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Modeling the Nitrogen Cycle

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The rapid increase in computer power observed over the last few decades has allowed the development of computer simulation models for C and N cycling in agricultural and natural ecosystems. Models of the N cycle may be useful to understand and manage ecosystems so as to protect environmental quality and ensure long-term sustainability. In this chapter, we first present general concepts on systems, models, and model development, followed by a review of current approaches used to model different transformations in the N cycle. We conclude with a general discussion of the current status and future research needs in the area of N models. We want to emphasize that it is not our intention to provide an exhaustive review of the different N models available, but instead to describe representative approaches used by the different models in existence. Detailed reviews of several C and N models can be found in publications by McGill (1996), Molina and Smith (1998), Ma and Shaffer (2001), and McGechan and Wu (2001).

Systems, Models, and Software Tools

Systems and Models

A system is a set of components that act and interact together to achieve a certain goal (Jones and Luyten, 1998). Systems are composed of subsystems, subsystems are composed of sub-subsystems, and so on until the maximum level of resolution allowed by current scientific knowledge is reached. An example of a system is the set of components of the N cycle in soil. A model is a simplified representation of a system (Ford, 1999), and as such it attempts to capture the main components and behavior of that system.

Classification of Models

Models can be classified according to different criteria (Ford, 1999). Based on their nature, they can be divided into mental, physical, and symbolic. Symbolic models can in turn be mathematical or nonmathematical (e.g., maps), and mathematical models can be divided into analytical and numerical (depending on the type of mathematical solution used). In general, computer simulation models are symbolic, mathematical, and numerical.

Based on the type of modeling approach, computer simulation models can be divided into empirical or mechanistic (Kelton et al., 1998). Empirical models use empirical relationships between variables, whereas mechanistic models attempt to model the detailed mechanisms through which variables interact. Values taken by the parameters of empirical models have no restrictions, while those of mechanistic (process-oriented) models are limited by their biophysical connotation; for example, 5 to 13 is a likely range for C/N ratios of microbes. As such, mechanistic models have more restrictions on their behavior but include more information than the empirical simulators. Based on time, simulation models are classified into static (variables do not change with time) and dynamic (variables change as a function of time), and, based on how variables change, they are divided into continuous and discrete. In continuous models, variables change smoothly over time and are not restricted to integer values. In discrete models, variables change in steps instead of smoothly and are usually restricted to integer values. Based on the role of probability, models are divided into deterministic (no probability used) and stochastic (probability used).

Most computer simulation models of the N cycle are partly mechanistic and partly empirical. They are also dynamic because they model changes with time, and they are continuous because the simulated variables (N pools) change smoothly over time. For the most part, simulation models of the N cycle have been deterministic because incorporating probability requires additional computational time, consequently slowing down program execution. Fortunately, the increase in computer power achieved over the last few decades has allowed model developers to start exploring stochastic implementations, which may generate more realistic representations of natural systems.

Terminology Used in Simulation Modeling

Common terms used in simulation models include *variable, parameter, constant,* and *time step*. A variable is a quantity that changes during a simulation. There are state variables, which describe the state of the system; rate variables, which determine the rate at which state variables change in dynamic models; auxiliary variables, which are used to compute other variables; and driving variables, which characterize the influence of external factors. Parameters of empirical models can take any value but remain constant during a simulation; their value can change between simulations. In contrast, a constant is a quantity whose value never changes, as in the case of the gravitational constant. Time step refers to the time increment used to advance time during the simulation. It defines the temporal resolution, which can change to fit the requirements of individual subsystems within the model or environmental circumstances. Similar considerations apply to the spatial resolution whereby a computational step is defined to integrate processes over distances. For example, gas diffusion in soil calls for lower temporal and spatial

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resolutions than N biological processes, a requirement that complicates the simulation of CO_2 release at the soil–air interface.

Steps in Model Development

Ideally, the development of a model would proceed according to the following steps: (i) statement of objectives, (ii) system identification, (iii) specification of component behavior, (iv) computer implementation, (v) verification, (vi) sensitivity analysis, (vii) calibration, and (viii) validation (Jones and Luyten, 1998; Ford, 1999).

Statement of Objectives

In this crucial but often overlooked step, the intended end product and its use should be clearly stated to serve as a guide in subsequent steps. In general, simulation models of the N cycle are developed for research or management purposes. Research models are helpful to test hypotheses and increase our understanding of a particular system. In contrast, management models are helpful to predict system behavior, with the goal of improving its management. Although the distinction between research and management models is not sharp because research models can eventually become management models, it is important to clearly define objectives at the start of a modeling exercise to have a well-defined project goal.

System Identification

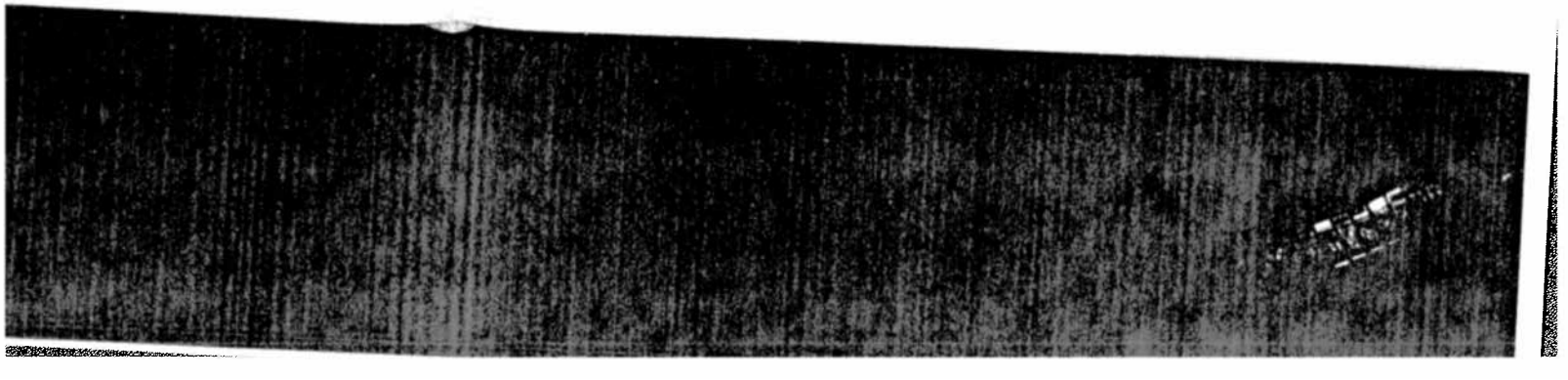
This step consists of identifying the system components (state variables and rate variables), as well as the system environment (driving variables such as management practices and climate). The system components to be included depend on the goals of the modeling exercise, as outlined in the first step. Once the system components are identified, the system environment needs to be identified. The environment is composed of all those variables that affect the system but are not affected by the system (Neelamkavil, 1987; Jones and Luyten, 1998).

Specification of Component Behavior

The first task in this step is to select names for the variables to be included in the model. Ideally, these names should be mnemonic to facilitate model development and use. After selecting variable names, a flow diagram of the model should be developed (Ford, 1999), and the mathematical form of the relationships between variables should be formulated. Coefficients, parameters, and constants for these mathematical relationships should be obtained from the literature, if available, or from experiments specifically conducted for that purpose.

Computer Implementation

If a programming language is used to implement the model, a sequence commonly used for the program consists of (i) declaration and documentation of variables, (ii) initialization of parameters and constants, (iii) initialization of state variables, and (iv) time/space loop. The time/space loop is an iterative calculation process in which time/space is incremented by an amount selected for the temporal and spatial resolution, rate variables are calculated, state variables are updated, and any desired output is generated. When the time/space loop has progressed to the spatio-temporal dimensions desired for the simulation, the program stops execution.



Implementation of models using a programming language requires expertise in the language of choice, as well as considerable time for correcting syntax errors. If a visual programming tool (see below) is used to implement the model, the programming code is written by the software as the flow diagram is developed on the screen, and as relationships between variables are defined. Although the model developer needs to become familiar with the visual programming tool of choice, learning these tools usually takes much less time than learning the syntax of a conventional programming language.

Verification

Verification consists of checking the computer code to ensure that it correctly represents the mathematical model of the system. This is a step that needs to be conducted independently of whether a regular programming language or a visual programming tool is used for model development.

Sensitivity Analysis

A sensitivity analysis is conducted to identify parameters and/or driving variables to which the model is very sensitive. Identifying these parameters and/or driving variables is important because it helps the developer to allocate resources to measure the parameters and driving variables needed, and to simplify the model by removing processes that do not impact on the dynamics of the system. Those parameters or variables to which the model is more sensitive should be measured with more accuracy than those to which the model is less sensitive.

A sensitivity analysis begins by identifying output variables of interest and establishing a set of best estimates of each parameter and driving variables. Simulations are then run with a range of values for each parameter to observe changes in the output variables of interest. There are several methods to combine the range of values for each parameter in the simulation runs for sensitivity analysis. The most comprehensive method uses a factorial combination of all parameter values to be tested, allowing the determination of not only the main effect of each parameter, but also the degree of interaction between parameters (Ford, 1999). One drawback of this method, however, is that it may require a large number of simulations, as indicated by the equation

$$\text{Number of Simulations} = (\text{Levels of Each Parameter})^{\text{Number of Parameters}}$$

According to this equation, it would require 177,000 simulations to run every combination of 11 parameters at three levels for each parameter. It is clear that conducting such a large number of simulations may require more time than the model developer has available. Consequently, other methods have been developed for sampling the different parameter combinations.

One of these methods is random sampling, in which the parameter values for each run are selected at random. For example, in the Monte Carlo approach, the value of each parameter for a given run is taken from a specified probability for each parameter. Although random sampling requires fewer simulations than a full factorial combination, it still requires a large number of simulations to ensure a reasonable exploration of the sample space. Thus, other methods have been used to reduce the number of simulations while still exploring all regions of interest of the sample space. For example, Taguchi methods (Clemson et al., 1995; Ross, 1996) use fractional factorial designs to evaluate the main effect of parameters as well

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Model Validation

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method that achieves a reasonable exploration of the sample space (Clemson
1995), although it assumes no interaction between parameters. In conclusion
method to be used in sensitivity analysis should be selected according to the
ber of parameters and levels involved, as well as the degree of interaction expe
between parameters.

Some model developers conduct an analysis that involves observing
changes in output caused by large changes in parameters or driving variat
This analysis is conducted to investigate the range of values in which the mode
stable, and as such it has been called a stability analysis.

Model Calibration

Calibration consists of refining the parameter values to be used in a particul
situation. Ideally, a model should be calibrated with a data set collected for th
particular situation of interest to obtain the parameter values to be later used ir
validation (see below). The data set used in calibration should preferably be inde
pendent of the data set used in validation.

Model Validation

Validation refers to the testing of the model to determine how well the simula-
tion results compare to reality (Smith et al., 1996). A paramount reality is the first
principle of chemistry: mass conservation. The model should display in the output a
balance between the masses coming in and out of the system (C, N, water, etc.). This
mass balance should be checked for every single simulation, as unwanted appari-
tions of mass gains and losses have an uncanny way of making their way even into
models that have been tested for many years, revealing an unsuspected mistake in
the coding. Once the mass balance has been checked, the comparison of simulated
to experimental data can be started. As stated above, ideally the validation data set
should be independent of the calibration data set. In some cases, however, models
are calibrated with several data sets, and the average parameter values are used to
validate the model with the same data sets. Some numerical procedures compute
the standard deviation on the estimated parameters, thus giving some insight on the
sensitivity of the parameter over the behavior of the system.

Several statistical tools have been used to calibrate a model and to evaluate
the "goodness of fit" between observed and simulated results. This evaluation uses
"figure of merit" functions such as the mean difference (M_d) between observed and
simulated values, the standard error of M_d, the average relative error of the simulat-
ed values, the maximum error, the root mean square error, the correlation coefficient,
confidence intervals for measured values, and analysis of lack of fit (Loague and
Green, 1991; Whitmore, 1991). In general, the root mean square error is the preferred
tool when measured values are not replicated, whereas the lack of fit analysis is the
preferred tool when measured values are replicated (Whitmore, 1991).

The statistical tools described above are useful but have limitations in that
they do not necessarily show trends of over- or underestimation. Graphical dis-
plays, on the other hand, can be useful to show trends and types of errors (Loague
and Green, 1991). For example, a graph of observed versus simulated results for a
given site can easily show trends in simulation errors. Similarly, a graph of maxi-
mum, minimum, and median values for observed and simulated results can be
useful to show types of errors across different sites.

