

# A comparison of the isotope-dilution and the difference method for estimating fertilizer nitrogen recovery fractions in crops. III. Experimental

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## Abstract

Fertilizer nitrogen (N) recovery fractions may be calculated by the difference or the isotope-dilution method. With the first method an apparent recovery fraction (ARF) and with the latter method a <sup>15</sup>N recovery fraction (<sup>15</sup>NRF) is calculated. The two methods may give different results, ARF generally being higher than <sup>15</sup>NRF, particularly in the higher range of ARF-values. Fertilizer N recovery fractions in crops calculated by the two methods were compared using experimental data derived from the literature. The experimental results could be largely explained on the basis of theoretical relationships between <sup>15</sup>NRF and ARF, based on the assumptions of (1) complete and instantaneous mixing of initial soil mineral N and fertilizer N, and (2) zero order kinetics for plant uptake, mineralization and immobilization reactions. In the lower range of ARF-values, values of <sup>15</sup>NRF exceeded those of ARF, presumably because the plant derives its N from fertilizer as well as soil N, even if there is no crop response to applied N. In the higher range of ARF-values, <sup>15</sup>NRF tended to be lower than ARF, presumably because of the occurrence of mineralization-immobilization turnover, which causes the <sup>15</sup>N content of the mineral N pool to decrease. This phenomenon, referred to as 'pool substitution', may be enhanced by increased uptake efficiency of soil N by fertilized crops or by increased mineralization in fertilized treatments. From an agronomic point of view, the use of ARF would be preferred, as this quantity accurately

reflects the overall effect of fertilizer application on crop N uptake.  $^{15}\text{NRF}$  is a meaningful quantity in N-balance studies. It accurately estimates the fertilizer N recovery in the crop, provided  $^{14}\text{N}$  released in mineralization-immobilization turnover in soil is not considered fertilizer N. The theory developed in the present series of papers may contribute to the understanding of the dynamics and transformations of fertilizer N in soil-crop systems and thus help to develop criteria for efficient and effective fertilizer N management.

*Additional keywords:* apparent recovery fraction,  $^{15}\text{N}$  recovery fraction, N fertilizer efficiency, mineralization, immobilization, pool substitution, added N interaction, organic N, mineral N

## Introduction

An important objective of the use of  $^{15}\text{N}$ -enriched fertilizers in agricultural research is to develop criteria for the efficient use of N fertilizers. By comparing different fertilizer sources and alternative types of application, the efficiency of these fertilizer management practices can be assessed in terms of increasing plant uptake and reducing losses of applied N from the soil-plant system.

To measure the amount of fertilizer N recovered in crops, two methods may be used: the difference or indirect method, and the isotope-dilution or direct method. With the difference method the apparent recovery fraction (ARF) of the amount of applied N taken up by a crop is calculated from the difference between total N uptake from fertilized and unfertilized plots per unit of N applied. With the isotope-dilution method the amount of applied N taken up by a crop is estimated from the results of total N uptake and N isotope-ratio analysis of plant materials from fertilized treatments (Harmsen, 2003a).

The difference method is generally assumed to give higher recoveries than the isotope-dilution method (Jansson, 1971; Hauck & Bremner, 1976; Hauck, 1982; Jansson & Persson, 1982). The discrepancy between the two methods has been ascribed to (1) a possible increase in the mineralization of organic N induced by the addition of fertilizer, (2) the irreversible uptake of  $^{15}\text{N}$  into the organic N pool as a result of mineralization-immobilization in the soil, and (3) increased availability of soil mineral N in fertilized treatments ('priming effect') possibly due to better root development (Jansson, 1971).

In two companion papers, simple models for the distribution of  $^{15}\text{N}$ -labeled N over different N pools in the soil-plant system have been presented and the ways these distributions would affect fertilizer N recoveries by crops, calculated by the two methods, have been investigated and discussed (Harmsen, 2003a, b). The objective of the present paper is to compare the predicted relationship between  $^{15}\text{NRF}$  and ARF with results of  $^{15}\text{N}$  research from field and greenhouse trials. An understanding of how the dynamics and transformations of N and the distribution of N over different pools in the soil-plant system affect  $^{15}\text{NRF}$  and ARF may help to focus research on the role of N in agricultural soils.

## Sources of experimental data

There is a vast amount of literature on the application of  $^{15}\text{N}$  in agricultural research. Hauck (1982), for instance, states that over 3000 papers reporting on the use of the stable isotope  $^{15}\text{N}$ , in depleted or enriched form, as a tracer in agricultural research had been published at the time of his review. Therefore a comparison of experimentally determined  $^{15}\text{NRF}$ - and  $\text{ARF}$ -values with model predictions is by necessity selective and cannot be more than the confirmation of some trends.

The Food and Agriculture Organization of the United Nations (FAO) and the International Atomic Energy Agency (IAEA), through their Joint FAO/IAEA Division of Atomic Energy in Food and Agriculture, based in Vienna, Austria, have strongly stimulated the use of isotopes in agricultural research, particularly in developing countries. The Joint FAO/IAEA Division has coordinated a significant number of worldwide studies on N fertilizer use efficiency by different crops, using  $^{15}\text{N}$  tracer techniques. This research programme started in 1962 with rice, soon to be followed by programmes on wheat and maize. One series of experiments on rainfed and irrigated wheat will be used here to investigate whether the predicted relationship between  $^{15}\text{NRF}$  and  $\text{ARF}$  is in agreement with experimental results. The dataset on wheat will be compared with results of a similar dataset on wetland rice. Because these large datasets cover a wide range of soil, climatic and crop conditions, it is not possible to relate the results to specific experimental conditions. However, the datasets show general trends that can be compared with model predictions and thus provide valuable materials for testing the relationship between  $^{15}\text{NRF}$  and  $\text{ARF}$ .

To illustrate how specific experimental conditions may affect the relationship between  $^{15}\text{NRF}$  and  $\text{ARF}$ , a dataset by Broadbent & Carlton (1978) was used as an example.

One of the explanations for the discrepancy between the difference and isotope-dilution method would be the increased native soil N uptake by fertilized crops, presumably because of a more prolific root development in fertilized soils. As this effect would not, or to a lesser extent occur in pot experiments, it is of interest to compare the results from greenhouse studies with those from field experiments. To this end, two datasets were compiled. The first dataset is from a series of greenhouse experiments conducted by the International Fertilizer Development Center (IFDC) in Muscle Shoals, Alabama. The objective of these experiments was to study the effect of N fertilizer management (N-sources, types, timings and rates of N application) on N losses and on fertilizer N recovery by crops under simulated semi-arid conditions. These experiments were conducted within the framework of collaborative N research between IFDC and the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Hyderabad, India, and the International Center for Agricultural Research in the Dry Areas (ICARDA), Aleppo, Syria. The most promising N fertilizer management strategies identified in the greenhouse studies were subsequently tested in field experiments at the ICRISAT and ICARDA experiment stations. These field experiments form the basis of the second dataset. As the soil, climatic and crop conditions were assumed to be similar between the greenhouse and field trials it is of interest to compare experimentally determined  $^{15}\text{NRF}$ - and  $\text{ARF}$ -values between the two

datasets and with predicted results.

Finally, a few case studies from the ICARDA research are presented and the relationship between  $^{15}\text{NRF}$  and ARF is discussed in terms of soil moisture use and N uptake during the growing season.

## Field experiments with wheat

Soper (1974) reported the results of a research programme on fertilizer N recovery by wheat, coordinated by the joint FAO/IAEA Division of Atomic Energy in Food and Agriculture. The main objective of this programme was to gain knowledge on the effects of time of application and N source on the utilization of N by wheat grown under rainfed as well as under irrigated conditions. Field experiments using  $^{15}\text{N}$ -enriched fertilizers were carried out in the period 1968–1972 in 15 countries in Africa, Asia, Europe and Latin America. Fertilizers used were urea, ammonium sulphate and ammonium nitrate. Labeled fertilizers were applied at a rate of  $120 \text{ kg ha}^{-1}$ , either as a single dressing at sowing or as a 60/60 split application.

Apparent recovery fractions and  $^{15}\text{N}$  recovery fractions have been calculated from the 1970/71 and 1971/72 data (Soper, 1974). This resulted in 172 ARF- $^{15}\text{NRF}$  data-pairs covering a range of ARF-values from 0.08 to 0.94 and of  $^{15}\text{NRF}$ -values from 0.14 to 0.74. About 50% of the ARF-values were in the range of 0.25–0.45, and about 75% in the range of 0.20–0.60 (Figure 1). The  $^{15}\text{NRF}$ -values were more concentrated than the ARF-values: about 70% of the  $^{15}\text{NRF}$ -values were in the range of 0.30–0.50 and about 85% in the range of 0.25–0.55. This means they were well below the range of 0.50–0.75 reported by Hauck (1982) for field experiments on pasture and field crops.

