5.2 Modelling of the behaviour of nitrogen in soil

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5.2.1 Introduction

In the last decade numerous mathematical models of the terrestrial nitrogen cycle have been developed. Depending on the ultimate goal, the models differ widely in concept. Moreover models were developed by scientists specialized in different fields, which hindered communication, so that even models with the same goal differed significantly in concept. For this reason a workshop on modelling N in soil-plant systems was organized. During this workshop about 29 nitrogen models and the present 'state of art' of the soil-physical, microbiological and plantphysiological aspects of the fate of N in the soil-plant system were discussed (Frissel & van Veen, 1981). Several classification devices of models of the soil N cycle were proposed. A rough classification is the division into budgeting and dynamic models; budgeting models consist mainly of material balances whereas dynamic models are based on a description of the processes of the system by rate equations, usually in the form of differential equations. Another classification device distinguishes between models which are mainly developed for better scientific understanding, for forecasting and for management purposes (cf. Subsection 1.3.1). A third classification dealt specially with dynamic models of the N cycle, dividing the models into groups depending on whether emphasis was on transport processes, on crop growth or on organic matter transformations.

Subsection 5.2.2 deals with the model developed by the authors, which is a typical representative of the last category (organic matter transformations) since it stresses growth and turnover of the soil microbial biomass and related N and carbon (C) transformations. Furthermore, the present 'state of art' with respect to the soil-physical, chemical and biological aspects of modelling the terrestrial N cycle will be discussed (Subsection 5.2.3). The text of this section is based on papers published elsewhere by van Veen (1977), van Veen et al. (1981) and Frissel & van Veen (1981).

5.2.2 Description of the model

The model, and some general microbiological features

A scheme of the model is shown in Figure 69. The present model does not include a detailed description of N uptake by plants. When the model is used to simulate the fate of N in soil in the presence of crops, the rate of uptake is calculated from the total observed N uptake and it is therefore a driving variable. The transformation processes presented in Figure 69 are described in separate