The steps in model development described above are general and do not necessarily guarantee the achievement of the stated objectives by the end of the last step. Once the validation step is completed, one or more iterations through the different steps may be needed to further refine the model or improve its performance.

Software Tools

Most computer simulation models have been implemented in process-oriented programming languages such as FORTRAN, which commonly lack the structure and flexibility to develop user- and developer-friendly models. The current availability of object-oriented languages such as C++ allows more structured and easier/understand implementations. Also, recent versions of FORTRAN (e.g., Absoft Pro FORTRAN and Lahey/Fujitsu) that support window and mixed-language programming promise to rejuvenate a simulation tool that has withstood the challenge of time. Although to date very few N models have been developed with these new languages (Shaffer et al., 2000), their use is expected to increase in the future.

One of the factors that has limited the development of simulation models is the need for developers to have expertise in the programming language of choice. In recognition of this limitation, new software tools have been designed to allow developers to create models without having to write programming code. These visual software tools use graphical icons to represent state and rate variables, allowing the user to build models by simply dropping icons on a "working space" and joining them according to the desired model structure. As the model structure is graphically built and the mathematical relationships between variables are defined, the software automatically writes the code to implements the model. Examples of these tools are Stella (High Performance Systems, Hanover, NH), ModelMaker (Cherwell Scientific Limited, Oxford, UK), Vensim (Ventana Systems, Belmont, MA), Powersim (Powersim Corp., Herndon, VA), and VisSim (Visual Solutions, Westford, MA). A Stella implementation of the N model NLEAP (Shaffer et al., 1991) is currently available (Bittman et al., 2001), and more implementation of N models with similar tools are likely in the future.

Nitrogen Models

Simulation models of the N cycle attempt to capture the main processes or transformations in the system of interest. Models simulate the rate of these processes or transformations by using different types of kinetics. In this section we first review the most commonly used types of kinetics and then we describe the different kinetic approaches used to model some of the most important transformations in the N cycle.

Common Kinetic Models

Zero-Order Kinetics

In zero-order kinetics, the rate of transformation of substrate S into product P is constant and independent of the concentration of S (zero order with respect to S):

$$S \rightarrow P$$

$$dS/dt = -k[S]^0 = -k$$

where k is a term comm
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ing Eq. [1] yields

$$S_t = S_0 + kt$$

where S_t is the substrate
tion at time 0.

First-Order Kinetics

In first-order kinetics,
is proportional to the conc

$$dS/dt = -k[S]^1 = -k[S$$

where k is the first-order rat

$$S_t = S_0 e^{-kt}$$

Second-Order Kinetics

In one type of second-or
into product P is proportional
with respect to S):

$$dS/dt = -k[S]^2$$

where k is the second-order ra

$$S_t = S_0/(S_0 kt + 1)$$

In another type of second-
S into product P is proportiona
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$$dS/dt = -k[S][B]$$

If the microbial biomass i

$$dS/dt = -k[S]B_0 e^{-rt}$$

where B_0 is biomass at time (
bial biomass.

Integrating Eq. [8] yields

$$S_t = S_0 \exp\{(kB_0/r)[\exp(rt$$

Michaelis–Menten Kinetic

Michaelis–Menten kinetic
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$$E + S \longleftrightarrow ES \xrightarrow{k} P$$

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$$[1]$$

where k is a term commonly called the zero-order rate constant. Accord
modeling terminology described above, k is a parameter rather th
stant, and therefore it will be referred as a zero-order rate coefficient.
ing Eq. [1] yields

$$S_t = S_0 + kt$$

where S_t is the substrate concentration at time t, and S_0 is the substrate con
tion at time 0.

First-Order Kinetics

In first-order kinetics, the rate of transformation of substrate S into prod
is proportional to the concentration of S (first order with respect to S):

$$dS/dt = -k[S]^1 = -k[S]$$

where k is the first-order rate coefficient. Integrating Eq. [3] yields

$$S_t = S_0 e^{-kt}$$

[

Second-Order Kinetics

In one type of second-order kinetics, the rate of transformation of substrate S
into product P is proportional to the square of the concentration of S (second order
with respect to S):

$$dS/dt = -k[S]^2$$

where k is the second-order rate coefficient. Integrating Eq. [5] yields

$$S_t = S_0/(S_0 kt + 1) \qquad [5]$$

In another type of second-order kinetics, the rate of transformation of substrate
S into product P is proportional to the concentration of S and to the concentration of
microbial biomass B (first order with respect to S and B) (Simkins et al., 1986).

$$dS/dt = -k[S][B] \qquad [6]$$

If the microbial biomass in turn grows according to first-order kinetics, then

$$dS/dt = -k[S]B_0 e^{-rt} \qquad [7]$$

where B_0 is biomass at time 0, and r is the first-order rate coefficient for micro-
bial biomass.

Integrating Eq. [8] yields

$$S_t = S_0 \exp\{(kB_0/r)[\exp(rt) - 1]\} \qquad [8]$$

Michaelis–Menten Kinetics

Michaelis–Menten kinetics was developed in 1913, when Michaelis and Men-
ten proposed a theory to explain the rate of a reaction that involves a substrate, an
enzyme, and a product:

$$E + S \longleftrightarrow ES \xrightarrow{k} P \qquad [9]$$

where E is the enzyme, S is the substrate, ES is the enzyme–substrate complex, P is the product, and k is a rate coefficient. The rate of formation of product P is first order with respect to ES:

$$dP/dt = k[ES] \quad [10]$$

The concentration of E a short time after the start of the reaction can be calculated as

$$[E] = [E]_0 - [ES] \quad [11]$$

where $[E]_0$ is the initial concentration of E. Also, the dissociation constant K_m for the ES complex can be calculated as

$$K_m = [E][S]/[ES] \quad [12]$$

Substituting Eq. [11] into Eq. [12] and solving for [ES] yields

$$[ES] = [E]_0[S]/(K_m + [S]) \quad [13]$$

Substituting Eq. [13] into Eq. [10] yields

$$dP/dt = i[E]_0[S]/(K_m + [S]) \quad [14]$$

The expression $k[E]_0$ represents the maximum velocity of the reaction, which occurs when all the enzyme molecules are in the complex form ES. Therefore if $V_m = k[E]_0$,

$$dP/dt = V_m[S]/(K_m + [S]) \quad [15]$$

Equation [15] is the common expression for Michaelis–Menten kinetics. The Michaelis–Menten constant, K_m, corresponds to the substrate concentration at which half of the maximum reaction rate ($1/2\ V_m$) is achieved. When the substrate concentration is very low, $K_m + [S]$ is approximately equal to K_m, and the reaction is equivalent to first-order kinetics. When the substrate concentration is very high, $K_m + [S]$ is approximately equal to $[S]$, and the reaction is equivalent to zero-order kinetics.

Michaelis–Menten kinetics is commonly used to model the transformation of substrates that are present in the soil solution. Parameters for the Michaelis–Menten equation (V_m and K_m) are best determined by nonlinear curve fitting of Eq. [15]. A less preferable approach is to convert Eq. [15] into a linear form and use linear regression to find slope and intercept values, which in turn can be used to estimate K_m and V_m values (Müller, 1999).

Monod Kinetics

In Monod kinetics, the rate of transformation of substrate S is proportional to the rate of growth of a microbial population B that uses substrate S (Koch, 1998). The rate of growth of the microbial population is given by

$$dB/dt = \mu B \quad [16]$$

where $\mu = (V_m[S])/(K_m + [S])$, V_m is the maximum rate of growth, and K_m is a constant. The rate of transformation of substrate S is modeled as

$$dS/dt = -dB/dt \times 1/Y \quad [17]$$

where Y is the efficiency of biomass B (biomass formed/substrate used).

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Temperature Factors

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Arrhenius Equation

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$$k = Ae^{-E_a/RT}$$

where k is a rate coefficient,
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is absolute temperature. The
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$$TF = k_2/k_1 = e^{Ea/R(T_2-T_1)/(T_1T}$$

If $T_2 - T_1 = 10$, then $TF = e^E$
which the rate of a reaction cl
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Van't Hoff Function

In the Van't Hoff functior
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$$TF = k_2/k_1 = Q_{10}^{(T_2-T_1)/10}$$

where Q_{10} is a constant repres
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substrate used).

In Monod kinetics it is necessary to model both B and S to obtain
S at any point in time. Simkins and Alexander (1984) derived a modifi
for Monod kinetics for cases in which modeling biomass B is not desir

$$dS/dt = -(V_m[S])/(K_m + [S])(S_0 + B_0/Y - S_t)$$

where S_0 is the concentration of S at time 0, S_t is the concentration of S at ti
the concentration of biomass B at time 0, and Y is the efficiency of biomass

Temperature and Moisture Factors in Simulation Mod

The kinetic equations described above are useful to describe the rate o
cess at constant environmental conditions. However, simulation models
oped to simulate field conditions need to have kinetic equations that are mo
based on environmental conditions. Therefore, simulation models usually inc
factors that reflect temperature and moisture conditions in the field.

Temperature Factors

Different approaches have been used to develop temperature factors for si
ulation models. Among them are the Arrhenius equation and the Van't Hoff fur
tion, as well as other linear and exponential functions.

Arrhenius Equation

In 1889 Arrhenius found that the effect of temperature on many reactions
could be described by the equation

$$k = Ae^{-E_a/RT} \qquad [19]$$

where k is a rate coefficient, A is the frequency factor (frequency of collisions be-
tween reactant molecules), E_a is the activation energy, R is the gas constant, and T
is absolute temperature. The following temperature factor (TF) can be derived to
correct a rate coefficient (k_1) measured at a given reference temperature (T_1) to be
used at a different temperature (T_2):

$$TF = k_2/k_1 = e^{Ea/R(T_2-T1)/(T_1T_2)} \qquad [20]$$

If $T_2 - T_1 = 10$, then $TF = e^{Ea/R(10)/(T_1T_2)} = Q_{10}$, which is defined as the proportion by
which the rate of a reaction changes as the temperature changes by 10°C. Accord-
ing to the Arrhenius equation, Q_{10} varies with temperature.

Van't Hoff Function

In the Van't Hoff function, the temperature factor for correction of a rate coef-
ficient can be calculated as follows:

$$TF = k_2/k_1 = Q_{10}^{(T_2-T_1)/10} \qquad [21]$$

where Q_{10} is a constant representing the ratio by which the rate coefficient changes
for a temperature increase of 10°C. In contrast to the Arrhenius equation, Q_{10} in the
Van't Hoff function does not vary with temperature.

Other Linear or Exponential Functions

Many authors have shown that the Q_{10} (defined as the ratio by which the
rate constant changes for a temperature increase of 10°C) for organic matter de-

composition and N mineralization varies with temperature (Addiscott, 1983; Ellert and Bettany, 1992; Kirschbaum, 1995). Because in many cases these changes in Q_{10} could not be adequately described by the Arrhenius equation, some researchers have proposed different functions. For example, Vigil and Kissel (1995) proposed polynomial ($TF = -0.010 + 0.039T - 0.014T^{1.5} + 0.00036T^{2.5}$) and exponential ($TF = 0.0106e^{0.1297T}$) temperature factors for N mineralization from crop residues. Exponential temperature factors have also been proposed by Jenkinson et al. (1987) ($TF = 47.9/(1 + \exp[106/(T + 18.3)])$) and Kirschbaum (1995) ($TF = \exp[-3.432 + 0.168T(1 - 0.5T)/36.9]$) for organic matter decomposition, and by McMeekin et al. (1988) ($TF = a(T - T_{min})\{1 - \exp[b(T - T_{max})]\}$) for bacterial growth. Stark (1996) used a generalized Poisson density function to describe the effect of temperature on nitrification. The different approaches used for temperature correction have in many cases led to different temperature factors for the same transformation process.

Soil Water Content Factors

The effect of soil water content on N processes has been expressed with factors based on soil water potential, soil water content, and water-filled porosity.

Functions Based on Soil Water Potential

Functions based on soil water potential are commonly of the following form (Andrén and Paustian, 1987):

$$MF = [\log(-\psi) - \log(\psi_{min})]/[\log(-\psi_{opt}) - \log(\psi_{min})], \text{ for } \psi < \psi_{opt} \qquad [22]$$

where MF is the moisture factor, ψ is the actual soil water potential in MPa, ψ_{min} is the minimum water potential at which there is activity, and ψ_{opt} is the optimum water potential for activity.

