

The development of models simulating nitrogen transport in soil and manure

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Hengnirun, S., Barrington, S., Prasher, S.O. and Lyew, D. 1999. **The development of models simulating nitrogen transport in soil and manure.** *Can. Agric. Eng.* 41:035-045. Three submodels were developed for simulating the transport of nitrogen in a manure-amended soil. RUNOFF and LEACH are the submodels for simulating nitrogen losses by runoff after a rainfall and for leaching into the subsoil. The effects of soil adsorption and the presence of both micro- and macropores were considered in the development of LEACH. The simulation of adsorption was accomplished by a third model called ADSORP which was coupled with LEACH. The consideration of macropores in addition to micropores contributed towards a more realistic simulation of leaching and adsorption in the soil. The three submodels were integrated into a model called MANIMEA (Manurial Nitrogen Management: Environmental Aspects). The MANIMEA model simulated the transformation and transport processes affecting nitrogen in a manure-soil system for a specified soil and meteorological conditions so as to predict the fate and distribution of nitrogen in this system. Such a model is a useful tool in the management of manure application so as to lessen the environmental impact of this manure. The integration of RUNOFF, LEACH, and ADSORP into MANIMEA was successfully realized. The simulation results indicated that the submodels were able to generate results that fell within reasonable limits.

Trois sous-modèles furent développés pour simuler les mécanismes de transport de l'azote dans un sol amendé avec des engrais organiques (fumier) et inorganiques. RUNOFF et LEACH sont les sous-modèles qui simulent les pertes d'azote par ruissellement et par lessivage dans le sous sol. Les effets de l'absorption du sol et de la présence de micro et macropores dans le sols furent considérés dans le sous-modèle LEACH. La simulation de l'adsorption fut réalisée par le sous-modèle ADSORP qui fut accouplé au sous-modèle LEACH. La considération des macropores du sol fait en sorte que le modèle est plus réaliste lors de la simulation de l'adsorption et du lessivage dans le sol. Les trois sous-modèles furent intégrés dans le modèle MANIMEA (Gestion de l'azote des fumiers: aspects environnementaux). Le modèle MANIMEA simule la transformation et le transport de l'azote dans tout système constitué de fumier et de sol, pour des conditions spécifiques de climat et de sol. Ce modèle fut développé dans le but d'offrir un outil de gestion des fumiers en tenant compte des aspects environnementaux et agronomiques. L'intégration des sous-modèles RUNOFF, LEACH et ADSORP avec MANIMEA fut réalisée avec succès car les données calculées sont réalistes.

INTRODUCTION

The MANIMEA model simulates the fate of nitrogen in manure-amended soils (Hengnirun et al. 1995). The MANIMEA model is modular in structure and is presently comprised of 11 submodels (Fig. 1) to simulate the environmental conditions of the manure-soil system, the

biological and chemical processes affecting nitrogenous components in the manure and soil, and the transport of nitrogenous compounds through the system. MANIMEA is a dynamic model which considers temporal and spatial changes in environmental factors. It also considers the manure as a separate component prior to its incorporation into the soil. Consequently, MANIMEA should provide a more realistic simulation of the manure-soil system.

The objective of this paper is to present the development of three submodels of MANIMEA which simulate solute transport in the manure-amended soils system, namely RUNOFF, LEACH, and ADSORP. Nitrogen losses in surface runoff were evaluated by RUNOFF, nitrogen movement and loss through the soil profile were simulated by LEACH, and the retention of charged species of nitrogen solutes moving through the soil was simulated by ADSORP coupled to LEACH. The effects of micropores and macropores on the transport of nitrogenous compounds in the soil were taken into account in the development of LEACH and ADSORP. These submodels were run using two scenarios: manure that was surface applied and left for a period before incorporation into the soil; and manure that was injected into the soil.

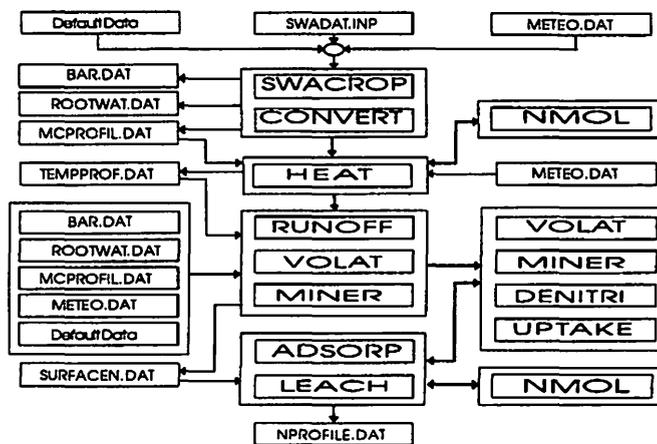


Fig. 1. Structure and organization of MANIMEA.

MODEL DEVELOPMENT

Manure and soil N in the form of NH_4^+ is generally bound to organic matter and the soil minerals, while NO_3^- and NO_2^- are

species present in the soil solution. The bound and dissolved nitrogen can be easily transported by surface runoff as part of the sediment to surface water. The dissolved NO_3^- can be moved to the groundwater by the leaching process. These two transport processes have been recognized as important pathways for the movement of nitrogen in soils.

Surface runoff occurs when the rate of rainfall exceeds the rate of infiltration during a rainfall event (Schwabb et al. 1981) and may lead to soil erosion and sediment loss. The overall process of surface runoff and soil erosion comprises four subprocesses: 1) detachment by rainfall; 2) detachment by runoff; 3) transport by rainfall; and 4) transport by runoff (Meyer and Wischmeier 1969). As the sediments are transported by surface runoff to surface waters, they constitute the most important non-point source of pollutants affecting surface water quality (McElroy et al. 1975).

Runoff and sediment losses from agricultural land receiving agricultural wastes depend on a number of variables, such as the intensity of rainfall, amount of rainfall, type of cover crop, soil characteristics, topography, type of tillage, and conservation practices (McElroy et al. 1975). Nutrient losses through runoff and sediment losses also depend on the concentration, rate of application, method of application, and time of application of manure and fertilizer. For example, uniform incorporation of manure by plowing or by injection into the soil at the rate required by the plants will minimize such losses tremendously.

RUNOFF SUBMODEL

The equations used in RUNOFF to simulate nitrogen losses in runoff are presented in the following section. Nitrogen can be found either adsorbed on particles or dissolved in solution. Nitrogen loss by surface runoff can, therefore, occur either as organic and ammonium nitrogen in the sediment or as nitrate dissolved in the runoff water.

