Fate and Transport of Nitrogen in Soils Based on a Coupled Nitrogen-Carbon Cycling Model Using the HP1 Code

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Abstract

In order to predict the fate and transport of nitrogen in soils as a result of decomposition of organic matter, we implemented within the PHREEQC program a coupled carbon and nitrogen cycling model based on the LEACHM code. Decay processes from organic carbon (Org-C) to biomass carbon (Bio-C), humus carbon (Hum-C), and carbon dioxide were described using first-order kinetics. Bio-C was recycled into the organic pool. Decomposition of Org-N was related to the carbon cycle using the C/N ratio. Mineralization and immobilization were determined based on available NH₄-N and the nitrogen demand for the formation of biomass and humus. Nitrogen transformations were also described with first-order chain reactions. The carbon and nitrogen cycling model described with PHREEQC was linked with HYDRUS-1D using the HP1 code. Various nitrogen transport scenarios were demonstrated for the application of organic matter to a variable-saturated soil under nonisothermal conditions.

1. Introduction

Nitrogen in soil can change its form through various microbial activities such as mineralization of ammonium from organic matter, nitrification from ammonium, and denitrification from nitrate. Nitrogen mineralization rates depend upon the rate of degradation of organic carbon, the N content of organic matter, and the carbon-to-nitrogen (C/N) ratio of the decomposition products. Because the biomass product usually has a higher C/N ratio than the parent manure, incorporation of biomass gradually increases the C/N ratio of the parent organic pool. The C/N ratios of humus and biomass determine how much N transforms to humus and biomass, while any excess N is released as mineral NH₄. If sufficient N for the production of humus and biomass is not released by mineralization, mineral N will be immobilized from the soil. In order to predict the dynamics and transport of nitrogen as a result of decomposition of organic matter in soils, it is necessary to link a coupled carbon and nitrogen cycling model with a water flow and solute transport model.

The LEACHM code (Hutson, 2005) used a coupled carbon and nitrogen cycling model developed by Johnsson (1987). Although LEACHM has been used widely for nitrogen transport problems, it is currently difficult to further modify the code for various applications. Furthermore, the basic properties of the coupled carbon and nitrogen cycling model have not been investigated thoroughly. In this study we firstly describe first-order kinetic equations for the carbon and nitrogen cycles in soils using the PHREEQC program (Parkhurst and Appelo, 1999). Then, the coupled cycling model is linked with the water flow and solute transport model of HYDRUS-1D (Šimůnek et al., 2005) within the HP1 code (Jacques and Šimůnek, 2010). Various nitrogen transport scenarios are demonstrated for the application of organic matters to a variable-saturated soil under nonisothermal conditions.

2. Coupled Nitrogen and Carbon Cycling Model

2.1. Degradation of Organic Matter

Figure 1 shows the coupled nitrogen and carbon cycling model of Johnsson et al. (1987) as implemented in LEACHM (Hutson, 2005). The blue lines are for the carbon cycle and the black lines for the nitrogen cycle. Numbers in the figure represent the reaction routes specified in the discussion that follows. Two types of principal organic matter were defined: a first cycling pool for litter and a slow cycling pool for stabilized humus. Separate litter pools were used for organic matter having different decay rates and carbon-to-nitrogen (C/N) ratios, such as plant residue and manure. Decay processes from organic carbon (Org-C) to biomass carbon (Bio-C), humus carbon (Hum-C), and carbon dioxide were described with a first-order kinetic. The biomass was recycled into a decomposable litter pool, forming a litter-decomposer complex. Decomposition from the Org-N to Bio-N and Hum-N were related to the carbon cycle using the C/N ratios of the organic matter, biomass and humus. Mineralization of ammonium (NH₄-N) from organic matter and immobilization of NH₄-N to organic matter were determined based on the available NH₄-N and the N demand for the formation of biomass and humus.



Figure 1. Coupled nitrogen and carbon cycling model based on the LEACHM code.