Functions Based on Soil Water Content

Functions that use soil water content commonly have a form similar or related to the following equation (Myers et al., 1982; Godwin and Jones, 1991):

$$MF = [\theta - \theta_b]/[\theta_{opt} - \theta_b], \text{ for } \theta < \theta_{opt} \qquad [23]$$

where θ is the actual soil water content, θ_b is the minimum soil water content at which there is activity, and θ_{opt} is the optimum soil water content for activity.

The optimum soil water content for a microbially mediated transformation would be expected to vary depending on the soil because microorganisms are expected to respond to water potential, not soil water content. Nevertheless, for a given soil, moisture factors expressed via soil water content may be as effective as moisture factors expressed via soil water potential. For example, Kladivko and Keeney (1987) found that N mineralization rates could be linearly related to relative soil water content or to the logarithm of soil water potential.

Functions Based on Water-Filled Porosity

Functions based on water-filled porosity are commonly linear or exponential. For example, Grundmann et al. (1995) proposed a moisture function for nitrification that is linear below the optimum water-filled porosity and exponential above the optimum water-filled porosity.

$$MF = [\exp(A/$$

where $A = (WFP_{max} -$ WFP is the actual wa gen reduces activity t tained, and WFP_{min} is

Relationship betwe

Both temperature a tions that describe the combined in different w proach is to multiply bot independent in their effec

$$dS/dt = -k \times S \times MF$$

where MF is the moisture f

Another approach is to that the most limiting facto tion process:

$$dS/dt = -k \times S \times \text{Minim}$$

Some models use the gec the existence of some interact

$$dS/dt = -k \times S \times (MF \times$$

A few models have used ture (T) and moisture (M), as

$$dS/dt = -k \times S \times f(M, T$$

This function has been d an interaction term (Kowalen and Cabrera, 1997b):

$$f(M, T) = a + bM + cT +$$

or as a combination of linear 1997b):

$$f(M, T) = a + bT + \exp[($$

Because many studies h perature and water content (Cassman and Munns, 1980; ra, 1997b), more effort shoul simulation models. As an alt itly modeling the effect of ter microbial activity. A

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$$\log(\psi_{min})], \text{ for } \psi < \psi_{opt} \qquad [22]$$

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$$MF = [\exp(A/B)/(WFP_{opt} - WFP_{min})](WFP - WFP_{min})$$

where $A = (WFP_{max} - WFP_{opt})(WFP - WFP_{opt})$, $B = (WFP_{opt} - WFP_{min})(WFP$
WFP is the actual water-filled porosity, WFP_{max} is the maximum WFP (l
gen reduces activity to zero), WFP_{opt} is the WFP at which maximum acti
tained, and WFP_{min} is the minimum WFP (lack of water reduces activity to

Relationship between Temperature and Water Content Fact

Both temperature and moisture factors are usually included in kineti
tions that describe the rate of N transformation processes. These factors
combined in different ways to express their overall effect on the process. C
proach is to multiply both factors, which implicitly assumes that the factor
independent in their effect:

$$dS/dt = -k \times S \times MF \times TF$$

where MF is the moisture factor, and TF is the temperature factor.

Another approach is to select the minimum of the two factors, which assum
that the most limiting factor is the one that controls the rate of the transform
tion process:

$$dS/dt = -k \times S \times \text{Minimum}(MF, TF) \qquad [26$$

Some models use the geometric means of the two factors, implicitly assuming
the existence of some interaction between the factors:

$$dS/dt = -k \times S \times (MF \times TF)^{1/2} \qquad [27]$$

A few models have used a function that describes the main effects of tempera-
ture (T) and moisture (M), as well as their interaction:

$$dS/dt = -k \times S \times f(M, T) \qquad [28]$$

This function has been described as a first- or second-order polynomial with
an interaction term (Kowalenko et al., 1978; Cassman and Munns, 1980; Quemada
and Cabrera, 1997b):

$$f(M, T) = a + bM + cT + dMT \qquad [29]$$

or as a combination of linear and exponential equations (Quemada and Cabrera,
1997b):

$$f(M, T) = a + bT + \exp[(d + c\ 1/T) \times M] \qquad [30]$$

Because many studies have shown the existence of interaction between tem-
perature and water content on decomposition and N mineralization processes
(Cassman and Munns, 1980; Ropper, 1985; Doel et al., 1990; Quemada and Cabre-
ra, 1997b), more effort should be spent on developing these types of functions for
simulation models. As an alternative, Grant and Rochette (1994) proposed implic-
itly modeling the effect of temperature and moisture on substrate availability and
microbial activity. A detailed modeling of these effects may adequately simulate
the observed interaction between temperature and moisture.

Models of Nitrogen Processes

The most important processes related to the N cycle in soil are N mineralization and immobilization, nitrification, denitrification, and ammonia volatilization. In this section we describe the different approaches used to model these processes.

Nitrogen Mineralization and Immobilization

Mineralization is the release of NH_4 from the soil organic matter (SOM); immobilization is the incorporation of inorganic N in the SOM. The first systematic study of rates of net N mineralization was performed by Stanford and Smith (1972), who found that the release of inorganic N in many soils was proportional to the concentration of a hypothetical soil organic fraction (first-order kinetics), which they called the potentially mineralizable N, or N_o. It is a one-pool model that is still used to quantify the release of inorganic N from SOM, crop residues, manures, and other organic compounds. The one-pool approach is sometimes replaced by several pools decaying in parallel to give a better account of net N mineralization kinetics (e.g., Bonde et al., 1988; Chen and Lee, 1997; Aggangan et al., 1998; Bridgham et al., 1998).

Nitrogen mineralization and immobilization are transformations driven by the energy accumulated in the soil heterotrophic microbial population through the decay of SOM and other organic compounds (Jansson and Persson, 1982). Thus, mechanistic models of mineralization and immobilization should include at least two types of organic pools, some with parameters and abiotic linkage functions relevant to the physiology of microbes, and some disposed in the flow structure to be a carbon source for the microbial biomass.

Inorganic N immobilization is observed when organic chemicals (e.g., plant residues) with high C/N ratio are added to soil. This transformation is rationalized as the process that maintains the C/N ratio of the microbial biomass that grows on the added residues. Thus immobilization starts if

$$(dC/dt)/CN_x < (dC/dt) \times EFFAC/CN_b \qquad [31]$$

where dC/dt is the rate of residue decay, EFFAC is the efficiency of C incorporation in the microbial biomass, and CN_x and CN_b are the C/N ratios of the residues and microbial biomass, respectively (Beek and Frisel, 1973). When the inequality is reversed (Eq. [31]), residues supply more N to the microbial biomass than needed, and the excess is mineralized as NH_4.

If the estimated amount of N required for immobilization is larger than the amount of inorganic N available in the soil,

$$[(dC/dt) \times EFFAC/CN_b - (dC/dt)/CN_x] > \text{Available Inorganic N} \qquad [32]$$

The amount of N immobilized has to be adjusted so that it is equal to the amount of inorganic N available. This is accomplished by any one of the following three options: (i) reducing the rate of decay (dC/dt); (ii) reducing the efficiency of the microbial population (EFFAC), thus increasing the rate of CO_2 release from soil; or (iii) increasing the C/N ratio of the microbial biomass (CN_b).

In the absence of residues (soils kept fallow for several years), soils mineralize the SOM to release NH_4, and the single exponential model (N_0 model) can be satisfactorily used. However, this release of NH_4 hides a gross N immobilization that runs concomitantly with gross N mineralization, as revealed by the

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NH_4 concentrations will be le
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NH_4 (Molina et al., 1990; Ha
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Because of the close relat
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In the following section
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bilization is called the mineralization–immobilization turnover (MIT). I
simulated by the N_0 mineralization model or Eq. [31], which assumes
eralization or immobilization, each process being triggered by the presei
dues. The simultaneous occurrence of mineralization and immobilizatior
the absence of residues is simulated by assuming that mineralization resu
the growth of microbes feeding on microbes (microbial successions) with
tios that fulfill the reverse of Eq. [31], while NH_4 immobilization is driver
growth of microbes on a soil organic pool with a high C/N ratio (Eq. [31])
formed during the microbial succession (Molina et al., 1983). There are, ho
other mechanisms that account for N immobilization even in the absence
dues with high C/N ratio.

Incorporation of N into the soil microbial biomass can occur through (i
direct absorption of organic molecules (e.g., amino acids added to soil) or (ii)
absorption of NH_4 after deamination (mineralization) of organic chemicals (
amino acids released from decaying microbes during microbial succession bef
they are absorbed by the growing cells). The direct absorption of residues' ami
acids has been amply documented (Barak et al., 1990; Barraclough, 1997). Wheth
endogenous amino-N compounds are directly absorbed or are first deaminate
is a question that has been resolved by considering that changes in added trace
NH_4 concentrations will be less pronounced when nontracer amino groups are di
rectly absorbed rather than first deaminated. Comparison of the two hypotheses
(amino-N vs. NH_4 incorporation) represented in two models of N transformations
showed that the microbial biomass in the absence of residues immobilizes N as
NH_4 (Molina et al., 1990; Hadas and Molina., 1993). Another peculiarity of this
process that has to be taken into consideration by models is that NO_3 is not immo-
bilized, in contrast to immobilization driven by residues that can use either NH_4 or
NO_3 (Broadbent, 1965). Analysis of N immobilization data by some models would
indicate that NO_3 immobilization can occur during MIT, albeit to a lesser degree
than with NH_4 (Mary et al., 1998).

Because of the close relationship that exists between organic N and C decom-
position, most models of N mineralization and immobilization include a model
of C decomposition. Also, because the heterotrophic microbial population plays a
key role in N mineralization and immobilization, many models of N mineraliza-
tion and immobilization also include a model for soil microbial biomass growth.

In the following section we review the general structure of selected models
(CERES-N, NCSOIL, CENTURY, Jenkinson model, van Veen and Frissel model,
PHOENIX, Verberne model, Hassink and Whitmore model). These models rep-
resent most of the different approaches that have been used to model residues
and SOM decay in concurrence with the mineralization–immobilization process.
Results of the evaluation of some of these models (CANDY, CENTURY, DAISY,
DNDC, Hurley-ITE, NCSOIL, Roth-26-3, SOMM, and VERBENE) in terms of their
ability to simulate the dynamics of the SOM during long-term field experiments
have been presented by Smith et al. (1996).

CERES-N

The CERES-N model (Godwin and Jones, 1991) is a relatively simple model
derived from the model PAPRAN (production of arid pastures limited by rainfall

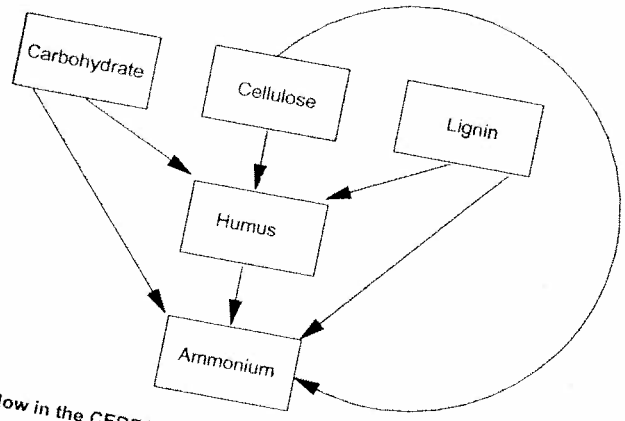

Fig. 18–1. Nitrogen flow in the CERES-N model.

and nitrogen) (Seligman and van Keulen, 1981). There is one SOM pool (humus) and three crop residue pools (carbohydrate, cellulose, and lignin) (Fig. 18–1).

The division of residues into carbohydrate, cellulose, and lignin pools is convenient for modeling purposes because these compounds decompose at different rates and can be measured with routine analytical procedures. CERES-N assumes that 20% of the residue organic matter goes to carbohydrates, 70% to cellulose, and 10% to lignin. The same assumptions are used to divide residue N into carbohydrate, cellulose, and lignin N pools. It should be noted that these percentages are reasonable for mature cereal residues, but they may lead to incorrect simulations for other crop residues. For example, Quemada and Cabrera (1995, 1997a) found that entering the actual values measured in cover crop residues (oats, rye, crimson clover, wheat) resulted in better CERES-N simulations of net N mineralized than using the default values.

