

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

II. Mineralization and immobilization of nitrogen

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Abstract

The recovery fractions of fertilizer nitrogen (N) by crops can be calculated by the difference or the isotope-dilution method. In the difference method, an apparent recovery fraction (ARF) is calculated from the N uptake by fertilized and unfertilized crops, whereas in the isotope-dilution method a ¹⁵N recovery fraction (¹⁵NRF) is calculated from isotope-ratio analysis and N uptake by fertilized crops. The recovery fractions calculated by the two methods are compared on the basis of simplified models for the distribution of ¹⁵N-labeled N over different N pools in the soil-crop system, considering plant uptake and mineralization-immobilization in soil. In N-deficient soils, ARF-values are likely to be higher than those of ¹⁵NRF, due to pool substitution. Plant uptake and immobilization do not affect the relationship between ARF and ¹⁵NRF, as these processes do not discriminate between ¹⁵N and ¹⁴N. However, immobilization reduces the range of values of ARF and ¹⁵NRF. Mineralization is the main factor causing the discrepancy between ARF and ¹⁵NRF. It results in dilution of the soil mineral N pool with soil-derived N and thus affects the ¹⁵N/¹⁴N ratio in the soil mineral N pool. The combined action of mineralization-immobilization and plant uptake increases the effect of dilution of the soil mineral N pool by (re)mineralized soil N. The effects of plant uptake and mineralization-immobilization on the relationship

between ^{15}NRF and ARF are discussed and analytical expressions are derived for the relevant quantities considered in the model. The difference and the isotope-dilution method measure essentially different quantities and complementary information can be derived from recovery fractions calculated by the two methods, thus contributing to the understanding of fertilizer N-dynamics and transformations in soil.

Additional keywords: apparent recovery fraction, ^{15}N recovery fraction, N fertilizer efficiency, added N interaction, biological interchange, pool substitution, organic N, mineral N

Introduction

The difference method and the isotope-dilution method for estimating fertilizer-nitrogen (N) recovery fractions in crops often give different results. In particular, biological interchange of ^{15}N -labeled N with unlabeled soil organic N (pool substitution) may confound the interpretation of fertilizer-N recovery fractions as calculated by the isotope-dilution method (Hauck & Bremner, 1976; Jenkinson *et al.*, 1985). 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}N in the organic N pool as a result of mineralization-immobilization turnover in the soil, and (3) increased availability of soil mineral N due to better root development in fertilized treatments ('priming effect'). The isotope-dilution method would correctly estimate the fertilizer N recovery fraction if the difference between the methods were due to increased mineralization in fertilized plots, but not so if mineralization-immobilization turnover in soils would cause the difference (Jansson, 1971). More recently, Jenkinson *et al.* (1985) discussed the 'priming effect' in terms of 'apparent' and 'real' added N interactions (ANI's) and developed a model to demonstrate how N transformations in soil, in particular mineralization and immobilization, may affect the interpretation of results of ^{15}N research in agricultural soils.

If fertilizer-N uptake by a crop were directly proportional to uptake of labeled N, then the ^{15}N -recovery fraction would accurately estimate the fertilizer-N recovery fraction. It is questionable, however, whether fertilizer-N uptake can be assumed to be directly proportional to uptake of labeled N in a situation where immobilization and mineralization of N occur in the soil. If part of the ^{15}N -enriched N applied to a soil is immobilized in the soil organic fraction, and subsequently remineralized, the remineralized N is likely to have a much lower ^{15}N concentration than the labeled N before it was immobilized. So the question is whether the remineralized N is considered to be fertilizer N or not (Hauck, 1978). If the remineralized N is considered to be fertilizer N, the ^{15}N -recovery fraction is likely to underestimate the fertilizer-N fraction. In that case the true value of the fertilizer-N recovery fraction might lie between the values obtained by the difference and the isotope-dilution method (Hauck, 1978).

In the past few decades, the processes causing discrepancies between the difference and the isotope-dilution method seem to have been largely clarified (Jansson, 1971; Hauck & Bremner, 1976; Jansson & Persson, 1982; Hauck, 1982; Jenkinson *et al.*, 1985; Hart *et al.*, 1986; Harmsen & Moraghan, 1988). Notwithstanding the progress made in this respect, the discussion as to whether to use the difference or the

isotope-dilution method still continues (Rao *et al.*, 1992; Stout, 1995; Roberts & Janzen, 1990; Jokela & Randall, 1997; MacKown & Sutton, 1997).

In a companion paper, a model is discussed in which plant uptake and loss of N from the soil are considered, but in which mineralization-immobilization does not occur (Harmsen, 2003). In that paper it is shown that of all the mechanisms and conditions considered, only an increased uptake of soil-derived N by fertilized crops would result in $ARF > {}^{15}NRF$, thus confirming that the commonly observed situation in field experiments that $ARF > {}^{15}NRF$, is most likely caused by mineralization-immobilization turnover in soil, possibly in combination with enhanced uptake of soil mineral N by fertilized crops. The treatment of mineralization-immobilization requires a time-dependent approach (Kirkham & Bartholomew, 1954, 1955; Jenkinson *et al.*, 1985; Hart *et al.*, 1986) and will be dealt with in the present paper.

The objectives of this paper are (1) to present a simplified model for plant uptake, immobilization and mineralization occurring in soils, (2) to investigate how these processes may affect the distribution of ${}^{15}N$ -labeled N over different N pools in the soil-plant system, and (3) to investigate how these distributions would affect fertilizer-N recoveries by crops, calculated by the difference and the isotope-dilution method. An understanding of these phenomena may help to focus research on the role of N in agricultural soils. In a companion paper (Harmsen & Garabet, 2003), the models discussed here are compared with results of ${}^{15}N$ research from field and greenhouse trials.

Description of the system

The system under consideration consists of a soil on which a crop is grown. It is assumed that soil nitrogen is divided over two pools: a mineral N and an organic N pool (Figure 1). The mineral N pool consists mainly of ammonium- and nitrate-N, but no distinction between different forms of mineral N will be made. The organic N pool consists of a range of organic N compounds and matrices, from the labile heterotrophic biomass to stable organic matter. Fertilizer N is assumed to mix completely and instantaneously with initial soil mineral N. Fertilizer-derived and soil-derived N in the soil mineral N pool are assumed to be equally available to the crop and taken up in proportion to their relative abundance. Furthermore, the initial fertilizer N is assumed to be enriched in ${}^{15}N$ such that the ratio of ${}^{15}N/{}^{14}N$ in the fertilizer is in the range of 1–5 atom%. It is further assumed that the crop does not discriminate between the two N isotopes and that all mineral N is plant-available and that organic N is not available to the plant. The plant thus derives its N only from the mineral N pool. Transformation of organic N into mineral N is referred to as mineralization, and the reverse process as immobilization. Furthermore, all processes considered, i.e., plant uptake, immobilization and mineralization, are assumed to follow zero-order kinetics, i.e., their rates do not depend on the concentrations of initial or final products. However, reaction rates of plant uptake and immobilization of N are assumed to be proportional to the relative abundance of soil- and fertilizer-derived N in the soil mineral N pool, in accordance with the law of mass action (Kirkham & Bartholomew, 1954; 1955). Fertilizer N and

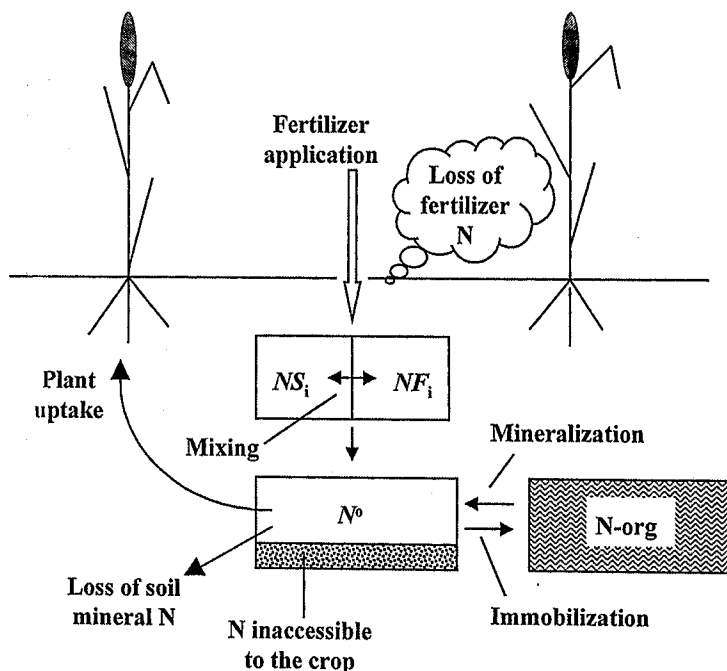


Figure 1. Schematic representation of the processes and transformations involving N considered in the present system: fertilizer N application (NF_i), loss of fertilizer N before mixing has occurred, instantaneous mixing of initial soil mineral N (NS_i) and fertilizer N (NF_i), the organic N pool (N-org), plant uptake, loss of N from the mixed soil mineral N pool, mineralization and immobilization, where the associated variables are given in parentheses. It is assumed that a fraction of the soil mineral N pool (N^0) is not accessible to the crop (shaded area).

soil mineral N are assumed to be equally available to the crop as well as to the (heterotrophic) biomass of the soil.

Soils in all treatments initially contain the same amount of N, denoted by NS_i (kg ha^{-1}). The amount of fertilizer N applied is denoted by NF_i (kg ha^{-1}). It is assumed that fertilizer is applied at the time of sowing and that mixing of NS_i and NF_i is complete and instantaneous. Hence:

$$N^0 = NS_i + NF_i$$

where N^0 is the total amount of mineral N in the soil mineral N pool at $t = 0$, after the addition of fertilizer N.

Plant uptake of N

Plant uptake in fertilized treatments is described by:

$$dNP_f/dt = v_{fp}$$

$$NP_{fh} = v_{fp}t_h$$

where

NP_f = the amount of N taken up by a fertilized crop at time t (kg ha^{-1}),

NP_{fh} = the amount of N taken up by a fertilized crop at harvest (kg ha^{-1}),

v_{fp} = a rate constant for plant uptake of N in fertilized treatments (kg ha^{-1} per day) and

t_h = the time from sowing to harvest (days), i.e., the length of the growing season.

For the present model it is relevant to distinguish between crop uptake of soil-derived (NP_{fs}) and fertilizer-derived N (NP_{ff}). Hence:

$$dNP_f/dt = dNP_{fs}/dt + dNP_{ff}/dt$$

If both forms of N in the soil mineral N pool are equally available to the crop and the crop derives all of its N from this pool, it follows from the law of mass action that:

$$dNP_{fs}/dt = (NS_{fs}/NS_f) v_{fp} \quad (1)$$

$$dNP_{ff}/dt = (NS_{ff}/NS_f) v_{fp} \quad (2)$$

with:

$$NS_f = NS_{fs} + NS_{ff}$$

where

NS_{fs} = soil-derived and NS_{ff} is fertilizer-derived mineral N at time t (kg ha^{-1}), and

NS_f = total soil mineral N at time t (kg ha^{-1}).

At $t = 0$, it follows that $NS_{fs} = NS_i$, $NS_{ff} = NF_i$ and $NS_f = N^0$.

Immobilization and mineralization of N

Immobilization of N from the soil mineral N pool in fertilized treatments is described by:

$$dNI_f/dt = v_{fi}$$

$$NI_{fh} = v_{fi}t_h$$

where

NI_f = the amount of N immobilized in fertilized treatments at time t (kg ha^{-1}),

NI_{fh} = the amount of N immobilized in fertilized treatments at harvest (kg ha^{-1}), and
 v_{fi} = a rate constant for immobilization of N in fertilized treatments (kg ha^{-1} per day).