2.2. Carbon Cycle

Organic carbon (Org-C) in the organic pool i (= 1, 2) degrades into three components (routes 1, 2 and 3 in Figure 1): microbial biomass carbon (Bio-C), humus carbon (Hum-C), and carbon dioxide (CO₂):

$$Org-C \rightarrow Bio-C + Hum-C + CO_2 \tag{1}$$

First-order kinetic is used for the degradation of organic carbon:

$$\frac{dC_{\text{Org-C}i(d)}}{dt} = -k_{\text{Org}i}C_{\text{Org-C}}$$
(2)

where *C* is concentration, expressed as mass per volume of soil, and k_{Org} is the first-order rate coefficient. In order to distinguish the route and direction of the reactions in Figure 1, the subscript (d) is used for degradation while the subscript (p) is used for production in the rate equations. The rate coefficient depends on temperature and water content, with a correction factor according to Johnsson et al. (1987).

The fractions of three products in Eq. (1) are assumed to be invariant. The efficiency factor, f_e , determines the relative production of CO₂ and biomass plus humus while the humification factor, f_h , determines the split between biomass and humus as follows:

$$f_e = \frac{\Delta \text{Bio-C} + \Delta \text{Hum-C}}{\Delta \text{Bio-C} + \Delta \text{Hum-C} + \Delta \text{CO}_2}$$
(3)

$$f_{h} = \frac{\Delta \text{Hum-C}}{\Delta \text{Bio-C} + \Delta \text{Hum-C}}$$
(4)

The fraction of each mineralized product can be described with these two factors: $f_e (1 - f_h)$ for Δ Bio-C, $f_e f_h$ for Δ Hum-C, and $1 - f_e$ for Δ CO₂. Johnsson et al. (1987) used $f_e = 0.5$ and $f_h = 0.2$ in their examples, assuming fractions of Δ Bio-C, Δ Hum-C, and Δ CO₂ are 0.4, 0.1, and 0.5, respectively. The fraction of persistent humus production may depend on the type of organic matter (Brady and Weil, 2008). Since f_e and f_h can be different for the different organic pools, the subscript i (= 1, 2) is used in this paper to distinguish between these two factors.

The production rate of Bio-C, Hum-C, and CO₂ of the organic pool i (= 1, 2) can be related to the degradation rate of Org-C (routes 1, 2, 3):

$$\frac{dC_{\text{Bio-Ci(p)}}}{dt} = -f_{\text{ei}} \left(1 - f_{\text{hi}}\right) \frac{dC_{\text{Org-Ci(d)}}}{dt}$$
(5)

$$\frac{dC_{\text{Hum-C}i(p)}}{dt} = -f_{ei}f_{hi}\frac{dC_{\text{Org-C}i(d)}}{dt}$$
(6)

$$\frac{dC_{\text{CO2}i(p)}}{dt} = -(1 - f_{ei})\frac{dC_{\text{Org-C}i(d)}}{dt}$$
(7)

Hum-C further decomposes into CO_2 and the degradation rate is also described with first-order kinetics (route 4):

$$\frac{dC_{\text{Hum-C(d)}}}{dt} = -k_{\text{Hum-C}}C_{\text{Hum-C}}$$
(8)

Note that $k_{\text{Hum-C}}$ is much smaller than $k_{\text{Org}i}$ since humus is a persistent substance.

The net reaction rate for each carbon component can be described with a mass balance for all the routes in Figure 1. The net reaction rate for Org-C is the sum of degradation described using Eq. (2) and Bio-C production described with Eq. (5), which is recycled in the organic pool (routes 2, 3):

$$\frac{dC_{\text{Org}-Ci}}{dt} = -k_{\text{Org}\,i}C_{\text{Org}-Ci} + f_{ei}\left(1 - f_{\text{h}i}\right)k_{\text{Org}\,i}C_{\text{Org}-Ci} \tag{9}$$

The net reaction rate for Hum-C is the sum of degradation according to Eq. (8) and production from the organic pools according to Eqs. (2) and (6) (routes 2, 4):

$$\frac{dC_{\text{Hum-C}}}{dt} = -k_{\text{Hum-C}}C_{\text{Hum-C}} + \sum_{i=1}^{2} f_{ei}f_{hi}k_{\text{Org}\,i}C_{\text{Org-C}i}$$
(10)

Carbon dioxide is produced from the organic pools according to Eq. (7) and Hum-C according to Eq. (8) (routes 3, 4):

$$\frac{dC_{\rm CO2}}{dt} = \sum_{i=1}^{2} (1 - f_{\rm ei}) k_{\rm Org\,i} C_{\rm Org-Ci} + k_{\rm Hum-C} C_{\rm Hum-C}$$
(11)

Note that since the biomass is recycled in the organic pool as shown by the second term on the right hand side of Eq. (9), Bio-C does not explicitly appear in the net rate equations.