Runoff equation

The Soil Conservation Service Curve Number Equation (Mockus 1972) was used in RUNOFF to estimate the amount of nitrate lost through surface runoff. This equation has been used to estimate pesticide losses in runoff (Haith 1980; Clemente et al. 1993) and to evaluate the effect of poultry manure on runoff quality (Edwards and Daniel 1992). The Curve Number equation is:

$$Q_t = \frac{(R_t - 0.2S_t)^2}{(R_t + 0.8S_t)} \quad (1)$$

where:

- Q_t = direct storm runoff (mm),
- R_t = storm rainfall (mm), and
- S_t = a retention parameter (mm) which is related to soil moisture and curve number (CN).

The value of R_t must be greater than $0.2S_t$, which represents the initial abstraction of surface storage, interception losses, and the amount of infiltration water prior to the runoff event. The relationship between the retention parameter and the curve number can be expressed as:

$$S_t = \frac{1000}{CN} - 10 \quad (2)$$

The curve number accounts for land use or crop cover, soil type, treatment or practice, and hydrological conditions. The curve number for different conditions can be found in the handbook issued by the U.S. Department of Agriculture Soil Conservation Service (1972).

Soil loss equation

The Modified Universal Soil Loss Equation (Williams 1975) was used in RUNOFF to estimate sediment loss from a rainfall event on day t:

$$X_t = \frac{11.8}{A} (V_t q_t)^{0.56} K_e L_t C_t F_{sp} \quad (3)$$

where:

- X_t = soil loss on day t (t/ha),
- A = field area (ha),
- $V_t = 100AQ_t$ = runoff volume (m^3),
- q_t = peak runoff rate (m^3/s),
- K_e = standard soil erodibility factor,
- L_t = topographic factor,
- C_t = cover factor, and
- F_{sp} = supporting practice factor.

The peak runoff rate was given as (Williams 1975):

$$q_t = 0.028A \left(\frac{R_t}{T_t} \right) \left(\frac{Q}{R_t - 0.2S_t} \right) \quad (4)$$

where T_t = rainstorm duration (h).

Nitrogen partitioning in surface runoff

Solid manure is more erodible than soil particles in the receiving land and richer in nitrogen content. Therefore, the nitrogen content of sediments following the surface application of solid manure will increase. As a result, the applied manure layer was a major contributor to total nitrogen losses in runoff and sediment until the manure was incorporated.

During runoff, the amount of nitrogen in the applied manure layer is the net amount remaining after volatilization and net mineralization-nitrification determined by MANIMEA for each time step of the simulation. This can be expressed as:

$$OrgN_{rw} = OrgN_{iw} - OrgN_{minw} \quad (5a)$$

$$NH_{4rw} = NH_{4iw} - NH_{4volw} \quad (5b)$$

$$NO_{3rw} = NO_{3iw} + NO_{3minw} \quad (5c)$$

where:

- $OrgN_{iw}, NH_{4iw}, NO_{3iw}$ = total amounts of organic, ammonium, and nitrate N in the applied manure layer (kg/ha),
- $OrgN_{iw}, NH_{4iw}, NO_{3iw}$ = initial amounts of organic, ammonium, and nitrate N in the applied manure layer (kg/ha),

$OrgN_{minw}$ = amount of organic N mineralized into nitrate as a net end product in the manure layer (kg/ha),
 NH_{4volw} = amount of ammonium volatilized from the manure layer (kg/ha), and
 NO_{3minw} = amount of manure-derived nitrate resulting from the net mineralization-nitrification process (kg/ha).

Similarly, the concentrations of N at time t in the soil can be written as:

$$OrgN_{ts} = OrgN_{is} - OrgN_{mins} \quad (6a)$$

$$NH_{4ts} = NH_{4is} - NH_{4volw} - NH_{4upt} \quad (6b)$$

$$NO_{3ts} = NO_{3is} + NO_{3mins} - NO_{3den} - NO_{3upt} \quad (6c)$$

where:

$OrgN_{ts}, NH_{4ts}, NO_{3ts}$ = total amounts of organic, ammonium, and nitrate N in the soil at time t (kg/ha),
 $OrgN_{is}, NH_{4is}, NO_{3is}$ = levels of organic, ammonium, and nitrate N, respectively, in the soil before manure was applied ($\mu\text{g/g}$),
 $OrgN_{mins}$ = amount of organic N mineralized ($\mu\text{g/g}$),
 NH_{4volw}, NH_{4upt} = ammonium volatilized and ammonium taken up by plants ($\mu\text{g/g}$), and
 $NO_{3mins}, NO_{3den}, NO_{3upt}$ = quantities of nitrate resulting from the net mineralization-nitrification, denitrification in the soil, and nitrate taken up by the plants ($\mu\text{g/g}$).

The net NO_{3ts} in the soil is also considered to be the net concentration after it has been transported by the leaching process.

The concentrations of N in the soil after incorporation will increase due to the residual N in the applied manure layer. MANIMEA assumes that the manure and soil were completely mixed so that the N levels were uniform throughout the entire incorporation depth. A general form of nitrogen, N, was used to represent the concentration of any one of the three different forms (organic nitrogen, ammonium, and nitrate) of N referred to in Eqs. 7 to 18. This was done to avoid repetitive derivation of equations for each species of N in the surface runoff. Subscripts will be used to indicate ionic association (adsorbed or dispersed), type of associate (solid or liquid), and the status (total or remaining) of that specific form of N.

When runoff occurs, N in the mixed soil surface layer can be found in both the adsorbed and dissolved phases. Assuming that the amount of N in the precipitation is negligible, the total amount of N can be described as:

$$N_{tot} = N_{ads} + N_{dis} \quad (7)$$

where:

N_{tot} = total amount of any one of the three forms of N (Org-N, NH_4 , NO_3)(kg/ha),
 N_{ads} = amount of N adsorbed to soil solids (kg/ha), and
 N_{dis} = amount of dissolved N in the soil solution (kg/ha).

Temperature and pH were found to have no significant effect on the adsorption rate (Deizman and Mostaghimi 1991). The partitioning of N concentrations between the adsorbed and dissolved phases can be written as:

$$C_{ads} = K_{ads} C_{sol} \quad (8)$$

where:

C_{ads} = concentration of a specific form of N adsorbed on the surfaces of mineral or organic particles ($\mu\text{g/g}$),
 K_{ads} = adsorption partition coefficient (m^3/g), and
 C_{sol} = concentration of that specific form of N in the soil solution (mg/L).

