nitrite oxidation at pH values above 7.8. In an alkaline environment, quantities of nitrite may accumulate for periods up to a few weeks, but these will disappear as nitrite formation lowers the pH and slows down as the ammonium supply is depleted. (Broadbent et al. 1957). The greater inhibition at high pH values may be due to toxicity of ammonia present at high pH values (Stojanovic and Alexander, 1958).

The conversion of ammonium to nitrite, is dependent upon the activity of organisms (Nitrosomonas) characterized by a high optimum pH which is toxic to many organisms. Conversion of ammonium to nitrite tends to lower the soil pH in the vicinity of the reaction due to the production of protons (acid). Nitrobacter organisms which are active in the conversion of nitrite to nitrate are favored by lower soil pH; optimum pH may be approximately 6.5 to 6.8. The conversion of nitrite to nitrate is not an acid producing reaction.

c. Temperature

Mineralization of nitrogen takes slowly at temperatures near freezing, because of the restricted microbial activity, and in-

creases up to temperatures above those at which plants grow. Blackman (1936) noted that higher soil temperatures increased the rate of herbage perennial ryegrass production in the absence of added nitrogen fertilizer. Blackman interpreted this behavior to be a result of increased mineralization of soil nitrogen.

The optimum temperature for ammonium oxidation is usually found to be in the range from 75 to 82 F. At a temperature of 125 F, nitrification practically ceases. At freezing and below freezing temperatures, nitrification will not take place, but at about 35 to 40 F it begins and slowly increases in intensity until the optimum temperature is reached. Lower temperatures do inhibit ammonium oxidation, as illustrated by the data of Sabey et al. (1956) reproduced in Figure 1.

d. Water supply

Since water is the major component of protoplasm, an adequate supply must be available for growth and development of soil microorganisms. The maximum soil bacterial density is found in regions of fairly high moisture content. The optimum level for the activities of aerobic bacteria often is at 50 to 75 per cent of soil's moisture-holding capacity. Excessive water limits gaseous exchange and lowers the available oxygen supply, creating an anaerobic environment. So water logging leads to a decrease of aerobic bacteria, sometimes following an initial but brief rise in the number of aerobes, and a simultaneous stimulation of strict anaerobes.

Figure 2 shows that the release of nitrogen through mineralization increased steadily as the water content of a soil during incubation increased from that corresponding to the air-dry condition up to 21 per cent moisture, which corresponded to the perma-

Fig. 1 - Rate of production of nitrate-nitrogen in ammonium-fertilized soil in the field in Iowa at different temperatures in the autumn. Each measurement was made on previously unfertilized areas of soil to which ammonium sulfate was added at the beginning of the test period to provide 112 and 224 kg of ammonium-nitrogen per hectare (Sabey et al. 1956).

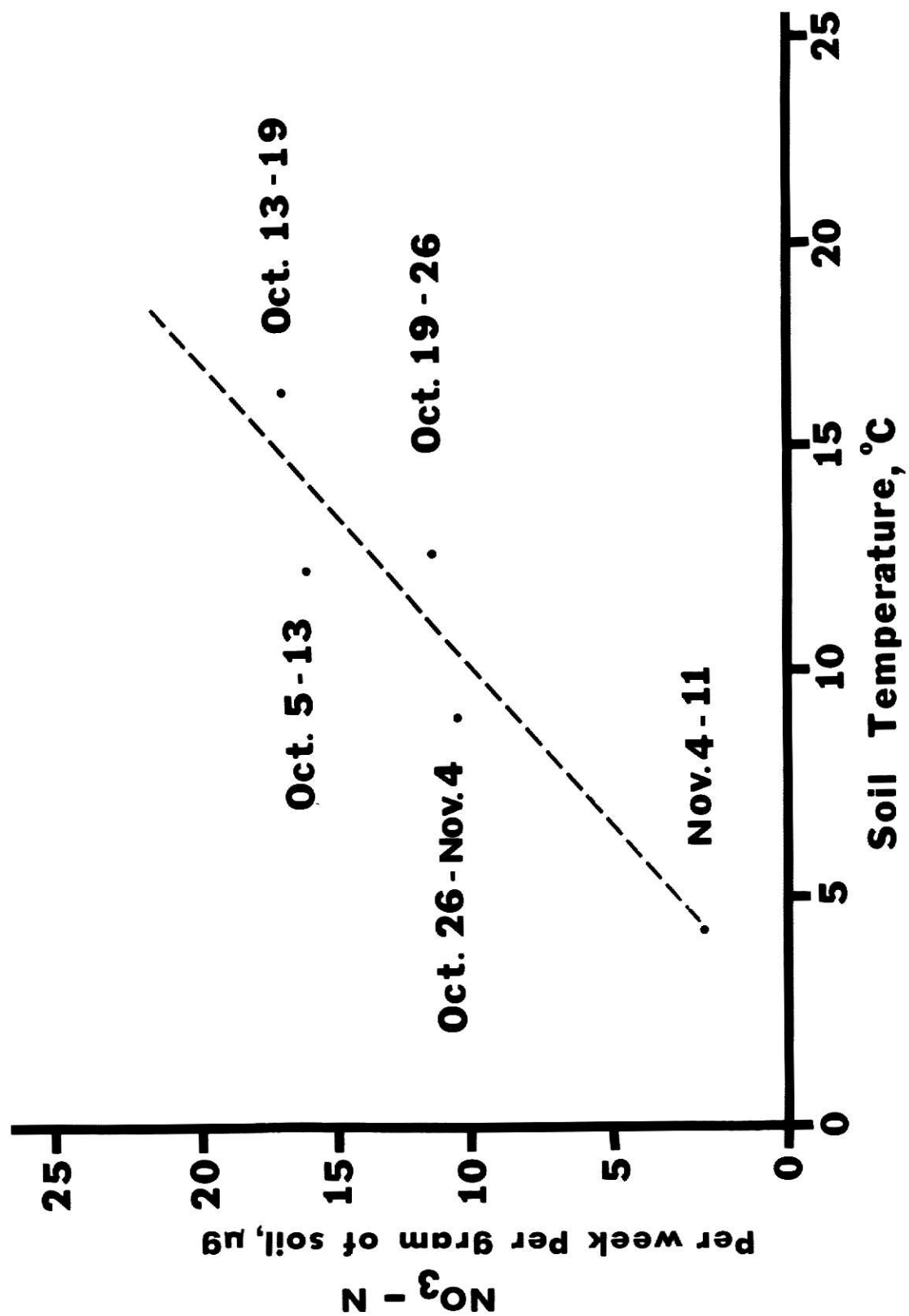
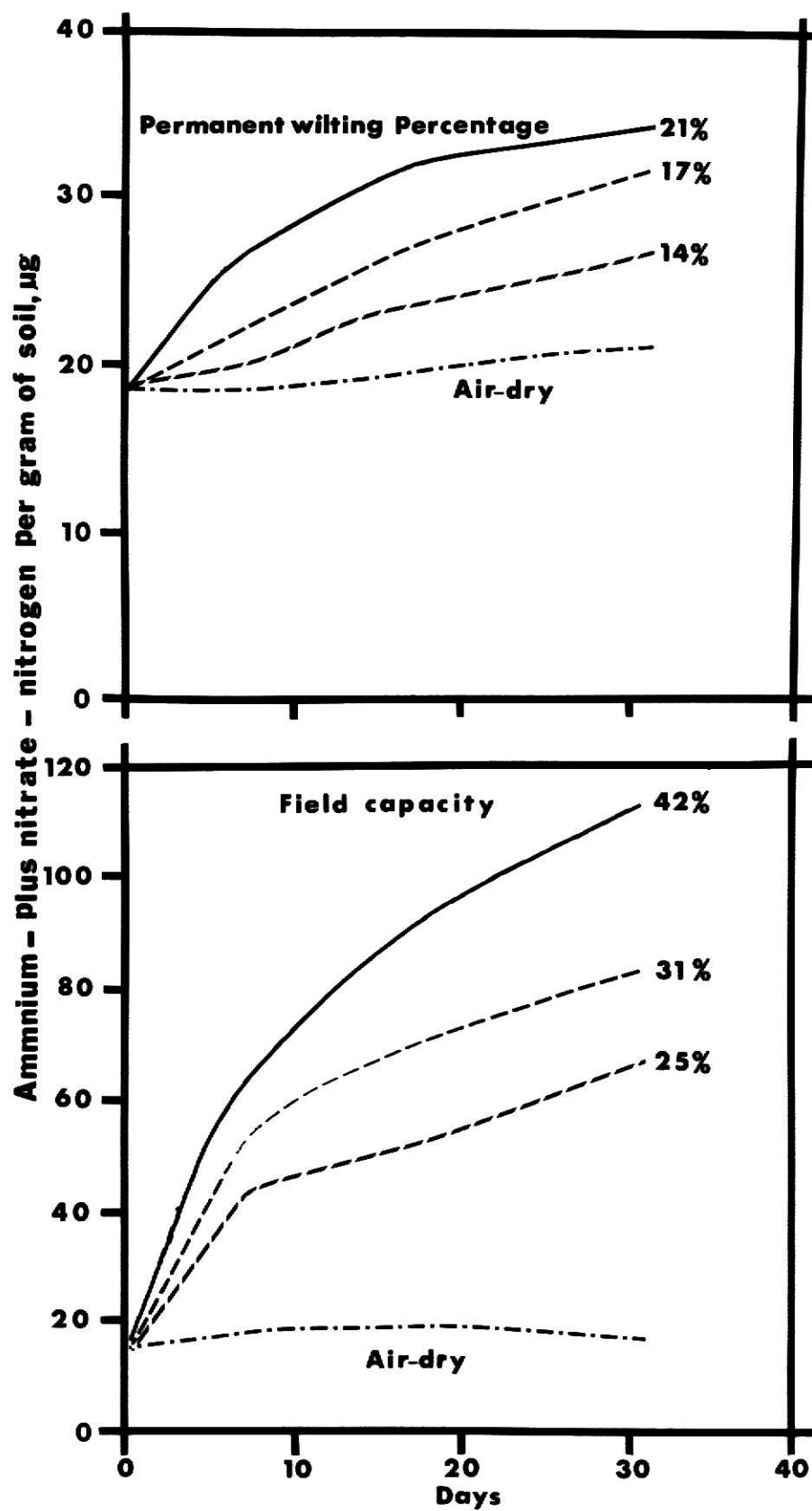


