MEASURING AND MODELLING THE FATE OF FERTILIZER AND SOIL NITROGEN IN A CROPPING SYSTEM

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ABSTRACT

Future trends in New Zealand cropping, anticipate an increased use of fertilizer nitrogen (N). In order to more efficiently utilise N in cropping systems, a better understanding of the N processes and their significance under New Zealand conditions, is required. To achieve such understanding, several small scale experiments were conducted.

Preliminary experiments, investigating the fate of N-15 urea applied to barley and oats, were conducted using soil cylinders. Total recovery of N-15 in plant and soil components varied between 50 to 90 percent. Initial urea N transformations were rapid, and most of fertilizer N uptake by plants occurred in the first five weeks following its application at sowing. Plants took up a greater proportion of their total N as native soil N. N-15 assay on soil and plant samples containing N-15 in excess of about 1 atom percent, was performed satisfactorily with emission spectrometry. The data obtained by the use of soil cylinders, were representative, particularly of short term field behaviour.

A five-week study was undertaken to account for the extent and pattern of immobilisation and leaching of N-15 urea applied to a barley crop. Two irrigation treatments (wet and normal) were imposed. Approximately 90% of the applied N was recovered. One week after application, 86% of urea N had been hydrolysed, while after two weeks 36% of it had been immobilised into organic matter. The increased leaching of N from the wet lysimeters compared with the normal lysimeters was at the expense of plant N uptake, having little effect on the amount of N immobilised. Net mineralisation of native soil N was calculated as 1.2 kgN/ha/day.

Using the data obtained from the preceding investigation, a five-week N model was developed. The model successfully predicted the increased leaching of fertilizer N from the wet compared with the normal lysimeters. The reduced plant uptake of fertilizer N, resulting from this increased leaching from

the wet lysimeters, was also quite successfully modelled. The model indicated that the amount of fertilizer N leached was strongly dependent on the timing of rainfall in relation to the time of fertilizer application.

A crop season model was developed by extending the five-week model to cover a full growth season of a barley crop, and the model was verified with data from a large scale field trial. The model prediction for N leaching losses, demonstrated better accuracy than for plant N uptake. The model has the potential to provide a continuous evaluation of possible adverse effects caused by unanticipated factors such as excessive rainfall, on plant N uptake.

The crop season model was further developed to predict long term changes in the N cycle of a double cropping system, in a soil that was previously under pasture. The model predicted quite accurately the N loads as well as the N concentrations in tile drainage effusing from experimental field plots. In general, the measured and predicted data for nitrate concentrations in tile drainage of field plots indicated that nitrate concentrations in tile effluent usually exceed 15 to 20 mgN/litre, regardless of fertilizer addition. The addition of fertilizer could increase these levels two-fold but only for a short time. The utility of the model as a research tool was illustrated.

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TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

Page

Page

LIST OF TABLES

Page

Page

LIST OF SYMBOLS

Symbol		Units
B	Reduction factor that accounts for soil temperature and moisture effects on rate constants (dimensionless).	
ENM	Effective net mineralisation over rooting depth Z	kgN/ha
ETp	Evapotranspiration estimate (Priestley and Taylor, 1972)	m
k_i	Rate constant for immobilisation	d^{-1}
k_L	N leaching coefficient (dimensionless)	
k_m	Rate constant for mineralisation	d^{-1}
$\underline{k}_m$	Coefficient for effective net mineralisation of native soil N	d^{-1}
k_n	Rate constant for nitrification	d^{-1}
k_p	Rate constant for plant N uptake	m^{-1}
k_u	Rate constant for urea hydrolysis	d^{-1}
$(k_x)_m$	Maximum value for a coefficient k_x when B = 1	d^{-1}
m_1	Mineralisation rate coefficient at optimum conditions of soil temperature and moisture (B = 1), for the short-cycle organic N of native soil N origin	d^{-1}

M_2	Constant rate of mineralisation at optimum conditions of soil temperature and moisture, from the long-cycle organic N of native soil N origin	kgN/ha/d
N_a	Fertilizer derived ammonium N content in unit soil area over rooting depth Z	kgN/ha
$\underline{N}_a$	Ammonium N content of native soil N origin, in unit soil area over rooting depth Z ...	kgN/ha
ΔN_L	Daily leaching losses of fertilizer and native N from rooting depth Z	kgN/ha
$\underline{N}_m$	Daily amount of N mineralised from native soil organic N pool ($\underline{N}_o$), over rooting depth Z	kgN/ha
$\Sigma \underline{N}_m$	Total amount of N mineralised over the 2 year period (1978-80) from soil organic N pool ($\underline{N}_o$), over rooting depth Z	kgN/ha
N_n	Fertilizer derived nitrate N content in unit soil area over rooting depth Z	kgN/ha
$\underline{N}_n$	Nitrate N content of native soil N origin, in unit soil area over rooting depth Z ...	kgN/ha
N_o	Fertilizer derived organic N content in unit soil area over rooting depth Z	kgN/ha
$\underline{N}_o$	Organic N content of native soil N origin, in unit soil area over rooting depth Z ...	kgN/ha
$\underline{N}_{o1}$	Short-cycle organic N of native soil N origin, in unit soil area over rooting depth Z	kgN/ha

$\underline{N}_{o2}$	Long-cycle organic N of native soil N origin, in unit soil area over rooting depth Z	kgN/ha
ΔN_p	Daily plant uptake of fertilizer N	kgN/ha
$\Delta \underline{N}_p$	Daily plant uptake of native N	kgN/ha
N_u	Amount of urea in unit soil area over rooting depth Z	kgN/ha
θ	Volumetric water content when drainage has just ceased (dimensionless)	
q	Drainage flux density	m d^{-1}
STE	Reduction factor for sub-optimal soil temperature (dimensionless)	
SSE	Reduction factor for sub-optimal soil moisture content (dimensionless)	
T	Transpiration	m
Z	Rooting depth	m

CHAPTER 1

INTRODUCTION

In many New Zealand farming districts, agricultural crops are grown in short term rotations between periods in pastures. Consequently, biologically fixed nitrogen (N) inputs from the pastoral phase of the rotation can be used by the crops without recourse to N fertilizers. The rapid increase in capital cost for land and farm machinery is promoting intensive cropping, which disrupts, in some cases permanently, the pasture-crop sequence. After growing two or three successive crops, N deficiency in such farming systems develop, even on soils that were initially, relatively high in organic matter status (Sears et al 1965; Douglas et al 1972). Eventually, the attainment of high levels of crop production will rely on continual use of fertilizer N, as inputs of biologically fixed N from the pastoral phase are reduced.

Additionally, land use in New Zealand is changing. Due to the recent prospect of increased export earnings from New Zealand horticultural products, first class cropping soils are now mostly used for horticultural cropping. This change in land use has reduced the area of first class soils for growing agricultural crops, and increased the cropping use of second and third class cropping soils. Greater inputs of N fertilizer would therefore be required to achieve optimal yields of agricultural crops. Horticultural crops also need large amounts of N fertilizers, notwithstanding the higher fertility status of first class soils.

Estimated predictions (Menzies 1980) indicate that the amounts of N fertilizer used in New Zealand agriculture and horticulture, could treble within the next decade, without any substantial increase in the land area under cropping.

Intensive cropping practices tend to localise in areas with appropriate soils and climates; barley in the Manawatu, wheat in Southland, maize in the Waikato, and horticultural crops in South Auckland. If fertilizer N quantities applied are in excess of crops' demand, drainage from such intensive farming districts, could carry excessive nitrate loads into the waterways. Excessive nitrate loads in waterways could cause health hazards like methaemoglobinaemia in young babies and livestock, and other environmental pollution problems such as eutrophication of natural waters (Keeney 1982). Thus, N management in the intensive cropping farms has a dual problem; (i) optimal N should be applied to the crops so that yields are not suppressed due to excessive or deficient N fertilization, and (ii) such N fertilization practices should not create environmental pollution problems.

In order to monitor or manage N in croplands, an understanding of the fate of applied N is essential. Toward this end, N balance studies have been valuable in identifying mechanisms of N transfer and in indicating the size of N pools in soil-plant system. Such studies, however, give only static accounts of the N gains, losses, and transfers; and such static accounts characteristically depend on the prevailing environments during the experimentation. This limits the application of experimental results to other sites where the environments

would be different. The utility of N balance studies in N management practices, would be enhanced if the results from such studies could be used to develop predictive models of the N behaviour in the soil-plant system. Such predictive models would find use in N fertilizer requirement models that are based on field trials, and/or in the evaluation of nitrate loads in agricultural drainage water.

Allison (1955, 1966) reported extensive reviews on the N balance experiments and found that quantitative data were usually lacking for N leaching and N gaseous losses. Today, N balance results are more complete and accurate (Legg and Meisinger 1982), chiefly due to the wide-spread use of N-15 technology. Surprisingly, for a cropping system, no N-15 balance experiment has been reported in New Zealand, which gives a complete accounting of all the N transfers and pools in a single experiment. N balance results obtained overseas (mainly USA), are not directly applicable to New Zealand agro-climatic conditions, because, although many of the basic processes may remain the same, the environment may modify the rates of these processes to such an extent that their relative importance may change completely. Meaningful predictive models applicable to New Zealand conditions can only be developed if accurate N balance data are available for New Zealand conditions.

The broad objectives for this study are to

(i) determine a N-15 balance for N-15 labelled urea applied to a barley crop;

(ii) develop, validate and where possible verify, a simple mechanistic N model for a cropping system to which N is added.

CHAPTER 2

REVIEW OF LITERATURE

2A. NITROGEN BALANCE EXPERIMENTS

2A.1 Methodology of fertilizer N balance experiments:

Fertilizer N balance experiments, using N-15 enriched materials, on conventional size field trial plots are prohibitive in terms of cost of N-15 isotope. On the other hand, field experiments using the less costly N-15 depleted fertilizer, have been conducted economically on plot sizes comparable to those used in conventional field experiments as reported by Broadbent and Carlton (1978). They measured crop uptake of fertilizer N with ease, but the measurement of residual N-15 in a soil with moderate organic N content (0.1%), could not be made as the N-15 depleted fertilizer lost its isotopic identity, through enrichment to baseline level, by the indigenous soil organic N. Since most New Zealand soils are relatively high in organic N content (>0.1%), fertilizer N balance studies would require the use of N-15 enriched fertilizers. The high cost of N-15 enriched compounds restricts the size of experimental plots to small areas.

2A.1.1 Small scale experiments

(a) Microplots and soil cylinders

Several studies on the fertilizer N balance in cropping systems (Carter et al 1967; Patrick and Reddy 1976; Kissel et al 1977; Kowalenko et al 1978; Kissel and Smith 1978; Olson et al 1979; Olson 1980) have been conducted using N-15 enriched fertilizers applied to microplots. In the study by Olson (1980), berms were built around square plots

measuring 12.7 m^2 each and N-15 enriched ammonium sulphate, dissolved in water, was applied evenly over each square. A metal box 710 x 710 x 100 mm was placed on the surface in the centre of each plot to prevent lateral movement of nitrogen with surface water. In other studies, metal boxes or cylinders were pushed into the soil to prevent lateral movement of N with both surface and subsurface water. Olson et al (1979) established microplots in field soil by pushing open-ended metal boxes, of size 534 x 470 mm to a depth of 1.42 m, with a large hydraulic ram. In the study by Kissel et al (1977), steel boxes of size 640 X 640 mm were forced into the field soil to a depth of 870 mm with a static load of weights as described by Tackett et al (1965). Two of their microplots were forced out of shape when pressed into the soil, suggesting that this technique could be unsuitable as deshaping of microplot rims could cause compaction, reduce water movement and create temporary anaerobic conditions for denitrification. Carter et al (1967) used cylinders of 600 and 300 mm diameter that were pushed into the soil to depths of 600 and 450 mm respectively. They showed that there were insignificant differences in the fertilizer N balance results for sudangrass obtained from the two different sizes of microplots. Considering the practical difficulties in placing large size cylinders in undisturbed soil and the increased cost of N-15 isotope, small size cylinders appear more suitable for fertilizer N balance studies.

(b) Lysimeters

Lysimeters are required if measurements of nitrogen leaching losses is included in the objectives of a N-15 balance study. Large lysimeters have been used in studies conducted for one or two successive cropping periods and with crops such as corn that need large volumes of soil. Owens (1960) studied the fate of N-15 enriched fertilizer applied to a corn crop in monolith lysimeters that were about a metre in diameter and a metre in depth. Chichester et al (1978) also studied the fate of N-15 fertilizer applied to two successive corn crops using monolith lysimeters that were 2.44 m deep and had a surface area of 8 m^2. Holmes et al (1967) and Scotter et al (1979) have reported the use of small lysimeters (9 litre capacity) of monolith type in their studies of soil water balance for pastures. Surprisingly, use of small lysimeters in fertilizer N balance studies for cropping systems has not been reported.

Lysimeters are either the filled-in type or the monolith type containing undisturbed soil. Harrold and Dreibelbis (1967) suggested the use of monolith lysimeters, in order to keep the soil in a lysimeter in its original undisturbed condition so that the hydrologic behaviour of the soil is not seriously altered. Also such monolith lysimeters should be weighable if estimates of evapotranspiration (ET) are required. In field studies, a weighing lysimeter is installed by placing the lysimeter containing the soil block inside a tank or liner that retains the surrounding soil (McIlroy and Angus 1964). Tanner (1967) suggested that the size of a lysimeter should

be such that the area of the lysimeter soil surface is large compared with the area of the gap between the lysimeter container and the liner (wall-gap area). He indicated that the ET in the lysimeter compared to that of its surrounds could increase with increasing wall-gap area as a large wall-gap area could increase the heat balance of the lysimeter. Lysimeters with wall-gap areas as small as 3% (Pruitt et al 1960) and as large as 30% (McIlroy and Angus 1964) of the lysimeter area have been used.

2A.1.2 N-15 isotope measurement:

In most fertilizer N balance studies (e.g., Carter et al 1967; Patrick and Reddy 1976; Kissel and Smith 1978; Olson et al 1979, olson 1980), N-15 isotope measurement has been made using mass spectrometry. Various types of mass spectrometers have been used including single and double collector instruments (Bremner 1965d; Fiedler and Proksch 1975). Regardless of the type, mass spectrometers, if properly maintained and operated, are capable of rendering a very accurate determination of small variations in the N isotope ratios (Hauck and Bremner 1976).

Emission spectrometry is available as an alternative to mass spectrometry (Broida and Chapman 1958). The advantages claimed for emission spectrometry (e.s.) over mass spectrometry (m.s.) are that the e.s. technique is simpler to operate, only a few micrograms (3 to 5) of nitrogen are needed for N-15 analysis, and that analysis of N gas sample can be repeated many times since the method is non-destructive (Fiedler and Proksch 19775). Other advantages are that the cost of e.s. instrument is less

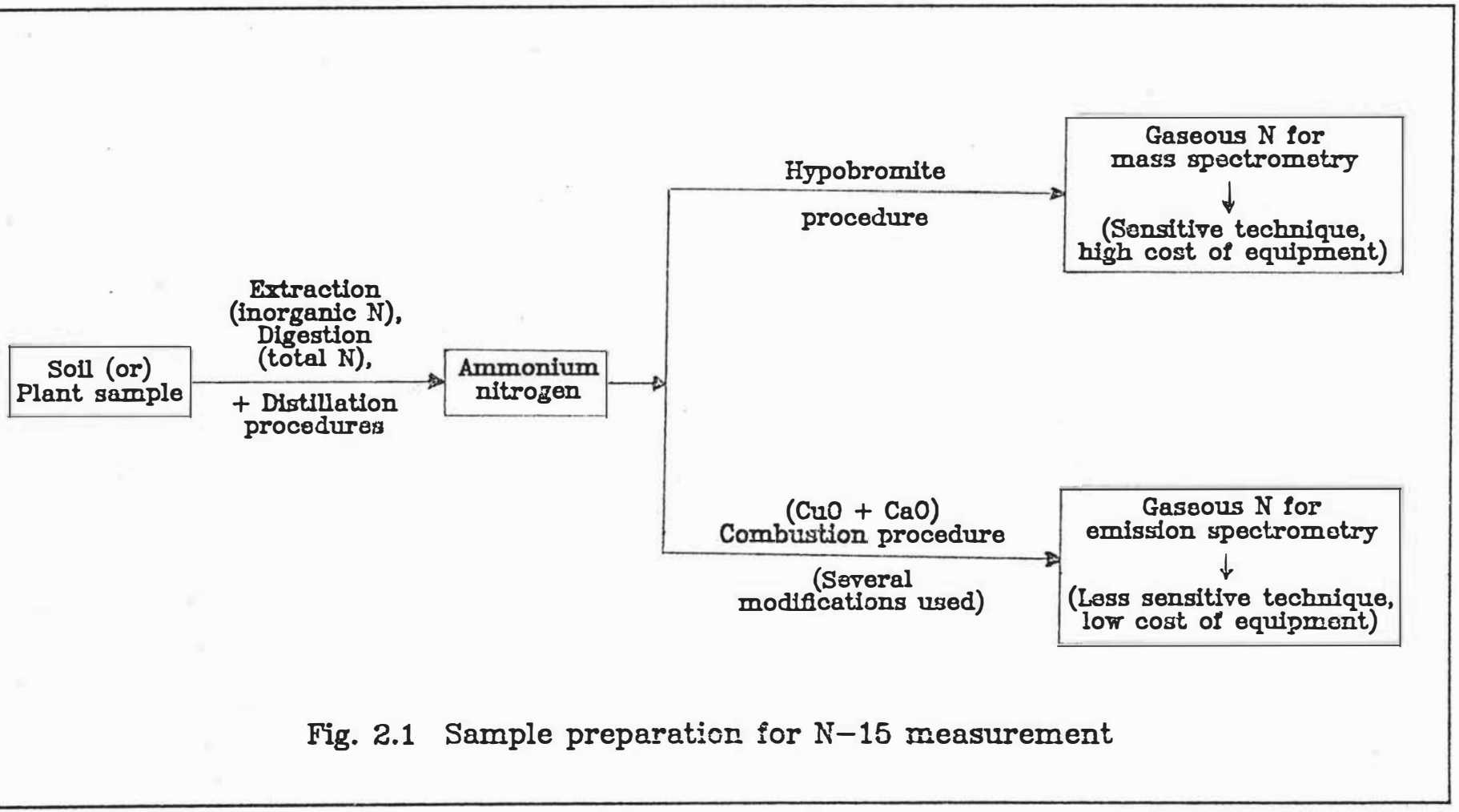

Fig. 2.1 Sample preparation for N–15 measurement

than one-half the cost of m.s. equipment and that the e.s. instrument can be installed and supervised by any experienced analyst (Hauck and Bremner 1976). However, considerable divergence of opinion exists in the literature concerning several aspects of N-15 analysis by e.s., including accuracy, amount of N needed, precision and memory effects (Perschke et al 1971; Keeney and Tedesco 1973; Meyer et al 1974; Fiedler and Proksch 1975).

Measurement of N-15 in the soil organic N fraction is required for studies involving immobilisation of added fertilizer N into soil organic matter. As most New Zealand soils are relatively high in organic N content, the expected isotopic dilution when the added N-15 is immobilised, would be large. No information is available on the measurement of N-15 by e.s., in the organic fraction of any New Zealand soil. Overseas work is limited to a study by Watanabe et al (1979), who have used e.s. to study the movement and recovery of applied N-15 down the profile of a fallow soil that was low in total N content (0.09%). They applied ammonium sulphate labelled with 10 atom percent N-15, to the soil enclosed by 185 mm diameter cylinders in field. N-15 enrichment was not detected by e.s., when the fertilizer N concentration in soil dropped below 0.02 ug/g in the mineral fraction and 3 ug/g in the organic fraaction. Unfortunately, the magnitude of isotopic dilution was not mentioned.

Regardless of the technique used for N-15 measurement in any N balance experiment, i.e., whether m.s. or e.s., a cumulative error could occur due to inaccuracies in measuring the various components of the N balance. Martin

and Skyring (1962) reviewed the sources of error in N balance experiments, and pointed out that the cumulative error could be partly of analytical origin and the remainder could be random error associated with all stages of a N balance experiment. Martin et al (1962) conducted a pot experiment for 35 days to identify the sources of error associated with fertilizer N balance experiment. Using mass spectrometry, they considered the sources of error in N-15 analysis such as memory effects, reference standards and back ground contributions and found them negligible compared with random errors arising due to soil heterogeneity. Olson (1980), in an attempt to evaluate the accumulated errors of sampling, sample preparation and analyses, applied N-15 to small confined areas in the field and recovered 94.8 $\pm$ 0.6% after 2 hours and 93.0 $\pm$ 2.6% after 24 hours. He concluded that this cumulative error may not exceed 6% of the applied N. Adequate replication, prevention of isotope contamination during storage and analysis, and caution in the conduct of analysis would help to keep the cumulative errors to a minimum possible level.

2A.2 Results of fertilizer N balance experiments

2A.2.1 Total recovery of applied fertilizer N :

Kissel et al (1976) and Olson et al (1979), in experiments with grain sorghum and wheat respectively, found about 50% of the applied N in crop, 30% in soil and 20% unaccounted for. Leaching was either insignificant ($\approx$ 1% , Kissel et al 1976) or was not measured (Olson et al 1979). Chichester et al (1978) reported 25-30% of applied N taken up by corn crop, 10-30% in the soil, about 30% leached and

6-26% unaccounted. Growing corn, Olson (1980) found 33% of applied N taken up by crop, 43% in the soil and 24% unaccounted. Craswell et al (1975) measured higher plant uptake (63%) for wheat and lower (6%) deficits. Thus, fertilizer N balance studies, in general, report recoveries in the crop of 25-65% with 10-45% retained in the soil, 1-30% removed by leaching and 5-25% unaccounted for and presumed lost. Similar ranges of values are reported in earlier reviews by Kundler (1970) and Hauck (1971).

The unaccounted for losses of 5-25% were considered in a review by Allison (1966), to be real losses and not the product of poor techniques or experimental errors. This view is still commonly held (Legg and Meisinger 1982). It appears that the extent of fertilizer N deficit in a N balance could differ with the nitrogenous source applied. Craswell (1979), in a microplot experiment studying the fate of three N fertilizers applied to fallow soil, found unaccounted losses of 9, 23 and 26% for urea, ammonium sulphate and calcium nitrate respectively. On the other hand, Dev and Rennie (1979), in a growth chamber experiment with barley as a test crop, showed the N deficit to be larger with urea ($\approx$ 10%) than potassium nitrate ($\approx$ 2%). Smith and Chalk (1980), in a pot experiment with ryegrass, showed that there were no significant differences in the total recoveries measured between the three fertilizer forms tested namely urea, aqueous ammonia and ammonium sulphate. In general, all the investigators mentioned above, report a consistant unaccounted for loss of about 10% of the applied amount when urea has been used.

The deficit in N-15 balance can be expected to be proportional to the amount of N applied at sowing the crop, as shown by Myers and Paul (1971). Using two rates of N application (56 and 112 kg/ha) to spring wheat, they found no significant difference in percent N deficit (≈ 25%) in the fertilizer N balance. On the other hand, the deficit in N-15 balance where N is applied in split applications, may be less than where all of the N is applied initially. For a rice crop, Patrick and Reddy (1976) reported lower N-15 deficits when half of the total N amount was applied early and half at mid season, than when all was applied in early season. Higher crop N uptake and lower denitrification losses, were suggested reasons for lower N-15 deficits when N was applied in split applications.

2A.2.2 Plant uptake

Few fertilizer N balance studies have investigated the crop uptake rates sequentially during its growth period under field conditions. In a review on the fertilizer N balance studies in the USSR, Zamyatina (1971) pointed out that almost all the fertilizer N uptake by oat crops on two different soils, occurred during the first 40 days following fertilizer application. Patrick and Reddy (1976) showed that, under flooded conditions, all of the fertilizer N uptake by rice plants (30 to 37% of applied N) occurred within a 3-4 week period following application with little further uptake. In field experiments with barley using unlabelled ammonium nitrate, Kowalenko et al (1978) showed that barley was capable of a high rate of N uptake (fertilizer plus non-fertilizer) early in its growth period.

They reported that the average N uptake rates were 3.13 kgN/ha/d during the first 30 days following sowing, 1.21 kgN/ha/d between days 30 to 44, 0.40 kgN/ha/d between days 44 to 69 and negligible uptake after 69 days. All this experimental evidence suggests that crop uptake of fertilizer N is of importance only during the first 4-6 weeks following its application at sowing.

The generally low recoveries of N-15 in crop plants, have been attributed to the degree of N-15 immobilisation into soil organic matter (Olson et al 1979) and also to the extent of N-15 leaching (Owens 1960). Olson et al (1979) reported that more N was taken up by a wheat crop and less remained in the soil from spring rather than an autumn application of ammonium sulphate. They suggested that this difference was due to a lesser amount of fertilizer N immobilisation into soil organic matter during spring than autumn.

Owens (1960), using monolith lysimeters, showed that excess leaching of fertilizer N resulted in low N-15 uptake by corn grown in those lysimeters. He reported that crop uptake was 22-24% of applied N in one treatment in which 5-7% of applied fertilizer N was leached. In another treatment where 16-19% of the applied N was leached, crop uptake was reduced to about 15% of the applied N. Regardless of the amount of applied N leached, immobilisation into soil organic matter was about 38% of applied N.

Crop uptake of N-15 has been shown to differ with irrigation rate, fertilizer application rate and time of

fertilizer application. Broadbent and Carlton (1978) reported that the N uptake efficiency (crop uptake as a percentage of the application rate) for a corn crop, under three irrigation regimes (200, 600 and 1000 mm water), was, in general, inversely related to the N fertilizer application rate in the range of 90 to 360 kgN/ha. The maximum uptake efficiency occurred at 90 kgN/ha application rate and differed between 35 and 65% depending on the irrigation rate. Olson (1980) reported that the average N uptake efficiency for two corn crops, under an irrigation regime of 1200 mm, were 30 and 35% for the 50 and 150 kgN/ha application rates respectively. Olson et al (1979) reported that, for wheat crops, there was no significant difference in fertilizer N uptake between autumn and spring applications at the 50 kgN/ha rate; but at a higher application rate (100 kgN/ha) plants recovered about 10% more N for the spring than for the autumn application. No explanation was suggested.

2A.2.3 Immobilisation of applied N into soil organic matter:

Fertilizer N balance studies with crops (Patrick and Reddy 1976; Chichester et al 1978; Kissel and Smith 1978; Olson 1980) have shown that a varying proportion of the applied N (10-45%) is immobilised into soil organic matter. An important factor causing this variation is the supply of energy material, particularly the relative proportion of available C and N. Allison and Klein (1962) reported that added N was immobilised at a maximum rate when the soil C:N ratio exceeded the range of 25 - 30 and mineralisation

occurred when the C:N ratio dropped below 20. Bartholomew (1965) suggested that the C:N ratios could not be used as indices for N immobilisation and mineralisation since all the C and all the N present in soil are not readily available to microbes and also the C and N values determined chemically rarely correlate to the biological availability. Thus, although C:N ratio is recognised as an important factor in the immobilisation - mineralisation processes, it has been of limited use in determining the amount of applied N immobilised.

It has long been known that many micro-organisms utilise ammonium more readily than nitrate for their metabolic activity, when both are present simultaneously (Alexander 1977). Jansson (1958) presented a cycle theory of N transformations in soil in which he proposed immobilisation to proceed from ammonium only. Nitrate was outside this internal N cycle. Contrary to this hypothesis, some workers (Stojanovic et al 1956; Broadbent et al 1962;) have shown that added nitrate could also be immobilised into soil organic matter. But these investigators had added nitrate to soil along with a readily available carbon source. More recently, Kissel et al (1977) who applied a relatively high rate of calcium nitrate (328 kgN/ha) to a sorghum crop, reported that about 20% of applied nitrate was immobilised. It appears that immobilisation could proceed from the nitrate form when nitrate N is the abundant source of mineral N in the soil.

In greenhouse studies, some investigators (Legg et al 1959; Stewart et al 1963) have found that with an increase

in the amount of N added to soils, there was increase in the amount of added N immobilised in the soil. This increase was non-linear. No regression analyses were reported for their data to establish a relationship between the amount of N added and its fraction immobilised. The results obtained by Westerman et al (1972) in field experiments where urea enriched with N-15 was applied to a sorghum crop, also demonstrated this non-linear relationship. They found that the amounts of applied N immobilised in the soil by the end of cropping season were 18, 35 and 35 kgN/ha respectively for the 56, 112 and 168 kgN/ha rates of application, which suggests that this soil may have a potential capacity to immobilise applied N. With 50 and 150 kgN/ha rates of application to a corn crop, Olson (1980) found 46% and 40% respectively of applied N immobilised after 2 years of successive cropping. Thus, the limited evidence suggests that N immobilisation as a percent of applied N would not increase linearly with increasing higher application rates (>100 kgN/ha) although there often is a significant increase in the actual amount of applied N immobilised with a higher rate of application.

There is a suggestion (Kissel et al 1977; Olson 1980) that continual net immobilisation of fertilizer N might in the long term, gradually increase the soil organic N content to a higher equilibrium level, as compared with no fertilizer N use. However, long term experiments at Rothamsted (Johnston 1976) where soils had been treated with N fertilizers (50 to 150 kgN/ha/year) for nearly a 100 years, indicate that the soil organic N had increased no

more than about 0.006%, equivalent to less than 5% of the N unaccounted for in the N balance. The soil heterogeneity and spatial variability in the soil organic N distribution is often so large (Biggar 1978) that trends in the soil organic N content are not measurable, particularly where only small N additions take place.

Experimental evidence suggests that immobilisation of added N-15 into soil organic matter is significant only in the surface layer down to a depth of about 400 mm, presumably where the highest level of microbial activity exists. Westerman et al (1972) found nearly all of the fertilizer N immobilised in the surface 250 mm soil layer. Johnston (1976) also reported a small increase in the soil organic N content in the surface layer (230 mm) due to fertilizer N application to wheat and barley; but there was no evidence to show that added N was immobilised in soil below 230 mm depth. Chichester et al (1978) applied fertilizer N to corn crops grown in monolith lysimeters and found almost all of the immobilised fertilizer N in the top 300 to 400 mm of the soil profile. Olson et al (1979) and Olson (1980) reported that from 65 to 100% of the fertilizer N immobilised was found in the surface 100 mm of soil.

2A.2.4 Mineralisation of soil organic N:

(i) Mineralisation of immobilised fertilizer N:

Limited experimental evidence (Ladd et al 1981a,b) on the mineralisation of immobilised fertilizer N, has indicated that a major portion (>50%) of the immobilised fertilizer N would not be mineralised during the same cropping season in which it was applied, and therefore would

not be available for current plant uptake. This study also indicated that the magnitude of subsequent mineralisation for future crops would be low. Ladd et al (1981a,b) studied the decomposition of legume residues that were doubly labelled with C-14 and N-15 and added to field microplots. They found that about 60-65% of the added legume N-15 remained in the soil as organic residues after decomposing for 32 weeks. Even after 4 years, nearly 50% of the added legume N-15 remained as relatively stable organic residue. Their findings confirmed the results of earlier studies (Broadbent and Nakashima 1965, 1967) which had suggested that the immobilised fertilizer N would be resistant to mineralisation. Broadbent and Nakashima (1965, 1967) postulated that the immobilised fertilizer N in the microbial tissue might undergo a non-biological reaction involving ammonia resulting in the formation of N-containing compounds much more stable than microbial N.

(ii) Net mineralisation of soil N

A 'priming' effect described as change in the soil N mineralisation rate, due to fertilizer N addition, has been reported by several investigators. A positive priming effect resulting in an increase in the soil N mineralisation rate has been reported in experiments with N-15 conducted in the laboratory (Broadbent 1965; Westerman and Tucker 1975), in the greenhouse (Low and Piper 1957) and in the field (Westerman and Kurtz 1973; Kissel and Smith 1978). On the other hand, a negative priming effect resulting in a depression in the soil N mineralisation rate, has also been reported (Megusar 1968). Other investigators (Fack 1965;

Olson 1980) found little change in the soil N mineralisation rate as a result of fertilizer N additions. Thus inconsistencies exist in the experimental results on priming effect of fertilizer N on native soil N mineralisation.

Several explanations for the priming action of fertilizer N addition have been given. Legg and Stanford (1967) considered priming action to be the result of decreased immobilisation and increased mineralisation in the rhizosphere. To Jansson (1971), priming effect is an erroneous interpretation of the N-15 data. Westerman and Kurtz (1973) took the view that fertilizer N additions could stimulate the microbial activity to release more soil N. Laura (1974, 1975) suggested that priming effect resulted from proton transfer reactions in soil rather than due to microbial action. In a review, Hauck and Bremner (1976) concluded that none of the suggested explanations for the priming effect, completely explain the observed net effects. Thus, the question of whether the priming effect is real, partly real or results from misinterpretation of N-15 data, still remains unanswered.

The relationship between N mineralisation rate and soil organic matter content has been the subject of many investigations. Harmsen and Shreven (1955), reviewing the early work, pointed out that the N mineralisation rate is likely to be associated with a small active pool of organic N. Attempts to fractionate the soil organic N to quantify the active pool (Bremner 1965c; Jenkinson 1966), have met with limited success as the soil organic matter has no well defined composition. As a result, most studies concerned

with net mineralisation (Gasser 1961; Greenland 1971; Russell 1975) have made no attempt to relate the N mineralisation rate to an active pool of organic N. Thus, although the concept of N mineralisation rate being dependent on an active pool of organic N has been suggested for a long time, it has not been possible to obtain a relationship between them due to the complex chemical nature of the soil organic matter and the inadequacy of methods available for its characterisation.

Several studies report on the mineralisation rates of organic N in New Zealand cropping soils. The estimated N mineralisation rates vary. Using data for field experiments with maize that were conducted on several soils in the Manawatu district, Elliott and Gregg (1979) calculated net mineralisation in the top 300 mm, to be in the range of 0.5 to 1 kgN/ha/day, over the growing season. Based on laboratory incubation experiments, a potential mineralisation rate of about 1 kgN/ha/day, has been reported for a Canterbury soil (Quin and Drewitt 1979) and for two Waikato soils (Ross et al 1982). Other workers (Ludecke and Tham 1971; Hart et al 1979) report a higher value of about 1.5 kgN/ha/day for the amount of N mineralised over a growing season, in the top 150 mm depth of some cropping soils in Canterbury district. There appears to be no published information available on the total amounts of native soil N mineralised annually for New Zealand soils under cropping conditions.

The varying soil temperature and moisture regimes profoundly affect the quantity of N mineralised during a

growing season (Stanford 1982). Soil temperature has been shown to influence the microbial activities of ammonifiers and nitrifiers, to different degrees (Alexander 1977). The activity of nitrifiers is near optimum in the mesophilic range, 20 to 35 C, whereas the activity of ammonifiers can proceed optimally up to about 50 C. The activities of both ammonifiers and nitrifiers cease near the freezing point.

Soil moisture in the range of 10 to 50 kPa, is conducive for optimal activities of both ammonifiers and nitrifiers (Stanford and Epstein 1974). Desiccation and subsequent wetting of soil could produce a flush of mineral N in the soil (Hardey 1946; Birch 1960). This 'desiccation' effect on the soil N mineralisation is explained by these workers in terms of C:N ratios of the organic material in soil. During dry periods, carbon decomposition exceeds N mineralisation, resulting in a decreased C:N ratio which enhances net mineralisation during the subsequent wet periods.

Few studies (Chichester 1969; Ladd et al 1977) report on the N mineralisation trends among various particle size classes of soil, with respect to quantity and relative susceptibility to mineralisation. Chichester (1969) reported that N mineralisation as a percent of organic N content, was higher in the finer fraction than in the coarser fraction of a soil, because the C:N ratio in the finer fraction was lower than that in the coarser fraction. Ladd et al (1977) showed that the silt fraction accumulated higher proportion of the more stable N residues. Such differences in N mineralisation trends, in addition to the

random distribution of soil particles in soil aggregates, could produce spatial differences in N mineralisation rates, not only among aggregates but also within aggregates. The effects of such spatial differences in N mineralisation, on N availability to plants have not been studied.

Soils under pasture have been shown (Jackman 1964; Ford and Greenland 1968) to accumulate organic N. In New Zealand, Jackman (1964) reported that such accumulations of organic N occurred mainly in the top 150 mm soil depth, and the organic N content reached steady state conditions after a period of time under pasture. The length of this time period depended upon the soil organic N content prior to pasture establishment, and whether the soil was developed from volcanic parent material. When established pastures are ploughed for cropping, mineralisation of this accumulated organic N is rapid at first because of the presence of large amount of decomposable plant material from roots, foliage and dung that was turned under (Greenland 1971). After a period of successive cropping, the organic N content tends to stabilise at a lower level relative to its steady state content under pasture (Walker and Ludecke 1982; Ross et al 1982).

2A.2.5 Leaching of fertilizer N:

Nitrate is the major form of N leached out of the root zone. Ammonium N is seldom found in the drainage water (Badzhov and Ikonomova 1971; Erickson and Ellis 1971; Jones et al 1977; Logan et al 1980). Thomas (1970), reviewing nitrogen mobility in soils, pointed out that although nitrate is the form of N generally leached in many

soils, ammonium ions could become freely mobile if they overload the soil system or exist in a soil with negligible cation exchange capacity. Urea N can also be leached as it is not strongly adsorbed in soils (Tomlinson 1970; Terman et al 1970). Small quantities of N may be leached in the form of dissolved gases (Dowdell et al 1979). Amounts of organic N leached are negligible (Chichester 1977).

Amounts of fertilizer N leaching losses, in general, are related to two factors: (i) rate of fertilizer N application (ii) amount of water that drains in the soil.

(i) Fertilizer N application rate: Experimental evidence (Chichester 1977; Gast et al 1978) suggests that the amount of fertilizer N leached would be in proportion to the N application rate. In a lysimeter study with a corn crop, Chichester (1977) reported that the amounts of fertilizer N leached were about 100-130 and 240 kgN/ha for the 178 and 336 kgN/ha rates of fertilizer application, when about 300 mm of drainage occurred. The N concentration in the leachate also followed similar trends; N concentrations being 30 and 70 ppm for the 178 and 336 kgN/ha application rates. In a three year study, Gast et al (1978) investigated nitrate leaching losses in a tile-drained clay loam soil with continuous corn crop fertilized with three rates of N application (112, 224 and 448 kgN/ha applied annually). They found that nitrate losses over three years, in 128 mm drainage through tile lines, were 25, 59, and 120 kgN/ha respectively for the three treatments, indicating that a proportional amount of the applied N (about 25 %) was leached.

(ii) Amount of drainage water: Hood (1976) showed that N leaching losses were dependent on the amount of drainage; but not on the total amount of rainfall. He reported that about 50% less nitrate was lost in leachate due to reduced amount of drainage, during a wet year (732 mm rainfall) that followed a dry year (432 mm rainfall), than when a wet year (709 mm rainfall) followed a wet year (700 mm rainfall). The amounts of drainage were 122 mm and 191 mm respectively, for the wet year following a dry year and for the wet year following a wet year. The reduced drainage in the wet year following a dry year, resulted from a part of the precipitation being used up to recharge the soil moisture deficit. McNeal and Pratt (1978) summarised the results on N leaching losses in irrigated croplands of California. Leaching losses commonly ranged from 25 to 50% of the N applied in most cropping situations, and were dependent on the amount of excess water passing through the crop root zone.

When preferential flow occurs, the amount of N leached is unlikely to be related to the amount of drainage. With preferential movement of water in soil, relatively larger amounts of surface applied fertilizer could remain near the soil surface while some fertilizer could be leached to greater depths, than predicted by miscible displacement theory. Kissel et al (1976) reported that most of the surface applied calcium nitrate remained near the soil surface following a heavy rainstorm (44 mm) that occurred 2 days after its application; while small amounts (1 ppm) of nitrate moved down to a depth of 1.2 m. Shuford et al (1977) also reported that the vertical distribution profiles of fertilizer nitrate obtained following a 178 mm drainage

event, showed little displacement of nitrate to lower depths, due to preferential flow of drainage water.

Thomas and Phillips (1979) pointed out, in a review, that the amount of N leached by preferential flow of drainage water in the soil would be related to the rate of water movement in the macropores as compared with that in the main matrix of the soil. These two rates of water movement would be affected by rainfall intensity, soil structure, relative proportion of micro and macro porosity, and antecedent soil water content. Unfortunately, the effects of these factors on the amount of N leached by preferential flow have not been quantified.

The conditions under which preferential flow is likely to occur have been reported by Scotter (1978), and Scotter and Kanchanasut (1981). Preferential flow in saturated soil is likely to be of greater magnitude than under unsaturated conditions. Root and worm channels, sometimes in association with incipient fracture planes, would be the main preferential pathways.

2B NITROGEN SIMULATION MODELLING

2B.1 Forms of N models :

2B.1.1 'Single N transformation' models and N system models:

Several 'single N transformation' models that simulate the various individual N transformations such as urea hydrolysis (Sankhayan and Shukla 1976) nitrification (McLaren 1969, 1971), immobilisation - mineralisation (Kirkham and Bartholomew 1954) plant uptake (Epstein and Hagen 1952; Rao and Rains 1976), leaching (Burns 1975,1976; Cho 1971) and mineralisation of soil organic matter (Greenland 1971; Russell 1975), have been reported. The purpose for developing such models has been to understand the nature of the basic mechanism involved by studying an individual N transformation under controlled and defined conditions. Such an approach is necessary as the simultaneous interplay of several N transformations in soil create a complicated N system. On the other hand, the study of a single N transformation in isolation of the rest of the transformations has limited application to the N system as a whole.

System level N models take an integrated approach to simulate simultaneously several N transformations occurring in a N system. Several N system models have been proposed which range from conceptual framework models (e.g. Endelman et al 1972) to computer simulation models (e.g. Tillotson and Wagenet 1982). Such N models are useful either as research tools that summarize and describe the complex N system (e.g., Tanji et al 1979), or as management tools

either in environmental nitrate pollution studies (e.g., Shaffer and Gupta 1981) or fertilizer N requirement studies (e.g., Geist et al 1970).