The mean values of all data-pairs were  $^{15}\text{NRF} = 0.392$  and  $\text{ARF} = 0.438$ , and the median values  $^{15}\text{NRF} = 0.375$  and  $\text{ARF} = 0.400$ . It may be noted that, with one exception, all  $^{15}\text{NRF}$ -values were below 0.70, which may well point at losses of N in the order of 20–30%. Loss of N might also reduce the range of ARF-values, but in a less consistent manner than in the case of  $^{15}\text{NRF}$ , as it depends on the values of the uptake coefficients,  $\epsilon_o$  and  $\epsilon_p$ , as well as on the nitrogen loss coefficients (after mixing),  $\lambda_o$  and  $\lambda_p$ , in unfertilized and fertilized treatments (Harmsen, 2003a). Nevertheless, it is noteworthy that virtually all ARF-values were below 0.80.

The theoretical relationship between  $^{15}\text{NRF}$  and ARF is given by Harmsen (2003b):

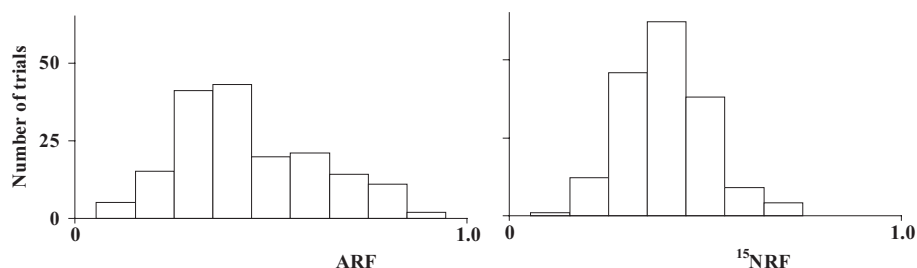


Figure 1. Frequency distributions of ARF (left) and  $^{15}\text{NRF}$  (right) in experiments on N fertilizer use by rainfed and irrigated wheat (after Soper, 1974).

$$^{15}\text{NRF} = \{ \text{ARF} + (1 + \mu_o - \kappa_o - \lambda_o) \varepsilon_o NS_i / NF_i \} \{ 1 - (1 - \varepsilon_f)^{1 + \mu_f} \} / \{ (1 + \mu_f) \varepsilon_f [ 1 + NS_i / (1 - \lambda_{ff}) NF_i ] \} \quad (1)$$

where

- $NS_i$  = initial soil mineral N ( $\text{kg ha}^{-1}$ ),  
 $NF_i$  = the amount of initial N fertilizer applied to the soil ( $\text{kg ha}^{-1}$ ),  
 $\mu_o$ ,  $\kappa_o$ ,  $\lambda_o$  and  $\varepsilon_o$  = coefficients for mineralization, immobilization, loss of N from the soil mineral N pool and plant uptake in unfertilized plots, respectively,  
 $\mu_f$  = a mineralization coefficient for fertilized plots, and  
 $\lambda_{ff}$  = a coefficient to account for loss of fertilizer N (all N coefficients are dimensionless).

It may be noted that not all coefficients required to define the physical system appear in Equation 1. For example,  $\kappa_f$  and  $\lambda_f$  do not appear as they do not affect the relationship between  $^{15}\text{NRF}$  and ARF (Harmsen, 2003a).

Figure 2 shows that the data do not conform to the relationship  $^{15}\text{NRF} = \text{ARF}$  (broken line). In the lower range of ARF-values ( $\text{ARF} \leq 0.20$ ) values of  $^{15}\text{NRF}$  exceed those of ARF, whereas in the higher range ( $\text{ARF} \geq 0.55$ ) values of  $^{15}\text{NRF}$  are lower than the values of ARF. The solid line in Figure 2 represents the linear regression equation:

$$^{15}\text{NRF} = 0.20 + 0.44\text{ARF} \quad (R^2 = 0.56; n = 172) \quad (2)$$

To compare the linear regression equation in Figure 2 (Equation 2) with the theoretical relationship (Equation 1), the values of the ratio  $NS_i/NF_i$  and of the coefficients  $\mu_o$ ,  $\kappa_o$ ,  $\varepsilon_o$ ,  $\mu_f$  and  $\lambda_{ff}$  have to be estimated. This was done on the assumption that (1) losses of fertilizer N were in the range of 20–30% ( $\lambda_{ff} = 0.2-0.3$ ), (2) the ratio  $NS_i/NF_i$  averaged 0.5 in the experiments, and (3) 30–40% of the fertilizer N (i.e.,  $^{15}\text{N}$ ) was immobilized in the organic phase of the soil at harvest ( $\mu_o = \kappa_o = \mu_f = \kappa_f = 0.3-0.4$ ,

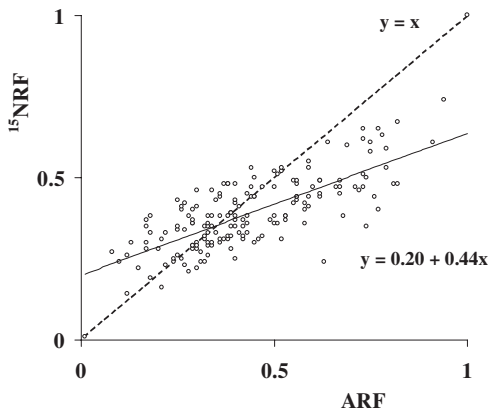


Figure 2.  $^{15}\text{NRF}$  as a function of ARF in experiments on N fertilizer use by rainfed and irrigated wheat (after Soper, 1974).

where subscripts 'o' refer to unfertilized and 'f' to fertilized treatments).

Of course, these are only rough estimates, and the experiments certainly would have covered a wide range of soil and environmental conditions. Nevertheless, the reduced range of  $^{15}\text{NRF}$  would suggest that fertilizer N losses in the order of 20–30% could have occurred. In the case of urea and ammonium sulphate – the N-sources used in the experiments reported – ammonia volatilization is the most likely loss mechanism. Losses in the order of 20–30% due to ammonia volatilization would be consistent with N losses reported in the literature (Craswell & Godwin, 1984). In the irrigated trials, additional losses due to leaching of nitrate, and possibly some denitrification, may have occurred ( $\lambda_f > 0$ ).

A ratio of  $NS_i/NF_i$  of 0.5 is no more than a rough estimate of the mean value in the trials: as the fertilizer rate used, 120 kg ha<sup>-1</sup>, was fairly high, it seems reasonable to assume that initial soil mineral N was lower in most of the experiments. The results in Figure 2 show that the actual soil mineral N contents must have covered a wide range of values, from deficient soils to soils with high mineral N contents, such that an estimated content of  $NS_i = 60 \text{ kg ha}^{-1}$  cannot be more than an approximation of the mean.

Finally, the most likely mechanism explaining the relatively low values of  $^{15}\text{NRF}$  in the higher range of ARF-values would be mineralization-immobilization turnover in the soils concerned. Although little is known about this under the conditions of the actual experiments, it is very unlikely that mineralization-immobilization turnover would *not* have occurred in these agricultural soils. So the question is what the rates of mineralization and immobilization might have been in the experiments. Again, they certainly would have covered a wide range of values, and the assumptions that (1) the rates were the same in unfertilized and fertilized treatments, (2) equilibrium existed between mineralization and immobilization, and (3) the coefficients  $\kappa_o$ ,  $\mu_o$ ,  $\kappa_f$  and  $\mu_f$  were all in the range of 0.3–0.4, cannot be more than an approximation. On the other hand, soil  $^{15}\text{N}$  recoveries of 30–40% are not uncommon in  $^{15}\text{N}$  field experiments (Craswell & Godwin, 1984).

Finally, one would have to estimate the uptake efficiencies of N by the wheat crops. As no specific information on this is available, it will be assumed that the uptake coefficients equal 1 ( $\epsilon_o$ ,  $\epsilon_f = 1$ ).