Distinguishing between the immobilization of soil-derived (NI_{fs}) and fertilizer-derived N (NI_{ff}) it follows that:

$$dNI_f/dt = dNI_{fs}/dt + dNI_{ff}/dt$$

If both forms of N in the mineral N pool are completely mixed and equally available to the heterotrophic biomass in the soil, it follows that:

$$dNI_{fs}/dt = (NS_{fs}/NS_f) v_{fi} \quad (3)$$

$$dNI_{ff}/dt = (NS_{ff}/NS_f) v_{fi} \quad (4)$$

With regard to mineralization in fertilized treatments, the overall process can be described in a way similar to plant uptake and immobilization:

$$dNM_f/dt = v_{fm}$$

$$NM_{fh} = v_{fm} t_h$$

where

NM_f = the total amount of N mineralized in fertilized treatments at time t (kg ha^{-1}),

NM_{fh} = the amount of N mineralized in fertilized treatments at harvest (kg ha^{-1}), and

v_{fm} = a rate constant for mineralization of N in fertilized treatments (kg ha^{-1} per day).

Furthermore:

$$dNM_f/dt = dNM_{fs}/dt + dNM_{ff}/dt$$

where

NM_{fs} = the amount of soil-derived N (kg ha^{-1}), and

NM_{ff} = the amount of fertilizer-derived N mineralized in fertilized treatments at time t (kg ha^{-1}).

To distinguish between the mineralization of soil- and fertilizer-derived N one would have to consider their relative occurrences in the organic N pool rather than in the mineral N pool. Hence, if soil- and fertilizer-derived N in the organic N phase are fully mixed and the organisms involved in the mineralization process do not discriminate between the two forms of N, it follows that:

$$dNM_{fs}/dt = (NO_{fs}/NO_f) v_{fm} \quad (5)$$

$$dNM_{ff}/dt = (NO_{ff}/NO_f) v_{fm} \quad (6)$$

with:

$$NO_f = NO_{fs} + NO_{ff}$$

Where NO_{fs} represents the amount of soil-derived (kg ha^{-1}), and NO_{ff} the amount of fertilizer-derived N (kg ha^{-1}) in the organic phase of the soil in fertilized treatments.

The notion 'fertilizer-derived' refers to the current experimental season and not to previous seasons, i.e., NO_{ff} essentially equals NI_{ff} . The organic N pool is assumed to be much larger than the mineral N pool in agricultural soils and therefore, as an approximation, it will be assumed that $NO_{ff}/NO_f = 0$ and $NO_{fs}/NO_f = 1$. Hence:

$$dNM_{fs}/dt = v_{fm} \quad (7)$$

$$dNM_{ff}/dt = 0 \quad (8)$$

The assumption that $dNM_{ff}/dt = 0$ is not required in the present model. One could also consider the remineralization of immobilized fertilizer N, in accordance to the law of mass action (Kirkham & Bartholomew, 1955). Nevertheless, the inclusion of this term would further complicate the equations to be derived and probably not add much to the treatment.

The composition of the soil mineral N pool

The composition and size of the soil mineral N pool will change in time as a result of plant uptake, mineralization and immobilization of N. The overall rate of change is given by:

$$dNS_t/dt = dNM_t/dt - dNI_t/dt - dNP_t/dt \quad (9)$$

and the size of the mineral N pool at time t is given by:

$$NS_t = N^0 + (v_{fm} - v_{fn} - v_{fp})t \quad (10)$$

where: $N^0 + (v_{fm} - v_{fn} - v_{fp})t \geq 0$, otherwise the system has no physical significance. The rate of change in the composition of the mineral N pool follows from:

$$dNS_{ff}/dt = - (NS_{ff}/NS_t)(v_{fn} + v_{fp}) \quad (11)$$

$$dNS_{fs}/dt = v_{fm} - (NS_{fs}/NS_t)(v_{fn} + v_{fp}) \quad (12)$$

In case the size of the mineral N pool changes with time, i.e., if $v_{fm} \neq v_{fn} + v_{fp}$, the solution to Equations 11 and 12 is given by:

$$NS_{ff} = NF_t \Theta \quad (13)$$

$$NS_{fs} = \{N^0 + (v_{fm} - v_{fn} - v_{fp})t\} - NS_{ff} \quad (14)$$

$$\text{where: } \Theta = \{[N^0 + (v_{fm} - v_{fn} - v_{fp})t] / N^0\}^{(v_{fn} + v_{fp}) / (v_{fn} + v_{fp} - v_{fm})} \quad (15)$$

In the limit for $NS_f = 0$ it follows that $\Theta = 0$ and thus $NS_{ff} = NS_{fs} = 0$.

In case the size of the mineral N pool does not change with time, i.e., if $v_{fm} = v_n + v_{fp}$, the solution to Equations 11 and 12 is given by:

$$NS_{ff} = NF_f \exp(-v_{fm}t/N^0) \quad (16)$$

$$NS_{fs} = N^0 - NS_{ff} \quad (17)$$

This solution also applies in case only plant uptake and mineralization occur:

$$v_n = 0 \quad v_{fp} = v_{fm}$$

or if only immobilization and mineralization occur:

$$v_{fp} = 0 \quad v_n = v_{fm}$$

The latter case is of interest for understanding the fate of ^{15}N -enriched fertilizer N in the soil and will be discussed in one of the following sections.

Plant uptake and mineralization-immobilization

The solution to Equations 1 and 2 for plant uptake from the mineral N pool is given by ($v_{fm} \neq v_n + v_{fp}$):

$$NP_{ff} = \{v_{fp}NF_i/(v_n + v_{fp})\}(1 - \Theta) \quad (18)$$

$$NP_{fs} = v_{fp}t - NP_{ff} \quad (19)$$

In case the size of the soil mineral N pool is constant with time ($v_{fm} = v_n + v_{fp}$), the solution is given by:

$$NP_{ff} = (v_{fp}NF_i/v_{fm})\{1 - \exp(-v_{fm}t/N^0)\} \quad (20)$$

$$NP_{fs} = v_{fp}t - NP_{ff} \quad (21)$$

Equations 20 and 21 also apply if either v_n or v_{fp} equals 0. The solution to Equations 3 and 4 describing the immobilization of nitrogen in soil takes a similar form:

$$NI_{ff} = \{v_nNF_i/(v_n + v_{fp})\}(1 - \Theta) \quad (22)$$

$$NI_{fs} = v_n t - NI_{ff} \quad (23)$$

if:

$$v_{fm} \neq v_n + v_{fp}$$

In case the size of the soil mineral nitrogen pool does not change with time ($v_{fm} = v_{fi} + v_{fp}$), the solution to Equations 3 and 4 is given by:

$$NI_{ff} = (v_{fi}NF_i/v_{fm}) \{1 - \exp(-v_{fm}t/N^0)\} \quad (24)$$

$$NI_{fs} = v_{fi}t - NI_{ff} \quad (25)$$

In the case of mineralization it is assumed that no remineralization of immobilized fertilizer N occurs. Hence the solution to Equations 7 and 8 becomes:

$$NM_{fs} = v_{fm}t \quad (26)$$

$$NM_{ff} = 0 \quad (27)$$

Nitrogen balance at harvest

The equations for the amounts of N in the soil-crop system at harvest can be written in terms of coefficients for plant uptake, immobilization and mineralization, while eliminating time as a variable and replacing the rate constants for the N transformations and plant uptake by their corresponding coefficients.

In unfertilized treatments, at harvest, it follows that:

$$\begin{aligned} NP_{oh} &= v_{op}t_h \\ NI_{oh} &= v_{oi}t_h \\ NM_{oh} &= v_{om}t_h \\ NS_{oh} &= NS_i - v_{oi}t_h - v_{op}t_h + v_{om}t_h \end{aligned}$$

If $v_{om} \neq v_{oi} + v_{op}$ it follows that:

$$t_h = (NS_i - NS_{oh}) / (v_{oi} + v_{op} - v_{om}) \quad (28a)$$

Hence, with:

$$\begin{aligned} \varepsilon_o &= (1 - NS_{oh}/NS_i) \\ \kappa_o &= v_{oi} / (v_{oi} + v_{op} - v_{om}) \\ \mu_o &= v_{om} / (v_{oi} + v_{op} - v_{om}) \end{aligned} \quad (29a)$$

it follows that:

$$\begin{aligned} NP_{oh} &= (1 + \mu_o - \kappa_o) \varepsilon_o NS_i \\ NI_{oh} &= \kappa_o \varepsilon_o NS_i \\ NM_{oh} &= \mu_o \varepsilon_o NS_i \\ NS_{oh} &= (1 - \varepsilon_o) NS_i \end{aligned} \quad (30a)$$

where

κ_o = a coefficient to account for immobilization of N,

μ_o = a coefficient to account for mineralization of N, and

ε_o = an uptake coefficient for N in unfertilized treatments.

It can be seen that $1-\varepsilon_o$ relates to the fraction of the soil mineral N pool inaccessible to the crop, e.g. because of limited root development or lack of water in a particular soil layer. It is thus assumed that plant uptake, immobilization and mineralization all occur in the accessible part of the soil mineral N pool.

Analogously, in fertilized treatments, at harvest:

$$NP_{fh} = v_{fp} t_h$$

$$NI_{fh} = v_{fi} t_h$$

$$NM_{fh} = v_{fm} t_h$$

$$NS_{fh} = N^o - v_{fi} t_h - v_{fp} t_h + v_{fm} t_h$$

If $v_{fm} \neq v_{fi} + v_{fp}$ it follows that:

$$t_h = (N^o - NS_{fh}) / (v_{fi} + v_{fp} - v_{fm}) \quad (28b)$$

Hence, with:

$$\varepsilon_f = (1 - NS_{fh} / N^o) \quad (29b)$$

$$\kappa_f = v_{fi} / (v_{fi} + v_{fp} - v_{fm})$$

$$\mu_f = v_{fm} / (v_{fi} + v_{fp} - v_{fm})$$

it follows that:

$$NP_{fh} = (1 + \mu_f - \kappa_f) \varepsilon_f N^o \quad (30b)$$

$$NI_{fh} = \kappa_f \varepsilon_f N^o$$

$$NM_{fh} = \mu_f \varepsilon_f N^o$$

$$NS_{fh} = (1 - \varepsilon_f) N^o$$

where

κ_f = a coefficient to account for immobilization of N,

μ_f = a coefficient to account for mineralization of N, and

ε_f = an uptake coefficient for N in fertilized treatments.

The same substitutions (Equations 28b–29b) can be used in the expressions for the quantities of N at harvest. From Equation 15 it follows that:

$$\Theta = (1 - \varepsilon_f)^{1 + \mu_f} \quad (31)$$

such that:

$$\begin{aligned} NS_{fth} &= NF_i(1-\varepsilon_f)^{1+\mu_f} \\ NS_{fsh} &= N^o(1-\varepsilon_f) - NS_{ff} \end{aligned} \quad (32)$$

$$\begin{aligned} NP_{fth} &= NF_i\{(1+\mu_f-\kappa_f)/(1+\mu_f)\}\{1-(1-\varepsilon_f)^{1+\mu_f}\} \\ NP_{fsh} &= N^o(1+\mu_f-\kappa_f)\varepsilon_f - NP_{ff} \end{aligned} \quad (33)$$

$$\begin{aligned} NI_{fth} &= NF_i\{\kappa_f/(1+\mu_f)\}\{1-(1-\varepsilon_f)^{1+\mu_f}\} \\ NI_{fsh} &= N^o\kappa_f\varepsilon_f - NI_{ff} \end{aligned} \quad (34)$$

$$\begin{aligned} NM_{fsh} &= N^o\mu_f\varepsilon_f \\ NM_{fth} &= 0 \end{aligned} \quad (35)$$

The equations are now written in forms similar to those in part I of this contribution (Harmsen, 2003). Although time does not explicitly appear in the equations, it does affect crop uptake of N and, thus, the amount of N remaining in the soil through:

$$\varepsilon_f N^o = t_h(v_{fi} + v_{fp} - v_{fm})$$

Hence, NS_{fh} decreases in the course of time until it equals 0 ($\varepsilon_f = 1$) or some other value > 0 ($\varepsilon_f < 1$) when the crop's demand for N has been satisfied. Of course, Equations 28a and 28b are not limited to time at harvest, but valid for any t , as long as $(v_{fi} + v_{fp} \neq v_{fm})$ and $(N^o - NS_{fh}) > 0$.