Regardless of the use to which N system models are put to, they vary widely in scope. Most N system models are small scale system models, and only a few are large scale system models. Small scale system models (e.g. Tillotson and Wagenet 1982) are developed with data obtained from small scale experiments (Wagenet et al 1977). Such models simulate N and water fluxes in small scale systems such as lysimeters (e.g., Dutt et al 1972), and incubation experiments (Reddy et al 1979a,b). Most of the small scale system models have been fully or partly verified with small scale studies.

Large scale system models have been designed to simulate N processes occurring in large scale systems such as watersheds and irrigation projects (e.g.,Shaffer and Gupta 1981). Where parameterisation of such models is made, data obtained from small scale studies are used. The results simulated in these large scale system models have not been verified with data obtained from large scale studies, presumably due to a lack of suitable data.

N models have characteristic time scales. The time scale for a N model developed for a cropping system (e.g.,Watts and Hanks 1978) is restricted by the duration of a crop (about 15 weeks). Models such as those (by Shaffer and Gupta, 1981) used by the U.S. Bureau of Reclamation to evaluate the water quality of return flows from irrigation projects, run continuously.

2B.1.2 Static and dynamic models:

Static models (Geist et al 1970; Soper et al 1971; Nuttall 1973; Stanford 1982) based on regression analysis of soil and plant test data for N obtained from field trials, make static accounting of N gains, losses and exchanges. Such models do not take into account the dynamic nature of N transport and transformations in soil and thus are not capable of predicting cause (e.g., rainfall) and effect (N leaching) relationships. This limits the application of such models to a different climatic situation. Dynamic models (Mehran and Tanji 1974; Duffy et al 1975,; Watts and Hanks 1978; Selim and Iskander 1981; Tillotson and Wagenet 1982), on the other hand, are based on rate of change equations of the given N forms in soil, with sink and source terms. Such models are process oriented in that physical, biological, and chemical processes are simulated simultaneously. They are capable of predicting N pool sizes, and the N losses and gains from these pools. However, they are not applicable to all soil- water- plant situations because each dynamic model has a degree of site-specificity, since each of these dynamic models has been formulated for a specific local condition. Application of a given dynamic model to a different set of experimental conditions usually requires recalibration of model parameters.

2B.1.3 Dynamic models of N transport and transformations in soil

The two important processes involved in N simulation are: (i) N movement (transport) caused mainly by water

movement; and (ii) biochemical processes (transformations). Models on N transformations alone (Mehran and Tanji 1974; Cameron and Kowalenko 1976) are formulated for simultaneous computation of several N transformations like ammonification, nitrification, denitrification, mineralisation, immobilisation, ion exchange and plant uptake. This type of a model takes into account the N transformations occurring in a spatial volume of soil and does not include N movement or transport in soil due to water movement. On the other hand, models on N transport and transformations simulate simultaneously the changes in N resulting from N movement and N transfers between different pools. Dynamic models on N transport and transformations are more valuable than the models on N transformations alone, since the former models take an integrated approach on N movement and transformations, and thus relate better to practical situations.

2B.2 Modelling principles and approaches

Mechanistic as well as empirical approaches have been used in developing dynamic models on N transport and transformations. In the mechanistic approach, physical laws and mathematical relations are used to quantify the N system, by invoking mass conservation principles. The empirical approach involves stochastic approximations, regression analysis and use of curve-fitting techniques on experimental data. More often both approaches are used simultaneously in model formulation.

Dynamic models on N transport and transformations simulate, simultaneously, the N movement and biochemical

transfers, but since not all of the N species are mobile, the N transport and the N transformations are considered independently for clarity.

2B.2.1 N transport:

The theoretical basis for the dynamic simulation of water and N fluxes is the equation of continuity expressed in the form (Bresler 1973):

$$d(\theta C_i)/dt = d/dz \{D(v,\theta)\ dC_i/dz\} - d/dz(qC_i/dz) \pm P_i \quad (2.1)$$

where C_i is the concentration of the solute N species i, θ is the volumetric soil water content, t is time, z is the verticle space coordinate, D is the dispersion coefficient, v is the average pore water velocity, q is the volumetric water flux, and P_i is the sink/source term for solute N species i.

Some models (e.g., Beek and Frissel 1973) utilise equation (2.1). Such models simulate water flow in discrete soil layers and calculations for the sink/source term are made independent of the dispersion and convection term, within a given soil layer over a given time interval, and the new concentration values of N are used in N transport from one layer to another. Some parameters (like dispersion coefficient) have unique values only in relation to a particular set of soil conditions and to the methods employed for their measurement. Also processes like the preferential flow of soil water and the resulting N fluxes are not considered. Because of such limitations, these models are unlikely to be successful under a wide range of field conditions.

More simplified models (e.g., Davidson and Rao 1978) take an integrated view of the N transformations and transport over the whole soil profile and simplify equation (2.1) to

$$d(\theta C_i)/dt = - d(qC_i)/dz \pm P_i \qquad (2.2)$$

Davidson and Rao (1978) tested their simplified model against experimental data published by NaNagara et al (1976) and Watts and Hanks (1978), and reported that the gross simplification of equation (2.1), contributed to large deviations in predicted data (upto $\pm$ 77%) over measured data for N uptake by corn. Thus, such simplifications may not produce the desired results in model predictions.

Saxton et al (1977) used a stochastic approach for modelling N transport in a well-aerated, permeable soil profile of 1.8 m depth. The soil profile was divided into 12 layers (segments) of 150 mm each. Assuming uniform nitrate concentration within each layer, nitrate quantities leaving or entering a layer were calculated as the product of the computed water movement and the computed nitrate concentration. The soil water fluxes were computed with a soil moisture-evapotranspiration submodel. The nitrate submodel was essentially a nitrate budget for the soil profile that was used to compute nitrate amounts and distribution in each soil layer. Testing this model for soil moisture conditions wetter than field capacity, they concluded that the model predicted excess nitrate movement, and suggested that a term reflecting the leaching efficiency may be required for excess soil moisture conditions. An opportunity exists to use their approach with suitable

modification such as inclusion of a proportionality constant in order to more closely approximate the measured data.

2B.2.2 N transformations

The N transformations include ammonification, nitrification, immobilisation, mineralisation, denitrification, ion exchange, ammonia volatilisation, biological N fixation, and urea hydrolysis. There is no N model that takes into account all these N transformations. Most models do not consider denitrification (Dutt et al 1972; Beek and Frissel 1973; Watts and Hanks 1978) and mineralisation - immobilisation (Selim and Iskandar 1981; Tillotson and Wagenet 1982). Such omission of one or more transformations in any model is often due to (i) a dearth of available data on such transformations, and (ii) site-specific conditions where such transformation(s) play(s) a minor role and thus negligible. A few models include transformations such as urea hydrolysis (e.g., Dutt et al 1972; Tillotson and Wagenet 1982), ammonia volatilisation (Reddy et al 1979b), ion exchange (Mehran and Tanji 1974; Selim and Iskander 1981), and biological N fixation (Duffy et al 1975).

N transformations are described by mechanistic or empirical models. Most mechanistic models involve chemical kinetics, mainly first order (e.g., Mehran and Tanji 1974;); or Michaelis-Menten type of kinetics as adopted by Beek and Frissel (1973) to describe the growth of ammonifiers and nitrifiers. Empirical models include multiple regression (Dutt et al 1972) or algebraic expressions (Duffy et al 1975; Watts and Hanks 1978; Reddy et al 1979a,b).

Empirical models require elaborate experimental data for individual transformations in order to obtain regression equations or algebraic expressions describing the transformations. The disadvantage with such empirical models is that they have a higher degree of site-specificity than mechanistic models, and so are not applicable to a wider range of soil - crop - climate conditions. On the other hand, mechanistic models do not completely describe the transformations, since the biological mechanism involved in any N transformation can not be fully described by chemical kinetics alone. However, for simple models, first order kinetics may be suitable for describing the microbially mediated N transformations (Tanji and Gupta 1978).

Some models (e.g., Watts and Hanks 1978) take into account effects of environmental conditions such as temperature on rate constants so that it partially regulates N transformations, but others ignore this factor (Mehran and Tanji 1974; Duffy et al 1975). A few models (Beek and Frissel 1973; Selim and Iskandar 1981) also take into account effects of soil moisture content on N transformations. It appears that there is no mechanistic approach that can be used to incorporate, into the model, the effect of environmental factors on N transformations; all models that take into account these effects have used only empirical approaches. Recently, Frissel and van Veen (1981) proposed an empirical approach of using reduction (correction) factors on the kinetic rate coefficients, in order to take into account a simultaneous effect (reduction

effect) of soil temperature, moisture and pH. Their equation is :

Reduction effect = TCOF x WCOF x PHF

where TCOF, WCOF, PHF are coefficients for soil temperature, moisture and pH, respectively. Soil temperature is considered as a primary factor because of synergistic as well as antagonistic interactions among these factors. Reduction effect is set equal to TCOF multiplied by the minimum value of WCOF and PHF. It appears that their approach may have some potential for use in simple models.

2B.2.3 N uptake by plants

Nitrogen uptake by plants involves the movement of water soluble N species (ammonium and nitrate) to the roots followed by their absorption across the root surfaces. Mass flow and diffusion are the two major processes by which these N species are transported to the roots (Nye and Spiers 1964; Olsen and Kemper 1968). Convective flow of water towards roots in response to transpiration results in mass transport of ammonium and nitrate, to the roots along with the water. The concentration of these ions at the root surface decreases when the rate of root uptake exceeds the rate of supply of these ions by mass flow. Diffusion of ammonium and nitrate towards the roots then occurs due to concentration gradient. It appears that data are not available to determine explicitly (i) the contribution of each process and (ii) the fractional uptake of ammonium and nitrate by plants when both species are equally available. This inherent complexity in the dynamic nature of water and N uptake by plants, makes formulation of mechanistic model for plant N uptake very difficult.

Some modelers (Davidson et al 1978; Selim and Iskandar 1981) have used Michaelis-Menten kinetics to describe plant N uptake. Such models require inputs such as root length per unit soil volume and maximum N uptake demand, which are difficult to determine in field experiments. Also these models assume that the Michaelis coefficient remains constant throughout the growth season, which is not fully valid even for plants grown in solution culture studies (Burns 1980). Tillotson and Wagenet (1982) modelled N uptake per unit root length as the product of root circumference, root absorbing power and N concentration in soil solution. The deficiency in this model is again the lack of data to parameterise root absorbing power, root radius, root growth and distribution in soil.

Several modelers (Dutt et al 1972; Duffy et al 1975; Saxton et al 1977; Tanji and Mehran 1979) have assumed the N uptake rate to be proportional to the rate of root water uptake and nitrate concentration in the soil solution. Tanji and Mehran (1979) considered uptake as proportional to the product of root water extraction and concentration of ammonium and nitrate in soil solution, with a proportionality constant which can be set to unity if uptake is assumed to be proportional to root water extraction. In the absence of data on several plant parameters like root absorbing power and root growth characteristics, the approach of Tanji and Mehran (1979) appears most suitable for purpose of developing a simple N model, since it needs less data input.

2B.3 Model formulation

2B.3.1 Approaches

Two main approaches seem to have been evolved in the model formulation procedure, depending upon the objective(s) for developing the model. Some models (e.g., Mehran and Tanji 1974) are developed to examine the theoretical aspects of a N model system, without basing the model on experimental data. The rate constants are estimated empirically and the model or part of the model is tested with experimental data reported in the literature. On the other hand, some models (e.g., Watts and Hanks 1978) are developed for field application with objectives such as to provide better management guidelines that would help in maximising crop production and/or minimising nitrate pollution in agricultural drainage. The approach taken by such models is to collect data from a field site documenting the effects of rate, amount, and timing of fertilizer and irrigation applications, on crop yield and N uptake. These data are partly used to develop the model, and partly to verify the model. This approach has an advantage in that the model so developed has better field applicability, since the model is based on field data.

2B.3.2 Steps in developing a N model

The N model development procedure, as summarised by Tanji and Gupta (1978), consists of calibration, validation and verification. Calibration refers to model parameterisation with synthetic and/or observed data; validation means testing the algorithm and verification means testing the model with data other than the set used to

calibrate the model. Model verification or model testing usually means comparing the computed results or model predictions, with experimentally measured data. Usually statistical correlations between predicted and measured values are not run; but the measured and predicted values are compared in graph form. More often the predicted values are at variance with the measured data; but it appears that there exist no rules on the acceptable variance for the purpose of declaring whether or not the predicted values are in good agreement with the measured data. The degree of agreement probably depends on the modelling objectives.

Some modelers choose to test only parts of their model. For example, Mehran and Tanji (1974) verified the nitrification sub-routine with incubation-type experimental data. This happened because their model was not designed in conformance with experimental data. However, several modelers (e.g., Duffy et al 1975; Watts and Hanks 1978) have tested all parts of their models, by simultaneous simulation of all sub-routines that constitute their N models. Most of the models (e.g., Duffy et al 1975; Watts and Hanks 1978) have been tested against only one set of experimental data. Only a few models have been tested against more than one set of experimental data; e.g., the model of Davidson and Rao (1978) has been tested against the data of NaNagara et al (1976) and Watts and Hanks (1978). Such attempts, as testing a model against more than one set of data, are made in order to develop models that have more generality. Since each model is developed with specific objective(s) and for specific conditions, most models have

unique specificity. Thus application of one model to a different set of experimental conditions, usually require modifications to the model parameters.

2B.3.3 Model construction procedure

In order to simplify the interactions within the complex N system, the system is divided into a water submodel and a nitrogen submodel (Tanji and Gupta 1978). Each submodel is, in turn, divided into subroutines that describe parts of the system. The system as a whole is then described in terms of the interconnections between these subroutines. Each subroutine consists of a set of mathematical equations which may need to be solved simultaneously. Sophisticated models (e.g., Selim and Iskandar 1981) consist of differential equations governing N transport and transformations in multilayered or stratified soil profiles. Analytical and/or numerical solutions for such equations require the use of computers. Computer science and numerical analyses have advanced to such levels that it is difficult to follow the computer jargon describing the sophisticated mathematical terms. Even computer specialists have difficulties deciphering computer models developed elsewhere (Tanji 1981). Contrary to such computer models, there is a group of simple models such as those that describe water requirements of crops (e.g., Kanemasu et al 1978), which are stored in and run with programmable calculators. It appears that there is no such N model reported that can be stored in and run with a programmable calculator. Such simple N models can find better use with managers or advisors engaged in determining N fertilizer requirements of crops or N pollution control.

CHAPTER 3

N-15 BALANCE STUDIES UTILISING EMISSION SPECTROMETRY IN SMALL SCALE EXPERIMENTS

3.1 INTRODUCTION

Preliminary investigations into the fate of N-15 labelled urea applied to barley and oat crops in a double cropping system, were conducted using soil cylinders in situ, and are reported in Appendix 1. In these investigations, plants were grown in soil confined by PVC pipe (soil cylinder) and N-15 analyses on soil and plant samples were performed using emission spectrometry. The purpose of these investigations was to evaluate the N-15 mass balance at various stages of crop growth, in order to better understand the fate of applied N and the likely pathways of major fertilizer N transformations. In this preliminary study, the total recovery of applied N in plant and soil components varied between 50 to 90 percent. The unaccounted component of the mass balance increased from about 10% at 1 week following fertilizer application to about 50% at harvest of the crop. These experimental results could only be taken as approximations, because experimental errors in this study due to

(i) reduced accuracy in N-15 assay by emission spectrometry compared with a mass spectrometer; and

(ii) artificial experimental conditions such as use of powdered N-15 labelled urea and confined soil volumes in which plants were grown,

were not evaluated. Thus, further investigations into the

use of emission spectrometry for N-15 assay, and the suitability of soil cylinders for growing plants, were necessary.

Emission spectrometric (e.s.) assay of N-15 is less precise compared with mass spectrometric (m.s.) assay (section 2A.1.2), particularly in the N-15 enrichment range close to natural abundance (0.366 atom percent). The major cause for low precision is attributed to the many possible sources of error involved in the N-15 sample preparation for e.s., as the chemical procedures for N-15 sample preparation are complex (Perschke et al 1971; Keeney and Tedesco 1973; Fiedler and Proksch 1975). Several modified procedures of the original Dumas method are in use as pointed out by Fiedler and Proksch (1975). Each modified procedure requires specialised apparatus (N-15 sample preparation unit). For the study in Appendix 1, owing to the available N-15 sample preparation unit, N-15 samples were prepared using a modified Dumas method which differed from other procedures in that the reagents of the Dumas mixture, namely copper oxide and calcium oxide, were degassed separately and placed as a mixed powder into the discharge tube. When N-15 samples are prepared by this method and measured by using a Statron NO1-5 analyser, the accuracy and precision of the N-15 assays are not known. An investigation was, therefore, necessary to determine, using N-15 standard samples, the accuracy and precision of N-15 assay when samples are prepared following this modified Dumas method and measured using a Statron NO1-5 analyser.

In the preliminary study (Appendix 1), the estimates of fertilizer N immobilisation were considered to be less precise than plant N uptake and soil inorganic N data, due to the lower precision of the N-15 data for soil organic N. This lower precision of the N-15 data for soil organic N, resulted from the manyfold isotopic dilution caused by the relatively large native soil N pool (0.2% organic N). Information is not available on the required initial N-15 enrichment in the fertilizer material that would facilitate, by reducing the dilution effect, the use of emission spectrometry in immobilisation studies with soils of relatively high organic N content. A further investigation was therefore necessary to determine the level of N-15 enrichment in urea, which would facilitate emission spectrometric assay of N-15 in the organic fraction of a Tokomaru silt loam soil.

Often artificial experimental conditions, such as use of powdered form of N-15 enriched urea and confined soil volumes for growing plants, are necessary in N-15 studies since the isotope is expensive for use on large field plots. Such artificial experimental conditions may alter the N transformations in experimental soils as compared with the soils under field conditions. Visual inspection during the twelth and subsequent weeks of the winter experiment reported in Appendix 1, indicated that the plants grown in soils confined by PVC pipe were stunted in growth as compared with plants in the surrounding field. The relevance of data collected from such small scale experiments to field situation does not appear to have been

evaluated. An investigation was therefore necessary to determine the relevance of N data obtained from small soil cylinders in situ, to large field plots.

In the preliminary study (Appendix 1), the fate of applied N-15 urea was determined at 3 to 4 weekly intervals during the crop season. The dynamic nature of the N-15 transformations was thus not fully evaluated. In order to develop a crop N model, the N transformations, particularly, the changes in soil inorganic N associated with its uptake by a growing crop, need to be investigated at more frequent (e.g., weekly) intervals. An additional experiment was conducted to characterise the dynamic nature of soil inorganic N changes associated with its uptake by a barley crop to which N-15 urea was added.

3.2 METHODS AND MATERIALS

The experimental site was located at the Tiritea Research Area, in part of a main plot prepared for sowing barley.Three field experiments were conducted in this main plot, using soil cylinders in situ. A soil cylinder was a confined soil volume obtained by pushing into soil in the field, a PVC pipe of 100 mm diameter to a depth of 150 or 400 mm. In each soil cylinder, 5 barley seeds were sown at the time of fertilizer application and thinned to three seedlings 4 days after plumule emergence. N-15 assay on plant and soil samples, collected from these soil cylinders were made using emission spectrometry.

3.2.1 Field experiments:

Experiment I: Emission spectrometric assay of N-15 in soil organic matter:

Fifteen soil cylinders of depth 150 mm, were established in field positions that were previously marked on a grid using 1 m between treatments and 1.5 m between blocks in the randomised block design (5 treatments x 3 blocks). Five enrichments of N-15 (30.156, 37.491, 47.303, 55.471 and 65.588 atom percent) as urea constituted the five treatments that were replicated three times. Urea in powder form was mixed with some dry soil as an extender and was surface applied to soil cylinders at a rate equivalent to 100 kgN/ha. The soil cylinders were removed 11 weeks later. The soil from each cylinder was pushed out of the PVC pipe and the plants with as many roots as possible, were separated from the soil cylinder. The soils were dried, ground and homogenised before samples were taken for Kjeldahl N analysis. On each soil sample, triplicate samples were prepared for N-15 analysis by emission spectrometry.

Experiment II: Relationship between soil cylinder data and field plot data:

An area of 4 x 6 m was marked out within the main plot and this area was divided into 24 plots of 1 square meter each. In the centre of each plot a soil cylinder of 400 mm depth was established. Non-enriched urea in granular form was applied to the field plots and in powder form to the soil cylinders, at a rate equivalent to 100 kgN/ha. The field plots were also sown with barley at an equivalent seed rate (250 seeds/ m^2) as of the soil cylinders.

Plant and soil samples were collected from both the field plots and soil cylinders, at five sampling times that were on 1, 2, 4, 7 and 11 weeks following urea application. At each of the first four samplings, five randomly chosen field plots were harvested manually for plant samples and 15 soil cores were taken from each of these plots, to a depth of 400 mm. At the same time, the soil cylinders in the corresponding field plots were removed from the field for soil analysis. Above-ground portions of plants were harvested from the cylinders prior to removal. During the final sampling at 11 weeks, 4 field plots and soil cylinders were sampled in the same manner as previous samplings.

The plant portions were oven-dried, weighed, powdered and sub-samples were taken for total N analysis. The soil cores from the field plots were divided into 3 sections of 0-150, 150-300 and 300-400 mm depth increments and the corresponding sections of the 15 cores from each plot were bulked, mixed thoroughly and duplicate samples taken for analysis. The soil cylinders were cut into three sections of the same depth increments as the field plot samples. Duplicate samples were taken from each section of the soil cylinder, after mixing the soil thoroughly. All soil samples were analysed for inorganic N.

Experiment III: An investigation to characterise the dynamic nature of urea N transformations:

Twelve positions were marked in the main plot, on a grid with three rows at approximately 7 m apart and four blocks at about 10 m apart. At each position a soil cylinder of 400 mm depth was established. Urea, in powder form, enriched with 65.223 atom percent N-15, was mixed with

some dry soil as an extender, and was applied to the soil cylinders, at a rate equivalent to 100 kgN/ha.

One soil cylinder, chosen randomly, was removed from the field at weekly intervals up to 12 weeks. Prior to removal of soil cylinder, the plants were harvested for the above-ground portions. The herbage was oven dried, weighed and ground (<1 mm). The soil cylinders were cut into 3 sections of 0-150, 150-300 and 300-400 mm depth increments. The soil from each section of the soil cylinder was removed, well mixed, and sub-samples were taken for soil inorganic N analysis.

Soil samples were collected from the main plot on day 0, i.e., prior to sowing the barley crop, in order to know the initial soil inorganic N content. Ten soil cores were collected to a depth of 400 mm, using a corer of 20 mm diameter. The soil cores were also cut into sections of the same depth increments as of the soil cylinders. Soil cores of the corresponding depths were bulked, mixed thoroughly, and sub-samples were taken for soil inorganic N analysis.

3.2.2 Analytical procedures:

(a) N-15 assay by emission spectrometry:

Samples of ammonium sulphate and urea enriched with N-15 at 23 different concentrations ranging from 0.395 to 65.588 atom percent N-15, were prepared and analysed for N-15 using mass and emission spectrometers. For preparing these N-15 standard samples, ammonium sulphate or urea with higher N-15 enrichment was isotopically diluted with compounds of the same chemical composition but with N-15 concentration at natural abundance level. Ammonium sulphate enriched with 40 atom percent N-15 was diluted to obtain 14

samples with N-15 enrichments ranging between 0.395 to 22.792 atom percent. Urea enriched with 99 atom percent N-15 was diluted to obtain 5 samples 30.156 to 65.588 atom percent N-15 enrichments (Table 3.1).

The N isotope ratios of the N-15 standard samples were determined using a mass spectrometer (Houlston and Shilton 1958) at the Institute of Nuclear Sciences, Wellington, New Zealand.

For N-15 analysis by emission spectrometry, N-15 samples were prepared in triplicate following a modified Dumas method in which the oxides of copper and calcium (reagents of the Dumas mixture) were degassed separately by heating in muffle furnaces at 600 and 1000 C respectively and the Dumas mixture was placed as powder into the discharge tube. Apart from this modification, the procedure described by Fiedler and Proksch (1975) was followed. Emission spectrometer model Statron NO1-5 was used to measure the N isotope ratios.

The N-15 standards were divided into 4 groups, as shown in Table 3.1, based on the amplifier gain settings used to differentially amplify the $^{14}N^{14}N$ and $^{15}N^{15}N$ bandheads. For all samples containing less than 30 atom percent N-15, the gain setting for $^{14}N^{14}N$ bandhead was kept constant at 100, and the gain setting for $^{14}N^{15}N$ was set at either 3000 (group 1) or 1000 (group 2) or 300 (group 3) depending on the N-15 content of sample. For samples with N-15 content in excess of 30 atom percent (group 4), the isotopic bandheads for $^{14}N^{15}N$ and $^{15}N^{15}N$ were measured.

(b) Soil and plant analysis:

The soil samples were extracted in a 10:1 suspension of 2M potassium chloride (KCl). The extracts were distilled for inorganic N that included ammonium, nitrate and nitrite (Bremner and Keeney 1966). The KCl extracts of soil samples collected from the main plot on day 0, were distilled for ammonium separately from nitrate and nitrite (Bremner and Keeney 1966). Kjeldahl N in the soil samples was determined by a salicylic acid-thiosulphate modification of the kjeldahl method as described by Bremner (1965a).

Plant samples were analysed for total N by a salicylic acid- thiosulphate modification of the kjeldahl method (Bremner 1965a).

3.3 RESULTS AND DISCUSSION

3.3.1 Accuracy and precision of N-15 assay by emission spectrometry:

The N-15 content of the standard samples as determined by the use of mass spectrometry (m.s.) and emission spectrometry (e.s.) is shown in Table 3.1. The m.s. values are from a single determination. The measurement error associated with this mass spectrometer is known to be $\pm$0.003 atom percent N-15, regardless of N-15 content in the sample being measured (personal communication with Dr.J.Houlston, Institute of Nuclear Sciences, Lower Hutt).

The measured e.s. values for N-15 samples in group (1) differed considerably from m.s. values, indicating poor accuracy of e.s. measurement for samples with N-15 enrichment of up to about 1.218 atom percent. With a similar e.s. instrument (Statron NO1-5), Meyer et al (1974)

Table 3.1 N-15 atom percent enrichment values of ammonium sulphate and urea samples determined by mass and emission spectrometers.

M.S. values of N-15 atom %	Emission spectrometric measurements: Gain setting (N14/N15)	Group	Atom percent N-15: Mean of 3 replicates	standard deviation	% Coefficient of variation
0.395	3000	(1)	0.99	0.04	4.0
0.541	3000	(1)	1.13	0.08	7.4
0.853	3000	(1)	1.39	0.16	11.7
0.865	3000	(1)	1.54	0.05	2.9
1.218	3000	(1)	1.78	0.09	4.8
1.661	1000	(2)	2.11	0.10	4.5
3.971	1000	(2)	4.25	0.02	0.5
5.708	1000	(2)	5.92	0.04	0.7
8.560	1000	(2)	8.96	0.28	3.1
9.273	300	(3)	9.14	0.08	0.9
9.771	300	(3)	9.92	0.27	2.8
14.005	300	(3)	13.65	0.21	1.5
15.740	300	(3)	14.88	0.20	1.3
21.253	300	(3)	19.46	0.22	1.2
22.792	300	(3)	20.41	0.26	1.3
30.156	100	(4)	29.05	0.58	2.0
37.491	100	(4)	34.48	0.74	2.1
47.303	100	(4)	47.54	3.15	6.6
55.471	100	(4)	56.13	1.67	3.0
65.588	100	(4)	65.78	0.85	1.3

measured several N-15 samples at natural abundance, using a gain setting of 3000/100, and their reported e.s. values were also in the range of 0.8 to 1.3 atom percent which compare well with the values shown in Table 3.1. It appears that, at 3000/100 gain settings, e.s. measurement N-15 is not accurate and the reasons for this are not known (Keeney and Tedesco 1973; Fiedler and Proksch 1975). For samples with N-15 enrichment in excess of 1.218 atom percent, gain settings of 1000/100 or 300/100 were used and the results in Table 3.1, indicate better accuracy for e.s. assay when compared with corresponding m.s. values.

The measured e.s. values differed between analytical replicates with a coefficient of variance (c.v.) ranging between 0.5 to 12 percent of mean values. The c.v. values for samples in groups (2), (3) and (4) were small (0.5 to 6.6%) when compared with the c.v. values of 3 to 12% for samples in group (1), indicating that the reproducible precision of this Statron NO1-5 analyser deteriorates as the N-15 content in sample becomes lower than about 1.218 atom percent. The reasons for such large variances in the e.s. measured data for N-15 samples in group (1), are not known. Possible explanations could include a combination of non-constant instrumental errors and sample preparation errors. However, the precision for e.s. measurement of N-15 samples in groups (2) to (4) is similar to that obtained by other workers (Keeney and Tedesco 1973; Blackburn 1979), and therefore appears to be constant.

In order to define the form of relationship between the measured e.s. and m.s. values, linear regression equations

were formulated for samples in groups (2) to (4), using the mean e.s. values (Xes) and m.s. values (Yms), and these equations are shown in Table 3.2. For a measured e.s. value, a corresponding m.s. value was found using one of these equations, only if the e.s. measurement was made with the appropriate gain setting listed for these groups in Table 3.1. These linear regressions were used to obtain the corrected e.s. values of N-15, reported in Tables 3.3 and 3.6.

3.3.2 Use of emission spectrometry for determining the N-15 excess in soil organic matter:

The values of N-15 excess in soil organic matter due to immobilisation from various rates of applied N-15, as measured using a Statron N01-5 analyser are shown in Table 3.3. The values are means and standard deviations calculated from three or nine N-15 assays. In the soil cylinders treated with urea at 30 atom percent N-15, the label in the soil organic N fraction was so close to natural abundance that N-15 atom percent excess values could not be calculated and thus are not shown in Table 3.3.

The N-15 excess values for organic N in Table 3.3, do not exceed 0.5 atom percent, indicating that fertilizer with N-15 enrichment as high as 65.588 atom percent would lose its isotopic identity through dilution to near baseline levels by the relatively large amount of indigenous soil organic N at this site. For determining immobilisation of applied N-15 at this site, e.s. measurements of N-15 would, therefore, not be useful since the precision and accuracy of e.s. measurement is not good in the range of natural abundance to 1.218 atom percent N-15.

Table 3.2 Regression equations for converting measured e.s. values (atom %) of N-15 (Xes) to m.s. values (atom %) (Yms).

Equation number	applicable to e.s. value in the range of	e.s. to m.s. conversion formulae	r^2 value
3.1	1.7 to 9.0	Yms = 1.02 Xes - 0.46	1.00
3.2	9.0 to 15.0	Yms = 1.17 Xes - 1.83	0.99
3.3	15.0 to 25.0	Yms = 1.44 Xes - 6.27	0.99
3.4	25.0 to 65.8	Yms = 0.93 Xes + 3.97	0.99

Table 3.3 Emission spectrometric measurement of N-15 excess (corrected) values in soil organic N pool. Values are means, standard deviations (S.D) and coefficient of variations (C.V.).

N-15 atom % in urea applied to soil cylinders	N-15 atom % excess in soil organic N due to immobilisation of urea N-15					
	Mean ± S.D. from 3 analytical replicates					
	Soil cylinder (1)	Soil cylinder (2)	Soil cylinder (3)	Mean	S.D.	C.V.
37.491	0.04 ± 0.04	0.04 ± 0.04	0.05 ± 0.01	0.04	0.03	62.75
47.303	0.22 ± 0.03	0.15 ± 0.05	0.20 ± 0.07	0.19	0.05	27.75
55.471	0.36 ± 0.06	0.42 ± 0.08	0.31 ± 0.04	0.37	0.07	19.83
65.588	0.41 ± 0.06	0.36 ± 0.03	0.41 ± 0.06	0.39	0.05	13.05

3.3.3 Relationship between soil cylinder data and field plot data:

(a) Soil inorganic N data:

The amounts of inorganic N measured in the soils of field plots and soil cylinders are shown in Table 3.4. The values are means and standard deviations calculated from 10 replicates. The mean values of soil inorganic N content for the field plots do not differ significantly from the soil cylinder values. However, the standard deviations for both sets of data are large, ranging from 10 to 45% of the means. These results thus indicate that the soil inorganic N data obtained by the use of soil cylinders, can be representative of field behaviour, although it must be realised that large variability in the data exists.

The coefficient of variance associated with the soil inorganic N data (also shown in Table 3.4) did not exceed 30% for the surface soils (0-150 mm), while greater variations (20 to 45%) occurred for sub-surface soils (150-400 mm). These coefficient of variance (c.v.) values are comparable to those reported in a review by Biggar (1978). He reported that the c.v. values associated with the soil inorganic N determinations could vary between 22 to 33% in soils of A horizon and 10 to 80% in soils of B horizon. The variability in soil inorganic N determinations is greater than the values of 15-20% in soil organic N determinations (Appendix 2), and this would be expected because of the greater mobility of inorganic than of organic forms of N in soils (Biggar 1978).

Table 3.4 Soil inorganic N content in field plots and soil cylinders. Values are means ± standard deviations in kg N ha^{-1}. Values in parentheses are coefficients of variations as percentages of means.

	Soil depth	Duration in weeks following urea application				
		(1)	(2)	(4)	(7)	(11)
Field plots	0 - 150 mm	92 ± 19 (21)	80 ± 10 (13)	59 ± 9 (15)	12 ± 2 (17)	11 ± 2 (18)
Soil cylinders	0 - 150 mm	122 ± 17 (14)	87 ± 22 (25)	54 ± 8 (15)	17 ± 5 (29)	9 ± 2 (22)
Field plots	150-300 mm	23 ± 5 (22)	26 ± 8 (31)	34 ± 8 (24)	14 ± 6 (43)	11 ± 3 (27)
Soil cylinders	150-300 mm	19 ± 4 (21)	28 ± 12 (43)	32 ± 6 (19)	12 ± 3 (25)	17 ± 5 (29)
Field plots	300-400 mm	15 ± 5 (33)	23 ± 10 (44)	18 ± 7 (39)	6 ± 2 (33)	9 ± 2 (22)
Soil cylinders	300-400 mm	11 ± 3 (27)	17 ± 4 (24)	15 ± 5 (33)	5 ± 1 (20)	7 ± 3 (43)

(b) Plant N data:

The values of dry matter yield and plant N uptake for plants grown in soil cylinders and field plots are shown in Table 3.5. The values are means and standard deviations calculated from 10 replicates. The soil cylinder values for dry matter yield and plant N uptake are not significantly different from the field plot values, up to week (7). On week (11), the mean value for dry matter yield in the soil cylinders is not significantly different from the field plot mean value, whereas the mean value for plant N uptake is significantly different. A possible cause for this difference in the soil cylinder data, may be that of root confinement in the soil cylinders. However, this experiment has shown that the data for plant N uptake obtained from soil cylinders can be representative of field plot data at least for the first seven weeks of plant growth.

3.3.4 Study to characterise the dynamic nature of urea N transformations:

(a) N-15 assay in soil and plant samples using emission spectrometry:

The values of N-15 atom percent excess in soil inorganic N fraction and plant N, are shown in Table 3.6. Use of 65.588 atom percent N-15 labelled urea had resulted in very high enrichments of N-15 (>20 atom percent) in plant material. Use of urea with N-15 enrichments as low as about 10 atom percent would have made possible calculations of fertilizer N in the plant. However, as the objective was to measure the N-15 label in both the plant and the soil inorganic N fraction, over a 12 week experimental period,

Table 3.5 Dry matter yield (kg/ha) and plant N uptake (kgN/ha) for plants grown in field plots and soil cylinders. Values are means and standard deviations.

For plants grown in	Duration in weeks following seed sowing			
	2	4	7	11
Field plots				
Dry matter yield	120 ± 19	1210 ± 186	4060 ± 1080	7320 ± 1260
Plant N uptake	5.4 ± 0.9	34.1 ± 4.7	70.4 ± 4.9	87.8 ± 3.1
Soil cylinders				
Dry matter yield	110 ± 24	1050 ± 310	3740 ± 1180	4580 ± 1730
Plant N uptake	6.1 ± 1.2	30.2 ± 5.9	59.2 ± 8.2	65.7 ± 12.3

Table 3.6 Changes in soil inorganic N and plant N uptake during a 12 week experimental period.
(NDE = Not detectable by emission spectrometry)

	Weeks following urea application and seed sowing											
	1	2	3	4	5	6	7	8	9	10	11	12
Plant uptake (kgN/ha)												
Total N uptake	2.4	10.8	24.5	52.1	70.3	96.7	97.3	106.0	107.8	100.4	89.5	83.4
N-15 atom % excess	38.05	28.99	27.69	25.16	24.49	20.10	20.51	19.94	19.97	22.41	17.64	22.99
Fertilizer N uptake	1.4	4.8	10.4	20.1	26.4	29.8	30.6	32.4	33.0	34.5	24.2	29.4
Soil inorganic N (kg/ha)												
0-150 mm soil depth												
Fertilizer + native soil N	88.7	73.5	51.7	27.8	23.9	19.2	17.3	17.0	15.6	16.2	17.0	16.5
N-15 atom % excess	41.69	39.75	38.48	28.39	19.65	4.76	2.26	1.92	1.67	1.21	1.15	1.58
Fertilizer N	56.7	44.8	30.5	12.1	7.2	1.4	0.6	0.5	0.4	0.3	0.3	0.4
150-300 mm soil depth												
Fertilizer + native soil N	40.7	31.8	25.5	22.9	19.1	20.4	24.2	25.5	22.9	19.1	20.8	17.7
N-15 atom % excess	NDE	NDE	NDE	NDE	NDE	NDE	NDE	NDE	NDE	NDE	NDE	NDE

use of 66 atom percent enriched urea was required. For short term (about 8 weeks) studies, about 30 atom percent N-15 enrichment may be adequate, since the N-15 label in the soil inorganic N fraction, resulting from 65.588 atom percent N-15 labelled urea, was high, particularly in the first 5 weeks following urea application.

(b) Soil inorganic N and its uptake by plants:

Amounts of N taken up by plants and found as soil inorganic N in the top soil of 300 mm, are shown in Table 3.6. As expected, fertilizer N appeared quickly in the inorganic N pool as a result of hydrolysis. On day 42, measured amounts of fertilizer N were about 1.4 kg N/ ha and thereafter fertilizer N could scarcely be detected in the inorganic N pool suggesting that initial urea N transformations are rapid. The plants took up about 26 kg/ ha of fertilizer N during the first 5 weeks following urea application and thereafter plant uptake was only about 9 kg N/ ha, indicating that most of fertilizer N uptake by plants occurs in the first 5 weeks.

The amounts of native soil N in the inorganic N pool in the top soil of 300 mm depth, dropped from about 60 kg N/ ha at seed sowing to about 35 kg N/ ha at harvest (Table 3.6). As plant uptake of native soil N was about 70 kg/ ha, at least 45 kg/ ha of N taken up by plants could have come from mineralisation of soil organic N.

Total plant N uptake and also fertilizer N uptake by plants appeared to decline after about 9-10 weeks (Table 3.5). The N concentrations in plant material, shown in Fig. 3.1, also demonstrate a decline in N concentrations after

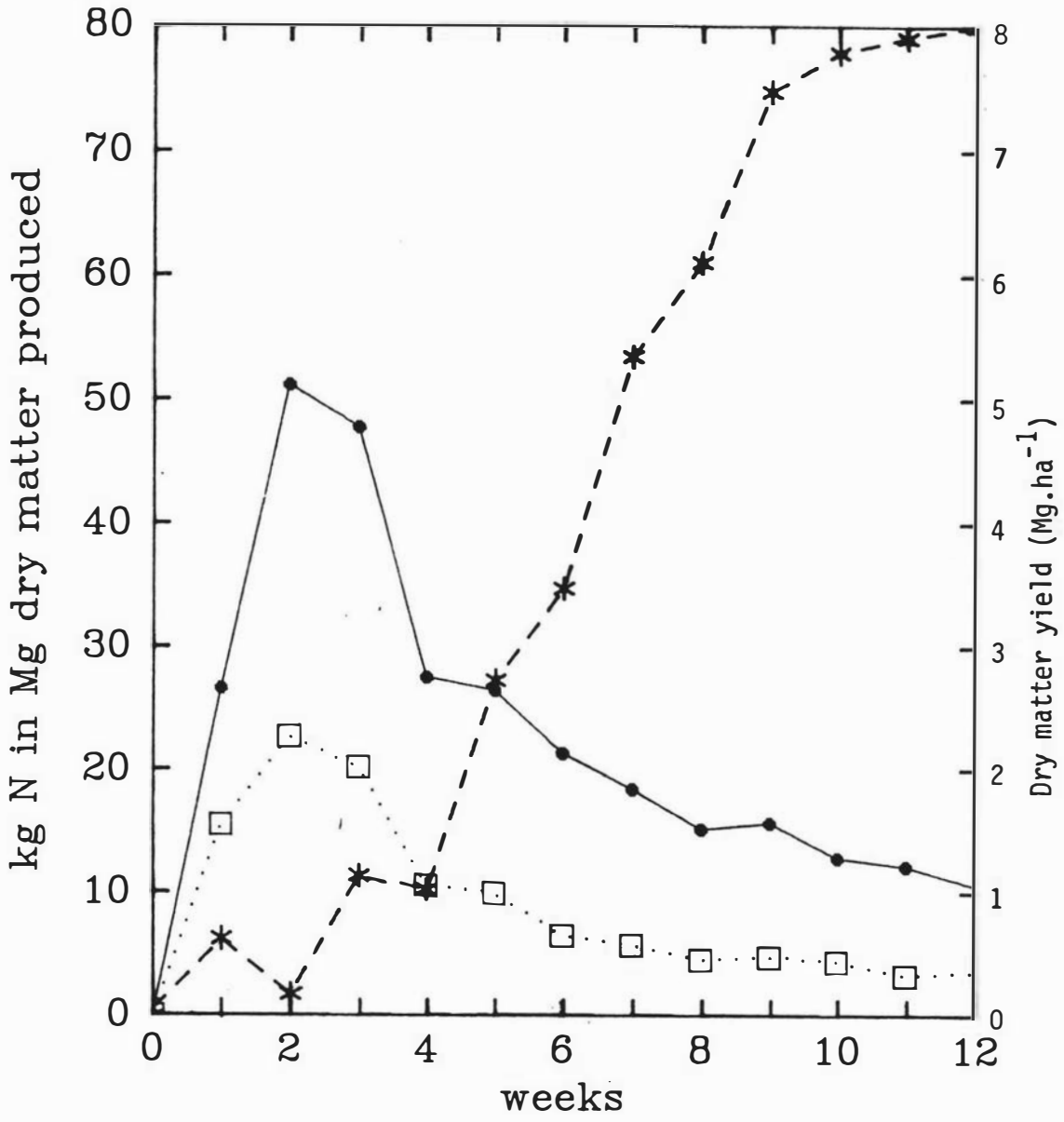

Fig. 3.1 The dry matter yields (*------*) of the above ground plant portions and the N concentrations in herbage of plants grown in soil cylinders. (●——●) Total N (fertilizer N plus soil native N) and (□·····□) fertilizer N concentrations are shown.

about 9 weeks. Such a decline has been observed in maize and was attributed to ammonia volatilisation from senescing leaves (Farquhar et al 1979). Ammonia volatilisation from barley leaf surfaces does not appear to have been reported.