Assuming that runoff losses occur only within the top 10 mm layer (Haith 1980) and based on a mass balance of this 10 mm layer, N_{ads} and N_{dis} can be expressed as:

$$N_{ads} = 0.1 C_{ads} \rho \quad (9)$$

$$N_{dis} = 0.1 C_{sol} \theta \quad (10)$$

where:

ρ = soil bulk density (mg/m^3),
 θ = volumetric moisture content (m^3/m^3), and
 0.1 = conversion factor to obtain N_{ads} and N_{dis} in kg/ha.

N_{ads} and N_{dis} can be expressed as functions of N_{tot} , θ , ρ , and K_{ads} using the relationships described in Eqs. 7 to 10:

$$N_{ads} = \left[\frac{1}{1 + \theta / (\rho K_{ads})} \right] N_{tot} \quad (11)$$

$$N_{dis} = \left[\frac{1}{1 + \rho K_{ads} / \theta} \right] N_{tot} \quad (12)$$

Equations 11 and 12 can be used when either surface applied manure has been incorporated or manure has been injected directly into the soil. In either case, only the top layer of exposed soil and manure will be considered for a mass balance. This layer was assumed to be 10 mm thick. After mixing or injection, N_{tot} , θ , ρ , and K_{ads} of the soil and manure are adjusted proportionally to reflect this event.

In practice, manure is surface-applied and left unincorporated for a certain period. In this case, the top soil and applied manure layers were considered in the mass balance as a layer consisting of two exposed surfaces, that of manure and the soil, and both 10 mm deep. The manure was assumed to occupy a fraction of the surface and layer volume, expressed as D_w . The value of N_{tot} in the top 10 mm layer can be defined as:

$$N_{tot} = \rho(1 - D_w) N_{ts} + N_{nw} \quad (13)$$

where N_{is} ($\mu\text{g/g}$), N_{tw} (kg/ha) = levels of a specified form of N in the top soil and in the manure layer obtained from Eqs. 5a, b, c and 6a, b, c, respectively. The average soil coverage of the applied manure can be 1.0 or less, however, in the absence of applicable data in the literature, D_w was assumed to be 0.5. Future users of this model can supply a different value of D_w as an input parameter, if one is available.

N losses in the sediment in surface runoff is equal to $X_t C_{ads}$ and can be written as:

$$N_{xt} = \frac{X_t N_{ads}}{100\rho} \quad (14)$$

where N_{xt} = N loss either in the form of Org-N, NH_4^+ , or NO_3^- in the sediment (kg/ha).

After a rainfall event, the amount of rainfall was distributed into runoff water (Q_t), residual water in the soil (θ), and percolation water ($R_t - Q_t - \theta$) (Haith 1980). Assuming that the dissolved N was distributed proportionally among these three components and that the soil was dry at the beginning of the rainfall, the dissolved nitrogen loss in surface runoff can be expressed as:

$$N_{Qt} = \frac{Q_t N_{dis}}{R_t} \quad (15)$$

where N_{Qt} = N loss either in the form of Org-N, $\text{NH}_4\text{-N}$, or $\text{NO}_3\text{-N}$ in the dissolved phase of runoff (kg/ha). If the total available dissolved N is the sum of N loss in sediment, N loss in percolation water and N remaining in soil water, then the dissolved N remaining in the soil after a rainfall event is:

$$N_{\theta t} = \frac{\theta N_{dis}}{R_t} \quad (16)$$

where $N_{\theta t}$ = remaining dissolved N for a specified form of N in the soil after a rainfall (kg/ha).

The total dissolved N lost in the surface layer is then equivalent to $N_{dis} - N_{\theta t}$ and the total N remaining (N_r) in the layer after a rainfall event is:

$$N_r = N_{tot} - N_{xt} - (N_{dis} - N_{\theta t}) \quad (17)$$

After replacing for $N_{\theta t}$ by Eq. 16 and rearranging, N_r can be defined as:

$$N_r = N_{tot} - N_{xt} - \left(1 - \frac{\theta}{R_t}\right) N_{dis} \quad (18)$$

where:

N_r = remaining N in the 10 mm layer (kg/ha), and
 N_{tot} = total amount of N which can be determined using Eq. 13 (kg/ha).

In the case when the applied manure layer is not incorporated, OrgN_{tw} and OrgN_{is} , NH_{4tw} and NH_{4is} , or NO_{3tw} and NO_{3is} are calculated by Eqs. 5a, b, c and 6a, b, c. When the applied manure layer is incorporated, the OrgN_{ts} or NH_{3ts} or NO_{3ts} in the mixed layer can be calculated by Eqs. 6a, b, c.

Equations 13 to 18 were derived for a general form of N, which represents any one of the three forms of Org-N, $\text{NH}_4\text{-N}$, or $\text{NO}_3\text{-N}$ considered in this study. The appropriately selected values for different forms of N in Eqs. 5a, b, c and 6a, b, c can be used to concurrently replace N_{is} and N_{tw} in Eq. 13 when calculating N_{tot} in the 10 mm combined layer. The N remaining in the 10 mm layer will be used as the upper boundary condition to determine N leaching in the complex manure-soil-water-plant system in the LEACH submodel.

LEACH and ADSORP SUBMODELS

The transport of nitrogenous compounds through the soil by leaching is affected by dissociation/adsorption and the presence of micro- and macropores present in the soil. The LEACH and ADSORP submodels were coupled and developed to simulate the leaching process and adsorption effect. The porous structures in the soil, and especially the macropores, were considered to cause preferential flow. The governing equations for the LEACH and ADSORP models are presented and discussed in this section, as are the equations for evaluating the effect of micro- and macropores in the soil on leaching and adsorption.

Leaching

Nitrogen leaching is a transport process involving the movement of water-soluble N out of a defined soil volume into a subsoil region which may or may not contain a watertable (White 1988). The leaching rate can be influenced by many factors including rainfall and evaporation, temperature, soil texture and structure, irrigation, fertilizer use and soil structure, and land use and management.

The movement of dissolved N ions in soil water is governed by two mechanisms: 1) convection or mass flow of ions with the moving soil solution; and 2) diffusion of ions within the solution (Jury and Nielsen 1989). The basic convection-dispersion equation for one-dimensional, steady-state solute movement in a homogenous soil is (Addiscott and Wagenet 1985):

$$J_s = -[\theta D_m + D_e] \frac{dc}{dz} + qc \quad (19)$$

where:

J_s = steady-state solute flux ($\text{mg m}^{-1} \text{h}^{-1}$),
 θ = volumetric water content (m^3/m^3),
 q = volumetric water flux (m/h),
 c = solute concentration (g/mm^3),
 z = depth (m),
 D_m = mechanical dispersion coefficient (m^2/h), and
 D_e = effective diffusion coefficient (m^2/h).