So, in summary, the coefficients in Equation 1 have been estimated to be in the range of values between two limiting cases:

$$\text{Case (1): } NS_i/NF_i = 0.5, \epsilon_o = \epsilon_f = 1, \lambda_{ff} = 0.2 \text{ and } \mu_o = \kappa_o = \mu_f = \kappa_f = 0.4$$

$$\text{Case (2): } NS_i/NF_i = 0.5, \epsilon_o = \epsilon_f = 1, \lambda_{ff} = 0.3 \text{ and } \mu_o = \kappa_o = \mu_f = \kappa_f = 0.3$$

where it is further assumed that the mean  $^{15}\text{N}$  recovery in the crop was 0.4. Inserting these values in Equation 1 results in the relationships:

$$^{15}\text{NRF} = 0.22 + 0.44\text{ARF} \quad (\text{case 1})$$

$$^{15}\text{NRF} = 0.22 + 0.45\text{ARF} \quad (\text{case 2})$$

which are in good agreement with the linear regression equation in Figure 2.

In fact, one would expect the linear regression equation for data calculated for the same conditions as in Equation 1 to be slightly 'flatter' than the theoretical curve, i.e., the intercept to increase and the slope to decrease slightly (Harmsen, 2003a, b). This 'flattening' of the regression equation was thought to be caused by variation in the values of  $NS_i/NF_i$  and the fact that the uptake efficiencies  $\epsilon_o$  and  $\epsilon_f$  decrease when available N exceeds the crop's demand.

Equation 1 is quite sensitive to the choice of the numerical values of the uptake coefficients  $\epsilon_o$  and  $\epsilon_f$ , and of the ratio  $NS_i/NF_i$ . For example, if this ratio is taken as 0.25, the calculated relationships become:

$$^{15}\text{NRF} = 0.14 + 0.54\text{ARF} \quad (\text{modified case 1})$$

$$^{15}\text{NRF} = 0.14 + 0.57\text{ARF} \quad (\text{modified case 2})$$

Therefore, in summary, a value of  $NS_i/NF_i$  between 0.25 and 0.50 would probably give the best over-all fit. This would suggest that initial mineral N in the soils concerned might have been in the range of 30–60 kg ha<sup>-1</sup>, which is not inconceivable for agricultural soils under wheat production.

The lower  $NS_i$ -values might seem to be at variance with the fact that the response to fertilizer N does not seem very high, i.e., ARF-values were in the range of 0.30–0.50. This, however, is thought to be due primarily to loss of fertilizer N, and may further be caused by growth-limiting factors, such as lack of available moisture in rainfed experiments, nutrient deficiencies (e.g. P or K), salinity and/or alkalinity in irrigated trials, or other factors constraining the uptake of N.

The relatively low value of the intercept of the linear regression equation in Figure 2 may point at increased uptake efficiency in fertilized treatments, i.e.,  $\epsilon_o < \epsilon_f$ .

In summary, it may be concluded that the relationship between  $^{15}\text{NRF}$  and ARF predicted on the basis of estimated values of N coefficients would be similar to the linear regression equation in Figure 2.

## Field experiments with wetland rice

It is of interest to compare the results for rainfed and irrigated wheat with results obtained for an entirely different agro-ecosystem: wetland rice. Results for rice have been compiled from a series of experiments on N efficiency in rice, coordinated by the Joint FAO/IAEA Division in Vienna (Anon., 1976), and fertilizer N recoveries have been published (Vlek & Fillery, 1984) following the methodology presented in Harmsen (2003a), based on an earlier version of the present paper.

In the case of the rice experiments, some 54% of the ARF-values were in the range of 0.20–0.50 and 77% in the range of 0.10–0.60 (Figure 3 – left). The frequency distribution of  $^{15}\text{NRF}$  was strongly concentrated in the lower range of recovery values: 80% of the  $^{15}\text{NRF}$ -values were in the range of 0.10–0.40 and virtually all  $^{15}\text{NRF}$ -values (98.6%) were below 0.60 (Figure 3 – right). This points at losses of fertilizer N in the order of 30–40%. With median values of the recovery fractions in the range of 0.28

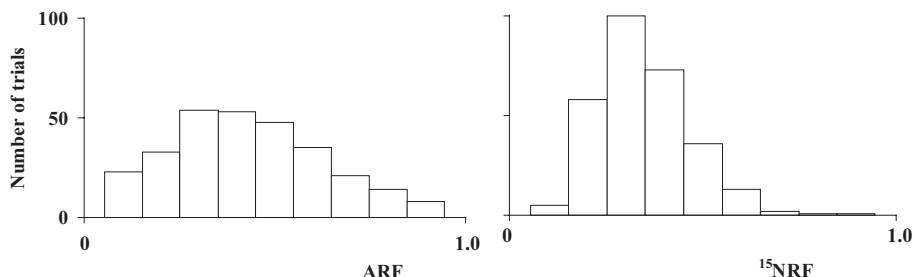


Figure 3. Frequency distributions of ARF (left) and  $^{15}\text{NRF}$  (right) in experiments on N fertilizer use by rice (after Anon., 1976).

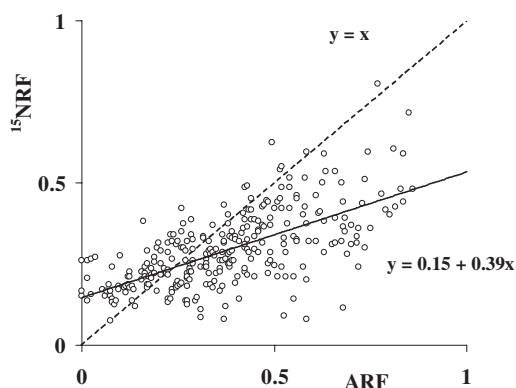


Figure 4.  $^{15}\text{NRF}$  as a function of ARF in experiments on N fertilizer use by rice (after Anon., 1976).

( $^{15}\text{NRF}$ ) to 0.37 (ARF), they were lower than the corresponding values in the wheat experiments reported by Soper (1974) and well below the range of 0.50–0.75 reported by Hauck (1982) for field crops and pasture.

A regression of  $^{15}\text{NRF}$  on ARF resulted in:

$$^{15}\text{NRF} = 0.15 + 0.39\text{ARF} \quad (R^2 = 0.42; n = 289) \quad (3)$$

and thus showed a trend similar to the data in the wheat experiments, even though the crop and land management systems were entirely different (Figure 4). However, in the case of the rice experiments, the intercept (0.15) and slope (0.39) of the linear regression equation were lower than in the case of the wheat experiment (0.20 and 0.44, respectively).

This difference is thought to be due to (1) lower initial soil mineral N and (2) higher losses of fertilizer N in wetland rice systems than in dry farming or well-managed irrigated wheat systems.

Ad (1): During the dry season, soil mineral N in wetland rice systems is mainly in the form of nitrate-N concentrated in the topsoil, because of capillary rise of soil mois-



ture and evaporation at the soil surface. Upon flooding and puddling of the soil, virtually all of this nitrate-N is denitrified in a short period following flooding, when the redox-potential drops quickly. Hence, the remainder of the initial soil mineral N is mainly in the form of ammonium-N. During the growing period there may be a net mineralization of soil organic-N, adding ammonium-N to the soil mineral N pool. Nevertheless, the initial soil mineral N is expected to be low because of the loss of virtually all nitrate-N through denitrification upon flooding.

Ad (2): The basal application of fertilizer N to wetland rice is often a broadcast application in the floodwater, at the time of transplanting. It has been shown that more than 50% of this fertilizer N may be lost from the floodwater, mainly due to ammonia volatilization (Mikkelsen & DeDatta, 1979; Craswell & Vlek, 1979; Weeraratna *et al.*, 1985). The growth of algae in the unshaded floodwater and the hydrolysis of urea and ammonium may raise the pH of the floodwater to values that are conducive to ammonia volatilization. Some of the ammonium in the floodwater may be nitrified and lost due to denitrification when nitrate-N enters the rooting zone of the rice crop, but ammonia volatilization is presumably the major N loss mechanism (Mikkelsen & DeDatta, 1979). The second application of fertilizer N (topdressing) generally occurs when the canopy of the rice crop shades the flood water and crop transpiration rates are high, thus resulting in less ammonia volatilization. Nevertheless, overall losses of fertilizer N in wetland rice systems may well be in the order of 30–40%.