Both gross N mineralization (dN/dt) and organic matter decay (dC/dt) from each of the residue pools follow first-order kinetics and take into account temperature (TF), soil water content (MF), and C/N ratio (CNRF) factors.

$$dC/dt \text{ or } dN/dt = -RDECR \times TF \times MF \times CNRF \times POOL \quad [33]$$

where RDECR is the first-order rate coefficient for carbohydrate, cellulose, or lignin; POOL is the organic matter or N in the carbohydrate, cellulose, or lignin pool.

It is assumed that 20% of the gross N mineralized goes to humus N and 80% goes to the inorganic N pool. Nitrogen immobilization is calculated taking into account that microorganisms require 0.02 g N per gram of organic matter decomposed. This value was obtained by assuming that microorganisms have an efficiency of 0.4 (g C assimilated per g of C decomposed) and a C/N ratio of 8, and that organic matter contains 400 g C kg^{-1}. The amount of N required for immobilization computed as the difference between the amount of N required by the microorganisms (0.02 g N/g OM) and the amount of N present in the decomposing residue (Pool N/Pool OM; g N/g OM).

$$dN/dt_{immob} = \text{Minimum}[dC/dt_{decomp} \times (0.02 - \text{Pool N/Pool OM}), \text{Inorganic N Available}] \quad [34]$$

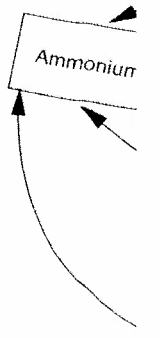

Fig. 18–2. NH_4 flow in the NCSOIL mc

If the estimated amount o
available in the inorganic N p
immobilized is set equal to the
rate of decay is not changed.
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Mineralization of N from
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MF) used for residue decompc
ture factors for residue and SO
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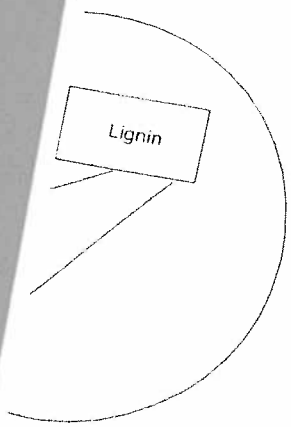
the soil surface (Quemada and

NCSOIL

NCSOIL is a submodel of t
al., 1983) developed as one of t
residue management model) (
into NCSWAP/NCSOIL (Clay e
soils.umn.edu/research/ncswap
program to simulate soil incul
structured around three SOM
biomass; Pool II and Pool III ar
tively. Organic N and C (not ra
Pool II, and Pool III



There is one SOM pool (humus)
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found that entering the actual val-
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s and take into account tempera-
(CNRF) factors.

$$\text{CNRF} \times \text{POOL} \qquad [33]$$

carbohydrate, cellulose, or lignin;
cellulose, or lignin pool.
ized goes to humus N and 80%
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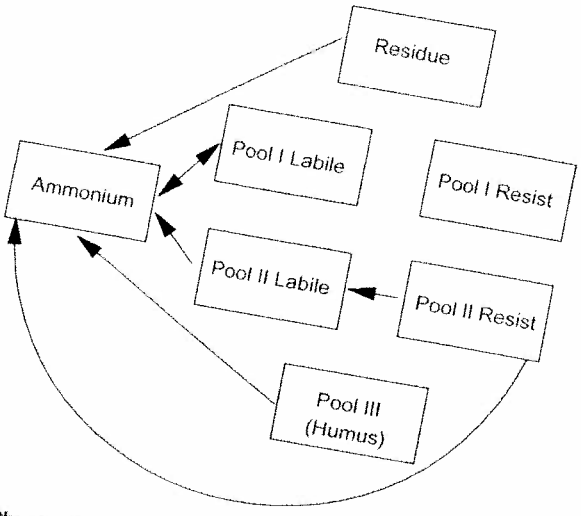

Fig. 18–2. NH_4 flow in the NCSOIL model.

If the estimated amount of N required for immobilization is larger than that available in the inorganic N pool (Inorganic N Available), then the amount of N immobilized is set equal to the amount available in the inorganic N pool, but the rate of decay is not changed. This is equivalent to reducing the amount of N required by microorganisms, which can be achieved by reducing their efficiency and/or increasing their C/N ratio.

Mineralization of N from humus follows first-order kinetics and is modified in a multiplicative manner by the same temperature and moisture factors (TF and MF) used for residue decomposition. The use of the same temperature and moisture factors for residue and SOM decomposition may be adequate when residues are incorporated into the soil but may not be appropriate when residues are left on the soil surface (Quemada and Cabrera, 1997b).

NCSOIL

NCSOIL is a submodel of total and tracer C and N transformations (Molina et al., 1983) developed as one of the C–N submodels of NTRM (N, tillage, and crop-residue management model) (Shaffer and Larson, 1987) and later incorporated into NCSWAP/NCSOIL (Clay et al., 1989; Molina, 1996; Molina et al., 2001) (www.soils.umn.edu/research/ncswap-ncsoil). NCSOIL is also available as a stand-alone program to simulate soil incubation in constant environmental conditions. It is structured around three SOM pools (Fig. 18–2). Pool I represents the microbial biomass; Pool II and Pool III are the easily mineralizable and stable SOM, respectively. Organic N and C (not represented in Fig. 18–2) flow from residues to Pool I, Pool II, and Pool III with feedback loops from the SOM pools to Pool I, including that from Pool I to Pool I to simulate microbial successions. Figure 18–2 illustrates the mineralization–immobilization turnover when N immobilization by Pool I involves NH_4 exclusively.

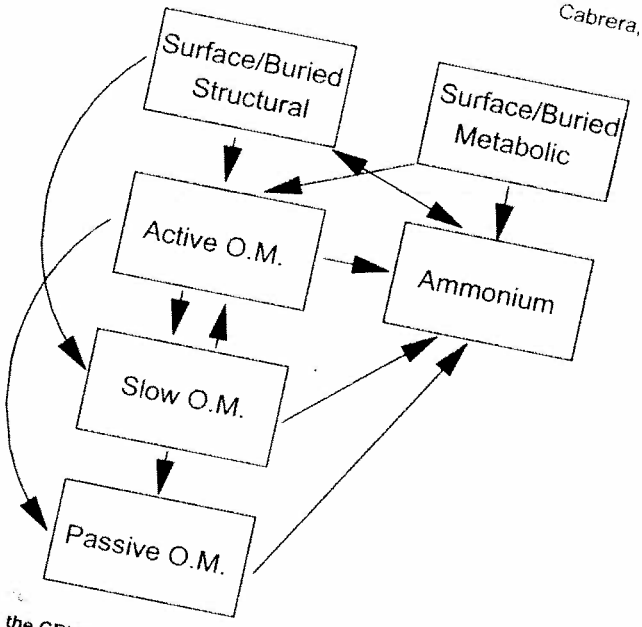

Fig. 18–3. Nitrogen flow in the CENTURY model. O.M., organic matter.

As a stand-alone model, NCSOIL has two residue pools and assumes constant temperature and moisture. As a subroutine of the model NCSWAP/NCSOIL, four organic chemical pools (e.g., manure, pesticides) in addition to roots, root exudates, and residues from three different crops are available; driving variables include management and climatic conditions. Residues, Pool II, and Pool III decay according to first-order kinetics, while Pool I decays with either first-order or Monod kinetics. Residues, Pool I, and Pool II are divided into labile and resistant components. Tillage moves C and N from the resistant fraction of Pool II to its labile fraction.

CENTURY

The CENTURY model was developed to analyze long-term changes in N and C in soil (Parton et al., 1987). It considers surface and buried residue, each of which has structural (slow) and metabolic (fast) components. Turnover times are 1 to 5 yr for structural components and 0.1 to 1 yr for metabolic components. The amounts of structural and metabolic components in the residue are determined by the lignin/N ratio. Soil organic matter is divided into active, slow, and passive pools (Fig. 18–3). The active pool consists of live microorganisms and microbial products, as well as organic compounds with a short turnover time (1–5 yr). The slow pool is organic matter that is physically or chemically protected and has a turnover time of 20 to 40 yr. The recalcitrant pool has compounds with a turnover time of 200 to 1500 yr.

The transfer of plant residue to structural or metabolic pools is determined by the lignin/N ratio (L/N) of the residue:

$$FM = 0.85 - 0.018L/N$$

where FM is the fraction of residue that goes to metabolic pool.

Fig. 18–4. Carbon flow in Jenkinson

This approach has the ac
nents to divide residue into di
lows first-order kinetics modif
in a multiplicative manner.

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and that for the active organic
plus clay in the soil increases. A
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Jenkinson et al.'s Model

Jenkinson et al. (1987) de
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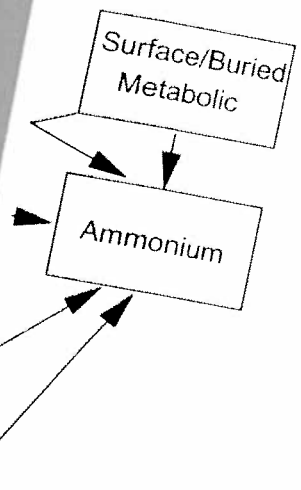

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the model NCSWAP/NCSOIL, four
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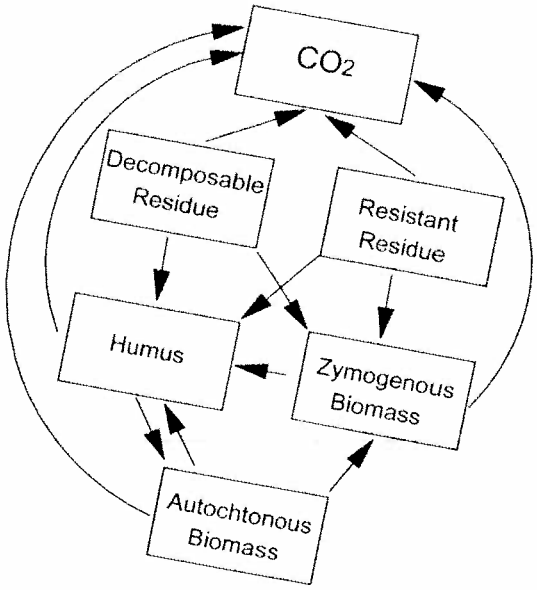

Fig. 18–4. Carbon flow in Jenkinson et al.'s model.

This approach has the advantage of using easily measurable plant components to divide residue into different pools. The decomposition of the C pools follows first-order kinetics modified by moisture (MF) and temperature (TF) factors in a multiplicative manner.

The rate coefficients for surface residue are assumed to be 20% lower than those for buried (root) residue. All rate coefficients of decomposition are constant, except for those for surface and buried structural litter, which decrease with lignin content, and that for the active organic matter pool, which decreases as the amount of silt plus clay in the soil increases. Also, as the amount of silt plus clay increases, the fraction of the decomposed active pool that is evolved as CO_2 decreases. These effects of silt plus clay are intended to model the protection of microbial biomass and SOM in fine-textured soils and are features not present in CERES-N and NCSOIL.

Jenkinson et al.'s Model

Jenkinson et al. (1987) developed a model that includes a relatively simple submodel of microbial biomass and its effect on organic matter decomposition (Fig. 18–4). This model was initially developed to study the dynamics of organic matter at Rothamsted and does not include separate C and N submodels. There are two residue pools (decomposable and resistant), two types of microbial biomass (zymogenous and autochtonous), and two pools of SOM (humus and biologically inert organic matter). The zymogenous biomass decomposes fresh residues to form zymogenous biomass, humus, and CO_2. The autochtonous biomass decomposes humus to form autochtonous biomass, humus, and CO_2.

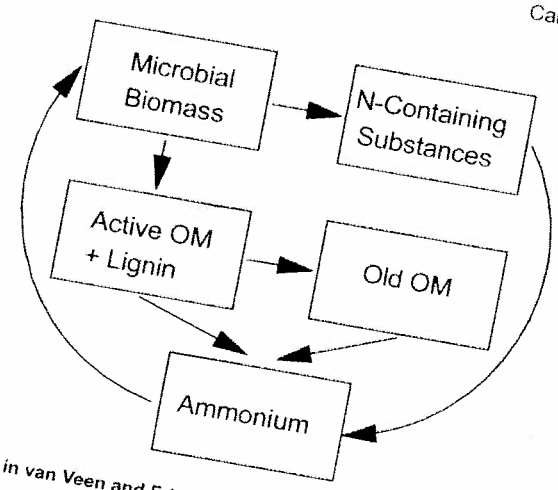

Fig. 18–5. Nitrogen flow in van Veen and Frissel's model. OM, organic matter.