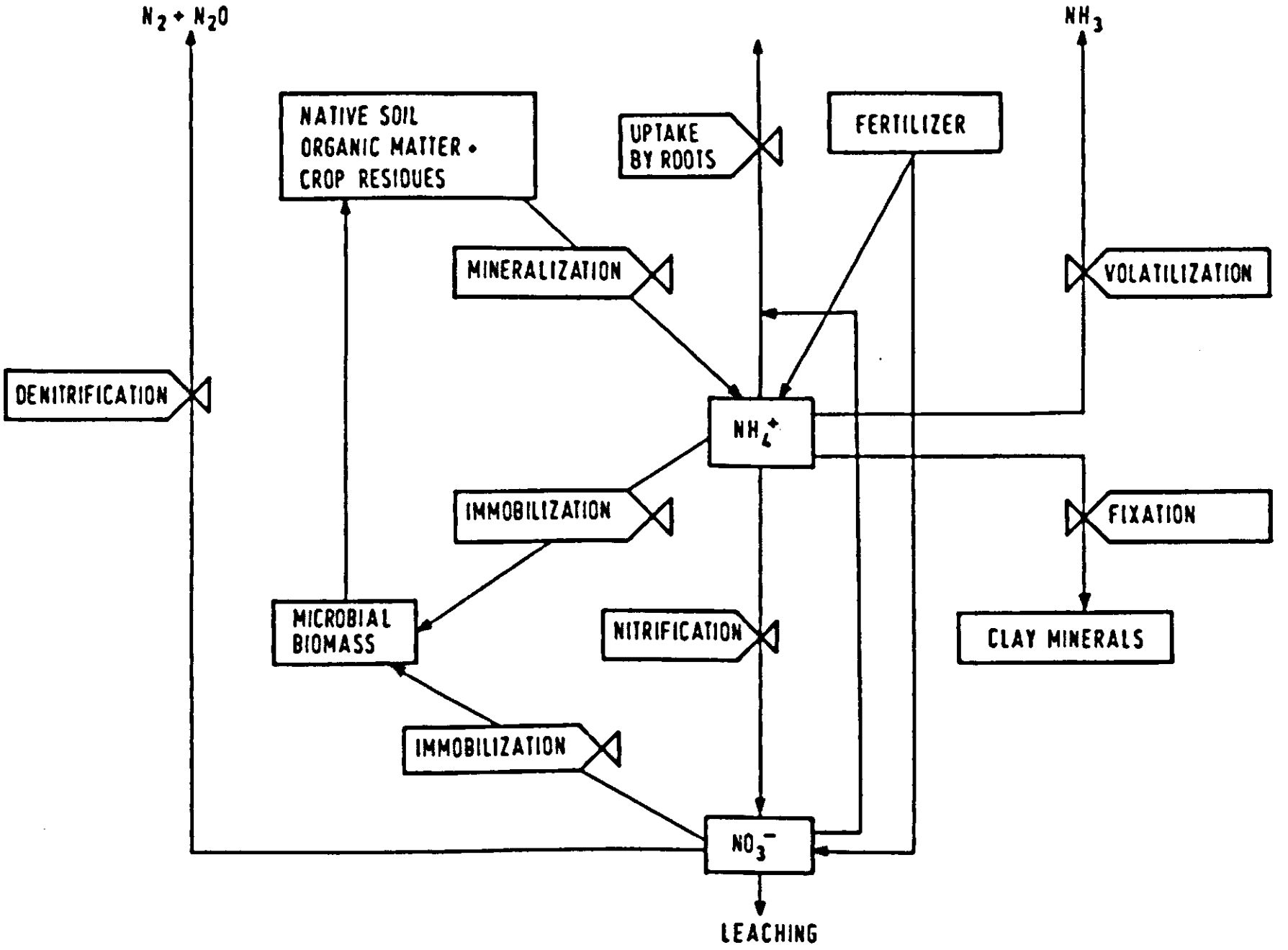

Figure 69. A simplified relational diagram of the N model (van Veen et al., 1981).

submodels. Submodels are: mineralization and immobilization, nitrification, denitrification, volatilization of ammonia, ammonium fixation on clay minerals and leaching. A detailed scheme of the mineralization and immobilization submodel in relation to NO_3^- production and transport is presented in Figure 70. The model is a multilayer model i.e., several layers of soil are distinguished. The equations, described below, are identical for all layers except in case of the first or upper and last or lower layer, for which adapted input and output equations are used. The number of layers, as well as their thickness, depends on the situation under study. Besides the vertical compartmentalization of the total model, in the submodel of denitrification a radial division of a soil volume around an airfilled pore is considered. In this description the number of layers is fixed (10), but their thickness is calculated depending on the relative air volume in the soil.

Growth of micro-organisms is considered to be determined by the concentration of a growth limiting substrate. This relationship is described according to the hyperbolic equation, Monod or Michaelis Menten equation. Thus:

$$GBIOM = GRMAX * BIOM * CX/(KX + CX) \quad (91)$$

where GBIOM is the gross growth rate of microbes, GRMAX the maximum specific growth rate, CX the concentration of the growth limiting substrate X, BIOM the amount of micro-organisms and KX the saturation constant. The

