

NITROGEN FERTILISER REACTION IN SOILS

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ABSTRACT

Characteristics of the soil immediately surrounding granules or bands of fertiliser nitrogen are particularly important in influencing subsequent soil-fertiliser nitrogen interactions.

Both ammonium sulphate and urea are popular sources of fertiliser nitrogen in New Zealand. General overseas evidence suggests that soon after placement of granules or bands, high concentrations (300 to 400 $\mu\text{g/g}$ of ammonium nitrogen develop at fertiliser microsites. Biological oxidation of ammonium nitrogen at the periphery of each fertiliser microsite often results in unusually high levels (200 to 300 $\mu\text{g/g}$) of nitrate. Nitrate under acidic soil conditions is known to chemically decompose to oxides of nitrogen and nitrogen gas, resulting in gaseous losses of nitrogen. Because nitrate is a non-specifically absorbed anion it is only weakly held by soil components, at the pH of most soils. Under conditions of high rainfall, significant amounts of nitrate may move below the rooting zone.

These and other fertiliser nitrogen reactions in soil are factors to be considered in formulating a rationale for optimum use of nitrogen fertiliser in agronomic systems.

INTRODUCTION

Recommendations for the use of nitrogen fertiliser in New Zealand, as elsewhere, are largely founded on factors having little or no apparent relationship to the efficiency with which the applied nitrogen fertiliser is used by the crop or pasture system. Recommendations are often based on yield increases during field trials, cost of fertiliser, and experience of the grower or farmer for the region concerned.

In field trials, plant response to nitrogen is usually measured by yield increases over a control area supplied with adequate levels of available nutrients except nitrogen. In a typical yield-nitrogen fertiliser response curve, however, the last 10% of maximum yield often requires approximately one half of the total fertiliser application (Stanford, 1973).

Fertiliser costs play a variable but often significant role in formulating recommendations. Nitrogen fertiliser popular at less than 10c a kilogram of N can understandably become relatively unpopular at twice this cost. But how meaningful are such cost assessments if it is possible to improve the effectiveness of use of applied nitrogen through better timing, placement, and use of water?

In certain areas with extensive documentation of cropping and yield histories, decisions to use nitrogen fertiliser may be made in order to attain yields typical or "normal" for that area.

Ideally, nitrogen fertiliser applications should supplement the potentially available soil nitrogen so that the total supply of plant available nitrogen does not exceed that necessary for optimum crop and pasture yields (Parr, 1973).

RATIONALE FOR FERTILISER RECOMMENDATIONS

In order to establish a rationale for nitrogen fertiliser applications, it is essential to have an understanding of several aspects of the soil-plant system in question. In

particular, information on the nitrogen requirement for a given crop is required. In the U.S.A. for example, maximum dry matter yields of maize are obtained when the nitrogen content of the grain + stover is 1.2 to 1.3% (Stanford, 1973). Also, a reliable estimate of the rate and extent of mineralisation of soil organic nitrogen is needed. Such estimates have been determined by incubating soils under specified conditions and performing quantitative analyses of the inorganic nitrogen released (Stanford and Smith, 1972). An estimate of the mineralisation of organic nitrogen in pasture soils converted into cropping systems in New Zealand would appear to be particularly meaningful.

In addition to having an estimate of the amount of residual nitrogen fertiliser from previous applications likely to remain available for plant uptake, it becomes necessary to estimate the efficiency with which a given plant system is capable of using plant-available nitrogen. The efficiency factor is probably the most difficult to determine because it is not only a function of plant and climatic conditions, but also of source, form, rate, time, and method of nitrogen fertiliser application, as well as extent of nitrogen immobilisation and general soil properties (Allison, 1966).

Efficiency values (proportion of nitrogen recovered in plant tissue to nitrogen fertiliser applied) of 50% are common for maize crops (Allison, 1966), and values ranging from 50 to 90% are reported for a sorghum-sudan hybrid grown in the presence of ^{15}N -labelled fertiliser (Westerman *et al.* 1972). It is obvious that in experiments designed to estimate plant recovery of applied nitrogen it is impossible to determine the proportion of plant nitrogen which originates from the fertiliser and that which originates from the mineralisation of soil organic nitrogen without employing a label of some kind. Significant amounts of ^{15}N -Nitrogen fertiliser may remain in the soil of cropping systems for up to five years after application (Allen *et al.*, 1973).

NITROGEN FERTILISER REACTIONS IN SOIL

There appears to be very little published work on fertiliser nitrogen reactions in New Zealand soils. This is no doubt related largely to New Zealand's dependence on the grass-clover association for plant available nitrogen. Due to dramatic increase in use of nitrogen fertiliser, basic information on the reactions of nitrogen fertiliser in New Zealand will inevitably be required. In 1952, Doak reported pH values of up to 9.2 and the accumulation of nitrite within pasture urine spots, both effects presumed to be due to the reaction of urea in soil. Phytotoxic effects of ammonia on certain vegetable crops were reported in the first New Zealand investigation into the use of anhydrous ammonia (Thomas, 1973).