(c) Dry matter production and N concentration in plants:

The dry matter (D.M.) yields of the above ground plant portions and the N concentrations in herbage measured at weekly intervals during the cropping period are shown in Fig. 3.1. During the first three weeks following seed sowing, the rate of dry matter production was slow relative to N uptake by plants, resulting in higher N concentration in plants. The total N (fertilizer derived N plus native soil N) concentration in plants reached a maximum of 51 kg N/ Mg D.M. on day 14 and did not drop very much until after day 21. The rate of dry matter production was fast after day 21 and the N concentrations were about 13 kg N/ Mg D.M. on day 70. This trend, in general, is similar to the results obtained by Kowalenko and Cameron (1978), who reported a field experiment with barley in which 80 kg N/ ha as ammonium nitrate was applied at the time of sowing. They reported that plant analysis at various stages of crop growth, for total N concentration showed a maximum of 54 kg N/ Mg D.M. on day 30 and a fairly constant concentration of about 18 kg N/ Mg D.M. between days 69 and 109. The N concentration in plants prior to day 30 was not measured in their study.

The concentration of fertilizer derived N in plants followed the same trend as the total N concentration

(Fig.3.1). The concentration of native soil N (as the difference between total N and fertilizer N concentrations) was consistently higher than the fertilizer N concentration in plants, after the first week, suggesting that plants took up a greater proportion of their total N as native soil N.

3.4 CONCLUSIONS

With the emission spectrometric technique used in this investigation, it appears that analysis of N-15 samples containing more than about 1 atom percent excess N-15 enrichments, can be performed satisfactorily. Consequently, the present e.s. technique is not useful in N-15 tracer studies investigating the immobilisation of applied fertilizer N with soils of relatively high organic N content ($\approx$ 0.2%), since such investigations require measurement of less than 1 atom percent N-15. The study showed that the present e.s. technique can be satisfactorily used to measure N-15 in plant and soil inorganic N fraction since the isotope dilution is much less than in the organic N fraction.

Data for changes in soil inorganic N content over time, obtained by the use of soil cylinders, can be representative of field behaviour, although it must be realised that large variability in the data exists. Data for plant N uptake obtained by growing plants in soil cylinders can be representative of field data at least for the first seven weeks of plant growth. At growth stages later than seven weeks, plants grown in soil cylinders appear to suffer from root confinement and therefore, plant N uptake data obtained after seven weeks, may underestimate the field plot values

The study into the dynamic nature of urea N transformations, indicated that the initial urea N transformations are rapid, and that most of fertilizer N uptake by plants occurs in the first five weeks. The study also indicated that plants take up a greater proportion of their total N as native soil N.

CHAPTER 4

SHORT TERM FATE OF UREA N-15 APPLIED TO A BARLEY CROP

4.1 INTRODUCTION

In the preceding chapter, the fate of N-15 labelled urea applied to a barley crop, was investigated at weekly intervals, using soil cylinders. Immobilisation of the applied N-15 into soil organic matter could not be investigated since the emission spectrometric technique used, did not permit measurement of N-15 enrichment close to natural abundance. Leaching losses of the applied N-15 were not investigated since the use of soil cylinders did not permit collection of leachate samples. The study, however, suggested that initial N transformations of the applied urea are rapid and most of the fertilizer N uptake by plants occurs in the first five weeks. A further study was undertaken to account for immobilisation and leaching of N-15 labelled urea applied to a barley crop, during the first five weeks following its application. The objectives were:

(i) to quantify immobilisation of applied N-15 using mass spectrometry,

(ii) to quantify leaching losses of N-15 applied to small lysimeters, under two moisture treatments that are representative of a normal and a wet season;

(iii) to assess the potential movement of nitrate in soil, using bromide as a double tracer for applied N; and

(iv) to obtain a more detailed N-15 mass balance.

4.2 METHODS AND MATERIALS

4.2.1 Microplots and lysimeters installation:

The experimental site was located at the Tiritea Research Area, in part of a main plot prepared for sowing barley. Within this main plot, microplots and lysimeters were used to isolate small areas for N-15 studies. Two microplots, each 0.44 m^2 in area, were formed by pushing thin galvanized iron rings into the bare cultivated soil to a depth of 250 mm. Adjacent to the microplots 8 cubic lysimeters with 200 mm side length were installed. These were filled by pushing thin galvanised iron frames 200 mm into the soil to obtain relatively undisturbed cores of the top soil, which was approximately 200 mm deep. After removal, the bottoms of the cores were covered with a thin layer of fine gravel, cheese-cloth and wire-mesh, with the frames becoming the lysimeter casings. The lysimeters were mounted flush with the soil surface, in metal liners deep enough to house a container to collect the drainage. The lysimeters could be removed for weighing.

4.2.2 Crop phenology:

Barley was sown at approximately 250 seeds/m^2 in both the microplots and lysimeters on December 4,1980 (day 0). On the same day, a powdered mixture containing urea (100 kgN/ha), potassium bromide (67 kgBr/ha) and a little dry soil as an extender, was sprinkled onto the microplots and lysimeters. The urea was enriched with 8.894 atom percent N-15 excess. The seeds had to be resown on day 6, due to slug damage. Emergence occurred in day 11, and the experiment was terminated on day 35 (January 8,1981). At

this time the barley was 250 mm tall, and had just achieved canopy closure.

4.2.3 Water inputs:

Two leaching treatments were imposed. Rainfall and irrigation inputs for the two leaching treatments are shown in Fig. 4.1. The two microplots and four of the lysimeters received rainfall (74 mm) and irrigation (29 mm applied in small increments after day 20) totalling the normal rainfall of 103 mm for a 35 day period at that time of the year (Anon 1979). The other four lysimeters were irrigated at approximately weekly intervals so that the total rainfall plus irrigation over the 35 days equalled the 90 percentile rainfall of 186 mm. These two treatments are referred to subsequently as the "normal" and "wet" treatments. Each day the lysimeters were weighed and the drainage measured; rainfall was also measured daily at the site.

4.2.4 Soil and plant sampling procedures:

The soil in the microplots was sampled on days 0 (before fertilization), 3, 7, 14, 23 and 35. At each sampling, five cores, 10 mm in diameter, were taken to a depth of 200 mm from each microplot. The holes left by the corer were immediately plugged with wooden rods. Each core was cut into four 50 mm long sections, and the corresponding sections from the 10 cores taken at each sampling bulked for analysis.

On day 35, the above-ground portions of the plants in the microplots and lysimeters were harvested, dried, weighed and ground for analysis. Root material was extracted manually from the lysimeter soil, washed free of soil, then

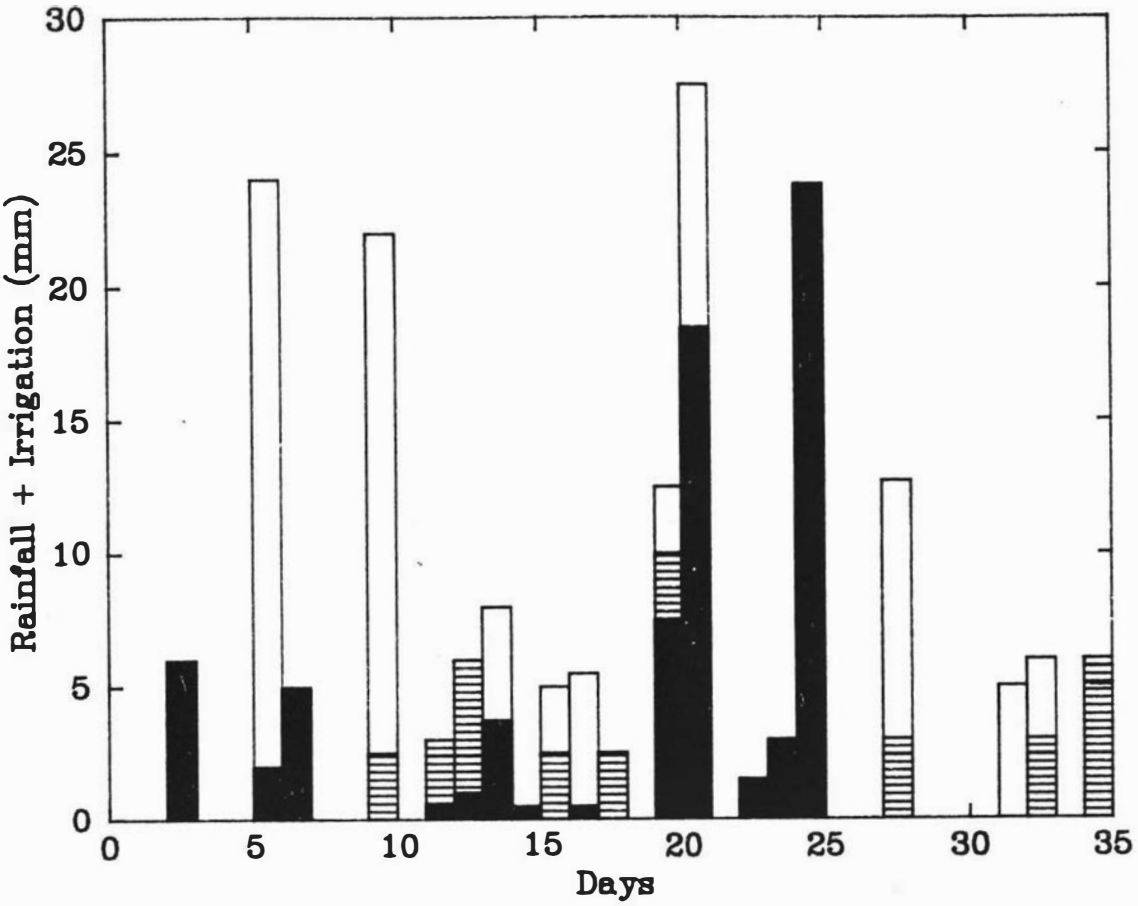

Fig. 4.1 Rainfall (▮) and additional water input as irrigation (▤) applied to both normal and wet lysimeters and additional irrigation (□) applied to wet lysimeters during the experiment.

also dried, weighed and ground for analysis. The soil from the lysimeters was well mixed and then sub-sampled for analysis.

4.2.5 Analytical procedures:

The following analytical procedures were used. Soil samples were first extracted using a 10:1 suspension of 0.5 M potassium sulphate, and extracts were analysed for inorganic N (ammonium + nitrate + nitrite) as described by Bremner and Keeney (1966). An exception was made for the microplot samples taken on day 0. They were analysed for ammonium separately from nitrate + nitrite, as described by Bremner and Keeney (1966). Soil residues after potassium sulphate extraction were dried at 60 C, ground, and analysed for organic N using the Kjeldahl procedure (Bremner 1965a). Kjeldahl analyses of potassium sulphate extracts, from the microplot samples collected on days 3 and 7, allowed urea N to be found as the difference between the total and inorganic N in these extracts. Total N in the plant samples was determined by a salicylic acid-thiosulphate modification of the Kjeldahl method (Bremner 1965a). The leachate samples were analysed for inorganic N as described by Bremner and Keeney (1966). The N-15 enrichments in the soil, plant and leachate samples were determined using a mass spectrometer, as described by Bremner (1965d).

The potassium sulphate soil extracts referred to above, and the leachate samples, were also analysed for bromide using a selective-ion electrode. Potassium sulphate (acting as an ionic strength adjuster) was added to the leachate samples and bromide standards to give 0.5 M concentration.

4.3 RESULTS AND DISCUSSION

The daily lysimeter drainage, totalling 30 ± 6 mm from the normal lysimeters, and 68 ± 6 mm from the wet lysimeters, is shown in Fig.4.2. The first drainage occurred from the wet lysimeters on day 5, but no drainage occurred from the normal lysimeters until day 20.

4.3.1 Total recovery of applied fertilizer N:

The fertilizer derived N, native soil N and bromide found in the soil, plant material and accumulated drainage on day 35, are shown in Table 4.1. Approximately 90% of the applied N was recovered from the lysimeters, so unaccounted for losses were not large. Gaseous N losses, due to volatilization of ammonia and denitrification of nitrate, constitute the most likely pathways for the unaccounted for losses. However, the soil to which the urea was applied had a mean temperature of 17 C, C:N ratio of 13 and a pH of about 6, so conditions were not conducive to excessive volatilization (Nelson 1982). Also, despite moist conditions, particularly in the wet lysimeters, the reasonable macroporosity and soil structure in the A horizon probably ensured adequate aeration and little denitrification (Firestone 1982). The leachates were not analysed for N in the urea form. Probably some N was lost from the wet lysimeters in this form on days 5 and 6, as urea was still present in the soil at this time. This may explain why the unaccounted fertilizer N losses from the wet lysimeters were slightly greater than in the normal lysimeters.

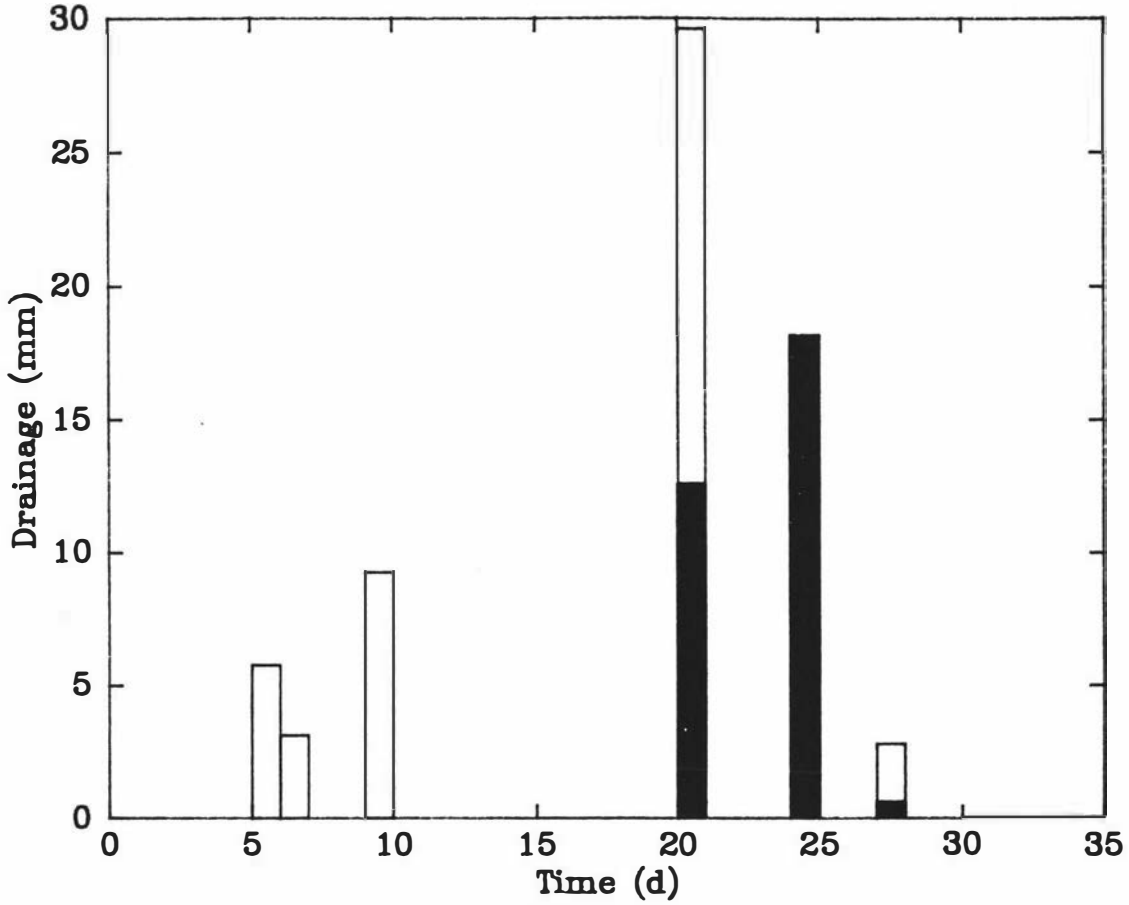

Fig. 4.2 Drainage from normal lysimeters (▮) and additional drainage from wet lysimeters (▯) as a function of time.

Table 4.1 Nitrogen and bromide in soil, plant and drainage water after 35 days. All values are in Kg N/ha. Means and standard deviations are given for the lysimeter data.

Species and pool	Microplots	Normal lysimeters	Wet lysimeters
Fertilizer N			
Application	100	100	100
Plant shoots	23	25 ± 2	18 ± 2
Plant roots	-	7 ± 1	4 ± 1
Leaching	-	6 ± 1	14 ± 1
Soil organic	47	45 ± 1	49 ± 3
Soil inorganic	9	9 ± 1	4 ± 1
Unaccounted for	-	8 ± 2	11 ± 3
Native N			
Plant shoots	47	42 ± 7	18 ± 3
Plant roots	-	15 ± 5	5 ± 2
Leaching	-	10 ± 1	17 ± 5
Soil organic	5879	5624 ± 143	5679 ± 588
Soil inorganic	51	59 ± 5	40 ± 7
Bromide			
Application	67	67	67
Soil	41	28 ± 6	12 ± 4
Leaching	-	30 ± 4	51 ± 2
Unaccounted for	-	9 ± 5	4 ± 3

4.3.2 Total recovery of applied bromide:

Over 90% of the bromide applied to the lysimeters was recovered from the soil and leachate. Plant uptake of bromide was not measured, and may account for much of the remaining 10%. Kanchanasut and Scotter (1982) found 13% of bromide applied to pasture was taken up by the plants.

The bromide data from the microplots are shown in Fig.4.3. On days 3,7 and 14, over 90% of the applied bromide was recovered from the soil, although the data show some redistribution from the top 100 mm to 100-200 mm depth during this period. By day 35, only 60% of the applied bromide was recovered from the microplots, most of the remaining 40% probably having been leached, as shown by the normal lysimeter data in Table 4.1. Also, on day 35, the bromide was relatively uniformly distributed throughout the 200 mm of soil in the microplots, although the highest concentration was still in the top 50 mm. This leaching pattern is similar to that observed by Kanchanasut and Scotter (1982), and suggests non-uniform water movement through the soil.

4.3.3 Fertilizer derived inorganic N

Analysis of soil samples taken from the microplots on days 3 and 7, showed that the amounts of urea N were 43 and 14 kg/ha respectively. The amounts of urea N hydrolysed were, therefore, 57 kg/ha during the first 3 days and 27 kg/ha during the following 4 days, indicating that, in the moist soil, urea hydrolysis would be rapid. This is in general agreement with the findings of laboratory studies (Overrein et al 1967; Ayanaba et al 1976; Sankhayam et al 1976) investigating urea hydrolysis.

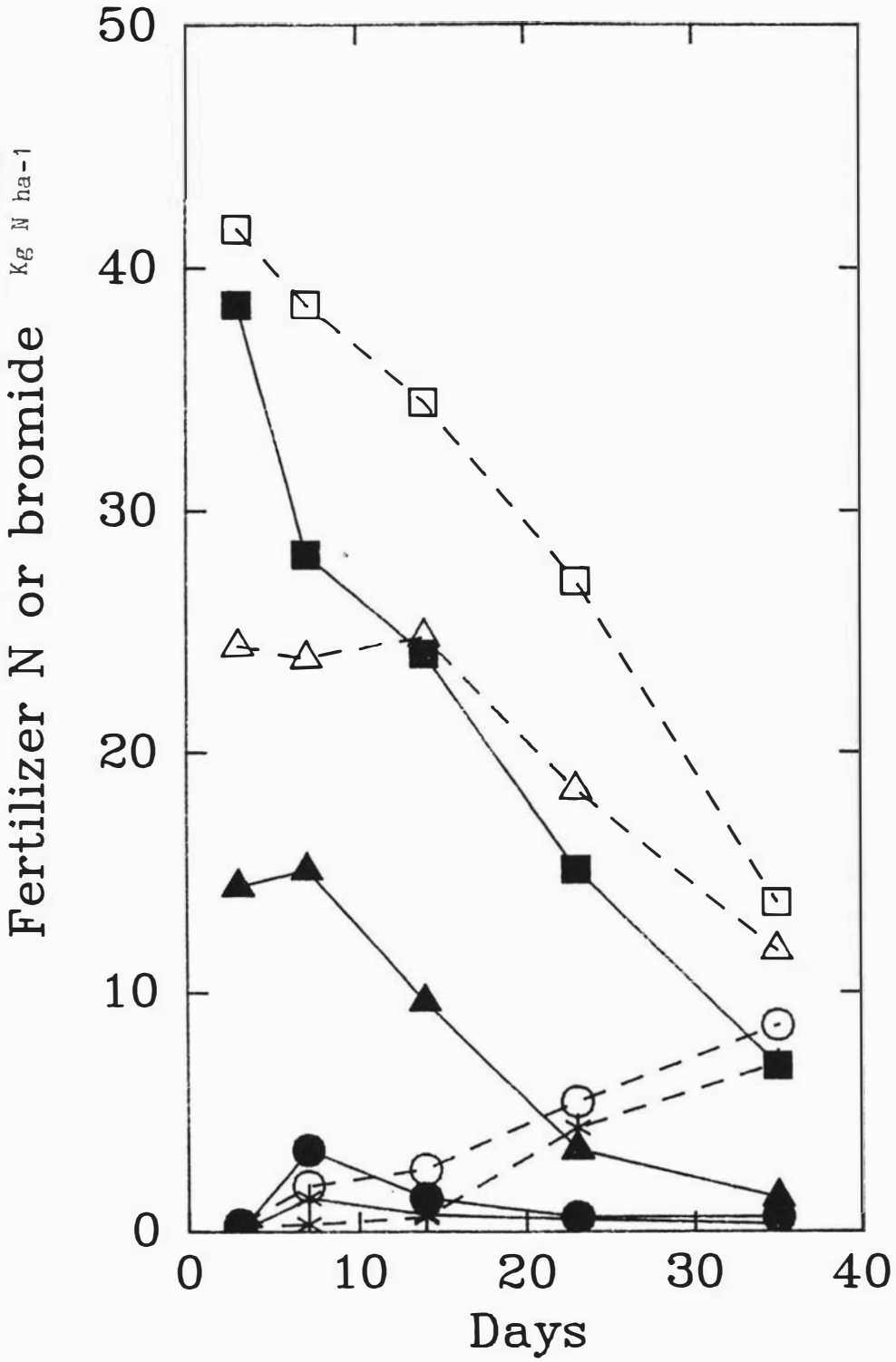

Fig. 4.3 Fertilizer derived inorganic N (——) and bromide (-----)in microplots at 0-50 mm (■ ,□), 50-100 mm (▲ ,△), 100-150 mm (● ,○) and 150-200 mm (*,*) depths, as a function of time after urea application.

Most of the urea measured in microplots on days 3 and 7, was found in the 50-100 mm depth samples, indicating displacement of urea occurred due to rainfall. The fertilizer-derived inorganic N measured in the microplots is shown in Fig. 4.3. In the 0-50 mm layer, it was highest on day 3; at other depths it was highest on day 7, which is consistent with the urea measurements quoted above. Table 4.1 shows that after 35 days, the microplots and normal lysimeters contained 9 kg/ha of inorganic fertilizer N, while the wet lysimeters only contained 4 kg/ha.

4.3.4 Fertilizer derived organic N

The fertilizer derived organic N data from the microplots are shown in Fig. 4.4. Most of the immobilisation occurred between days 3 and 14. By day 35, nearly half of the applied N was present in the organic form, indicating that immobilisation can be very significant and rapid. The immobilised fertilizer N was fairly uniformly distributed throughout the top 200 mm of soil. Very similar amounts of N were immobilised in both the normal and wet lysimeters (Table 4.1).

In other field studies (Westerman et al 1972; Craswell 1979; Legg and Meisinger 1982), the extent of N-15 immobilisation has been reported to vary between 11 to 44%, under a similar rate of about 100 kgN/ha application to crops. These studies measured N-15 immobilisation by the end of the growing season; and the extent of N-15 immobilisation during the early stages of crop growth is not known. Rapid immobilisation of N-15 applied to pasture has

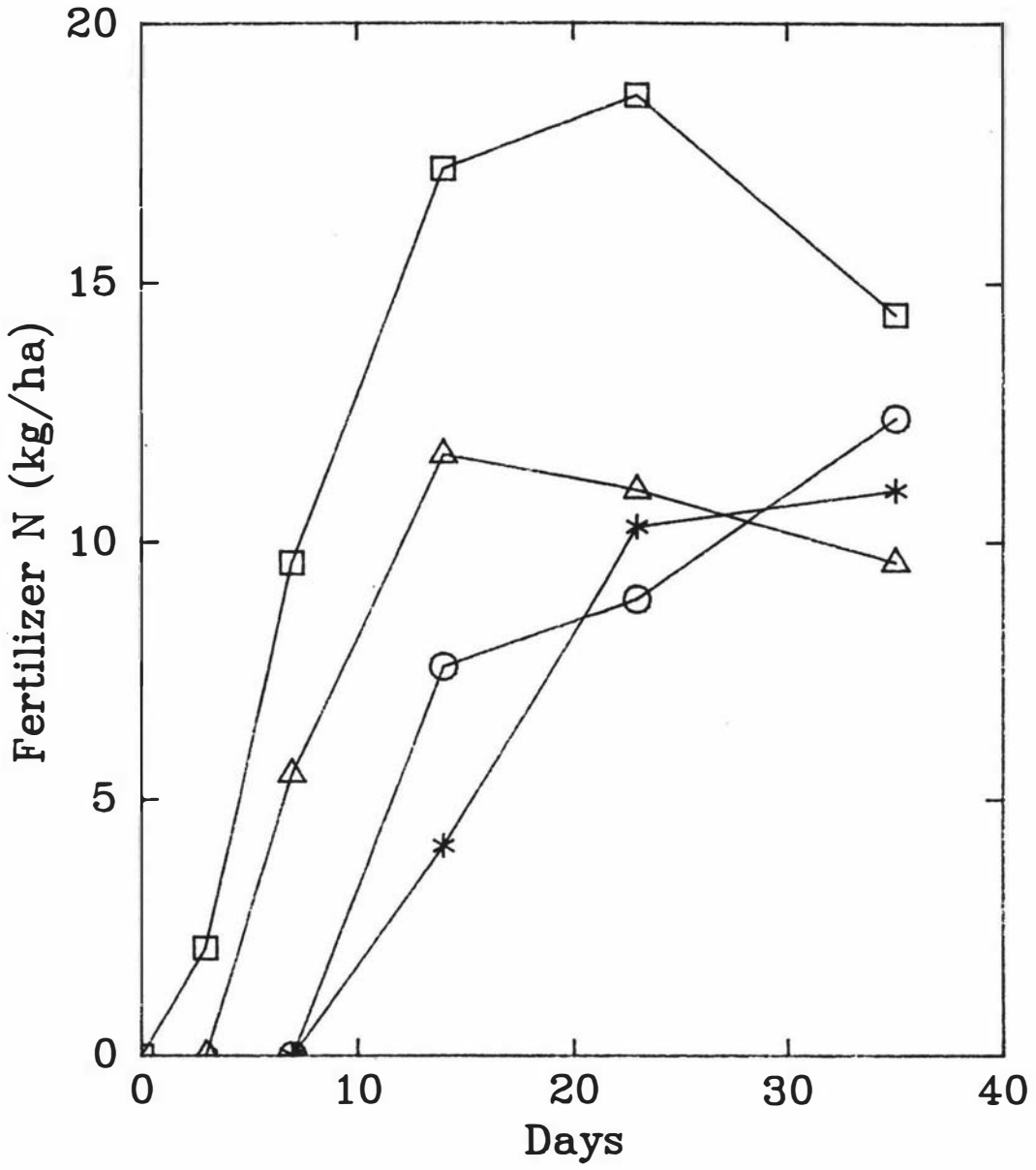

Fig. 4.4 Fertilizer derived organic N in microplots at 0-50 mm (□), 50-100 mm (Δ), 100-150 mm (○), and 150-200 mm (*) depths, as a function of time after urea application.

been reported in a New Zealand investigation (Keeney and Macgregor 1978). They reported that over 9% (about 27 kgN/ha) of the urea N applied at 300 kgN/ha, was immobilised within a day and 13% (about 49 kgN/ha) by the end of 7 days, suggesting that the soil had a high degree of biological activity. Studies on the short-term fate of S-35 labelled gypsum fertilizer (Goh and Gregg 1982) also indicate rapid immobilisation of sulphur by the biological activity. This might be expected in a pasture soil; and where a pasture is ploughed for cropping, it is possible that a relatively high degree of biological activity might persist during the early stages of cropping phase. In the present investigation, the soil was cropped for 4 years since ploughing from pasture. A relatively high degree of biological activity could have predisposed towards the extent of N-15 immobilisation measured.

4.3.5 Leaching losses of nitrogen and bromide:

Total leaching losses of N and Br from the wet lysimeters were nearly twice the losses from the normal lysimeters (Table 4.1). The amounts of Br and inorganic N leached from the wet lysimeters on different days are shown in Table 4.2. As expected, given that preferential flow occurred, the greatest losses of bromide and native soil N per mm of drainage were from the early drainage events. However, this was not true for fertilizer derived inorganic N, presumably due to more of it being present as nitrate (and less as ammonium) on days 20 to 27 than days 5 to 9. It is interesting that 76% of the applied bromide, but only 14% of the fertilizer N, appeared in the drainage from the

Table 4.2 Inorganic N and bromide leached from wet lysimeters. Means and standard deviations are given.

Period	Drainage	Fertilizer N	Native N	Bromide
	mm	kg/ha	kg/ha	kg/ha
Days 5,6 and 9	18 ± 2	1.9 ± 0.4	5.4 ± 1.0	22 ± 3
Day 20	30 ± 2	8.8 ± 1.0	7.6 ± 3.3	20 ± 3
Days 24 and 27	20 ± 4	3.3 ± 0.7	4.4 ± 1.7	9 ± 5

wet lysimeters. This is a consequence of the rapid hydrolysis and immobilisation of much of the urea N into ammonium and organic N, two N forms not prone to leaching. On the other hand, urea, nitrate and bromide have been observed to move readily with soil water (Smith and Davis 1974; Wagenet et al 1977).

4.3.6 Plant uptake of N

Above ground dry matter yields at harvest on day 35 from the microplots, normal lysimeters and wet lysimeters were 2580 $\pm$ 270, 2170 $\pm$ 380 and 2380 $\pm$ 500 kg/ha respectively. The root dry masses were 910 $\pm$ 170 and 1120 $\pm$ 280 kg/ha for the normal and wet lysimeters respectively. Thus dry matter yields did not differ significantly between the microplots and the normal and wet lysimeters.

Plant uptake of both fertilizer and native N was similar in the microplots and normal lysimeters (Table 4.1). However considerably less fertilizer and native N was taken up by both shoots and roots in the wet lysimeters than in the normal lysimeters. This difference can be explained in part by the enhanced leaching and lower inorganic N values in the wet lysimeters. While the lower N uptake does not seem to have affected dry matter yield on day 35 from the wet lysimeters, it may well have affected later dry matter production and grain yield. Plant uptake of native N was about twice that of fertilizer N in the microplots and normal lysimeters. However in the wet lysimeters the amounts of native and fertilizer N taken up were the same. Whether this difference is real or an experimental artifact is not clear.

4.3.7 Native soil N

In the microplots, the amounts of ammonium and nitrate were 40 and 22 kg N/ ha (200 mm surface soil) respectively, prior to urea application (day 0).

Native soil inorganic and organic N present on day 35, and cumulative plant uptake and leaching of native N over the 35 days, are shown in Table 4.1. The amounts of native inorganic N present on day 35 in the microplots and lysimeters were 5 to 10 times greater than the fertilizer-derived inorganic N. As expected increased drainage affected leaching losses, the wet lysimeters losing 70% more native N by leaching than normal lysimeters.

The net mineralisation rate of native soil N could not be inferred from changes in organic N measurements, as the spatial variability of approximately $\pm$ 500 kg/ha associated with such measurements was an order of magnitude greater than the amount of N likely to be mineralised over the 35 days. So net mineralisation of native soil N was assumed equal to the sum of the amount leached and taken up by the plants in the normal lysimeters, less the decrease in native inorganic soil N from day 0 to day 35 in the microplots. The net mineralisation calculated this way was 42 kg N/ha, or 1.2 kg N/ha/day. This mineralisation rate is within the range of values (0.5 to 1.5 kgN/ha/day), that are reported in the literature (2A.2.4.ii) for several New Zealand soils.

4.4 CONCLUSIONS

The recovery of 90% of the applied fertilizer N indicates that relatively little volatilization and denitrification occurred.

Hydrolysis and immobilisation of the urea N occurred rapidly. One week after application, 86% of urea N had been hydrolysed, while after two weeks 36% of it had been immobilised into organic matter. Rapid immobilisation of fertilizer N probably resulted due to a relatively high degree of biological activity.

As expected, leaching was a function of drainage. But whereas 76% of the bromide applied was leached from the wet lysimeters, only 14% of the fertilizer N was leached, presumably due to its rapid transformation into ammonium and organic N.

The increased leaching of N from the wet lysimeters compared with the normal lysimeters was at the expense of plant uptake, having little effect on the amount of N immobilised.

CHAPTER 5

MODELLING THE SHORT TERM FATE OF UREA NITROGEN APPLIED TO A BARLEY CROP

5.1 INTRODUCTION

In the preceding chapter, the results of an investigation into the fate of urea applied to a barley crop were presented. In this chapter, the objective is to develop, using the data presented in chapter 4, a model that can be used to predict the fate of urea N in the five weeks following its application to a barley crop. The aim of the model is mainly to predict the effects on the fate of urea N, of different rainfall regimes following late spring application. Rainfall is the meteorological variable most likely to cause year to year differences in N response (Walker and Ludecke 1982). Provided that the model is capable of predicting N leaching losses, the model would be of agronomic value in alerting advisors or growers to possible ameliorative measures that may have to be taken to obtain maximum economic yield, when rainfall conditions after sowing are atypical.

5.2 MODEL STRUCTURE

The processes explicitly taken into account in the model are shown in Fig.5.1. There are three separate but inter-related sub-models. The soil water sub-model leads to estimates of drainage and transpiration, which are needed to estimate leaching and plant uptake of N respectively. As plant uptake includes both native soil N and fertilizer derived N, the latter cannot be considered in isolation. So separate pools and sub-models for fertilizer N and native N

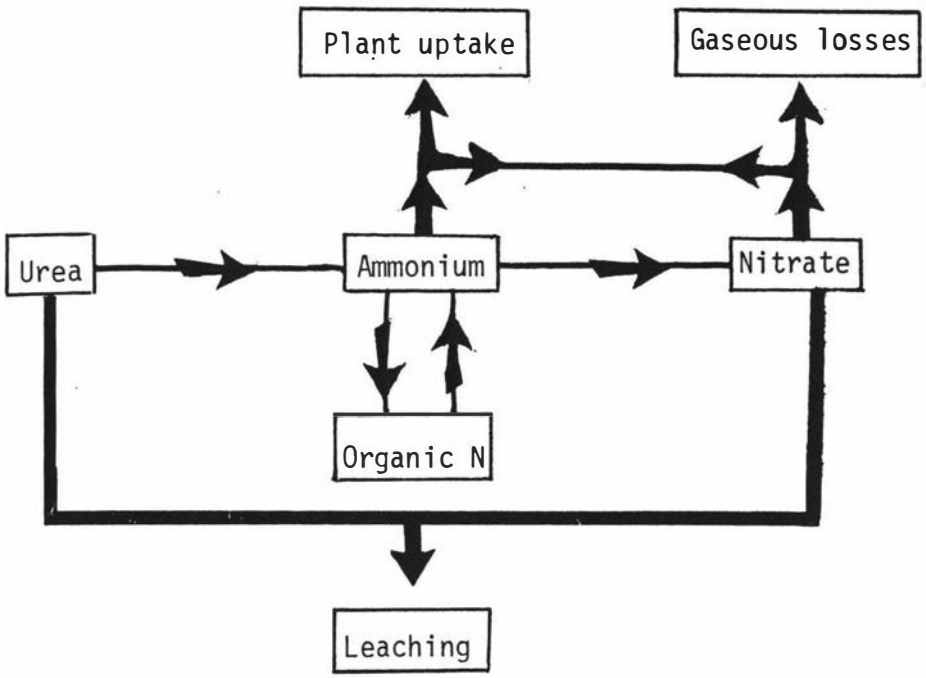

Fig. 5.1 Processes and pathways considered in soil nitrogen sub-models.

are used. For simplicity in the model, the soil is treated as a single uniform layer of depth Z (m). Since fertilizer additions to cropping soils, N uptake by crops and N leaching losses are usually calculated for unit area of soil, the N quantities in this model are expressed for a unit area (kgN/ha), assuming rooting depth (Z) as a function of time and space to be invariant. An advantage of this simplifying assumption is that the simulation calculations become easier to perform on a programmable calculator.

5.2.1 Soil water sub-model

Rainfall, irrigation if applicable, mean air temperature, incoming short-wave radiation (sunshine hours) and crop height are the daily inputs needed to run the soil water sub-model. The model is essentially that described by Scotter et al (1979) for pasture, except that transpiration and soil evaporation are calculated separately, and the total evapotranspiration taken as the greater of the two values. For bare or partially-covered soil, the maximum surface layer soil water storage was taken as the total evaporation occuring from an initially wet bare soil, before the surface becomes dry and the evaporation rate approaches zero. Daily soil evaporation was taken as the Priestley and Taylor (1972) evapotranspiration estimate (ETp, m) if water was available in the surface layer, and zero if it was not.

Given no water stress, transpiration (T,m) was assumed equal to ETp once the crop effectively covered the soil. Following Kerr and Clothier (1975), between emergence and full-cover the daily transpiration was taken as the ratio of crop height to the crop height when full-cover was attained, multiplied by ETp.

5.2.2 Nitrogen sub-model

The sub-models used for fertilizer derived N and native soil N were structurally identical, but used different coefficients for some of the processes involved. Irreversible first-order kinetics were assumed for urea hydrolysis to ammonium (obviously zero for native N) and the nitrification of ammonium to nitrate, as found by Wagenet et al (1977). For urea,

$$dN_u/dt = -k_u N_u \qquad (5.1)$$

where N_u is the amount of urea in unit soil area (kgN/ha) over rooting depth (Z), and k_u a rate constant (d^{-1}). Using daily time steps the finite-difference form of equation (5.1) is not sufficiently accurate, due to the relatively fast urea hydrolysis rate. Integration and rearrangement of equation (5.1) gives

$$(\Delta N_u)_H = -(\Delta N_a)_H = N_u\,[\exp(-k_u) - 1] \qquad (5.2)$$

Here N_a is the amount of ammonium N in the unit soil area (kgN/ha) over rooting depth (Z), the symbol Δ indicates the daily gain (or loss) of a certain N form from one day to the next due to a particular process, and the subscript H indicates hydrolysis is, in this case, the process involved.

For nitrification

$$dN_a/dt = -k_n N_a \qquad (5.3)$$

where k_n is a rate constant (d^{-1}). Nitrification is a slower process than hydrolysis, so equation (3) can be approximated by

$$(\Delta N_a)_I = -(\Delta N_n)_I = -k_n N_a \qquad (5.4)$$

where N_n is the amount of nitrate N and the subscript I indicates nitrification is the process involved.

For fertilizer derived N, reversible first-order kinetics were assumed for immobilisation -mineralisation reactions between ammonium and organic N forms, as data from the microplot experiment (chapter 4) showed early net immobilisation and later net mineralisation. Thus, in finite-difference form,

$$(\Delta N_a)_{im} = -(\Delta N_o)_{im} = k_m N_o - k_i N_a \qquad (5.5)$$

where N_o is the amount of organic N in soil, k_i and k_m are rate constants for immobilisation and mineralisation respectively, and the subscript im denotes immobilisation and mineralisation are the processes involved. A short inactive period immediately after application (when $k_n = k_i = k_m = 0$) was assumed before immobilisation and nitrification commenced, to allow the appropriate bacteria populations to build up (Sabey et al 1959).

For native soil N, net mineralisation was assumed to follow first-order rate reaction (Greenland 1971). In finite- difference form,

$$(\Delta \underline{N}_a)_m = -(\Delta \underline{N}_o)_m = -\underline{k}_m \underline{N}_o \qquad (5.6)$$

where $\underline{N}_a$ and $\underline{N}_o$ are the amounts of ammonium and organic N forms of native soil N origin respectively and k_m (d^{-1}) is a rate constant.

Immobilisation of nitrate was assumed negligible, as soil microorganism prefer ammonium as a N source (Alexander 1977).