Fig. 2 - Ammonium plus nitrate-nitrogen in a soil during incubation at 35 C in two experiments. The numbers at the right of individual lines are the water percentages in the soil during incubation (Robinson, 1957).



ment wilting percentage. Release of nitrogen further increased as the water content of soil was increased to 42 per cent which corresponds to the field capacity (Robinson, 1957).

Figure 3 shows a plot of the increase in ammonium-nitrogen produced under anaerobic conditions against the increase in the sum of ammonium-, nitrite-, and nitrate-nitrogen produced under aerobic conditions during incubation of samples for two weeks at 30 C (Waring, 1963). The results of these investigations suggest that mineralization of soil organic nitrogen occurs at a gradually increasing rate as the water content of the soil increased from air-dry condition to complete submergence. If submergence conditions were prolonged, soil aerobes decreased so that mineralization decreased.

Generally the greatest nitrifying activity is observed at about half to two-thirds of the soil's moisture-holding capacity. Nitrate is not formed in air-dry soil nor is it produced at very low moisture levels, although the mineralization of nitrogen may proceed when water is present in sub-optimal conditions. Nitrate is produced rapidly in the wet-period following a prolonged drought or in a rainy season following a drought (Jacquemin and Berlier, 1956). Dommergues (1960) showed nitrification would not occur in soils with pF values greater than 4.3 to 4.7. Miller and Johnson (1964) obtained much the same results and also showed that maximum rates of nitrification occur at pF values of 2.2 to 2.7.

Justice et al. (1962) showed that 100 per cent of the ammonium was nitrified in 21 days when 150 ppm of nitrogen as ammonium sulfate was applied to a soil under low moisture tension (7 bars). At the approximate wilting percentage (15 bars), more than half

Fig. 3 - Ammonium-nitrogen produced under anaerobic conditions versus (ammonium + nitrite + nitrate)-nitrogen produced under aerobic conditions during incubation of samples of 39 soils for two weeks at 30 C (Waring, 1963).

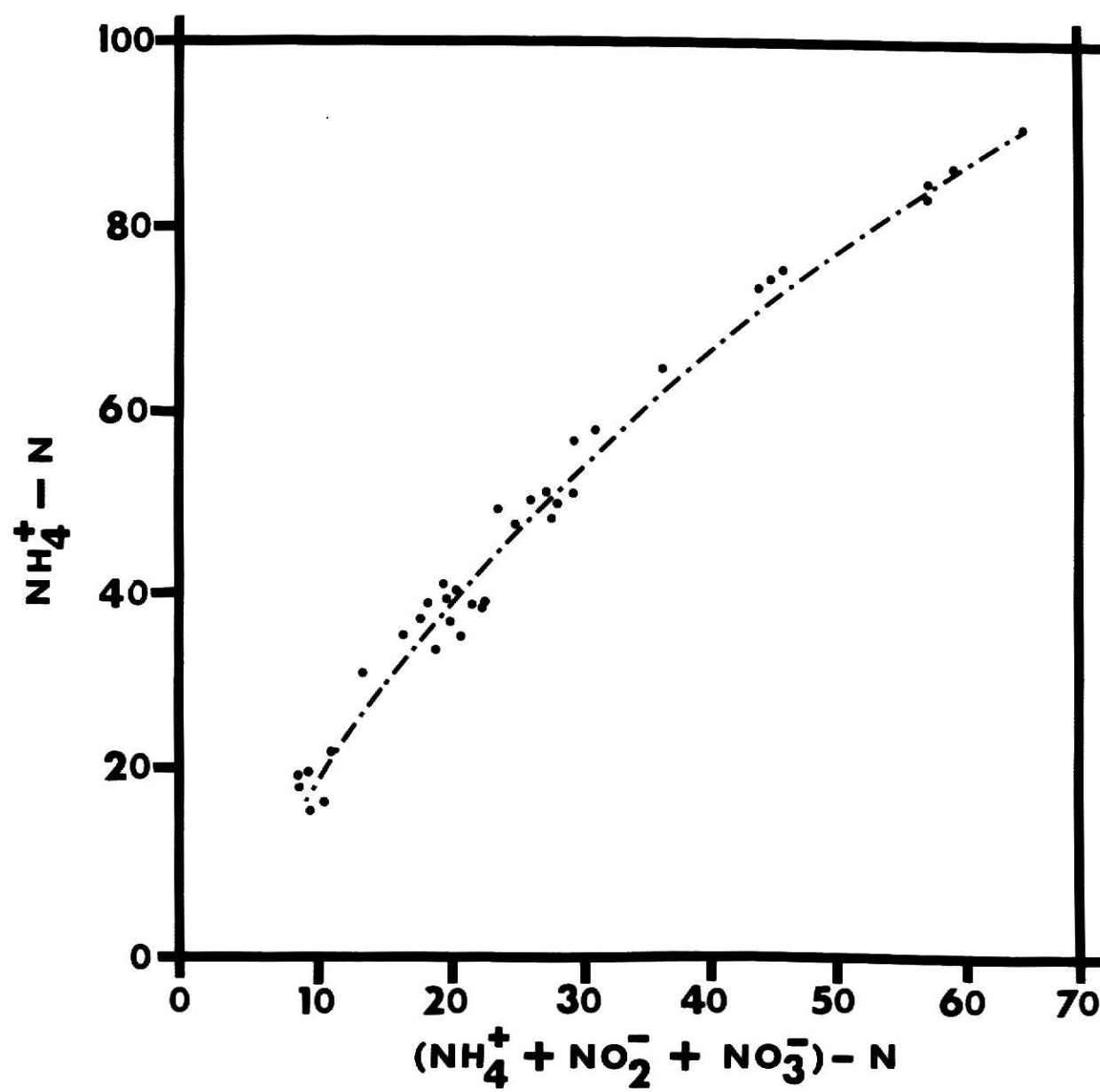
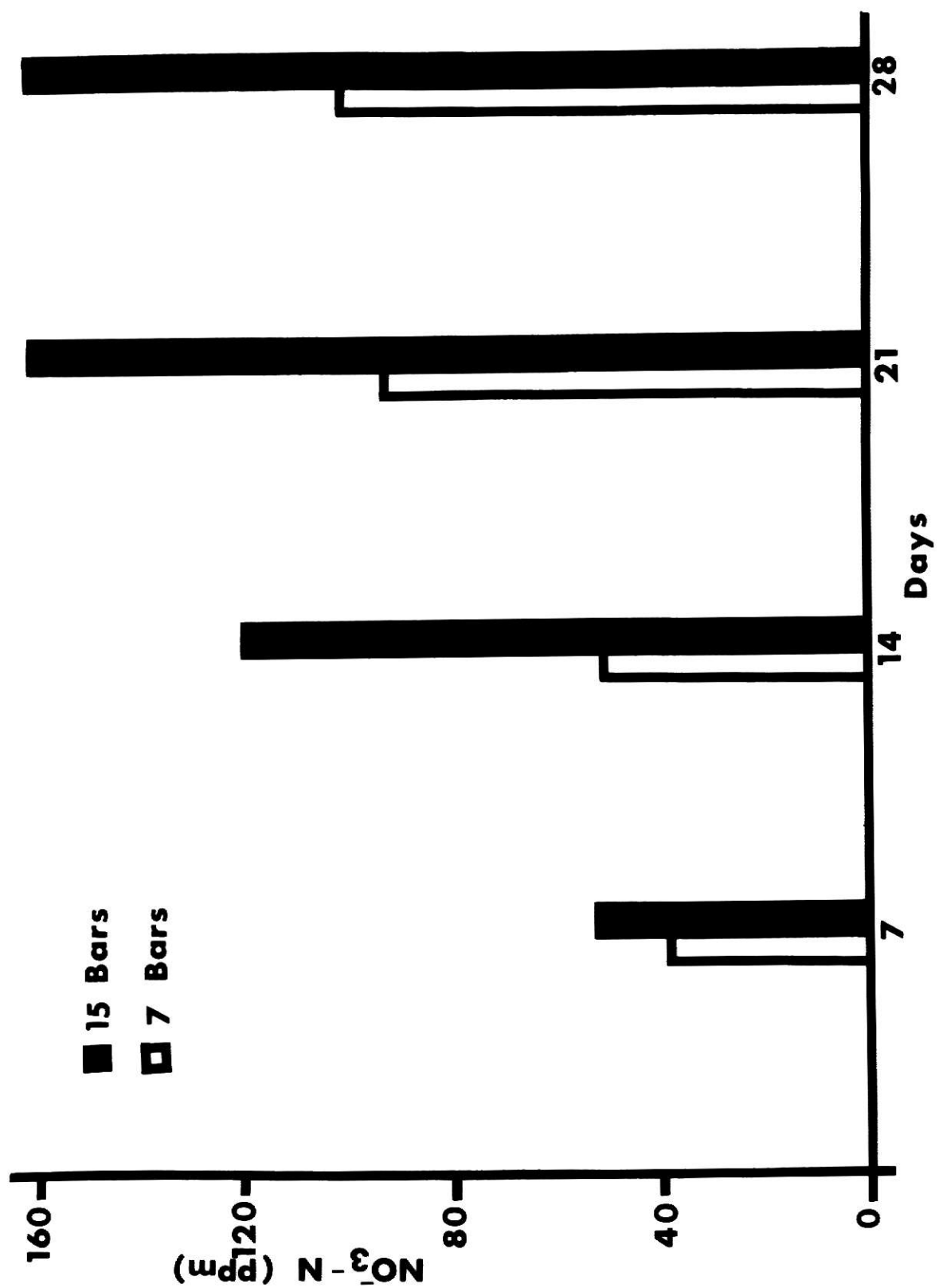