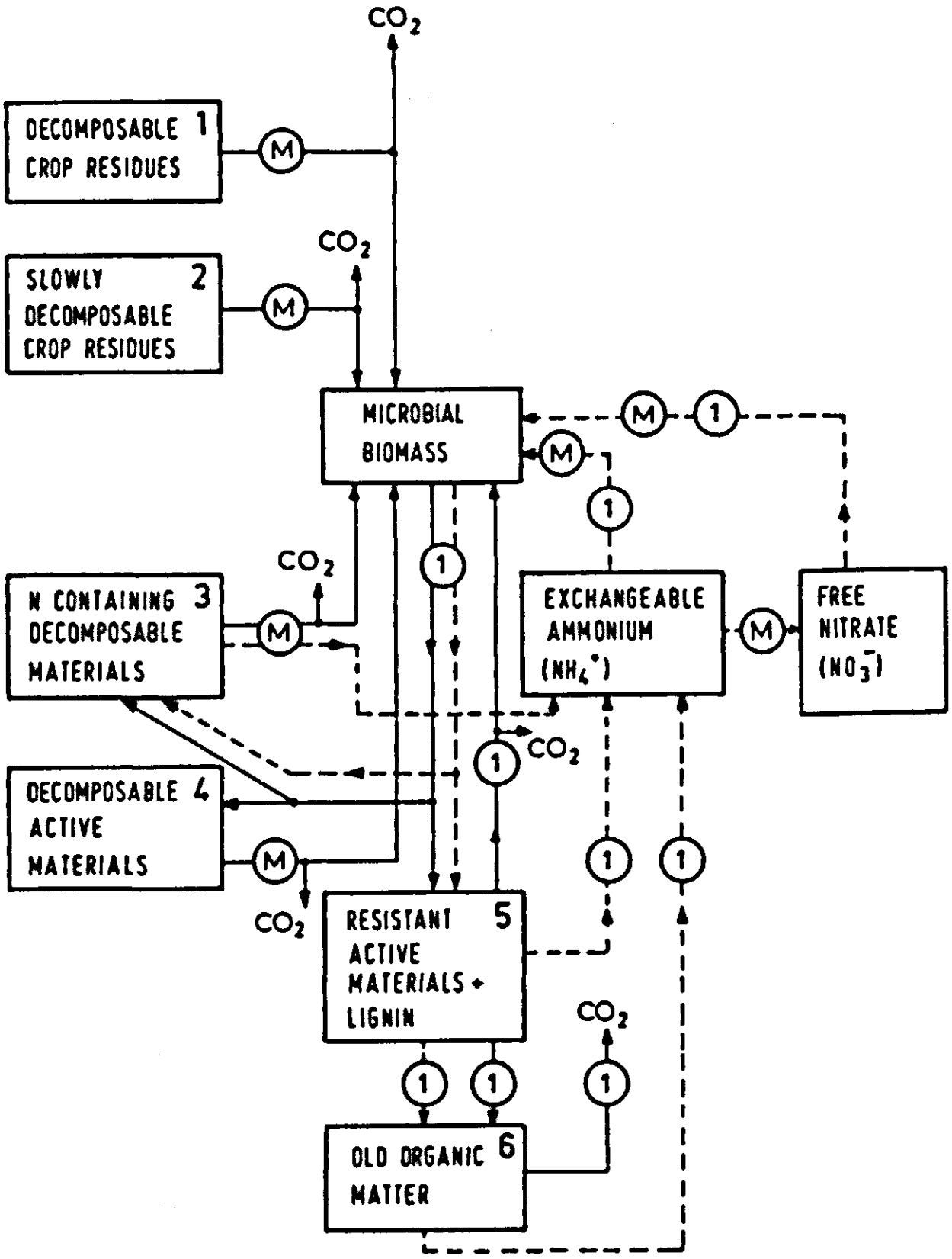

Figure 70. Schematic presentation of the third version of the submodel of mineralization and immobilization (van Veen et al., 1981). Drawn lines represent the flux of carbon, dashed lines represent the flow of nitrogen. Ⓜ stands for Michaelis-Menten kinetics, ① for first order kinetics. The numbers 1-6 of state variables are explained in the text.

consumption rate (= transformation rate) of a substrate, DCX, is linearly related to the gross growth rate GBIOM:

$$DCX = -GBIOM * 1./EFFX \tag{92}$$

where EFFX is the growth yield (amount of micro-organisms formed per unit of substrate consumed).

The hyperbolic model describes the reactions in which a certain compound is transformed due to catalytic action with a limited 'reach'. This means that the transformation rate not only depends on the amount of the transformed material but also on the amount of transformer, which is not transformed itself. Enzymatic (soil microbiological) reactions are these kind of reactions and are therefore properly described by the hyperbolic model.