The high losses of fertilizer N combined with a low  $NS_i/NF_i$  ratio and a high biological activity in the soil would explain the lower intercept of the linear regression equation in the case of wetland rice in comparison with the wheat experiment. Hence, the initial values and parameters in Equation 1 have been estimated to be in the range of values between two limiting cases:

$$\text{Case (3): } NS_i/NF_i = 0.25, \epsilon_o = \epsilon_f = 1, \lambda_{ff} = 0.3 \text{ and } \mu_o = \kappa_o = \mu_f = \kappa_f = 0.4$$

$$\text{Case (4): } NS_i/NF_i = 0.25, \epsilon_o = \epsilon_f = 0.4 \text{ and } \mu_o = \kappa_o = \mu_f = \kappa_f = 0.3$$

where it is further assumed that the mean  $^{15}\text{N}$  recovery in the crop was 0.3. Inserting these values in Equation 1 results in:

$$^{15}\text{NRF} = 0.13 + 0.53\text{ARF} \quad (\text{case 3})$$

$$^{15}\text{NRF} = 0.14 + 0.54\text{ARF} \quad (\text{case 4})$$

which is in fairly good agreement with the linear regression equation for wetland rice, considering that the regression equation for the calculated values tends to be 'flatter' than the theoretical curve. If the ratio  $NS_i/NF_i$  is taken as 0.50, the calculated relationship becomes:

$$^{15}\text{NRF} = 0.21 + 0.42\text{ARF} \quad (\text{modified cases 3 and 4})$$

Hence, a value of  $NS_i/NF_i$  in the range of 0.25–0.50 would give a reasonably good fit.

Only the intercept of the linear regression equation of the rice data seems to be slightly lower, which suggests that in the rice experiments  $\epsilon_0$  may have been smaller than 1.

The relatively low response to fertilizer N, i.e., ARF-values in the range of 0.20–0.50, presumably reflects the high losses of fertilizer N in wetland rice systems. Other factors that may have contributed to this include inefficient water management, deficiency of nutrients such as P or K, occurrence of Al-toxicity, competition with weeds or the incidence of other factors constraining the uptake of N.

### Field experiments with maize

Broadbent & Carlton (1978) reported results of field trials utilizing  $^{15}\text{N}$ -depleted N fertilizers on a Yolo fine sandy loam at Davis, California, with maize as the test crop, during three consecutive years, from 1973 to 1975. Experimental treatments included 3 irrigation regimes (20, 60 and 100 cm of water) and 3 fertilizer application rates (90, 180 and 360 kg N ha<sup>-1</sup>). The N fertilizer used was ammonium sulphate.

The soils were initially high in mineral N, and in 1973 there was no yield response to fertilizer N at all; in 1974 there was a yield response up to 90 kg N ha<sup>-1</sup> and in 1975 up to 180 kg N ha<sup>-1</sup>. The higher response in 1975 may have been caused in part by the use of a longer-season (i.e., higher-yielding) maize variety as the test crop in that year.

The ARF- and  $^{15}\text{NRF}$ -values for the three years, averaged over the three irrigation regimes, are plotted in Figure 5. In all years, the recovery fractions decreased with increasing fertilizer application rate. In 1973 – when there was no yield response to fertilizer application – the  $^{15}\text{NRF}$  was higher than the ARF, consistent with the mixing model, i.e., the crop is taking up fertilizer-derived N from the soil mineral N pool in proportion to its relative abundance in this pool, even if there is little or no yield response to fertilizer application (Fried & Dean, 1952; Harmsen, 2003a).

In 1973, the amount of soil-derived N in the crop (Nd<sub>fs</sub>) decreased with increasing fertilizer application rate (Figure 5). So there was a negative (presumably 'real') added N interaction (ANI) (Jenkinson *et al.*, 1985; Hart *et al.*, 1986; Stout, 1995): the crop taking up less soil-derived N because of the increasing proportion of fertilizer-derived N in the soil mineral N pool. In 1974 and 1975 there were positive ANI's, presumably caused by pool substitution of mineralized soil-derived N for immobilized fertilizer-derived N. It may be noted that although the yield response was limited, the crop appeared to take up increasing amounts of total N with increasing N rate, in particular during the 1974 and 1975 growing seasons.

This is also reflected in positive N recovery fractions, decreasing with increasing N rate. Values of  $^{15}\text{NRF}$  as a function of ARF, calculated for the Davis experiment, are plotted in Figure 6 for the three experimental years. It can be seen that the 1973 data are all in the lower range of ARF-values and that  $^{15}\text{NRF} > \text{ARF}$  for this year. The 1974 and 1975 years generated similar datasets, with some ARF-values larger than 1, because of the positive ANI's.

The linear regression equation for the entire dataset was estimated as:

$$^{15}\text{NRF} = 0.32 + 0.29\text{ARF} \quad (R^2 = 0.74; n = 27) \quad (4)$$

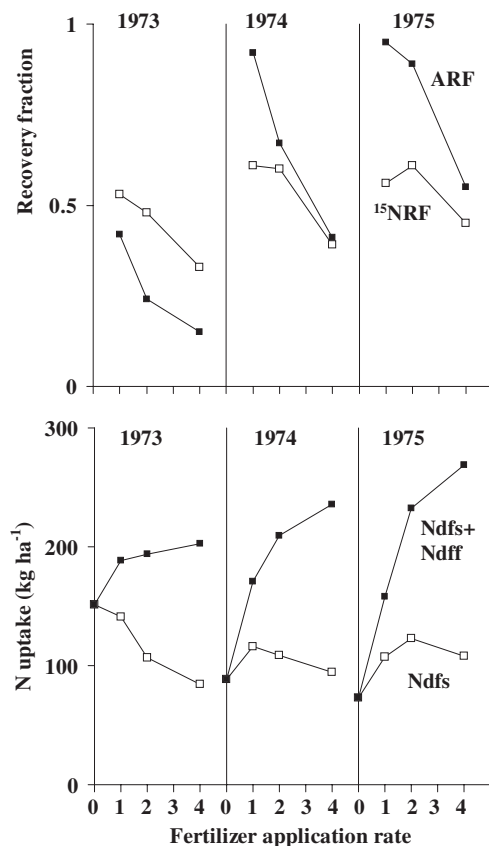


Figure 5. <sup>15</sup>NRF and ARF (top) and soil- (Ndfs) and fertilizer-derived N in the crop (Ndff) (bottom) as functions of fertilizer application rates for three years of experiments on N fertilizer use by maize (after Broadbent & Carlton, 1978). N rates were 0 (0), 90 (1), 180 (2) and 360 kg ha<sup>-1</sup> (4).

from which it can be seen that the linear regression equation is relatively 'flat', i.e., the intercept is relatively high compared with the regression equations in Figures 2 and 4, whereas the slope is relatively low.

Broadbent & Carlton (1978) reported leaching losses of inorganic N at the highest N rate in the order of 128 kg N ha<sup>-1</sup> in 1975, out of which 102 kg N ha<sup>-1</sup> presumably was fertilizer-derived N. No leaching losses were reported for the other seasons and therefore it is assumed that losses of fertilizer N due to leaching were in the order of 5–10% of the fertilizer N applied in the experiment ( $\lambda_{\text{ff}} = 0.05\text{--}0.10$ ). Furthermore, from a nearby experimental site (Kearney) where a similar experiment with irrigated maize was conducted, the fraction of fertilizer N that was unaccounted for in the <sup>15</sup>N balance averaged about 20%. These losses were thought to be due to denitrification. Assuming that the Kearney site was comparable to the Davis site in this respect and that denitrification losses equally affected soil- and fertilizer-derived N, this would

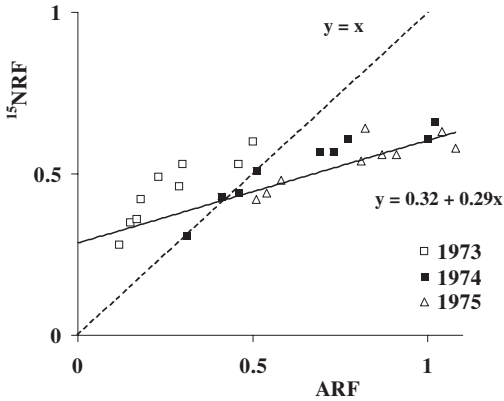


Figure 6.  $^{15}\text{NRF}$  as a function of ARF for three years of experiments on N fertilizer use by irrigated maize (after Broadbent & Carlton, 1978).

result in  $\lambda_o = \lambda_f = 0.2$ , where  $\lambda_o$  and  $\lambda_f$  denote the N losses from the soil mineral N pool, in the case of fertilized treatments, after mixing of soil- and fertilizer-N has occurred.

