12 Nitrification and denitrification module NITDEN

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12.1 Introduction

A subroutine has been added to FUSSIM2 that simulates NITrification and DENitrification (NITDEN). This subroutine was used to simulate the dynamics in conversion and production rates of ammonium and nitrate in the soil and the gaseous losses of N_2 and N_2O due to denitrification from grassland. Most of the underlying equations have been taken from Bril *et al.* (1994). Below the relevant aspects will be briefly described. The reader is referred to chapter 15 '*User's Guide*' to see the structure of the input file and some typical values and ranges for values of the parameters used below.

12.2 Nitrification

The conversion of ammonium through nitrification is given by

$$\frac{\mathrm{dNH}_4^+}{\mathrm{d}t} = f_{W,1} f_{T,1} f_{pH,1} f_{CEC} \frac{\mathrm{NH}_4^+}{n_1 + \left(\frac{10^3\,\mathrm{NH}_4^+}{14 M_{ws}} \right)^2} \qquad (12\text{-}1)$$

where

NH_4^+	ammonium concentration	mg cm^{-3} (soil)
t	time	d
M_{ws}	mass of wet soil	g cm^{-3} (soil)
14	molar mass of nitrogen	g mol^{-1}
10^3	conversion factor	g kg^{-1}
n_1	parameter used to calculate a multiplication factor which represents the effect of the NH_4 concentration in the soil on nitrification rate	$mmol^2$ kg^{-2} (wet soil)

The functional relationships f are explained below. The effect of soil water content via water filled pore space *WFPS* (-) on nitrification is given by the functional relationship $f_{W,1}$

$$f_{W,1} = \mathrm{MAX}\left[0, \left(\sin\left(p\, WFPS^{n_2} \right) \right)^{n_3} \right] \qquad (12\text{-}2)$$

where

n_2	curve shape parameter for the effect of water filled pore space on nitrification rate that determines the value of the optimum *WFPS*, where $f_{W,1} = 1$	-
n_3	curve shape parameter for the effect of water filled pore space on nitrification rate that determines the area underneath the optimum curve	-

The effect of soil temperature T (^{0}C) on nitrification is given by the functional relationship $f_{T,1}$

$$f_{T,1} = \begin{cases} 0 & T < 0 \\ \dfrac{n_4 T^{n_5}}{1 + n_6 T^{n_7}} & T \geq 0 \end{cases} \qquad (12\text{-}3)$$

where

$n_{4,5,6,7}$	curve shape parameters	-

The effect of soil pH on nitrification is given by the functional relationship $f_{pH,1}$

$$f_{pH,1} = \frac{1}{1 + n_8 10^{-pH}} \qquad (12\text{-}4)$$

where

n_8	curve shape parameter for the effect of pH on nitrification rate, that determines the value of the pH, where $f_{pH,1} = 0.5$	-

The effect of cation exchange capacity of the soil *CEC* (cmol$^+$ kg^{-1}) on nitrification is given by the functional relationship f_{CEC}

$$f_{CEC} = n_9 - n_{10} \log(CEC) \qquad (12\text{-}5)$$

where

n_9	intercept of relationship between f_{CEC} and log (*CEC*)	mmol^2 kg^{-2} (wet soil) d^{-1}
n_{10}	slope of relationship between f_{CEC} and log (*CEC*)	mmol^2 kg^{-2} (wet soil) d^{-1}

Nitrification of ammonium produces not only NO_3, but also N_2O. This has been modeled by using a dimensionless partitioning factor PF_1, which is described as a function of soil *WFPS*:

$$PF_1 = \begin{cases} n_{11} & WFPS < n_{13} \\ n_{11} + n_{12}\left(\dfrac{WFPS - n_{13}}{1 - n_{13}}\right)^{n_{14}} & WFPS \geq n_{13} \end{cases} \qquad (12\text{-}6)$$

where

n_{11}	minimum fraction of total nitrification that is converted into N_2O	-
n_{12}	maximum fraction of total nitrification that is converted into N_2O	-
n_{13}	*WFPS* threshold value below which the effect of *WFPS* on N_2O production from nitrification equals zero	-
n_{14}	curve shape parameter that determines the steepness of the curve relating the fraction converted into N_2O to *WFPS*	-

PF_1 gives the part of the total nitrification of equation 12-1 that is converted into N_2O. The production of NO_3 from nitrification is then given by the product of total nitrification and $(1 - PF_1)$.

In the above equations M_{ws}, *WFPS* and T are dynamically computed by FUSSIM2. *pH*, *CEC* and n_1 through n_{14} are all assumed constant and taken from the input file.