To investigate the effect of mineralization-immobilization on the fate of fertilizer N (i.e., ^{15}N) in soil, three cases will be considered:

1. Plant uptake and immobilization ($v_{fm} = 0$);
2. Plant uptake and mineralization ($v_{fi} = 0$);
3. Plant uptake and mineralization-immobilization.

In each case the effects of the processes involving N on the recoveries of N as calculated by the isotope-dilution and the difference method will be evaluated.

Nitrogen recovery fractions

In the difference method, an apparent recovery fraction (ARF) of the amount of fertilizer N taken up by a crop is defined as:

$$ARF = (NP_{fh} - NP_{oh})/NF_i \quad (36)$$

where it is assumed that all other growth-limiting factors that may affect N uptake by crops are at optimal levels and constant between fertilized and unfertilized treatments. In the isotope-dilution method, a ^{15}N recovery fraction (^{15}NRF) is defined as:

$$^{15}NRF = c_{xp} NP_{fh} / c_{xf} NF_i \quad (37)$$

where

c_{xp} = the atom% ^{15}N excess concentration in fertilized crops (%), and

c_{xf} = the atom% ^{15}N excess concentration in the applied N fertilizer (%).

If mixing of soil and fertilizer N is instantaneous and complete, the initial atom% excess ^{15}N of the soil mineral N pool (c_{xs}) at $t = 0$ can be calculated from the mass conservation equation in the form:

$$c_{xs} = c_{xf}NF_i/N^0 \quad (38)$$

If the crop derives all of its N from the soil mineral N pool without discrimination between ^{14}N and ^{15}N , and the $^{15}\text{N}/^{14}\text{N}$ ratio in the soil mineral N pool does not change in the course of time it follows that:

$$c_{xp} = c_{xs} \quad (39)$$

Hence, from Equations 36–39 it follows that:

$$\text{ARF} = \varepsilon_f + (\varepsilon_f - \varepsilon_o)NS_i/NF_i \quad (40)$$

$$^{15}\text{NRF} = \varepsilon_f \quad (41)$$

$$^{15}\text{NRF} = (\text{ARF} + \varepsilon_o NS_i/NF_i) / (1 + NS_i/NF_i) \quad (42)$$

Equations 38 and 39 would hold in the case of plant uptake and immobilization ($v_{fm} = 0$), but not in the case of plant uptake and mineralization ($v_{fi} = 0$) or in the case of plant uptake and mineralization-immobilization. In those cases, one may define a 'mean pool ^{15}N abundance' (\bar{c}_{xs}) for the soil mineral N pool, similar to the concept introduced by Barraclough (1991) for the ammonium and nitrate pools in the soil. From:

$$c_{xs}/c_{xf} = NS_{fi}/NS_f$$

it follows that (Equations 13–15):

$$c_{xs} = c_{xf}(NF_i/N^0)[\{N^0 + (v_{fm} - v_{fi} - v_{fp})t\}/N^0]^{v_{fm}/(v_{fp} + v_{fi} - v_{fm})} \quad (43)$$

and defining the 'mean pool ^{15}N abundance' by:

$$\bar{c}_{xs} = (1/\Delta t) \int_t^{t+\Delta t} c_{xs} dt$$

it follows that:

$$\bar{c}_{xs} = \{c_{xf}NF_i/(v_{fi} + v_{fp})\Delta t\} [1 - \{N^0 + (v_{fm} - v_{fi} - v_{fp})\Delta t\}/N^0]^{(v_{fp} + v_{fi})/(v_{fp} + v_{fi} - v_{fm})} \quad (44)$$

where t has been set equal to zero and where Δt is assumed to be the length of the

growing season or any other period of time relevant to a ^{15}N tracer experiment, starting at $t = 0$. It further follows that:

$$\hat{c}_{\text{xs}} = c_{\text{xp}}$$

In case $v_{\text{fm}} = 0$, both Equations 43 and 44 reduce to:

$$c_{\text{xs}} = c_{\text{xf}}(NF_i/N^0)$$

In the case of plant uptake and mineralization-immobilization, ARF may be written as:

$$\text{ARF} = (1 + \mu_f - \kappa_f) \varepsilon_f + \{(1 + \mu_f - \kappa_f) \varepsilon_f - (1 + \mu_o - \kappa_o) \varepsilon_o\} NS_i / NF_i \quad (45)$$

which reduces to Equation 40 if $\mu_f = \kappa_f$ and $\mu_o = \kappa_o$, i.e., if equilibrium exists between mineralization and immobilization. An expression for ^{15}NRF can be derived from:

$$^{15}\text{NRF} = NP_{\text{ff}} / NF_i$$

with the use of Equations 15 and 18 it follows that ($v_{\text{fm}} \neq v_{\text{a}} + v_{\text{fp}}$):

$$^{15}\text{NRF} = \{(1 + \mu_f - \kappa_f) / (1 + \mu_f)\} \{1 - (1 - \varepsilon_f)^{1 + \mu_f}\} \quad (46)$$

In case $v_{\text{fm}} = v_{\text{a}} + v_{\text{fp}}$ similar expressions can be derived for ARF, NP_{ff} and NP_{fs} with the use of Equations 20 and 21.

From Equations 45 and 46 a relationship between ^{15}NRF and ARF can be derived:

$$^{15}\text{NRF} = \{\text{ARF} + (1 + \mu_o - \kappa_o) \varepsilon_o NS_i / NF_i\} \{1 - (1 - \varepsilon_f)^{1 + \mu_f}\} / \{(1 + \mu_f) \varepsilon_f (1 + NS_i / NF_i)\} \quad (47)$$

Equations 45–47 describe ARF, ^{15}NRF and the relationship between them and consider plant uptake, immobilization and mineralization. If mineralization does not occur ($\mu_o = \mu_f = 0$), Equations 45–47 become similar in form to the equations describing loss of N from the mixed soil mineral N pool (Harmsen, 2003, Equations 14–16). In fact, if one substitutes the loss coefficients λ_o , λ_f for the immobilization coefficients κ_o , κ_f in Equations 45–47, they become identical to the set of equations describing losses from the mixed soil mineral N pool ($\mu_o = \mu_f = 0$).

The only phenomenon considered in Harmsen (2003) and not yet included in the current Equations 45–47 is the case of losses occurring from the initial fertilizer N (NF_i), before mixing with the initial soil mineral N (NS_i) has occurred. Equations 45–47 can be generalized further to include this case as well. Defining:

$$N^0 = NS_i + (1 - \lambda_{\text{ff}}) NF_i$$

where λ_{ff} is a coefficient to account for loss of fertilizer-derived N prior to mixing with soil mineral N, and inserting this expression for N^0 in Equations 45–47 results in:

$$\text{ARF} = (1 + \mu_f - \kappa_f)(1 - \lambda_{ff})\varepsilon_f + \{(1 + \mu_f - \kappa_f)\varepsilon_f - (1 + \mu_o - \kappa_o)\varepsilon_o\}NS_i/NF_i \quad (48)$$

$$^{15}\text{NRF} = \{(1 + \mu_f - \kappa_f)/(1 + \mu_f)\}[(1 - \lambda_{ff})\{1 - (1 - \varepsilon_f)^{1+\mu_f}\}] \quad (49)$$

$$^{15}\text{NRF} = \{\text{ARF} + (1 + \mu_o - \kappa_o)\varepsilon_o NS_i/NF_i\} \{1 - (1 - \varepsilon_f)^{1+\mu_f}\} / \{(1 + \mu_f)\varepsilon_f(1 + NS_i/(1 - \lambda_{ff})NF_i)\} \quad (50)$$

which is a comprehensive set of equations, describing ARF, ^{15}NRF and the relationship between them, for soil-plant systems considering plant uptake, immobilization (or loss of N from the mixed soil mineral N pool), mineralization, and loss of fertilizer N before mixing with the soil mineral N pool has occurred. Equations 48–50 are relevant, because in fertilizer experiments conducted under field conditions, some losses of fertilizer N are inevitable (e.g. ammonia volatilization from applied urea), whereas mineralization and immobilization occur in virtually all natural soils during the crop growing season.

Added nitrogen interaction

The notion of ‘added N interaction’ (ANI) is defined by Jenkinson *et al.* (1985) as “any increase (or decrease) in the quantity of soil-derived N in a compartment caused by added N” and ‘compartment’ is defined as “a particular assemblage of N atoms”. The term ‘compartment’ in the definition of ANI could be replaced by ‘pool’, where ‘pool’ is defined as “a compartment containing material that is chemically indistinguishable and equally accessible to plants (or to the soil population)”. From the definition of ANI it follows that for the plant N pool ANI can be written as:

$$\text{ANI} = NP_{\text{fsh}} - NP_{\text{oh}}$$

where NP_{fsh} denotes soil-derived N in fertilized crops at harvest (kg ha^{-1}). From this it follows that:

$$\text{ANI}/NF_i = \text{ARF} - ^{15}\text{NRF} \quad (51)$$

This expression for ANI would generally apply to ANI’s, whether they be negative or positive and apparent or real. Equation 51 may be helpful in the interpretation of ^{15}N tracer studies in which both ARF and ^{15}NRF have been determined (Stout, 1995). From the definition of ANI it further follows that:

$$\text{ANI} = NS_i\{(1 + \mu_f - \kappa_f)\varepsilon_f - (1 + \mu_o - \kappa_o)\varepsilon_o\} + NF_i(1 + \mu_f - \kappa_f)[\varepsilon_f - \{1 - (1 - \varepsilon_f)^{1+\mu_f}\}/(1 + \mu_f)] \quad (52)$$

Hence, if mineralization does not occur ($\mu_o = \mu_f = 0$):

$$\text{ANI} = NS_i\{(1 - \kappa_f)\varepsilon_f - (1 + \lambda_o)\varepsilon_o\}$$

which is the ‘real’ ANI resulting from different ‘effective’ uptake efficiencies in fertil-

ized and unfertilized treatments, i.e., $(1-\kappa_f)\varepsilon_f \neq (1+\kappa_o)\varepsilon_o$. This ANI is negative if $(1-\kappa_f)\varepsilon_f < (1+\kappa_o)\varepsilon_o$, which is likely to be the case when unfertilized treatments are N deficient ($\varepsilon_o = 1$) and fertilized treatments contain N in excess of the crop's demand ($\varepsilon_f < 1$).

Plant uptake and immobilization

In this section, plant uptake and immobilization are considered. If mineralization does not occur, i.e., if $v_{om} = v_{im} = 0$, it follows that:

$$\mu_o = \mu_f = 0$$

and thus Equation 15 reduces to:

$$\Theta = \{N^0 - (v_{fi} + v_{fp})t\} / N^0$$

and the equations describing the composition of the soil mineral N pool, plant uptake, and immobilization change accordingly. Hence, the composition of the system changes linearly with time and soil- and fertilizer-derived N fractions are proportional to their initial ratio. Also, the $^{15}\text{N}/^{14}\text{N}$ ratio in the soil mineral N pool does not change in the course of time.