Only urea and nitrate N were considered prone to leaching (section 2A.2.5). Other leaching studies (Scotter and Kanchanasut 1981; Kanchanasut and Scotter 1982) on the

same mole-tile drain soil as used in the lysimeter experiment (chapter 4) showed that the classical miscible displacement theory (Gardner 1965; Biggar and Nielsen 1967) was not applicable, due to preferential flow. A simple leaching relationship assumed is,

$$dN_x/\,dt = -k_L\, N_x\, q/\,\theta Z \qquad (5.7)$$

where the subscript x indicates the ion or molecule involved, q is the drainage flux density ($m\ d^{-1}$), θ is the volumetric water content when drainage has just ceased, and k_L is a dimensionless constant. If the soil solution behaved as a well-mixed system, k_L would equal one. As only daily q values are given by the water sub-model, and on certain days a lot of drainage and leaching can occur, the simple finite-difference form of equation (5.7) is not suitable for the model. Integration and rearrangement gives

$$(\Delta N_x)_L = N_x\,[\exp(-k_L\, q/\,\theta Z) - 1] \qquad (5.8)$$

where subscript L indicates leaching is the process involved. The daily leaching losses of fertilizer and native N (ΔN_L, kgN/ha) is found as

$$\Delta N_L = (\Delta N_u)_L + (\Delta N_n)_L \qquad (5.9)$$

Ammonium and nitrate were assumed to be equally available for plant uptake (Selim and Iskander 1981). N uptake was considered proportional to transpiration and to $(N_a + N_n)$. Thus

$$(\Delta N_x)_P = -k_P\, T\, N_x \qquad (5.10)$$

where k_P is a rate constant (m^{-1}) and the subscript x indicates nitrate or ammonium involved. The daily plant uptake of fertilizer or native N (ΔN_P, kgN/ha) is found as

$$\Delta N_P = (\Delta N_a)_P + (\Delta N_n)_P \qquad (5.11)$$

Equations (5.10) and (5.11) model plant N uptake in a very simplistic manner. This approach is justified as the aim of the model is to use the results of a particular experiment to predict what would happen under somewhat different climatic conditions at a different site or in a different year, not to model N uptake a priori. In the model, climate affects uptake directly through T, and indirectly through the effect of leaching of N_n.

The order in which the various processes were accounted for each day was first hydrolysis, then nitrification, immobilisation -mineralisation, leaching, and lastly plant uptake. Volatilisation and denitrification of fertilizer N were only crudely accounted for, by assuming a relatively small fraction of the applied fertilizer N was lost from the system after application.

5.3 MODEL PARAMETERISATION

The only parameter needed for the soil water sub-model is the evaporation occurring from moist bare soil before the surface becomes dry. For the silt loam soil used, a value of 10 mm was chosen following Kanemasu et al (1978). The time when the barley crop attained full-cover was visually, and somewhat subjectively, assessed as 35 days after sowing and fertilizer application, the last day of the experimental study. The crop was then approximately 250 mm high.

A problem arose in applying the water balance sub-model to the lysimeter data from chapter 4. The lysimeter were small (200 x 200 mm square surface area) with a gap of 20 mm between the metal lysimeter casing and liner. This meant that radiation and sensible heat exchange occurred over a

larger area than actual lysimeter soil surface, enhancing evapotranspiration from them, relative to that from the microplots and the rest of the crop (Tanner 1967). To account for this, the effective area for evapotranspiration of the lysimeters was taken as the soil surface plus half the area of the gap between the casing and the liner. This meant ETp estimates for the lysimeters, on a per unit soil area basis, were enhanced by 22% compared with ETp values for the microplots. There was close agreement between the modelled drainage from both the normal and the wet lysimeters of 27 mm and 63 mm respectively and the measured values of 30 $\pm$ 6 mm and 68 $\pm$ 6 mm. The predicted soil water storage in the normal and wet lysimeters agreed also closely with the measured values as shown in Fig.5.2.

Z was taken as 200 mm, the lysimeter depth. Within the first 5 weeks probably nearly all the N uptake was from the top 200 mm of soil which was approximate depth of the topsoil. Also in loessial soils drainage from 200 mm depth to mole drains at approximately 400 mm moves preferentially through the soil (Scotter and Kanchanasut 1981), reacting very little with soil matrix. The amount of N leached below 200 mm depth is thus probably similar to the amount reaching the mole drains.

Data from chapter 4 for the microplots and normal lysimeters were used to initialise and parameterise the N sub-models, while data from the wet lysimeters were used to test them. As approximately 10% of the 100 kg/ha of urea N applied to the lysimeters was unaccounted for and assumed to be lost by volatilisation and/or denitrification, gaseous

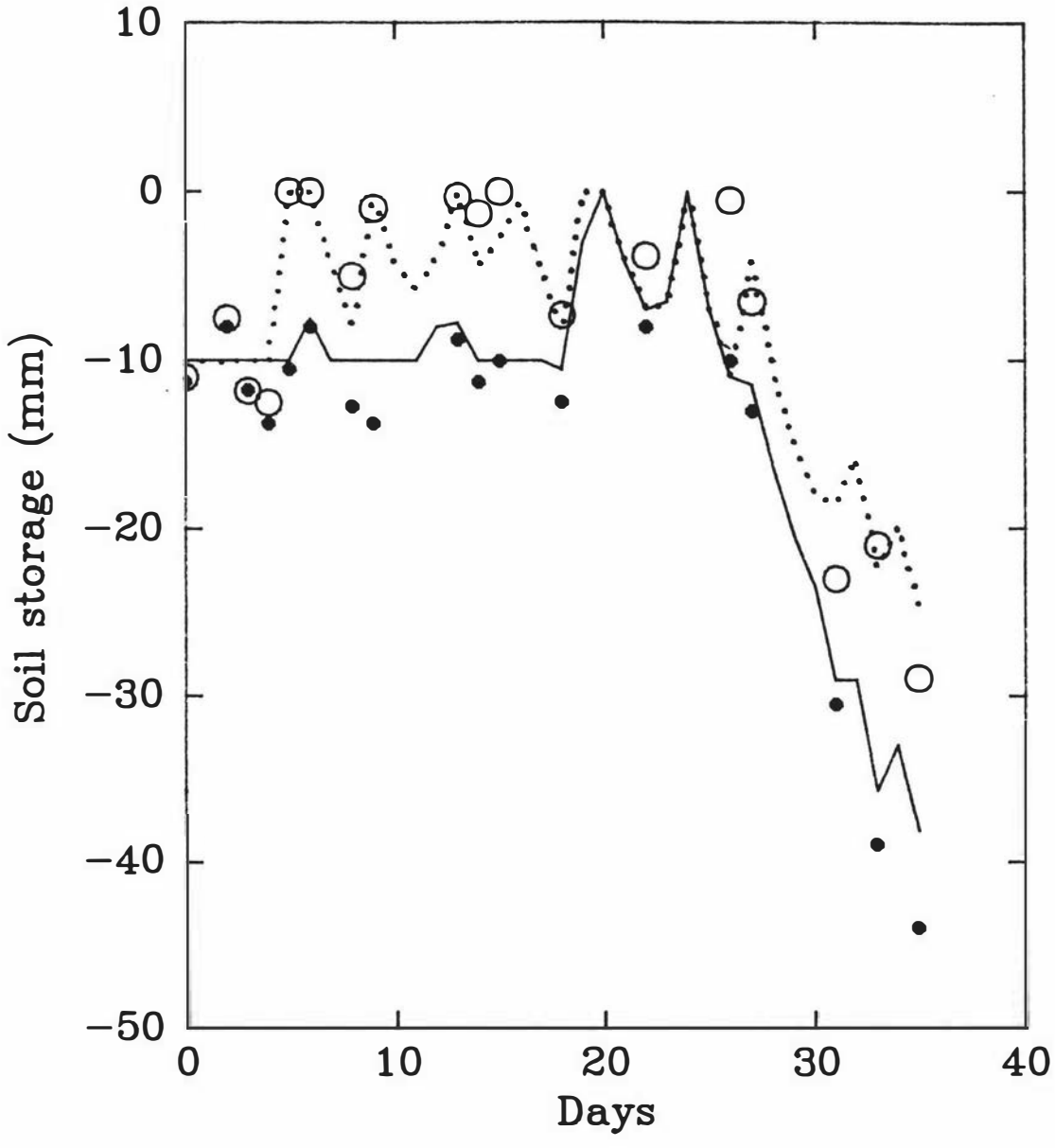

Fig. 5.2 Measured (data points) and modelled (lines) soil water storage relative to field capacity, for the normal (• and——) and wet (o and ·····) lysimeters as a function of time.

losses of urea N in the microplots on days 3 and 7 after application enabled k_u to be calculated as 0.28 d^{-1}. The modelled decline in N_u, and the measured values, are shown in Fig.5.3.

For nitrification, the same value for k_n was used for both fertilizer and native N. A value of 0.03 d^{-1} was obtained by assuming the rate of nitrification of native N equalled the observed rate of net mineralisation during the experiment of 1.2 kgN/ha/d, and that N_a for native N relatively constant and equal to the value of 40 kgN/ha measured on day 0. The net mineralisation rate, and the measured N_o value for native N of 6 Mg/ha in the microplots, allowed k_m for native N to be evaluated as 2 x 10-4 d^{-1}, while k_i for native N was taken as zero. For nitrification, and for immobilisation of fertilizer N, a two day inactive period was assumed to occur immediately after urea application.

Inorganic and organic fertilizer N data from the microplots (Figs. 5.3 and 5.4) were used to evaluate the rate constants for the immobilisation and mineralisation of fertilizer N. About day 26, $dN_o/dt = 0$ (Fig.5.4) so then from equation (5.5)

$$k_i/k_m = N_o/N_a \qquad (5.11)$$

Values for the separate amounts of ammonium and nitrate were not available, because the soil samples were analysed for inorganic N which included ammonium and nitrate N. Other data from the associated long-term experiment (described in chapter 7) showed native plus fertilizer N_a and N_n values to be of similar magnitude. Thus on day 26, fertilizer-derived N_a and N_n values were

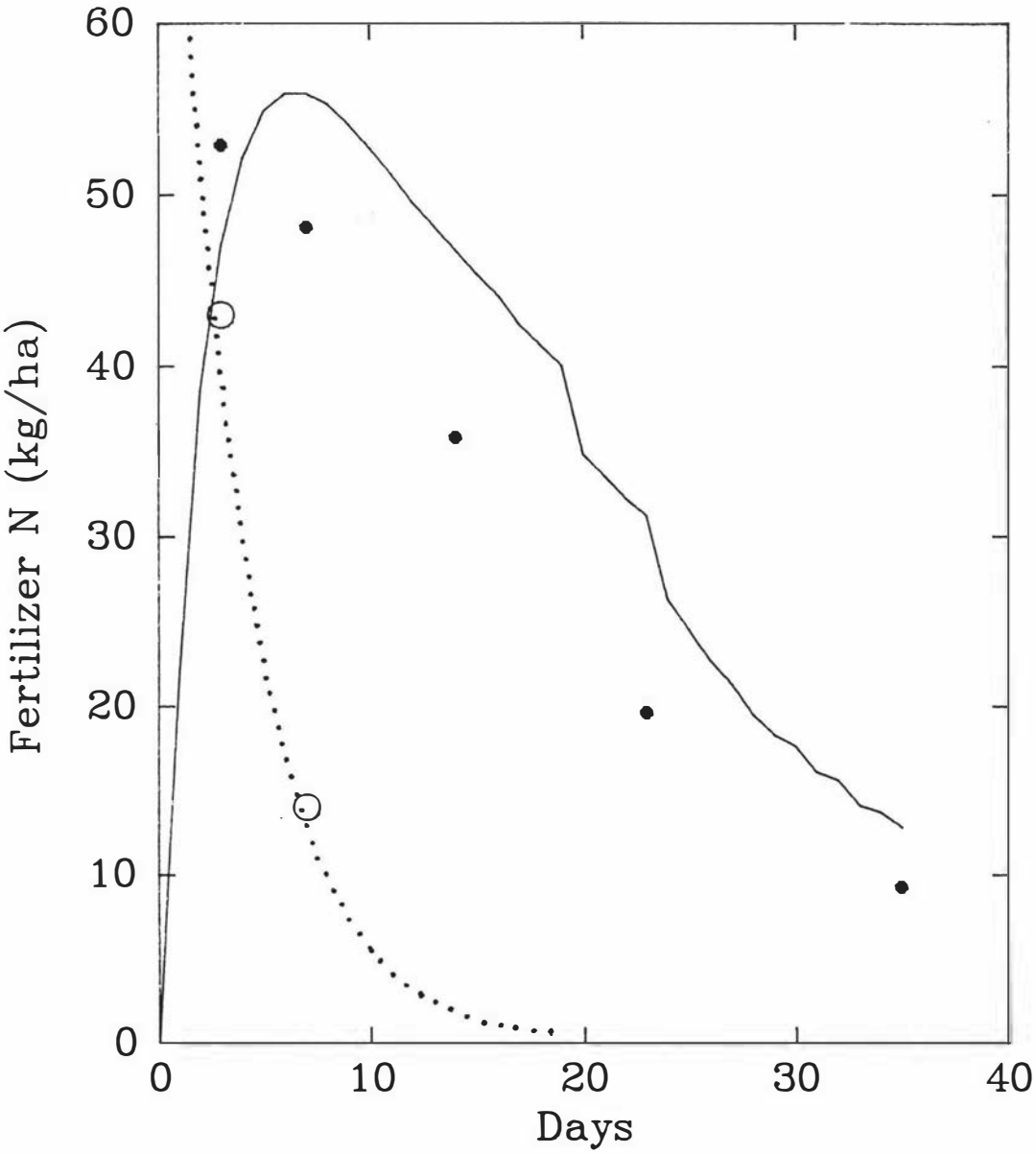

Fig. 5.3 Measured (data points) and modelled (lines) urea N (o and • • • •) and fertilizer derived inorganic N (• and ——) in microplots as a function of time after urea application.

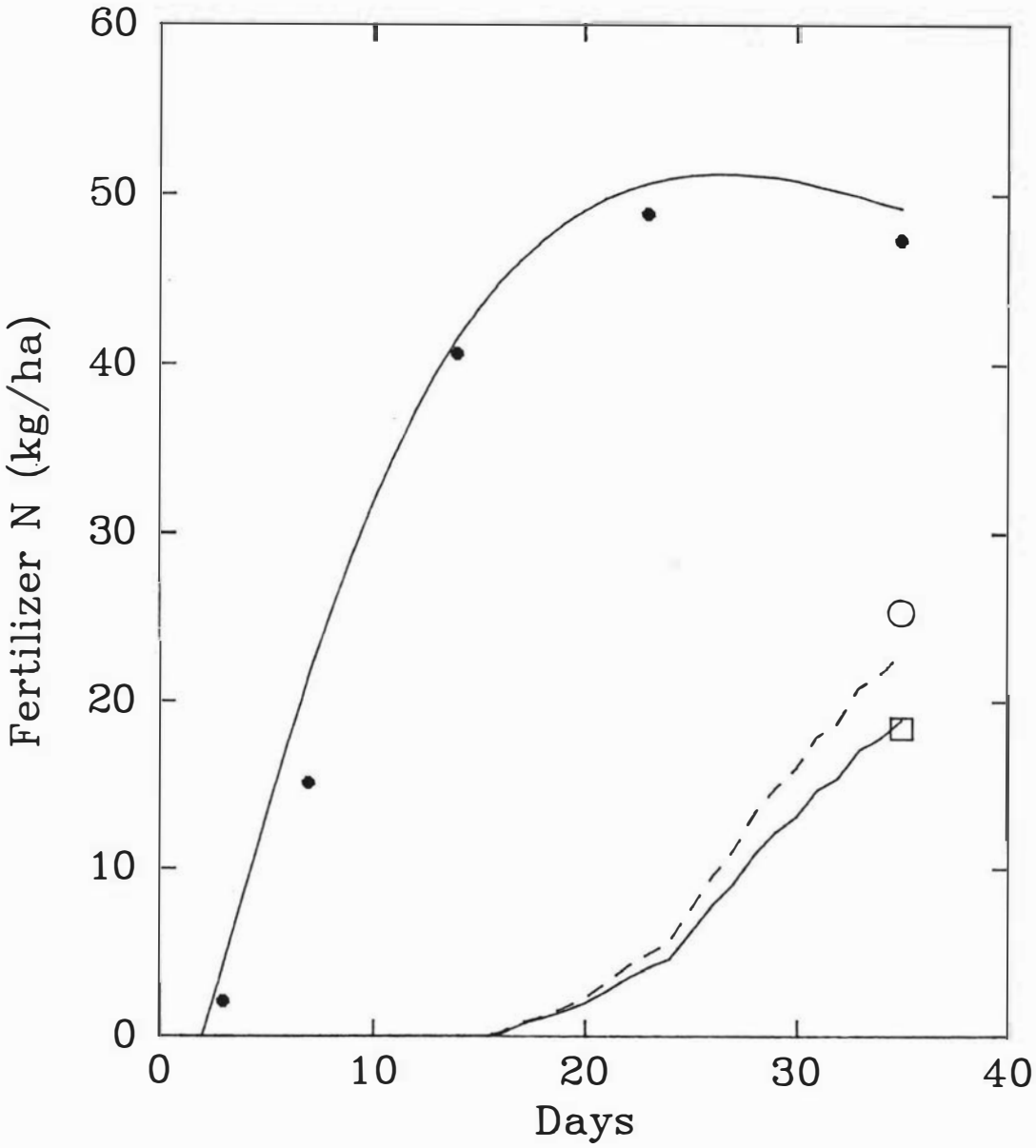

Fig. 5.4 Measured (data points) and modelled (lines) fertilizer derived organic N in microplots (• and ——) and fertilizer N in plants on normal (O and - - - -) and wet (□ and ——) lysimeters as a function of time after urea application.

assumed equal, and so a value for N_a obtained and k_i/k_m evaluated. A reasonable value for k_i (and so k_m) was then obtained by running the fertilizer N sub-model with various k_i values, and comparing predicted and measured ($N_a + N_n$) and N_o values (Figs. 5.3 and 5.4). The values obtained were 0.084 d^{-1} and 0.017 d^{-1} for k_i and k_m respectively. k_i was the only parameter in the fertilizer sub-model evaluated using optimisation, all other parameters were obtained independently.

The coefficient k_L for the leaching of fertilizer N was evaluated using the microplot bromide leaching data presented in chapter 4. Bromide and nitrate have been found to move similarly through soil (Smith and Davis 1974). Urea probably also moves in a similar way to nitrate, particularly when preferential flow occurs and anion exclusion and adsorption reactions are less important. Drainage through the microplots was calculated using the water balance sub-model. Then, taking θ as 0.45, and using measured values of N_x in equation (5.8) a k_L value of 1.4 was found. This implies that the leachate bromide concentration was higher than that of the soil solution. This apparent anamoly is explainable in terms of the preferential flow pattern occurring in the soil when it is near saturation, causing the surface-applied bromide to bypass much of the soil matrix as it moves through the soil.

From the above discussion it will be apparent that a lower k_L value would be expected to model the leaching of the more uniformly distributed native soil N than the surface-applied fertilizer N. A k_L value of 1.0 for native

N was found by optimising the native N sub-model, using the data from the normal lysimeters. This was the only parameter in the native N sub-model found this way.

To evaluate the plant uptake parameter k_p, daily measured and interpolated values of $T(N_a + N_n)$ for both fertilizer and native N in the microplots were summed over the 35 day experimental period. This sum was divided into the total N plant uptake over the period to give k_p as 0.021 mm^{-1}. This value was used for fertilizer and native N.

5.4 MODEL VALIDATION AND VERIFICATION

The data from the microplots and normal lysimeters were used to develop and parameterise the model. Thus, the measured and modelled results from the microplots and normal lysimeters have been, to some extent, forced into agreement. However, this is not so for the wet lysimeters, and as the model was developed to predict the effect of perturbations such as increased rainfall and drainage, the results for them provide a suitable test for the model.

It can be seen in Table 5.1 and Fig 5.5, that the model successfully predicted the approximate doubling of the leachate fertilizer N from the wet compared to the normal lysimeters. The reduced plant uptake of fertilizer N resulting from the increased leaching from the wet lysimeters is also quite successfully modelled. For native soil N (Table 5.1) and bromide (Fig.5.5) the increased leaching from the wet lysimeters is also modelled quite well. However measured and modelled values for native inorganic N and plant uptake of native N in the wet lysimeters are in poor agreement. Whether it is mainly the

Table 5.1 Measured and predicted amounts of N (kg/ha) in the soil, plants and drainage, 35 days after sowing and application of 100 kg N/ha as urea. Means and standard deviations are given for lysimeter data.

Treatment and N form	Fertilizer N		Native N	
	Measured	Modelled	Measured	Modelled
Microplots				
Plant N uptake	23	20	47	51
Soil organic N	47	49	5879	5462
Soil inorganic N	9	13	51	36
Normal lysimeters				
N leached	6 ± 1	7	10 ± 1	11
Plant N uptake	25 ± 2	23	42 ± 7	58
Soil organic N	45 ± 1	49	5624 ± 143	5462
Soil inorganic N	9 ± 1	11	59 ± 5	30
Wet lysimeters				
N leached	14 ± 1	11	17 ± 5	20
Plant N uptake	18 ± 2	19	18 ± 3	52
Soil organic N	49 ± 3	46	5679 ± 588	5462
Soil inorganic N	4 ± 1	9	40 ± 7	28

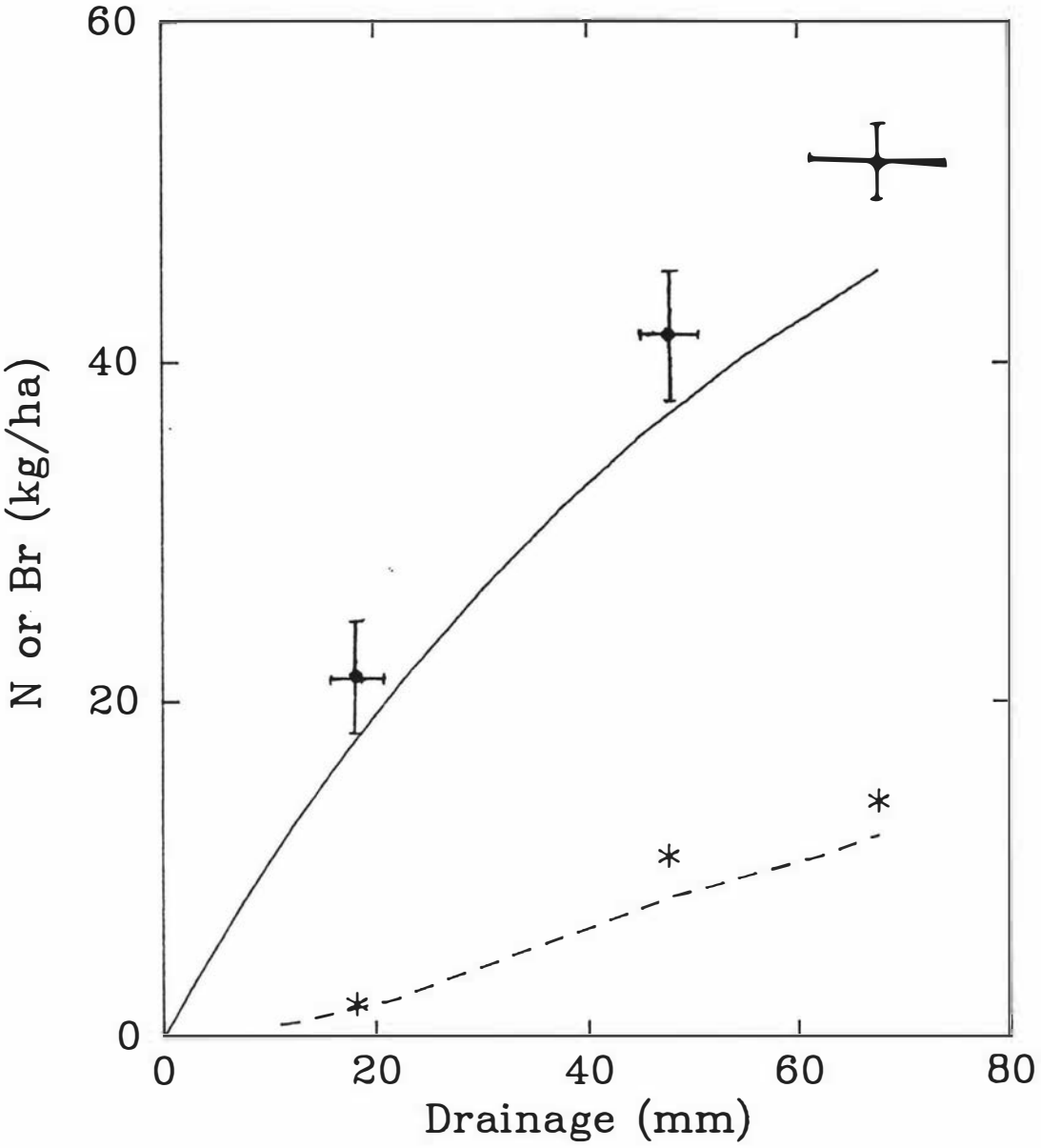

Fig. 5.5 Measured (data points) and modelled (lines) bromide (• and ——) and fertilizer derived nitrate N (* and ----) leached from wet lysimeters as a function of amount of drainage. Standard deviations are shown for the measured values.

model or the measurement that is in error in this case is not clear.

As an example of how the model may be used, the predicted effect on leaching of a very wet day is shown in Fig.5.6. Analysis of rainfall data for Palmerston North shows that over 30 mm rain on a single day can be expected approximately 4 times per year. So 30 mm was taken as representing the drainage on a very wet day, assuming the soil was near field capacity when the rain started. The predicted amount of fertilizer N leached is shown to depend very strongly on when the day occurs, relative to the fertilizer application. A very wet day immediately after urea application causes an estimated loss of 34% of the applied urea, whereas the same amount of rainfall 7 days after urea application (assuming no previous drainage) results in a loss of only 8%. Fig.5.6 also shows the predicted gradual change with time in the form of N leached from urea to nitrate.

Apart from the utility of the model in extending the applicability of fertilizer trial results, its ability to predict changes in soil N status during the first few weeks after sowing is of considerable agronomic value. Researchers have stressed the importance of adequate N nutrition in the early growth stages of the cereals (Storrier 1965; Stephen 1982). The model has the potential to alert both advisors and growers to the need for ameliorative measures (e.g. either more or less N fertilizer at early to mid-tillering) to obtain maximum economic yields, when atypical rainfall conditions occur during the early stages of growth.

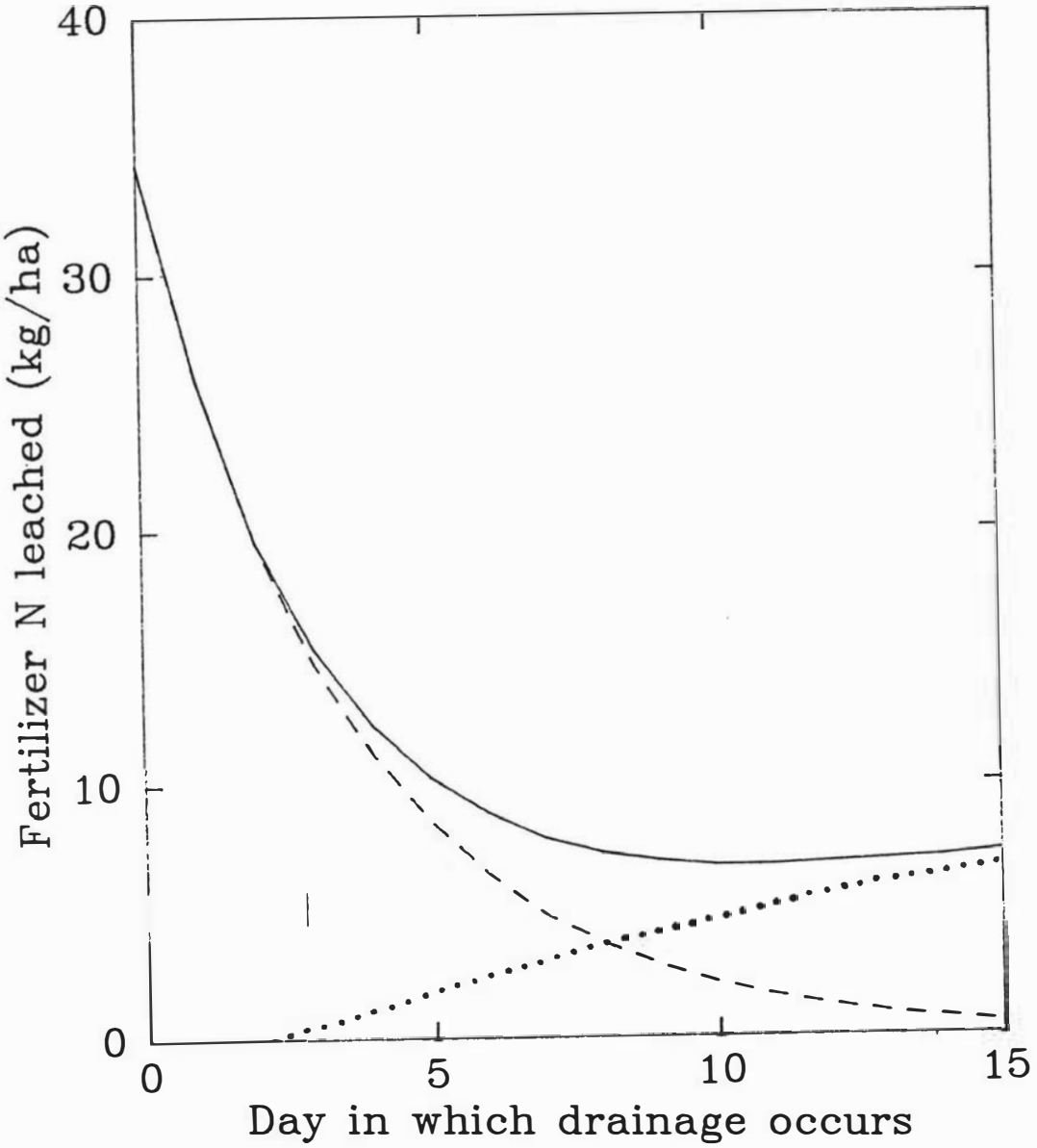

Fig. 5.6 Simulated amounts of fertilizer N leached by 30 mm of drainage, as a function of time after urea application when drainage occurs. (----) urea N, (.....) nitrate N, and (——) urea + nitrate N.

For practical models, simplicity can be more important than generality. Even complex models are not usually applicable to quite different environments, as is illustrated by considering the model of Tillotson and Wagenet (1982) pertaining to the application of urea to a cereal crop. It models in detail the movement of heat, water and solutes in soil, as well as considering more simplistically N transformations and plant uptake. But the model ignores immobilisation and mineralisation. This is apparently reasonable for the Utah maize crop considered, but clearly would be quite unrealistic for the soil at the Tiritea Research Area where nearly half of the applied N was immobilised in two weeks. Rather than existing in isolation, the model presented in this chapter provides a framework for interpreting and extrapolating a set of experimental data.

5.5 CONCLUSIONS

The model described is relatively specific, considering only the major variables in a particular soil-plant system. In other situations a somewhat different model, and certainly different values for the model parameters would be needed. In chapter 6, the model is extended to longer periods, and different moisture and temperature conditions are taken into account.

The main purpose of the model is to predict leaching and plant uptake of fertilizer N for different rainfall conditions in the 5 weeks following application. The agreement between the measured and modelled leaching and

plant uptake from the wet lysimeters suggest the model fulfills this purpose. The model indicates that the amount of fertilizer N leached is strongly dependent on the timing of rainfall in relation to the time of fertilizer application.

CHAPTER 6

MODELLING NITROGEN TRANSFORMATIONS IN A CROPPING SEASON

6.1 INTRODUCTION

In the preceding chapter, a simple N model was formulated for simulating N transformations in the first five weeks following urea application to a barley crop. The usefulness of the model would be extended if N transformations were simulated over a full growth season. Such a model would be helpful in predicting the consequential effects of early large variations in weather (particularly rainfall) on the total plant N uptake at harvest, In this chapter two objectives exist, viz.,

(i) to develop a simple crop-season model by extending the short term model formulated in chapter 5; and

(ii) to verify the crop-season model with data obtained from a large scale field trial.

6.2 MODEL PARAMETERISATION

The model presented in chapter 5 considered model coefficients as constants. These model coefficients did not take into account any effects caused by (i) environmental conditions such as changing soil temperature and moisture, and (ii) plant growth and development stage of the crop. In the present model extension, the empirical approach of Frissel and van Veen (1981) is adapted to account for environmental effects as described later in section (6.2.3). To account for the effects caused by plant growth and development stage, the total duration of plant growth from sowing to harvest, is divided into phenological periods and different values for the plant uptake coefficient are used in each period.

6.2.1 Plant uptake coefficient

The data obtained from experiment III described in Chapter 3, were used to divide the crop season into periods and to parameterise the plant uptake coefficient (k_p) for each period. The crop season was divided into periods based on the N concentration changes with time in herbage. The data for the N concentration in herbage as shown in Fig.3.1, indicate that the initial changes in N concentration were rapid, followed by gradual changes and finally the N concentrations reached a fairly constant value. The crop season was thus divided into three periods: period (1) representing the duration from seed sowing to the growth stage when the N concentration changes in herbage were rapid, period (2) when these changes were gradual, and period (3) when the N concentrations were fairly constant. The days in which periods (2) and (3) began were approximated to coincide with crop phenological events.

The data in Fig.3.1 indirectly show that nearly 77% of the total (final) plant N uptake occurred in the first five weeks following seed sowing and fertilizer application, and also this is the period when the N concentration changes in herbage were most rapid. By the end of week (5), the crop in the main plot (where the soil cylinders were located) had just attained "full-cover" over the soil. The plants in the soil cylinders and also in the main plot, were visually observed to be at "stem elongation stage". This five week duration was considered as period (1).

From the data in Fig.3.1, it was assessed, to some extent subjectively, that the crop attained a fairly constant N concentration in herbage, at about day 44, when the crop was phenologically at the end of "tillering stage". The duration between stem elongation and end of tillering was considered as period (2).

The soil cylinder experiment was terminated at 12 weeks and the crop at this time was at the "grain ripening stage". It was assumed in the model that the barley crop would stop taking up N once it reached the grain ripening stage, since the plant N uptake data from the associated long-term experiment showed for a barley crop in a previous year, that the crop uptake of N was negligible after the grain ripening stage. The duration between end of tillering and grain ripening stages was considered as period (3).

For the short-term model presented in chapter 5, the rooting depth (Z) was taken as 200 mm (lysimeter depth),and this rooting depth as a function of time and space was assumed to be invariant. In the soil cylinder experiment, visual inspection of soil cylinders collected after the first 5 weeks showed presence of most of the roots in the top soil of 300 mm depth, although the root growth in the soil cylinders collected during the first 5 weeks was mostly in the top 200 mm soil depth. For purpose of keeping the crop season model simple, a single value of 300 mm was chosen for Z and assumed to be invariant with time and depth.

The plant uptake coefficient (k_p) was evaluated for individual periods in the same manner as described in

chapter 5. Daily values of $T(N_a + N_n)$ for both fertilizer and native N in the soil cylinders were summed over each period and this sum was divided into total N taken up by plants during that period. The k_p values were evaluated as 0.028, 0.015 and 0.0039 mm^{-1} for periods (1), (2) and (3) respectively.

The k_p value of 0.021 mm^{-1}, evaluated in chapter 5 from the data for the microplot experiment, is about 25% lower than the value (0.028 mm^{-1}) evaluated for the corresponding period in this soil cylinder experiment. This difference may be attributed, in part, to the effect of climatic conditions of different years on the rate of plant growth (not accounted for in the transpiration value) and to the initial seedling damage that occurred in the microplot experiment (section 4.2).

The effect of using a higher value for k_p in period (1), on model predictions of N leaching and uptake by plants over this period, was examined by substituting the k_p value of 0.028 mm^{-1} in place of 0.021 mm^{-1} in the short-term model simulation of chapter 5 (lysimeter experiment). The results are shown in Table 6.1. The model (1) predictions in the table are from the simulation run (with k_p = 0.021 mm^{-1}) as reported in chapter 5. The model (2) predictions were made using the higher value of 0.028 mm^{-1} for k_p. With model (2), the predicted values of plant uptake of fertilizer and native soil N, over the 5 week period, were 19% and 16% respectively, higher than the corresponding values predicted with model (1). The predicted values of plant uptake of fertilizer N by both models are in good agreement with

Table 6.1 Measured and predicted data (in kgN/ha) for the lysimeter experiment. Means and standard deviations are given for the measured data. Predicted data for models (1) and (2) were obtained using k_p values of 0.021 mm^{-1} and 0.028 mm^{-1} respectively.

Treatment and N form	Fertilizer N			Native soil N		
	Measured	Modelled		Measured	Modelled	
		(1)	(2)		(1)	(2)
Normal lysimeters						
Plant N uptake	25 ± 2	23	27	42 ± 7	58	68
Leaching	6 ± 1	7	7	10 ± 1	11	11
Soil inorganic	9 ± 1	11	8	59 ± 5	30	21
Soil organic	45 ± 1	49	48	5624 ± 143	5462	5462
Wet lysimeters						
Plant N uptake	18 ± 2	19	23	18 ± 3	52	61
Leaching	14 ± 1	16	16	17 ± 5	20	20
Soil inorganic	4 ± 1	9	7	40 ± 7	28	19
Soil organic	49 ± 3	46	45	5679 ± 588	5462	5462

measured values. However, the model (2) prediction for plant uptake of native soil N remains [as with model (1)] in poor agreement with the measured values, especially when wet lysimeters are considered. The use of a higher value for k_p has not altered the prediction of leaching losses and they remain in good agreement with the measured values. Based on the above assessments, the use of higher k_p value (as evaluated from the soil cylinder experiment) in period (1) of the crop season model, is considered justifiable. An advantage of using this higher k_p value is that the k_p values for periods (2) and (3) were also evaluated in the same growing season.

6.2.2 Mineralisation of organic N:

It has long been suggested that the mineralisation rate is likely to be associated with an active pool of organic N (Crowther and Mirchandani 1931). Keeney and Bremner (1967) proposed a soil incubation test to determine the mineralisable soil organic N fraction. Using this test for the soil at the experimental site, A.N.Macgregor (personal communication) found a mineralisable soil organic N pool of about 250 kgN/ha in the top 300 mm soil layer. Assuming the observed rate of 1.2 kgN/ha/d of net mineralisation during the microplot experiment (chapter 4), originated from a mineralisable organic pool of 250 kgN/ha, a value for $\underline{k}_m$ (coefficient for effective net mineralisation of native soil N) was evaluated as 0.0048 d^{-1}.

Experimental evidence in the literature [section 2A.2.4(i)] on the mineralisation of immobilised fertilizer N suggested that a major portion (>50%) of the immobilised

fertilizer N would end up in a stable organic pool in the soil and would not be available for plant uptake during the growth season. It was assumed for this simple season model that only a small fraction (25%) of the immobilised fertilizer N was mineralised during the cropping season, and is incorporated into the model as explained in section (6.2.5).

6.2.3 Environmental effects on the model coefficients

Experimental data on the simultaneous effect of environmental factors on N transformations are lacking (section 2B.2.2) and modelling their mutual action is therefore empirical. A simple approach that was proposed by Frissel and van Veen (1981), was adopted here. Temperature (ST) and moisture content (SS) of the soil were taken into account using reduction factors. These factors, with values between 0 and 1, were found by interpolation from graphs shown in Fig. 6.1. If the reduction factors for soil temperature and moisture content were represented by STE and SSE respectively, the net effect B was obtained by multiplying the two factors.