Fig. 4 - The effect of moisture levels near the wilting point on the nitrification of 150 ppm. of nitrogen applied as ammonium sulfate to a Millville loam and incubated at 25 C (Justice et al. 1962).



the ammonium was nitrified at the end of 28 days. These results (Figure 4) indicate that the nitrobacteria function well even in reasonably dry soils.

e. Aeration

Since nitrification is a process of oxidation, oxygen is required in both steps of the process. Any increase of soil aeration up to a certain point, increases the nitrification rate. The optimum percentage of oxygen for rapid nitrate production in soil is similar to that found in air, 20%, (Amer and Bartholomew, 1951; Grechin and Ch' eng, 1960). Figure 5 gives an example of the effect of higher percentages of oxygen on the production of nitrate. Maximum nitrification occurred when the percentage of oxygen reached 20 (Amer, 1949).

f. Effects of Accumulated Salts

Higher rates of animal waste application to the soil results in accumulation of cations such as sodium, potassium and ammonium and causes the soil colloidal particles to be dispersed with alteration of soil structure and reduction of water movement (Travis et al. 1971). Even with more than normal leaching, large amounts of salts accumulated after manure applications greater than 22 tons per ha (Mathers and Stewart, 1971). Electrical conductivity values up to 5.3 mmhos ($\times 10^3$) were observed due to large increases in the amounts of soluble and exchangeable Na and K in soil resulting from heavy application of animal wastes (Figures 6-7, Murphy et al. 1972).

There may be a possibility of increase in soil pH due to accumulation of cations, which is helpful to Nitrosomonas organisms as they are characterized by a high optimum pH. Nitro-

Fig. 5 - Increase in nitrite-nitrogen during incubation of a silt loam soil with ammonium sulfate for three weeks at 30 C under continuous aeration with air-nitrogen mixtures differing in oxygen percentage (Amer, 1949).

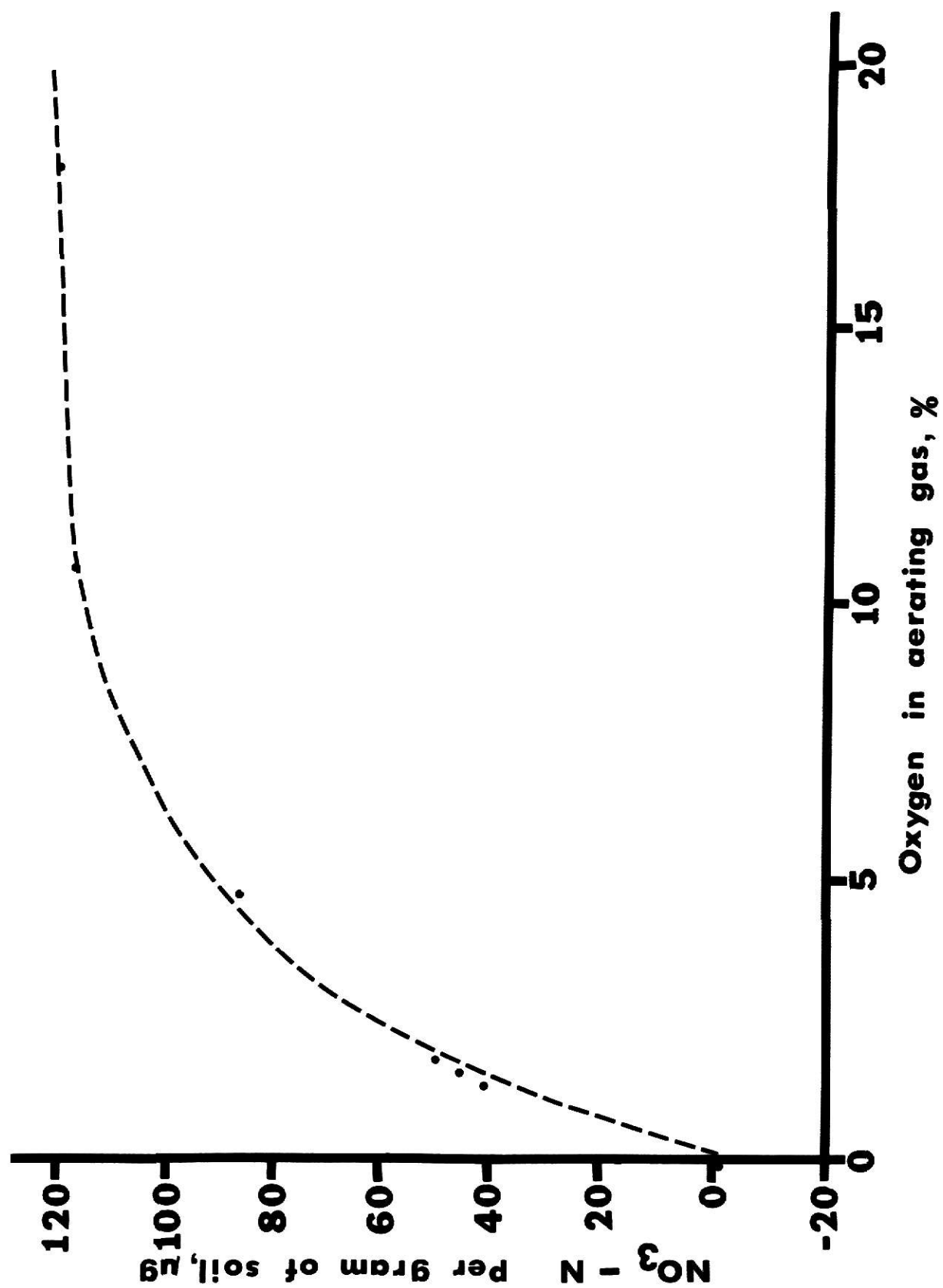


Fig. 6 - Exchangeable + soluble soil sodium in the top
30 cm of soil as affected by manure treatment
and sampling date (Murphy et al. 1972).