2.3. Nitrogen Cycle

Organic nitrogen (Org-N) decomposes to microbial biomass nitrogen (Bio-N) and humus nitrogen (Hum-N) as in the case of carbon of Eq. (1):

$$Org - N \rightarrow Bio - N + Hum - N$$
 (12)

The C/N ratios, r, for organic matter, biomass and humus are defined as

$$r_{\text{Org}\,i} = \frac{C_{\text{Org-C}i}}{C_{\text{Org-N}i}}, \quad r_{\text{Bio}} = \frac{C_{\text{Bio-C}i}}{C_{\text{Bio-N}i}}, \quad r_{\text{Hum}} = \frac{C_{\text{Hum-C}}}{C_{\text{Hum-N}}}$$
(13)

Note that $r_{\text{Org }i}$ changes with time as the organic matter degrades, whereas r_{Bio} and r_{Hum} , are constant (≈ 10).

The degradation rate of Org-N in Eq. (12) can be related to the degradation rate of Org-C using $r_{\text{Org }i}$ as

$$\frac{dC_{\text{Org-N}i(d)}}{dt} = \frac{1}{r_{\text{Org}\,i}} \frac{dC_{\text{Org-C}i(d)}}{dt}$$
(14)

The production rates for Bio-N and Hum-N are also transformed to the carbon concentration rates and further related with the degradation rate for the organic carbon using Eqs. (5) and (6):

$$\frac{dC_{\rm Bio-Ni(p)}}{dt} = \frac{1}{r_{\rm Bio}} \frac{dC_{\rm Bio-Ci(p)}}{dt} = -\frac{f_{\rm ei}(1 - f_{\rm hi})}{r_{\rm Bio}} \frac{dC_{\rm Org-Ci(d)}}{dt}$$
(15)

$$\frac{dC_{\text{Hum-N(p)}}}{dt} = \frac{1}{r_{\text{Hum}}} \frac{dC_{\text{Hum-C(p)}}}{dt} = -\frac{f_{ei}f_{hi}}{r_{\text{Hum}}} \frac{dC_{\text{Org-Ci(d)}}}{dt}$$
(16)

The difference between the nitrogen supplies from Org-N and the demands for Bio-N and Hum-N production gives the production rate of ammonium (NH₄-N):

$$\frac{dC_{\mathrm{NH}_{i}i(\mathrm{p})}}{dt} = -\frac{dC_{\mathrm{Org-N}i(\mathrm{d})}}{dt} - \left(\frac{dC_{\mathrm{Bio-N}i(\mathrm{p})}}{dt} + \frac{dC_{\mathrm{Hum-N}(\mathrm{p})}}{dt}\right)$$

$$= -\left(\frac{1}{r_{\mathrm{Org}\,i}} - \frac{f_{\mathrm{e}i}\left(1 - f_{\mathrm{h}i}\right)}{r_{\mathrm{Bio}}} - \frac{f_{\mathrm{e}i}f_{\mathrm{h}i}}{r_{\mathrm{Hum}}}\right)\frac{dC_{\mathrm{Org-C}i(\mathrm{d})}}{dt}$$

$$= \left(\frac{1}{r_{\mathrm{Org}\,i}} - \frac{f_{\mathrm{e}i}\left(1 - f_{\mathrm{h}i}\right)}{r_{\mathrm{Bio}}} - \frac{f_{\mathrm{e}i}f_{\mathrm{h}i}}{r_{\mathrm{Hum}}}\right)k_{\mathrm{Org}\,i}C_{\mathrm{Org-C}i}$$
(17)