Mineralization-immobilization turnover did probably occur in the soils at Davis, as suggested by the positive ANI's in 1974 and 1975, and the ARF-values in excess of 1. Hence, from the  $^{15}\text{N}$  balance (about 50%  $^{15}\text{N}$  recovered in the crop), the coefficients are estimated to be  $\mu_o = \kappa_o = \mu_f = \kappa_f = 0.2$ , i.e., it is further assumed that there was equilibrium between mineralization and immobilization, and that the coefficients were the same for fertilized and unfertilized treatments.

Therefore, with  $\varepsilon_o = \varepsilon_f = 1$ ,  $\lambda_o = \lambda_f = 0.2$ ,  $\lambda_{ff} = 0.1$  and  $\mu_o = \kappa_o = \mu_f = \kappa_f = 0.2$ , Equation 1 becomes:

$$^{15}\text{NRF} = \{\text{ARF} + 0.80 \text{NS}_i/\text{NF}_i\} / \{1.20(1.00 + 1.11 \text{NS}_i/\text{NF}_i)\}$$

The ratio  $\text{NS}_i/\text{NF}_i$  presumably was quite high in the present experiment, higher than in the series of wheat and rice experiments reported earlier. Calculated A-values (Fried & Dean, 1952), where  $A = \text{NF}_i(\text{Ndfs}/\text{Ndff})$ , were in the range of 190–270 kg ha<sup>-1</sup>. From this the  $\text{NS}_i/\text{NF}_i$  ratios, averaged over irrigation regimes and years, were calculated as:  $\text{NS}_i/\text{NF}_i = 2.38$  ( $\text{NF}_i = 90$  kg ha<sup>-1</sup>), 1.14 ( $\text{NF}_i = 180$  kg ha<sup>-1</sup>), and 0.68 ( $\text{NF}_i = 360$  kg ha<sup>-1</sup>). Hence, rather than using a single value of  $\text{NS}_i/\text{NF}_i$  in Equation 1, it will be assumed that  $\text{NS}_i/\text{NF}_i$  decreased from 2 at ARF = 0 to 1 at ARF = 1. This means that the relationship sought should be intermediate between:

$$\begin{aligned} ^{15}\text{NRF} &= 0.41 + 0.26\text{ARF} & (\text{NS}_i/\text{NF}_i = 2) \text{ at ARF} = 0 \\ \text{and} \\ ^{15}\text{NRF} &= 0.32 + 0.39\text{ARF} & (\text{NS}_i/\text{NF}_i = 1) \text{ at ARF} = 1. \end{aligned}$$

So if  $\text{NS}_i/\text{NF}_i$  decreases with increasing ARF, the intercept tends to increase and the

slope tends to decrease, resulting in a 'flattening' of the curve, consistent with the data in Figure 6. The relationship:

$$^{15}\text{NRF} = 0.41 + 0.30\text{ARF}$$

which is obtained as the straight line through  $^{15}\text{NRF} = 0.41$  at  $\text{ARF} = 0$  (and  $N\text{S}_i/N\text{F}_i = 2$ ) and  $^{15}\text{NRF} = 0.71$  at  $\text{ARF} = 1$  (and  $N\text{S}_i/N\text{F}_i = 1$ ) is close to the linear regression curve in Figure 6. The intercept is slightly higher than the one of the regression curve in Figure 6, which may point at a slightly lower uptake efficiency in unfertilized plots, e.g.  $\epsilon_0 = 0.8$  would result in an intercept of 0.33 in the calculated relationship. So the model predictions appear to be in general agreement with the data from Broadbent & Carlton (1978).

### Greenhouse experiments with wheat and sorghum

The results of the greenhouse experiments conducted at IFDC, Muscle Shoals, Alabama, have been published in several publications, including Buresh *et al.* (1984; 1990) and Stumpe & Abdel Monem (1986). The experiments were conducted under simulated semi-arid tropical (ICRISAT) or Mediterranean (ICARDA) conditions, with wheat (2 experiments) and sorghum (4 experiments), respectively. The major objective of the experiments was to study N fertilizer use efficiency as affected by fertilizer N sources, timing and type of application, and soil and crop conditions. In most experiments, losses of fertilizer N were determined, by difference, from the amounts of  $^{15}\text{N}$  labeled fertilizer applied and  $^{15}\text{N}$  analysis in soil and plant materials.

The data plotted in Figure 7 represent means for treatments, rather than individual pot yields. The solid curve in Figure 7 represents the linear regression equation:

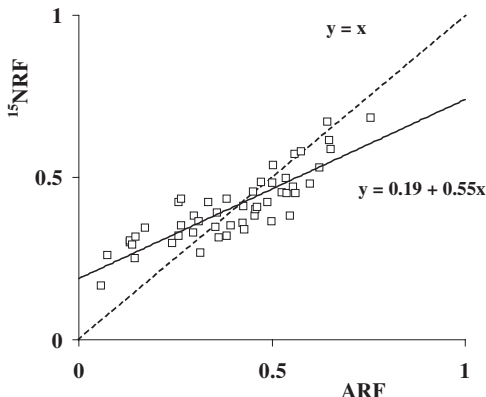


Figure 7.  $^{15}\text{NRF}$  as a function of  $\text{ARF}$  in a series of greenhouse experiments with wheat and sorghum under simulated semi-arid conditions (after Buresh *et al.*, 1984, 1986; Stumpe & Abdel Monem, 1986).

$$^{15}\text{NRF} = 0.19 + 0.55\text{ARF} \quad (R^2 = 0.73; n = 50) \quad (5)$$

One of the soils used in the wheat trials (Uvalde soil) was high in initial soil mineral N, which resulted in low ARF-values. Loss of  $^{15}\text{N}$ , i.e., estimated as the  $^{15}\text{N}$  unaccounted for in the  $^{15}\text{N}$  soil-crop balance, ranged from 11.3 to 26.5% and averaged 17.9%. Main factors affecting losses were soil type (pH), N-source and type of application. For example, losses decreased in the order urea phosphate > urea > ammonium nitrate > sodium nitrate, and were higher for surface application than for incorporation (placement) of urea-N sources. Losses were not much affected by moisture conditions (simulated rainfall), but the effect of moisture on the distribution of  $^{15}\text{N}$  over the soil and plant N pools was highly significant: the quantity of  $^{15}\text{N}$  recovered in the plant increased linearly with increasing moisture availability c.q. simulated rainfall (Buresh *et al.*, 1990).

At low available moisture, virtually all  $^{15}\text{N}$  was recovered in the soil, whereas at high available moisture most of the  $^{15}\text{N}$  was recovered in the crop, leaving about 30% of the applied  $^{15}\text{N}$  in the organic N fraction of the soil. This confirms that under dry farming conditions the amount of N taken up by the crop is determined by available moisture and the moisture-limited potential yield (Harmsen, 2000). So, in general, the uptake efficiencies of N by the crop may be expected to be smaller than 1 under rainfed farming conditions in the dry areas. Against this background it was assumed that  $\epsilon_o = \epsilon_f = 0.5$  in the greenhouse experiments. Of course, this is only an approximation and in reality the uptake coefficients must have ranged from about 0.3 to 0.4 at low moisture availability to close to 1 at the highest moisture levels. Nevertheless, the assumption that  $\epsilon_o = \epsilon_f = 0.5$  underlines the point that under dry farming conditions the availability (or accessibility) of N to the crop is likely to be constrained by available moisture.

Averaged over all trials, about equal amounts of  $^{15}\text{N}$  were recovered in soil and plant materials (41% each). Assuming that (1) about half of the residual N in the soil was in inorganic form and about half in organic form, (2) there was equilibrium between mineralization and immobilization ( $\mu_{o,f} = \kappa_{o,f} = 0.2$ ) and that (3) loss of N was 20% ( $\lambda_{ff} = 0.2$ ), the relationship between  $^{15}\text{NRF}$  and ARF becomes:

$$^{15}\text{NRF} = \{\text{ARF} + \epsilon_o \text{NS}_i/\text{NF}_i\} \{1 - (1 - \epsilon_f)^{1.2}\} / \{1.2\epsilon_f(1 + \text{NS}_i/0.8\text{NF}_i)\}$$

Hence, with  $\epsilon_f = \epsilon_o = 0.5$  (moisture constraint) it follows that:

$$^{15}\text{NRF} = 0.94\{\text{ARF} + 0.5\text{NS}_i/\text{NF}_i\} / (1 + \text{NS}_i/0.8\text{NF}_i)$$

Assuming that  $\text{NS}_i/\text{NF}_i$  was in the range of 0.5–1.0, it follows that:

$$^{15}\text{NRF} = 0.15 + 0.58\text{ARF} \quad (\text{NS}_i/\text{NF}_i = 0.5)$$

or:

$$^{15}\text{NRF} = 0.21 + 0.42\text{ARF} \quad (\text{NS}_i/\text{NF}_i = 1.0)$$

The actual regression equation in Figure 7 is in between these two cases and would thus be well described by a value of  $\text{NS}_i/\text{NF}_i$  in the range of 0.5–1.0.