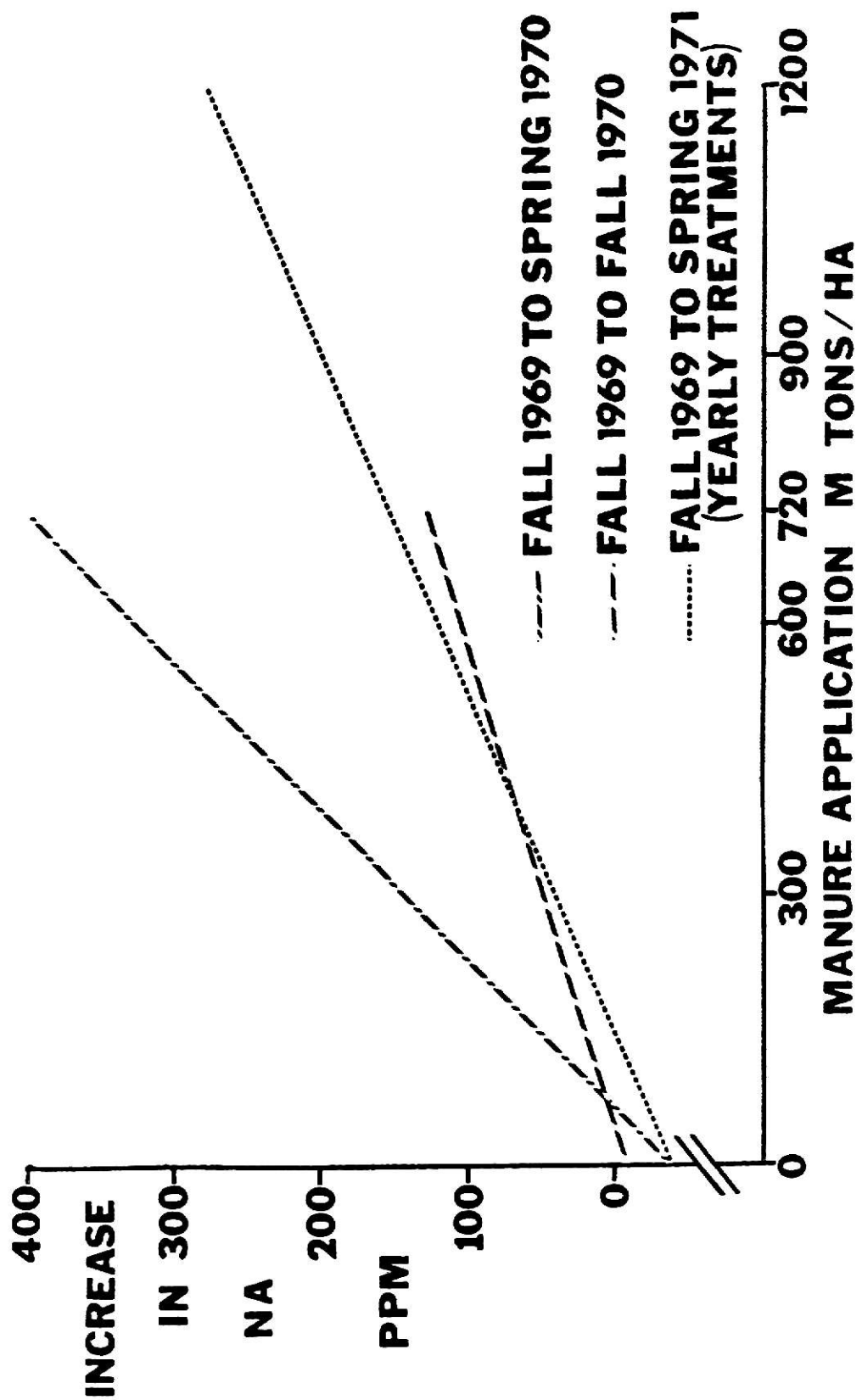
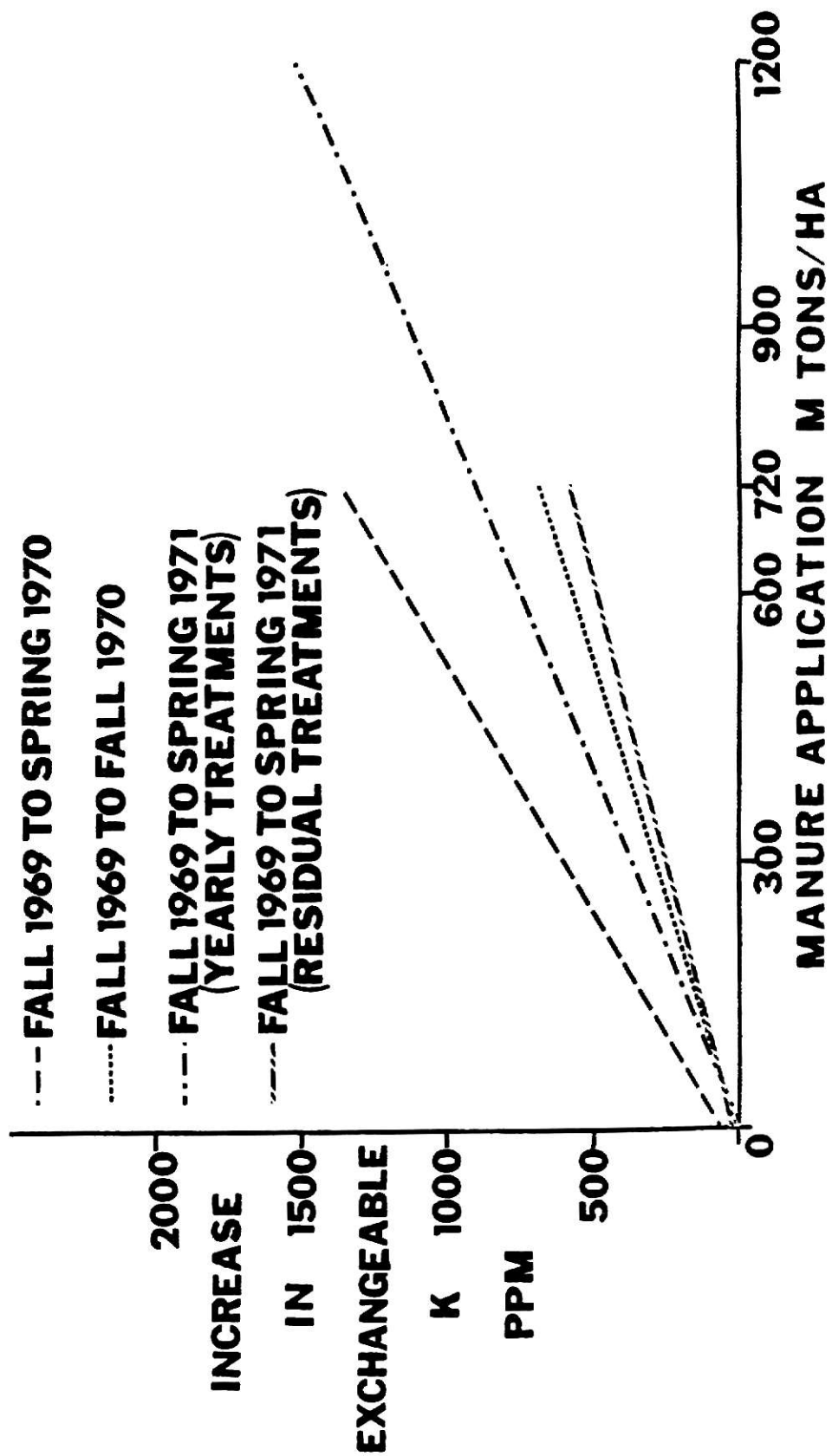


Fig. 7 - Exchangeable soil potassium in the top 30 cm of
soil as affected by manure treatment and sampling
date (Murphy et al. 1972).



bacter can not function well under high soil pH conditions which may lead to accumulation of nitrite in the soil. As nitrite production increases in the soil however soil pH decreases, which in turn improves conditions conducive to Nitrobacter activity and accumulation of nitrate.