In case of $r_{\text{Bio}} = r_{\text{Hum}} = r_0$, Eq. (17) can be simplified as

$$\frac{dC_{\mathrm{NH}_{4}i(\mathrm{p})}}{dt} = -\left(\frac{1}{r_{\mathrm{Org}\,i}} - \frac{f_{\mathrm{e}i}}{r_{0}}\right) \frac{dC_{\mathrm{Org-C}i(\mathrm{d})}}{dt}$$

$$= \left(\frac{1}{r_{\mathrm{Org}\,i}} - \frac{f_{\mathrm{e}i}}{r_{0}}\right) k_{\mathrm{Org}\,i} C_{\mathrm{Org-C}i}$$
(18)

When the NH₄-N production rate described with Eq. (17) or (18) is positive, the surplus nitrogen is used for the mineralization of NH₄-N. On the other hand, when the production rate is negative, immobilization of NH₄-N occurs to compensate the nitrogen deficiency (route 7). If f_{ei} and r_0 are constant, the sign of the parenthesis in Eq. (18) simply depends on the $r_{\text{Org }i}$ value. A negative production rate for $r_{\text{Org }i} > r_0 / f_{ei}$ leads to immobilization while a positive production rate for $r_{\text{Org }i}$ $< r_0 / f_{ei}$ results in mineralization. In case $f_{ei} = 0.5$ and $r_0 = 10$, the immobilization occurs for $r_{\text{Org }i} > 20$ while the mineralization for $r_{\text{Org }i} < 20$.

The net reaction rate for each nitrogen component can be described with a mass balance scheme similarly as shown in Figure 1 for the carbon cycle. The net reaction rate for Org-N is the sum of reductions due to ammonium production as given by Eq. (18) and Hum-N production as given by Eq. (16) (routes 6, 7):

$$\frac{dC_{\text{Org-N}i}}{dt} = -\frac{dC_{\text{NH}_{4}(\text{p})}}{dt} - \frac{dC_{\text{Hum-N}(\text{p})}}{dt} = -\left\{\frac{1}{r_{\text{Org}\,i}} - \frac{f_{ei}\left(1 - f_{hi}\right)}{r_{0}}\right\} k_{\text{Org}\,i} C_{\text{Org-C}i}$$
(19)

Notice that Bio-N production does not explicitly appear in Eq. (19) since Bio-N is recycled in the organic pool (route 5). Although a similar expression can be obtained when $r_{\text{Bio}} \neq r_{\text{Hum}}$, for simplicity we assume in the discussion to follow that $r_{\text{Bio}} = r_{\text{Hum}} (= r_0)$.

Hum-N also produces ammonium as a result of first-order degradation (route 8):

$$\frac{dC_{\text{Hum-N(d)}}}{dt} = -k_{\text{Hum-N}}C_{\text{Hum-N}}$$
(20)

The net reaction rate for Hum-N is degradation and production from the organic pools as described with Eq. (16) (route 6):

$$\frac{dC_{\text{Hum-N}}}{dt} = -k_{\text{Hum-N}}C_{\text{Hum-N}} + \frac{1}{r_0}\sum_{i=1}^2 f_{ei}f_{hi}k_{\text{Org}\,i}C_{\text{Org-C}i}$$
(21)

As in the case of carbon, since $k_{\text{Hum-N}} \ll k_{\text{Org}i}$, it is possible to neglect Hum-N degradation as given by Eq. (20) for relatively short time periods.

2.4. Immobilization of Ammonium

If the C/N ratio for organic matter, $r_{\text{Org}i}$, is smaller than r_0/f_{ei} , mineralization of NH₄-N ammonium occurs according to Eq. (18). In that case, the NH₄-N concentration does not affect the degradation rate of organic matter. On the other hand, in case $r_{\text{Org}i}$ is larger than r_0/f_{ei} , the biomass and humus are produced using the immobilized NH₄-N. If the NH₄-N concentration is small enough for immobilization, the decay rate may slow down because of NH₄-N deficiency. According to the LEACHM program (Hutson, 2005), three immobilization stages can be defined depending upon the available amount of NH₄-N.