For the total mass of non-reactive solutes, such as nitrate, under transient conditions, the equation for continuity of mass can be written as:

$$\frac{\partial(\theta c)}{\partial t} = -\frac{\partial}{\partial z} \left[-(\theta D_m + D_e) \frac{dc}{dz} + qc \right] \quad (20)$$

where t = time (h).

Rao and Jessup (1983) used Eq. 20 to describe the transport of a solute adsorbed and volatilized during transport. Source and sink mechanisms, such as volatilization, mineralization, and plant uptake were included in Eq. 20:

$$\frac{\partial}{\partial t}(\theta c + \rho s + \epsilon K_H c) = \frac{\partial}{\partial z} \left(\theta D \frac{\partial c}{\partial z} - q c \right) \pm \Phi(z, t) \quad (21)$$

where:

- ρ = bulk density of dry soil (mg/m³),
- s = mass of solute adsorbed per unit mass of soil (mg/mg),
- ϵ = air-filled porosity (dimensionless),
- K_H = Henry's constant (dimensionless),
- D = apparent diffusion coefficient combining D_m and D_c (m²/h), and
- $\Phi(z, t)$ = source or the sink term of the solute at the depth, z and at time, t (mg m⁻¹ h⁻¹), such as plant uptake and other transformation processes.

Equilibrium models for adsorption

Most of the models developed to describe the adsorption process are based on one of three equilibrium equations proposed by (1) Langmuir, (2) Brunauer-Emmett Teller (BET), and (3) Freundlich (Bohn et al. 1985). The first and second equations were developed to describe the adsorption of gases by solids (Langmuir 1918, Brunauer et al. 1938). The third equation (Freundlich 1926) is the one most commonly used to describe solute adsorption during transport through a soil-water system. The adsorption is assumed to be instantaneous and the relationship between the solute concentration and the mass of solute adsorbed is linear. The general form of this equation is:

$$s = K_d c^n \quad (22)$$

where:

- s = mass of solute adsorbed per unit mass of soil (g/g),
- K_d = sorption coefficient (mm³/g),
- c = equilibrium solute concentration (g/mm³), and
- n = empirical exponent which is equal to 1 for the linear type equilibrium adsorption.

This study is concerned with negative (NO₃⁻) and positive (NH₄⁺) ions of N in soils with clay particles with negative charges. For nitrogen sorption in micropores, Eq. 22 becomes:

$$s_1 = K_d C_N \quad (23)$$

where:

- s_1 = mass of N adsorbed in micropores per unit mass of soil (g/g), and
- C_N = concentration of Org-N, NH₄⁺ and NO₃⁻ in the soil (g/mm³).

Equation 22 is mathematically simple to handle but limited to a narrow range of concentrations (Nielsen et al. 1986). In addition, adsorption in the field is not always linear and many influencing factors are involved. Non-equilibrium models were introduced to improve the prediction of the adsorption process.

Non-equilibrium models for adsorption

The simplest form of the non-equilibrium equation was introduced by Lapidus and Amundson (1952):

$$\frac{\partial s}{\partial t} = \alpha (K_d c - s) \quad (24)$$

where:

- t = time (d), and
- α = first-order rate coefficient for mass transfer (d⁻¹).

The prediction results were improved as compared to the equilibrium model when this equation was used for miscible displacement experiments in the laboratory. However, it has been limited to conditions with relatively low pore water velocities (van Genuchten et al. 1974).

Sorption sites have been divided into two types: first fraction or type-1 sites where sorption occurs instantaneously and is governed by the equilibrium equation; and second fraction or type-2 sites where sorption occurs over time (van Genuchten and Wagenet 1989):

$$\frac{\partial s_2}{\partial t} = \alpha [(1 - F)K_d c - s_2] \quad (25)$$

where:

- s_2 = sorption at type-2 sites (g/g), and
- F = fraction of type-1 sites.

This two-site concept was used successfully by Syers et al. (1973) to describe the two-site adsorption for phosphorus.

For the adsorption of Org-N, NH₄⁺ and NO₃⁻, Eq. 25 can be written as:

$$\frac{\partial s_2}{\partial t} = \alpha [(1 - F)K_d C_N - s_2] \quad (26)$$

where:

- s_2 = concentration of adsorbed N in macropores at time, t (g/g),
- F = fraction of macropores, and
- C_N = concentration of Org-N, NH₄⁺, and NO₃⁻ in the soil (g/mm³).

Microporous flow

The convective-dispersive equation (Eq. 21) has been widely used to describe water flow and solute transport in microporous soil including the source and sink terms. Therefore, this equation was used in MANIMEA to evaluate the transient, one-dimensional flow of water and the transport of N under homogeneous soil conditions in this study. The governing equation for N transport is:

$$\frac{\partial}{\partial t}(\theta N + \rho s + \epsilon K_H N) = \frac{\partial}{\partial z} \left(\theta D \frac{\partial N}{\partial z} - q N \right) \pm \Phi \quad (27)$$

where:

- t = time (h),
- θ = volumetric water content (mm³/mm³),
- N = concentration of N (g/mm³),

ρ = bulk density of dry soil (g/mm³),
 ε = air filled porosity,
 K_H = Henry's constant,
 s = concentration of N adsorbed (g/g),
 z = distance along the flow path (mm),
 D = apparent diffusion coefficient (mm²/h),
 q = volumetric water flux (mm/h), and
 Φ = net sink/source term of N due to transformation and plant uptake processes (g mm⁻³ h⁻¹).

As stated earlier, three major forms of N: organic N (Org-N), ammonium N (NH₄⁺), and nitrate (NO₃⁻) were considered in this model. Nitrate is the only one of the three forms known to be significantly transported by the leaching process and not to exist in gaseous state. Therefore, only nitrate leaching was considered in this study by the following equations:

$$\frac{\partial}{\partial t} (\theta C_{NO_3} + \rho s_1) = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C_{NO_3}}{\partial z} - q C_{NO_3} \right) + \Phi_{min} - \Phi_{upt} - \Phi_{den} \quad (28)$$

where:

C_{NO_3} = concentration of nitrate (g/mm³),
 s_1 = concentration of adsorbed NO₃⁻ (g/g),
 Φ_{min} = source term of NO₃⁻ due to mineralization (g mm⁻³ h⁻¹),
 Φ_{upt} = sink term of NO₃⁻ due to plant uptake (g mm⁻³ h⁻¹), and
 Φ_{den} = sink term of NO₃⁻ due to denitrification (g mm⁻³ h⁻¹).