From Equations 45–47 it follows that:

$$\text{ARF} = \varepsilon_f(1-\kappa_f) + \{\varepsilon_f(1-\kappa_f) - \varepsilon_o(1-\kappa_o)\} NS_i/NF_i$$

$$^{15}\text{NRF} = (1-\kappa_f)\varepsilon_f$$

$$^{15}\text{NRF} = \{\text{ARF} + (1-\kappa_o)\varepsilon_o NS_i/NF_i\} / (1 + NS_i/NF_i) \quad (53)$$

Hence, the expressions for ARF and ^{15}NRF are essentially the same as in the case of plant uptake and loss of N from the mixed soil mineral N pool (Harmsen, 2003). In other words immobilization can be described as a loss mechanism of fertilizer N from the soil mineral N pool, the soil organic N phase acting as a sink for fertilizer N. Equation 53 is plotted in Figure 2. The intercept and slope are given by:

$$\text{intercept} = \{(1-\kappa_o)\varepsilon_o NS_i/NF_i\} / (1 + NS_i/NF_i)$$

$$\text{slope} = 1 / (1 + NS_i/NF_i)$$

and it can be seen that the intercept decreases with increasing value of κ_o at constant NS_i/NF_i . The value of κ_o does not affect the slope and κ_f does not affect intercept nor slope. However, κ_f does affect ARF and ^{15}NRF : the range of ^{15}NRF -values is reduced by a factor $(1-\kappa_f)$ and the same applies to ARF, if $(1-\kappa_o)\varepsilon_o = (1-\kappa_f)\varepsilon_f$. Both the intercept and the slope are affected by the ratio NS_i/NF_i : the intercept increases and the slope decreases with increasing values of NS_i/NF_i . In other words, the intercept decreases

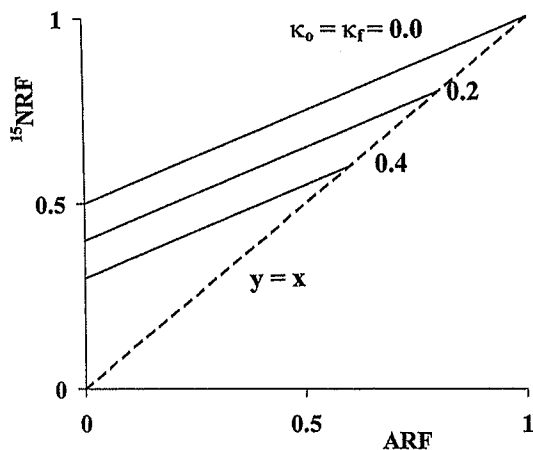


Figure 2. ^{15}NRF as a function of ARF for the case of plant uptake and immobilization, for $NS_i/NF_i = 1.0$, $\varepsilon_o = \varepsilon_f = 1.0$, $\mu_o = \mu_f = 0$, and $\kappa_o = \kappa_f = 0, 0.2$ and 0.4 , according to Equation 53.

and the slope increases with increasing fertilizer rate (NF_i) at constant initial soil mineral N (NS_i). The situation that only immobilization occurs in soil may be approached under field conditions where large quantities of straw or other organic materials with high C/N ratios have been incorporated in the soil prior to the start of the growing season. Under such conditions, the soil system would be N limited and both soil- and fertilizer-derived mineral N may be immobilized. Of course, mineralization and immobilization always occur simultaneously, but if the system is (initially) N limited, immobilization of N will predominate.

Plant uptake and mineralization

In this section plant uptake and mineralization are considered, i.e., immobilization does not occur, such that:

$$V_{oi} = V_{fi} = 0$$

and consequently:

$$\kappa_o = \kappa_f = 0$$

If the organic N pool does not contain any ^{15}N in excess of natural abundance, then mineralization contributes to soil-derived mineral N only.

If plant uptake and mineralization of N occur simultaneously, the ratio NS_{ff}/NS_{fs} changes in the course of time and the amount of fertilizer-derived N taken up by the crop decreases in proportion to the decreasing NS_{ff}/NS_{fs} ratio (Figure 3). The ratio NP_{ff}/NP_{fs} decreases more slowly than the ratio NS_{ff}/NS_{fs} because crop uptake reflects the cumulative effect of the changing NS_{ff}/NS_{fs} ratio over time. It may be noted that the ratio NS_{ff}/NS_f equals the ratio c_{xs}/c_{xf} where c_{xs}/c_{xf} is given by Equation 43. Hence:

$$NS_{ff}/NS_{fs} = (c_{xs}/c_{xf}) / (1 - c_{xs}/c_{xf})$$

As the ratio of $^{15}\text{N}/^{14}\text{N}$ in the soil mineral N pool is decreasing during the growing season, it follows that NP_{ff}/NP_{fs} equals the ratio $\hat{c}_{xs}/\hat{c}_{xf}$, where \hat{c}_{xs} is given by Equation 44. Hence:

$$NP_{ff}/NP_{fs} = (\hat{c}_{xs}/\hat{c}_{xf}) / (1 - \hat{c}_{xs}/\hat{c}_{xf})$$

These examples illustrate that if the ratio $^{15}\text{N}/^{14}\text{N}$ decreases during the growing season the atom% excess ^{15}N concentration in the crop is given by $c_{xp} = \hat{c}_{xs}$. For the examples in Figure 3, the ratios are calculated as follows: $c_{xs}/c_{xf} = 0.394$ and $c_{xp}/c_{xf} = 0.448$ ($v_{fm} = 0.2$) and $c_{xs}/c_{xf} = 0.328$ and $c_{xp}/c_{xf} = 0.410$ ($v_{fm} = 0.4$).

Figure 3 illustrates that mineralization results in dilution of the soil mineral N pool with soil-derived mineral N, which has a strong effect on the ratio of NS_{ff}/NS_{fs} and thus on the $^{15}\text{N}/^{14}\text{N}$ ratio in the crop. In the case that only mineralization and plant uptake occur, Equations 45–47 become:

$$\begin{aligned} \text{ARF} &= (1 + \mu_f)\varepsilon_f + \{(1 + \mu_f)\varepsilon_f - (1 + \mu_o)\varepsilon_o\}NS_i/NF_i \\ {}^{15}\text{NRF} &= \{1 - (1 - \varepsilon_f)^{1 + \mu_f}\} / (1 + \mu_f) \\ {}^{15}\text{NRF} &= \{\text{ARF} + (1 + \mu_o)\varepsilon_oNS_i/NF_i\} \{1 - (1 - \varepsilon_f)^{1 + \mu_f}\} / \{(1 + \mu_f)\varepsilon_f(1 + NS_i/NF_i)\} \end{aligned} \quad (54)$$

Equation 54 is plotted in Figure 4 and it follows that ($\varepsilon_f = \varepsilon_o = 1$):

$$\text{intercept} = \{(1 + \mu_o)NS_i/NF_i\} / \{(1 + \mu_f)(1 + NS_i/NF_i)\}$$

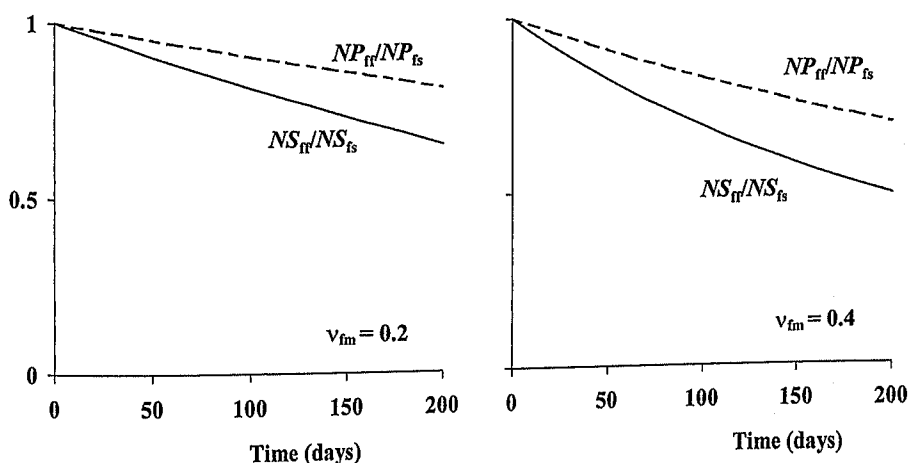


Figure 3. The ratios of fertilizer- to soil-derived N in the soil mineral N pool (NS_{ff}/NS_{fs}) and in the plant N pool (NP_{ff}/NP_{fs}) as functions of time, in case only plant uptake and mineralization occur. Curves are plotted for $NS_i = NF_i = 100 \text{ kg ha}^{-1}$, $v_n = 0$, $v_{ip} = 0.50 \text{ kg ha}^{-1}$ per day and $v_{fm} = 0.2$ (left) or $v_{fm} = 0.4 \text{ kg ha}^{-1}$ per day (right) and a growing season of 200 days, according to Equations 32 and 33.

Hence, if $\mu_o = \mu_f$, the intercept is not affected by μ_o or μ_f . Furthermore, from:

$$\text{slope} = 1 / \{(1 + \mu_f)(1 + NS_i/NF_i)\}$$

it follows that the slope decreases with increasing value of μ_f , at constant NS_i/NF_i (Figure 4). Also, if $(1 + \mu_f)\epsilon_f = (1 + \mu_o)\epsilon_o$ it follows that $ARF = (1 + \mu_f)\epsilon_f$. So contrary to the case of immobilization (or loss of N from the mixed soil mineral N pool), where the range of ARF-values was reduced, in the case of mineralization the range of values of ARF is expanded by a factor $(1 + \mu_f)$. However, if $(1 + \mu_f)\epsilon_f < (1 + \mu_o)\epsilon_o$, as may well be the case in N-deficient soils, the modification of the range of ARF-values is more complex, but ARF may still be >1 , in particular if NS_i/NF_i is very small. In the case of ^{15}NRF , if $\epsilon_f = 1$, it follows that $^{15}NRF = 1/(1 + \mu_f)$ which is < 1 if $\mu_f > 0$. Hence, in N-deficient soils, the values of ^{15}NRF would be reduced by a factor $1/(1 + \mu_f)$. If $\epsilon_f < 1$, the relationship is slightly more complex, but from:

$$\{1 - (1 - \epsilon_f)^{1 + \mu_f}\} / (1 + \mu_f) < \epsilon_f \text{ if } \epsilon_f, \mu_f > 0$$

it follows that the range of ^{15}NRF -values is reduced by a variable factor, ranging from close to 1 to $1/(1 + \mu_f)$ if $\epsilon_f, \mu_f > 0$.

The relationship between ^{15}NRF and ARF is more complex than might appear from Figures 2 and 4, because the variables and parameters in Equation 37 are not independent of each other. For example, values of ϵ_o and ϵ_f are expected initially to be close to 1 in N-deficient soils, but to decrease at soil mineral N levels in excess of the crop's demand for N. Similarly, the ratio NS_i/NF_i is not normally kept constant in fertilizer response trials, as there is one initial soil mineral N level across all plots at the experimental site, but usually there are several rates of fertilizer N application.