The decomposition rate of all pools follows first-order kinetics and is modified by temperature and moisture factors in a multiplicative manner. The emission of CO_2 is determined by the amount of inorganic colloids in the soil, as indicated by the cation exchange capacity of the inorganic soil components. As the inorganic cation exchange capacity increases, the proportion of decomposed C released as CO_2 decreases to simulate the protective effect of inorganic colloids on soil microbial biomass and organic matter.

Van Veen and Frissel's Model

Van Veen and Frissel (1981) developed a model to study the behavior of N in agroecosystems in which they assumed that each pool was decomposed by a different type of microbial population. The model has three residue pools (carbohydrate, cellulose, and N-containing organic substances) and three organic matter pools (active, active plus lignin, and old). Two of the residue pools (carbohydrate, cellulose) contain only C, whereas the third pool (N-containing substances) contains C and N. One of the organic matter pools (active) contains only C, and the other two pools (active plus lignin, old) contain both C and N (Fig. 18–5).

It is assumed that only a fraction of the total microbial biomass is involved in the decomposition of a given C pool x. This fraction is proportional to the ratio of the amount of C in pool x (C_x) to the total amount of C in all pools (C_t). The growth of this fraction of the total microbial biomass is estimated using Monod kinetics for the three residue pools and for the active organic matter pool.

$$dB/df_{(\text{growth},x)} = (V_{m,x}C_x)/(K_{m,x} + C_x)BC_x/C_t \qquad [36]$$

here $V_{m,x}$ is the maximum rate of microbial growth on pool x, C_x is the C in pool $K_{m,x}$ is the C concentration at which one-half of $V_{m,x}$ is achieved, B is the total mibial biomass, and C_t is the sum of C in all pools.

The total decomposition of pool x (decomposing under Monod kinetics) is ested taking into account the efficiency of the microbial biomass (Y_x). The active lignin organic matter pool (C_s) decomposes according to first-order kinetics,

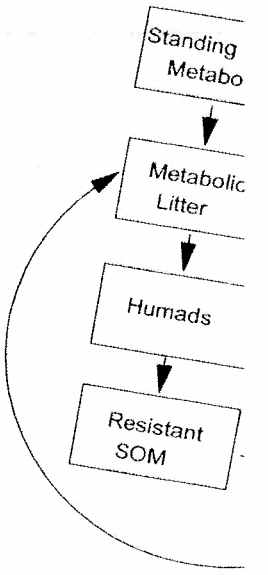

Fig. 18–6. Nitrogen flow in the Phoenix

and the growth of the correspon
the microbial biomass efficiency

Nitrogen mineralization fr
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immobilization, then growth of
is stopped.

Phoenix

The Phoenix model was de
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standing dead structural, metal
(humads and resistant), and two
cetes, and fungi (Fig. 18–6).

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N/C ratio of the residue and on
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$$F_S = (B_D - B_N)/(B_S - B_N)$$

where F_S is the fraction of C alloc
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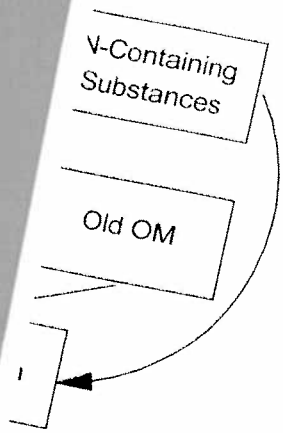

OM, organic matter.

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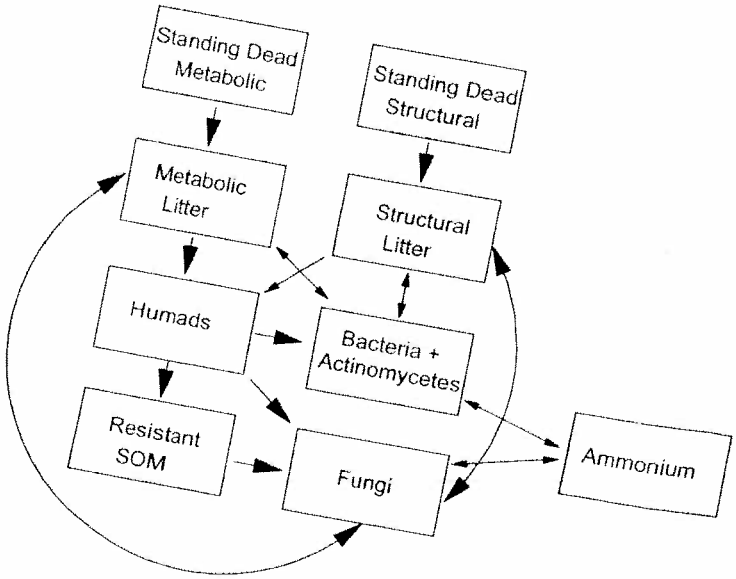

Fig. 18–6. Nitrogen flow in the Phoenix model. SOM, soil organic matter.

and the growth of the corresponding biomass (B_s) is calculated taking into account the microbial biomass efficiency (Y_s).

Nitrogen mineralization from pools that contain N is estimated by dividing the rate of decomposition by the C/N ratio of the decomposing pool. Nitrogen immobilization by microbial biomass is calculated by dividing the growth of the biomass by the C/N ratio of the biomass. If there is not enough N for microbial immobilization, then growth of the biomass is reduced to zero and decomposition is stopped.

Phoenix

The Phoenix model was developed to study C and N dynamics in grassland soils (McGill et al., 1981). It includes four residue pools (standing dead metabolic, standing dead structural, metabolic litter, and structural litter), two SOM pools (humads and resistant), and two microbial biomass pools: bacteria plus actinomycetes, and fungi (Fig. 18–6).

The allocation of residue into metabolic and structural pools is based on the N/C ratio of the residue and on assumed N/C ratios for metabolic and structural components in plants and microorganisms:

$$F_S = (B_D - B_N)/(B_S - B_N) \qquad [37]$$

where F_S is the fraction of C allocated to structural components, B_D is the N/C ratio of residue (shoots, roots, or microorganisms), B_N is the N/C ratio of metabolic components (0.2 for plants, 0.33 for microorganisms), B_S is the N/C ratio of structural components (0.0066 for plants, 0.033 for microorganisms).

A fraction of the metabolic litter is assumed to be in the soil solution and is subject to uptake by microorganisms according to Monod kinetics:

$$dC_m/dt = TF \times MF \times (V_{max} C_m)/(K_m + C_m)M \quad [38]$$

where dC_m/dt is the rate of uptake of metabolic litter C, TF and MF are temperature and moisture factors, V_{max} is the maximum rate of uptake, K_m is the concentration at which one-half of V_{max} is achieved, M is the microbial C, and C_m is the metabolic litter in solution.

The structural litter is insoluble in water and constitutes not only substrate but also habitat for the microorganisms. Its rate of decomposition (dC_s/dt) is first order with respect to microbial biomass and is modified by factors for temperature (TF), moisture (MF), C/N ratio of the microbial population (CNRF), and microbial density (MDF).

To simulate competition between microorganims, the microbial density factor (MDF) reduces the rate of decomposition as the ratio of microbial C to structural C increases. To maintain the C/N ratio of microorganisms within certain limits, the C/N ratio factor (CNRF) reduces the rate of decomposition when the C/N ratio is below 15 for bacteria and below 20 for fungi. It is assumed that 97.5% of the decomposed structural litter is retained by the microbial pools, with the remaining 2.5% going to the humads pool.

The humads pool also receives a transfer of C from the metabolic litter, which is modeled according to first-order kinetics and is modified by a temperature factor. As in the case of metabolic litter, a fraction of the humads pool is in solution and decomposes according to Monod kinetics, modified by temperature and moisture factors. It is assumed that 50% of the decomposed humads is retained by the microbial pools, and the remaining 50% is transferred to the resistant SOM pool.

The decomposition of the resistant SOM is first order with respect to the amount of C in that pool and with respect to the microbial population, and it is modified by temperature and moisture factors. All the decomposed C is retained by microorganisms.

In contrast to N immobilization in the previously described models, N immobilization in the PHOENIX model is modeled using Monod kinetics modified by factors for temperature (TF), moisture (MF), and the variable CNRF set to either 1 or 0 ("on–off" flag).

$$dN_{immob}/dt = TF \times MF \times CNRF \times (V_{max} N_i)/(K_m + N_i)M \quad [39]$$

where V_{max} is the maximum rate of immobilization, K_m is the concentration at which one-half of V_{max} is achieved, N_i is inorganic N in solution, and M is microbial C.

Similarly, N mineralization is modeled using first-order kinetics modified by factors for temperature (TF), moisture (MF), and CNRF:

$$dN_{min}/dt = TF \times MF \times CNRF \times k \times N_m \quad [40]$$

where k is the first-order rate constant and N_m is N in microbial biomass.

To control the C/N ratio of the microbial biomass, N immobilization is decreased to zero when the C/N ratio falls below 5 for bacteria and below 10 for fungi, and N mineralization is reduced to zero when the C/N ratio reaches 15 for bacteria and 20 for fungi. The C/N ratios of the bacterial and fungal biomasses are used to control CNRF (0–1) to initiate N mineralization or immobilization so that the C/N ratios of bacteria and fungi are maintained within specified ranges. This approach is to fluctuating C/N ratios for the microbial biomass. This is in contrast to the C/N ratios used in many of the previously described models.

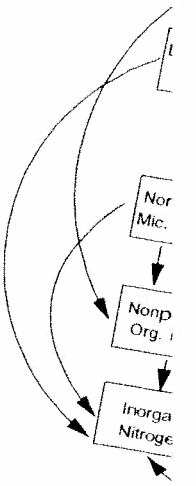

Fig. 18–7. Nitrogen flow in the Verberne

Verberne Model

Verberne et al. (1990) develop
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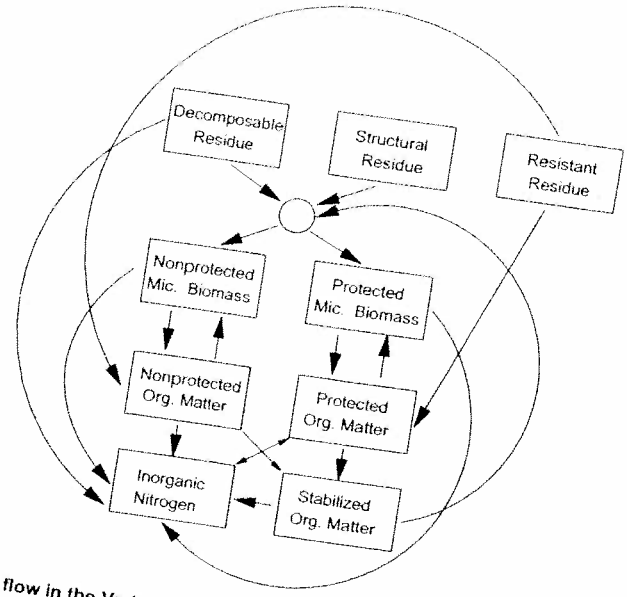

Fig. 18–7. Nitrogen flow in the Verberne model.

Verberne Model

Verberne et al. (1990) developed a model to describe C and N cycling in soil, taking into account the effect of soil texture on decomposition processes. The model has three residue pools that correspond to carbohydrates and proteins (decomposable), cellulose and hemicellulose (structural), and lignified materials (resistant). There are two pools of microbial biomass (protected and nonprotected), two pools of active organic matter (protected and nonprotected), and one pool of stabilized organic matter (Fig. 18–7). The division of microbial biomass and active organic matter into protected and nonprotected pools is intended to simulate protection by clay and silt fractions. All the pools decompose according to first-order kinetics.

The maximum amount of protected microbial biomass is defined as a fraction of total organic soil C. If the microbial population is below this maximum capacity, then the whole population is protected. If, on the contrary, the microbial population is above this maximum capacity, then the amount in excess is considered nonprotected. Nonprotected biomass decomposes at a much higher rate than protected biomass (k = 0.5 vs. 0.005 d^{-1}).