12.3 Denitrification

Decay of organic matter in the soil by aerobic micro-organisms requires oxygen. At low O_2 levels in the soil, the oxygen can also be provided by NO_3 and N_2O. In this process electrons are transferred from the organic matter to NO_3 and N_2O. NO_3 is then denitrified to N_2O and N_2O is denitrified to N_2. Total denitrification, expressed as total electron production accepted by either NO_3 or N_2O, is given by

$$\frac{\mathrm{d}e_\mathrm{p}}{\mathrm{d}t} = f_{W,2}\, f_{T,2} DPR \frac{\left(0.8\frac{\mathrm{NO_3^-}}{14M_{ws}} + 0.4\frac{\mathrm{N_2O}}{28M_{ws}}\right)}{d_1 + \left(0.8\frac{\mathrm{NO_3^-}}{14M_{ws}} + 0.4\frac{\mathrm{N_2O}}{28M_{ws}}\right)} \qquad (12\text{-}7)$$

where

e_p	electrons produced	mmol electron cm^{-3} (soil) d^{-1}
NO_3^-	nitrate concentration	mg cm^{-3} (soil)
N_2O	total nitrous oxide concentration	mg cm^{-3} (soil)
DPR	potential denitrification rate of the soil	mmol electron cm^{-3} (soil) d^{-1}
14	molar mass of N	g mol^{-1}
28	= 2 * 14	g mol^{-1}
0.4	electron equivalent ratio of N_2O	-
0.8	electron equivalent ratio of NO_3	-
d_1	amount of source in terms of both NO_3 and N_2O corrected for their electron-equivalents, at which the denitrification rate equals half its maximum rate at optimal conditions for denitrification (the half-value constant in a Monod function)	mol N kg^{-1} (wet soil)

DPR is defined as the maximum denitrification at a reference temperature of 20 ^{0}C in the absence of O_2 and unlimited supply of NO_3. It is thus strongly related to the decomposition rate of organic matter in the soil. Via a small adaptation of NITDEN CO_2 production from a module that simulates organic matter decay can be used instead of *DPR*. The dynamics in the soil organic matter, e.g. by using organic fertilizers, then also determines the denitrification rates.

The effect of soil water content via water filled pore space *WFPS* (-) on total denitrification is given by the functional relationship $f_{W,2}$

$$f_{W,2} = \begin{cases} 0 & WFPS < d_2 \\ \left(\dfrac{WFPS - d_2}{1 - d_2}\right)^{d_3} & WFPS \geq d_2 \end{cases} \tag{12-8}$$

where

d_2	*WFPS* threshold value below which the denitrification rate equals zero	-
d_3	curve shape parameter that determines the steepness of the curve for the effect of *WFPS* on denitrification rate	-

The effect of soil temperature *T* (^{0}C) on total denitrification is given by the functional relationship $f_{T,2}$

$$f_{T,2} = \begin{cases} 0 & T < 0 \\ \dfrac{d_4 T^{d_5}}{\left(1 + d_6 T^{d_7}\right) f_{T=20,2}} & T \geq 0 \end{cases} \tag{12-9}$$

where

$d_{4,5,6,7}$	curve shape parameters	-

In the denitrifcation process NO_3 and N_2O compete for the electrons produced during decay of organic matter. Reduction of NO_3 is given by

$$\frac{dNO_3^-}{dt} = \frac{NO_3^-}{\left(\dfrac{4NO_3^-}{14} + \dfrac{2N_2O}{28} d_8 f_{pH,2}\right)} \frac{de_p}{dt} \tag{12-10}$$

where

2	electron equivalent ratio of N_2O	-
4	electron equivalent ratio of NO_3	-
d_8	parameter that accounts for the sink strength of N_2O in consuming electrons relative to that of NO_3	-

and reduction of N_2O is given by

$$\left(\frac{\mathrm{dN_2O}}{\mathrm{d}t}\right)_R = \frac{\mathrm{N_2O}\, d_8\, f_{pH,2}}{\left(\frac{4\mathrm{NO_3^-}}{14} + \frac{2\mathrm{N_2O}}{28} d_8\, f_{pH,2}\right)} \frac{\mathrm{de_p}}{\mathrm{d}t} \qquad (12\text{-}11)$$

The effect of soil pH on reduction of NO_3 and N_2O is given by the functional relationship $f_{pH,2}$

$$f_{pH,2} = MAX\left[d_{11}, 10^{\frac{pH - d_9}{d_{10}}}\right] \qquad (12\text{-}12)$$

where

d_9	pH value at which the factor for the sink strength of N_2O in consuming electrons relative to that of NO_3 equals d_8	-
d_{10}	curve shape parameter	-
d_{11}	minimum value for the multiplication factor for the effect of pH on the sink strength of N_2O in consuming electrons relative to that of NO_3	-

The N_2O production from denitrification of NO_3 is given by $\mathrm{dNO_3}/\mathrm{d}t$ and the N_2 production equals $(\mathrm{dN_2O}/\mathrm{d}t)_R$.