Replacing s_1 by Eq. 23 yields:

$$\frac{\partial}{\partial t} (\theta C_{NO_3} + \rho K_d C_{NO_3}) = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C_{NO_3}}{\partial z} - q C_{NO_3} \right) + \Phi_{min} - \Phi_{upt} - \Phi_{den} \quad (29)$$

where K_d = sorption coefficient (mm³/g).

Macroporous flow

The importance of macropores (e.g. cracks and channels formed by roots and soil fauna) on water flow and solute transport in soil has been increasingly recognized. Macropores allow for the rapid flow of water resulting in a rapid breakthrough of surface-applied solutes through the unsaturated zone to the ground water. The effect of macroporous flow can be introduced into Eq. 29 by using Eqs. 24 to 26:

$$\left(1 + \frac{\rho F K_d}{\theta} \right) \frac{\partial C_{NO_3}}{\partial t} + \frac{\rho}{\theta} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 C_{NO_3}}{\partial z^2} - v \frac{\partial C_{NO_3}}{\partial z} + \frac{\Phi_{min} - \Phi_{upt} - \Phi_{den}}{\theta} \quad (30)$$

where:

F = fraction of micropores,
 s_2 = concentration of adsorbed NO₃⁻ in macropores (g/g) which can be evaluated using Eq. 26, and
 v = average pore-water velocity (mm/h) which is equivalent to q/θ .

Table I. conditions used for surface application and injection in the simulation.

	Surface application	Injection
<u>Manure</u>		
Type of manure	dairy solid manure	dairy slurry
Total Solids (%wb)	20.5	6.9
Total Nitrogen (TN) (%wb)	0.49	0.30
NO ₃ -N/TN	0.01	0.01
TAN/TN	0.45	0.45
NH ₄ -N/TAN	0.95	0.90
pH	7.2	7.3
C/N ratio	10.5	10.2
<u>Soil</u>		
Type of soil	clay loam	clay loam
Bulk density (g/cm ³)	1.30	1.30
Depth of root zone (mm)	200	200
TN in root zone (μg/g of soil)	1485	1485
TN beyond root zone (μg/g of soil)	150	150
NO ₃ -N/TN	0.01	0.01
TAN/TN	0.43	0.43
NH ₄ -N/TAN	0.93	0.93
CEC (meq/100 g)	17	17
pH	6.9	6.9
<u>Farming practice</u>		
Application rates:		
- Manure (t/ha)	100	140
- TN from manure (kg/ha)	490	420
Days before	5	-
Incorporation/injection depth (mm)	150	150
Crop	corn	corn

Equation 30 was used as the governing equation to numerically solve for nitrate leaching in this study.

MODEL COMPUTATION

The evaluation of the submodels was achieved by integrating and running the submodels within the MANIMEA model. This was necessary as the input data for the models arose from other submodels in MANIMEA. In the case of RUNOFF, the submodel was run with other nitrogen process submodels occurring in the top 10-mm layer of the soil. The array of remaining NO₃-N levels in the 10-mm layer, after calculating the NO₃-N loss in runoff, was then used as the upper boundary conditions for the prediction of NO₃-N movement in the leaching process as simulated by LEACH.

The conditions and properties of the manure and the soil used by MANIMEA in the simulation of volatilization,

mineralization-immobilization, denitrification, and plant uptake are given in Table I. Two different manure management procedures or options were investigated. In Option A, the manure was broadcast onto the land on Julian day 152 and left there for a period of four days prior to being incorporated into the soil on Julian day 156 at a depth of 150 mm. In Option B, the manure was injected into the soil at a depth of 150 mm on Julian day 152. A corn crop had been planted on Julian day 141.

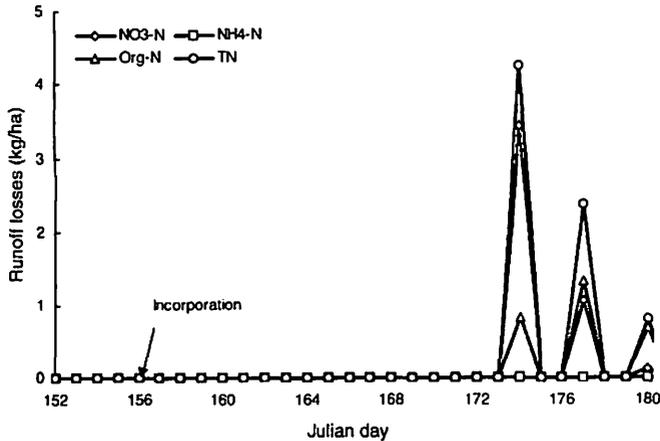


Fig. 2. Nitrogen losses in surface runoff over time: Option A (surface application).

Runoff

A default curve number (CN) value of 82 was used in Eqs. 1 and 2 to calculate the storm runoff. This number represents contoured tillage, good hydrological conditions, and moderately high runoff potential with row crops. The minimum amount of rain which will cause storm runoff was calculated by Eq. 1 to be 4.4 mm. The N losses in runoff for Options A and B are shown in Figs. 2 and 3, respectively. The results demonstrated that runoff losses did not occur until Julian day 174 in spite of rainfalls under 4.4 mm on Julian day 162 and 172.

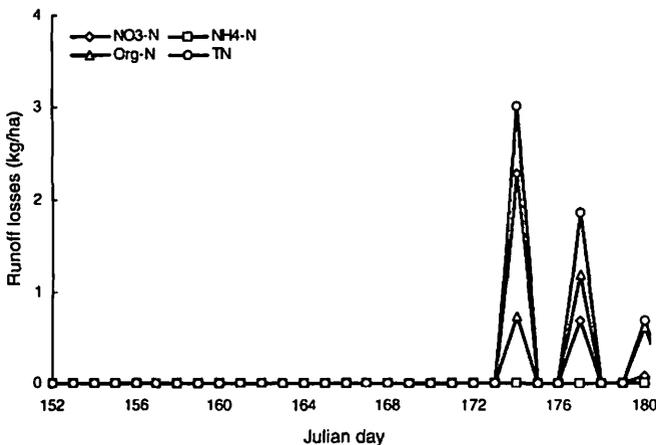


Fig. 3. Nitrogen losses in surface runoff over time: Option B (injection).