Although the hyperbolic model itself is considered to be a correct description of microbial growth and concurrent decomposition of organic matter in soil, it requires data on the maximum specific growth rate and the saturation constant, which cannot or can only very roughly, be determined in soil. Therefore the more simple first-order rate kinetics are often used. The latter model implies that the decomposition rate of an organic component is only dependent on its concentration and that the biological potential to decompose organic matter in soil is not limiting.

Exercise 62
Derive zero and first-order rate equations from the hyperbolic model and discuss the use of zero and first-order rate kinetics to describe microbially mediated transformations.

Nitrifications

Nitrification is described as the result of the activity of only two genera of bacteria, *Nitrosomonas* and *Nitrobacter*. The hyperbolic model is used to describe growth with NH_4^+ and NO_2^- being the growth limiting substrates. The size of the nitrifier population is controlled by the balance between growth and death of the organisms. The latter process is described with first-order rate kinetics.

Mineralization and immobilization

The submodel for immobilization and mineralization has passed three stages during its development. At the first stage the C/N ratio of the organic material was used to control mineralization and immobilization. In a second stage, differences in the decomposability of the several compounds of plant residues were realized and five types of organic compounds were included: (hemi-) cellulose, lignin, sugar, protein and microbial biomass. C/N ratios of the organic matter were no longer used to control the decomposition, but the uptake of C by the growing biomass was determining the decomposition rate. At a third stage the substrates arrangement was revised so that it corresponded better with organic matter distributions as they are used by soil scientists. In this contribution we will deal with the last version only (Figure 70). For the other two versions see Beek & Frissel (1973), van Veen (1977) or Frissel & van Veen (1980).

Mineralization and immobilization are considered to be controlled by the growth and activity of the total microbial biomass in soil. C and N are considered to be the growth limiting substrates, with N being limiting at very low concentrations only (1-2 mg kg^{-1}). To recognize the differences in availability of organic matter compounds as substrates for micro-organisms, both plant residues and soil organic matter are divided into several components.

Crop residue C is split into sugars and other well decomposable carbohydra-

tes (Pool 1, Figure 70) and slowly decomposable material, mostly (hemi-) cellulose (Pool 2). The third pool contains all easily decomposable N containing substances, proteins and aminosugars. The fourth and fifth pool contain microbial debris products and lignins, which thus provide a base for chemical stabilization of organic matter. Those fractions can be considered together as the active fraction, according to Jansson's (1958) nomenclature. The difference between Pool 4 and Pool 5 is based on the consideration that material of Pool 5 consists of organic matter, which is adsorbed on clay minerals or entrapped in soil aggregates, but which is chemically identical to the material in the Pool 4 (Paul & van Veen, 1978). In contrast, the material of Pool 6 is considered to be chemically resistant, i.e. recalcitrant, old organic matter.

When C is used for synthesis of microbial biomass, a corresponding quantity of N (depending on the C/N ratio of the biomass and the substrate) is transferred to the inorganic N pool. But the N flux from the old organic matter (6) to the inorganic N pool is the only one which is not controlled by the soil microbial biomass because of its resistance, and biomass growth is not considered with C of this pool of substrate. The types of the conversion processes in Figure 70 are indicated with ① for processes described by first-order rate kinetics and with Ⓜ for those ones described by the hyperbolic or Monod model.

When using the hyperbolic model, the reaction rates depend on the amount of microbial biomass which is involved in the utilization of a particular substrate, X. Therefore it is assumed that each of the C pools is utilized by a fraction of the total microbial biomass, this fraction being proportional to the ratios of the amount of the particular C compound (CX) to the total amount of C in Pools 1-5 (CT).

The decay rate of the microbial biomass is specific for each type of microorganisms. The types which grow on easily available compounds are assumed to have a fast turnover rate, the types which grow on the resistant fractions turnover slowly. When assuming that the fraction of the biomass, which is involved in the decomposition of compound X, BIOMX, is proportional to the ratio CX/CT, i.e.:

$$BIOMX = CX/CT * BIOM \quad (93)$$

then the decay rate, KBIOMX, will be:

$$KBIOMX = KB * BIOMX \quad (94)$$

where KB is the decay rate constant. The net growth of the biomass is calculated from the difference between the growth rate and the decay rate.