Daily values of soil temperature in the top 300 mm soil layer were obtained from the meteorological measurements made at Grasslands Division, DSIR, about 2 km away from the trial site. The daily measured values of soil temperature and the daily values of soil water storage computed with the soil water sub-model, were averaged over a calender month. These monthly values of ST and SS were used to find values for STE and SSE from Fig. 6.1, and thus a value for B was evaluated for the calender month. A value of 0.576 for B

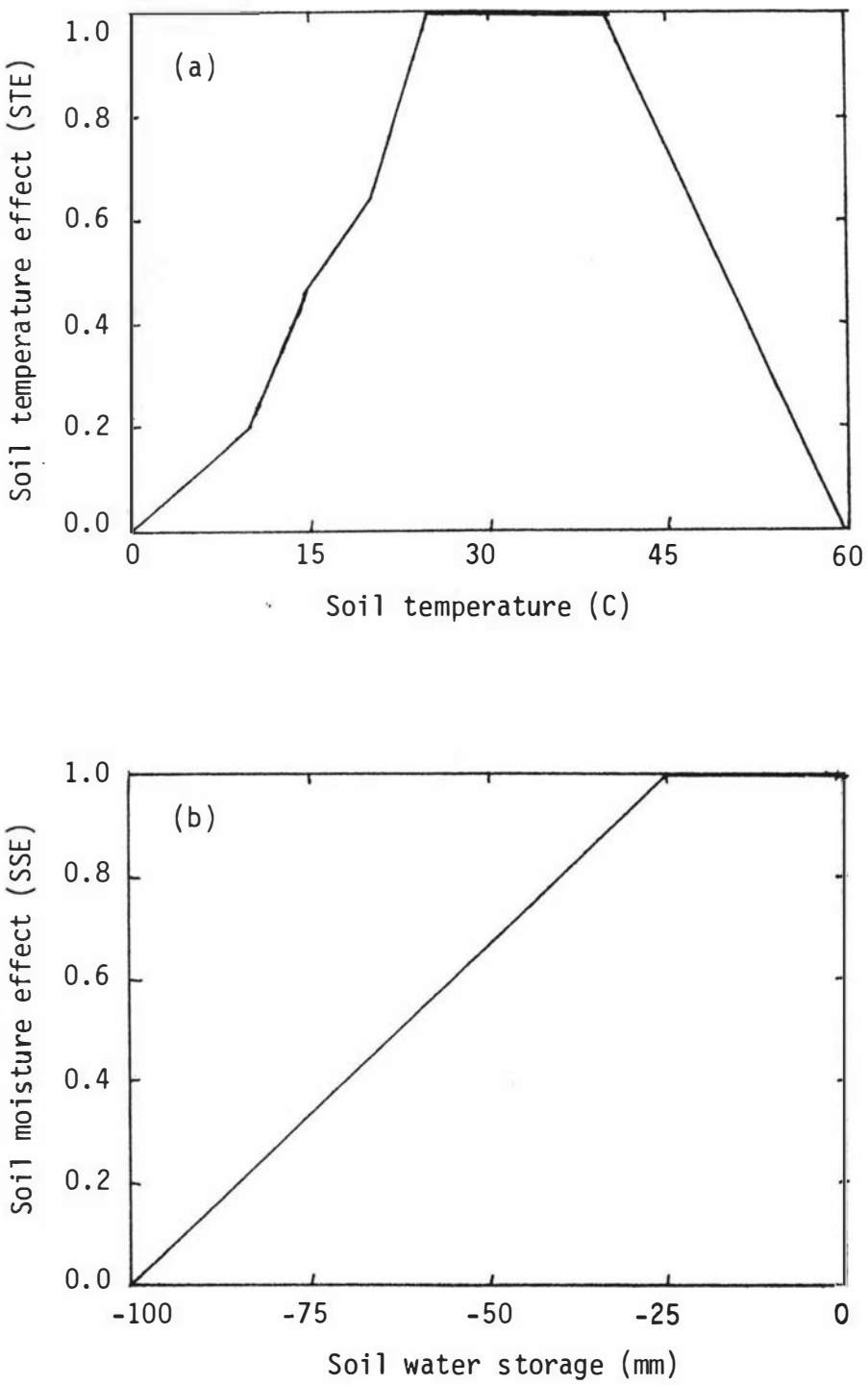

Fig. 6.1 Some typical functions for environmental effects on the decomposition rate of soil organic matter. (a) soil temperature effect; (b) soil moisture effect. From J.K.R.Gasser, (ed). 1979. Modelling Nitrogen from Farm Waste.

was obtained for the five week experimental period described in chapter 4. For a model coefficient k_x evaluated for this period, a value $(k_x)_m$ was found when B = 1, and these values are shown in Table 6.2. A value for k_x for a different time period was calculated by multiplying $(k_x)_m$ with the B value calculated for that time period. The effect of ST and SS on the plant uptake coefficient was accounted for in the transpiration value and the effect of ST and SS on urea hydrolysis was assumed to be negligible as found by Shingo Mitsui (1968).

6.2.4 Nitrogen leaching

In the crop season model, N leaching was simulated using the simple leaching relationship as stated in equation (5.7). The k_L values of 1.4 and 1.0 for the leaching of fertilizer derived N and native soil N respectively, were used as in the short-term model (chapter 5). The value of 200 mm (lysimeter depth) for Z in equation (5.7) also remained the same for leaching of fertilizer N, assuming that any fertilizer N leached below 200 mm depth would reach the mole drains and the unleached fertilizer N would tend to remain in the top 200 mm soil depth, due to preferential flow in this soil. This assumption is justified since the results of the soil cylinder experiment (Table 3.6) showed that the inorganic fertilizer N content in the 150-300 mm soil depth was minimal despite estimated leaching of about 7 kgN/ha. Also other leaching studies at the same (Tiritea Research Area) experimental site (Scotter and Kanchanasut 1981; Kanchanasut and Scotter 1982) have shown the movement of surface applied anions (bromide, chloride and phosphorus)

Table 6.2 Values of model coefficients used in model simulations of N transformations during barley cropping seasons of 1978-79 and 1979-80. Mineralisation of fertilizer N or native soil N denotes mineralisation process up to formation of ammonium. Nitrification refers to convertion of ammonium to nitrate.

		Dec 1980	Optimum values	Barley grown during 1978-79				Barley grown during 1979-80			
				Oct 1978	Nov 1978	Dec 1978	Jan 1979	Nov 1979	Dec 1979	Jan 1980	Feb 1980
Mean monthly soil temperature	ST, C	17.0	25-35	12.7	15.2	18.0	19.2	16.0	17.9	18.8	19.5
Mean monthly soil water storage	SS, mm	-13	-25 to 0	-8	-19	-94	-110	-8	-12	-42	-107
Reduction factor	B	0.576	1.0	0.348	0.481	0.050	0.000	0.523	0.624	0.519	0.000
Immobilisation of fertilizer N	k_i, d^{-1}	0.084	0.1458	0.051	0.070	0.007	0.000	0.076	0.091	0.076	0.000
Mineralisation of fertilizer N	k_m, d^{-1}	0.017	0.0295	0.010	0.014	0.001	0.000	0.015	0.018	0.015	0.000
Net mineralisation of native soil N	$\underline{k}_m$, d^{-1}	0.0048	0.0083	0.0029	0.0040	0.0004	0.0000	0.0044	0.0052	0.0043	0.0000
Nitrification	k_n, d^{-1}	0.0300	0.0521	0.0180	0.0250	0.0026	0.0000	0.0270	0.0330	0.0270	0.0000

to be highly preferential and, as a consequence, the unleached solute tended to remain in the surface 50 mm of top soil.

For the more uniformly distributed native soil N, Z was taken to be 300 mm, assuming that the inorganic N content in the 300-400 mm soil depth was a small quantity that remained fairly constant during the crop season. This assumption is justified, since the soil analysis for the inorganic N content in the 300-400 mm soil cylinder sections (Experiment III, Chapter 3) showed that the inorganic N content over this depth remained about 8-10 kgN/ha with little change over the 12 week experimental period.

6.2.5 Data inputs and simulation procedure:

The soil water sub-model described in chapter 5 was used to estimate drainage and transpiration. During period (1), separate pools and sub-models for fertilizer derived N and native soil N were used. At the end of period (1), these two pools were combined and only the sub-model for native soil N was used for periods (2) and (3). Plant uptake of N and transpiration were considered negligible once grain ripening commenced.

An initial mineralisable organic N pool was assumed to be 250 kgN/ha. At the end of period (1), when the fertilizer and soil N pools were merged, 25% of the immobilised fertilizer N amount was added to this mineralisable organic N pool.

6.3 MODEL VALIDATION

In order to check the attunement of the model assumptions and the values for the model parameters, the major N transformations occurring in the soil cylinder experiment (Experiment III, Chapter 3) were simulated with the model. The soil N sub-model was initialised with the values of soil inorganic ammonium and nitrate measured at the start of the field experiment (t=0), when soil cylinders were established. The simulated values for the amounts of inorganic N in soil from fertilizer and fertilizer plus native soil N (total N) sources are shown along with measured values in Fig.6.2. The measured and predicted values for total soil inorganic N as well as for fertilizer N are in good agreement.

The simulated values for N taken up by plants from fertilizer and soil N sources are shown in Fig.6.3, along with the measured values. The predicted values for fertilizer N taken up by plants, are in good agreement with the measured values. The predicted values for total N taken up by plants agree reasonably well with the measured values during the first 9 weeks of crop growth, but during the final 3 weeks, the measured and predicted values are in poor agreement. The measured plant N uptake appear to decline during this period, and such a decline, if real, could be due to ammonia volatilisation from senescing leaf surfaces, as discussed in section (3.3.4b). The model is not structured to account for N losses from plant canopy, because of the uncertainty of the loss mechanism and quantities involved and lack of experimental data on such losses.

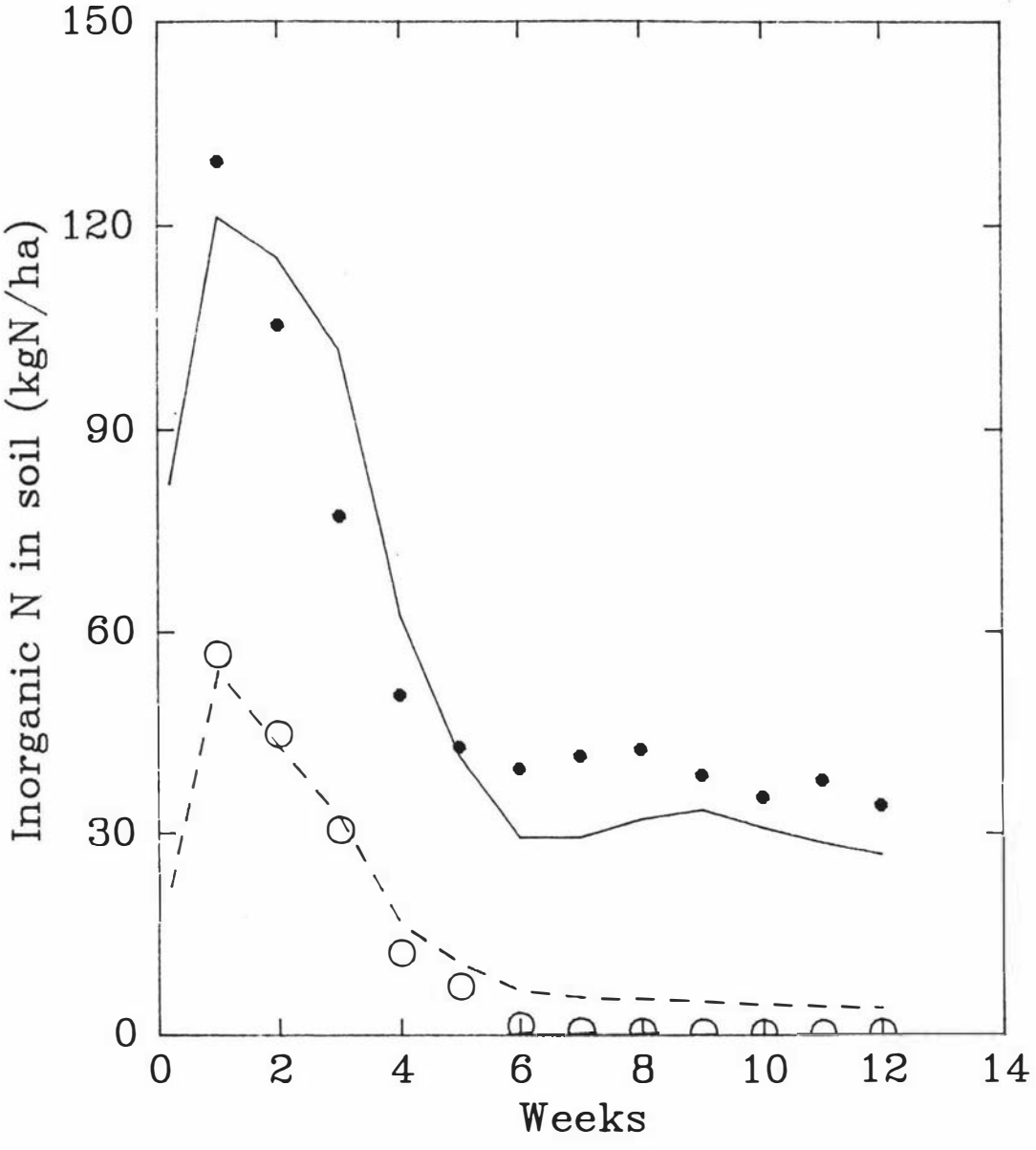

Fig. 6.2 Measured (data points) and modelled (lines) values of soil inorganic N from fertilizer (o and - - -), and fertilizer plus native soil N (• and ——) sources for the soil cylinder experiment.

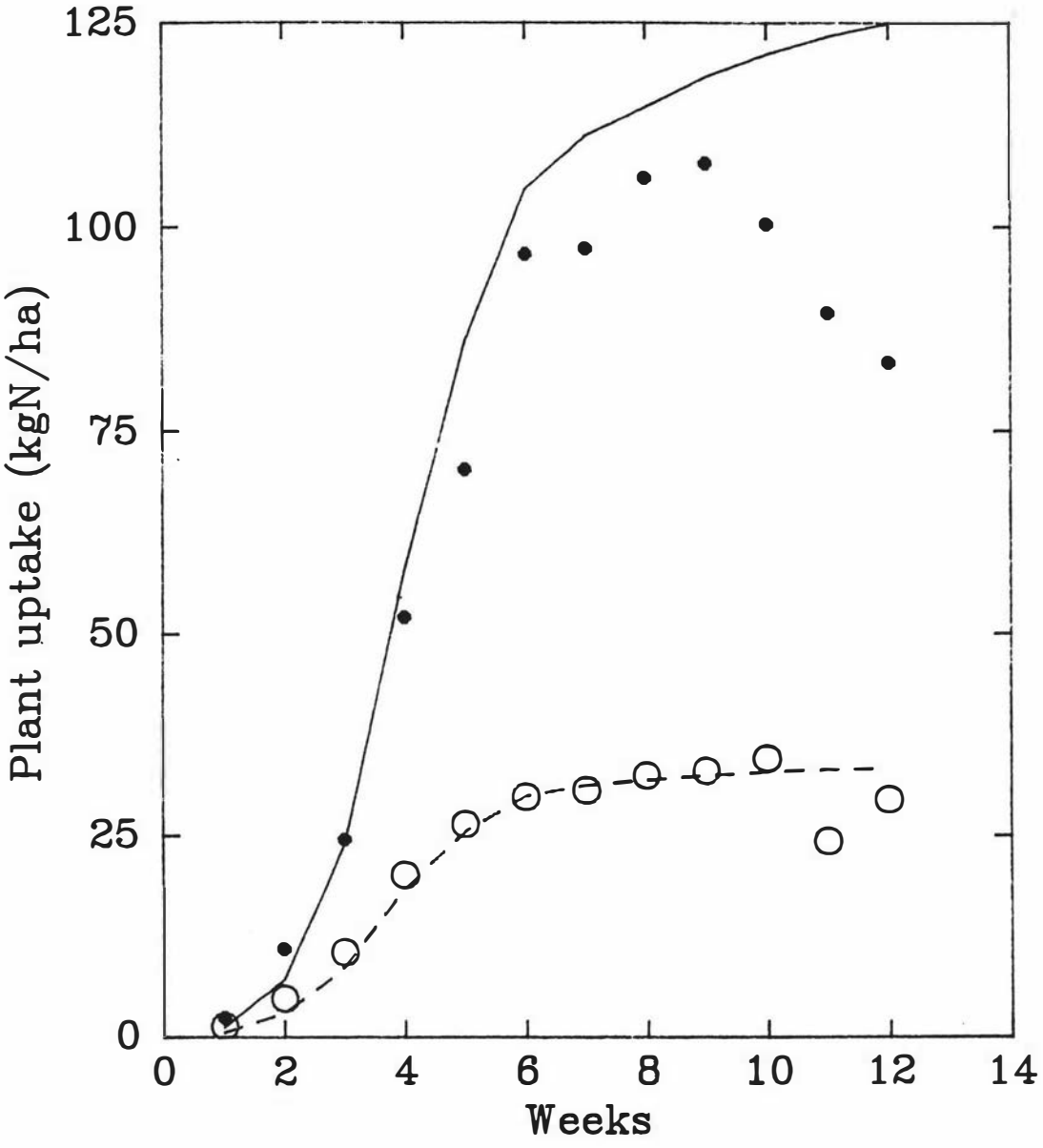

Fig. 6.3 Measured (data points) and modelled (lines) values of plant N uptake from fertilizer (o and - - -) and fertilizer plus native soil N (• and ———) sources for the soil cylinder experiment.

6.4 MODEL VERIFICATION

In order to verify the crop season model, the N transformations occurring in a large scale field trial with barley, were simulated with the crop season model. The model simulations were compared with measured data from the field trials, which were obtained independently of the data used to develop and parameterise the model.

The experimental field for the trial was located at the same site (Tiritea Research Area) where the small scale experiments using lysimeters, microplots and soil cylinders, were conducted. The field trial involved a double cropping rotation using barley and oats. Results from the 1978-79 and 1979-80 barley crops are used for the purpose of model verification. During each cropping season one field plot of 30 x 100 m size was fertilized with 100 kgN/ha and a 'control' plot of the same size had no N fertilizer application. The growing seasons were different for the two barley crops as the barley crop of 1978-79 was sown early in the season (2 October) and the barley crop of 1979-80 was sown almost two months later (22 November). Fuller details of the large scale field trial are given in chapter 7.

During each season, barley was sown on both the control and fertilized plots on the same day. In the model, it was assumed that crop canopy closure, end of tillering and beginning of grain ripening occurred on both plots on the same day. This assumption was necessary due to a lack of detailed phenological observations for crops on each plot. The calculations for the soil water sub-model were essentially the same for both plots. The N transformations occurring in the control plot were simulated with the soil N

sub-model. For the fertilized plot, the N transformations resulting from fertilizer application were simulated with the fertilizer N sub-model and added to the soil N sub-model simulation.

6.4.1 Drainage and N leaching

For the barley crop season of 1978-79, the model predicted 111 mm of drainage during two events that occurred during weeks (3) and (5) following urea application. This predicted value compared well with the measured drainage of 113 mm for the fertilized plot; but was an overestimation for the control plot as only 79 mm of drainage was measured in this plot. Visual inspection of the control plot over this period, showed water ponding over localised areas during wet periods, suggesting that some mole channels failed to conduct water into the drain, and hence surface runoff losses may have been higher than in the fertilized plot. Water ponding might have resulted from a deterioration in soil structure due to lower biomass returns in this unfertilized plot over the years since ploughed from pasture. The model prediction of 53 mm drainage during the barley season of 1979-80 could not be used for model verification as drainage was not measured for this season.

During the barley season of 1978-79, a total of 34 and 18 kgN/ha were measured in the tile drain effluent of the fertilized and control plots respectively. The model predicted these N leaching losses accurately as the predicted values were 30 and 17 kgN/ha for the respective plots. In 1979-80, the predicted values of 20 and 9 kg/ha for N leaching losses from the fertilized and control plots

respectively, although less than in 1978-79, displayed a similar proportional difference between the fertilized and control plots. The good agreement between predicted and measured values for N leaching losses indicate that the model is capable of predicting N leaching losses under field conditions with reasonable accuracy.

6.4.2 Nitrogen uptake by plants and soil inorganic N

The simulated and measured values of N taken up by barley crop of 1979-80 are shown in Fig. 6.4. The model predicts reasonably well the measured plant N uptake in the fertilized plot up to about week 11 (Fig. 6.4a). To some extent, this was expected as the soil cylinder experiment (section 3.2.1.III) from which the plant uptake coefficient (k_p) was evaluated, was also conducted (for a period of 12 weeks) during 1979-80 under the same cropping conditions and fertilizer addition, but in a small scale experiment.

In the control plot, the model overestimates plant N uptake (Fig. 6.4b). This could have resulted partly due to an invalid assumption made in the model simulation. In the model simulation, development stages for the crop on the control plot were assumed to be the same as for the crop on the fertilized plot. Such an assumption was necessary due to a lack of detailed phenological data (development stages such as stem elongation, end of tillering and grain ripening) for the crop on the control plot. This assumption is not valid, if the crop on the control plot had a slower growth rate. Over the growing season, the dry matter yields recorded at regular intervals for the N fertilized and control plots, indicated that the overall growth rate was

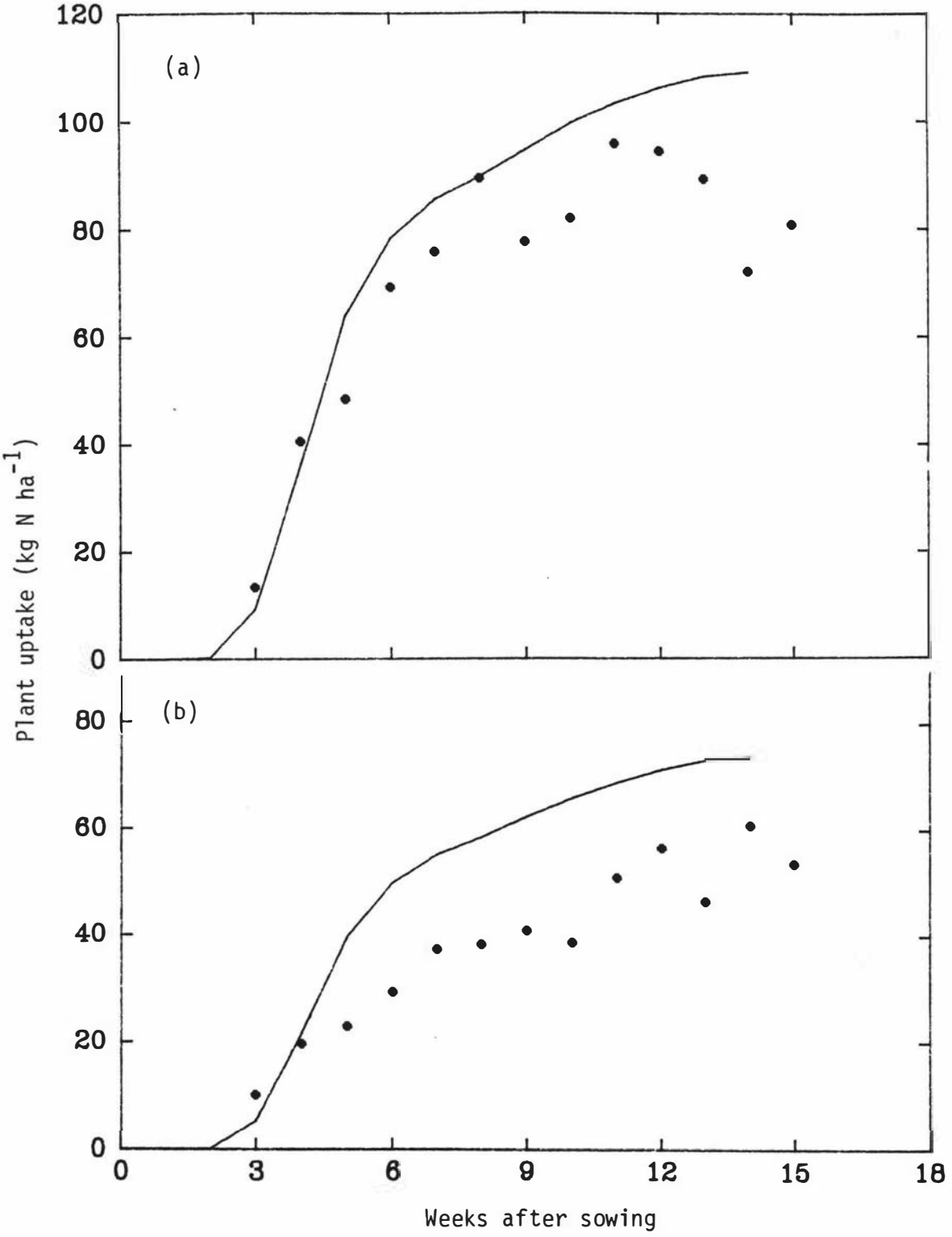

Fig. 6.4 Measured (data points) and modelled (lines) values of N taken up by barley crop of 1979-80. (a) N fertilized plot; and (b) control plot.

slower on the control plot compared with the fertilized plot. At harvest, the dry matter yields were 7600 and 4500 kg/ha respectively for the fertilized and control plots. This slower crop growth rate would cause a reduction in transpiration and consequently plant N uptake would be less. This effect of slower crop growth rate due to N deficiency, on transpiration was ignored in the model simulation by assuming the crop development stages to be the same for the fertilized and control plots.

Additionally, the model assumed that the amount of native soil N mineralised in the control plot, was the same as in the N fertilized plot, and thus any 'priming' effect due to fertilizer N addition on native soil N mineralisation was ignored. If 'priming' did occur in the fertilized plot, then the amount of native soil N mineralised in the control plot, could be less than the amount of native soil N mineralised in the fertilized plot. In the model formulation, this 'priming' effect was not included because the reality of this process is uncertain [section 2A.2.4(ii)] and thus the effect could not be predicted.

The simulated and measured values of N taken up by barley crop of 1978-79 are shown in Fig. 6.5, for (a) fertilized plot and (b) control plot. For both plots, the model predictions for plant N uptake are in very good agreement with the measured amounts at weeks (4) and (7).

At weeks (11) and (15), the model underestimates plant N uptake for both the fertilized and control plots. The plant uptake parameter (k_p), used for simulating these N uptake curves for the barley crop of 1978-79, was calibrated

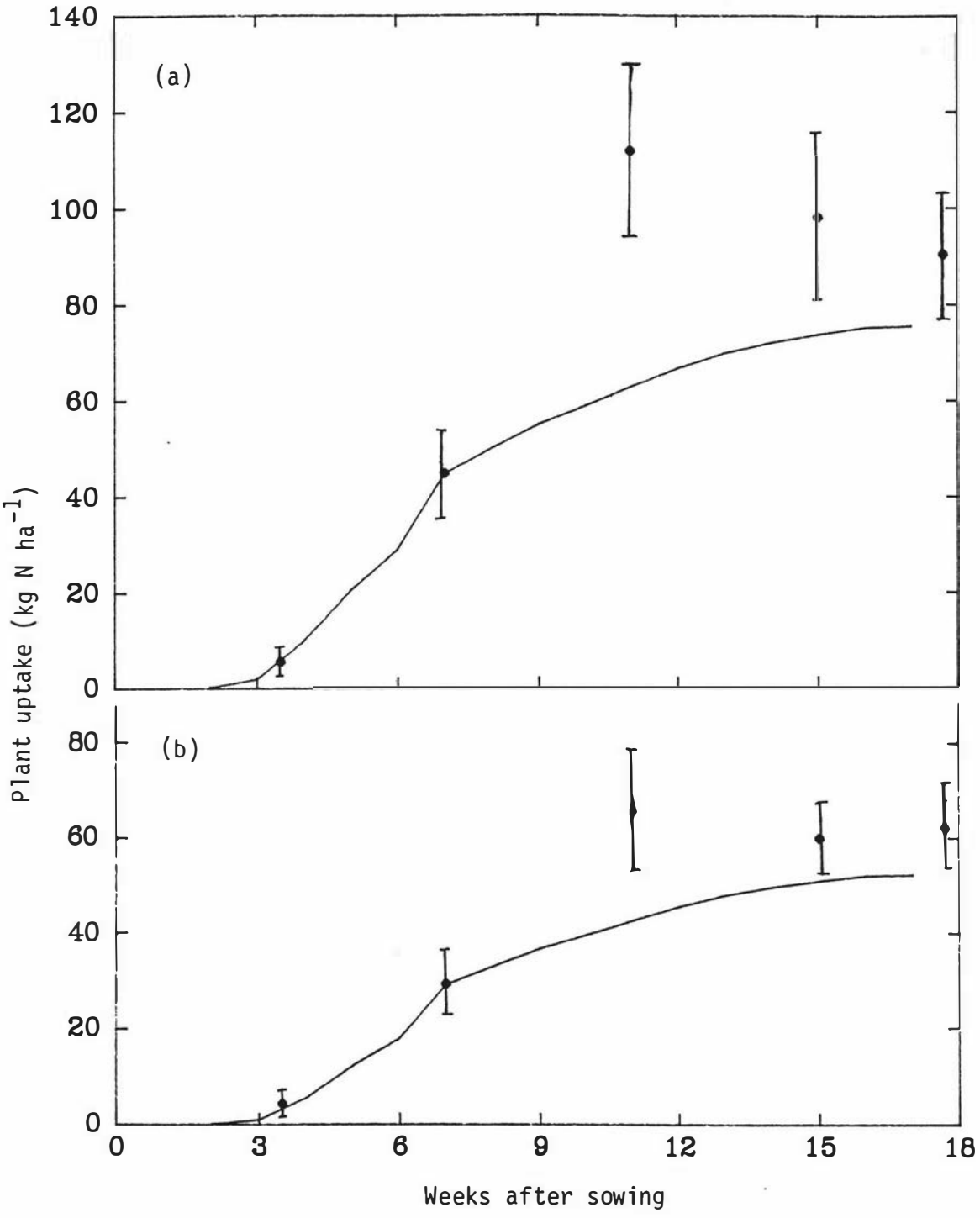

Fig. 6.5 Measured (data points) and modelled (lines) values of N taken up by barley crop of 1978-79. (a) N fertilized plot; and (b) control plot. Measured mean values are given with confidence intervals (95%).

during 1979-80 season in which the barley crop was sown 2 months later (than the barley crop of 1978-79). The overall growth rate for the 1978-79 barley crop, was much slower compared with the barley crop of 1979-80 season, as illustrated by the dry matter yields (at harvest) in the N fertilized plot during 1978-79 (7,600 kg/ha) and 1979-80 (11,000 kg/ha). The value for k_p can change depending on growth rate, as shown in section (6.2.1) by comparing the k_p values determined for the soil cylinder experiment (1979-80) and the microplot experiment (1980-81). Using the value of k_p determined in 1979-80 season for simulating crop uptake in 1978-79 season, could have partly contributed to the poor agreement in the modelled and measured values on weeks (11) and (15).

Additionally, the higher amounts of plant N uptake measured at weeks (11) and (15), could have resulted, in part, due to more rapid rate of native soil N mineralisation than predicted by the model. A 'desiccation' effect (not included in the model) caused by drying and rewetting of soil [section 2A.2.4(ii)], on the native soil N mineralisation, could have produced a flush of mineral N. The simulated data for soil water storage in Fig. 6.6, indicate that the soil was very dry (-90 mm) during week (9) and subsequent rainfall rewetted the soil and the soil water storage raised to -27 mm. This may have caused a 'desiccation' effect on the native soil N mineralisation which was not predicted by the model. The model parameters do not take this effect into account due to lack of detailed data for the changes in C:N ratios in the soil organic matter during the growth season.

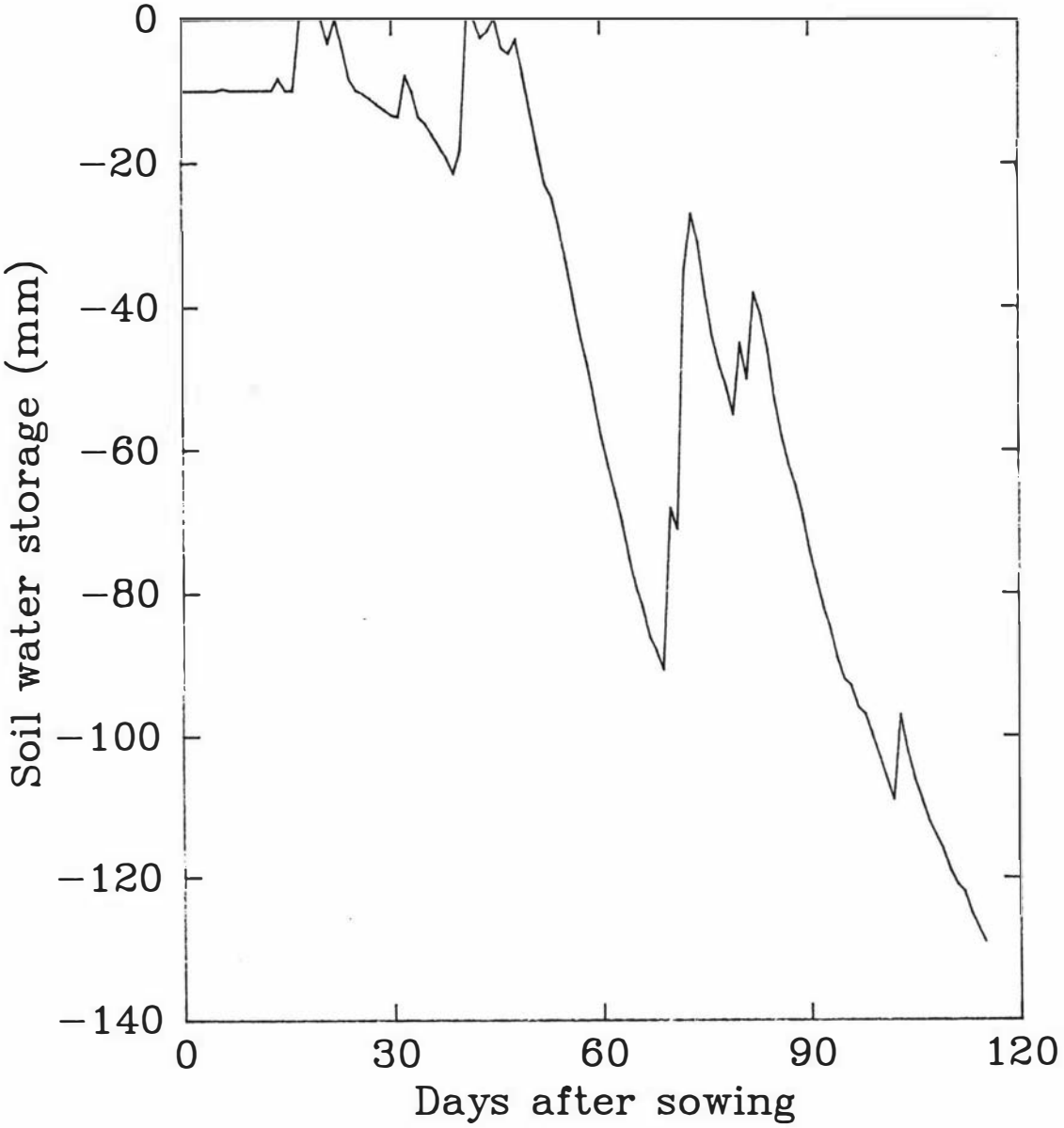

Fig. 6.6 Simulated soil water storage data for the barley crop of 1978-79. Crop was sown on 2 October 1978 and harvested on 25 January 1979.

The simulated values for inorganic ammonium and nitrate in the soils of N fertilized and control plots are shown in Fig.6.7 for the crop season of 1978-79 and in Fig.6.8 for the crop season of 1979-80, along with the corresponding measured values. There is considerable temporal variation in the measured data. In both years, the agreement between predicted and measured values, is generally not good, even after allowing for the 20% measured variance limits on the means of data for field plots, to account for spatial variabilty. As the model did not account for possible 'priming' and 'desiccation' effects on the native soil N mineralisation, the model predictions for inorganic ammonium and nitrate levels could only be considered as first approximations and therefore, a good agreement with the measured values could not be expected. However, the trends in the measured values, particularly the nitrate values, resemble the simulated values.

Overall, there is good agreement between measured and simulated values for N leaching losses and to a less extent, for N uptake by barley.

6.5 GENERAL DISCUSSION

The validity of using models developed from small scale studies, to predict N behaviour in large scale systems (of paddock size), appears not to have been evaluated for a cropping system (section 2B.1.1). The crop season model presented in this chapter was developed with data from small scale experiments. This model, in general, successfully simulated the N transformations occurring in a large scale

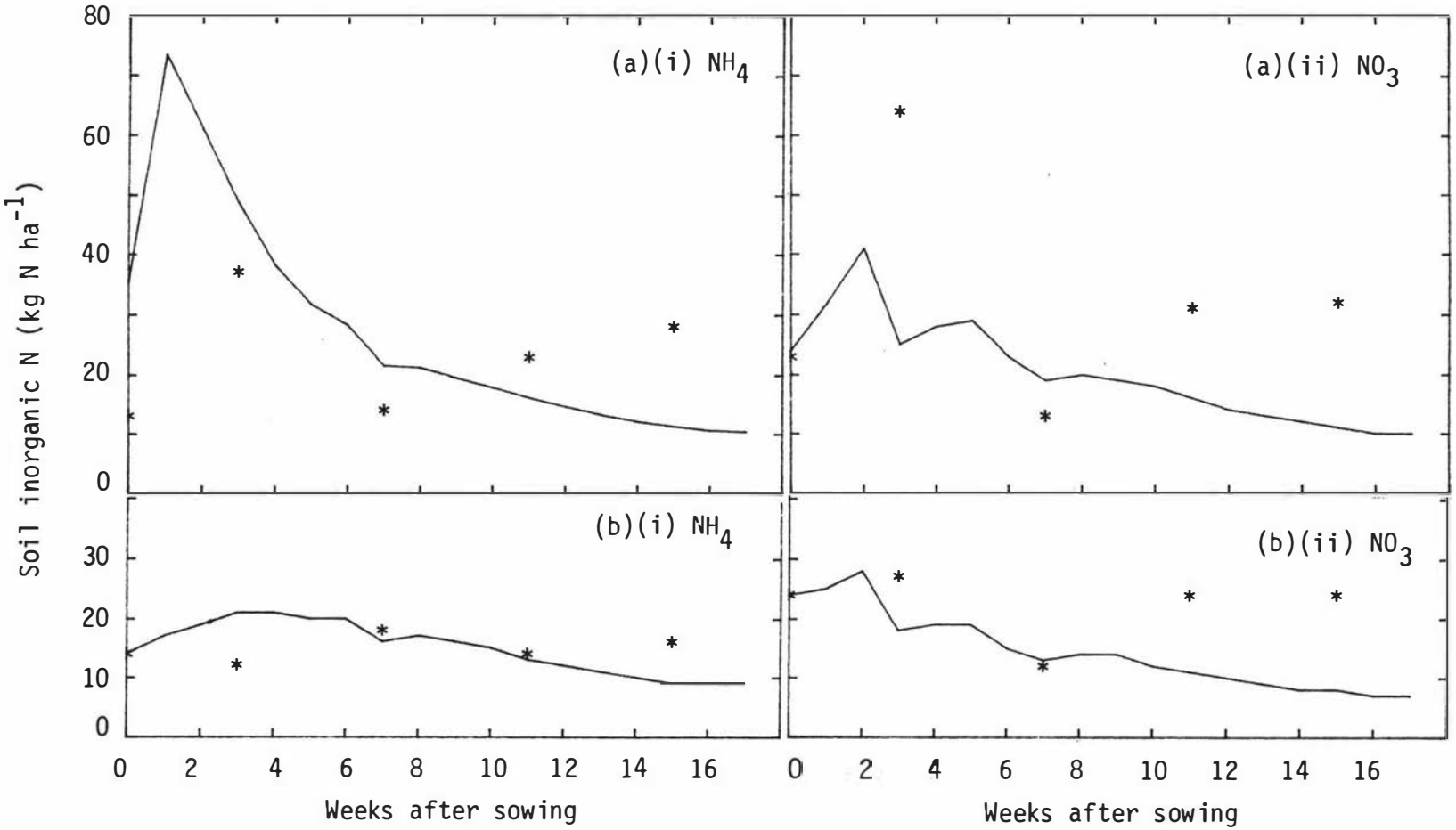

Fig. 6.7 Measured (data points) and modelled (lines) values of soil inorganic N during the barley season of 1978-79. (a) N fertilized and (b) control plots; (i) ammonium N and (ii) nitrate N.

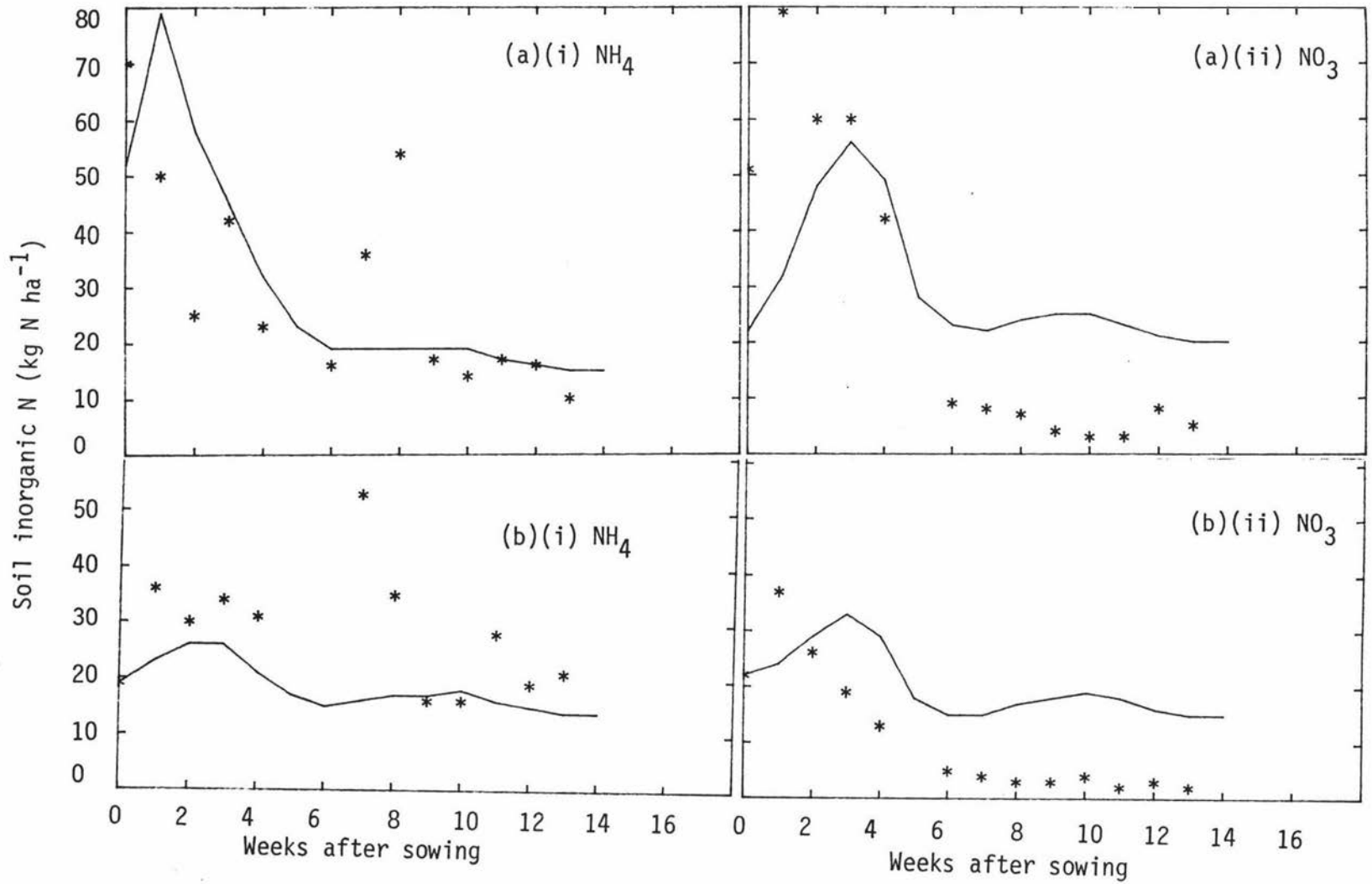

Fig. 6.8 Measured (data points) and modelled (lines) values of soil inorganic N during the barley season of 1979-80. (a) N fertilized and (b) control plots; (i) ammonium N and (ii) nitrate N.

field study, indicating that small scale experimentation and models developed from them are likely to have direct application to field situations with similar crops and soils.