For Option A, MANIMEA determined the levels of $\text{NO}_3\text{-N}$, Org-N, and $\text{NH}_4\text{-N}$ remaining after nitrogen transformation in the 10-mm mixed layer of manure and soil on Julian day 174, to be 17.7, 114.8, and 0.5 kg/ha, respectively. $\text{NO}_3\text{-N}$ was assumed to be totally dissolved in the liquid phase ($K_{\text{ads}}=0$), and Org-N was assumed to be in both the liquid and solid phases ($K_{\text{ads}}=3.2$). Consequently, $\text{NO}_3\text{-N}$ loss in runoff was a function of the total amount of $\text{NO}_3\text{-N}$ and of the ratio of storm runoff to rainfall, while Org-N loss in runoff was a fraction of the total Org-N as the other part was associated with the sediment. Thus, as shown in Fig. 2, the total loss of Org-N was less than the loss of $\text{NO}_3\text{-N}$ on Julian Day 174. The loss of $\text{NO}_3\text{-N}$ became less than that for Org-N on Julian day 177, because the remaining levels of $\text{NO}_3\text{-N}$ were lower than that of Org-N.

In Option B, the runoff losses from the top 10-mm of the soil were determined rather than from the top 10-mm of the mixed layer of manure and soil. This was because the slurry-soil mixed zone was 60 to 150 mm beneath the surface. MANIMEA determined the levels of $\text{NO}_3\text{-N}$, Org-N, and $\text{NH}_4\text{-N}$ remaining in the top 10-mm layer on Julian day 174 to be 11.8, 102.5, and 0.4 kg/ha, respectively. The results followed the same trends obtained for Option A (Fig. 3) and can be explained using the reasons given for Option A. While the trends were the same, the peaks obtained for Option B were lower than that for Option A even though the manure application rate for Option A was lower (Table I). This difference was due to the higher TN content of the solid manure (0.49%) used in Option A than that of the dairy slurry (0.30%) used in Option B.

LEACH and ADSORP

Transient $\text{NO}_3\text{-N}$ levels and $\text{NO}_3\text{-N}$ leaching losses were evaluated by the LEACH submodel. This submodel used the Numerical Method of Lines (NMOL) technique to solve the governing partial differential equation described above. The $\text{NO}_3\text{-N}$ source term in the equation was the result of net mineralization and the $\text{NO}_3\text{-N}$ sink terms were the results of denitrification and plant uptake processes. The results predicted by the LEACH model are presented in Figs. 4 and 6 as changes in $\text{NO}_3\text{-N}$ levels over time and in Figs. 5 and 7 as $\text{NO}_3\text{-N}$ leaching losses over time.

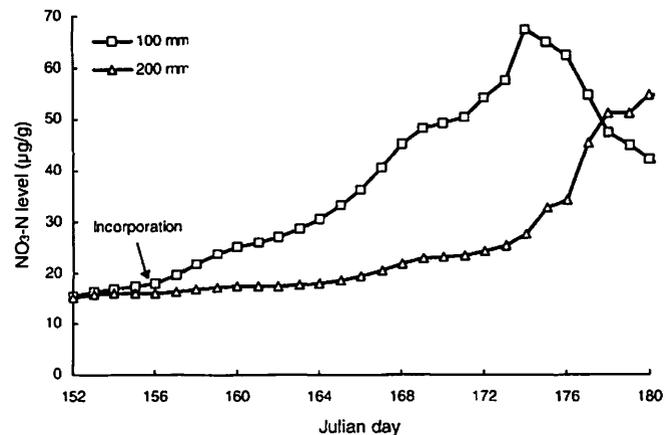


Fig. 4. Changes in $\text{NO}_3\text{-N}$ levels over time at soil depths of 100 and 200 mm: Option A (surface application).

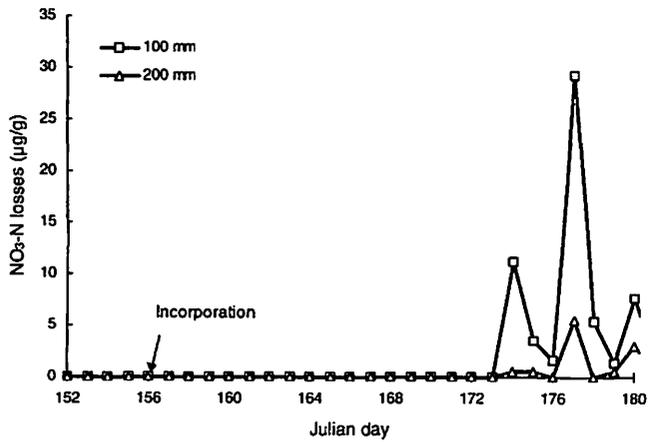


Fig. 5. $\text{NO}_3\text{-N}$ leaching losses over time at soil depths of 100 and 200 mm: Option A (surface application).

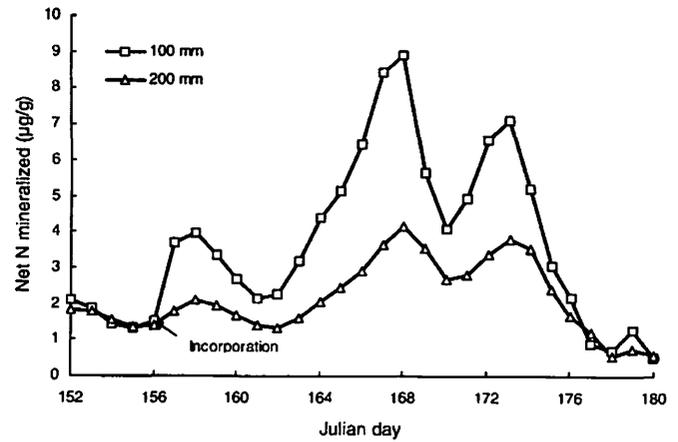


Fig. 8. Net N mineralized from the soil component over time at soil depths of 100 and 200 mm: Option A

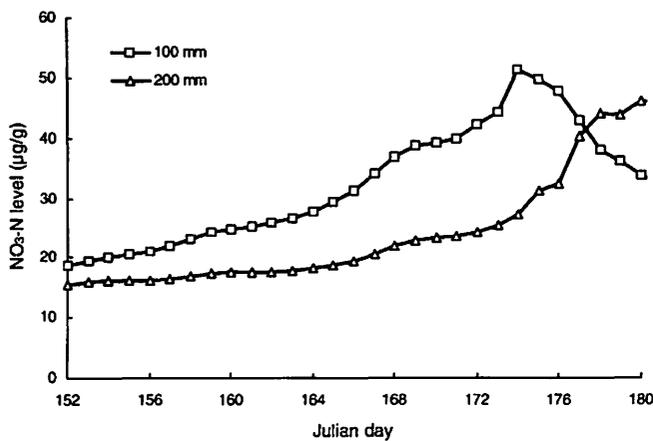


Fig. 6. Changes in $\text{NO}_3\text{-N}$ levels over time at soil depths of 100 and 200 mm: Option B (injection).