Decomposing microbial biomass is distributed between the protected and nonprotected organic matter according to a parameter that is a function of soil texture. In soils with high clay content, a larger proportion of the decomposing microbial biomass is routed to the protected organic matter. The rate of decomposition of this protected organic matter is much lower than that of the nonprotected organic matter. The C/N ratio of all the pools is constant, and therefore the N fluxes are assumed to be proportional to the C fluxes.

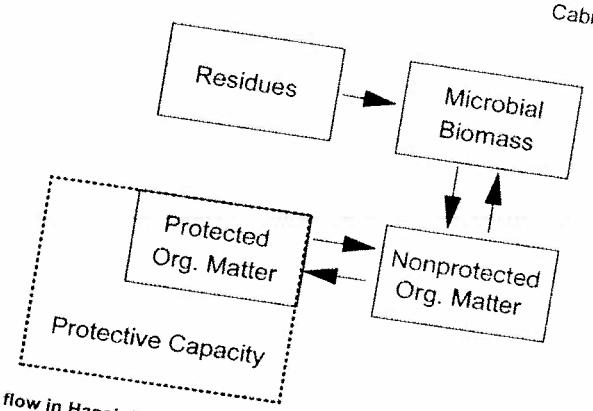

Fig. 18–8. Nitrogen flow in Hassink and Whitmore's model.

Hassink and Whitmore's Model

Hassink and Whitmore (1997) proposed a new model of the physical protection of organic matter in soil (Fig 18–8). Previous models had simulated physical protection by using the clay content of the soil to change the efficiency of utilization (CENTURY, Jenkinson's model), the rate of organic matter decomposition (CENTURY), or the partitioning between protected and nonprotected organic matter (Verberne model). These approaches have the drawback of not limiting the amount of organic matter protection. In their model, Hassink and Whitmore introduced the concept of a limited capacity for protection, similar to the concept introduced in the Verberne model for the protection of microbial biomass.

The rate of formation of protected organic matter ($C_{protected}$) is calculated taking into account the fraction of the protective capacity of the soil that is currently available for protecting organic matter.

$$dC_{protected}/dt = k_p \times (1 - \theta)C_{nonprotected} \quad [41]$$

where k_p is the rate coefficient of protection, θ is the protected organic matter divided by the protective capacity of the soil, and $C_{nonprotected}$ is the nonprotected organic matter.

By calibrating their model with a 10-yr data set including eight soils, Hassink and Whitmore (1997) found that the protective capacity of the soil was related to the soil clay content ($R^2 = 0.76$).

Protected organic matter can become unprotected through desorption, which is modeled as a first-order reaction:

$$dC_{protected}/dt = -k_d \times C_{protected} \quad [42]$$

where k_d is the first-order rate coefficient of desorption.

The use of sorption–desorption kinetics appears to be a reasonable approach to modeling the protection of SOM by clay and silt in soil.

Controlling Factors in Mineralization/Immobilization

As mentioned above, simulation of the N mineralization–immobilization involves the participation of a microbial succession driven by the energy provided

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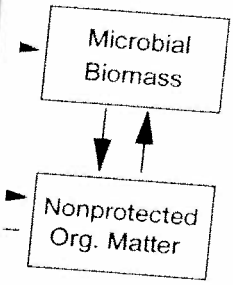

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by the decay of either the SOM pools (microbial pool included) or residues. Al models simulate the residue-driven process of N mineralization–immobilizatior but NCSWAP/NCSOIL is the only model that simulates the MIT and accounts for the dynamics of tracer N (Molina et al., 1990; Nicolardot et al., 1994). The observed exchange between inorganic and organic N is so rapid even in the absence of residues that its simulation requires a high rate of microbial succession obtained by a high decay rate for the microbial pool (Nelson et al., 1979). Nevertheless, the microbial biomass is sustained by the decay of the other SOM pools that can drive the MIT with the net result of N mineralization for many years. When the MIT is not simulated and the model does not account for tracer N kinetics, net N mineralization in the absence of residues is obtained by the release of inorganic N from one or several SOM pools, as described in its simplest form by the N_0 model.

Mineralization–immobilization rates are controlled by the rates of residues and SOM decay, which in turn are controlled by temperature. In general, these rates are very small near 0°C and increase linearly or exponentially until they reach a maximum at 30 to 40°C (Li et al., 1992; Rodrigo et al., 1997). Rates are commonly considered to decrease as temperatures increase above the maximum temperature. Rodrigo et al. (1997) compared the temperature factors of nine C and N transformation models and found large differences among them. Because these differences can lead to different results for the same environmental conditions, the authors concluded that more attention should be paid to consistency between models. The use of the same temperature and moisture factors for residue and SOM decomposition may be adequate when residues are incorporated into the soil but may not be appropriate when residues are left on the soil surface (Quemada and Cabrera, 1997b).

Similarly, rates of mineralization–immobilization are small at low water contents, increase up to field capacity, and decrease as the soil becomes water saturated. In CERES-N (Godwin and Jones, 1991), the moisture factor is 0 when the soil is air dry and increases linearly to reach 1 at the drained upper limit (field capacity). As water content increases above the drained upper limit, the moisture factor decreases linearly to reach a value of 0.5 at saturation. DNDC (Li et al., 1992) and NCSWAP/NCSOIL use a relationship observed for several soils by Linn and Doran (1984): the moisture factor is 0 below 10% water-filled porosity and increases linearly to reach 1 at 60% water-filled porosity. Above 60% water-filled porosity, the moisture factor decreases linearly to reach values of 0.5 at 80% water-filled porosity and 0.4 at 100% water-filled porosity. The optimum water potential for C decomposition processes has been reported to vary from –0.010 (Andrén et al., 1992) to –0.178 MPa (Moore, 1986). In PHOENIX (McGill et al., 1981), different water potential functions are used for bacterial and fungal activity to reflect their different tolerance to water stress. In some cases, the moisture response functions differ among models, which may lead to different simulated results under the same environmental conditions (Ma and Shaffer, 2001; McGechan and Wu, 2001).

The effect of the C/N ratio of the residues and SOM pools on the rate of residue decay is considered by several models. The overall effect is to reduce the rate of residue decomposition when the agents that decay are N starved. In CERES-N, the C/N ratio factor has a value of 1 when C/N ratio is 25 and decreases exponentially as the C/N ratio increases above 25. In NCSOIL/NCSWAWP, the C/N ratio factor decreases exponentially as the ratio of the daily potential C decomposition to the available N (N potentially released during decomposition + inorganic N) increases (Molina et al.,

1983). In NLEAP (Shaffer et al., 2001) the C/N ratio factor has a value of 2.6 at C/N = 9, 1.0 at C/N = 25, 0.57 at C/N = 40, and 0.29 at C/N = 100. The value of the C/N ratio factor between these points is calculated by linear interpolation.

Nitrification

Nitrification is a two-step biological oxidation in which NH_4^+ is first oxidized to NO_2^-, and NO_2^- is subsequently oxidized to NO_3^- (Alexander, 1977). The microorganisms responsible for this process (*Nitrosomonas* and *Nitrobacter*) derive energy from the oxidation reactions and require only CO_2 as a C source.

Modeling Approaches

The second step of nitrification is usually faster than the first step, and as a result it is rare for NO_2^- to accumulate in soils (Paul and Clarke, 1989). Consequently, many simulation models consider nitrification as a direct conversion of NH_4^+ to NO_3^-.

The rate of nitrification has been modeled with a linear equation containing NH_4^+, NO_3^-, and soil temperature (T) as independent variables (NTRM model [Shaffer and Larson, 1987]):

$$dNO_3^-/dt = a + b \times T \times NH_4^+ - N + c[\log_{10}(NH_4^+\text{–}N)] + d(\log 10)\,(NO_3^- - N) \quad [43]$$

Nitrification has also been modeled as a zero-order reaction modified by temperature and moisture factors in a multiplicative manner (NLEAP model [Shaffer et al., 1991]; GLEAMS model [Knisel, 1993]):

$$dNO_3^-/dt = k_0 \times TF \times MF \quad [44]$$

or modified by the minimum of temperature and moisture factors (NCSWAP model [Molina et al., 1983]):

$$dNO_3^-/dt = k_0 \times \text{Minimum}(TF, MF) \quad [45]$$

The EPIC model uses first-order kinetics to model nitrification in soils (Williams, 1995):

$$dNO_3^-/dt = NH_3[1 - \exp(TF \times MF \times pHF)] \quad [46]$$

where NH_3 is the ammonia in soil, and TF, MF, and pHF are temperature, moisture, and pH factors.

SOILN is another example of a model that uses first-order kinetics for nitrification. The ammonium that undergoes nitrification is that in excess of a maximum nitrate/ammonium ratio (r_{max}). The rate is also modified by moisture (MF), temperature (TF), and pH (pHF) factors (Johnsson et al., 1987).

$$dNO_3^-/dt = k \times (NH_4 - NO_3/r_{max}) \times TF \times MF \times pHF \quad [47]$$

In CERES-N, nitrification is modeled according to Michaelis–Menten kinetics (Godwin and Jones, 1991):

$$dNO_3^-/dt = (40 \times NH_4)/(90 + NH_4) \times SNH_4 \times \text{Minimum}(MF, TF, pHF, NPF) \quad [48]$$

where NH_4 is the concentration of ammonium in soil layer; SNH_4 is the total amount of ammonium in soil layer; MF, TF, and pHF are moisture, temperature,

pH factors; and NPF is
potential and current e

Similar approache
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$$dNB_1/dt = (V_{m1}NH_4$$

where NB_1 is *Nitrosomon*
V_{m1} is the maximum rate c
growth rate equals 1/2 V_{m1}
IF is the inhibition factor d

The production rate o
nas population:

$$dNO_2^-/dt = dNB_1 \times 1/$$

where Y_1 is biomass formed c

The growth of *Nitrobacte*

$$dNB_2/dt = (V_{m2}NO_2)/(K$$

where NB_2 is *Nitrobacter* biom
mum rate of growth, K_{m2} is t
one-half of V_{m2}, TF and MF
inhibition factor due to pH a

The rate of production o
ter population:

$$dNO_3^-/dt = dNB_2 \times 1/Y$$

where Y_2 is the biomass forme

Models that use Monod k
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growth is as follows:

$$dNB_1/dt = TF \times MF \times V_m \times (CO_2/(K_{CO2} + CO_2) \times N$$

where NB_1 is the *Nitrosomona*
lution, CO_2 is the CO_2 concen
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CO_2 concentration at which gr
and moisture factors.

ratio factor has a value of 2.6 at C/N = C/N = 100. The value of the C/N ratio ıear interpolation.

lation in which NH_4^+ is first oxidized o NO_3^- (Alexander, 1977). The micro- *osomonas* and *Nitrobacter*) derive en- e only CO_2 as a C source.

ly faster than the first step, and as a (Paul and Clarke, 1989). Consequently, as a direct conversion of NH_4^+ to NO_3^-. ed with a linear equation containing dependent variables (NTRM model

N) [43]

zero-order reaction modified by tem- ıtive manner (NLEAP model [Shaffer

[44]

ıre and moisture factors (NCSWAP

[45]

:s to model nitrification in soils (Wil-

ɔHF)] [46]

F, and pHF are temperature, moisture,

ıat uses first-order kinetics for nitrifi- :ation is that in excess of a maximum so modified by moisture (MF), tem- n et al., 1987).

× MF × pHF [47]

ɔrding to Michaelis–Menten kinetics

[48]

m in soil layer; SNH_4 is the total ıd pHF are moisture, temperature,

pH factors; and NPF is the nitrification potential factor based on past nitrification potential and current environmental limits on nitrification.

Similar approaches are used to model nitrification in the models DAISY (Hansen et al., 1991) and CANDY (Franko et al., 1995).

In more detailed models, Monod kinetics has been used to simulate the independent growth of each of the two nitrifier populations: *Nitrosomonas* and *Nitrobacter* (Darrah et al., 1985a, 1985b, 1986a, 1986b). The growth of *Nitrosomonas* has been modeled as

$$dNB_1/dt = (V_{m1}NH_4)/(K_{m1} + NH_4) \times NB_1 \times TF \times MF \times IF \quad [49]$$

where NB_1 is *Nitrosomonas* biomass, NH_4 is the ammonium in the soil solution, V_{m1} is the maximum rate of growth, K_{m1} is the ammonium concentration at which growth rate equals 1/2 V_{m1}, TF and MF are temperature and moisture factors, and IF is the inhibition factor due to pH and osmotic potential.