Accumulations of soluble salts due to high rates of manure application may cause an increased osmotic potential of the soil solution and subsequently depressed crop yields. Potentially toxic accumulations of ammonium were found in the surface 30 cm of soil due to heavy application of solid beef feedlot waste (Murphy et al. 1972). Accumulations of ammonium could also be toxic to Nitrobacter organisms thus slowing nitrate production.

Possible Mechanisms of Nitrogen Loss
Under High Rates of Manure Application

Losses of nitrogen may occur through several mechanisms, among these are:

1. Leaching
2. Losses as organic substances from plants
3. Losses as oxides of nitrogen by mechanisms other than biological denitrification
4. Losses as nitrogen gas by non-biological chemical reactions
5. Losses as ammonia
6. Losses as nitrogen gas by bacterial denitrification

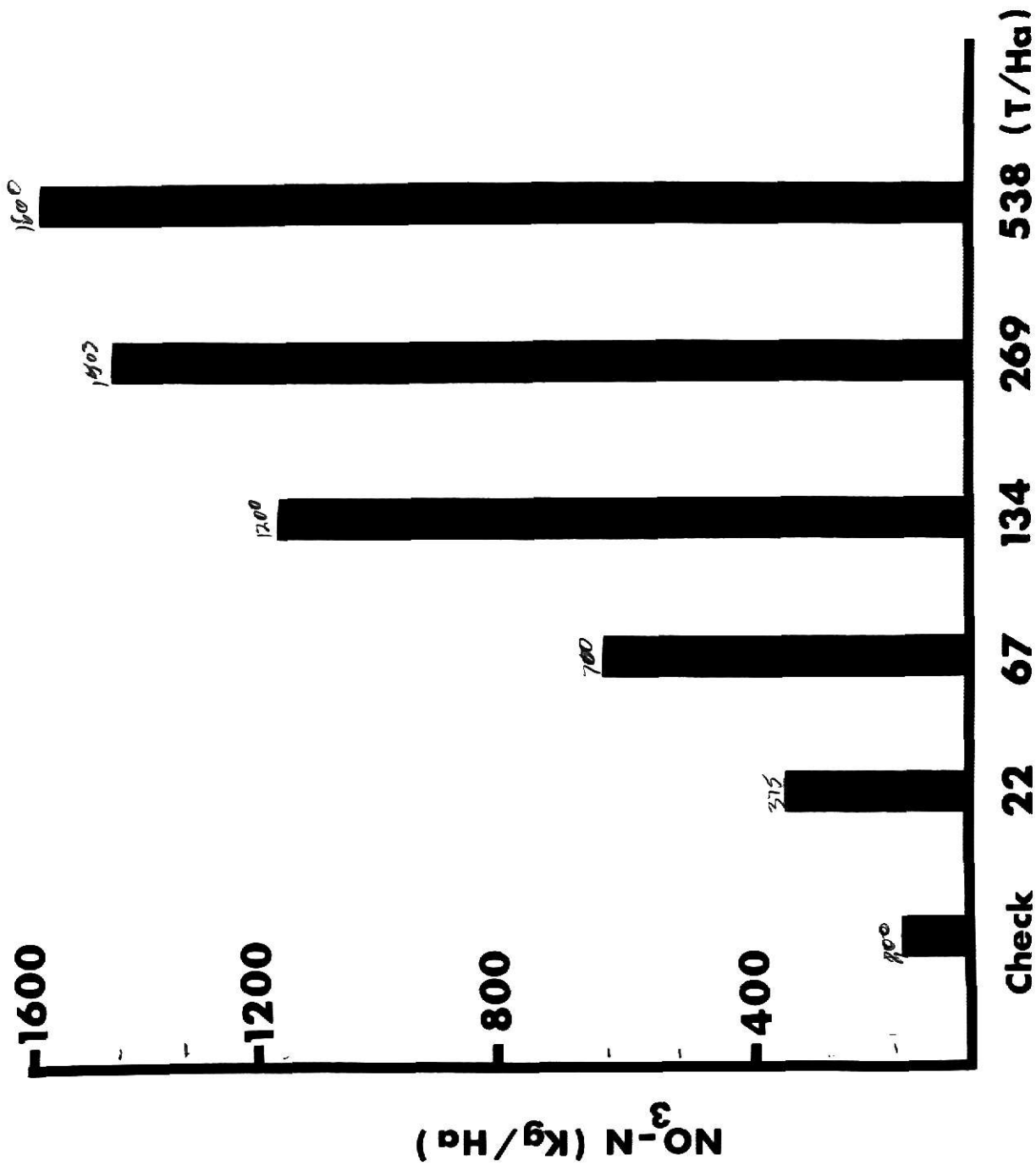
Leaching Losses

High rates of animal waste application to the soil have resulted in accumulation of nitrate-nitrogen (Figure 8). Accumulated nitrate-nitrogen may be lost when rainfall is sufficient to cause water to percolate through the soil profile (Allison, 1966). When a field is irrigated with excess water the water may move most of the nitrate that was present in the top soil to lower levels where it can either accumulate, be lost in the drainage, or be subject to denitrification.

Losses of nitrate-nitrogen by leaching occur more readily from soils of coarse texture than from those of fine texture (Morgan and Street, 1939).

There can be no nitrate leaching if soil moisture is not above field capacity initially and if during a period of a few

Fig. 8 - Total amount of nitrate-nitrogen accumulated in 360 cm profiles following two cropping seasons with the indicated manure applications (Mathers and Stewart, 1971).



days evapotranspiration exceeds precipitation (Allison, 1965). When precipitation exceeds evapotranspiration, leaching can occur after the soil has reached field capacity. Such studies show that there is little likelihood of loss of nitrates from regions where the annual rainfall is below 50 inches unless the soil is very sandy or the rainfall is unusually heavy during short periods. In winter months, however much movement of water through the soil profile may be expected unless the soil is frozen (Allison, 1965).

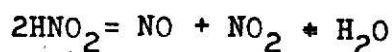
Losses as organic substances from plants

A few organic substances, such as methylamine, trimethylamine, hydrocyanic acid, and nicotine, are known to be exuded from plants and a portion of these compounds may be lost by volatilization. Nitrites, nitrates and ammonia, also commonly occur in plant exudates, but most of this nitrogen returns to the soil (Allison, 1966).

Losses as oxides of nitrogen by mechanisms other than biological denitrification

Nelson (1967) found that loss of nitrite-nitrogen was as great in the absence of microbial activity as in its presence from incubated sterile soils under moist but aerobic conditions for a week after an addition of 100 ug of nitrite-nitrogen per gram of soil. This shows that the principal reaction or reactions responsible for the nitrite loss were not biological in nature.

Several chemical reactions have been implicated in nonbiological loss of nitrogen from nitrite (Nelson, 1967). The most important reaction seem to be the spontaneous decomposition of nitrous acid:



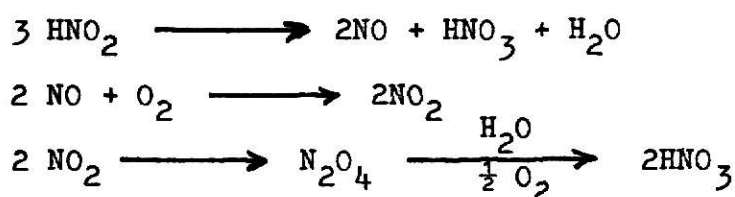
Nelson also noted the evolution of nitric oxide (NO), as indicated in the equation, but only in the absence of oxygen. In the presence of low concentrations of oxygen, nitric oxide was oxidized rapidly to NO₂.

Losses as nitrogen gas by non-biological chemical reactions

Several inorganic chemical reactions have been implicated in non-biological loss of nitrogen from nitrite. It is assumed that the nitrogen losses are the consequence of the chemical decomposition of nitrite under acid conditions, as the highest losses were found in the soils which accumulated nitrite and which were originally acid, or which became acid during incubation (Mulder et al. 1969).

It was found that N₂, N₂O and NO were formed as the result of chemical decomposition. Suggested mechanisms are:

1. The decomposition of nitrous acid leading ultimately to the formation of nitric acid:



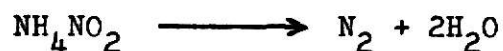
In the presence of low concentration of oxygen, nitric oxide may be oxidized rapidly to nitrogen dioxide (Nelson, 1967).