An alternative way of investigating the relationship between ^{15}NRF and ARF is by

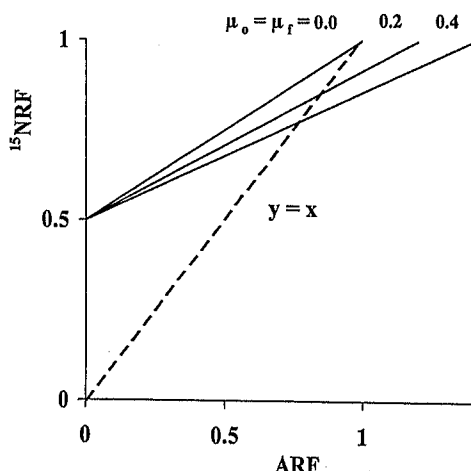


Figure 4. ^{15}NRF as a function of ARF for the case of plant uptake and mineralization, for $NS_i/NF_i = 1.0$, $\epsilon_o = \epsilon_f = 1.0$, $\kappa_o = \kappa_f = 0$ and $\mu_o = \mu_f = 0.0, 0.2$ and 0.4 , according to Equation 54.

calculating their values for a standard dataset. This is done in Figure 5 for the following conditions:

$$\begin{aligned}
 NS_i &= 10, 20, \dots, 80 \text{ kg ha}^{-1} \\
 NF_i &= 10, 20, \dots, 100 \text{ kg ha}^{-1} \\
 \varepsilon_o &= 1 && \text{if } (1+\mu_o)NS_i \leq 100 \text{ kg ha}^{-1} \\
 \varepsilon_o &= 100/(1+\mu_o)NS_i && \text{if } (1+\mu_o)NS_i > 100 \text{ kg ha}^{-1} \\
 \varepsilon_f &= 1 && \text{if } (1+\mu_f)N^o \leq 100 \text{ kg ha}^{-1} \\
 \varepsilon_f &= 100/(1+\mu_f)N^o && \text{if } (1+\mu_f)N^o > 100 \text{ kg ha}^{-1} \\
 \kappa_o &= \kappa_f = 0 \\
 \mu_o &= \mu_f = 0.20 \text{ or } 0.40
 \end{aligned}$$

In Figure 5 only data for which ${}^{15}\text{NRF} < 1/(1+\mu_f)$, $\text{ARF} > 0$ and $NP_f = 100$ are plotted. It can be seen that the slope of the regression lines increases if $\mu_o = \mu_f$ increases from 0.20 to 0.40. The scatter is caused by the different NS_i/NF_i ratios and by the decreasing value of ε_f when the crop's demand for N has been satisfied.

In Figures 4 and 5 it is assumed that $\mu_o = \mu_f$. This implies that mineralization in fertilized plots would be effectively higher than in unfertilized plots if $NS_i > 0$ and $\varepsilon_o = \varepsilon_f = 1$. This is also the reason why ARF-values > 1 can be seen in Figure 5. In this case, ARF would tend to overestimate the fertilizer N recovery fraction as the increased plant uptake in fertilized plots would contain more soil mineral N than in unfertilized plots, whereas ${}^{15}\text{NRF}$ would accurately estimate fertilizer N recovery. If, however, the increased mineralization in fertilized treatments would be considered an 'indirect' fertilizer effect, i.e., induced by fertilizer application, then ${}^{15}\text{NRF}$ would underestimate the overall fertilizer effect.

It is questionable, however, whether fertilizer application is likely to enhance mineralization. If the system were N-limited, application of fertilizer N would enhance

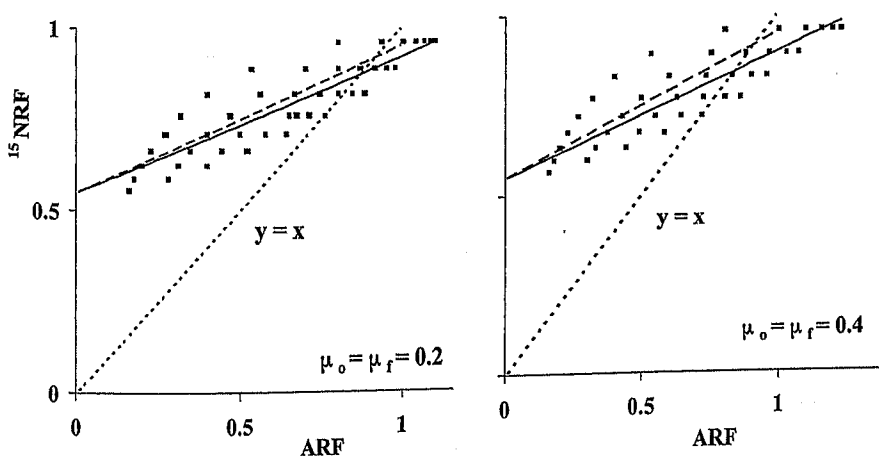


Figure 5. Calculated ${}^{15}\text{NRF}$ -values as a function of ARF for $\varepsilon_o = \varepsilon_f = 1.0$, $\kappa_o = \kappa_f = 0$ and $\mu_o = \mu_f = 0.2$ (left) or 0.4 (right), and NP_{oh} , $NP_{fh} \leq 100 \text{ kg ha}^{-1}$. The solid line represents the linear regression line through the calculated values. The broken line represents the linear regression equation of ${}^{15}\text{NRF}$ as a function of ARF for $\varepsilon_o = \varepsilon_f = 1.0$ (plant uptake only).

immobilization rather than mineralization. Alternatively, if the system were carbon-limited, application of fertilizer N would have little direct effect on the rate of mineralization. Enhanced root growth might stimulate biological activity in a fertilized soil, e.g. through the release of organic root exudates, if the C/N ratio of the organic substrate would be sufficiently low. Nevertheless, the increased accessibility of soil mineral N in case of increased root development might well be the more important phenomenon under such circumstances.

Plant uptake and mineralization-immobilization

In this section it is assumed that plant uptake and immobilization-mineralization occur simultaneously. For simplicity it will be assumed that the rate of mineralization equals the rate of immobilization within the same treatment, so that $v_{om} = v_{oi}$ and $v_{fm} = v_{fi}$. This restriction is not required, but it simplifies the analytical expressions and thus makes it easier to see how the different conditions affect the N parameters and the recovery fractions. If there is equilibrium between mineralization and immobilization, the size of the mineral N pool decreases only due to plant uptake. The composition of the soil mineral N pool and the amounts of N taken up by the crop, immobilized and mineralized at harvest, are given by Equations 32–35. To assess the effects of plant uptake and mineralization-immobilization on the $^{15}\text{N}/^{14}\text{N}$ ratio in the soil mineral N pool, and on the different quantities of N considered in the model, the ^{15}N excess concentration in the soil mineral N pool, c_{xs} , is plotted in Figure 6 for 4 cases: (1) immobilization and plant uptake, (2) mineralization and plant uptake, (3) immobilization and mineralization, and (4) plant uptake and immobilization-mineralization. Case (3) assumes that plant uptake does not occur, i.e., $v_{op} = v_{fp} = 0$. In this case the system consists of a soil only on which no crop is grown (i.e., fallow land). As the rates of mineralization and immobilization are assumed to be equal, the size of the mineral N pool does not change in time but the $^{15}\text{N}/^{14}\text{N}$ ratio does decrease, because of immobilization of ^{15}N . It follows from Figure 6 that plant uptake and immobilization alone do not alter the ^{15}N excess concentration in the soil mineral N pool, as these processes do not discriminate between ^{15}N and ^{14}N . The main process affecting c_{xs} is mineralization. Also, mineralization and immobilization, without plant uptake, affect c_{xs} in about the same way as mineralization and plant uptake, the difference only being in the choice of the numerical values of the rate constants ($v_{fp} = 0.5$ and $v_{fi} = 0.4$). This is because both immobilization and plant uptake result in the removal of N from the soil mineral N pool, without discrimination between N isotopes. The combined effect of immobilization and plant uptake results in a slightly steeper decrease in c_{xs} , but, again, the main factor is mineralization.

In case there is equilibrium between immobilization and mineralization, and assuming that fertilizer-derived N is proportional to labeled N, the decrease of c_{xs} results in a decrease in the ratio NS_{ff}/NS_{fs} . This would imply that the amount of fertilizer-derived N in the soil mineral N pool decreases in time, even if the size of the mineral N pool does not change, i.e., in case plant uptake does not occur. This illustrates the paradox resulting from the organic N pool acting as a sink for ^{15}N (pool

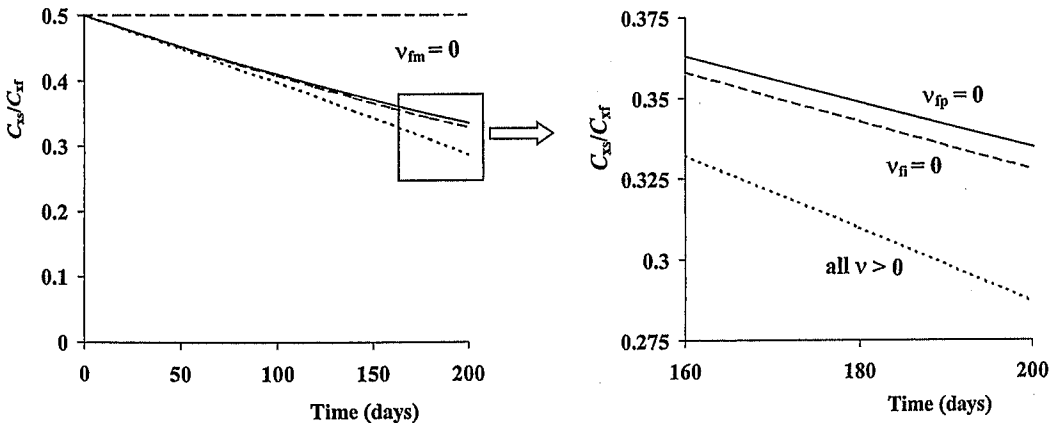


Figure 6. The ratio of the ^{15}N excess concentrations in the soil mineral N pool and the fertilizer, C_{xs}/C_{xf} , as a function of time, according to Equations 16 and 17 for case 1 and Equations 13 and 14 for cases 2–4, for $NS_i = NF_i = 100 \text{ kg ha}^{-1}$, and $v_{fp} = 0.5$, $v_N = 0.4$ and $v_{fm} = 0.4 \text{ kg ha}^{-1}$ per day, except for: (1) $v_{fm} = 0$, (2) $v_N = 0$, (3) $v_{fp} = 0$ and (4) all $v_f > 0$.

substitution) and the interpretation of that phenomenon in terms of NS_{ff} and NS_{fs} . If there is no plant uptake, the size of the soil mineral N pool remains constant in time. However, the amount of fertilizer-derived soil mineral N decreases in time through immobilization. If there would be no mineralization, this case would be similar to loss of N due to denitrification or leaching of nitrate. However, because the rate of mineralization equals the rate of immobilization, an equivalent amount of soil-derived mineral N is released through mineralization. Therefore, the soil mineral N pool is 'diluted' with soil-derived mineralized N. If only mineralization would occur, the soil mineral N pool would be diluted, i.e., the ^{15}N concentration would decrease but the total amount of ^{15}N would remain constant. So it is the combination of the two processes that causes the pool substitution.

If $\kappa_o = \mu_o$ and $\kappa_f = \mu_f$ the N recovery fractions and the relationship between them (Equations 45–47) become:

$$\begin{aligned} \text{ARF} &= \varepsilon_f + \{\varepsilon_f - \varepsilon_o\} NS_i / NF_i \\ {}^{15}\text{NRF} &= \{1 - (1 - \varepsilon_f)^{1+\mu_f}\} / (1 + \mu_f) \\ {}^{15}\text{NRF} &= \{\text{ARF} + \varepsilon_o NS_i / NF_i\} \{1 - (1 - \varepsilon_f)^{1+\mu_f}\} / \{(1 + \mu_f) \varepsilon_f (1 + NS_i / NF_i)\} \end{aligned} \quad (55)$$

Equation 55 is plotted in Figure 7 for $\varepsilon_f = \varepsilon_o = 1$ and $NS_i / NF_i = 1$. In this case, the intercept and slope are both given by:

$$\text{intercept} = \text{slope} = 1 / \{2(1 + \mu_f)\}$$

from which it follows that the intercept and slope both decrease with increasing value of μ_f . If $\varepsilon_f = \varepsilon_o = 1$ it further follows that $\text{ARF} = 1$ and ${}^{15}\text{NRF} = 1 / (1 + \mu_f)$ (see Figure 7).