The production rate of NO_2^- is proportional to the growth of the *Nitrosomonas* population:

$$dNO_2^-/dt = dNB_1 \times 1/Y_1 \quad [50]$$

where Y_1 is biomass formed divided by mol of NH_4^+ used (or mol of NO_2^- produced).

The growth of *Nitrobacter* has been similarly modeled as

$$dNB_2/dt = (V_{m2}NO_2)/(K_{m2} + NO_2) \times NB_2 \times TF \times MF \times IF \quad [51]$$

where NB_2 is *Nitrobacter* biomass, NO_2 is nitrite in the soil solution, V_{m2} is the maximum rate of growth, K_{m2} is the nitrite concentration at which growth rate equals one-half of V_{m2}, TF and MF are temperature and moisture factors, and IF is the inhibition factor due to pH and osmotic potential.

The rate of production of NO_3^- is proportional to the growth of the *Nitrobacter* population:

$$dNO_3^-/dt = dNB_2 \times 1/Y_2 \quad [52]$$

where Y_2 is the biomass formed per mole of NO_2^- used (or mol of NO_3^- produced).

Models that use Monod kinetics for nitrification include Phoenix (McGill et al., 1981) and van Veen and Frissel's model (van Veen and Frissel, 1981). This detailed modeling approach to nitrification may be useful to study and describe situations that lead to NO_2^- accumulation in soils (Gee et al., 1990; Jones and Schwab, 1993; Burnes et al., 1995; Smith et al., 1997; Chandran and Smets, 2000).

Because nitrifiers are autotrophic and require CO_2 for their growth, Grant (1994) developed a model for nitrifier growth that includes CO_2 as substrate and NH_3 or NO_2^- as the source of energy. The equation used to model *Nitrosomonas* growth is as follows:

$$dNB_1/dt = TF \times MF \times V_{m1} \times [NH_3/(K_{m1} + NH_3)] \times (CO_2/(K_{CO2} + CO_2) \times NB_1 \quad [53]$$

where NB_1 is the *Nitrosomonas* biomass, NH_3 is ammonia concentration in soil solution, CO_2 is the CO_2 concentration in soil solution, V_{m1} is the maximum rate of growth, K_{m1} is the ammonium concentration at which growth rate is 1/2 V_{m1}, K_{CO2} is CO_2 concentration at which growth rate is 1/2 V_{m1}, and TF and MF are temperature and moisture factors.

In later work, Grant (1995) extended this model of nitrification by including N_2O evolution during nitrification, which is an important process for environmental reasons.

Controlling Factors

The general form of temperature factors used to modify nitrification rates has been described previously. Nitrification is considered to increase as temperature increases from 0°C to a maximum temperature that varies from 20 to 35°C, depending on soil type and geographic location (Malhi and McGill, 1981; Godwin and Jones, 1991; Li et al., 1992; Grundmann et al., 1995).

The different functions of soil moisture used to modify nitrification rates have also been described previously. In general, the effect of soil moisture on nitrification varies among models. In CERES-N (Godwin and Jones, 1991), the moisture factor is 0 at the lower limit of water content and increases linearly to reach 1 at the drained upper limit (field capacity). Beyond the drained upper limit, the moisture factor decreases linearly until it reaches 0 at saturation. In NCSWAP/NCSOIL and DNDC, the percentage of water saturation is used to control the rate of nitrification (Linn and Doran, 1984): the moisture factor is 0 when the water-filled porosity is 0%, and increases linearly to reach 1 at 60% water-filled porosity; beyond that point, the factor decreases linearly until it reaches a value of 0 at 100% water-filled porosity. In PHOENIX (McGill et al., 1981), the moisture factor is 0 at a water potential of –6 MPa and increases exponentially to reach 1 at 0 MPa (saturation). It should be clear from these examples that models differ in their effects of moisture on nitrification. For example, at saturation the moisture factor is 0 for CERES-N and 1 for PHOENIX. More research in this area seems warranted to obtain consistency between models.

The soil pH effect on nitrification (pHF, 0–1) has been modeled with first-order (EPIC [Williams, 1995]; CERES-N [Godwin and Jones, 1991]) or higher-order (Darrah et al., 1986b) polynomials. SOILN (Johnsson et al., 1987) uses a pH factor of the form

$$pHF = (pH - pH_{min})/(pH_{max} - pH_{min}) \qquad [54]$$

where pH is the soil pH, pH_{min} is the minimum pH for nitrification, and pH_{max} is the maximum pH for nitrification.

The effect of osmotic potential (OP) on nitrification has been modeled with a second-order polynomial (Darrah et al., 1986a) and with exponential functions of the form $k = a + b \exp(c \times OP)$, where k is the rate of nitrification (Low et al., 1997).

Denitrification

Denitrification is a biological process in which microorganisms use NO_3^-, NO_2^-, and N_2O as electron acceptors (instead of O_2), with the consequent production and evolution of N_2O and N_2 gases. The process occurs under anoxic conditions and the microorganisms responsible for it require organic compounds as energy and C sources (Alexander, 1977).

Modeling Approaches

Modeling denitrification presents a special problem because of the difficulty of modeling anoxic microsites in the soil. Consequently, most comprehensive

models of soil–plant syst
out the soil according to
uses zero-order kinetics,
2000) use first-order kine
Jones, 1991) use second-o

$$-dNO_3/dt = k \times MF \times$$

where k is the second-orde
ture factors, C is the conce
the nitrate concentration in

Michaelis–Menten kin
2000) and SOILN (Johnssor

$$-dNO_3/dt = MF \times TF \times$$

A similar type of Micha
(DB) is used in the Phoenix

$$-dNO_3/dt = MF \times TF(V$$

Van Veen and Frissel (1
mass (B) under anoxic condi
to calculate the rate of denitri

$$-dNO_3/dt = dB/dt \times 1/Y$$

Leffelaar and Wessel (198
soil samples incubated in the
late the growth of denitrifiers
NO_3^-, NO_2^-, and N_2O):

$$dB/dt = \mu B$$

where B is the denitrifier popu
$C)(E_i/(K_{Ei} + E_i)]$ is the growth r
tion of electron acceptor i; i =
tively; $\mu_{Ei\ max}$ is the maximum
in solution; K_c and K_{Ei} are the

The use of each electron a
maintenance requirements:

$$dE_i/dt = (\mu_{Ei}/Y_{Ei\ max} + m_E$$

where $Y_{Ei\ max}$ is the maximum
maintenance coefficient with

The gases produced by d

$$dN_2O/dt = (dE_3/dt - dE$$

$$dN_2/dt = (dE_4/dt)$$

The model of Leffelaar a
(Li et al., 1992), a model that
agricultural soils. To take into
rates based on each electron

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d to modify nitrification rates has
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ıes, 1991]) or higher-order (Darrah
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[54]

pH for nitrification, and pH_{max} is

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of nitrification (Low et al., 1997).

hich microorganisms use NO_3^-,
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cess occurs under anoxic condi-
require organic compounds as

roblem because of the difficul-
equently, most comprehensive

models of soil–plant systems consider denitrification to occur uniformly throughout the soil according to a specified type of kinetics. NCSOIL (Molina et al., 1983) uses zero-order kinetics, NLEAP (Shaffer et al., 1991) and RZWQM (Ahuja et al., 2000) use first-order kinetics, and other models such as CERES-N (Godwin and Jones, 1991) use second-order kinetics:

$$-dNO_3/dt = k \times MF \times TF \times C \times NO_3 \quad [55]$$

where k is the second-order coefficient, MF and TF are the moisture and temperature factors, C is the concentration of water-extractable C in soil layer, and NO_3 is the nitrate concentration in soil layer.

Michaelis–Menten kinetics is used in models such as LEACHM (Hutson, 2000) and SOILN (Johnsson et al., 1987):

$$-dNO_3/dt = MF \times TF \times (V_m NO_3)/(K_m + NO_3) \quad [56]$$

A similar type of Michaelis–Menten expression including denitrifier biomass (DB) is used in the Phoenix model (McGill et al., 1981):

$$-dNO_3/dt = MF \times TF(V_m\ NO_3)/(K_m + NO_3)DB \quad [57]$$

Van Veen and Frissel (1981) use the rate of growth of the heterotrophic biomass (B) under anoxic conditions together with its efficiency of use of NO_3 (Y_{NO3}) to calculate the rate of denitrification:

$$-dNO_3/dt = dB/dt \times 1/Y_{NO3} \quad [58]$$

Leffelaar and Wessel (1988) developed a detailed model of denitrification for soil samples incubated in the laboratory. The model uses Monod kinetics to simulate the growth of denitrifiers and their use of the different electron acceptors (O_2, NO_3^-, NO_2^-, and N_2O):

$$dB/dt = \mu B \quad [59]$$

where B is the denitrifier population; μ is the growth rate $= \Sigma\ \mu_{Ei}$; $\mu_{Ei} = \mu_{Ei\ max}[C/(K_c + C)(E_i/(K_{Ei} + E_i)]$ is the growth rate based on electron acceptor E_i; E_i is the concentration of electron acceptor i; i = 1, 2, 3, 4 refers to O_2, NO_3^-, NO_2^-, and N_2O, respectively; $\mu_{Ei\ max}$ is the maximum growth rate based on electron acceptor E_i; C is the C in solution; K_c and K_{Ei} are the Michaelis–Menten constants for C and E_i.

The use of each electron acceptor is calculated taking into account growth and maintenance requirements:

$$dE_i/dt = (\mu_{Ei}/Y_{Ei\ max} + m_{Ei}\ E_i/E)B \quad [60]$$

where $Y_{Ei\ max}$ is the maximum growth yield on electron acceptor E_i, and m_{Ei} is the maintenance coefficient with respect to electron acceptor E_i.

The gases produced by denitrification are then estimated as

$$dN_2O/dt = (dE_3/dt - dE_4/dt) \quad [61]$$

$$dN_2/dt = (dE_4/dt) \quad [62]$$

The model of Leffelaar and Wessel (1988) was later incorporated into DNDC (Li et al., 1992), a model that simulates the evolution of N_2O, CO_2, and N_2 from agricultural soils. To take into account field environmental conditions, the growth rates based on each electron acceptor are multiplied by temperature and pH fac-

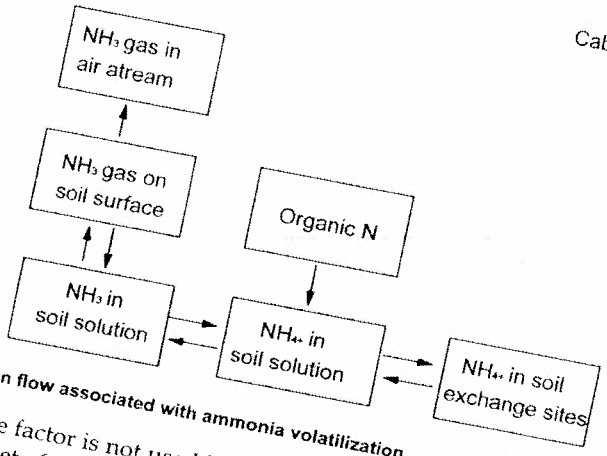

Fig. 18–9. Nitrogen flow associated with ammonia volatilization.

tors. A moisture factor is not used because it is assumed that denitrifiers become active at the onset of a rainfall event and remain active until the water-filled porosity decreases to 40%.

Although most comprehensive models of soil–plant systems do not model the development of anoxic microsites in soil, some researchers have developed models of anoxia and denitrification (McConnaughey and Bouldin, 1985; Arah and Vinten, 1995; Sierra et al., 1995). Furthermore, Arah and Vinten (1995) have developed simplified approximations of these models for incorporation into larger models. These simplified approximations have been added to SLIM (Addiscott and Whitmore, 1991), a solute leaching model, to estimate denitrification under field conditions (Vinten et al., 1996). Future models of field denitrification are likely to include similar approaches.

Controlling Factors

The different functions used to modify denitrification rates based on temperature are similar to the general temperature functions previously described. Denitrification is considered to increase from 0°C until it reaches a maximum at 40°C (PHOENIX [McGill et al., 1981]) to 60°C (DNDC [Li et al., 1992]).