## Field experiments with wheat and sorghum

A series of  $^{15}\text{N}$  field experiments with wheat and sorghum in a semi-arid environment was compiled from the following sources: (1) field experiments conducted at the ICRISAT experiment station at Patancheru, India (Moraghan *et al.*, 1984a, b) and (2) field experiments conducted at the ICARDA experiment stations at Tel Hadya and Breda in NW Syria during the 1980/81 growing season (Harmsen, Buresh & Vlek, 1982, *unpublished data*; Anon., 1983), the 1983/84 and 1984/85 seasons (Abdel Monem, 1986; Abdelmonem *et al.*, 1988) and the 1991/92 and 1992/93 seasons (Garabet, 1995; Garabet *et al.*, 1998a, b).

The pooled data are plotted in Figure 8. The solid line in Figure 8 represents the linear regression equation:

$$^{15}\text{NRF} = 0.17 + 0.50 \text{ ARF} \quad (R^2 = 0.38; n = 57) \quad (6)$$

This relationship appears to be quite similar to the regression equation obtained for the greenhouse data in the previous chapter, suggesting that the conditions in the greenhouse experiments were indeed comparable to those in the field at ICARDA and ICRISAT.

In the greenhouse experiments some of the  $^{15}\text{NRF}$ -values in the lower range of ARF-values were clearly higher than the corresponding values of ARF, presumably because of the relatively high initial soil mineral N contents. In the field experiments soils were probably lower in available soil mineral N, as there are no values of  $^{15}\text{NRF}$  exceeding ARF in the lower range of ARF-values. In fact, there are very few observations in the lower range, suggesting that, in general, crops responded positively to N application (Figure 8).

The experiments at ICRISAT were on two soil types: Vertisols and Alfisols. Crop

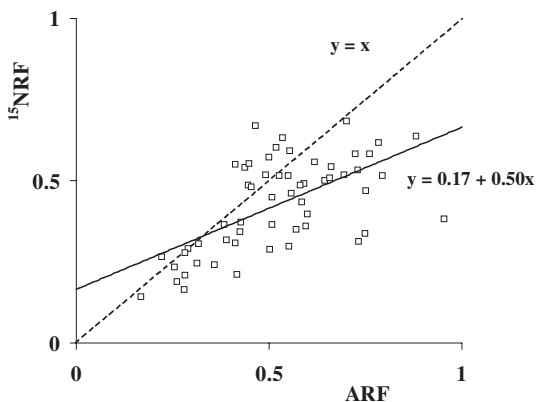


Figure 8.  $^{15}\text{NRF}$  as a function of ARF in a series of field experiments with sorghum and wheat under semi-arid Mediterranean (after K. Harmsen, R.J. Buresh & P.L.G. Vlek, 1982, *unpublished data*; Anon., 1983; Abdel Monem, 1986; Abdelmonem *et al.*, 1988; Garabet, 1995; Garabet *et al.*, 1998a,b) and tropical conditions (after Moraghan *et al.*, 1984a,b; Harmsen & Moraghan, 1988).

response to applied N was highest on the Alfisols in 1981, with ARF-values in the range of 0.65–0.88 and  $^{15}\text{N}$ RF-values in the range of 0.47–0.64. Losses of N were in the range of 12.1 (Alfisols) to 19.7% (Vertisols), ammonia volatilization presumably being the major loss mechanism. It was shown that discrepancies between the difference and isotope-dilution method could be explained in a satisfactory fashion by losses of fertilizer N prior to mixing with the soil mineral N pool and immobilization (pool substitution) of  $^{15}\text{N}$  in the soil organic N fraction (Harmsen & Moraghan, 1988).

## $^{15}\text{N}$ recoveries and balances

The early  $^{15}\text{N}$  research at ICARDA on N transformations and dynamics in soil-crop systems concentrated on the dynamics of inorganic N in soils as this was thought to be relevant for the development of N fertilizer recommendations (Anon., 1983; Harmsen, 1984; 1987). It was shown that losses of fertilizer N were limited, generally in the range of 10–20%. This was confirmed by later research (Abdel Monem, 1986; Garabet, 1995), although a series of experiments conducted by Pilbeam *et al.* (1997a, b) would suggest that N losses could be much higher, in the order of 40–70%. The difference between the two series of experiments is not yet fully understood, but possibly the mode of application of ammonium sulphate solution could explain some of the high N losses (Pilbeam *et al.*, 1997a).

From the data in Table 1 it would appear that (1) N losses were in the range of 0–29%, with median values in the range of 10–17%, (2)  $^{15}\text{N}$  recoveries in the crop ranged from 0.20 to 0.53 and tended to increase with increasing rainfall, and (3)  $^{15}\text{N}$  recoveries in the soil ranged from 0.30 to 0.73 and tended to decrease with increasing rainfall.

The crop  $^{15}\text{N}$  recoveries tended to increase with increasing rainfall (Figure 9),

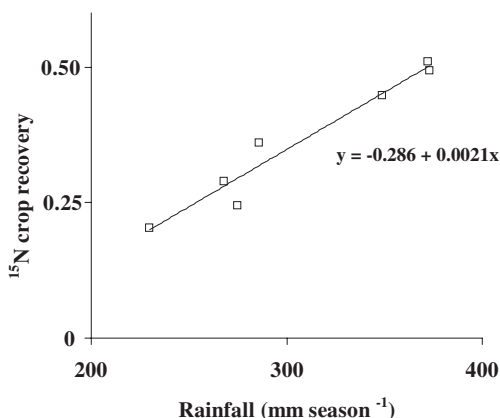


Figure 9.  $^{15}\text{N}$ RF as a function of seasonal rainfall in a series of field experiments with wheat under semi-arid Mediterranean conditions (after K. Harmsen, R.J. Buresh & P.L.G. Vlek, 1982, *unpublished data*; Abdel Monem, 1986; Garabet, 1995).



Table 1. Nitrogen balances of rainfed (mm of seasonal rainfall) and irrigated (IRR) cereal trials at two locations in NW Syria: Breda and Tel Hadya. The sources of nitrogen fertilizer used were ammonium- ( $^{15}\text{NH}_4$ ), nitrate- ( $^{15}\text{NO}_3$ ) and double-labeled ammonium nitrate (AN), ammonium sulphate (AS) and urea. The apparent recovery fraction (ARF) and the  $^{15}\text{N}$  recovery are expressed as a fraction of the amount of  $^{15}\text{N}$  applied. The loss of  $^{15}\text{N}$  is estimated by difference from the amounts applied and recovered in the crop plus the soil.

Site Season	Rain  (mm)	N fertilizer		ARF	<sup>15</sup> N recovery fraction					Ref.
		Source/ Labeled	Rate (kg ha <sup>-1</sup> )		Crop				Loss	
						Mineral	Organic	Total		
Tel Hadya 1980/81[May]	372	AN double	20/40	—	0.53	0.09	0.21	0.30	0.17	(1)
Tel Hadya 1980/81[June]	372	AN double	20/40	0.87	0.49	0.05	0.41	0.46	0.05	(1)
Breda 1980/81	286	AN <sup>15</sup> NH <sub>4</sub>	20/40	—	0.36	0.03	0.32	0.35	0.29	(1)
Breda 1980/81	286	AN <sup>15</sup> NO <sub>3</sub>	20/40	—	0.50	0.06	0.33	0.39	0.11	(1)
Breda 1980/81	286	AN double	20/40	0.38	0.43	0.04	0.33	0.37	0.20	(1)
Tel Hadya 1983/84	230	urea	0/40	0.27	0.20	—	—	0.69	0.11	(2)
Breda 1984/85	268	urea	0/40	0.36	0.29	0.25	0.28	0.53	0.18	(2)
Tel Hadya 1984/85	373	urea	0/40	0.55	0.49	0.04	0.29	0.33	0.18	(2)
Tel Hadya 1991/92	349	AS	100	0.51	0.45	0.21	0.35	0.56	-0.01	(3)
Tel Hadya 1991/92	IRR	AS	100	0.59	0.49	0.03	0.40	0.43	0.08	(3)
Tel Hadya 1992/93	275	AS	100	0.31	0.25	0.30	0.43	0.73	0.02	(3)
Tel Hadya 1992/93	IRR	AS	100	0.43	0.37	0.01	0.52	0.53	0.10	(3)

<sup>1</sup> (1) = Harmsen, K., R.J. Buresh & P.L.G. Vlek, 1982, unpublished; (2) = Abdel Monem, M.A.S., 1986.  
(3) = Garabet, S., 1995.

which is consistent with the results of the greenhouse experiments (Buresh *et al.*, 1990) and field trials in other parts of the world (Pilbeam, 1996). The solid line in Figure 9 represents the linear regression equation:

$$^{15}\text{NRF} = -28.6 + 0.21\text{Rainfall} \quad (R^2 = 0.95; n = 7) \quad (7)$$

which confirms that the correlation between  $^{15}\text{NRF}$  and rainfall (mm per season) is highly significant.