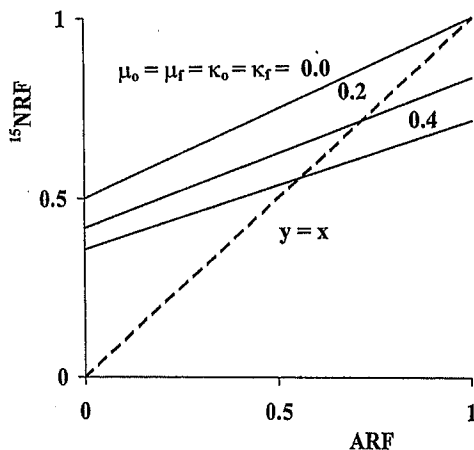


Figure 7. ^{15}NRF as a function of ARF for the case of plant uptake and mineralization-immobilization, for $NS_i/NF_i = 1.0$, $\varepsilon_o = \varepsilon_f = 1.0$, $\mu_o = \mu_f = \kappa_o = \kappa_f = 0.0, 0.2$ and 0.4 , according to Equation 55.

To investigate the effect of varying values of NS_i/NF_i and of decreasing values of ε_f , if $N^o > NP_f$, on the relationship between ^{15}NRF and ARF, values of ^{15}NRF and ARF were calculated for a standard dataset as follows:

$$\begin{aligned}
 NS_i &= 10, 20, \dots, 100 \text{ kg ha}^{-1} \\
 NF_i &= 10, 20, \dots, 100 \text{ kg ha}^{-1} \\
 NP_f &\leq 100 \text{ kg ha}^{-1} \\
 \varepsilon_o &= 1 \\
 \varepsilon_f &= 1 \quad \text{if } N^o \leq 100 \text{ kg ha}^{-1} \\
 \varepsilon_f &= 100/N^o \quad \text{if } N^o > 100 \text{ kg ha}^{-1} \\
 \kappa_o &= \mu_o = 0.20 \text{ or } 0.40 \\
 \kappa_f &= \mu_f = 0.20 \text{ or } 0.40
 \end{aligned}$$

In Figure 8, only data for which $^{15}\text{NRF} < 1/(1+\mu_f)$, $\text{ARF} > 0$ and $NP_f = 100 \text{ kg ha}^{-1}$ are plotted. It can be seen that the intercept as well as the slope decrease with increasing values of $\kappa_{o,f} = \mu_{o,f}$ in accordance with Equation 55.

To further examine the behaviour of the different quantities of N in fertilized treatments as a function of fertilizer rate, these quantities were calculated using Equations 32–35 for a situation in which mineralization and immobilization occur in fertilized treatments only, i.e., $\kappa_o = \mu_o = 0$ and $\kappa_f = \mu_f = 0.40$, where κ_f and μ_f increase stepwise with increasing fertilizer rate in increments of 0.10 units per 10 kg of fertilizer N per ha, i.e., from $\kappa_f = \mu_f = 0$ at $NF_i = 0$ to $\kappa_f = \mu_f = 0.40$ for $NF_i \geq 40 \text{ kg ha}^{-1}$. It can be seen from Figure 9 that $NS_f = 0$ up to a fertilizer application rate of 50 kg ha^{-1} . This is because if $\varepsilon_f = \varepsilon_o = 1$ all available soil mineral N is taken up by the crop until the crop's need for N ($NP_f = 100 \text{ kg ha}^{-1}$) has been satisfied at $N^o = 100 \text{ kg ha}^{-1}$. In case $N^o > 100 \text{ kg ha}^{-1}$, NS_f increases linearly with increasing fertilizer application rate, as plant uptake ceases beyond this N level. As the rate of immobilization equals the rate of mineralization, the net effect of these two compensating processes is that the size of

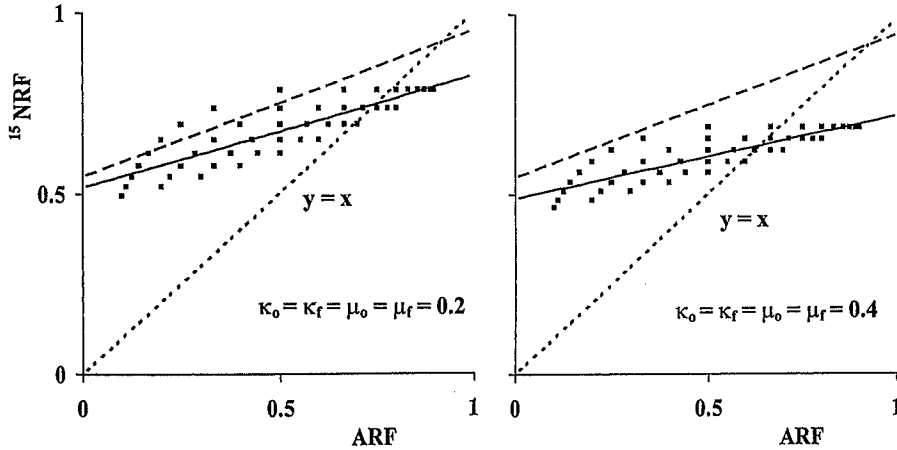


Figure 8. Calculated ^{15}NRF -values as a function of ARF for $\epsilon_o = \epsilon_f = 1.0$, $\kappa_o = \kappa_f = \mu_o = \mu_f = 0.2$ (left) or 0.4 (right), and NP_{oh} , $\text{NP}_{\text{h}} \leq 100 \text{ kg ha}^{-1}$. The solid line represents the linear regression line through the calculated values. The broken line represents the linear regression equation of ^{15}NRF as a function of ARF for $\epsilon_o = \epsilon_f = 1.0$ (plant uptake only).

the soil mineral N pool remains constant, i.e., is affected by plant uptake only. It can be seen from Figure 9 that NI_f increases with increasing fertilizer application rate until NP_f is 100 kg ha^{-1} at $\text{N}^o = 100 \text{ kg ha}^{-1}$, after which ϵ_f decreases with increasing N^o , which causes NI_f to remain constant. However, the isotopic composition of NI_f continues to change, i.e., the $^{15}\text{N}/^{14}\text{N}$ ratio continues to increase because of the increase of fertilizer derived N in the soil mineral N pool.

Total plant uptake (NP_f) increases linearly up to $\text{N}^o = 100 \text{ kg ha}^{-1}$ and remains constant thereafter. However, the isotopic composition of NP_f continues to change, because of the changing $^{15}\text{N}/^{14}\text{N}$ ratio in the soil mineral N pool with increasing fertilizer application rates. Initially, NP_{fs} exceeds NP_o ($= 50 \text{ kg ha}^{-1}$). This is a positive, apparent ANI, caused by pool substitution. If $\text{N}^o > 100 \text{ kg ha}^{-1}$, NP_{fs} decreases to values below 50 kg ha^{-1} , due to the increasing $^{15}\text{N}/^{14}\text{N}$ ratio and decreasing ϵ_f in the soil mineral N pool with increasing fertilizer application rates, when the crop's N requirement has been satisfied.

At low fertilizer application rates ($\text{NP}_f \leq 100 \text{ kg ha}^{-1}$) the ARF is larger than ^{15}NRF , the latter being equal to $1/(1+\mu_f)$. At higher rates, ARF decreases more strongly than ^{15}NRF , such that eventually $^{15}\text{NRF} > \text{ARF}$. It can be seen that the difference $\text{ARF} - ^{15}\text{NRF}$ follows essentially the same pattern as $\text{NP}_{\text{fs}} - \text{NP}_o$. Hence, if $\text{N}^o \leq 100 \text{ kg ha}^{-1}$, it follows that $\text{NS}_f = 0$ and $\epsilon_f = 1$, such that $\text{ANI} = \text{NI}_{\text{ff}}$, i.e., the excess soil-derived N in the crop is equivalent to the immobilized fertilizer-derived N. This point was also noted by Stout (1995) in his evaluation of the added nitrogen interaction in forage grasses. However, if $\text{N}^o > 100 \text{ kg ha}^{-1}$, it follows that $\text{NS}_f > 0$ and $\epsilon_f < 1$, such that that $\text{ANI} < \text{NI}_{\text{ff}}$. In this particular case:

$$\text{ANI} = \text{NI}_{\text{ff}} - \Delta\text{NS}_{\text{ff}}$$

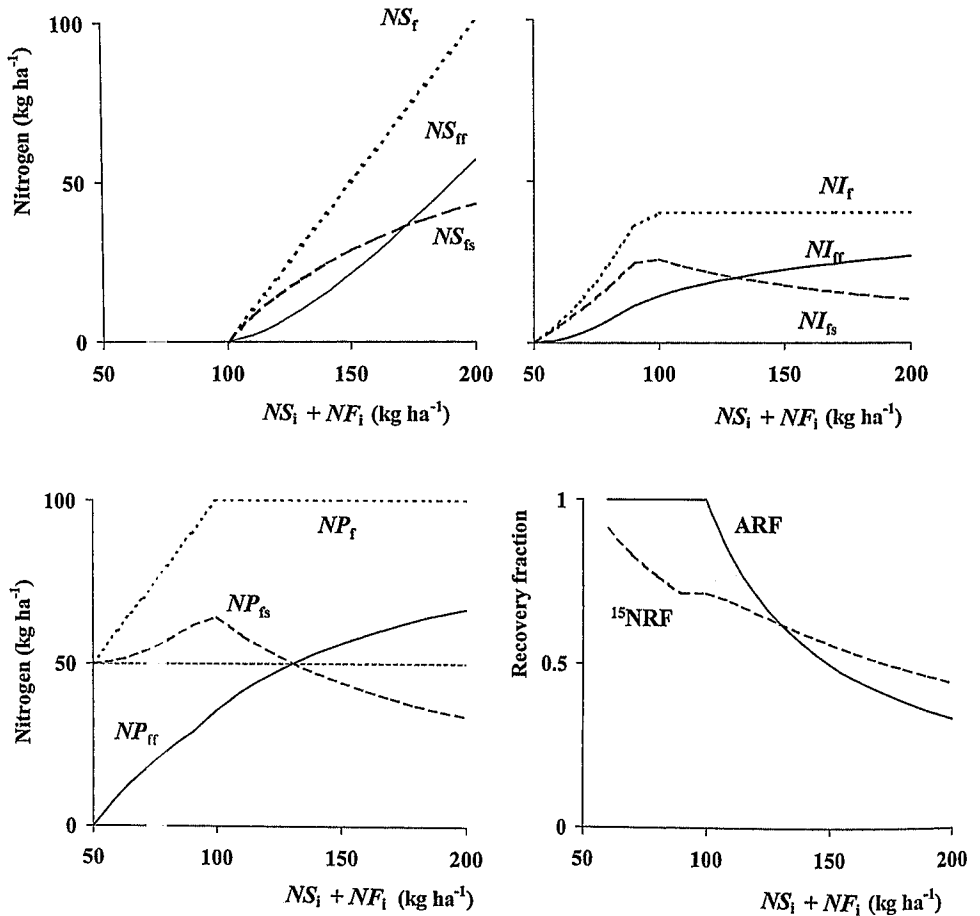


Figure 9. Soil-derived (NS_{fs}), fertilizer-derived (NS_{fr}) and total amount of soil mineral N (NS_f) (top left), soil-derived (NI_r), fertilizer-derived (NI_{fr}) and total immobilized N (NI_{fs}) (top right), soil-derived (NP_{fs}), fertilizer-derived (NP_{fr}) and total plant N (NP_t) in fertilized treatments (bottom left), and ARF and ^{15}NRF (bottom right), as functions of total soil mineral N, with $N^0 = NS_i + NF_i$ for $NS_i = 50$ kg ha⁻¹, $NP_{fs} \leq 100$ kg ha⁻¹, $\mu_o = \kappa_o = 0$, and $\mu_r = \kappa_r$ stepwise increasing from 0.10 at $N^0 = 60$ to 0.40 at $N^0 \geq 90$ kg ha⁻¹, according to Equations 13 and 14 for soil mineral N, Equations 18 and 19 for plant uptake, Equations 22 and 23 for immobilized N and Equations 35 and 36 for ARF and ^{15}NRF , respectively.

where

$$\Delta NS_{fr} = (NF_i/N^0)NS_f - NS_{fr} = NS_{fs} - (NS_i/N^0)NS_f$$

In other words, in this case there are two ANI's: one in the plant N pool and one in the soil mineral N pool, and the equivalent of NI_{fr} is distributed over these two pools:

$$NI_{fr} = (NP_{fs} - NP_o) + \{NS_{fs} - (NS_i/N^0)NS_f\}$$

Finally, the relationship between ^{15}NRF and ARF was investigated in 4 contrasting cases, all of which include plant uptake and either (1) mineralization and immobilization occur in all treatments, (2) mineralization in all treatments, but immobilization not ($\kappa_o = \kappa_f = 0$), (3) an increased uptake efficiency in fertilized plots ($\varepsilon_f = 0.8$, $\varepsilon_o = 1.0$), or (4) mineralization in fertilized treatments only ($\kappa_o = \mu_o = 0$, $\kappa_f = 0$, $\mu_f = 0.2$). All cases would result in 'real' ANI's. In the cases 1 and 2, the mineralization coefficients are the same for fertilized and unfertilized treatments ($\mu_o = \mu_f$), but the amounts of N mineralized increase in fertilized treatments, because of $\mu_f N^o > \mu_o N S_i$ if $N F_i > 0$, which may be considered a fertilizer-induced effect. In all cases, ^{15}NRF exceeds ARF at higher rates of N^o , when the crop has ceased to take up N. This is simply an effect of increasing $^{15}\text{N}/^{14}\text{N}$ ratio in the soil mineral N pool with increasing fertilizer application rate. This effect could be termed a 'real' ANI, as it is not caused by pool substitution or a similar mechanism.