To obtain the C losses from substrate Pools 1-4 (Figure 70), it must be taken into account that part of each compound is used for biosynthesis and the other part for energy production and related CO_2 production. So the utilization rate of C for biosynthesis, UBIOMX, is equal to the growth rate GBIOMX. The rate of CO_2 production equals:

$$DCO2X = GBIOMX * (1. - EFFX)/EFFX \quad (95)$$

and the total utilization rate of C is found by summation of UBIOMX and DCO2X. The rate of loss of C from Pools 5 and 6 is calculated according to first-order rate kinetics.

Finally, the N mineralization rate is calculated from the decomposition rate of the N containing components by dividing the C transfer rate by the C/N ratio of the components. The immobilization rate is proportional to the growth rate of microbial biomass (expressed in C equivalents) and is thus calculated by dividing the growth rate of the biomass by the C/N ratio of the biomass.

Exercise 63

Write a computer program to simulate the decomposition of two organic matter components, P and L.

The initial concentration of P, ICP, expressed as a mass fraction of C in soil is 100 $\mu g\ g^{-1}$. P contains nitrogen, its C/N ratio equals 3. Parameters to describe the decomposition of P are: the maximum specific growth rate of microbial biomass on P, GRMAP, equals 0.5 (d^{-1}), the growth yield of biomass on P, EFFP, is 0.6 ($g\ g^{-1}$), the saturation constant, KCP is 50 ($\mu g\ g^{-1}$ soil) and the death rate of biomass involved in decomposition of P, KBP is 0.3 (d^{-1}).

The initial microbial content, IBIOM also expressed in C is 100 $\mu g\ g^{-1}$soil. The initial inorganic N concentration, INIT, is 100 $\mu g\ g^{-1}$ soil and the C/N ratio of the biomass is 8.

L does not contain nitrogen. The important parameters to describe the decomposition of L are: the maximum specific growth rate of the microbial biomass on L, GRMAL, is 0.05 (d^{-1}); the growth yield of biomass on L, EFFL, is 0.1 ($g\ g^{-1}$); the saturation constant KCL is 200 ($\mu g\ g^{-1}$ soil); the initial concentration, ICL, also expressed in C, is 400 ($\mu g\ g^{-1}$ soil); and the death rate of biomass involved in decomposition of L, KBL, is 0.02 (d^{-1}).

Run the program for 15 days, and study the sensitivity of the inorganic N content for an assumed variation in the value of the growth yields.

Denitrification

The submodel of denitrification contains a description of the behaviour of oxygen (O_2) in water-saturated soils and in non-water-logged soils, to determine the occurrence of anaerobic zones in which denitrification is considered to occur. Therefore the number of air-filled pores per soil volume unit is calculated depending on the soil-water content and the pF curve of the soil (see Subsection 4.2.2). Transport of O_2 and NO_3^- from the pores into the surrounding soil is considered as being the result of diffusion due to concentration gradients.

Consumption of O_2, and of NO_3^- in the absence of O_2, is assumed to result from microbial activity, which is calculated in the submodel of mineralization and immobilization.

Ammonia volatilization

Ammonia (NH_3) volatilization is calculated as a function of the following equilibria:

$$NH_4^+ \text{ (exchangeable)} \rightleftharpoons NH_4^+ \text{ (dissolved)} \rightleftharpoons NH_3 \text{ (dissolved)} \rightleftharpoons NH_3 \text{ (gas)} \quad (96)$$

Instantaneous equilibria are assumed, with the equilibrium constants dependent upon temperature. This treatment allows surface soil pH and moisture to be considered. The dynamic step is the calculation of the amount of NH_3 that diffuses from the surface soil into the atmosphere.