If the amount of Org-C_i degradation per day according to Eq. (2) is given as $\Delta C_{\text{Org-Ci}}$, the amount of immobilized NH₄-N per day, ΔC_{NH4} , can be related with $\Delta C_{\text{Org-Ci}}$ using Eq. (18):

$$\Delta C_{\rm NH4} = \left(\frac{1}{r_{\rm Org\,i}} - \frac{f_{\rm ei}}{r_{\rm 0}}\right) \Delta C_{\rm Org-Ci}$$
(22)

It is assumed that not more than one tenth of the total NH₄-N concentration including solution and adsorbed phases, C_{NH4} , is available for each organic pool per day. The maximum amount of degradable Org-C_i per day can be defined as:

$$\Delta C_{\text{Org-C}i, \text{Max}} = \frac{C_{\text{NH}_4}}{10} \frac{r_{\text{Org}\,i} r_0}{r_0 - r_{\text{Org}\,i} f_{ei}}$$
(23)

Three immobilization stages can be defined depending on the $\Delta C_{\text{Org-C}i, \text{ max}}$ value:

- Stage 1: $\Delta C_{\text{Org-C}i, \text{ max}} > \Delta C_{\text{Org-C}i}$ Since enough NH₄-N exists, immobilization does not affect the degradation rate of the organic pool.
- Stage 2: $\Delta C_{\text{Org-C}i} > \Delta C_{\text{Org-C}i, \max} > 0.1 \Delta C_{\text{Org-C}i}$ The degradation rate of the organic pool is now reduced by multiplying Eq. (2) with $\Delta C_{\text{Org-C}i, \max} / \Delta C_{\text{Org-C}i}$ because of a deficiency in available NH₄-N. The reduction, however, is not less than 10 %.
- Stage 3: $\Delta C_{\text{Org-C}i, \text{max}} < 0.1 \Delta C_{\text{Org-C}i}$ When the available NH₄-N is further reduced, $\Delta C_{\text{Org-C}i, \text{max}}$ becomes less than $0.1 \Delta C_{\text{Org-C}i}$. In this case, immobilization for biomass and humus production ceases. Degradation of Org-C now only produces CO₂ without biomass and humus production at the 10 % rate of Eq. (2). Degradation of Org-N according to Eq. (14) mineralizes only NH₄-N. Hence, the C/N ratio for the organic pool, r_{Org} , does not change since no immobilization of NH₄-N occurs. When the NH₄-N concentration increases, $\Delta C_{\text{Org-C}i, \text{max}}$ becomes greater than $0.1 \Delta C_{\text{Org-C}i}$. However, the immobilization of Stage 2 starts using the mineralized NH₄-N.

Since $\Delta C_{\text{Org-C}i, \text{max}}$ is defined for each organic pool, the immobilization stage can be different between the organic pools. Although we consider two organic pools as in the case of the LEACHM program, it is straightforward to increase the number of organic pools by simply letting *i* run from 1 to *n* in the summations of the above equations.

2.5. Nitrogen transformation

The inorganic N pools in Figure 1 consist of urea, ammonium and nitrate. The degradation processes of inorganic N are also described using first-order kinetics. Urea fertilizers are rapidly transformed to NH_4 -N in soils:

$$\frac{dC_{\text{Urea}}}{dt} = -k_{\text{Urea}}C_{\text{Urea}}$$
(24)

where k_{Urea} is the ammonification constant. The net reaction rate for NH₄-N is the sum of nitrification (route 10), mineralization from urea (route 9) and humus (route 8), and mineralization or immobilization for biomass and humus production as described with Eq. (18) (route 7):

$$\frac{dC_{\rm NH4}}{dt} = -k_{\rm nit}C_{\rm NH4} + k_{\rm Urea}C_{\rm Urea} + k_{\rm Hum-N}C_{\rm Hum-N} / r_0 + \sum_{i=1}^2 \left(\frac{1}{r_{\rm Org\,i}} - \frac{f_{ei}}{r_0}\right) k_{\rm Org\,i}C_{\rm Org-Ci}$$
(25)

where k_{nit} is the nitrification constant. When the available NH₄-N for immobilization is limited, the last term is modified for Stages 2 and 3 of the immobilization process. The net reaction rate for the nitrate is denitrification and production from NH₄-N:

$$\frac{dC_{\rm NO3}}{dt} = -k_{\rm den}C_{\rm NO3} + k_{\rm nit}C_{\rm NH4}$$
(26)

where k_{den} is the denitrification constant.