Figure 10 includes all cases listed by Jansson (1971) that could cause a discrepancy between the difference and isotope-dilution methods: (1) increased mineralization of organic N induced by the addition of fertilizer (cases 2 and 4), (2) irreversible uptake of ^{15}N in the organic N pool as a result of mineralization-immobilization turnover in the soil (case 1), and (3) increased availability of soil mineral N due to better root development in fertilized treatments (case 3). It may be noted again that immobilization alone would not cause a discrepancy between the two methods: only a combination of mineralization and immobilization would do so.

Discussion

The present model assumes that (1) initial soil mineral N and fertilizer N mix instantaneously and completely, (2) there is only one soil mineral N pool, i.e., there is no need to distinguish between ammonium- and nitrate-N, (3) none of the processes occurring in the soil-crop system discriminates between ^{15}N and ^{14}N , (4) all time-dependent processes follow zero-order kinetics, and (5) their rate constants are proportional to the relative abundance of the reactants in the reactant pool (law of mass action). Most of these assumptions have been discussed in Harmsen (2003), except for the zero-order kinetics and the associated rate constants of plant uptake, mineralization and immobilization, as the latter two processes were not considered earlier.

Soil mineral N pool and reaction kinetics

With regard to the assumption that there is only one soil mineral N pool it may be noted that in the presence of mineralization and immobilization, the composition of the soil mineral N pool changes continuously. Both mineralization and immobilization primarily affect the ammonium-N pool, as soil organisms have a preference for ammonium-N, which is energetically more favourable, whereas all (re)mineralized N is initially in the form of ammonium-N. The dynamics of the system are determined by the rates of mineralization and immobilization, nitrification, plant uptake and possibly processes such as denitrification, nitrate leaching, ammonia volatilization and ammonium fixation. The nitrification of $^{15}\text{NH}_4\text{-N}$ is not a reversible process and once

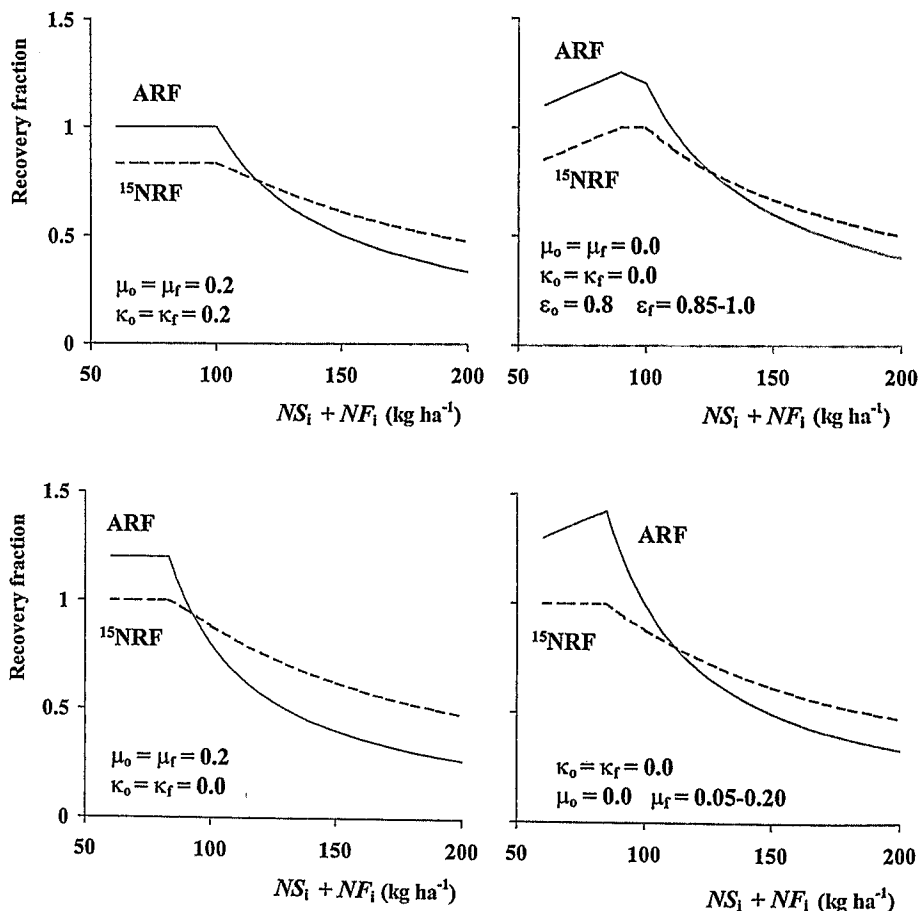


Figure 10. ARF and ^{15}NRF as functions of total soil mineral N, with $N^* = NS_i + NF_i$ (kg ha^{-1}) for $NS_i = 50$ kg ha^{-1} , $NP_{\text{in}} \leq 100$ kg ha^{-1} and $\varepsilon_o = \varepsilon_f = 1$ (except for case 3), and for 4 cases: (1) $\mu_o = \mu_f = 0.2$ and $\kappa_o = \kappa_f = 0.2$ (top left), (2) $\mu_o = \mu_f = 0.2$ and $\kappa_o = \kappa_f = 0.0$ (bottom left), (3) $\mu_o = \mu_f = 0.0$, $\kappa_o = \kappa_f = 0.0$, $\varepsilon_o = 0.8$ and ε_f increasing from 0.85 at $NF_i = 10$ to 1.00 at $NF_i \geq 40$ kg ha^{-1} (top right), and (4) $\kappa_o = \kappa_f = 0.0$, $\mu_o = 0.0$ and μ_f increasing from 0.05 at $NF_i = 10$ to 0.20 at $NF_i \geq 40$ kg ha^{-1} (bottom right), according to Equations 35 and 36.

ammonium-N is nitrified the $^{15}\text{NO}_3\text{-N}$ cannot be transformed back into ammonium. That is, there is no chemical equilibrium between ^{15}N in the two pools.

The assumption that the distribution of ^{15}N over the ammonium- and nitrate-pools is proportional to the distribution of fertilizer-derived N over these pools would be correct if none of the processes involved would discriminate between ^{15}N and ^{14}N . This would not apply to the remineralization of immobilized fertilizer-derived N. If the mineralized ^{14}N is apportioned to the soil- and fertilizer-derived soil mineral N fractions in proportion to the immobilized soil- and fertilizer-derived fractions, then the ammonium-N pool will be too low in ^{15}N .

The assumption that all processes follow zero-order kinetics and that the rates are

proportional to the relative abundance of the reactants (mass action) may not be realistic for soil-plant systems under field conditions. For example, rates of mineralization and immobilization depend, amongst other things, on temperature and moisture conditions, and these will change during the growing season. However, the question is whether ^{15}N can be considered a tracer for fertilizer-derived N and this will be the case, irrespective of the kinetics of the processes occurring in the system.

Mineralization and immobilization

The remineralization of immobilized fertilizer-derived N was assumed to be zero (Equations 7 and 8). Although, in principle, this assumption is not required and the relevant differential equations (Equations 5 and 6) can be solved for the general case (Kirkham & Bartholomew, 1955), it helps to simplify the treatment without losing much relevant information.

In most soils, the organic N pool is much larger than the mineral N pool. A soil with 1% organic N contains about $2 \times 10^4 \text{ kg ha}^{-1}$ in the top 20 cm layer. Typically, the amount of mineral N in agricultural soils would be in the range of 10–100 kg ha^{-1} in the top 20 cm layer. Hence, the organic N pool would be larger by a factor 10^2 – 10^3 . So even if one could distinguish between soil-derived and fertilizer-derived N, the organic N pool would act as a sink for fertilizer N. If 20–40 kg of fertilizer-derived N per hectare would be immobilized during a growing season, the fraction of that nitrogen that is remineralized would be minimal, of the order of 10^{-3} . However, the fertilizer N used in ^{15}N tracer experiments is enriched in ^{15}N and it is assumed that ^{15}N may be considered a tracer for fertilizer N. In the case of mineralization-immobilization, however, the organic N phase acts as a sink for ^{15}N . The initial ^{15}N content of the organic N pool will be close to natural abundance. If 100 kg of fertilizer N with a ^{15}N enrichment of 5 atom% is applied per hectare and all of this N is immobilized in the organic N pool, then this would raise the ^{15}N content of the organic N pool by about 0.025% above natural abundance (0.3663 atom%). Therefore, the ^{15}N content in the organic N pool will remain close to natural abundance during one growing season and thus act as a sink for ^{15}N . Even if it is assumed that most of the immobilization-mineralization is confined to an 'active' fraction of the total organic N pool, it is not likely that significant quantities of immobilized ^{15}N will be remineralized during the same growing season. Remineralization of immobilized ^{15}N in the second growing season is typically in the range of 1–10%. If during the first season some 40 kg of fertilizer-derived N per hectare is immobilized and during the second season the amount of this N that is remineralized is in the range of 1–10%, then the size of the 'active' organic N pool would be in the range of 400–4000 kg ha^{-1} , or 0.02–0.20% of the N in the top 20 cm of the soil, assuming that remineralization follows the law of mass action. So even in the case of 400 kg ha^{-1} , remineralization during the growing season would therefore be quite low.

Relationship between ^{15}NRF and ARF

Table 1 summarizes the way the N coefficients and the ratio NS_i/NF_i affect the rela-

Table 1. The effect of N coefficients and the ratio NS_i/NF_i on intercept and slope of the relationship between ^{15}NRF and ARF, according to Equation 50. In the case of loss of N from the mixed soil mineral N pool, λ_o and λ_f can be substituted for κ_o and κ_f in Equation 50. An increase in a quantity is denoted by ++, a decrease by --, whereas +/- denotes either a decrease or an increase.