It follows from Table 1 that the proportion of residual soil N in inorganic form decreased with increasing rainfall. The difference between rainfed and irrigated trials at Tel Hadya during the 1991/92 and 1992/93 seasons is remarkable in this respect. In both seasons there were significant amounts of fertilizer-derived inorganic N left in the soil in the rainfed experiments at harvest (21–30 kg ha<sup>-1</sup>), whereas in the irrigated experiments virtually all of this N was either taken up by the crop or transformed into organic N, leaving only 1–3 kg ha<sup>-1</sup> in inorganic form in the soil at harvest (Garabet, 1995).

It may be noted that irrigated treatments are not directly comparable with high-rainfall non-irrigated systems in the same agro-ecological environment. In rainfed systems most of the rainfall occurs during the winter months and early spring, when temperatures and evapo-transpiration rates are low. In irrigated systems, water is supplied in spring, when temperature and evaporative demand are high. This may result in intense biological activity (mineralization-immobilization turnover) to occur in the soil, which would otherwise not have occurred because of the lack of available moisture.

From the data in Table 1 the coefficients in Equation 1 can thus be estimated as follows:  $\epsilon_o = \epsilon_f = 0.5$  (moisture constraint),  $\lambda_{ff} = 0.15$  and  $\mu_o = \kappa_o = \mu_f = \kappa_f = 0.3$ , such that Equation 1 becomes:

$$^{15}\text{NRF} = 0.91\{\text{ARF} + 0.5\text{NS}_i/\text{NF}_i\}/(1 + 1.18\text{NS}_i/\text{NF}_i)$$

Hence, if  $\text{NS}_i/\text{NF}_i = 1$ :

$$^{15}\text{NRF} = 0.21 + 0.42\text{ARF}$$

and if  $\text{NS}_i/\text{NF}_i = 0.5$ :

$$^{15}\text{NRF} = 0.14 + 0.58\text{ARF}$$

The linear regression equation in Figure 8 is intermediate between these two equations and would thus be well described by Equation 1 with a value of  $\text{NS}_i/\text{NF}_i$  between 0.5 and 1.0.

## Dynamics of moisture and nitrogen during the growing season

Values of  $^{15}\text{NRF}$  and ARF not only differ between datasets and with N-rates, they also change in time during the growing season. To illustrate this, one experiment conducted during two seasons at ICARDA will be examined in some more detail. The behav-

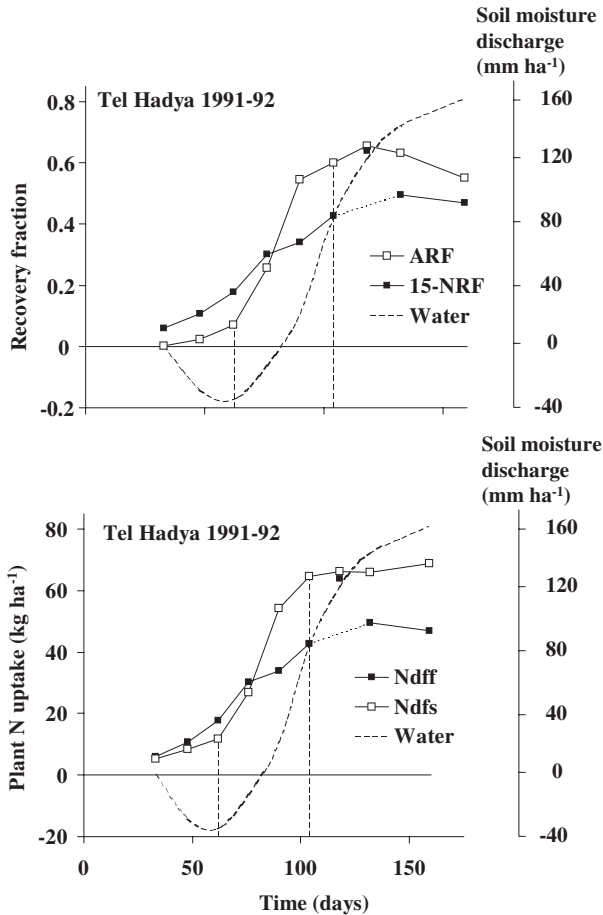


Figure 10. <sup>15</sup>NRF and ARF (top) and Ndff and Ndfs (bottom) as functions of time for N fertilizer use experiments with wheat, conducted at Tel Hadya during the 1991–1992 growing season (after Garabet, 1995).

Four of <sup>15</sup>NRF and ARF as a function of time after January 1 is plotted in Figures 10 and 11 for two contrasting growing seasons at Tel Hadya: a season with above-average rainfall (1991/92: 349 mm) and a season with below-average rainfall (1992/93: 275 mm).

The <sup>15</sup>NRF increased quite smoothly during the entire 1991/92 season (Figure 10), except for one data-point ( $t = 118$  days) which seems to be out of tune with the other and therefore the values of <sup>15</sup>NRF (= Ndff) at 104 and 132 days are connected directly by a broken line, skipping the value at 118 days. In Figures 10 and 11 crop N derived from fertilizer is denoted by Ndff and N derived from soil by Ndfs.

ARF-values increased slowly during the first 50 days of 1992, then increased quite steeply for some 50–60 days and finally leveled off or even decreased during the

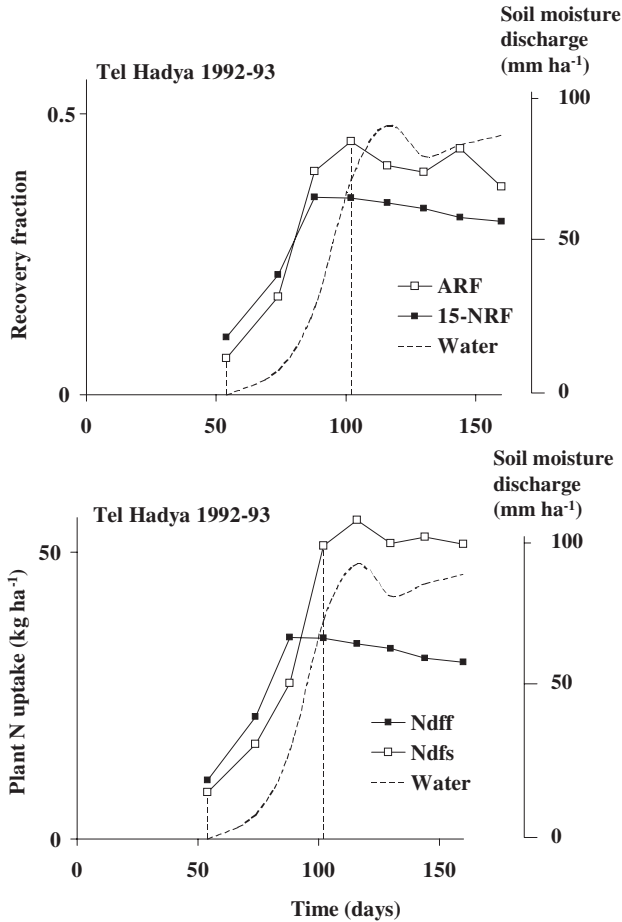


Figure 11. <sup>15</sup>NRF and ARF (top) and Ndff and Ndfs (bottom) as functions of time for N fertilizer use experiments with wheat, conducted at Tel Hadya during the 1992–1993 growing season (after Garabet, 1995).

remainder of the season. The Ndfs-values followed the same pattern as ARF, except for the leveling off after 104 days.