Ammonium fixation

Fixation of ammonium ions (NH_4^+) on clay minerals is described by the equilibrium:

$$NH_4^+ \text{ (free)} \rightleftharpoons NH_4^+ \text{ (fixed)} \quad (97)$$

This means that the fixation of NH_4^+ is assumed to be a reversible process between free NH_4^+, i.e. exchangeable and dissolving NH_4^+ and fixed NH_4^+. It should be pointed out, however, that the fixation rate greatly exceeds the rate of release of fixed NH_4^+.

Leaching

Leaching is described by a multicompartment submodel. A typical model suitable for combination with the N conversion equations may consider five soil layers of 20 cm each. It is assumed that NO_3^- is the only N component which migrates, because transport of NH_4^+ is negligible. The simplified transport equation is:

$$TNO3 = DIFN * (NO3(I) - NO3(I+1))/DX + LE * WFU * (NO3(I) + NO3(I+1))/2 \quad (98)$$

where TNO3 is the flux of NO_3^- which passes the boundary between the layers I and I+1

NO3(I) is the concentration of NO_3^- in compartment I (g m^{-3})
DX is the distance between centres of compartments I and I+1 (m)
WFU is the moisture flux (m^3 m^{-2} s^{-1})
LE is the leaching efficiency factor (−)
DIFN is the apparent diffusion coefficient (m^2 s^{-1}), computed as:

$$DIFN = TET * TORT * DIFNW + DISP * WFU \quad (99)$$

where TET is the moisture content (m^3 m^{-3})
TORT is the tortuosity factor (−)
DIFNW is the diffusion coefficient of NO_3^- in water (m^2 s^{-1})
DSIP is the dispersion distance (m).
(Dispersion results from the random direction of diffusion of NO_3^-; tortuosity accounts for the elongation of the diffusion pathway that results from the heterogeneity of the soil pores filled with water.)

Environmental factors

Effects of environmental factors, such as temperature and moisture on the microbially mediated processes are included by using multiplicative reduction factors. The way in which combined effects of environmental factors are expressed in simulation models has a profound impact on the calculations (Frissel & van Veen, 1978). If the reduction factors for temperature, moisture content, and O_2 pressure are represented by TCOF, WCOF and O2COF, respectively, many possibilities exist for combining them (cf. Subsection 3.3.3). An extreme view is the assumption that all factors act independently, which leads to the multiplication of all factors.

$$\text{EFFECT} = \text{TCOF} * \text{WCOF} * \text{O2COF} \qquad (100)$$

If the values of the reduction factors (dimensionless) are, 0.8, 0.7 and 0.4, respectively, Equation 100 results in EFFECT = 0.2. Another extreme view is consideration of the minimum value only, giving EFFECT = 0.4. A third possibility is consideration of temperature separately and its multiplication with the minimum value of the other two reduction factors, resulting in EFFECT = 0.3.

In this model the last possibility was chosen. The effect of pH on biological processes was not included. It was assumed that changes of the pH of a soil did not influence bacterial growth and that thus the microbial population was adapted to the pH of a soil.

5.2.3 The 'state of art' on modelling the terrestrial nitrogen cycle

In general, it appears that our mathematical skills exceed our knowledge of the biological system being described and the quality of input data available. Thus, care should be taken when evaluating output from N models based on minimal knowledge and inadequate input data. The 'state of the art' on modelling the terrestrial N cycle will be considered briefly on the level of the individual processes.

Nitrification

Nitrification has been the most intensively examined of all the processes of the nitrogen cycle. Several other simulation models of nitrification in both aquatic and terrestrial systems have been developed (see van Veen et al., 1981). However, not one model includes microbial growth, death, non-steady state conditions, saturation kinetics for N oxidation, diffusional effects on oxidation under static water conditions (which do exist often in soil), and ion-exchange effects on NH_4^+ supply and movement together.

Nitrification is usually modelled as the result of the activity of chemoautotrophic micro-organisms: *Nitrosomonas* for oxidation of NH_4^+ and *Nitrobacter* for oxidation of NO_2^-. Heterotrophic nitrification is not considered explicitly in modelling.