2. The reaction between nitrous acid and amino acids (Van Slyke reaction) :



The interaction of nitrous acid and aliphatic amino groups with release of nitrogen gas is known as Van Slyke reaction.

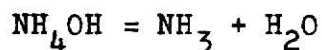
3. The decomposition of ammonium nitrite:



Nelson (1967) examined the ammonium nitrite reaction and obtained no losses of gaseous nitrogen by this mechanism from relatively high concentrations of ammonium and nitrite in acid or alkaline solutions and moist soils. If alkaline soils containing high concentrations of ammonium and nitrite were air-dried, however losses of N from decomposition of ammonium nitrite were found. The losses due to air-drying were large in neutral sand, but in alkaline or acid soil were less significant than losses due to other mechanisms.

Losses as ammonia

Under alkaline conditions the ammonium ion is unstable and subject to conversion to ammonia gas.



Ammonia losses can be high when nitrogenous organic substances, such as animal waste are applied to the soil and permitted to decompose on the surface. Localized increase in pH resulting from ammonia formation produces conditions conducive to ammonia volatilization (Stevenson, 1968). Heavy manure applications resulted in accumulation of ammonium nitrogen at high concentrations in the top 30 cm of a soil profile (Table 6, Murphy et al. 1972).

Ammonia losses are greatest from soils of low cation-exchange capacities. Clay and humus absorb ammonium ions and prevent volatilization. Volatilization losses increase with temperature and may be appreciable when neutral or alkaline soils containing ammonium near the surface are dried out (Allison, 1955).

Volatilization losses to the atmosphere are dependent upon the conversion of ammonium nitrogen back to the ammonia form or to

Table 6.

Ammonium concentrations in soil resulting from high rates of solid manure application. Values existed in April following manure application in October (Murphy et al. 1972)

Average annual manual application, metric tons/hectare

Depth cm	0	ppm $\text{NH}_4 - \text{N}$										Average annual manual application, metric tons/hectare							
		'70	'71	'70	'71	'70	'71	'70	'71	'70	'71	'70	'71	'70	'71	'70	'71	'70	'71
0-10	10	14	8	25	18	21	8	22	9	33	47	266	154	230	26	26	12	7	332
10-20	11	13	27	20	105	14	17	17	149	25	198	49	491	228	269	16	185	14	557
20-30	11	13	6	14	13	7	13	12	86	12	20	8	134	28	27	13	140	14	114
30-40	7	8	3	8	8	7	7	11	9	11	5	6	15	36	7	10	7	12	35
40-50	5	9	3	8	4	6	4	12	8	9	4	1	7	32	5	7	4	10	7
50-60	5	11	2	9	6	5	2	9	16	7	4	0	6	31	4	6	5	7	6
60-70	3	6	2	7	4	3	3	10	5	6	2	0	6	5	5	5	5	7	5
70-80	2	6	2	7	6	3	3	8	2	6	3	0	6	2	4	4	4	4	5
80-90	2	8	1	2	2	2	2	8	3	5	2	2	7	2	2	3	2	5	3
90-100	2	8	1	4	2	4	2	8	3	6	1	2	4	0	2	2	3	5	3

¹First year application only (Fall 1969) no manure in 1970.

a lack of adsorption capacity of soil. Excessively wet soil conditions may also enhance ammonia volatilization.

Losses as nitrogen gas by bacterial denitrification

Most of the gaseous losses of nitrogen from soil other than by ammonia volatilization are brought about by denitrifying bacteria. Denitrification generally refers to the biological reduction of nitrite and nitrate to volatile gases. These gases usually are nitrous oxide and/or molecular nitrogen. The process is accomplished by facultative anaerobic bacteria capable of using nitrate in place of oxygen as an electron acceptor in their respirational process.

In general, denitrifying microorganisms are abundant and counts in excess of a million per gram of field soil are not uncommon. The population is typically large in the immediate vicinity of plant roots. The potential for volatilization of nitrogen is therefore enormous, but conditions must be suitable for organisms to change from aerobic respiration to denitrifying types of metabolism.

N_2 and N_2O are the common gaseous products of this process as mentioned above. Elemental nitrogen is usually the dominant product but N_2O is evolved under some conditions as well (Alexander, 1964). The process normally occurs only when the partial pressure of oxygen is low (Turner and Patrick, 1968).

Only a relatively small number of bacterial species can bring about denitrification. The active species are largely limited to the genera Pseudomonas, Achromobacter, Bacillus, and Micrococcus as well as Thiobacillus denitrificans. Occasionally Chromobacterium, Mycoplana, Serratia, or Vibrio species may take part in the denitri-

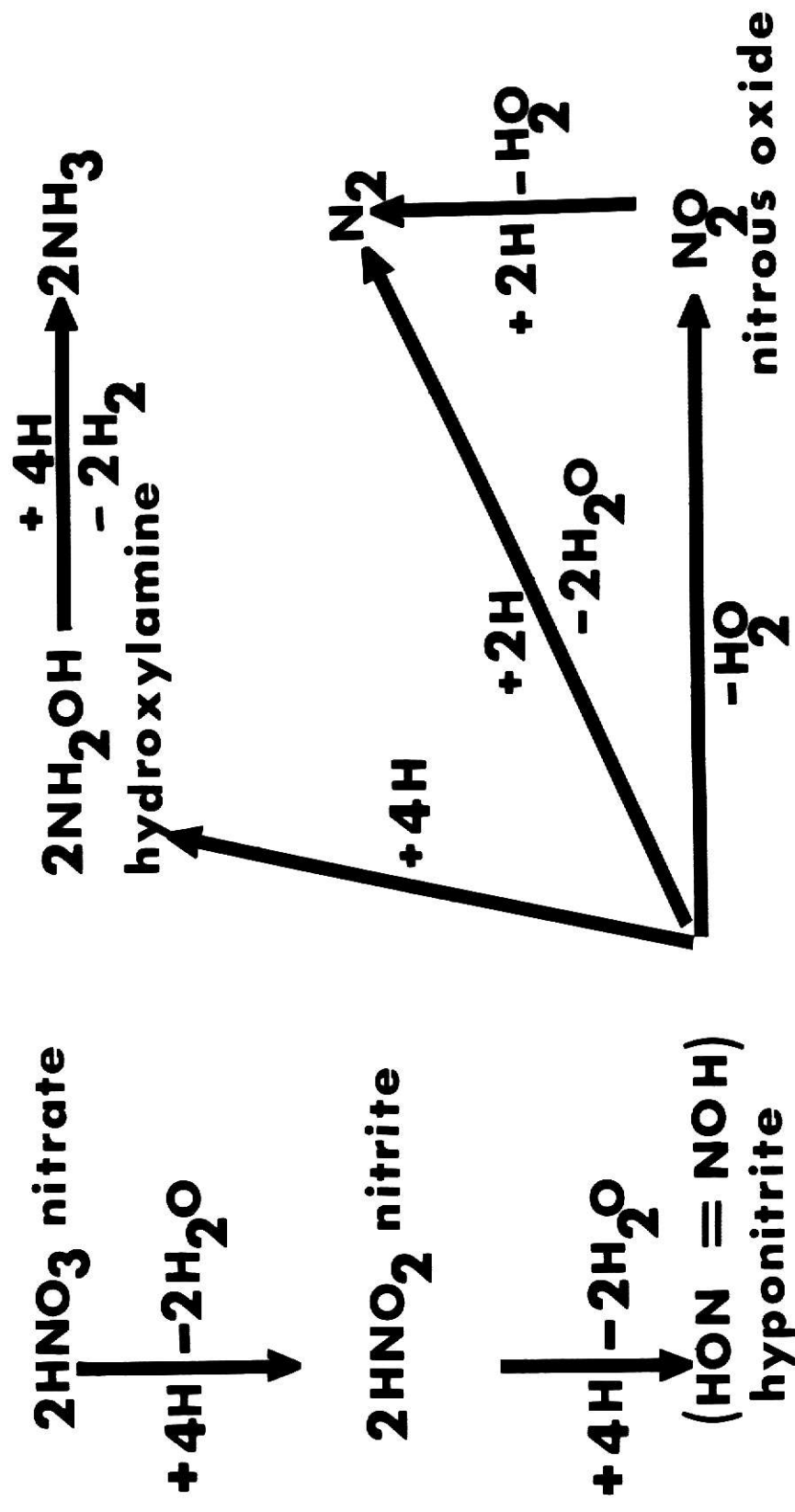
fication process (Alexander, 1964).