Quantity	Change	Effect on intercept	Effect on slope	Remarks
ε_o	--	--	none	compare λ_o and κ_o
ε_f	+/-	none	none	if $\mu_f = 0$
ε_f	--	++	++	if $\mu_f > 0$
NS_i/NF_i	++	++	--	
	--	--	++	
λ_{if}	++	--	--	reduces ARF and ^{15}NRF
λ_o	++	--	none	$1-\lambda_o$ same effect as ε_o
λ_f	+/-	none	none	compare κ_f ; reduces ARF and ^{15}NRF
μ_o	++	++	none	$\mu_o \neq \mu_f$
μ_f	++	--	--	$\mu_o \neq \mu_f$
$\mu_o = \mu_f$	++	(+)	--	intercept nearly constant
κ_o	++	--	none	$1-\kappa_o$ same effect as ε_o
κ_f	+/-	none	none	compare λ_f ; reduces ARF and ^{15}NRF

relationship between ^{15}NRF and ARF (Equation 50). The uptake coefficient for unfertilized plots (ε_o) affects the intercept of Equation 50 but not the slope: the intercept decreases if ε_o decreases. An increase in the loss of N from the soil mineral N pool (λ_o) or in the amount of N immobilized in unfertilized treatments (κ_o) has a similar effect as a decrease of ε_o , because the intercept decreases if the term $(1-\lambda_o-\kappa_o)\varepsilon_o$ decreases. A change in ε_f has no effect if $\mu_f = 0$, but does affect both the slope and the intercept if $\mu_f \neq 0$ (see Equation 50). This is because:

$$0 \leq \{1 - (1 - \varepsilon_f)^{1+\mu_f}\} / \varepsilon_f < (1 + \mu_f) \quad \text{if } \varepsilon_f, \mu_f > 0$$

So the effect of a change in ε_f on the slope and intercept is larger for smaller values of ε_f .

The effect of the ratio NS_i/NF_i on the relationship between ^{15}NRF and ARF is quite pronounced, both on the slope and the intercept, as was the case if mineralization and immobilization do not occur (Harmsen, 2003).

Loss of fertilizer N prior to mixing with the soil mineral N affects both the slope and

the intercept. Also, λ_{ff} reduces the range of values of ^{15}NRF by a factor $(1-\lambda_{ff})$ and of ARF by the same factor, if $(1+\mu_f-\kappa_f)\varepsilon_f = (1+\mu_o-\kappa_o)\varepsilon_o$ (Equations 48 and 49). This also follows directly from the mass balance: if fertilizer N is applied at a rate of 100 kg ha⁻¹ and 30% of this N is lost due to ammonia volatilization, then the maximum amount of fertilizer N that can be recovered by the crop is 70 kg ha⁻¹ which is equivalent to $^{15}\text{NRF} = 0.70$.

Loss of N from the mixed soil mineral N pool in the present model has the same effect as in the absence of mineralization-immobilization (Harmsen, 2003). The range of values of ^{15}NRF is reduced by a factor $1-\lambda_f$ and the same applies to ARF if $(1-\lambda_f)\varepsilon_f = (1-\lambda_o)\varepsilon_o$. Mineralization in unfertilized (μ_o) and fertilized plots (μ_f) has opposite effects on the intercept, whereas the slope is only affected by μ_f in both cases if $\mu_o \neq \mu_f$. In case $\mu_o = \mu_f$, the effect on the intercept is slightly positive (nearly constant) and on the slope negative, with increasing $\mu_o = \mu_f$. From Equation 49 it follows that both μ_f and κ_f affect the range of values of ^{15}NRF . If $\kappa_f > 0$ and $\varepsilon_f = 1$ it follows that ^{15}NRF is reduced by a factor $(1+\mu_f-\kappa_f)/(1+\mu_o)$, which is < 1 if $\mu_f > 0$. However, if $\varepsilon_f < 1$ the inequality becomes slightly more complex:

$$(1+\mu_f-\kappa_f)/(1+\mu_o) \leq ^{15}\text{NRF}/\varepsilon_f < (1+\mu_f-\kappa_f)$$

from which it follows that the actual effect on the $^{15}\text{NRF}/\varepsilon_f$ depends on the values of μ_f and κ_f .

The effect of κ_o and κ_f on ^{15}NRF and ARF, and on the relationship between them, is similar to the case of loss of N from the mixed soil mineral N pool (λ_o , λ_f).

In summary, it follows that the intercept in Equation 50 is decreased by decreasing values of ε_o and NS_i/NF_i and by increasing values of λ_o and κ_o , and μ_f if $\mu_o \neq \mu_f$. The effect of NS_i/NF_i is variable, because of varying values of NS_i and NF_i within and between experiments. In many cases the effects of λ_o and κ_o will be reduced by values of λ_f and κ_f of the same order of magnitude as λ_o and κ_o , in which case the range of ^{15}NRF will be reduced, such that $\text{ARF} \leq ^{15}\text{NRF}$. Therefore, the main factors resulting in a decrease in the intercept over the entire range of values of ARF, would be values of $\varepsilon_o < 1$ and $\mu_f > 0$. In other words, increased uptake of soil-derived N and mineralization in fertilized plots are the main factors causing ^{15}NRF to be smaller than ARF in the higher range of ARF-values (e.g. 0.6–1.0). These cases have been discussed in connection with Figures 9 and 10 and it has been shown that the difference between ARF and ^{15}NRF is a measure for the added N interaction, which in turn provides information on the fate of fertilizer N in the soil-plant system (Jenkinson *et al.*, 1985; Stout, 1995).

Finally, it has been shown that the linear regression lines through the calculated values of ^{15}NRF as a function of ARF in the 'scatter-diagrams' (Figures 5 and 8) tend to be 'flatter' than the theoretical relationships. For example, for $\varepsilon_o = \varepsilon_f = 1$, $NS_i/NF_i = 1$, $\lambda_{ff} = 0$ and $\kappa_o = \mu_o = 0$, 0.2 or 0.4 and $\kappa_f = \mu_f = 0$, 0.2 or 0.4, the exact relationships (Equation 50) would be:

$$^{15}\text{NRF} = 0.50 + 0.50\text{ARF}$$

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

$$^{15}\text{NRF} = 0.36 + 0.36\text{ARF}$$

whereas the linear regression equations for the same conditions and $NP_f \leq 100 \text{ kg ha}^{-1}$ would be:

$$^{15}\text{NRF} = 0.55 + 0.40\text{ARF}$$

$$^{15}\text{NRF} = 0.52 + 0.31\text{ARF}$$

$$^{15}\text{NRF} = 0.49 + 0.23\text{ARF}$$

Hence, the intercept increases and the slope decreases in the case of the linear regression equations as compared with the theoretical relationship. In the case of Figures 5 and 8 this is due to the choice of the initial values of NS_i and NF_i and the condition that $NP_i, NP_o \leq 100 \text{ kg ha}^{-1}$, which results in variation in the values of ϵ_f and NS_i/NF_i . The relation between the theoretical relationship and the linear regression equations cannot be generalized on the basis of these examples, but it is believed that similar trends may be observed in experiments conducted under field conditions.

Conclusions

Increased uptake of soil-derived mineral N and mineralization in fertilized plots may cause ^{15}NRF to be smaller than ARF in the higher range of ARF-values (N-deficient soils). The effect of mineralization in diluting ^{15}N in the soil mineral N pool is increased by plant uptake and immobilization. Losses of N from the fertilizer or the mixed soil mineral N pool reduce the range of ^{15}NRF -values and may similarly affect ARF-values. The difference between ARF and ^{15}NRF is a measure of the added N interaction in the plant N pool and provides information on the fate of fertilizer N in the soil-plant system. The ^{15}N recovery fraction accurately measures the fertilizer N recovery by the crop, but does not include any soil-derived N mineralized in exchange for immobilized fertilizer-derived N.

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Appendix

List of symbols

All quantities of N are in kg ha⁻¹, atom% ¹⁵N (excess) concentrations are in %, time in days, rate constants are in kg ha⁻¹ day⁻¹, and factors, recovery fractions and coefficients are dimensionless. Symbols that occur only once are defined in the text and are not repeated here.

- ARF = apparent N recovery fraction at harvest
 c_{xf} = atom% ¹⁵N excess concentration in N fertilizer
 c_{xp} = atom% ¹⁵N excess concentration in fertilized crop at harvest
 c_{xs} = atom% ¹⁵N excess concentration in the soil mineral-N pool
 \bar{c}_{xs} = mean atom% ¹⁵N excess concentration in the soil mineral-N pool, averaged over a specified time interval
 N^o = $NF_i + NS_i$
 NF_i = initial N fertilizer applied to the soil
 NI_f = $NI_{fs} + NI_{fh}$
 NI_{ff} = fertilizer-derived immobilized N in fertilized treatment at time t
 NI_{fh} = $NI_{fsh} + NI_{fth}$
 NI_{fth} = fertilizer-derived immobilized N in fertilized treatment at harvest
 NI_{fs} = soil-derived immobilized N in fertilized treatment at time t
 NI_{fsh} = soil-derived immobilized N in fertilized treatment at harvest
 NI_o = immobilized N in unfertilized treatment at time t
 NI_{oh} = immobilized N in unfertilized treatment at harvest
 NM_f = $NM_{fs} + NM_{ff}$
 NM_{ff} = fertilizer-derived mineralized N in fertilized treatment at time t
 NM_{fth} = fertilizer-derived mineralized N in fertilized treatment at harvest
 NM_{fh} = $NM_{fsh} + NM_{fth}$
 NM_{fs} = soil-derived mineralized N in fertilized treatment at time t
 NM_{fsh} = soil-derived mineralized N in fertilized treatment at harvest
 NM_o = mineralized N in unfertilized treatment at time t
 NM_{oh} = mineralized N in unfertilized treatment at harvest
 NO_f = $NO_{fs} + NO_{ff}$
 NO_{ff} = fertilizer-derived organic N in fertilized treatment at time t
 NO_{fs} = soil-derived organic N in fertilized treatment at time t
 NP_f = $NP_{fs} + NP_{ff}$
 NP_{ff} = uptake of fertilizer-derived N by fertilized crop at time t
 NP_{fth} = uptake of fertilizer-derived N by fertilized crop at harvest
 NP_{fh} = $NP_{fsh} + NP_{fth}$
 NP_{fs} = uptake of soil-derived N by fertilized crop at time t
 NP_{fsh} = uptake of soil-derived N by fertilized crop at harvest
 NP_o = uptake of N by unfertilized crop at time t
 NP_{oh} = uptake of N by unfertilized crop at harvest
¹⁵NRF = fertilizer N recovery fraction

NS_f	$= NS_{fs} + NS_{ff}$
NS_{ff}	= fertilizer-derived mineral N in fertilized treatment at time t
NS_{fth}	= fertilizer-derived mineral N in fertilized treatment at harvest
NS_{fth}	$= NS_{fsh} + NS_{ffh}$
NS_{fs}	= soil-derived mineral N in fertilized treatment at time t
NS_{fsh}	= soil-derived mineral N in fertilized treatment at harvest
NS_i	= initial soil mineral N
NS_o	= soil mineral N in unfertilized treatment at time t
NS_{oh}	= soil mineral N in unfertilized treatment at harvest
t	= time
t_h	= time until harvest
e_f	= uptake coefficient for N in fertilized treatment
e_{ff}	= uptake coefficient for fertilizer-derived N in fertilized treatment
e_{fs}	= uptake coefficient for soil-derived N in fertilized treatment
e_o	= uptake coefficient for N in unfertilized treatment
κ_f	= immobilization coefficient for N in fertilized treatment
κ_o	= immobilization coefficient for N in unfertilized treatment
λ_f	= loss coefficient for N in fertilized treatment
λ_{ff}	= loss coefficient for fertilizer-derived N in fertilized treatment
λ_o	= loss coefficient for N in unfertilized treatment
μ_f	= mineralization coefficient for N in fertilized treatment
μ_o	= mineralization coefficient for N in unfertilized treatment
v_{fi}	= rate constant for immobilization of N in fertilized treatment
v_{fm}	= rate constant for mineralization of N in fertilized treatment
v_{fp}	= rate constant for plant uptake of N in fertilized treatment
v_{oi}	= rate constant for immobilization of N in unfertilized treatment
v_{om}	= rate constant for mineralization of N in unfertilized treatment
v_{op}	= rate constant for plant uptake of N in unfertilized treatment