For general overseas literature the important reactions of nitrogen fertilisers are those occurring in the soil microsites surrounding fertiliser granules or bands. Nitrogen sources such as ammonium sulphate and urea, two currently popular nitrogen fertilisers in New Zealand, give rise to ammonium-nitrogen concentrations of 2000 to 3000, $\mu\text{g/g}$ within the soil-granule microsite (Wetselaar et al., 1972). Because the pH within this high ammonium-nitrogen zone can be either acidic (for ammonium sulphate) or alkaline (for urea) quantitative aspects of nitrification at the soil-granule microsite are governed by inhibitory conditions within the microsite as

well as conditions outside the microsite. Nitrate accumulations as high as 260 $\mu\text{g/g}$ have been reported (Bezdicsek et al., 1971) as being typical of microsites containing urea granules in soil at pH 7. At soil-microsite pH values of 8 or more, NH_3 (deprotonated) may be liberated and exert both phytotoxic effects on plants and preferentially inhibit the activity of *Nitrobacter* species (Aleen et al., 1957). Nitrate itself is capable of inhibiting the normal biological oxidation of NO_2 to NO_3 by *Nitrobacter* (Lees and Simpson, 1957).

Within the acidic environment of a soil-granule microsite containing ammonium sulphate, no gaseous NH_3 is generated, but the pH values suggest that nitrification of the ammonium-nitrogen occurs with difficulty (Hauck and Stephenson, 1965) and any nitrite so formed may be subject to chemical decomposition to NO_2 (nitric oxide), NO_2 (nitrogen dioxide) and N_2 (Bollay et al., 1973), particularly if the soil has a pH value of 6 or less.

The data in Tables 1 and 2 indicate the nature of the products of nitrification when a silty clay loam, pH 8.2 and a fine sandy loam pH 5.2, are treated with varying rates of urea or ammonium sulphate (between 4 to 6 mesh (Hauck and Stephenson, 1965). In this incubation study, soil temperature was maintained at 30C for 25 days.

TABLE 1: Nitrification of urea and ammonium sulphate granules in pH 5.2 fine sandy loam.

N-source	Rate	Percent of applied N recovered		
		NO_2 -N	NO_3 -N	Total
Urea	x1	0	76	88
	x2	54	26	92
	x3	67	3	85
$(\text{NH}_4)_2\text{SO}_4$	x1	0	88	99
	x2	10	85	103
	x3	45	30	93

Treatment x1 = 300 $\mu\text{g/g}$
Values corrected for control soil.

(Hauck and Stephenson, 1965)

TABLE 2: Nitrification of urea and ammonium sulphate granules in pH 5.2 fine sandy loam.

N-source	Rate	Percent of applied N recovered		
		NO_2 -N	NO_3 -N	Total
Urea	x1	0	74	99
	x2	14	< C	58
	x3	9	< C	45
$(\text{NH}_4)_2\text{SO}_4$	x1	0	3	102
	x2	0	2	100
	x3	0	< C	101

Treatment x1 = 300 $\mu\text{g/g}$
Values corrected for control soil
C = control soil

(Hauck and Stephenson, 1965)

The experimental data in Table 1 indicate that nitrification of both nitrogen sources occurs with accumulation of nitrite. Quantitative differences in nitrite and nitrate recovered are interpreted as being due to volatilisation losses of NH_3 (urea) and chemical instability of nitrite in the vicinity of the granule microsite (ammonium sulphate). The data in Table 2 suggest that nitrification of urea resulted in nitrite which was subject to chemical decomposition once the nitrite so formed became exposed to the normal soil pH of 5.2. Nitrification of ammonium sulphate was insignificant due to the highly acidic conditions which developed at the soil-granule microsite. Other factors possibly influencing nitrification in the vicinity of fertiliser granules are precipitation reactions and salt concentration (Hauck and Stephenson, 1965). Suggestions of a "priming effect" by nitrogen fertilisers may be partly due to solubilisation of soil organic nitrogen in a high salt solution environment and consequent mineralisation (Broadbent and Nakashima, 1971).

Apart from the obvious impact of nitrogen fertilisers on plant nutrition, both nitrite and nitrate may be significantly involved in broader based environmental issues. Certain vegetables may have nitrate levels of up to 3000 $\mu\text{g/g}$ when grown in the presence of high soil nitrate levels (Wolf and Wasserman, 1972). Furthermore, nitrate as a non-specifically absorbed anion in soil is readily leached out of the root zone (Martin and Skyring, 1962). The role of nitrogen fertilisers as a possible source of nitrate enrichment of surface and groundwaters (Kohl et al., 1971) requires careful evaluation. The possibility of allophanic soils providing sorption sites for nitrate under acid conditions (Schalscha et al., 1974) is of interest in New Zealand. Nitrite can react with certain amines forming N-nitroso compounds, many of which are known to be carcinogenic (Wolf and Wasserman, 1972).

SUMMARY

Quantitative information concerning the fate of fertiliser nitrogen in soil is helpful in estimating the amount of applied nitrogen available for plant uptake. There is a paucity of such information for New Zealand soils.

The reactions of nitrogen fertilisers in soil are essentially determined by the chemistry of soil-fertiliser granule microsites. Nitrification of nitrogen from sources such as urea or ammonium sulphate appears to proceed at a rate dependent on the pH which develops at the soil-granule microsite as well as the soil pH some distance from the granule.

Nitrate accumulation and/or gaseous losses of fertiliser nitrogen are probably unavoidable where fertiliser is applied as granules or in bands.

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