The change in the stored-moisture content of the soil, measured by neutron probe down to 1.80 m depth (Garabet, 1995), is indicated by a smoothened broken line in Figures 10 and 11. The soil moisture profile is still being recharged between 33 and 62 days in 1992, and after that the stored soil moisture is being discharged. The main factor in the discharge is the uptake of moisture by the crop (transpiration), although some soil evaporation also occurs, notably from the upper part of the soil profile. Towards the end of the season, when deep cracks form in the soil, moisture evaporates down to greater depth in the soil (0.5–1.0 m depth).

Therefore, what is shown in Figure 10 between 62 and 104 days is mainly crop tran-

spiration and it can be seen that the steep increase in ARF (c.q. Ndfs) coincides with the use of stored soil moisture by the crop. Assuming that most of the fertilizer N is concentrated in the top 20–40 cm of the soil (Harmsen, 1987) this explains why Ndfs increased steeply during this period, whereas Ndff continued to increase at a much lower rate. The stored soil moisture at depth in the soil contains mainly soil-derived mineral N and when the plant starts using stored soil moisture all of this N enters the crop, thus diluting the crop N pool with soil-derived N. This results in a rather steep increase in ARF (c.q. Ndfs), whereas  $^{15}\text{NRF}$  is not much affected by this, as the uptake of  $^{15}\text{N}$  occurs mainly from the surface layer, with the rains occurring in late winter and early spring.

During the 1992/93 season, which was relatively dry (Figure 11), total stored soil moisture was much lower than in 1991/92 – in the order of 90 mm ha<sup>-1</sup> – compared with some 160 mm ha<sup>-1</sup> during the previous season. The crop started using stored soil moisture with the rising temperatures in late February – early March, as was the case during the previous season. Initially this resulted in both ARF and  $^{15}\text{NRF}$  to increase, suggesting that some of the fertilizer N, which was all applied at sowing, had leached down with the early rains.

However, after 88 days the increase in  $^{15}\text{NRF}$  ended abruptly and  $^{15}\text{NRF}$  remained constant or even decreased slightly. It can be seen from the soil moisture discharge curve that there were some late rains, in late April – early May, but these rains were of little use to the crop. This behaviour of  $^{15}\text{NRF}$  (c.q. Ndff) is quite remarkable and suggests that the fertilizer-derived N in the topsoil was not accessible to the crop from 88 days onwards, presumably because of lack of moisture in the topsoil. The slight decrease in Ndff after 88 days could point at translocation of assimilates from the above-ground parts of the crop to the roots, or to losses of N, in gaseous form or through litter fall (Wetselaar & Farquhar, 1980).

So Figures 10 and 11 illustrate that under dry farming conditions, fertilizer N is likely to concentrate in the upper part of the soil profile and that the availability of this N depends on moisture conditions. Fertilizer-derived N is taken up throughout the season, as long as moisture contents in the upper part of the soil profile are high enough. Uptake of soil-derived N increases strongly when the plant starts using stored soil moisture. The result of these uptake patterns is that early in the season  $^{15}\text{NRF} > \text{ARF}$ , whereas towards the end of the season  $^{15}\text{NRF} < \text{ARF}$ .

Finally, it may be noted that the steepest increase in Ndfs seems to occur during the early stages of soil moisture discharge, suggesting that the soil solution that is taken up first, has a relatively high N concentration. This trend has been observed before (Harmsen, 1987) and is thought to be due to anion exclusion, involving nitrate ions and negatively charged surfaces of clay minerals in heavy-textured soils.

Neutron probe measurements suggest that when the crop starts using stored moisture its root system is already fully developed with depth and the crop extracts a particular fraction of moisture over the entire depth of the soil moisture profile, rather than 'emptying' the soil layer by layer. It is thought that this soil moisture fraction is held with approximately the same tension (free energy) over the entire length of the soil profile. In other words, if a soil is at field capacity and it is assumed that the water held at tensions between  $pF = 2.0$  and  $pF = 4.2$  is crop available, then the neutron probe data suggest that the fraction of soil moisture held at tensions between, say,  $pF$

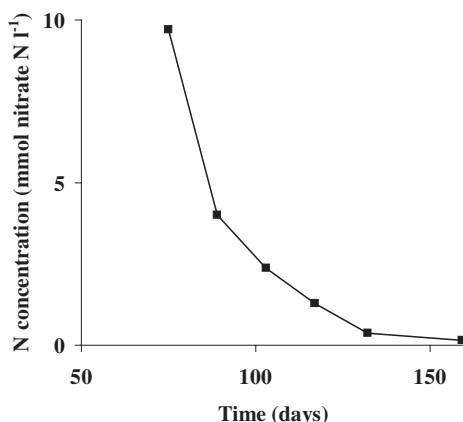


Figure 12. Estimated concentration of nitrate-N, averaged over treatments and seasons, in stored soil moisture taken up by the wheat crop in N fertilizer use experiments conducted at Tel Hadya during the 1991–1992 and 1992–1993 growing seasons.

= 2.0 and 2.2 over the entire length of the soil profile is used by the crop when it starts using stored soil moisture.

As the soils are high in negatively charged clay mineral surfaces, nitrate N is likely to be concentrated in the soil solution in the larger pores, away from the negative surface charge. This is also the moisture fraction that is held with the lowest tension, i.e., the most available to the crop, which is the first to be taken up by the crop when it starts using soil moisture.

Figure 12 gives the estimated N concentrations in the soil solution taken up by the crop. The estimates are obtained by estimating the increase in plant N ( $\Delta N P_f$ ) and the decrease in stored soil moisture ( $\Delta \theta$ ) for each time period and each treatment, and by averaging the resulting  $\Delta N P_f / \Delta \theta$  ratios over treatments and seasons. Of course, the estimates are approximate only: the  $\Delta N P_f$  estimates will include some N uptake from the surface horizon and  $\Delta \theta$  will include some moisture lost through soil evaporation.

Nevertheless, the trend in Figure 12 is clear: N concentrations are initially high in the stored soil moisture used by the crop and decrease when soil moisture discharge proceeds with time.

## Conclusions

The data presented in this paper are a selection of the data available in the literature and as such may not prove whether the models presented in the two companion papers (Harmsen, 2003a, b) are correct or not. In fact, some of the assumptions on which these simple mixing models are based cannot be more than a rough approximation of N dynamics in soil-crop systems under field conditions and therefore one cannot expect these models to really apply to field conditions. Nevertheless, the data presented in this paper do not seem to contradict the model predictions and that, in

turn, the models help to understand the observed relationships between  $^{15}\text{NRF}$  and ARF.

The relationships between  $^{15}\text{NRF}$  and ARF as they emerge from the extensive wheat and rice datasets compiled from the FAO/IAEA-coordinated field experiments are quite different from what would be expected on the basis of the assumption that  $^{15}\text{NRF}$  should equal ARF and seem to be in line with what would be expected on the basis of the models presented by Harmsen (2003a, b).

Model predictions are for fixed values of  $NS_i/NF_i$  and N coefficients, whereas these quantities are likely to vary in field experiments: not only between experiments, but also within experiments, with time and with N rates. This is particularly true for  $NS_i/NF_i$ . Therefore, in a number of cases it had to be assumed that  $NS_i/NF_i$  decreased from a certain value at ARF = 0 (no response to N, i.e.,  $NS_i$  relatively high) to another value at ARF = 1 (N deficient soils, i.e.,  $NS_i$  relatively low). This does not invalidate the present models as explanatory models, but it shows the limitations of the models in describing real field experiments. It may be noted though that the present model could easily be used with actual  $NS_i/NF_i$  ratios if this information would be available.

The experimental data presented in this paper seem to indicate that mineralization-immobilization turnover is generally one of the two most important factors in explaining the differences between  $^{15}\text{NRF}$  and ARF. The other important factor seems to be N losses before mixing with soil mineral N as well as from the soil mineral N pool after mixing of  $NS_i$  and  $NF_i$ . In a number of cases, experimental data seem to point at  $\epsilon_o < 1$  (uptake constraint), possibly caused by drought (lack of moisture at some depth in the soil profile). Under field conditions increased uptake efficiency in fertilized treatments ( $\epsilon_o < \epsilon_f$ ) may play a role too.

In summary, it may be concluded that the models presented in the two companion papers (Harmsen, 2003a, b) are not contradicted by experimental data from the N literature and that, in fact, the models help to understand the differences between  $^{15}\text{NRF}$  and ARF and thus may contribute to understanding the fate of fertilizer N in soil-crop systems.

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