Because only a few species of micro-organisms are involved, the effects of the

principal environmental variables affecting nitrification (temperature, pH, moisture and O_2 status) are well defined. Moreover, the process occurs within a much narrower range as compared to other processes, where a more diverse population of micro-organisms is involved. Thus, modelling of the effect of a particular environmental factor is comparatively easy and excellent fits with reality have been obtained. However, the combined effect of several factors has not yet been well defined. The lack of data and experimental evidence on correct mathematical expressions of the combined effects has appeared to be a very serious limitation to modelling, not only of nitrification, but also of other N cycle processes.

Mineralization and immobilization

As in most of the more comprehensive models of mineralization and immobilization, in this model the exogenous and soil substrates are divided into several components. Although this approach is superior to a description in which soil organic matter is considered to be an entity, it should be pointed out that the possibilities to measure quantity and turnover rate of the several soil organic matter fractions are limited.

The role of soil in protecting organic matter against decomposition and so, in controlling organic matter dynamics, together with tillage effects on this protection, requires further elucidation. Long-term modelling studies indicate that changes in the amount of protected compounds might be instrumental in controlling the decrease of soil organic-matter content of virgin grassland after cultivation (Paul & van Veen, 1978). Models usually treat stable soil N as consisting of several components. Good methods to partition soil N among these components are still lacking, and this probably constitutes one of the most severe single deficiencies in our understanding of soil N dynamics, regardless of the type of model used. This lack of good methodology exists because, in spite of our reasonably good understanding of what causes N to cycle, we do not understand the mechanisms, unique to soil systems, which prevent N from cycling. The presence of considerable quantities of organic compounds, such as sugars and amino acids, in soil among a large abundance of mostly starving micro-organisms which are capable of decomposition of these compounds, continues to be a highly remarkable observation.

Models explicitly including micro-organisms may be of no more value as general predictive tools for a given site with defined management or environment, than those without micro-organisms. (The model PAPRAN, e.g. discussed in the next section, does not consider micro-organisms explicitly.) The value of the larger models lies in a greater requirement to treat (if even superficially for lack of good data) mechanisms of action and control, resulting in greater applicability and flexibility. The range of conditions that can be examined is greater because mechanisms, and not only observations, are modelled with such explanatory models (Subsection 1.1.2). A proper understanding of mechanisms controlling processes is necessary to understand the terrestrial N cycles.

Soil microbial biomass measurements are essential and continue to be a problem. Comparisons between different methods such as plate counting, direct microscopic techniques, and chemical techniques, such as ATP measurements and CO_2 production measurement after fumigation, show that the data obtained are rather inconsistent, with the chemical techniques giving the highest biomass values (Paul & van Veen, 1978). There is a need for methods, which can be conveniently applied, to obtain reliable and comparable biomass values in soil ecosystem studies.

Many parameter values describing microbial processes are based on data from laboratory experiments with continuous cultures in chemostats. The use of these data in soil ecosystem studies has been justified on the basis of the continuous supply of nutrients in growth limiting concentrations in both systems (Veldkamp & Kuenen, 1973). Although this hypothesis seems reasonable, it should be carefully checked, especially since the continuously changing conditions in soil may lead to important differences between the systems. A case in point is the discrepancy between estimates of maintenance respiration rates in soil and in liquid culture.

The description of microbial organic matter transformation, which actually is biomass turnover, is a key point in N simulation models. Sound data are necessary on the rate of uptake, the efficiency of the use of organic compounds for biosynthesis or energy supply, the rate of release from the biomass and the quality of the released products. The first two aspects are quite well described in the literature with respect to uptake from solution, but substrate supply to the solution in soil is still poorly understood. On the quality and quantity of N and C compounds being released from the biomass in soil, no data are available.

The concept of concurrent growth, maintenance and death or debris production of micro-organisms is inadequately defined and most data provide only net growth rates. Death, endogenous metabolism and debris production have traditionally been handled by high maintenance rates. This is unacceptable (van Veen, 1977).