Pseudomonas and Achromobacter are the dominant genera in the soil. Several chemoautotrophs are capable of reducing nitrate to molecular nitrogen. Micrococcus denitrificans, a facultative autotroph, develops aerobically or anaerobically with either organic compounds or hydrogen as sources of energy and oxygen or nitrate as electron acceptors (Alexander, 1964; Mulder, 1969).

The possible actions of the denitrifiers on nitrate include: (a) complete reduction to ammonium frequently with the transitory appearance of nitrite; (b) an incomplete reduction to nitrite and an accumulation of nitrite in the medium; and (c) a reduction to nitrite followed by the evolution of gaseous compounds, i.e., denitrification (Alexander, 1964). Cady and Bartholomew (1960) reported that the initial gaseous denitrification product was found to be small amounts of nitric oxide which is attributed to decomposition of nitrous acid. Nitrous oxide then appeared and nitric oxide decreased. After an increase in nitrous oxide, molecular nitrogen was produced. Wijler and Delwiche (1954) found nitrous oxide to be the major denitrification product under most soil conditions, but noted that relative proportions of N_2O and N_2 depend on pH. Above pH 7 nitrous oxide could be readily reduced to nitrogen, but below pH 6 its reduction was strongly inhibited. Proposed biochemical pathways are shown in Figure 9.

Denitrification is inhibited by oxygen, probably because oxygen competes with nitrite for the role of electron acceptor. Consequently highest denitrification rates are found in waterlogged soils, especially those supplied with nitrate fertilizers or in which nitrification has recently taken place. The lowest rates occur

Fig. 9 - Possible pathways of denitrification (Alexander,
1964).



Possible Pathway Of Dentrification

in well aerated soils (Bremner and Shaw, 1958). Conditions conducive for denitrification are waterlogging, high soil pH, high soil temperature, a large amount of oxidizable carbon, and a large number of soil microorganisms (Tisdale and Nelson, 1966).

Factors affecting denitrification

a. Carbon content of the soil

Denitrifying organisms need a source of H^+ ions and electrons to reduce nitrate and carbon sources and a source of ammonia for cell protein synthesis. In soils, organic matter is the source of all these. Thus denitrification is absent or slow in soils low in organic matter and is enhanced in such soils by adding organic matter (Bremner and Shaw, 1958). Most soils presumably contain adequate amounts of organic compounds to bring about denitrification when oxygen is lacking. Bremner and Shaw (1958) found denitrification to be absent only when the content of soil organic matter was less than 1 percent.

High rates of manure application leads to an increase of soil organic matter and carbon. Mathers and Stewart (1971) and Murphy et al. (1972) have reported accumulation of nitrate-nitrogen and ammonium nitrogen in soil with high rates of manure application under irrigated conditons. The low nitrogen requirement of the anaerobic organisms responsible for organic matter decomposition results in ammonia being released to the soil solution at much wider C:N ratios than would the case with aerobic decomposition (Alexander, 1964). Solid animal wastes contain large amounts of carbon and much higher percentages of N than has been reported in the past (Mathers and Stewart, 1971), and (Murphy et al., 1972).

b. Oxygen supply

Oxygen availability is another of the critical environmental detriments for denitrification. Aeration affects the transformation in two apparently contrasting ways: on the one hand, denitrification proceeds only when the oxygen supply is insufficient to satisfy the microbiological demand; at the same time, oxygen is necessary for the formation of nitrite and nitrate, which are essential for denitrification. Decreasing the partial pressure of oxygen enhances the probability of denitrification in the soil. Anaerobic micro-environments exist at microscopic sites in well-drained soil whenever the biological oxygen demand exceeds the supply denitrification occur (Alexander, 1964).

c. Effect of pH

Rate of denitrification is profoundly influenced by soil pH, being very slow in acid soils, and very rapid in soils of high pH (Bremner and Shaw, 1958) Jansson and Clark (1952) found that an alkaline soil pH was required for any extensive denitrification and nitrite toxicity appeared to inhibit denitrification in an acid soil. Hiltbold and Adams (1960) noted that soil pH was increased by denitrification regardless of the probable gaseous form of loss and suggested that this helps to counteract the drop in pH which results from nitrification.

d. Temperature

Denitrification is highly temperature dependent. The process will proceed slowly down to as low as 2 C. The optimum for the reaction is 25 C and above. The transformation is rapid at elevated temperatures and will proceed to about 60 to 65 but not at 70 C. The relative proportions of N_2O and N_2 in the denitrification

gas vary with temperature, nitrous oxide being predominant at lower temperatures and molecular nitrogen predominant at higher temperature (Alexander, 1964).

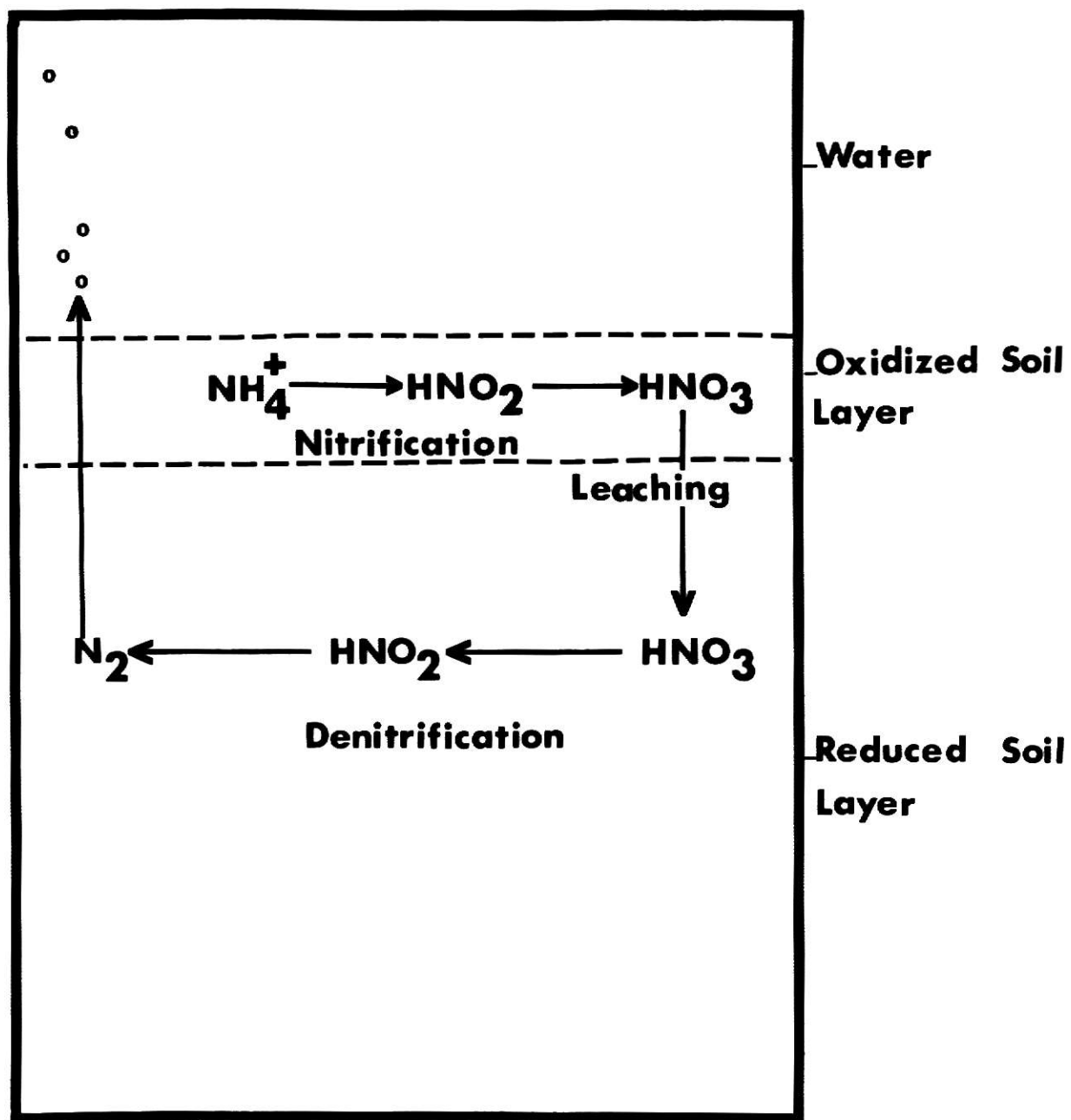
e. Moisture

The moisture level in the soil affects denitrification mainly from the standpoint of its affect upon oxygen diffusion rate into the soil. Denitrification is completely stopped at moisture levels below 60% of the water holding capacity of the soil and is fairly slow at 80% (Alexander, 1964). Nitrogen losses are the highest under waterlogged conditions and continue to increase up to 450% of the water holding capacity of the soil (Bremner and Shaw, 1958). Alternate wetting and drying increases the denitrification loss (Patrick and Wyatt, 1964); continuous submergence minimizes it and may even lead to a substantial accumulation of nitrogen (IRRI, 1969).