Several simplifying assumptions were made in the model, including the assumption that the rooting depth as a function of time and space is invariant, following Dutt et al (1972). But, unlike the mass-balance models (e.g. Tanji et al 1979) which aggregate time and space and thus are only capable of predicting N changes over long time intervals (such as between sowing and harvest of crop), this simple crop season model has the resolution to simulate daily values for N transformations. This adds to the usefulness of the model as a management tool, for the model should be of use in making decisions on the N fertilizer requirements of crops.

Stanford (1982) described a direct approach to estimate N requirements of crops as follows:

$$N_f = (N_c - N_i - N_m)/ E \qquad (6.1)$$

In this equation, N_f denotes the amount of fertilizer N needed, N_c is the crop uptake of N associated with a specific maximum or attainable economic yield, N_i is the measured initial quantity of inorganic N in the soil, N_m is the estimated quantity of N mineralised from soil organic N pool during the cropping season and E is an efficiency factor. Recently in New Zealand, a similar kind of approach has been used for evaluating the fertilizer N requirement of maize (Steele et al 1982) and wheat (Quin et al 1982). A limitation to this approach arises when factors affecting

the availability of both fertilizer N and native soil N, depart from the perceived 'norm'. This limitation could be reduced if mechanistic models were used to take into account the above factors under New Zealand conditions. This approach would be in line with the recent developments in England, where the fertilizer requirements of vegetable crops are determined by a combination of mechanistic and empirical approaches (Greenwood 1979).

A mechanistic approach would take into account soil and environmental conditions influencing N availability to crops. For example, heavy rainfall soon after fertilizer application may affect the availability to plants, of both fertilizer N and native soil N. The model presented in this chapter, can be used to assess the possible effect of excessive rain, that falls early in the crop season, on the crop N uptake pattern. If, for example, it is assumed that 90 percentile rainfall events occurred during the first 5 weeks (November-December) of the barley crop of 1979-80 that was fertilized with urea at 100 kgN/ha, their effects on crop N uptake can be simulated with the model. Actual rainfall measured during these two months was 105 and 114 mm respectively. In order to simulate 90 percentile rainfall of 126 and 173 mm respectively for the two months, an excess of 21 and 59 mm rain over the measured rainfall for the respective months, was assumed. The excess rainfall of 21 mm for November was assumed to have occurred on day 7 (November 29) following urea application. The excess rainfall of 59 mm for December was equally divided between two events and assumed to have occurred on days 14 (December 6) and 21 (December 13) following urea application.

The simulated pattern of crop N uptake with 90 percentile rainfall is shown in Fig. 6.9, along with the simulation with actual rainfall. At the end of week 5, the crop that received 90 percentile rainfall, took up 20% less N than the crop receiving actual rainfall. At harvest, the crop receiving 90 percentile rainfall had taken up 15% less N than the crop receiving actual rainfall. The model thus can provide a continuous evaluation of possible adverse effects caused by unforeseable factors such as excessive rainfall, on plant N uptake.

Adverse effects on plant N uptake can cause suppression of crop yield, since a positive relationship exists between plant N uptake and crop yields, as demonstrated in several studies that are well summarised by Olson and Kurtz (1982). If a reduction in plant N uptake can be predicted, steps such as top dressing with additional N fertilizer, could then be taken by growers or advisers to rectify any trend in plant N uptake which departs from that planned to obtain maximum economic yield. This approach would require a good knowledge of optimal N requirements in crop throughout its growth season, particularly in the early stages of its growth.

The crop season model was developed with the soil and plant data, obtained from plots fertilized with 100 kgN/ha. If lower application rates (<100 kgN/ha) are to be considered for this site, the current model will provide output (in terms of fertilizer N leached in drainage water, and taken up by plants), in proportion to the output

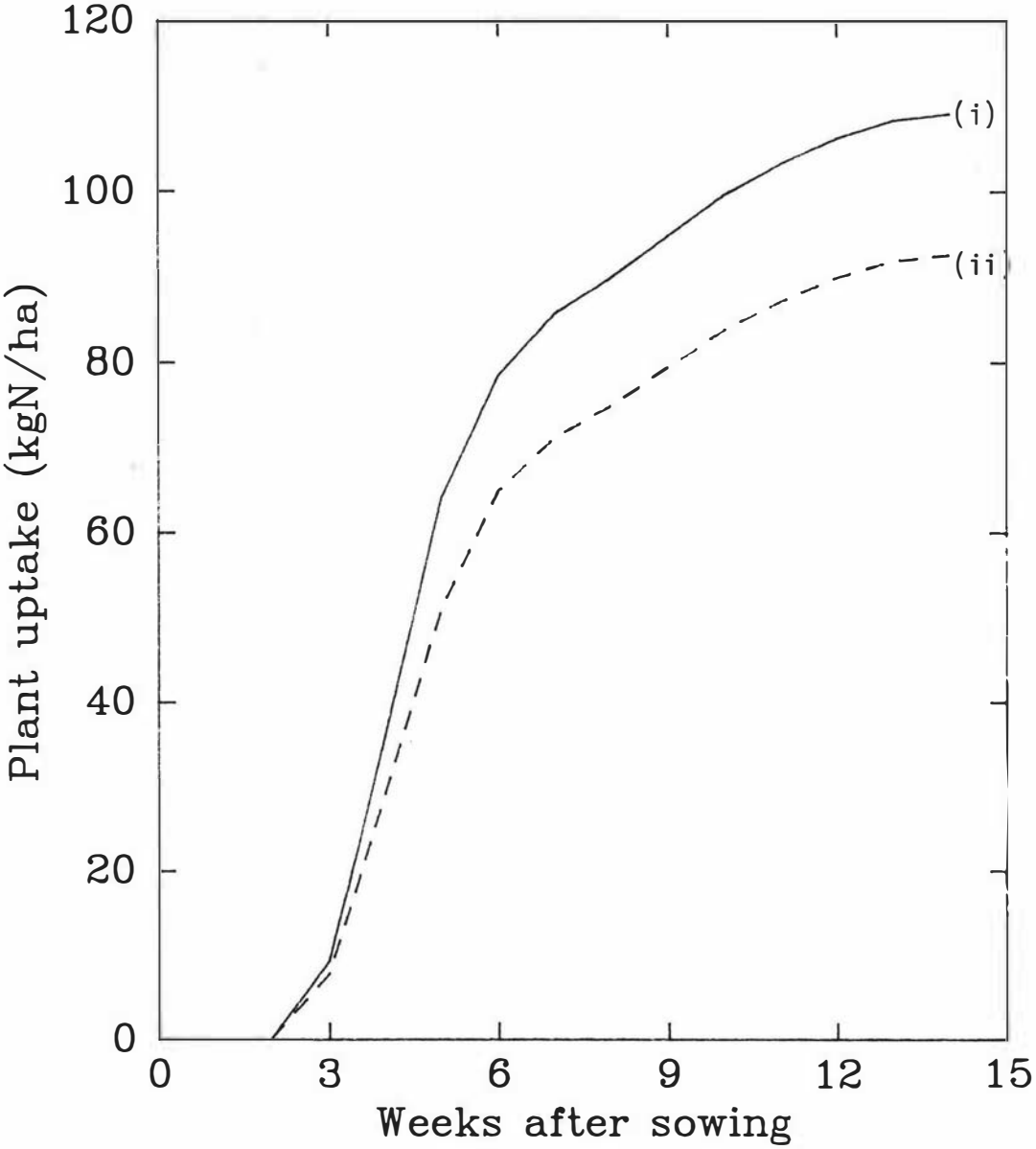

Fig. 6.9 Simulated values for N taken up by barley crop of 1979-80, in the N fertilized plot; (i) simulations with actual rainfall (———), and (ii) simulations with 90 percentile rainfall (- - -).

obtained with 100 kgN/ha application rate. Verification of these predicted values with measured data will be necessary. Where differences between the modelled and the measured values are observed, recalibration (with N-15 experiments) of some model parameters (such as immobilisation - mineralisation coefficients) will be required.

The crop season model predicted N leaching losses with better accuracy than plant N uptake. To improve the accuracy of model prediction on plant N uptake, some refinements are required on this component of the model. Since a major portion of total plant N uptake originates from native soil N (section 3.3.4c), it is necessary to predict more accurately the amounts of native soil N mineralised daily.

At present, soil temperature and moisture are the only environmental factors that were considered in the model to affect net mineralisation. Although the dominant factors usually are soil temperature and moisture, other conditions associated with soil properties, e.g., cultivation, other essential nutrients, liming and soil pH are also influential (Campbell 1978) and could therefore be taken into account in the model simulation, if their effects are known.

Morever, the model only crudely takes into account the effect of soil temperature and moisture, by taking monthly averages of soil temperature and moisture (section 6.2.3). This is an oversimplification and further refinement to the model should possibly consider soil temperature-moisture effect on net mineralisation on a daily basis. Soil temperatures can either be given as an input data to the

model or alternatively a soil temperature sub-model can be added to the model structure in order to simulate the daily soil temperatures, as done in some models (e.g. Watts and Hanks 1978; Tillotson and Wagenet 1982).

Like most models, the model presented in this chapter has a degree of site-specificity. Although it is developed for a site-specific situation (i.e., for tile-drained fragiaqualf), it could be adapted to other situations where different crops are grown on different soils with different N fertilizers at different rates of application. The model would need to be reparameterised with data from process-oriented experiments, and depending on how different the situation is, the mathematical structure (e.g., calculation of correction factors for different soil temperature and soil moisture conditions) may also need modification.

Provided a set of field data on N leaching and plant N uptake are available for use to verify the model output, the model, as it is, could be used to predict this output. Where differences result, research can be directed at reparameterising the model to obtain better model predictions. Such research efforts would lead to a few process-oriented experiments, and the results from them could be extended to a wider range of 'soil-crop-climate' situations. The model thus has the potential to be used in soil fertility studies where N fertilizer requirements of crops are being determined.

6.6 CONCLUSIONS

The crop season model presented in this chapter was formulated and parameterised with data from small scale experiments. This model, in general, successfully simulated the N transformations occurring in a large scale field study in which fertilizer N was added, indicating that small scale experimentation and models developed from them are likely to have direct application to field situations with similar crops and soils.

The usefulness of the model as a management tool is illustrated by using the model to predict the adverse effect of excessive rain, that falls early in the crop season, on the crop N uptake pattern. The model is capable of providing a continuous evaluation of possible adverse effects caused by unforeseable factors such as excessive rainfall, on plant N uptake.

The model prediction for N leaching losses has demonstrated better accuracy than for plant N uptake. To improve the accuracy of model prediction on plant N uptake, some refinements are required on the plant N uptake component of the model. For making such refinements, more soil and plant information would be required.

Also the model, like most other models, has a degree of site-specificity. However, with modifications, it could be adapted to other situations where different crops are grown on different soils with different N fertilizers at different rates of application.

CHAPTER 7

LONG-TERM SIMULATION OF N TRANSFORMATIONS IN A SUMMER BARLEY-WINTER OATS ROTATION

7.1 INTRODUCTION

Drainage waters from agricultural land flow into bodies of surface water or seep into ground water basins. Such drainage waters carry N loads, since removal of nitrates from soil by drainage is inevitable in agricultural practice, regardless of fertilizer use (Cooke 1976). The effects of this N load, in agricultural drainage, on the N content of natural waters causes concern as N has potential environmental and health impacts (Keeney 1982). The concentration of nitrate in potable water at times may exceed the recommended level (10 mg N/litre) set by the World Health Organisation on the basis of nitrate causing 'methaemoglobinaemia' in young babies. A 'point source' for such nitrate pollution of surface waters could be the tile drained farm lands as reported in several overseas studies (e.g. Baker et al 1975; Hood 1976; Miller 1979). Predicting nitrate concentration in tile drain effluent is, therefore, a desirable objective, for pollution control studies.

The New Zealand data on N losses from pasture watersheds (Turner et al 1977; Sharpley and Syers 1981) indicate that nitrate concentrations in tile drainage only occasionally exceed 10 mg N/litre; although higher nitrate levels (>25 mg N/litre) in ground waters have been reported (Baber and Wilson 1972). These latter workers considered the high nitrate levels in ground waters, to be due to deep

percolation of drainage water from an intensively grazed pasture on porous pumice soil. There appears to be no published information available on the effects of cropping on nitrate levels in either tile drainage or in ground waters.

The soil inorganic N levels are usually high following the ploughing of pastures, due to rapid initial mineralisation of soil organic matter [section 2A.2.4(ii)]. If a greater area of pasture land is tile drained and cultivated for crops, higher nitrate losses in tile discharge would seem inevitable.

Recent trends in New Zealand farming indicate that a greater area of pasture land is likely to be ploughed for growing forage crops (Taylor and Hughes 1978; Stephen 1982). Additionally, with longer cropping rotation, increased N fertilizer use could be expected because response to N fertilizer develops within a few years of successive cropping following pasture. The potential for increased N fertilizer use also exists with the establishment of ammonia-urea plant in Taranaki (Menzies 1980). With such trends in New Zealand farming, a N model developed for New Zealand conditions, should be capable of evaluating the extent to which tile drained crop land could become a point source for nitrate pollution, when fertilizer N is used to achieve high levels of crop production.

The objective for this chapter is to further develop the model outlined in the preceding chapters 5 and 6, in order to predict, over a two year period, the N leaching losses in tile discharge from a recently ploughed pasture

subjected to a double cropping rotation to which fertilizer N is added. Such a model may help in determining the best farm management practices which may minimise pollution.

7.2 NITROGEN SIMULATION IN A LARGE SCALE FIELD TRIAL

7.2.1 Large scale field trial

At the Tiritea Research Area (DSIR), adjacent to the Massey University campus, a long-term N balance experiment investigating N cycling in cropping rotation, was initiated in 1976. The objectives and the design of this large scale field trial, are fully described by Gandar and Gregg (1979). The field trial comprised five N treatments, that were imposed on five large plots (110 x 30 m each). Experimental data collected from two of these plots [plot (1) and (2)] between April 1978 and March 1980 are used for model verification.

7.2.1.1 Description of the experimental site

The soil at the experimental site is a Tokamaru silt loam, a moderately gleyed yellow grey earth derived from loess (Fragiaqualf). The soil under natural conditions has a perched water table during winter periods. In February 1976, a field drainage system was established comprising a tile line for each large plot and mole channels spaced at 2 m intervals and at a depth of about 400 mm. For purpose of monitoring tile discharge and N leaching, Stevens 'F' water-level recorders and calibrated automatic effluent samplers were installed for each plot at the outlet of each tile line. In April 1976, the plots were ploughed from pasture (five years old) and were immediately sown to winter oat crop. The land was subsequently cropped with a summer

maize-winter oat rotation during 1976-77. A barley crop followed during the summer crop season of 1977-78. In order to create a N responsive condition, all crops grown on plots (1) and (2) did not receive any N fertilizer, since the time the plots were ploughed from pasture.

7.2.1.2 Description of the field trial

(a) Crops grown during the experimental period

Following the summer barley crop of 1977-78, the plots were left fallow during the winter of 1978, and subsequently were continuously cropped with an annual crop rotation of summer barley-winter oats. The sowing, harvest and other phenological dates for these crops are shown in Table 7.1. Fertilizer N as urea was added to plot (1) at a rate of 100 kgN/ha prior to sowing of each barley crop, while no fertilizer N was applied to plot (2). On both plots, the winter oat crop did not receive N fertilizer.

(b) Sampling procedures

(i) Soil samples: Soil samples were collected from plots (1) and (2) at monthly intervals until March 1979 and thereafter at weekly intervals. At each sampling time, 10-15 soil cores were collected from each plot to a depth of 400 mm. Each core was divided into three sections of 0-150, 150-300 and 300-400 mm depth increments. Soil cores of the corresponding depths were pooled together and subsamples taken for N analysis.

(ii) Plant samples: For each crop grown, plant samples were collected regularly from plots (1) and (2) at intervals of approximately three weeks from sowing until harvest. At each sampling, plant samples were collected from 20 quadrats

Table 7.1 Crop phenological dates

Crop phenology	Barley	Oats	Barley
Sowing	2-10-78	3- 4-79	22-11-79
Crop emergence	8-10-78	18- 4-79	3-12-79
Full crop cover	6-11-78	1- 8-79	27-12-79
End of tillering	21-11-78	--	5- 1-80
Grain ripening	25 -1-79	--	25- 2-80
Harvest	2 -2-79	17-10-79	7- 3-80

During winter 1978, plots (1) and (2) were in fallow.

(0.2 m^2) for each plot. The quadrats were selected using random numbers from a grid layout. Dry matter yields and N content determinations were made on these samples.

(iii) Leachate samples: During each drainage event, tile flow measurements were made and "representative" samples were collected for determination of nitrate concentration. In order to justify the use of representative samples for measuring leaching losses of N, a comparison was made with the automatic sampling taken at fixed intervals during two tile flow events that were less than 15 mm discharge per day. Agreement between the two methods was satisfactory.

(c) Analytical procedures

The soil samples were extracted in 10:1 suspension of 2 M potassium chloride. The extracts were distilled with magnesium oxide to release ammonium N and distillation was continued with Devarda alloy to determine nitrate and nitrite N (Bremner and Keeney 1966). Leachate samples were filtered and distilled with Devarda alloy to determine nitrate and nitrite N (Bremner and Keeney 1966). Total N in plant samples was determined by a salicylic acid-thiosulphate modification of the kjeldahl method (Bremner 1965a).

7.2.2 Model parameterisation and calculations

For purpose of simulating N transformations over a two year period (April 1978 to March 1980) the crop season model described in Chapter 6, needs further development since it did not take account of the long term changes in soil organic N following the ploughing of pasture.

7.2.2.1 Mineralisation of soil organic N

For calculating daily amounts of N mineralised ($\underline{N}_m$) from native soil organic N pool, the total organic N in soil ($\underline{N}_o$) was divided between a short-cycle ($\underline{N}_{o1}$) and a long-cycle ($\underline{N}_{o2}$) organic N pools. Daily $\underline{N}_m$ values were estimated as

$$\underline{N}_m = - \Delta \underline{N}_o = - \Delta \underline{N}_{o1} - \Delta \underline{N}_{o2} \qquad (7.1)$$

where Δ denoted daily change in amounts of N. The mineralisation rate of the short-cycle organic N was assumed to follow irreversible first order kinetics and that of the long-cycle organic N to approximate a zero order rate equation.

$$-d\underline{N}_{o1}/\, dt = B\, m_1\, \underline{N}_{o1} \qquad (7.2)$$

$$- \Delta \underline{N}_{o2} = B\, M_2 \qquad (7.3)$$

where B is, as in chapter 6, a reduction factor that accounts for soil temperature and moisture effects on mineralisation rate, m_1 is mineralisation rate coefficient (d^{-1}) at optimum conditions of soil temperature and moisture (B = 1) for the short-cycle organic N pool ($\underline{N}_{o1}$), and M_2 is a constant rate of mineralisation (kgN/ha/d) at optimum conditions of soil temperature and moisture from the long-cycle organic N pool ($\underline{N}_{o2}$).

Numerical values were estimated for the N pools and parameters in equations (7.2) and (7.3) using the measured data from plot (2) where no N fertilizer was added (section 7.2.1). The total amount of N mineralised ($\Sigma \underline{N}_m$) over the 2 year period (April 1978 to March 1980) from soil organic N pool ($\underline{N}_o$) was evaluated assuming an effective net mineralisation (ENM) as in chapter 4. The amount of ($\Sigma \underline{N}_m$)

over the period was considered equal to the sum of the amount taken up by plants and leached in drainage during the period, ignoring any changes in native soil inorganic N content.

Over the two year period, plant uptake by one oat and two barley crops amounted to about 190 kgN/ha and the amount of N measured in tile discharge was about 90 kgN/ha and thus a value of 280 kgN/ha for ($\Sigma \underline{N}_m$) was obtained. If calculated as an average daily value over the two year period, this average mineralisation rate would be about 0.4 kgN/ha. This mineralisation rate is near the lower range of values reported for mineralisation rates of other New Zealand cropping soils [section 2A.2.4(ii)]. A higher value (>0.4 kgN/ha/day) would be expected if the above calculations had included amounts of mineralised N that could have been lost by denitrification, gaseous losses from crop foliage to the atmosphere, uptake by weeds and by downward N movement bypassing drainage system.

The amount of ($\Sigma \underline{N}_m$) evaluated above, was divided between $[\Sigma(\Delta \underline{N}_{o1})]$ and $[\Sigma(\Delta \underline{N}_{o2})]$, the total net amounts of N mineralised from the short-cycle and long-cycle organic N pools respectively, over the 2 year period. It was assumed that an effective net amount of N mineralised annually from the long-cycle organic N pool was approximately equal to the amount of N taken up (60 kgN/ha) by the barley crop of 1979-80. For the two year period, $[\Sigma(\Delta \underline{N}_{o2})]$ would thus be 120 kgN/ha. The total amount of N mineralised from the short-cycle organic N pool $[\Sigma(\Delta \underline{N}_{o1})]$ was then found by difference $\{\Sigma \underline{N}_m - [\Sigma(\Delta \underline{N}_{o2})]\}$, as 160 kgN/ha for the 2 year period.

The mineralisation coefficient, m_1, for the short-cycle organic N pool, was evaluated by integration of equation (7.2). Integration and rearrangement of equation (7.2) gives

$$\Delta \underline{N}_{o1} = \underline{N}_{o1} [\exp(-Bm_1) - 1] \qquad (7.4)$$

Assuming that the short-cycle organic N pool was reduced to a small amount ($\approx$ 20 kgN/ha) by the end of the 2 year period and using an estimated average value for B of 0.2, a value for m_1 was found as 0.015 d^{-1}.

The constant rate of mineralisation (M_2) from the long-cycle organic N pool was found as 0.822 kg N/ha/d by using in equation (7.3) the estimated total amount of N mineralised from this pool over the 2 years and the average value for B of 0.2.

7.2.2.2 Calculations for N model simulation

The model calculations were made essentially in the same manner as in chapter 6, except for the mineralisation of soil organic N. The model was initialised on 4 April 1978 and run continuously up to 10 March 1980, using daily time steps. The soil water sub-model described in chapter 5 was used to estimate drainage and transpiration. These values were the daily inputs for the native soil N model that was used to simulate N transformations in plot (2). To simulate changes in fertilizer derived N and native soil N in plot (1), the sub-model for fertilizer derived N was run separately for period (1) following fertilizer addition and the simulated values were added to the native soil N sub-model as described in chapter 6.

Reduction factors (B) to account for the environmental variations were estimated as described in chapter 6, for each month of the experimental period using values of mean monthly soil temperature (ST) and soil water storage (SS). The values of Bm_1 and BM_2 for use in equations (7.4) and (7.3) were calculated for each month and assumed to remain constant over a month as the reduction factor was averaged over the month. Table 7.2 shows these values that were used in the model calculations. The values for model coefficients, k_i and k_m, for immobilisation-mineralisation of fertilizer derived N were also found by using reduction factors on $(k_x)_m$ values as described in chapter 6 and these values are shown in Table 7.3.

The values of plant uptake coefficient determined in chapter 6 for the three crop-development periods of a barley crop, were used for the barley crops grown during the trial period. For the winter oat crop, the cropping season was divided into two periods, and the "full-crop-cover" was taken as the crop phenological stage dividing these periods. The values of plant uptake coefficients determined for periods (1) and (2) for barley were used for the two periods of winter oat crop. The dates in which the periods started and ended (Table 7.1) were assessed by visual observation. Leaching losses of native soil N and fertilizer derived N were calculated as described in chapter 6.

7.3 MODEL VERIFICATION

7.3.1 Drainage and leaching losses of N

Cumulative drainage predicted using the soil water balance sub-model and the measured values of tile discharge

Table 7.2 Values of model coefficients used in model simulation of N transformations occurring in a large scale field trial, during a two year period.

Year and month	ST C	SS mm	B	BM_2 kgN/ha/d	$\exp(-Bm_1)-1$ d^{-1}	k_n d^{-1}
1978						
April	16.4	-97	0.022	0.0181	-0.0003	0.0011
May	12.1	-33	0.282	0.2318	-0.0042	0.0150
June	9.4	-10	0.173	0.1422	-0.0026	0.0090
July	8.6	-1	0.131	0.1077	-0.0019	0.0068
August	9.2	-2	0.163	0.1340	-0.0024	0.0085
September	11.1	-5	0.263	0.2162	-0.0039	0.0140
October	12.7	-8	0.348	0.2860	-0.0052	0.0180
November	15.2	-19	0.481	0.3953	-0.0071	0.0250
December	18.0	-94	0.050	0.0411	-0.0007	0.0026
1979						
January	19.2	-110	0.000	0.0000	-0.0000	0.0000
February	18.8	-123	0.000	0.0000	-0.0000	0.0000
March	18.3	-92	0.069	0.0567	-0.0010	0.0036
April	15.4	-22	0.491	0.4036	-0.0073	0.0260
May	12.2	-2	0.322	0.2647	-0.0048	0.0170
June	10.1	-3	0.210	0.1726	-0.0031	0.0110
July	9.2	-6	0.163	0.1340	-0.0024	0.0085
August	9.3	-1	0.168	0.1381	-0.0025	0.0087
September	11.4	-3	0.279	0.2293	-0.0041	0.0150
October	12.7	-7	0.348	0.2860	-0.0052	0.0180
November	16.0	-8	0.523	0.4299	-0.0078	0.0270
December	17.9	-12	0.624	0.5129	-0.0093	0.0330
1980						
January	18.8	-42	0.519	0.4266	-0.0077	0.0270
February	19.5	-107	0.000	0.0000	-0.0000	0.0000
March	16.5	-97	0.022	0.0181	-0.0003	0.0011

Table 7.3 Immobilisation - mineralisation coefficients for fertilizer N sub-model.

	Reduction factor	Immobilisation coefficient d^{-1}	Mineralisation coefficient d^{-1}
$(k_x)_m$ value	1.0	0.146	0.030
Barley crop 1978			
October	0.348	0.051	0.010
November	0.481	0.070	0.014
Barley crop 1979			
November	0.523	0.076	0.015
December	0.624	0.091	0.018

from plots (1) and (2) are shown in Fig. 7.1. In the measured data, up to 20% variation exists between plots (1) and (2) at any one time. The model predictions are in good agreement with the measured data, and are within the measurement variation. Part of this variation between plots in the measured drainage, could have been caused due to ineffective mole drainage in plot (2), as explained in chapter 6.

The results indicate that the soil water balance method, which does not take into account preferential movement of water through soil cracks and biogenic channels, can predict tile discharge with reasonable accuracy under these site conditions.

Measured amounts of N in tile discharge and the model values for N leaching losses are shown in Fig.7.2. In general, the model values are in reasonable agreement with the measured amounts of N leached. Closer inspection of the predicted and measured values indicate that, if drainage during any day exceeds about 15 mm, the measured amount of N leached is always lower than that predicted. It is possible that the "representative" sampling method for tile discharge measurement could have underestimated the N losses in drainage when a large amount of tile flow (>15 mm) occurred during any single day.

7.3.2 Crop uptake of N and the soil inorganic N

The measured and simulated values for the amounts of N taken up by crops grown in plots (1) and (2) are shown in Fig.7.3. The model predicts reasonably well N uptake by the two barley crops. The measured values for N uptake by

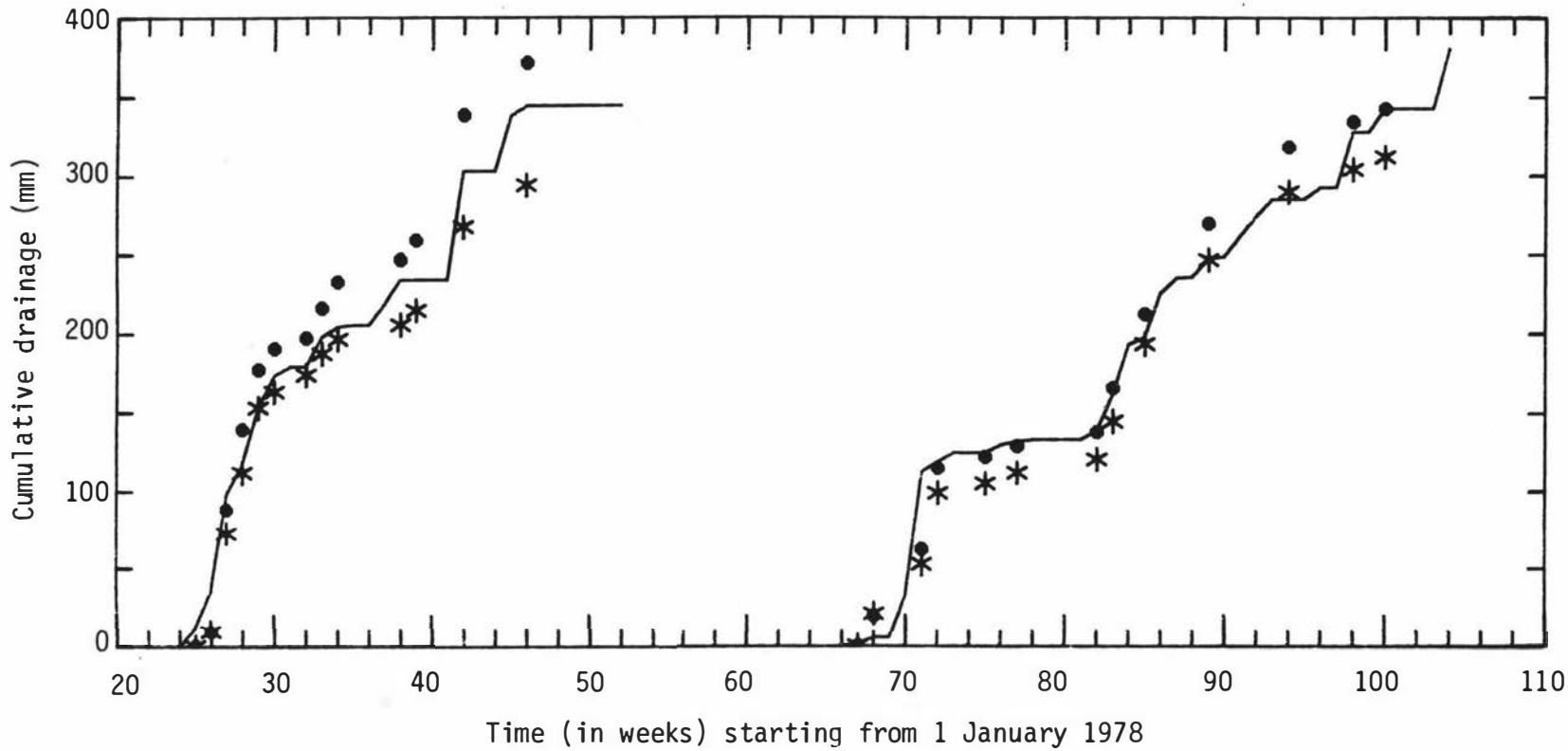

Fig. 7.1 Cumulative drainage (mm) measured in the tile drains of plot I (●) and plot II (✱); and predicted drainage (lines).

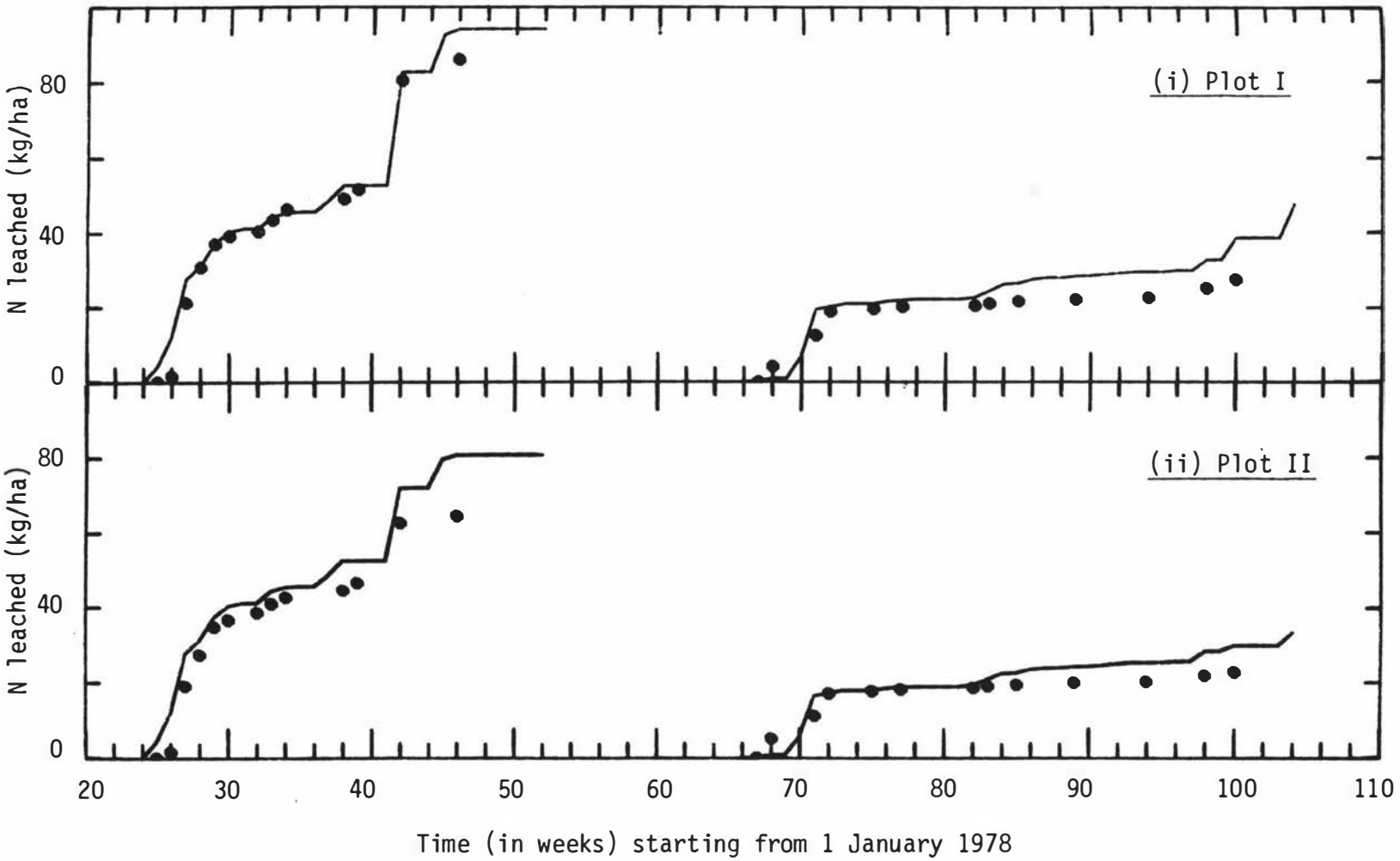

Fig. 7.2 Measured (data points) and modelled (lines) values of cumulative losses of N by leaching, from (i) plot I (N fertilized plot), and (ii) plot II (control plot).

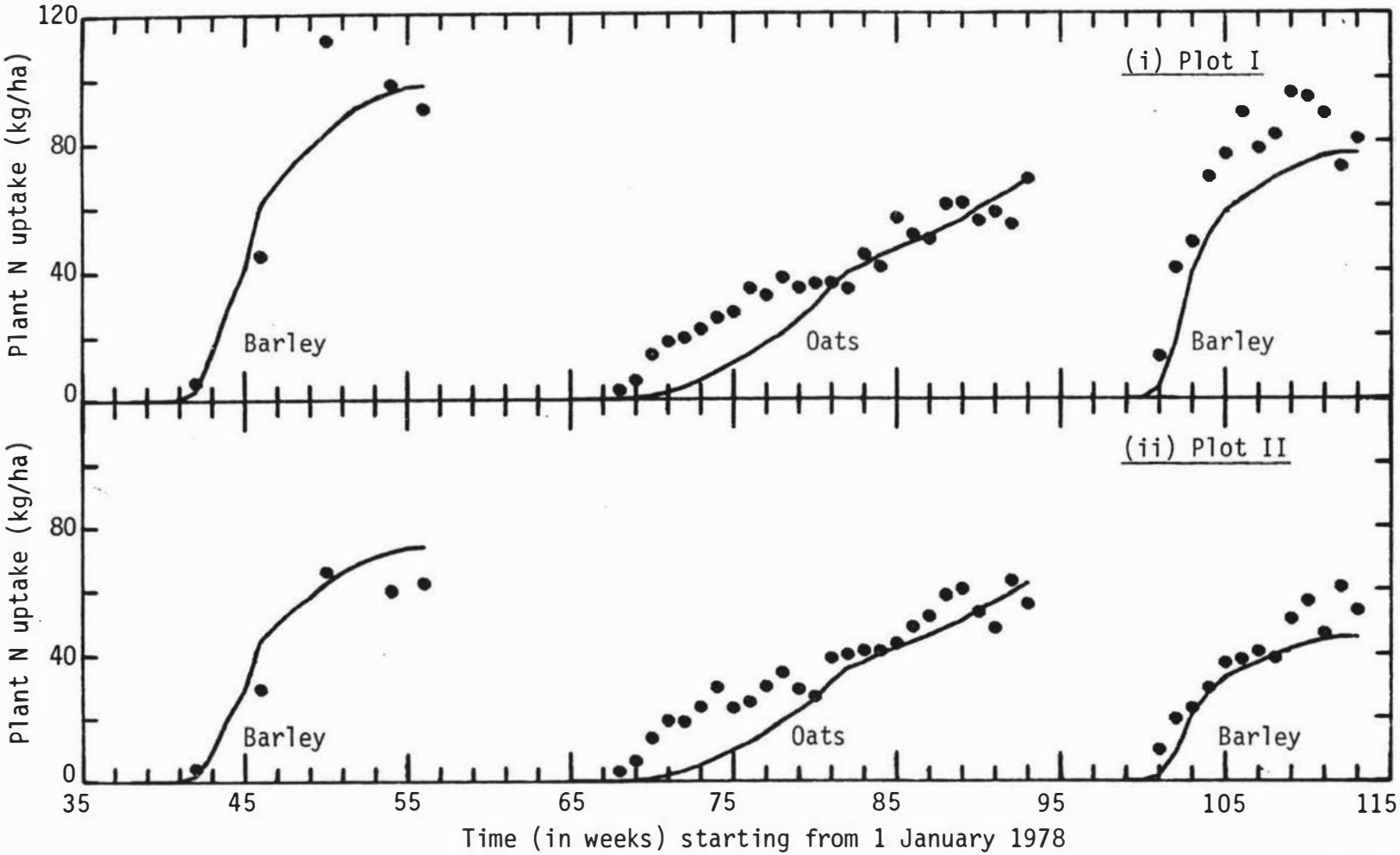

Fig. 7.3 Measured (data points) and modelled (lines) values of N taken up by crops from, (i) Plot I (N fertilized plot), and (ii) Plot II (control plot).

barley crops appear to decline after about 10 to 11 weeks of crop growth, during both years and on both plots; but in year 1978-79, the decline was not statistically significant, probably due to large variance associated with the measured data.

It is of interest to compare the predicted values for N uptake by barley crops shown in Fig. 7.3, with those in Figs. 6.4 and 6.5. During both years (1978-79 and 1979-80), the agreement between measured and predicted values is better in Fig. 7.3 than in Figs. 6.4 and 6.5. This better agreement has resulted partly due to the fact that, in the model simulations, different values for the soil ammonium and nitrate content were used to initialise the models. For the simulations shown in Figs. 6.4 and 6.5, actual measured values for the soil ammonium and nitrate content (see Figs. 6.7 and 6.8) were used to initialise the crop season model (Chapter 6); whereas, for the simulations shown in Fig. 7.3, predicted values (see Figs. 7.4 and 7.5) were used, since the long-term model was initialised in week 12 of 1978.

In comparison with the initial (measured) values of soil ammonium and nitrate that were used in the crop season model, the initial (predicted) values used in the long-term model, were higher for 1978-79 season and lower for 1979-80 season. As a result, the long-term model predicts higher plant N uptake for 1978-79 barley crop, and lower plant N uptake for 1979-80 barley crop, than predicted by the crop season model. This comparison provides evidence that the model prediction of plant N uptake is quite sensitive to the

initial values of soil ammonium and nitrate that are used to initialise the model.

For the oat crop grown during 1979, the model predictions of N uptake agree well with the measured values after the first 14 weeks of crop growth. During the first 14 week period which is approximately the period (1) considered in model simulation, the model predictions of N uptake are underestimates compared with the measured values. This indicates that a single value of 0.028 mm^{-1} for the uptake coefficient k_p for the period (1) is not adequate. By inspection of measured data, it appears that the model predictions for N uptake by oat crop, could be improved if period (1) is subdivided and a higher value (>0.028 mm^{-1}) for k_p is used for the first part and a lower value for k_p (<0.028 mm^{-1}) for the second part. This could not be justified in the present model due to lack of experimental data on soil and plant parameters.