Alternatively, a portion of the population has been considered active with a high maintenance rate, while the remainder is inactive with a low maintenance rate (Hunt, 1977; Frissel & van Veen, 1978). It is generally accepted that the most realistic modelling results are obtained with an explicit treatment of death or decay plus debris production. Further development of either treatment requires more experimental data on the mechanisms controlling the release in soil of C and N from biomass either through death or waste production.

Denitrification

Our submodel of denitrification should be considered to be a first attempt to simulate the complex process of the occurrence of anaerobic sites in soil and subsequent denitrification at these sites. The concept of cylindrical pores filled with water or air, depending on the actual moisture content and the soil pF curve, may be used as was described above, or a more detailed description con-

sidering aggregate sizes and the occurrence of anaerobic zones within aggregates (Leffelaar, 1979; Smith, 1980) may be employed.

Further development of denitrification models and testing on experimental results are seriously hampered by great uncertainties in the reliability of existing methods for measuring denitrification. Newly developed methods for direct measurements, using acetylene blockage of N_2O reduction, are promising. The current interest in N_2O-N_2 ratios in the gases evolved has drawn attention to some of the fundamental problems related to this process in soil.

In addition to limitations to the O_2 supply, questions on the energy supply to denitrifiers in soil, and on the NO_3^- concentration and denitrifier population controlling the overall rate, are of continuing concern. For instance, in describing the effect of NO_3^- concentration on denitrification rate with the hyperbolic model, a 800-fold difference has been observed between values reported in the literature for the saturation constant in aquatic systems and in soil (van Veen, 1977).

Volatilization of NH_3

Significant losses of N from the soil can occur through volatilization of NH_3. These losses occur when high concentrations of urea are placed on the soil surface. The volatilization occurs from shallow soil surface layers (0-5 cm); very little NH_3 volatilizes from deeper soil layers. The diffusion of NH_3 through the soil can be modelled using Fick's diffusion equation. The major problem centres around estimating the diffusion coefficient as a function of soil-water content and soil type. Volatilization of NH_3 from the top soil layers into the atmosphere can be modelled using the diffusion equation. This flux is a function of the boundary layer resistance which is controlled by wind speed and air stability (Freney et al., 1981).

NH_3 volatilization from the soil may not, however, be a loss from the system since NH_3 can be absorbed by the plant canopy (cf. Subsection 5.1.4). Preliminary models for describing volatilization of NH_3 have been developed (e.g. van Veen, 1977; Parton et al., 1981), however these models are not appropriate for field applications.

Ammonium fixation

Soils that have potential for NH_4^+ fixation are rare, but if clay minerals such as vermiculite and illite not saturated with K^+ or NH_4^+ are present they must be included in any model at the research level. In other cases, a suitable parameter in the ion-exchange part of the model will handle NH_4^+, which is temporarily, but strongly, held.

Leaching

The leaching of NO_3^- is entirely controlled by the flow of water through the system. The only uncertainty is that the NO_3^- concentration in a part of the water flowing downward might not be in equilibrium with the NO_3^- concentra-

tion in other, adjacent, parts of the liquid phase. Although this uncertainty is increased because of NO_3^- production by nitrification, this non-equilibrium phenomenon will be equal for all anions. So the leaching of NO_3^- is the only part of the N model which can be derived from data collected for other materials, e.g., water itself and chloride ions. There is a wealth of hydrology literature: there are three-dimensional models, models that consider a stagnant phase and a moving phase with exchange between the two phases, and models that specialize in the spatial distribution of the water flux (e.g. Burns, 1974; Rowse & Stone, 1978; Addescott, 1981). The only problem seems to be selecting the appropriate approach from the many ones available. More details on modelling of water transport in soils and related topics are given in the Sections 4.2 and 4.3.

An interesting observation from a comparison of output of our model with results of an experiment in one of the newly reclaimed Lake IJssel polders is the observation that a considerable portion of the water that flows downward through wide pores and cracks does not contribute, or does so only to a small extent, to the transport of NO_3^-. This phenomenon is described, using the leaching efficiency factor, LE of Equation 98.