Denitrification in cultivated soils is undesirable because it causes the loss of a valuable plant nutrient. However, with heavy soil applications of manure, loss of nitrogen by denitrification is desirable because it helps to prevent the accumulation of nitrate nitrogen in the soil and subsequently diminishes the chances for contamination of ground water by nitrate.

A schematic diagram of denitrification process in waterlogged soils is shown in Figure 10.

Fig. 10 - Schematic diagram of the process by which ammonium
fertilizer can be lost from waterlogged soil
(Mitsui, 1954).



Conclusion

Whenever animal wastes are applied to the soil, ammonium ions are released by microbial processes involving decomposition of nitrogen containing compounds such as proteins and amino acids. Ammonium ions produced by the ammonification process may accumulate to toxic levels and depress the germination and growth of crop plants. Potentially toxic accumulations of ammonium nitrogen have been noted in the surface 30 cm of soils following heavy manure applications. Higher concentrations of ammonium nitrogen may also be detrimental to Nitrosomonas organisms involved in the first reaction of the nitrification process.

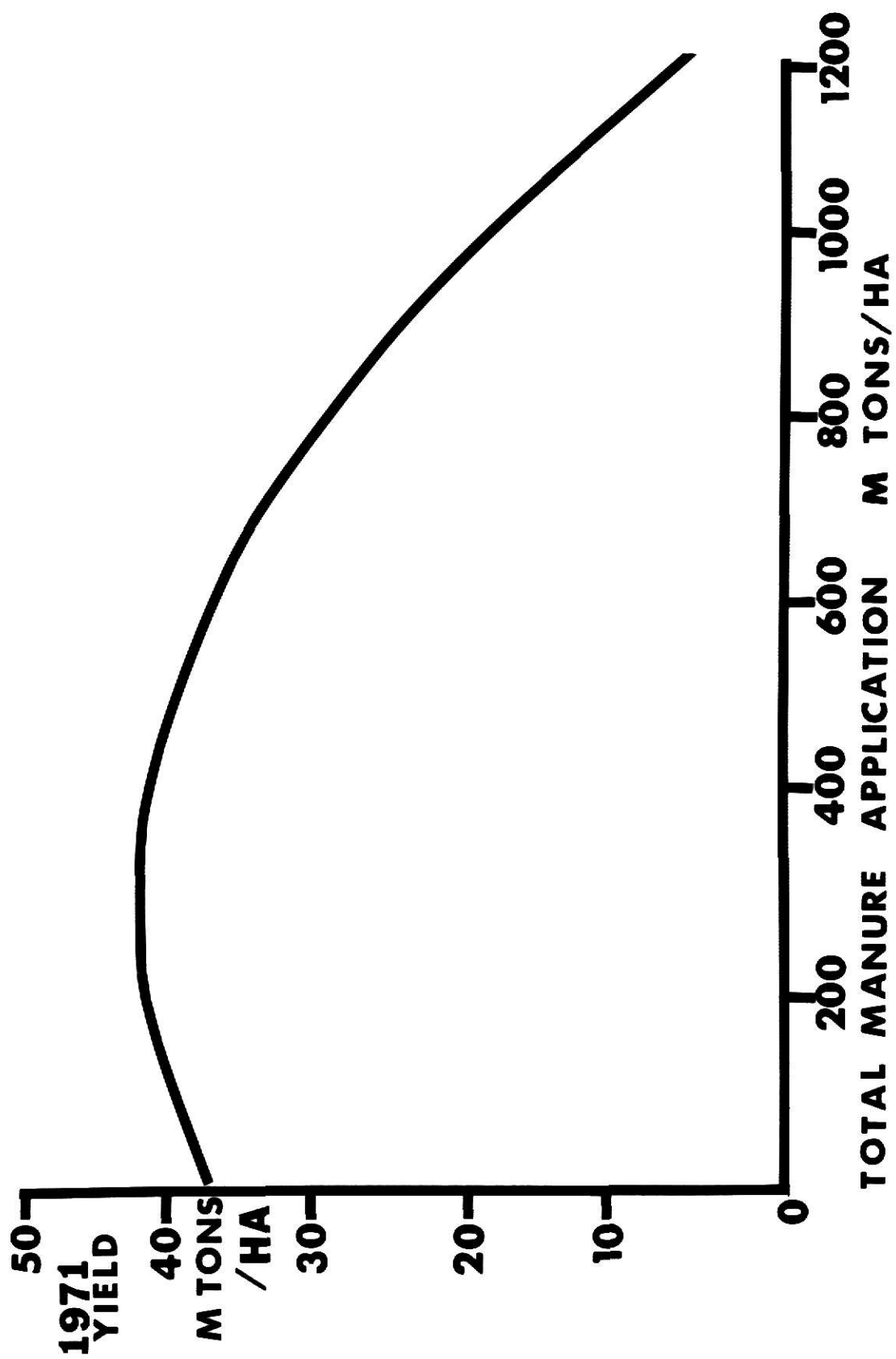
Irrespective of the original source of the ammonium ions present in the soil, either from manure or from fertilizer, nitrification occurs as soon as soil conditions are conducive for bacterial activity. As a result of nitrification, nitrate-nitrogen may accumulate in soil profiles from large applications of manure. Such accumulated nitrate may eventually contaminate ground water and produce excessive accumulations of this ion in plants.

Denitrification may represent an important mechanism of nitrogen loss from soil receiving large amounts of animal waste. High amounts of oxidizable carbon added to the soil in manure coupled with poor drainage favors denitrification. Salt accumulations resulting from heavy manure applications affect soil structure through colloidal dispersion, with resulting lowered permeability to water. Periodic anaerobic conditions may then be produced particularly under irrigated conditions. Nitrogen converted to the nitrate form during the period when the soil is aerobic may be subsequently lost through denitrification when

the soil is anaerobic. On the other hand, it is conceivable that soil microbial activity could be depressed due to effects of increased salinity resulting from manure applications. The relationships of increased salinity to nitrification and denitrification reactions have not been extensively examined.

Existing data relative on the losses of nitrogen from soil and by the process of denitrification in general are inadequate. From the information reviewed here, it can not be positively concluded that denitrification is the main mechanism of nitrogen loss from soils receiving large amounts of animal waste but it is undoubtedly an important factor. The extent of denitrification and how this microbial process can be managed in the interest of waste disposal needs to be investigated further. Additional research on the denitrification process in soils at various moisture levels and at various temperatures is necessary to allow adequate management of the problem of nitrogen pollution arising from waste disposal. Generally, the effects of heavy applications of feedlot manure to the soil are drastic and even crop yields may be severely reduced (Figure 11).

Fig. 11 - Corn forage yields as affected by continuing
manure applications (Murphy et al. 1972).



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SOIL REACTIONS OF
ANIMAL WASTE NITROGEN

by

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B. S., Andhra Pradesh Agr. University, 1970

AN ABSTRACT OF A MASTER'S REPORT

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One of the major problems associated with disposal of large amounts of animal wastes or soil is the possible pollution of surface and ground water with inorganic nitrogen compounds. The nitrate ion released from animal waste or manure through mineralization is very mobile. Excess amounts of nitrate-nitrogen may accumulate in crops and be hazardous to humans and livestock. Nitrate-nitrogen may also be leached from the soil and contaminate domestic water supplies.

Depressed crop yields have been caused by accumulation of soluble salts in the soil from heavy manure applications. This is from the effect of soluble salts and increased osmotic potential of the soil solution.

Accumulation of ammonium nitrogen toxic to plants has also been noted in the surface of 30 cm soil following heavy manure applications even under irrigated conditions. Such accumulation may hinder mineralization reactions since Nitrobacter organisms are very sensitive to higher concentration of ammonia and do not function well at high pH values (above pH 7).

Under irrigated conditions denitrification may be an important mechanism of loss of soil N which accumulates from animal waste applications. Large amounts of carbon present in animal waste accumulate in the soil and promote denitrification.