The measured amounts and simulated values of inorganic N in soils of plots (1) and (2) are shown in Fig.7.4 for ammonium N and Fig.7.5 for nitrate N. As discussed in chapter 6, no cognizance was taken in the model simulation, of the possible effects of 'priming' and 'desiccation' on the soil organic N mineralisation and therefore a good agreement between measured and predicted values for ammonium and nitrate levels in soil, could not be expected. However, a general comparison of measured and predicted values indicates that agreement for nitrate values is better than for ammonium values. The measured ammonium N content in soils of both plots was consistently higher throughout the

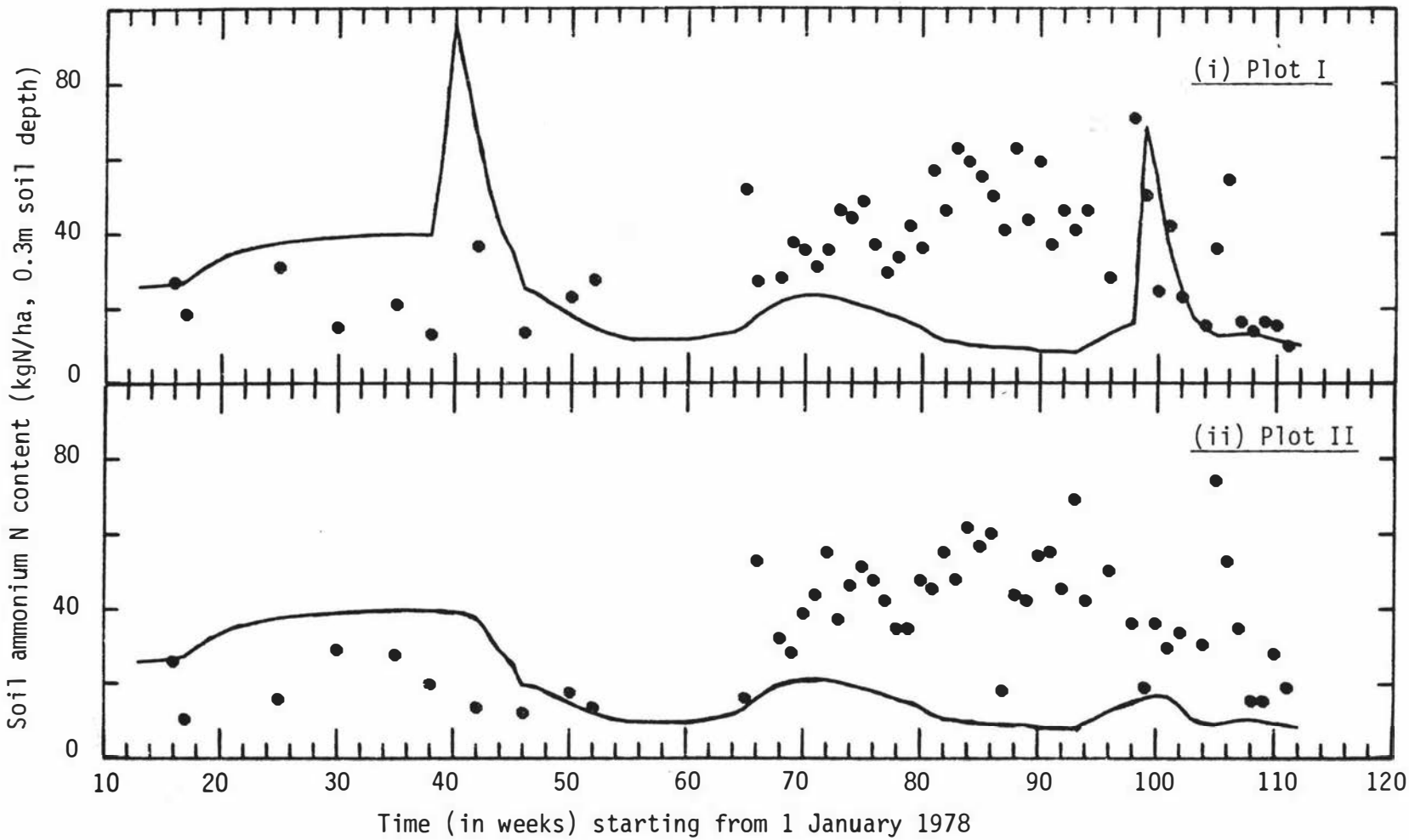

Fig.7.4 Measured (data points) and modelled (lines) values of ammonium in soils of (i) Plot I (N fertilized), and (ii) Plot II (control plot).

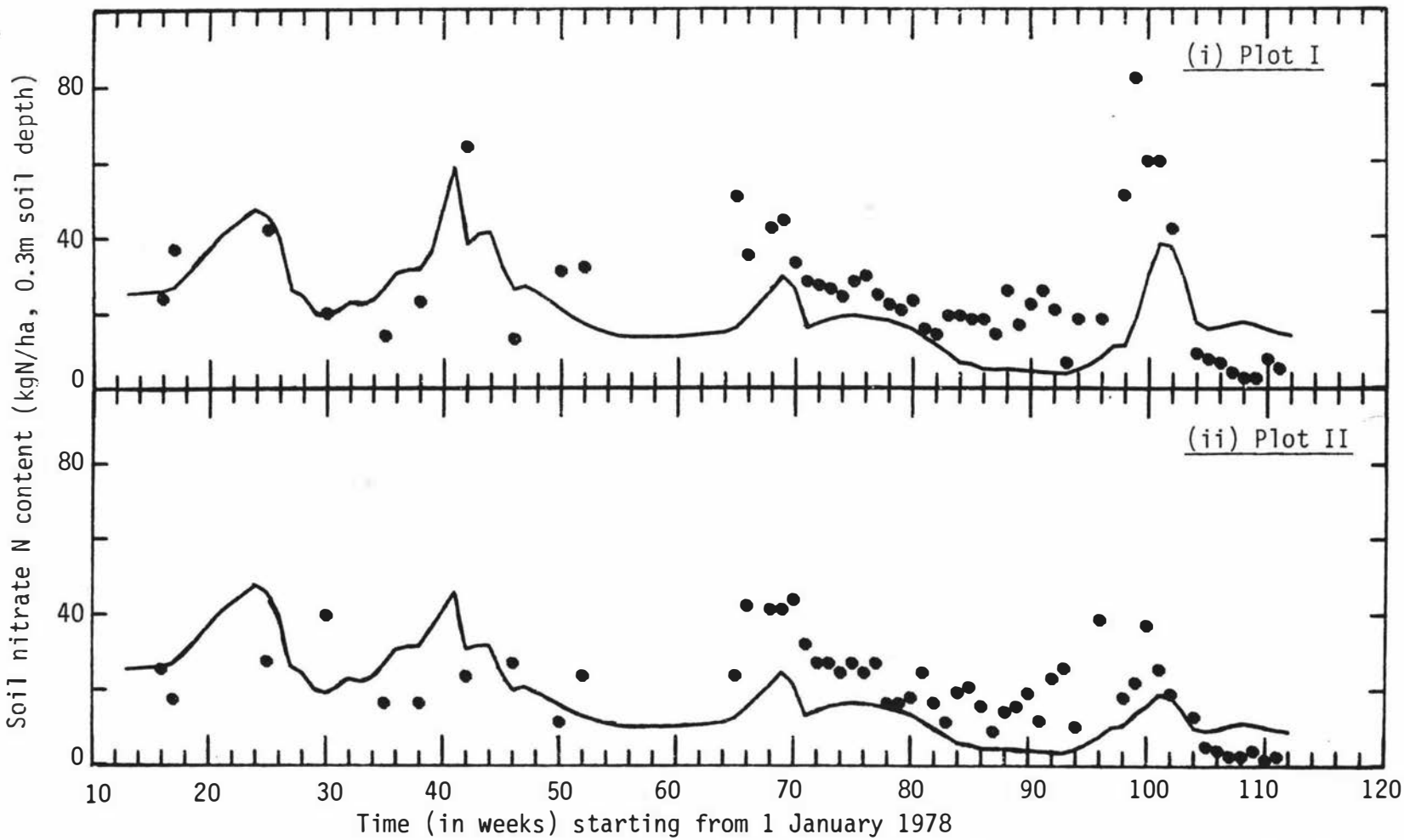

Fig. 7.5 Measured (data points) and modelled (lines) values of nitrate N in soils of (i) Plot I (N fertilized) and (ii) Plot II (control plot).

winter season of 1979 than it was during the previous winter season. This difference was not expected as the plots were fallow during the winter of 1978 and were in an oat crop during the winter of 1979. Cultivated soils in temperate regions generally contain a fairly constant and low content of ammonium N (Russell 1973). Whether it is mainly the model or the measurement that is in error in this case is not clear.

In general, the N simulation model, although simple in design, is reasonably accurate in its prediction of N leaching losses in tile discharge and N uptake by crops over the two year period studied.

7.4 DISCUSSION

Studies on the nitrate pollution of surface water often express nitrate content as nitrate concentration, since it is the nitrate concentration and not amounts that are used as the criteria for the suitability of potable water. The model presented in this chapter satisfactorily predicted the amounts of nitrate N discharged from tile drained cropland (Fig.7.2) under conditions of different N status. These amounts can readily be converted to nitrate concentrations knowing drainage volumes that are also predicted by the model. The simulated and measured nitrate concentrations in tile discharge during 1978 are shown in Fig.7.6. The model, in general, predicts reasonably well the nitrate concentrations in tile discharge effusing from both N fertilized and unfertilized plots. However, some differences in predicted and measured values do exist and these differences relate to two model assumptions:

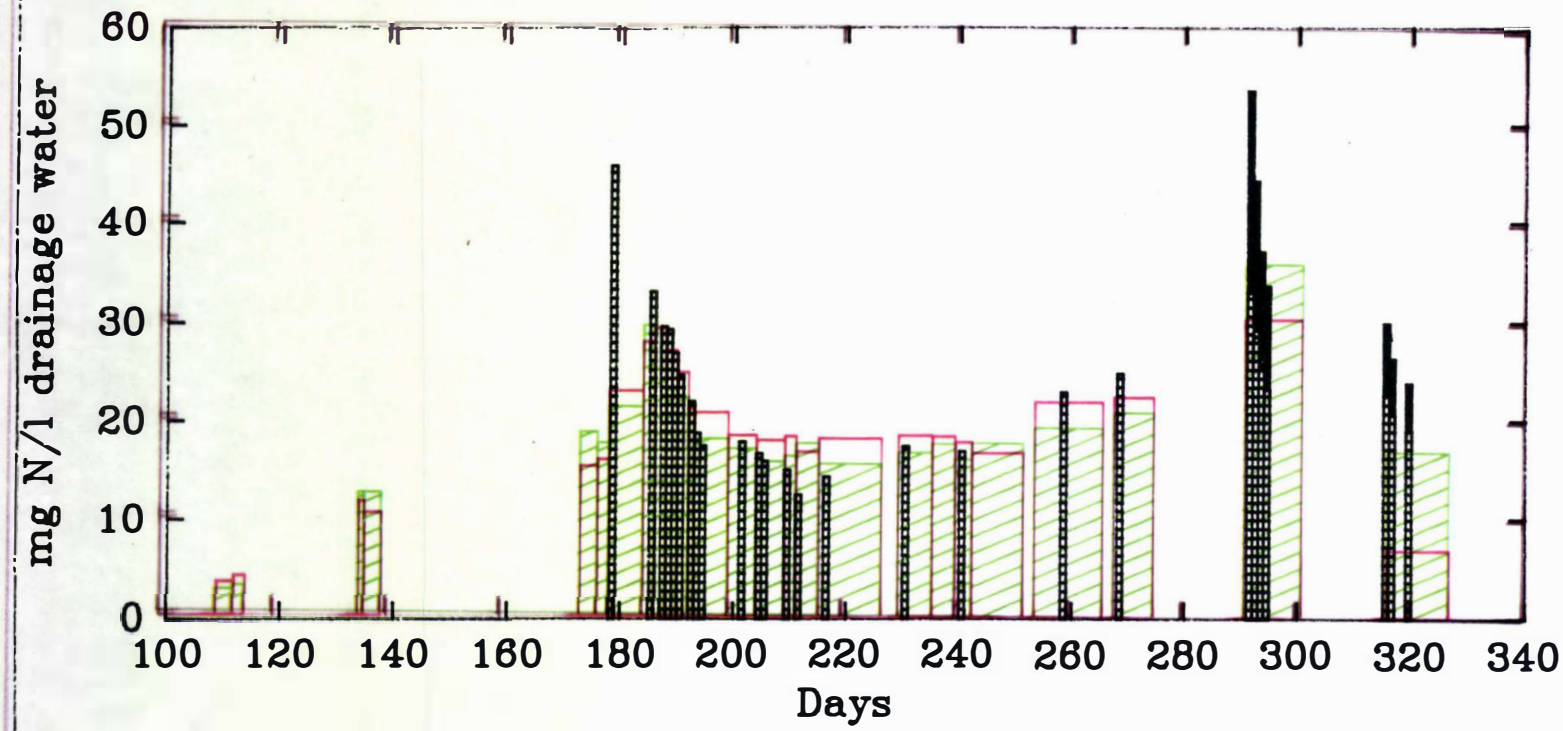

Fig. 7.6 Nitrate-N concentrations in tile discharge during 1978. (i) modelled values: (▌) N fertilized and (▯) control plots; (ii) measured values for plot I (N fertilized), and (iii) measured values for plot II (control plot).

(i) The model assumes that drainage does not occur until the soil water storage reaches 'field capacity'. In practice, this assumption does not hold as small amounts of water drain preferentially through cracks and channels in the soil, even before the soil water storage reaches 'field capacity' (Thomas and Phillips 1979; White et al 1983). Small amounts of drainage ranging between 0.7 to 3.8 mm were measured during three storm periods prior to day 178 (Fig.7.1). The model did not predict these drainage flows since it predicted that prior to day 178, the soil water storage did not reach 'field capacity'. These storm periods occurred on days 110 to 114, 135 to 139 and 174 to 176 when rainfall amounted to 105, 37 and 22 mm and drainage measured amounted to 0.7, 3.3 and 3.8 mm respectively. Measured nitrate concentrations in tile discharge during these drainage events are shown in Fig.7.6. As amounts of drainage were small, the N loads in tile flow were small and almost negligible.

(ii) The model assumes that, when the soil water storage is at 'field capacity', any excess rainfall,over evapotranspiration, would leave the soil profile as drainage within the same calender day, as the model output is on a daily basis. Nitrate leaching losses were, therefore, predicted with the model on a daily basis as shown in Fig.7.6 (i). On several occasions, depending upon the intensity of rainfall, the measured tile flow occurred for more than a day; but the model took no account of this time-lag in tile flow. The measured values for nitrate concentrations in tile flow, as shown in Fig.7.6 (ii) and

(iii), are thus distributed over several days. The measured values are only average nitrate concentrations measured in 'representative' samples.

In general, the measured and predicted data in Fig.7.6 indicate that nitrate concentrations in tile effluent usually exceed 15 to 20 mgN/litre, regardless of fertilizer addition. The addition of fertilizer N at 100 kgN/ha, increased these levels two-fold but only for a short time.

Similar results were reported by Cooke (1976) for British soils under cropping. He reported that drainage from intensively managed arable land often contained, on average of a year's flow, 10-15 mg N/litre. At some periods of the year, concentrations were much larger (upto 90 mgN/litre) for short periods due to fertilizer additions.

Reviewing the results for soils in USA, Keeney (1982) concluded that, for many crops, with good agronomic practices and profitable production, about 20 mg/litre of nitrate N in drainage effluent may be the best achievable. Furthermore, such high nitrate concentrations in drainage effluent may be of little significance if the tile effluent enters, shortly after discharge, into larger volumes of water flow of low nitrate content (MacKenzie and Viets 1974).

The model presented in this chapter is capable of predicting the N loads as well as the N concentrations in tile drain effluent and thus would be useful in environmental pollution assessments where catchment waters are influenced by tile drain discharge.

The measured and simulated data in Fig.7.2 for N leaching losses indicate that N losses during 1979 were nearly 50% less than in 1978; although similar amounts of drainage were measured during the two years (Fig.7.1). This was partly due to the fact that the land was under fallow conditions during the winter of 1978, but was cropped with a winter oats during 1979. The oat crop, by taking up the mineralised soil N, should have contributed to the reduced N leaching losses. However, the magnitude of this 'scavenging effect' of the crop on N leaching losses can not be fully evaluated due to the confounding effect of different years. The soil during 1979 was one year further away from the pasture phase than it was during 1978.

In order to better evaluate the benefit of growing a crop during the winter season, the model described in this chapter, was used to simulate N transformations in the control plot during the winter of 1979, assuming the plot was either fallow or cropped. The results of this simulation run are shown in Fig.7.7. The predicted N leaching losses under fallow conditions are twice as much as under cropping conditions. The simulated amount of drainage, however, remained the same (334 mm) under both fallow and cropping conditions, since evapotranspiration under both conditions proceeded at the potential rate and therefore remained the same. Thus, under New Zealand conditions, a winter crop might not reduce, the amount of drainage, but it could reduce the N leaching losses by removing N from soil solution which otherwise could be leached. The ability of crops to reduce N leaching losses

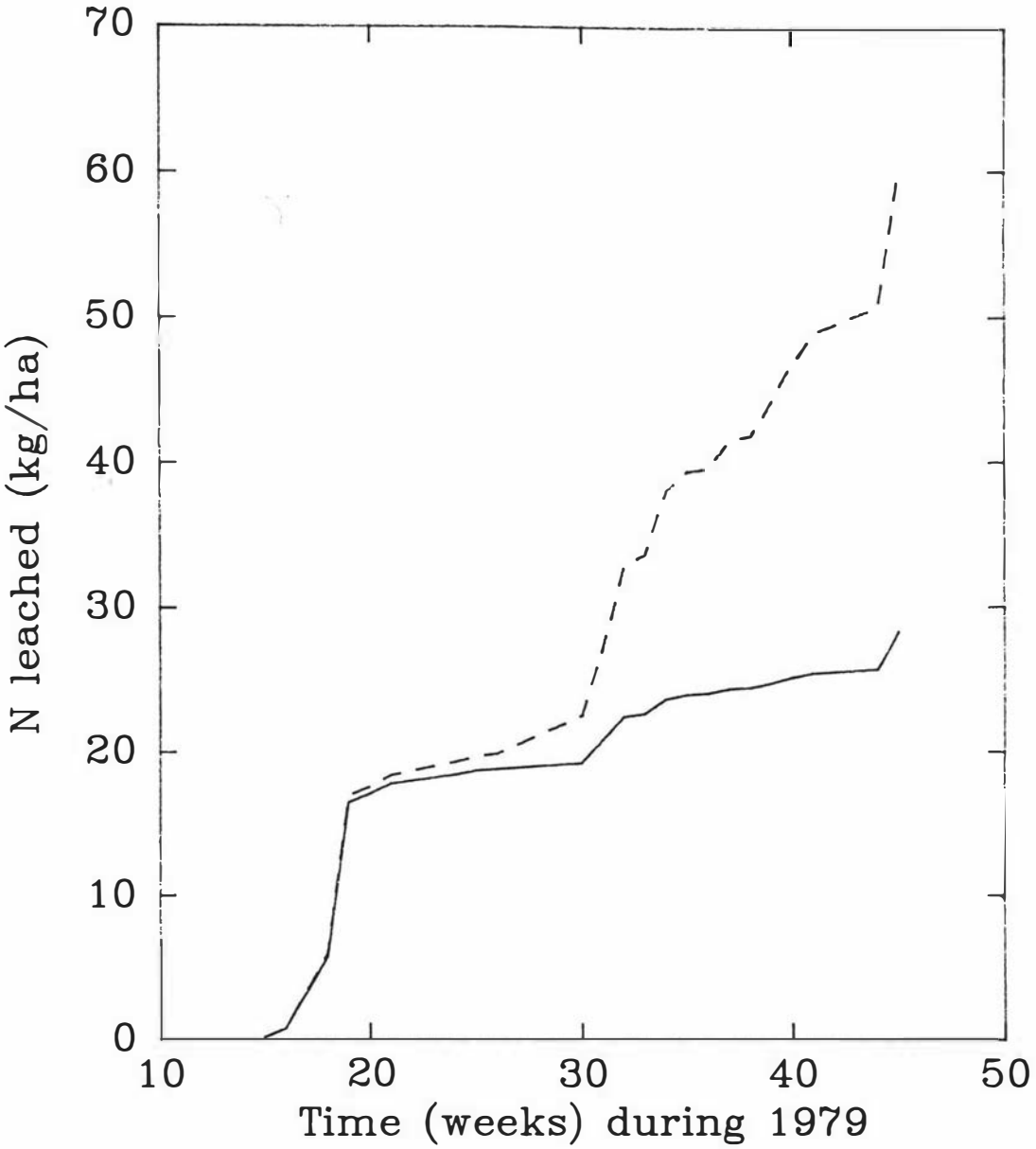

Fig. 7.7 Effect of an oat crop on N leaching during winter 1979. Predicted N leaching under cropping (———) and under fallow (- - - -) conditions.

by taking up N from soil solution, has also been reported by Olson et al (1970) and Keeney (1982).

Simulation approaches used to model mineralisation of soil organic matter vary. Simple models (e.g., Greenland 1971) describe the change in total soil N with a simple first-order rate equation. More complex models (e.g., Frissel and van Veen 1981), consider mineralisation of soil organic matter by dividing the soil organic matter into several carbon (C) and nitrogen (N) pools. Since data for all the C and N pools are not usually available, it is difficult to calibrate and verify such complex models. Hence, such complex models have limited use. In the long-term model described in this chapter, mineralisation of soil organic matter was described by zero-order and first-order chemical kinetics on long-cycle and short-cycle organic N pools respectively. The overall good agreement between modelled and measured values for leaching and plant uptake indicate that this approach has potential for use in simple models.

The agricultural management practices that have been proposed for minimising N losses from cropland and maximising N efficiency, are many and diverse, and are well summarised by Keeney (1982). Evaluation of the effectiveness of all these practices in New Zealand, would require elaborate experimentation requiring time and money. N model simulations for cropping systems in which management practices are varied, could complement efforts that are directed at altering the existing management practice in order to minimise N losses and maximise N efficiency. For

example, during winter the amounts of N likely to be leached from a soil under various cropping practices (including fallow) can be simulated, and depending on one's objectives, the most promising practices can then be selected and experimentation can be more selective. The model described in this chapter could be adapted to meet such requirements.

7.5 CONCLUSIONS

The model presented in this chapter predicted quite accurately the N loads as well as the N concentrations in tile drain effluent effusing from experimental field plots and thus would be useful in environmental pollution assessments where catchment waters are influenced by tile drain discharge.

In general, the measured and predicted data for nitrate concentrations in tile drain effluent of the field plots indicated that nitrate concentrations in tile effluent often exceed 10 mgN/litre, but rarely exceed 30 mgN/litre, regardless of fertilizer addition. The addition of fertilizer at 100 kgN/ha, increased nitrate levels to about 50 mgN/litre, but only for a short time.

In order to illustrate the utility of the model presented in this chapter, it was used to simulate N transformations occurring in an experimental plot assuming the plot was either fallow or cropped. The model predicted that during winter, N leaching losses could be 50% less from soil under crop as compared with fallow condition. These results could not be verified with experimental data.

The model could, with further modification, be used to identify the most promising management practices that might

minimise N pollution from agricultural lands, and research could then be directed to evaluate experimentally the effectiveness of these management practices.

CHAPTER 8

SUMMARY

8.1. The literature relating to, (A) N-15 balance experiments in cropping systems, and (B) modelling N transport and transformations in cropping systems, was reviewed.

8.1A. The following points were noted from the literature pertaining to N-15 balance experiments:

(i) Methodology of N-15 balance experiments:

(a) Fertilizer N balance studies on soils with relatively large soil native N pool, would require the use of N-15 enriched fertilizers. The high cost of N-15 enriched compounds has restricted the size of experimental plots to small areas. Microplots, small size cylinders and large lysimeters have been used. Use of small lysimeters in fertilizer N balance studies for cropping systems has not been reported.

(b) In most fertilizer N balance studies N-15 isotope measurement has been made using mass spectrometry. Emission spectrometry (e.s.) is available as an alternative to mass spectrometry. The e.s. technique has not been widely used and considerable divergence of opinion exists on several aspects of N-15 analysis by e.s., including accuracy, amount of N needed, precision and memory effects.

(ii) Results of N-15 balance experiments:

(a) N-15 balance studies, in general, report recoveries in the crop of 25-65% with 10-45% retained in the soil, 1-30% removed by leaching and 5-25% unaccounted for and presumed lost.

(b) The experimental results relating to crop uptake of applied fertilizer N suggested that, (i) crop uptake of fertilizer N is most important only during the first 4-6 weeks following its application at sowing; (ii) immobilisation of applied N into soil organic matter could cause low fertilizer N uptake by crops; (iii) excess leaching of fertilizer N could result in low N uptake by crops; (iv) crop uptake of N could differ with irrigation rate, and rate and time of fertilizer application.

(c) The experimental results relating to the immobilisation of fertilizer N into soil organic matter suggested that, (i) a varying proportion of the applied N (10-45%) could be immobilised into soil organic matter; (ii) a major portion (> 50%) of the immobilised fertilizer N might not be mineralised during the same cropping season in which it was applied, and therefore would not be available for plant uptake during that season; (iii) immobilisation of added N in soil would be significant only in the surface layer of varying depths upto about 400 mm; (iv) the amount of N immobilised, as a percent of applied N, might not increase linearly with increasing application rates. Although there often has been a significant increase in the actual amount of applied N immobilised with a higher rate of application; (v) a continual net immobilisation of applied fertilizer N might not increase soil organic N content to reach a higher equilibrium level under continuous cropping.

(d) The experimental results relating to the leaching of applied fertilizer N suggested that, (i) nitrate was the major form of N leached out of the root zone and ammonium N

was seldom found in the drainage water; (ii) urea N could also be leached as it would not be strongly adsorbed in soils; (iii) amounts of fertilizer N leached, in general, could be related to two factors: (a) rate of fertilizer N application (b) amount of water that drains in the soil; (iv) when preferential flow occurred, the amount of N leached was not related to the amount of drainage; (v) by preferential movement of water in soil, relatively larger amounts of surface applied fertilizer could remain near the soil surface while some fertilizer could be leached to greater depths, than predicted by miscible displacement theory.

(e) The results on soil native N mineralisation suggested that, (i) soils under pasture accumulated organic N, and when such established pastures were ploughed for cropping, mineralisation of this accumulated organic N was rapid; (ii) the soil heterogeneity and spatial variability in the soil organic N distribution could often be so large that measurement of short term changes in the soil organic N content could be difficult; (iii) the N mineralisation rate would likely to be associated with a small active pool of organic N, but no relationship between them has been reported; (iv) the experimental results on priming effect of fertilizer N on soil native N mineralisation were inconsistent and none of the suggested explanations for the priming effect, appeared to completely explain the observed net effects.

8.1B. The following points were noted from the literature pertaining to the modelling of N transport and transformations in cropping systems:

(a) Most N system models are small scale system models, and only a few are large scale system models. Small scale system models are developed and verified with data obtained from small scale experiments, such as lysimeter and incubation experiments. Large scale system models have been designed to simulate N processes occurring in large scale systems such as watersheds and irrigation projects. Where parameterisation of such models is made, data obtained from small scale studies are used. The results simulated in these large scale system models have not been verified with data obtained from large scale studies, presumably due to a lack of suitable data.

(b) Dynamic N models were process oriented in that the physical, biological, and chemical N processes occurring in the soil-plant system were simulated simultaneously. These N processes could be broadly classified into two categories: (i) N movement (transport) caused by water movement; and (ii) biochemical processes (transformations).

(c) Dynamic models were not applicable to all soil-water- plant situations because each dynamic model had a degree of site-specificity, as each dynamic model had been formulated for a specific local condition. Application of a given dynamic model to a different set of experimental conditions usually required modifications to model parameters.

(d) Two main approaches seemed to have been evolved in the model formulation procedure, depending upon the objective(s) for developing the model. Models developed to

examine the theoretical aspects of a N model system, took the approach to develop a theoretical or conceptual framework model without basing the model on any experimental data. Models developed for field application with objectives such as to provide better N management guidelines, took the approach to base the model on field data that document the effects of rate, amount, and timing of fertilizer and irrigation applications, on crop yield and N uptake.

(e) Sophisticated dynamic models required the use of computers. It appeared that there has been no simple N model reported that could be stored in and run with a programmable calculator. Such simple N models would be useful for managers or advisors engaged in routine N fertility evaluation or N pollution control.

(f) Mechanistic and empirical approaches have been adapted in dynamic models. Most mechanistic models involved chemical kinetics, mainly first order or Michaelis-Menten type of kinetics. Empirical models included multiple regression or algebraic expressions and such models required elaborate experimental data for individual transformations in order to obtain regression equations or algebraic expressions describing the transformations. The disadvantage with such empirical models was that they acquire a higher degree of site-specificity than mechanistic models. On the other hand, mechanistic models would not completely describe N transformations, since the biological mechanism involved in any N transformation could not be fully described by chemical kinetics alone. But it appeared

that, for simple models, first order kinetics might describe the microbially mediated N transformations just as well as empirical models.

(g) Few models took into account effects of environmental conditions such as soil temperature and moisture on rate constants. It appeared that there was no mechanistic approach that could be used to incorporate, into the model, the effect of environmental factors on N transformations; all models that took into account these effects have used only empirical approaches.

(h) The N model development procedure consisted of calibration, validation and verification. Calibration referred to model parameterisation with synthetic and/or observed data; validation meant testing the algorithm and verification meant testing the model with data other than the set used to calibrate the model.

(i) Some modelers have verified only parts of their model. However, several modelers have tested all parts of their models, by simultaneous simulation of all sub-routines that constitute their N models.

8.2. The study reported in this thesis can be divided into two stages: (A) Several N-15 experiments were conducted in order to better understand the N transport and transformations in soil - plant system; (B) The data obtained from these experiments were used to develop and verify N models.

8.2A. N-15 experiments:

(a) Preliminary investigations into the fate of N-15 labelled urea applied to barley and oat crops in a double cropping system, were conducted using soil cylinders in situ, during 1978-79. In these investigations, plants were grown in soil confined by PVC pipe (soil cylinder) and N-15 analyses on soil and plant samples were performed using emission spectrometry. The results of this study indicated that the total recovery of applied N in plant and soil components could vary between 50 to 90 percent.

(b) This preliminary study pointed out the needs for further investigations: (i) Measurement error in N-15 analyses and other N loss mechanisms, such as N leaching should be investigated in order to obtain a better N-15 balance sheet. (ii) Investigations would also be required to determine the initial N-15 enrichment in fertilizer material, that would facilitate emission spectrometric assay of N-15 in the organic fraction of the Tokomaru silt loam soil. (iii) The relevance of plant N uptake data collected by growing plants in soil cylinders, to the plant N uptake in the main plot needed to be evaluated.

(c) Further experiments were designed and conducted, based on the needs that emerged from the preliminary study: (i) Experiment I was conducted to determine the level of N-15 enrichment in urea, which would facilitate emission spectrometric assay of N-15 in the organic fraction of a Tokomaru silt loam soil; (ii) Experiment II was conducted to determine the relevance of N data obtained from small soil cylinders in situ, to large field plots; (iii) Experiment III was conducted to characterise the dynamic

nature of soil inorganic N changes associated with its uptake by a barley crop to which N-15 urea was added. Additionally,the accuracy and precision of N-15 assay by emission spectrometry, relative to mass spectrometry, were determined, using N-15 standard samples. Also, the analytical error and the spatial variabilty associated with soil organic N determinations, were determined.

(d) The results of these further experiments showed: (i) analysis of N-15 samples containing more than about 1 atom percent excess N-15 enrichments, can be performed satisfactorily, with the present emission spectrometric technique using Statron NO1-5 analyser; (ii) the current emission spectrometric technique will not be useful in N-15 tracer studies investigating the immobilisation of applied fertilizer N with soils of relatively high organic N content (~0.2%), since such investigations require measurement of less than 1 atom percent N-15; (iii) the emission spectrometric technique can be satisfactorily used to measure N-15 in plant and soil inorganic N fraction since the isotope dilution is much less than in the organic N fraction; (iv) the analytical errors in soil organic N determinations were small (2.8% of the mean value) compared with the spatial variability of about 15% of the mean value; (v) data for changes in soil inorganic N content over time, obtained by the use of soil cylinders, can be representative of field behaviour; (vi) data for plant N uptake obtained by growing plants in soil cylinders can be representative of field data at least for the first seven weeks of plant growth; (vii) initial urea N transformations are rapid, and

most of fertilizer N uptake by plants occurs in the first five weeks following its application at sowing; (viii) plants take up a greater proportion of their total N as native soil N.

(e) A further study was undertaken to account for immobilisation and leaching of N-15 labelled urea applied to a barley crop, during the first five weeks following its application. Microplots and small lysimeters were used. Two leaching treatments, "normal" and "wet", were imposed. N-15 labelled urea and potassium bromide were applied at the time of sowing barley.

Approximately 90% of the applied N was recovered, indicating that gaseous N losses were small. Hydrolysis and immobilisation of the urea N occurred rapidly. One week after application, 86% of urea N had been hydrolysed, while after two weeks 36% of it had been immobilised into organic matter. As expected, leaching was a function of drainage. Only 14% of the fertilizer N was leached from the wet lysimeters, whereas 76% of the bromide applied was leached, presumably due to rapid urea N transformation into ammonium and organic N, the two N forms not prone to leaching. The increased leaching of N from the wet lysimeters compared with the normal lysimeters was at the expense of plant N uptake, having little effect on the amount of N immobilised. Net mineralisation of native soil N was calculated as 42 kg N/ha, or 1.2 kgN/ha/day.

8.2B. N models:

(a) An initial short-term N-model was developed. The model was relatively specific, considering only the major variables in the soil-plant system studied. It consisted of a soil water sub-model and separate sub-models for fertilizer N and native N transformations. First-order kinetics were assumed for all microbially mediated N transformations. Plant N uptake was considered proportional to the amounts of ammonium and nitrate in soil and to transpiration. A simple leaching relationship was assumed, where the amount of N leached was considered proportional to the amount of nitrate in the soil and to the number of 'pore volumes' of drainage.

The model successfully predicted the leaching of fertilizer N, native soil N and bromide. The reduced plant uptake of fertilizer N resulting from the increased leaching, was also quite successfully modelled. The model indicated that the amount of fertilizer N leached was strongly dependent on the timing of rainfall in relation to the time of fertilizer application.

(b) A crop-season N-model was developed by extending the short-term N-model to cover a full growth season of a barley crop. The effects caused by changing soil temperature and moisture, and plant growth and development stage were incorporated in the model parameters. The model was validated by simulating the N transformations occurring in a soil cylinder experiment with barley. The model was verified with measured data from a large scale field trial.

The model prediction for N leaching losses, demonstrated better accuracy than for plant N uptake. To

improve the accuracy of model prediction on plant N uptake, some refinements to the model were suggested. Also the model had a degree of site-specificity; but it could be adapted to other situations with suitable modifications to the model parameters.

The usefulness of the model as a management tool was illustrated by using the model to predict the adverse effect of excessive rain, that fell early in the crop season, on the crop N uptake pattern. The model was found to be capable of providing a continuous evaluation of possible adverse effects caused by unforeseable factors such as excessive rainfall, on plant N uptake.

(c) A long-term N-model was developed in order to predict, over a two year period, the N leaching losses in tile discharge from a recently ploughed pasture subjected to a double cropping rotation to which fertilizer N was added. The model predicted quite accurately the N loads as well as the N concentrations in tile drain effluent effusing from experimental field plots. In general, the measured and predicted data for nitrate concentrations in tile drained effluent of the field plots indicated that nitrate concentrations in tile effluent are often above 10 mgN/litre, but rarely exceed 30 mgN/litre, regardless of fertilizer N addition. The addition of fertilizer N could increase these levels two-fold but only for a short time.

The utility of the model in assessing N leaching was illustrated by using the model to simulate N transformations occurring in an experimental plot assuming the plot was either fallow or cropped. Such predictive ability of the

model would be useful in directing further research to evaluate experimentally the effectiveness of a management practice such as cropping as against fallowing.

REFERENCES

Alexander,M. 1977. Intoduction to soil microbiology. John Wiley and Sons, New York.

Allison,F.E. 1955. The enigma of nitrogen balance sheets. Adv. Agron. 7:213-250

Allison,F.E. 1966. The fate of nitrogen applied to soils. Adv. Agron. 18:219-258.

Allison,F.E., and C.J.Klein. 1962. Rates of immobilisation and release of nitrogen following additions of carbonaceous materials and nitrogen to soils. Soil Sci. 93:383-6.

Anon. 1979. Rainfall parameters for stations in New Zealand and the Pacific Islands. N.Z. Meteorological Service Misc. Pub. 163.

Ayanaba,A., and B.T.Kang. 1976. Urea transformation in some tropical soils. Soil Biol. Biochem. 8:313-6.

Baber,H.L., and A.T.Wilson. 1972. Nitrate pollution of groundwater in the Waikato region. Chemistry in New Zealand 36:179-183.

Badzhov,K., and E.Ikonomova. 1971. N-15 for studying nitrogen transformations in soil, nitrogen nutrition of plants, and in assessing available nitrogen in soil. In Nitrogen-15 in Soil - Plant Studies. IAEA, Vienna, Austria.

Baker,J.L., J.L.Laflen, H.P.Johnson, and J.J.Hanway. 1975. Nitrate, phosphorus, ans sulphate in subsurface drainage water. J. Environ. Qual. 4:406-412.

Bartholomew,W.V. 1965. Mineralisation - immoobilisation of nitrogen in decomposition of plants and

animal residues. In W.V.Bartholomew and F.E.Clark (ed.) Soil Nitrogen. Agronomy 10:285-306. Am. Soc. of Agron., Madison, Wisc.

Beek,J., and M.J.Frissel. 1973. Simulation of nitrogen behaviour in soils. Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands.

Biggar,J.W. 1978. Spatial variability of nitrogen in soils. In Nitrogen behaviour in field soil. p.201-211. In D.R.Nielsen and J.G.MacDonald (ed.) Nitrogen in the environment. Vol.I. Academic Press, Inc., London.

Bigger,J.W., and D.R.Nielsen. 1967. Miscible displacement and leaching phenomenon. In R.M.Hagan, H.R.Haise and T.W.Edminster (ed.) Irrigation of agricultural lands. Agronomy 11:254-274. Am. Soc. Agron., Madison, Wisc.

Birch,H.S. 1960. Soil drying and soil fertility. J. Trop. Agr. (Trinidad) 37:3-10.

Blackburn,T.H. 1979. Method for measuring rates of ammonium turnover in anoxic marine sediments, using a N-15 ammonium dilution technique. Appl. Environ. Microbiol. 37:760-765.

Bremner,J.M. 1965a. Total Nitrogen. In C.A.Black (ed.) Methods of Soil Analysis. Agronomy 9:1148-1178. Am. Soc. Agron., Madison, Wisc.

Bremner,J.M. 1965b. Inorganic forms of nitrogen. In C.A.Black (ed.) Methods of Soil Analysis. Agronomy 9:1179-1237. Am. Soc. Agron., Madison, Wisc.

Bremner,J.M. 1965c. Organic forms of nitrogen. In C.A.Black (ed.) Methods of Soil Analysis. Agronomy 9:1238-1255. Am. Soc. Agron., Madison, Wisc.

Bremner,J.M. 1965d. Isotope ratio analysis of nitrogen in nitrogen-15 tracer investigations. In C.A.Black (ed.) Methods of Soil Analysis. Agronomy 9:1256-1286. Am. Soc. Agron., Madison, Wisc.

Bremner,J.M., and D.R.Keeney. 1966. Determination and isotope ratio analysis of different forms of nitrogen in soils: 3. Exchangeable ammonium, nitrate, and nitrite by extraction distillation methods. Soil. Sci. Soc. Am. Proc. 30:577-582.

Bresler,E. 1973. Simultaneous transport of solute and water under transient unsaturated flow conditions. Water Resour. Res. 9:975-986.

Broadbent.F.E. 1965. Effect of fertilizer nitrogen on the release of soil nitrogen. Soil Sci. Soc. Am. Proc. 29:692-696.

Broadbent,F.E., and K.B.Tyler. 1962. Laboratory and greenhouse investigations of nitrogen immobilisation. Soil Sci. Soc. Am. Proc. 26:459-462.

Broadbent,F.E., and T.Nakashima. 1965. Plant recovery of immobilised nitrogen in greenhouse experiments. Soil Sci. Soc. Am. Proc. 29:55-60.

Broadbent,F.E., and T.Nakashima. 1967. Reversion of fertilizer nitrogen in soils. Soil Sci. Soc. Am. Proc. 31:648-652.

Broadbent,F.E., and A.B.Carlton. 1978. Field trials with isotopically labeled nitrogen fertilizer. p.1-77. In D.R.Nielsen and J.G.MacDonald (ed.) Nitrogen in the environment. Vol. I. Nitrogen behaviour in field soil. Academic Press, Inc., London.

Broida,H.P., and M.W.Chapman. 1958. Stable nitrogen isotope analysis by emission spectroscopy. Anal. Chem. 30:2049-2055.

Burns,I.G. 1975. An equation to predict surface-applied nitrate. J. Agric. Sci. 85:443-454.

Burns,I.G. 1976. An equation to predict the leaching of nitrate uniformly incorporated to a known depth or uniformly distributed throughout a soil profile. J. Agric. Sci. 86:305-313.

Burns,I.G. 1980. Influence of the spatial distribution of nitrate on the uptake of N by plants: A review and a model for rooting depth. J. Soil Sci. 31:155-173.

Cameron,D.R., and C.G.Kowalenko. 1976. Modelling nitrogen processes in soil: mathematical development and relationships. Can. J. Soil Sci. 56:71-78.

Campbell,C.A. 1978. Soil organic carbon, nitrogen and fertility. p.173-271. In M.Schnitzer and S.U.Khan (ed.) Soil organic matter. Developments in soil science 8. Elsevier Scientific Publishing Co., New York.

Carter,J.N., O.L.Bennett, and R.W.Pearson. 1967. Recovery of fertilizer nitrogen under field conditions using N-15. Soil Sci. Soc. Am. Proc. 31:50-6.