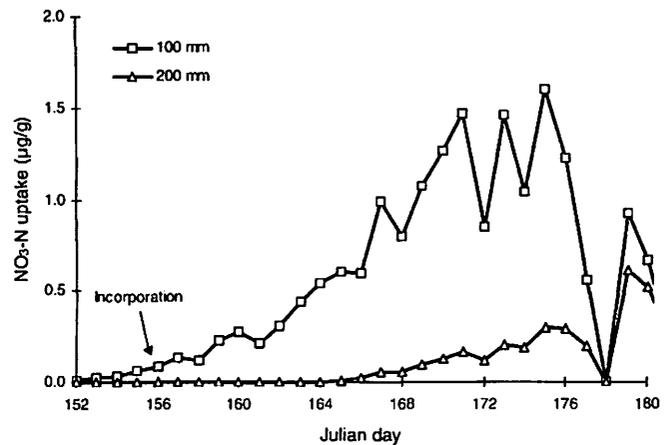


Fig. 9. $\text{NO}_3\text{-N}$ uptake by corn over time at soil depths of 100 and 200 mm: Option A (surface application).

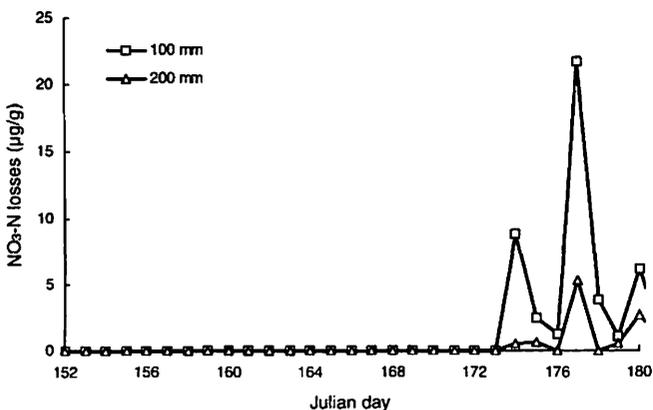


Fig. 7. $\text{NO}_3\text{-N}$ leaching losses over time at soil depths of 100 and 200 mm: Option B (injection).

For Option A, the $\text{NO}_3\text{-N}$ levels at depths of 100 and 200 mm were the same on the first day of simulation (Fig. 4), because both depths lie within the root zone where the initial $\text{NO}_3\text{-N}$ levels were assumed to be the same. The manure layer

was incorporated on Julian day 156 and the $\text{NO}_3\text{-N}$ level at 100 mm became higher than that at 200 mm, due to high net mineralization rates (Fig. 8) which produced more $\text{NO}_3\text{-N}$ at 100 mm than at 200 mm. The rates of $\text{NO}_3\text{-N}$ losses due to corn uptake and denitrification also increased, but the effects of these processes were small as compared to the rate of $\text{NO}_3\text{-N}$ production by net mineralization. The steep and continual decrease in $\text{NO}_3\text{-N}$ levels at 100 mm, starting on Julian day 174 (Fig. 4), was due to leaching. Decreasing rates of net mineralization also contributed to this effect. The gradual increase in $\text{NO}_3\text{-N}$ levels at 200 mm between the start of the simulation and Julian day 174 was due to increasing rates of net mineralization (Fig. 8). After Julian day 174, $\text{NO}_3\text{-N}$ levels rose markedly despite reduced net mineralization, $\text{NO}_3\text{-N}$ losses due to leaching (Fig. 5), plant uptake (Fig. 9), and denitrification (Fig. 10), since the amount of $\text{NO}_3\text{-N}$ percolating from the upper layer was higher than that lost from this depth.

In Option B, a difference in the $\text{NO}_3\text{-N}$ levels at 100 and 200 mm was present from the start of the simulation (Fig. 6), because the 100 mm depth was part of the slurry-soil mixed zone (60-150 mm) where the initial $\text{NO}_3\text{-N}$ level was higher

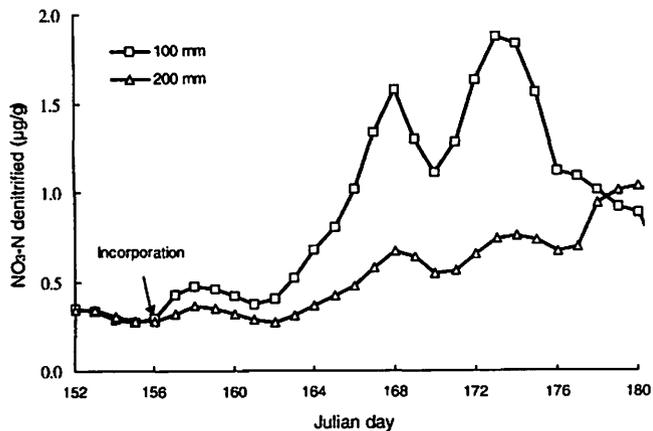


Fig. 10. $\text{NO}_3\text{-N}$ denitrified in the soil component over time at soil depths of 100 and 200 mm: Option A

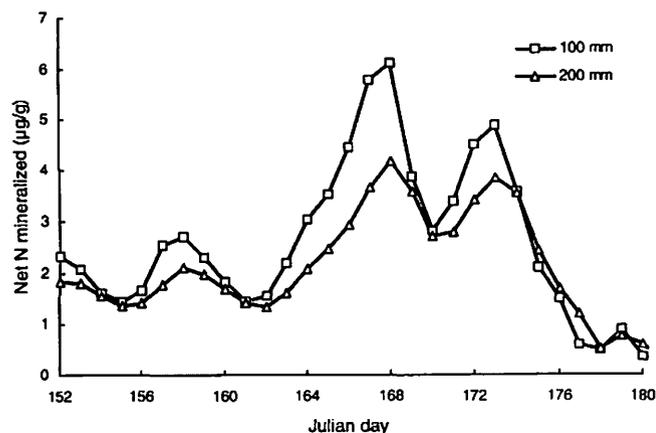


Fig. 11. Net N mineralized from the soil component over time at soil depths of 100 and 200 mm: Option B (injection).

than that at 200 mm. The $\text{NO}_3\text{-N}$ levels at both depths increased gradually until Julian day 174 as a result of a net increase in the difference between $\text{NO}_3\text{-N}$ production by net mineralization (Fig. 11) and $\text{NO}_3\text{-N}$ losses due to plant uptake (Fig. 12) and denitrification (Fig. 13). The $\text{NO}_3\text{-N}$ losses due to leaching began to affect $\text{NO}_3\text{-N}$ levels at both depths on Julian day 174, since $\text{NO}_3\text{-N}$ levels at 100 mm decreased while $\text{NO}_3\text{-N}$ levels at 200 mm increased. The changes in $\text{NO}_3\text{-N}$ levels at both depths can be interpreted using the same explanations used for Option A.