2.6. Transport of Ammonium and Nitrate

Transport of nitrogen in soils can be predicted by coupling the first-order kinetic equations for the carbon and nitrogen cycles with the convective-dispersive equation (CDE). The total concentration, C, expressed as solute mass per volume of soil, can be related with the solute concentration, C_l , expressed as solute mass per volume of soil solution, and adsorbed concentration, S, expressed as adsorbed mass per mass of dry soil as follows:

$$C = \theta C_l + \rho_b S \tag{27}$$

where θ is the volumetric water content, and ρ_b is the soil bulk density. Adsorption of urea and ammonium is described with the Freundlich isotherm:

$$S = K_d C_l^n \tag{28}$$

where K_d and *n* are constants. Nitrate is assumed to be a nonreactive solute. The CDE for urea, ammonium, and nitrate are given by:

$$\frac{\partial C_{\text{Uera}}}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_{\text{Uera}} \frac{\partial C_{l,\text{Uera}}}{\partial z} \right) - \frac{\partial q_{\text{w}} C_{l,\text{Uera}}}{\partial z} - k_{\text{Urea}} C_{\text{Uera}}$$
(29)

$$\frac{\partial C_{\rm NH4}}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_{\rm NH4} \frac{\partial C_{l,\rm NH4}}{\partial z} \right) - \frac{\partial q_{\rm w} C_{l,\rm NH4}}{\partial z} - k_{\rm nit} C_{\rm NH4} + k_{\rm Urea} C_{\rm Urea} + k_{\rm Hum-C} C_{\rm Hum-C} / r_0 + \sum_{i=1}^{2} \left(\frac{1}{r_{\rm Org\,i}} - \frac{f_e}{r_0} \right) k_{\rm Org\,i} C_{\rm Org-Ci}$$
(30)

$$\frac{\partial \theta C_{l,\text{NO3}}}{\partial t} = \frac{\partial}{\partial z} \left(\theta D_{\text{NO3}} \frac{\partial C_{l,\text{NO3}}}{\partial z} \right) - \frac{\partial q_w C_{l,\text{NO3}}}{\partial z} + k_{\text{nit}} C_{\text{NH4}} - k_{\text{den}} \theta C_{l,\text{NO3}}$$
(31)

where D is the dispersion coefficient, q_w is the volumetric water flux density, z is the vertical position, and t is time.

The first-order kinetic equations for the carbon and nitrogen cycles can be described with the PHREEQC program, which can be readily implemented into HYDRUS-1D using the HP1 code for solute transport simulations.

3. Examples

We demonstrated the decomposition processes of organic matter and resultant nitrogen transport in soils for transient water flow and nonisothermal conditions. A constant flux of water of 0.5 cm d⁻¹ was applied to the surface of a 100-cm deep silty soil profile having an initial pressure head h_i of -2000 cm. The soil bulk density, ρ_b , is 1.5 g cm⁻³. Constant temperature boundary conditions were applied: 40 °C at the surface and 10 °C at the bottom. Four types of organic matter with different C/N ratios (= 5, 20, 30, and 100) were uniformly applied from the surface to 25 cm depth. The amount of carbon per volume of soil was 0.152 mg cm⁻³, while the carbon content was taken to be the same for each type of organic matter. Linear adsorption was assumed for NH₄-N with $K_d = 2.5$. A negligible amount of NH₄-N initially existed and the initial C_{NH4} was set at 3.9 ×10-5 g kg⁻¹. A single carbon pool (i = 1) was used with $k_{\text{Org}} = 0.04 \text{ d}^{-1}$, $k_{\text{Hum-C}} = k_{\text{Hum-N}} =$ 0.0001 d⁻¹, $f_e = 0.5$, $f_h=0.2$, and $r_0 = 10$. Nitrification was neglected, $k_{\text{nit}} = 0 \text{ d}^{-1}$. Figures 2 and 3 show volumetric water content and temperature profiles during infiltration. Results for low and high C/N rations with mineralization are presented below in sections 3.1 and 3.2, respectively.