Chichester,F.W. 1977. Effects of increased fertilizer rates on nitrogen content of runoff and percolate from monolith lysimeters. J. Environ. Qual. 6:211-216.

Chichester,F.W. 1969. Nitrogen in soil organo-mineral sedimentation fractions. Soil Sci. 107:356-363.

Chichester,F.W., and S.J.Smith. 1978. Disposition of N-15 labelled fertilizer nitrate applied during corn culture in field lysimeters. J. Environ. Qual. 7:227-233.

Cho,C.M. 1971. Convective transport of ammonium with nitrification in soil. Can. J. Soil Sci. 51:339-30.

Cooke,G.W. 1976. A review of the effects of agriculture on the chemical composition and quality of surface and underground waters. p.5-57. In Agriculture and water quality. MAFF Tech. Bull. 32. HMSO, London.

Craswell,E.T., and A.E.Martin. 1975. Isotopic studies of the nitrogen balance in a cracking clay. II. Recovery of nitrate N-15 added to columns of packed soil and microplots growing wheat in the field. Aust. J. Soil Res. 13:53-61.

Craswell,E.T. 1979. Isotopic studies of the nitrogen balance in a cracking clay. IV. Fate of the three nitrogen fertilizers in fallow soil in the field. Aust. J. Soil Res. 17:317-323.

Crowther,E.M., and T.J.Mirchandani. 1931. Winter leaching and manurial value of green manures and crop residues for winter wheat. J. Agric. Sci. 21:493-525.

Davidson,J.M., and P.S.C.Rao. 1978. Use of mathematical relationships to describe the behaviour of nitrogen in the crop root zone. p.291-319. In P.F.Pratt (ed.) Management of Nitrogen in Irrigated Agriculture. Proc. Natl. Conf. 15-18 May 1978. University of California, Riverside.

Davidson,J.M., P.S.C.Rao, and R.E.Jessup. 1978. Crititique of computer simulation modelling for nitrogen in

irrigated croplands. p.131-143. In D.R.Nielson and J.G.MacDonald (ed.) Nitrogen in the environment, vol.1. Academic Press,Inc., New York.

Dev,G., and D.A.Rennie. 1979. Isotope studies on the comparative efficiency of nitrogenous sources. Aust. J. Soil Res. 17:155-162.

Douglas,J.A., D.P.Sinclair, and T.E.Ludecke .1972. A maize crop rotation study in Poverty Bay. Proc. Agron. Soc. N.Z. 2:21-30.

Dowdell,R.J., J.R.Burford and R.Crees. 1979. Losses of nitrous oxide dissolved in drainage water from agricultural land. Nature 278:342-3.

Duffy,J., C.Chung, C.Boast, and M.Franklin. 1975. A simulation model of biophysiochemical transformations of nitrogen in tile drained corn belt soil. J. Environ. Qual. 4: 477-486.

Dutt,G.R., M.J.Shaffer, and W.J.Moore. 1972. Computer simulation model of dynamic biophysiochemical processes in soils. Tech. Bull. 196, Agric. Exp. Stn., University of Arizona.

Elliott,J.C. and P.E.H.Gregg. 1979. Preliminary investigations into some aspects of maize fertilizer nitrogen requirements. Proc. N.Z. Fertilizer Manufacturers Association. 17th Conference. pp. 119-123.

Endelman,F.J., M.L.Northup, D.R.Keeney, J.R.Boyle, and R.R.Hughes. 1972. A systems approach to an analysis of the terrestrial nitrogen cycle. J. Environ. Sys. 2:3-19.

Epstein,E., and C.E.Hagen. 1952. A kinetic study of the absorption of alkali cations by barley roots. Plant Physiol. 27:457-474.

Erickson,A.E., and B.G.Ellis. 1971. The nutrient content of drainage water from agricultural land. Michigan Agrl. Exp. Sta. Res. Bull. 31, 16p.

Fack,H.J. 1965. Tracer studies on nitrogen transformations in Ontario soils. Agron. Abs. 83. Am. Soc. Agron., Madison, Wisc.

Farquhar,G.D., R.Wetselaar, and P.M.Firth. 1979. Ammonia volatilisation from senescing leaves of maize. Science, 203:1257-8.

Fiedler,R., and G.Proksch. 1975. The determination of nitrogen-15 by emission and mass spectrometry in biochemical analysis. A review. Anal. Chim. Acta. 78:1-62.

Firestone,M.K. 1982. Biological denitrification. p.289-326. In F.J.Stevenson (ed.) Nitrogen in Agricultural Soils, Agronomy 22, Am. Soc. Agron., Madison, Wisc.

Ford,G.W., and D.J.Greenland. 1968. The dynamics of partly humified organic matter in some arable soils. Trans. Ninth Int. Cong. Soil Sci. 2:403-410.

Frissel,M.J., and J.A.van Veen. 1981. Simulation model for nitrogen immobilisation and mineralisation. p.359-381. In I.K.Iskandar (ed.) Modelling waste water renovation by land disposal. John Wiley and Sons, Inc., New York.

Gandar,P.W., and P.E.H.Gregg. 1979. Designing a long-term nitrogen balance experiment. Proc. Agron. Soc. N.Z. 9:29-34.

Gardner,W.R. 1965. Movement of nitrogen in soil. p.550-572. In Soil Nitrogen. Agronomy 10. Am. Soc. Agron., Madison, Wisc.

Gasser,J.K.R. 1961. Soil nitrogen. IV. Correlations between laboratory measurements of soil mineral N and crop yields and responses in pot and field experiments. J. Sci. Food Agric. 12:562-5.

Gast,R.G., W.W.Nelson, and G.D.Randall. 1978. Nitrate accumulation in soils and loss in tile drainage following nitrogen applications in continuous corn. J. Environ. Qual. 7:258-261.

Geist,J.M., J.O.Reuss, and D.D.Johnson. 1970. Prediction of nitrogen fertilizer requirements of field crops. II. Application of theoretical models to malting barley. Agron. J. 62:385-9.

Goh,K.M., and P.E.H.Gregg. 1982. Field studies on the fate of radioactive sulphur fertilizer applied to pastures. Fert. Res. 3:337-351.

Goleb,J.A., and V.Middelboe. 1968. Optical nitrogen-15 analysis of small nitrogen samples with a mixture of helium and xenon to sustain the discharge in an electrodeless tube. Anal. Chim. Acta 43:229-234.

Greenland,D.J. 1971. Changes in N status and physical condition of soils under pastures, with special reference to the maintanance of the fertility of Australian soils used for growing wheat. Soils and Fertilizers 34:237-251.

Greenwood,D.J. 1979. New approaches to forecasting the fertilizer requirements of vegetable crops. J. Royal Agric. Soc. England. 140:101-8.

Hardey,F. 1946. Seasonal fluctuations of soil moisture and nitrate in humid tropical climates. Trop. Agr. (Trinidad). 23:40-49.

Harmsen,G.W. and D.A.van Shreven. 1955. Mineralisation of organic N in soils. Adv. Agron. 7:299-398.

Harrold,L.L., and F.R.Dreibelbis. 1967. Evaluation of agricultural hydrology by monolith lysimeters. USDA Tech. Bull. 1367, 123p. Washington DC.

Hart,P.B.S., K.M.Goh, and T.E.Ludecke. 1979. Nitrogen mineralisation in fallow and wheat soils under field and laboratory conditions. N.Z. J. Agric. Res. 22:115-125.

Hauck,R.D. 1971. Quantitative estimates of nitrogen cycle processes - concepts and review. p.65-80. In Nitrogen-15 in soil - plant studies. IAEA, Vienna.

Hauck,R.D. and J.M.Bremner. 1976. Use of tracers for soil and fertilizer N research. Adv. Agron. 28:219-266.

Holmes,J.W., and C.L.Watson. 1967. The water budget of irrigated pasture and land near Murray bridge, South Australia. Agrl. Met. 4:177-188.

Hood,A.E.M. 1976. The leaching of nitrates from intensively managed grassland at Jealott's Hill. p.201-221. In Agriculture and water quality. MAFF Tech. Bull. 32. HMSO, London.

Houlston,J.R., and B.W.Shilton. 1958. Sulphur isotope variations in nature - part 4. Measurement of sulphur isotopic ratio by mass spectrometry. N.Z. J. Sci. 1:91-102.

Jackman,R.H. 1964. Accumulation of organic matter in some New Zealand soils under permanent pasture. II. Rates of mineralisation of organic matter and supply of available nutrients. N.Z. J. Agric. Res. 7:472-9.

Jansson,S.L. 1958. Tracer studies on nitrogen transformations in soil with special attention to mineralisation - immobilisation relationship. Ann. Roy. Agr. Coll., Sweden. 24:101-361.

Jansson,S.L. 1971. Use of N-15 in studies of soil nitrogen. p.129-166. In A.D.McLaren and J.Skujins (ed.) Soil Biochemistry II. Marcel Dekker Inc., New York.

Jenkinson,D.S. 1966. The priming action. p.199-208. In The use of isotopes in soil organic matter studies. FAO/IAEA, Pergamon Press, Inc., New York.

Johnston,A.E. 1976. Additions and removals of N and P in long term experiments at Rothamsted and Woburn and the effect of the residues on total soil N and P. p.111-144. In Agriculture and water quality. Technical Bull. 32, MAFF, HMSO, London.

Jones,M.B., C.C.Delwiche, and W.A.Williams. 1977. Uptake and losses of N-15 applied to annual grass and clover in lysimeters. Agron. J. 69:1019-1023.

Kanchanasut,P., and D.R.Scotter. 1982. Leaching patterns in soil under pasture and crop. Aust. J. Soil Res. 20:193-202.

Kanemasu,E.T., V.P.Rasmussen, and J.Bagley. 1978. Estimating water requirements for corn with a "pocket" calculator. Bulletin 615, Agri. Expt. Sta., Kansas University.

Keeney,D.R. 1982. Nitrogen management for maximum efficiency and minimum pollution. p.605-649. In F.J.Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22. Am. Soc. Agron., Madison, Wisc.

Keeney,D.R., and A.N.Macgregor. 1978. Short-term cycling of N-15 urea in a ryegrass- white clover pasture. N.Z. J. Agric. Res. 21:443-8.

Keeney,D.R., and M.J.Tedesco. 1973. Sample preparation for and nitrogen isotope analysis by the NOl-4 emission spectroscope. Anal. Chim. Acta 65:19-34.

Keeney,D.R., and J.M.Bremner. 1967. Determination and isotope ratio analysis of different forms of nitrogen in soils: 4. Mineralisable nitrogen. Soil. Sci. Soc. Am. Proc. 31:34-9.

Kerr,J.P., and B.E.Clothier. 1975. Modelling evapotranspiration of a maize crop. Proc. Agron. Soc. N.Z., 5:49-53.

Kirkham,D., and W.V.Bartholomew. 1954. Equations for following nutrient transformations in soil, utilizing tracer data. Soil Sci. Soc. Am. Proc. 18:33-4.

Kissel,D.E., S.J.Smith, and D.W.Dillow. 1976. Disposition of fertilizer nitrate applied to swelling clay soil in the field. J. Environ. Qual., 5:66-71.

Kissel,D.E., S.J.Smith, W.L.Hargrove, and D.W.Dillow. 1977. Immobilisation of fertilizer nitrate applied to a swelling clay soil in the field. Soil Sci. Soc. Am. J. 41:346-9.

Kissel,D.E., and S.J.Smith. 1978. Fate of fertilizer nitrate applied to coastal bermudagrass on a swelling clay soil. Soil Sci. Soc. Am. J. 42:77-80.

Kowalenko,C.G., and D.R.Cameron. 1978. Nitrogen transformations in soil - plant systems in three years of

field experiments using tracer and non-tracer methods on an ammonium-fixing soil. Can. J. Soil Sci. 58:195-208.

Kundler,P. 1970. Utilisation, fixation, and loss of fertilizer nitrogen. (Review of international results of the last 10 years basic research). Albrecht-Thaer-Arch. 14(3):191-210.

Ladd,J.N., J.W.Parsons, and M.Amato. 1977. Studies on nitrogen immobilisation and mineralisation in calcareous soils: II. Mineralisation of immobilised nitrogen from soil fractions of different particle size and density. Soil Biol. Biochem. 9:319-325.

Ladd,J.N., J.M.Oades, and M.Amato. 1981a. Microbial biomass formed from C-14, N-15 labelled plant material, decomposing in soils in the field. Soil Biol. Biochem. 13:119-126.

Ladd,J.N., J.M.Oades, and M.Amato. 1981b. Distribution and recovery of N from legume residues decomposing in soils sown to wheat in the field. Soil Biol. Biochem. 13:251-6.

Laura,R.D. 1974. Effects of neutral salts on carbon and nitrogen mineralisation of organic matter in soils. Plant Soil 41:113-127.

Laura,R.D. 1975. On the "priming effect" of ammonium fertilizers. Soil Sci. Soc. Am. Proc. 39:385.

Legg,J.O., and F.E.Allison. 1959. Recovery of N-15 tagged nitrogen from ammonium-fixing soils. Soil Sci. Soc. Am. Proc. 23:131-4.

Legg,J.O., and G.Stanford. 1967. Utilisation of soil and fertilizer N by oats in relation to the available N status of soils. Soil Sci. Soc. Am. Proc. 31:215-9.

Legg,J.O., and J.J.Meisinger. 1982. Soil nitrogen budgets. p.503-66. In F.J.Stevenson (ed.). Nitrogen in Agricultural Soils. Agronomy 22. Am. Soc. Agron., Madison, Wisc.

Logan,T.J., G.W.Randall, and D.R.Timmons. 1980. Nutrient content of tile drainage from cropland in the north central region of USA. Res. Bull. 1119. Ohio Agrl. Res. Development center. Ohio.

Low,A.J., and F.J.Piper. 1957. Nitrogen, sulphur, and carbon uptake from some nitrogenous fertilizers using N-15, S-35, and C-13 as tracers. J. Agr. Sci. 49:56-59.

Ludecke,T.E., and K.C.Tham. 1971. Seasonal variations in the levels of mineral nitrogen in two soils under different management systems. Proc. Agron. Soc. N.Z. 1:203-214.

MacKenzie,A.J., and F.G.Viets. 1974. Nutrient and other chemicals in agricultural drainage waters. p.489-511. In J.van Schilfgaarde (ed.) Drainage for agriculture. Agronomy 17. Am. Soc. Agron., Madison, Wisc.

Martin,A.E., and G.W.Skyring. 1962. Losses of nitrogen from soil - plant system. p.19-34. In A review of nitrogen in the tropics with particular reference to pastures. Commonw. Bur. Past. Field Crops, Tech. Bull. 46., Hurley (England).

Martin,A.E., E.F.Henzell, P.J.Ross and K.P.Haydock. 1962. Isotopic studies on the uptake of nitrogen by pasture grasses. I. Recovery of fertilizer nitrogen from the soil : plant system using rhodes grass in pots. Aust. J. Soil Res. 1:169-184.

McIlroy,I.C., and D.E.Angus. 1964. Grass, water, and soil evaporation at Aspendale. Agr. Meteorol. 1:201-224.

McLaren,A.D. 1969. Steady state studies of nitrification in soil: Theoretical considerations. Soil Sci. Soc. Am. Proc. 33:273-6.

McLaren,A.D. 1971. Kinetics of nitrification in soil: Growth of the nitrifiers. Soil Sci. Soc. Am. Proc. 35:91-5.

McNeal,B.L., and P.F.Pratt. 1978. Leaching of nitrate from soils. p.195-230. In Management of nitrogen in irrigated agriculture. Proc. Natl. Conf. 15-18 May 1978. University of California, Riverside.

Megusar.F. 1968. Depressing effects on mineralisation caused by the addition of mineral nitrogen to soil. p.143-149. In Isotopes and radiation in soil organic matter studies. IAEA. Vienna.

Mehran,M., and K.K.Tanji. 1974. Computer modelling of nitrogen transformations in soils. J. Environ. Qual. 3:391-395.

Menzies,I.G. 1980. Trends in nitrogen fertilizer use. N.Z. Agric. Sci. 14:105-8.

Meyer,G.W., B.D.McCaslin, and R.G.Gast. 1974. Sample preparation and N-15 analysis using a Statron NO1-5 optical analyzer. Soil Sci. 117:378-385.

Miller,M.H. 1979. Contribution of nitrogen and phosphorus to subsurface drainage water from intensively cropped mineral and organic soils in Ontario. J. Environ. Qual. 8:42-8.

Myers,R.J.K., and E.A.Paul. 1971. Plant uptake and immobilisation of N-15 labelled ammonium nitrate in a field experiment with wheat. p.55-64. In Nitrogen-15 in Soil-Plant Studies. IAEA. Vienna.

NaNagara,T., R.E.Phillips, and J.E.Leggett. 1976. Diffusion and mass flow of nitrate N into corn roots under field conditions. Agron. J. 68:67-72.

Nelson,D.W. 1982. Gaseous losses of nitrogen other than through denitrification. p.327-362. In F.J.Stevenson (ed.). Nitrogen in Agricultural Soils, Agronomy 22. Am. Soc. Agron., Madison, Wisc.

Nuttall,W.F. 1973. Yield response of Conquest barley as affected by nitrogen fertilizer and soil tests for ammonium and nitrate nitrogen. Can. J. Soil Sci. 53:163-8.

Nye,P.H., and J.A.Spiers. 1964. Simultaneous diffusion and mass flow to plant roots. Trans. 8th Int. Cong. Soil Sci. 3:535-542. Bucharest.

Olsen,S.R., and W.D.Kemper. 1968. Movement of nutrients to plant roots. Adv. Agron. 20:91-151.

Olsen,R.J., R.F.Hensler, O.J.Attoc, S.A.Witzel, and L.A.Peterson. 1970. Fertilizer nitrogen and crop rotation in relation to movement of nitrate nitrogen through soil profiles. Soil Sci. Soc. Am. Proc. 34:448-452.

Olson,R.A., and L.T.Kurtz. Crop nitrogen requirements, utilization, and fertilization. p.567-604. In F.J.Stevenson (ed.). Nitrogen in Agricultural Soils. Agronomy 22. Am. Soc. Agron., Madison, Wisc.

Olson,R.V., L.S.Murphy, H.C.Moser, and C.W.Swallow. 1979. Fate of tagged nitrogen applied to winter wheat. Soil Sci. Soc. Am. J. 43:973-5.

Olson,R.V. 1980. Fate of tagged nitrogen fertilizer applied to irrigated corn. Soil Sci. Soc. Am. J. 44:514-7.

Overrein,L.N., and P.G.Moe. 1967. Factors affecting urea hydrolysis and ammonia volatilization in soil. Soil Sci. Soc. Am. Proc. 31:57-61.

Owens,L.D. 1960. Nitrogen movement and transformations in soils as evaluated by a lysimeter study utilising isotopic nitrogen. Soil Sci. Soc. Am. Proc. 24:372-6.

Patrick,W.H., and K.R.Reddy. 1976. Fate of fertilizer nitrogen in flooded rice soil. Soil Sci. Soc. Am. J. 40:678-681.

Perschke,,H., G.Proksch, E.A.Keroe, and A.Muehl. 1971. Improvements in the determination of N-15 in the low concentration range by emission spectrometry. Anal. Chim. Acta. 53:459-463..

Priestley,C.H.B., and R.J.Taylor. 1972. On the assessment of surface heat flux and evaporation using large-scaale parameters. Month. Weather Rev., 100:81-92.

Pruitt,W.O., and D.E.Angus. 1960. Large weighing lysimeter for measuring evapotranspiration. Am. Soc. Agr. Eng. Trans. 3:13-15.

Quin,B.F. 1982. Indirect evidence for large-scale nitrogen losses from wheat foliage to the atmosphere. In Nitrogen balances in New Zealand ecosystems. DSIR, New Zealand. pp.205-8.

Quin,B.F., and E.G.Drewitt. 1979. The growth, nitrogen uptake and yield of spring-sown wheat on Lismore silt loam. Proc. Agron. Soc. N.Z. 9:133-8.

Quinn,B.F., E.G.Drewitt and R.C.Stephen. 1982. A soil incubation test for estimating wheat yields and nitrogen requirements. Proc. Agron. Soc. N.Z. 12:35-40.

Rao,K.P. and D.W.Rains. 1976. Nitrate absorption by barley. 1. Kinetics and energetics. Plant Physiol. 57:55-8.

Reddy,K.R., R.Khaleel, M.R.Overcash, and P.W.Westerman. 1979a. A non-point source model for land areas receiving animal waste: I. Mineralisation of organic nitrogen. Trans. ASAE 22:863-872.

Reddy,K.R., R.Khaleel, M.R.Overcash, and P.W.Westerman. 1979b. A non-point source model for land areas receiving animal waste: II. Ammonia volatilisation. Trans. ASAE 22:1398-1405.

Ross,D.J., K.R.Tate, and A.Cairns. 1982. Biochemical changes in a yellow - brown loam and a central gley soil converted from pasture to maize in the Waikato area. N.Z. J. Agric. Res. 25:35-42.

Russell,E.W. 1973. Soil condition and plant growth. 10th ed., Longmans, London.

Russell,J.S. 1975. A mathematical treatment of the effect of cropping systems on soil organic nitrogen in two long term sequential experiments. J. Soil Sci. 120:37-44.

Sabey,B.R., L.R.Frederick, and W.V.Bartholomew. 1959. The formation of nitrate from ammonium nitrogen in soils.

III. Influence of temperature and initial population of nitrifying organisms on the maximum rate and delay period. Soil Sci. Soc. Am. Proc. 23:462-5.

Sankhayan,S.D., and U.C.Shukla. 1976. Rates of urea hydrolysis in five soils of India. Geoderma 16:171-8.

Saxton,K.E., G.E.Schuman, and R.E.Burwell. 1977. Modelling nitrate movement and dissipation in fertilized soils. Soil Sci. Soc. Am. J. 41:265-271.

Scotter,D.R. 1978. Preferential solute movement through larger soil voids. I. Some computations using simple theory. Aust. J. Soil Res. 16:257-267.

Scotter,D.R., B.E.Clothier and M.A.Turner. 1979. The soil water balance in a Fragiaqualf and its effect on pasture growth in central New Zealand. Aust. J. Soil Res. 17:455-465.

Scotter,D.R. and P.Kanchanasut. 1981. Anion movement in a soil under pasture. Aust. J. Soil Res. 19:299-307.

Sears,P.D., V.C.Goodall, and R.H.Jackman. 1965. Pasture growth and soil fertility. IX. Repeated cropping of a soil previously under high quality permanent pasture. N.Z. J. Agr. Res. 8:497-510.

Selim,H.M., and I.K.Iskandar. 1981. Modelling nitrogen transport and transformations in soils: I. Theoretical considerations. Soil Sci. 131:233--241.

Shaffer,M.J., and S.C.Gupta. 1981. Hydrosalinity models and field validation. p.137-181. In I.K.Iskandar (ed.) Modelling wastewater renovation by land treatment. John Wiley and Sons, Inc., New York.

Sharpley,A.N., and J.K.Syers. 1981. Amounts and relative significance of runoff types in the transport of nitrogen into a stream draining an agricultural watershed. Water, Air, and Soil Pollut. 15:299-308.

Shingo Mitsui. 1968. Urea, its characteristics and efficient use as fertilizer in Japan. Published by Urea Research Organisation of Japan ammonium sulphate industry association, Tokyo.

Shuford,J.W., D.D.Fritton, and D.E.Baker. 1977. Nitrate nitrogen and chloride movement through undisturbed field soil. J. Environ. Qual. 6:736-9.

Smith,S.J., and R.J.Davis. 1974. Relative movement of bromide and nitrate through soils. J. Environ. Qual. 3:152-5.

Smith,C.J., and P.M.Chalk. 1980. Comparison of the efficiency of urea, aqueous ammonia and ammonium sulphate as nitrogen fertilizers. Plant and Soil, 55:333-7.

Soper,R.J., G.J.Racz, and P.I.Fehr. 1971. Nitrate nitrogen in the soil as a means of predicting the fertilizer nitrogen requirements of barley. Can. J. Soil Sci. 51:45-9.

Stanford,G. 1982. Assessment of soil nitrogen availability. p.651-688. In F.J.Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22. Am. Soc. Agron. Madison, Wisc.

Stanford,G., and E.Epstein. 1974. Nitrogen mineralisation - water relations in soils. Soil Sci. Soc. Am. Proc. 38:103-6.

Steele,K.W. 1982. The nitrogen economy of crop systems. In Nitrogen balances in New Zealand ecosystems. DSIR, New Zealand. pp.157-162.

Steele,K.W., D.M.Cooper, and C.B.Dyson. 1982. Estimating nitrogen fertilizer requirements in maize grain production. I. Determination of available soil nitrogen and prediction of grain yield increase to applied nitrogen. N.Z. J. Agr. Res. 25:199-206.

Stephen,R.C. 1982. Nitrogen fertilizers in cereal production. p.77-94. In P.B.Lynch (ed.) Nitrogen fertilizers in New Zealand agriculture. NZIAS, Wellington.

Stewart,B.A., D.D.Johnson and L.K.Porter. 1963. The availability of fertilizer nitrogen immobilised during decomposition of straw. Soil Sci. Soc. Am. Proc. 27:656-9.

Stojanovic,B.J., and F.E.Broadbent. 1956. Immobilisation and mineralisation of nitrogen during decomposition of plant residues in soil. Soil Sci. Soc. Am. Proc. 20:213-8.

Storrier,R.R. 1965. The availability of mineral nitrogen in a wheat soil from southern New South Wales. Aust. J. Exp. Agric. Anim. Husb., 5:323-328.

Tackett,J.L., E.Burnett, and D.W.Fryrear. 1965. A rapid procedure for securing large, undisturbed soil cores. Soil Sci. Soc. Am. Proc. 29:218-220.

Tanji,K.K. 1981. Approaches and philosophy in modelling. p.20-41. In I.K.Iskandar (ed.) Modelling wastewater renovation by land treatment of wastewater. John Wiley and Sons, Inc., New York.

Tanji.K.K. 1982. Modelling of the soil nitrogen cycle. p.721-772. In F.J. Stevenson (ed.) Nitrogen in Agricultural Soils. Agronomy 22. American Society of Agronomy, Madison, Wisc.

Tanji,K.K. and S.K.Gupta. 1978. Computer simulation modelling for nitrogen in irrigated croplands. p.79-130. In D.R. Nielson and J.G.MacDonald (ed.) Nitrogen in the environment, Vol.I. Academic Press, Inc., London.

Tanji,K.K., F.E.Broadbent, M.Mehran, and M.Fried. 1979. An extended version of a conceptual model for evaluating annual nitrogen leaching losses from croplands. J. Environ. Qual. 8:114-120.

Tanner,C.B. 1967. Measurement of evapotranspiration. p.534-574. In R.M.Hagan, H.R.Haise, and T.W.Edminster. (ed.), Irrigation of Agricultural Lands, Agronomy 11, Am. Soc. Agron., Madison, Wisc.

Taylor,A.O., and K.A.Hughes. 1978. Conservation based forage crop systems for major or complete replacement of pasture. Proc. Agron. Soc. N.Z. 8: 161-6.

Terman,G.L., and S.E.Allen. 1970. Leaching of soluable and slow-release N and K fertilizers from lakeland sand under grass and fallow. Soil and Crop Sci. Soc. of Florida Proc. 30:130-140.

Thomas,G.W. 1970. Soil and climatic factors which affect nutrient mobility. p.1-20. In O.P.Engelsted (ed.) Nutrient mobility in soils: Accumulation and losses. Soil Sci. Soc. Am., Special Pub. 4. Madison, Wisc.

Thomas,G.W., and R.E.Phillips. 1979. Consequences of water movement in macropores. J. Environ. Qual. 8:149-152.

Tillotson,W.R., and R.J.Wagenet. 1982. Simulation of fertilizer nitrogen under cropped situations. Soil Sci. 133:133-143.

Tomlinson,T.E. 1970. Urea-Agronomic Implications. Proc. Fert. Soc. (London) :113.

Turner,M.A., D.R.Scotter, D.G.Bowler, and R.W.Tillman. 1977. Water harvesting: concept and use in a humid climate. DSIR, N.Z., Information Series No. 126:168-174.

Wagenet,R.J., J.W.Biggar, and D.R.Nielsen. 1977. Tracing the transformations of urea fertilizer during leaching. Soil Sci. Soc. Am. J. 41:896-902.

Walker,T.W., and T.E.Ludecke. 1982. An economic evaluation of the use of nitrogen fertilizers on field crops in New Zealand. p.95-120. In P.B.Lynch (ed.) Nitrogen fertilizers in New Zealand agriculture. NZIAS, Wellington.

Watanabe,I., and B.C.Padre. 1979. Inorganic nitrogen movement in tropical soils. II. The fate of ammonium fertilizer in well and poorly drained soils in the rainy season. Soil Sci. and Plant Nutr., 25:627-635.

Watts,D.G., and R.J.Hanks. 1978. A soil - water - nitrogen model for irrigated corn on sandy soils. Soil Sci. Soc. Am. J. 42:492-499.

Westerman,R.L., L.T.Kurtz, and R.D.Hauck. 1972. Recovery of N-15 fertilizer in field experiments. Soil Sci. Soc. Am. Proc. 36:82-6.

Westerman,R.L., and L.T.Kurtz. 1973. Priming effect of N-15 labelled fertilizer on soil nitrogen in field experiments. Soil Sci. Soc. Am. Proc. 37:725-7.

Westerman,R.L., and T.C.Tucker, 1979. In situ transformations of nitrogen-15 labelled materials in Sonoran desert soils. Soil Sci. Soc. Am. J. 43:95-100.

White,R.E., S.R.Wellings, and J.P.Bell. 1983. Seasonal variations in nitrate leaching in structured clay soils under mixed land use. Agic. Water Manage. 7:391-410.

Zamyatina,V.B. 1971. Nitrogen balance studies using N-15 labelled fertilizers based on N-15 studies in the USSR. p.33-45. In Nitrogen-15 in soil, plant studies. IAEA, Vienna.

APPENDIX 1

PRELIMINARY STUDIES USING SOIL CYLINDERS AND EMISSION SPECTROMETRY TO INVESTIGATE THE FATE OF N-15 UREA APPLIED TO A DOUBLE CROPPING SYSTEM

A1.1 INTRODUCTION

The purpose of this preliminary investigation was to measure the N-15 mass balance at various stages of crop growth, in order to understand better the fate of applied N and the likely pathways of major fertilizer N transformations. An additional purpose was to evaluate the use of emission spectrometry for N-15 assay in N-15 balance studies.

A1.2 METHODS AND MATERIALS

At the Tiritea Research Area (see Chapter 7), two experiments with either barley or oats as test crops, were conducted during the summer barley crop season of 1978-79 and winter oat crop season of 1979. In both experiments, twenty soil cylinders were established in the field, in part of a main plot, recently sown with either barley or oats. The soil cylinders were PVC pipes, forced into the soil during the first week of plumule emergence, around single barley plants or around three oat plants. The soil cylinders for the summer experiment were 75 mm in diameter and 150 mm in depth; and for the winter experiment 100 mm in diameter and 450 mm in depth. In both experiments, urea, equivalent of 46 mg N, and enriched with 30 atom percent N-15, was mixed with some soil as an extender and was surface applied to each soil cylinder. This rate corresponds to approximately 100 kgN/ha for summer barley and 60 kgN/ha for winter oats.

At approximately monthly intervals, 4 or 5 randomly chosen soil cylinders were removed from field (4 during the winter experiment and 5 during the summer experiment). The plants in the soil cylinders were harvested prior to removal. The soil cylinders were cut into sections, in depth increments of 50 mm (for the summer experiment) or 75 mm (for the winter experiment). The soil from each section was hand mixed and sub-samples were taken for N-15 analysis. Plant samples were dried and ground.

The soil inorganic N (that includes ammonium, nitrite and nitrate) was extracted in 2 M potassium chloride (KCl) and steam distilled following the procedure described by Bremner and Keeney (1966). Plant and KCl-extracted- soil samples were analysed for total N following the procedure of Bremner (1965a). For N-15 analysis by emission spectrometry, electrodeless discharge tubes were prepared in duplicate, from the N-15 distillates (plant and soil), following a modified Dumas method. This modified Dumas method involved degassing the oxides of copper and calcium (reagents of the Dumas mixture) separately by heating in muffle furnaces at 600 and 1000 C respectively and placing them as a mixture into the discharge tube. Apart from this modification, the procedure described by Fiedler and Proksch (1975) was followed. Emission spectrometer model Statron NO1-5 was used to measure the N isotope ratios.

A1.3 RESULTS AND DISCUSSION

The results of the two experiments are summarised in Table A1.1. The total recovery of applied N in plant and soil components varied between 50 to 90 percent. The

Table A1.1 Fate of N-15 applied to barley and oat crops. Both crops were fertilized with urea, equivalent of 46 mg N, at 30 atom percent N-15 enrichment. Means and standard errors (in parentheses) are given. Soil organic and inorganic N data are for the top 50 mm (*) or 150 mm (#) soil depth for barley, and 450 mm soil depth for oats. N.D. signifies not detectable.

Form of recovered N	Amount of fertilizer N recovered (mg)								
	Days after application (Summer barley)				Days after application (winter oats)				
	13	28	62	120	7	41	71	98	150
Plant	3	7	8(2.9)	10(2.2)	6(0.2)	10(1.2)	14(1.1)	16(2.0)	18(2.2)
Soil organic	4(1.2)*	6(0.4)*	10(1.4)#	12(1.2)#	30(1.8)	21(2.2)	17(0.7)	13(2.4)	7(1.1)
Soil inorganic	31(1.0)*	19(2.2)*	N.D.	N.D.	6(1.3)	1(0.2)	1(0.2)	N.D.	N.D.
Total recovery	38	25	18	22	42(2.2)	32(2.5)	32(1.4)	29(1.9)	24(1.8)
Unaccounted for	8	21	28	24	4(2.2)	14(2.5)	14(1.4)	17(1.9)	22(1.8)

unaccounted for component of the mass balance increased from about 10% at 1 week following urea application to about 50% at harvest of the crop. Measurement error in N-15 analyses by emission spectrometry, was not evaluated. This error component could not be deduced from the literature since the N-15 samples were prepared following a procedure different from that followed by other workers. However, since about 90% recovery of the applied N was obtained at 1 week following urea application, it is speculated that measurement error alone could not account for deficits as high as 50% in the N-15 balance. Other N loss mechanisms, particularly N leaching could be significant.

The amounts and the trends of fertilizer N immobilisation into the soil organic matter, during the two experiments differed (Table A1.1). It is not clear whether such differences were real or resulted from errors in N-15 analyses. The results of N-15 analyses on soil samples for the organic fraction, shown in Table A1.2, indicated that the N-15 enrichment in those samples was close to natural abundance level of N-15 (0.366 atom percent). Emission spectrometric analyses of N-15 in this range may not be accurate as pointed out by Hauck and Bremner (1976), and thus the calculated amounts of fertilizer N immobilised might also not be accurate. Further investigations would therefore be necessary to determine the precision and accuracy of N-15 assay by emission spectrometry.

Table A1.2 N-15 enrichment (atom percent) in soil organic N fraction, resulting from immobilisation of urea N-15 at 30 atom percent enrichment. Urea was applied at sowing the oat crop during winter, 1979. Values are means and standard deviations.

Soil depth mm	Atom % N-15 enrichment in soil organic N — Days following urea application				
	7	41	71	98	150
0-75	0.65 ± 0.13	0.64 ± 0.15	0.53 ± 0.07	0.53 ± 0.10	0.44 ± 0.05
75-150	0.62 ± 0.04	0.37 ± 0.03	0.48 ± 0.09	0.42 ± 0.05	0.39 ± 0.10
150-225	0.42 ± 0.04	0.42 ± 0.03	0.40 ± 0.03	0.42 ± 0.10	0.41 ± 0.12
225-300	0.46 ± 0.06	0.42 ± 0.06	0.44 ± 0.08	0.43 ± 0.07	0.33 ± 0.09
300-450	0.42 ± 0.04	0.47 ± 0.10	0.52 ± 0.06	0.42 ± 0.07	0.43 ± 0.12

Table A1.3 Estimated amounts of N taken up by barley and oat crops from soil and fertilizer N sources. Means and standard errors (in parentheses) are given.

Form of N in the crop	Amount of soil & fertilizer N in crop (kg/ha)							
	Days after application (Summer barley)			Days after application (winter oats)				
	13	62	120	7	41	71	98	150
Fertilizer N	5	17(2.3)	21(1.7)	8(0.3)	13(1.5)	18(1.5)	21(2.4)	23(2.8)
Soil N	6	29(4.5)	52(5.6)	22(0.9)	23(3.3)	41(3.1)	85(7.5)	93(9.3)
Total N	11	46(6.3)	73(6.8)	30(0.7)	36(4.8)	59(4.0)	106(8.7)	116(9.8)

The N-15 values for the soil organic N fraction shown in Table A1.2, indicate that the dilution of the N-15 label could be manyfold since Tokomaru silt loam has a large soil organic N pool (5500 $\pm$ 500 kg N/ha in the top 200 mm of soil depth). Investigations would be required to determine the initial N-15 enrichment in fertilizer material, that would facilitate emission spectrometric assay of N-15 in the organic fraction of the Tokomaru silt loam soil.

Plant uptake of fertilizer N, when expressed as kg/ha (Table A1.3), was similar at the time of final harvest for both crops, despite the fact that the barley crop received 1.7 times more fertilizer N than the oats crop. This could be partly due to different N uptake patterns in the barley and oat crops, and also due to differences in plant density between the summer and winter soil cylinders. These measurements of plant N uptake could only be taken as approximations, since visual inspection during the twelth and subsequent weeks of the winter experiment, indicated that the plants grown in soil cylinders were stunted in growth as compared with plants in the surrounding field. The relevance of plant N uptake data collected by growing plants in soil cylinders, to the plant N uptake in the main plot where the soil cylinders were located, therefore, needed to be evaluated, if small scale experimental data were to be applied to the field situation.

A1.4 CONCLUSIONS

The results of this study indicated that

(1) the total recovery of applied N in plant and soil components could vary between 50 to 90 percent depending on when the N-15 balance determinations were made;

(2) measurement error in N-15 analyses and other N loss mechanisms, such as N leaching should be investigated in order to obtain a more complete N-15 balance sheet;

(3) investigations would also be required to determine the initial N-15 enrichment in fertilizer material, that would facilitate emission spectrometric assay of N-15 in the organic fraction of the Tokomaru silt loam soil;

(4) the estimates of plant N uptake obtained in this study, could only be taken as approximations. The relevance of plant N uptake data, collected by growing plants in soil cylinders, to the plant N uptake in the main plot needed to be evaluated.

APPENDIX 2

SPATIAL AND ANALYTICAL VARIABILITY ASSOCIATED WITH SOIL ORGANIC NITROGEN DETERMINATIONS IN FIELD SOILS

A2.1 INTRODUCTION

The current practice of relying on a mean value for organic N content in the field soils, is open to question in view of large variabilities encountered in soil organic N determinations (Beckett and Webster 1971). Spatial variability of soil organic N, defined in terms of the spatial difference in soil organic N content from site to site in the field (Biggar 1978), is most often not distinguished from analytical errors in determining the soil organic N content. An investigation was taken up to evaluate the analytical error and the spatial variabilty associated with soil organic N determinations.

A2.2 METHODS AND MATERIALS

This investigation was carried out as part of an experiment described more fully in Chapter 3 (Experiment I, described in section 3.2.1). Briefly, this experiment consisted of 15 soil cylinders that were laid out in the field in a randomised block design (5 treatments x 3 blocks). Soil samples obtained from this experiment were analysed for total N following the procedure described by Bremner (1965a).

A2.3 RESULTS AND DISCUSSION

The results of soil organic N determinations are shown in Table A2.1. The values are means [U(j)] and standard deviations calculated from individual kjeldahl N determinations [Y(i)(j)] of three soil samples [j = 1,2,3]

Table A2.1 Soil organic N values (kg N/ha) for soil cylinders. Values are means and standard deviations (S.D.)

Rows	Blocks			Row means
	(1)	(2)	(3)	± S.D.
(1)	4860 ± 113	3638 ± 114	5724 ± 117	4740 ± 913
(2)	6010 ± 102	4496 ± 117	3938 ± 135	4815 ± 934
(3)	3693 ± 158	5301 ± 162	4387 ± 155	4460 ± 712
(4)	5064 ± 156	3583 ± 114	5348 ± 107	4665 ± 828
(5)	4077 ± 98	5795 ± 137	4319 ± 138	4730 ± 813
Block mean ± S.D.	4741 ± 844	4563 ± 919	4743 ± 708	4682 ± 814

taken from each of the 15 soil cylinders [i = 1,2, ..., 15]. Using all the 45 N values [Y(i)(j)], a pooled mean [U] and standard deviation was calculated and found to be 4682 $\pm$ 814 kgN/ha, indicating that the coefficient of variance for the measured data was 17.4% of the mean value. A portion of this variance is likely to be associated with analytical errors while the rest can be attributed to spatial variability associated with the soil organic N content in the field.

In order to partition the variance into its components a simple statistical model was assumed as follows:

$$Y(i)(j) = U \pm A(i) \pm E(ij)$$

where Y(i)(j) is the jth kjeldahl N determination on the ith soil cylinder, U is the mean value for soil organic N content, A(i) is the error due to ith field replicate and E(i)(j) is the error due to analytical replication. Using a one-way analysis of variance test (Freund 1962) on the measured data the error associated with analytical determination [E(i)(j)] was evaluated to be $\pm$ 130 kgN/ha. This suggested that the variance in measured data due to analytical errors was only a small percentage (2.8%) of the mean value while the variance representing spatial variability in the field was large (14.6%). This value for the spatial variability of organic N compares well with the values compiled by Beckett and Webster (1971) for the spatial variability of organic N in soils under crops.

A2.4 CONCLUSIONS

The results of this investigation showed that the analytical errors in soil organic N determinations were

small (2.8% of the mean value) compared with the spatial variability of about 15% of the mean value. Thus, the study indicated that analytical methods used were reliable and accurate. Spatial variability of about 15% in field measurements would be expected.