CONCLUSIONS

The RUNOFF, LEACH, and ADSORP submodels were successfully integrated within the MANIMEA model to generate predictions on the movement of N in manure-amended soils for two manure application methods. The simulation results indicated that the submodels were able to generate results that fell within reasonable limits and that could be readily interpreted with the context of results generated by

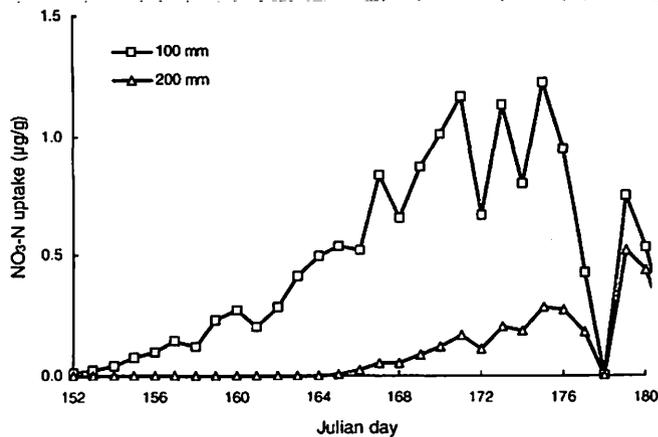


Fig. 12. $\text{NO}_3\text{-N}$ uptake by corn with time at soil depths of 100 and 200 mm: Option B (injection).

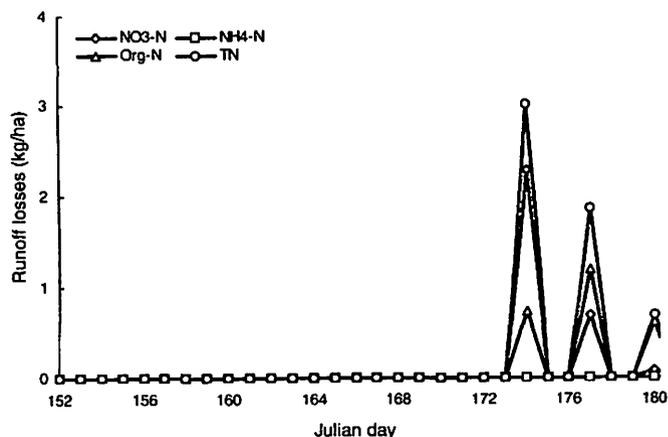


Fig. 13. $\text{NO}_3\text{-N}$ denitrified in the soil component over time at soil depths of 100 and 200 mm: Option B (injection).

models simulating mineralization, volatilization, and denitrification processes affecting nitrogenous compounds in the manure-soil system. Also, the MANIMEA model takes into consideration soil characteristics, application rates, meteorological conditions, and temperature. Consequently, an overall analog scheme of the fate of nitrogen in manure-amended soils can be attained by MANIMEA.

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NOMENCLATURE

A	field area (ha)
c	solute concentration (g/mm ³)
C _i	cover factor
C _{ads}	concentration of a specific form of N adsorbed on the surfaces of mineral or organic particles (μg/g)
C _N	concentration of nitrogenous compounds in the soil (g/mm ³)
C _{NO₃}	concentration of nitrate (g/mm ³)
C _{sol}	concentration of a specific form of N in the soil solution (mg/L)
D	thickness (mm); apparent diffusion coefficient combining D _m and D _e in Eq. 21 (m ² /h)
D _m	mechanical dispersion coefficient (m ² /h)
D _e	effective diffusion coefficient (m ² /h)
F	fraction of type-1 sites of macropores
F _{sp}	supporting practice factor
J _s	steady-state solute flux (mg m ⁻¹ h ⁻¹)
K _{ads}	adsorption partition coefficient (m ³ /g)
K _d	sorption coefficient (mm ³ /g)
K _e	standard soil erodibility factor
K _H	Henry's constant (dimensionless)
L _t	topographic factor
n	empirical exponent in Eq. 22
N	general form of nitrogen (Org-N, NH ₄ , NO ₃)
N _{ads}	amount of N adsorbed to the soil solids (kg/ha)
N _{dis}	amount of dissolved N in the soil solution (kg/ha)
N _{Qt}	amount of N in the dissolved phase of runoff (kg/ha)
N _r	total dissolved nitrogen remaining in the soil layer of interest after a rainfall (kg/ha)
N _{ts}	concentration of a specified form of N in the soil (μg/g)
N _{tw}	concentrations of a specified form of N in the manure (kg/ha)
N _{Xt}	amount of N loss in the runoff sediment (kg/ha)
N _{0t}	amount of dissolved N remaining in the soil after a rainfall (kg/ha)
NH ₄	amount of ammonium nitrogen
NO ₃	amount of nitrate nitrogen

OrgN	amount of organic nitrogen
q	volumetric water flux (m/h)
q _i	peak runoff rate (m ³ /s)
Q _t	storm runoff (mm)
R _t	storm rainfall (mm)
s	mass of solute adsorbed per unit mass of soil (g/g)
s ₁	mass of N adsorbed in micropores per unit mass of soil (g/g)
s ₂	mass of N adsorbed in type-2 sites of macropores (g/g)
S _t	retention parameter (m) related to soil moisture and curve number (CN)
t	time
T _t	rainstorm duration (h)
V _t	runoff volume (m ³) and is equivalent to 100AQ _t
X _t	soil loss on day t (t/ha)
z	depth; distance along flow path (mm)

Subscripts

ads	adsorbed
den	denitrified
dis	dissolved
i	initial
min	mineralized
N	nitrogen
NO ₃	nitrate
o	organic
s	soil
sol	solution
t, tot	total
upt	uptake
vol	volatilized
w	waste or manure

Greek symbols

α	first-order rate coefficient for mass transfer (d ⁻¹)
ε	air-filled porosity (dimensionless)
θ	volumetric moisture content (m ³ m ⁻³)
θ	residual water in the soil in Eqs. 16 and 18
v	average pore-water velocity (mm/h)
ρ	bulk density of dry soil (mg/m ³)
Φ	source or sink term (g mm ⁻³ h ⁻¹)
Φ(z,t)	net source or sink term of the solute at depth, z and at time, t (mg m ⁻¹ h ⁻¹)