Figure 2. Volumetric water content profiles during infiltration into silt with a constant flux of $0.5 \text{ cm } \text{d}^{-1}$.

 $(\overline{\underline{B}})^{-20}_{N} -60_{-80}_{-80}_{-100}_{10}_{10}_{20}_{20}_{20}_{-100}_{-100}_{10}_{10}_{20}_{20}_{30}_{30}_{40}_{40}_{-10$

Figure 3. Temperature profiles during infiltration into silt with boundary conditions of 40 $^{\circ}$ C at the surface and 10 $^{\circ}$ C at the bottom.

3.1. Low C/N Ratio with Mineralization

When the C/N ratio of organic matter is below 20 ($=r_0/f_e$), sufficient N for humus and biomass production results in the mineralization of NH₄-N. Since the NH₄-N concentration did not affect the degradation rate of the organic matter, Org-C concentrations were identical for C/N = 5 and 20 (Fig. 2). Faster degradation near the surface was due to effects of temperature. At 40 days, Org-C and Org-N became almost negligible and the C/N ratio became close to 10 ($=r_0$). Increased mineralization resulted in higher NH₄-N concentrations for C/N = 5.





Figure 2. Organic carbon (Org-C) concentration profiles for C/N = 5 and 20 with mineralization of ammonium.

-10 10 20 20 -20 z (cm) 40 -30 -40 C/N_{Initial}=20 C/N_{Initial}=5 -50 0 10 20 30 10 20 30 C/N (-)

Figure 4. C/N ratio profiles in the organic pool for C/N = 5 and 20 with mineralization of ammonium.

Figure 3. Organic nitrogen (Org-N) concentration profiles for C/N = 5 and 20 with mineralization of ammonium.



Figure 5. Total ammonium (NH₄-N) concentration profiles for O(N) = 5 and 20 with mineralization of ammonium.

3.2. High C/N Ratio with Immobilization

On the other hand, when the C/N ratio of organic matter was above $20 (=r_0/f_e)$, NH₄-N in a soil is immobilized for humus and biomass production. The N deficiency now slowed down the degradation process in that it took more than 200 days until the degradation almost finished for C/N = 100. As shown in Figure 7, C/N became less than 20 near the surface in case of C/N = 30, indicating mineralization started near the surface whereas immobilization continued in the lower part of the soil. Stage 3 immobilization continued for C/N =100. During this stage, very slow degradation at a 90 % reduced rate produced only CO₂ and NH₄-N without biomass and humus production. Stage 2 stated in the lower part of the soil at 100 days because of NH₄-N supply from the upper part of the profile.



Figure 6. Organic carbon (Org-C) concentration profiles for C/N = 30 and 100 with immobilization of ammonium.



Figure 7. Organic nitrogen (Org-N) concentration profiles for C/N = 30 and 100 with immobilization of ammonium.



Figure 8. C/N ratio profiles in the organic pool for C/N = 30 and 100 with immobilization of ammonium.

l0d 1`00 200 C/N_{Initial}=100 $0.0004 \quad 0.0008 \quad 0.0012 \quad 0.0016 \quad 0.0004 \quad 0.0008 \quad 0.0012 \quad 0.0016$

Figure 9. Total ammonium (NH₄-N) concentration profiles for C/N = 30 and 100 with immobilization of ammonium.

4. Conclusions

The carbon and nitrogen cycling model used in the LEACHM code was reformulated using the PHREEQC program and linked with HYDRUS-1D using the HP1 code. We confirmed that the HP1 code could accurately calculate carbon and nitrogen cycles and various nitrogen transport scenarios as a result of the application of organic matter to a variably-saturated soil profile under nonisothermal conditions. We further showed that coupled carbon and nitrogen cycling is especially important when organic matter with a high C/N ratio is applied to a soil. Although we only showed results for a single organic pool, it is possible to demonstrate various interactions between the different organic matter pools. We are planning to extend the program to include multiple organic pools, passive and active root uptake, CO₂ diffusion in the gas phase, cation and

anion exchange for ammonium and nitrate, and several other chemical reactions judged to be important.

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