In PHOENIX, the moisture factor is 0 at water potentials lower than –0.1 MPa and increases linearly to reach 1 at –0.03 MPa (field capacity). The factor stays at 1 between –0.03 and 0 MPa (saturation). NCSWAP/NCSOIL and DNDC refer to the same percentages of water saturation as those used to control nitrification: the denitrification moisture factor is 0 from 0 to 60% water saturation; beyond that point, the factor increases until it reaches a value of 1 at 100% water saturation. Thus, nitrification and denitrification occur simultaneously in the range of 60 to 100% water saturation.

The effect of pH on denitrification is not taken into account in most models. However, in DNDC (Li et al., 1992), a linear pH factor is used to achieve a decreased reduction of N_2O, as well as an overall decrease in denitrification as soil pH decreases.

Ammonia Volatilization

Ammonia volatilization is the process of molecular diffusion and convective transport of NH_3 gas from the soil surface to the free air stream in the atmosphere (Fig. 18–9).

Modeling App

Several models
ammonia loss from n
models was presentec
tion, the transfer of Ni
function of a concentra

$$NH_3 \text{ Flux} = r([NH$$

where r is the convective
at the soil surface, and [N
Because in open field
tration to be zero. Therefc
vective transfer coefficient
The mass transfer coef
of the following variables: a
and air viscosity. Ni (1999) F
models to estimate this coeff
The NH_3 gas concentrat
Henry's constant and the NH_3

$$[NH_3]_{surf} = [NH_3]_{sol}/Kh$$

where $[NH_3]_{surf}$ is the NH_3 con
the soil solution (mol N L^{-1}),
sionless ratio.
In this equation, the Henr
the liquid gas phase and molar
perature increases (log Kh = -
[Sherlock and Goh, 1985]). The
surface increases with tempera
The concentration of NH_3
the dissociation constant of NH

$$[NH_3]_{sol} = (Kd[NH_4^+]_{sol})/[$$

where Kd is the dissociation con
solution (mol N L^{-1}), and $[H^+]$ is
The dissociation constant
– 2729.92/T, where T is absolu
concentration of NH_3 in soluti
different forms of the dissociati
To estimate the concentrati
a mechanistic model of soil alk
al., 1988), whereas Ni (1999) us
release to NH_3 release.
Because it may not be prac
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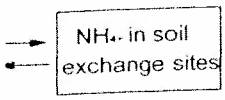

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AP/NCSOIL and DNDC refer to
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en into account in most models.
H factor is used to achieve a de-
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ular diffusion and convective trans-
eam in the atmosphere (Fig. 18–9).

Modeling Approaches and Controlling Factors

Several models of ammonia volatilization have been developed to simulate ammonia loss from manures and fertilizers. A detailed review of several of these models was presented by Ni (1999). In most mechanistic models of NH_3 volatilization, the transfer of NH_3 from the soil surface to the atmosphere is expressed as a function of a concentration gradient:

$$NH_3 \text{ Flux} = r([NH_3]_{surf} - [NH_3]_{atm}) \quad [63]$$

where r is the convective transfer coefficient, $[NH_3]_{surf}$ is the NH_3 gas concentration at the soil surface, and $[NH_3]_{atm}$ is the NH_3 gas concentration in the free air stream.

Because in open fields $[NH_3]_{atm}$ is very low, many models assume this concentration to be zero. Therefore, the NH_3 flux can be calculated by knowing the convective transfer coefficient and the NH_3 gas concentration at the soil surface.

The mass transfer coefficient is usually modeled as a function of one or more of the following variables: air velocity, temperature, surface roughness, air density, and air viscosity. Ni (1999) presented a table with 12 approaches used by different models to estimate this coefficient.

The NH_3 gas concentration at the soil surface is commonly estimated from Henry's constant and the NH_3 concentration in the soil solution:

$$[NH_3]_{surf} = [NH_3]_{sol}/Kh \quad [64]$$

where $[NH_3]_{surf}$ is the NH_3 concentration at the soil surface, $[NH_3]_{sol}$ is the NH_3 in the soil solution (mol N L^{-1}), and Kh is Henry's constant expressed as a dimensionless ratio.

In this equation, the Henry's constant is defined as a dimensionless ratio of the liquid gas phase and molar gas phase concentrations, and it decreases as temperature increases (log Kh = -1.69 + 1477.7/T, where T is absolute temperature [Sherlock and Goh, 1985]). Therefore, the concentration of gaseous NH_3 at the soil surface increases with temperature.

The concentration of NH_3 in the soil solution can in turn be estimated from the dissociation constant of NH_4^+, the concentration of NH_4^+ in solution, and pH:

$$[NH_3]_{sol} = (Kd[NH_4^+]_{sol})/[H^+] \quad [65]$$

where Kd is the dissociation constant, $[NH_4^+]_{sol}$ is the concentration of NH_4^+ in the soil solution (mol N L^{-1}), and $[H^+]$ is the concentration of H^+ in the soil solution (mol L^{-1}).

The dissociation constant increases with temperature (log Kd = –0.09018 – 2729.92/T, where T is absolute temperature [Sherlock and Goh, 1985]), so the concentration of NH_3 in solution also increases with temperature. Ni (1999) lists different forms of the dissociation constant used in different models.

To estimate the concentration of H^+ in the soil solution, some models include a mechanistic model of soil alkalinity (Rachhpal-Singh and Nye, 1986; Sadeghi et al., 1988), whereas Ni (1999) uses a regression equation based on the ratio of CO_2 release to NH_3 release.

Because it may not be practical to model or measure NH_4^+ in solution to calculate the concentration of NH_3 in solution, Sherlock and Goh (1985) derived an equation to estimate NH_3 in solution from total ammoniacal N in soil, which is a variable commonly measured. Total ammoniacal N is made up of ammoniacal N in exchangeable sites (mol N kg^{-1}) and ammoniacal N in solution (mol N L^{-1}). To

express both pools of N in the same units (mol N m^{-3}), ammoniacal N in exchangeable sites (mol N kg^{-1}) is multiplied by bulk density (kg m^{-3}), and ammoniacal N in solution (mol N L^{-1}) is multiplied by volumetric soil water content (L m^{-3}):

$$[NH_3]_{soil} = [NH_x]_{tot}/[\theta(1 + D)(1 + [H^+]/Kd)] \quad [66]$$

where $[NH_x]_{tot}$ is the total ammoniacal N in soil (mol N m^{-3}), θ is the volumetric soil water content (L m^{-3}), and D is the ammoniacal N in exhangeable sites divided by the ammoniacal N in solution.

Combining the equations presented above, Sherlock and Goh (1985) derived the following equation for estimation of ammonia volatilization:

$$NH_3 \text{ Flux} = (r[NH_x]_{tot})/[(Kh \times \theta(1 + D)(1 + [H^+]/Kd)] \quad [67]$$

This equation reflects the effects of water content, pH, and cation exchange capacity on the rate of ammonia loss. Other factors implicitly reflected in the equation are air velocity (which affects r) and temperature (which affects Kh and Kd).

Hengnirum et al. (1999) presented a model of ammonia volatilization that is also based on total ammoniacal N. This model considers the effects of temperature, cation exchange capacity, and air velocity:

$$NH_3 \text{ Flux} = K[NH_x]_{tot} \times 1.08^{(T-Tbase)} \times F_{CEC} \times F_{air} \quad [68]$$

where K is the transfer coefficient, T is the temperature (°C), T_{base} is the base temperature at which K was determined, F_{CEC} is the cation exchange capacity factor = 1 − 0.033 CEC ($cmol_c$ 100 μg g^{-1}), and F_{air} = 1.44 + 0.16 ln(air velocity; km h^{-1}).

Ammonia volatilization has also been modeled with empirical regression equations. For example, Katz et al. (1998) developed an equation to estimate ammonia volatilization after application of liquid cattle manure to grassland. The variables included are total ammoniacal N in the manure, saturation deficit of the air, and application rate:

$$NH_3 \text{ Flux (kg N ha}^{-1}) = (19.41 \text{ TAN} + 1.10 \text{ SD} - 9.51)(0.02 \text{ AR} + 0.36) \quad [69]$$

where TAN is the total ammoniacal N of the manure (g N kg^{-1}), SD is the saturation deficit of the air (mbar), SD = (1 − RH) × 6.112 exp[(17.67 T)/(243.5 T)], T is temperature (°C), RH is relative humidity, and AR is application rate (t ha^{-1}).

Although empirical regression equations are limited in terms of improving our understanding of the processes involved, they may be useful for managing applications under specific conditions.

Current Status and Research Needs

Mechanistic models moved our knowledge of the C and N cycles from a qualitative description to a dynamic dimension controlled by rates of transformations. Models have shown the large extent to which those rates are sensitive to climatic variations on a day to day basis—a fact the field practitioner is keenly aware of. It is thus not surprising to find that models have not been of great help to define crop and environmental management, considering the vagaries of climate prediction. Thirty years are required to characterize mean climatic data at one site. Management practices based on simulated scenarios for average climates must therefore take a long-term view, which is not realistic in today's socioeconomic context. It

can be said, however, that rel
models have been refined.

The soil–crop system is e
rates of N and C transforma
examples of successful simul
in soil and crop have been ob
obtain a quantitative underst
is, of course, room for improv
tion of the soil fauna on C and
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the rate of N immobilization
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The definition of the soil
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Fine tuning of some para
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imatic data at one site. Manage-
average climates must therefore
oday's socioeconomic context. It

can be said, however, that reliable soil–crop models will be available when climate models have been refined.

The soil–crop system is extremely complex, yet, through the interaction of a few rates of N and C transformations expressed by simple mathematical expressions, examples of successful simulation of complex kinetics of total and tracer C and N in soil and crop have been obtained. Thus, the reductionist approach seems valid to obtain a quantitative understanding of C and N dynamics in agroecosystems. There is, of course, room for improvement with models of increased complexity. The function of the soil fauna on C and N transformations requires more attention (De Ruiter et al., 1994; Fu et al., 2000). For example, soil nematodes and protozoa that increase the rate of N immobilization may have a large impact on the effect of elevated CO_2 concentrations on the global C and N cycles (Brimecombe et al., 2000).

The definition of the soil initial conditions, particularly the initial levels of residues and SOM pools, is still performed by calibration. However, progress can be made to alleviate this difficulty either by identifying those chemical fractions that correspond to the SOM pools, or by including chemically and physically defined fractions into deterministic simulation models (Xin-Tao He et al., 1988; Lemaitre et al., 1995; Cambardella, 1997; Paul et al., 1997; Xu et al., 1997; Curtin and Wen, 1999; Schmidt et al., 1999; Selles et al., 1999). Similarly, crop residues are categorized in model pools that reflect the chemical composition of the residues. The definition of residues' pools by proximate analysis has proven to be helpful to quantify their decay kinetics and impact on N transformations (Corbeels et al., 1999; Henriksen and Breland, 1999; Trinsoutrot et al., 2000a, 2000b).

Fine tuning of some parameters of N transformations requires more attention. Simulated N kinetics are very sensitive to the efficiency of C incorporation in the biomass, and the C/N ratio of biomass pools. Efficiency factors of 0.5 and C/N ratio values ranging from 6 for bacteria to 12 for fungi are usually assumed. However, adjustment of these values is often needed to fit simulated to experimental data (Blagodatsky and Richter, 1998; Henriksen and Breland, 1999; Verburg et al., 1999;). Not only is growth but also the C/N ratio of plants increased by elevated CO_2 concentrations, thus modifying the MIT in ways that must be included in mechanistic models of global ecological changes (Berntson and Bazzaz, 1996; Hungate et al., 1997).

Finally but not least is the simulation of N dynamics between plants and soil, essential for the simulation of plant growth limitation by N stress. Usually, a reduction factor on plant growth is activated when the simulated N concentrations in some plant organs cross a threshold value—the higher the N deficit in the organ, the more pronounced the reduction on growth. The relationship between the reduction factor and the N deficit is not linear and varies among plants (Cabelguenne et al., 1999). The form of the relationship is important but is usually not reported in publications, as if this aspect of the agroecosystem dynamics were not important. Also often omitted in publications is a description of the algorithms used to treat the interaction between water and N stress, which, of course, varies with plants. Another aspect of the soil–plant interaction that is not considered by modelers is the impact of root N exudation on plant growth, although some models do consider the impact of C exudation on the SOM C and N turnover (Bottner et al., 1999; Kuzyakov and Domanski, 2000; Molina et al., 2001;). The recycling of N root exudation back into the same plant has been documented (Jimenez et al., 2002). Information about the rates of this N feedback loop would be best treated by simulation modeling.

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While the vast majority of soi
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