In the above equations M_{ws}, $WFPS$ and T are used as in the equations for nitrification. DPR, pH and d_1 through d_{11} are all assumed constant and taken from the input file.

12.4 N2O emission

As gas transport is not modelled, emission of N_2O from the soil surface towards the atmosphere is estimated as follows

$$\left(\frac{\mathrm{dN_2O}}{\mathrm{d}t}\right)_E = EF\left(\frac{\left(1 - WFPS^{e_1}\right)}{f_a}\mathrm{N_2O} - \mathrm{N_2O}_{air}\right) \qquad (12\text{-}13)$$

where

N_2O_{air}	N_2O concentration of the atmosphere	mg cm^3 (air)
f_a	volumetric gas content	cm^3 cm^{-3} (soil)
e_1	parameter used in calculating the N_2O concentration in soil air by partitioning of total N_2O between soil water and soil air as a function of water filled pore space	-

No intrusion from atmosphere to the soil has been considered in NITDEN. The emission factor EF (d^{-1}) is given by a sigmoidal function

$$EF = \frac{e_4}{1 + \left(\dfrac{WFPS}{e_2} \right)^{e_3}} \tag{12-14}$$

where

e_2	$WFPS$ at which EF equals half of its maximum value e_4	-
e_3	curve shape parameter for the function relating EF to $WFPS$	-
e_4	maximum fraction of the difference in N_2O concentration between soil air and atmosphere that leaves the soil as N_2O emission at $WFPS = 0$	d^{-1}

f_a and $WFPS$ are dynamically computed by FUSSIM2. N_2O_{air} and e_1 through e_4 are all assumed constant and taken from the input file.

12.5 N₂O dynamics in the soil

The governing N_2O equation describes the net N_2O rate of change in the soil as the sum of two N_2O production processes minus the sum of two N_2O consumption processes. The production processes are nitrification of NH_4 to N_2O and reduction of NO_3 to N_2O, and the two consumption processes are N_2O reduction to N_2 and N_2O emission. The governing equation reads

$$\underbrace{\frac{\mathrm{dN_2O}}{\mathrm{d}t}}_{\text{net N}_2\text{O production}} = \underbrace{PF_1 \frac{\mathrm{dNH_4^+}}{\mathrm{d}t}}_{\text{nitrification}} + \underbrace{\frac{\mathrm{dNO_3^-}}{\mathrm{d}t}}_{\text{NO}_3\text{ reduction}} - \underbrace{\left(\frac{\mathrm{dN_2O}}{\mathrm{d}t} \right)_R}_{\text{N}_2\text{O reduction}} - \underbrace{\left(\frac{\mathrm{dN_2O}}{\mathrm{d}t} \right)_E}_{\text{N}_2\text{O emission}} \tag{12-15}$$

12.6 Numerical solution

Equation (12-15) is solved numerically using a semi-implicit Euler scheme. Our experience is that using explicit Euler resulted in very small time-step requirements. The semi-implicit Euler scheme reads (Press *et al*, 1992; their Eq. (16.6.17))

$$y^{t+\Delta t} = y^t + \frac{\Delta t \dfrac{\mathrm{d}y^t}{\mathrm{d}t}}{1 - \Delta t \dfrac{\mathrm{d}y^t / \mathrm{d}t}{\mathrm{d}y^t}} \tag{12-16}$$

The derivative $\mathrm{d}y/\mathrm{d}t$ is computed according to Eqs. (12-1)-(12-15), where y represents the N_2O concentration in the soil. The derivative of $\mathrm{d}y/\mathrm{d}t$ to y is numerically estimated by computing $\mathrm{d}y/\mathrm{d}t$ for two values of N_2O, one somewhat less than current N_2O and one somewhat larger than current N_2O:

$$\frac{\mathrm{d}y^t/\mathrm{d}t}{\mathrm{d}y^t} = \frac{\left(\mathrm{d}y/\mathrm{d}t\right)\Big|_{N_2O(1+\alpha)} - \left(\mathrm{d}y/\mathrm{d}t\right)\Big|_{N_2O(1-\alpha)}}{2\alpha N_2O} \tag{12-17}$$

A typical value for α equals 0.01.

12.7 The input file NITDENIN.DAT

In chapter 15 (section 15.4.17) an example of the input file NITDENIN.DAT is presented. Here we indicate which parameter of the Eqs. (12-1) through (12-14) corresponds to which variable in this file (Table 12-1).

Table 12-1 Correspondence between variables used in text and the parameter names as occurring in the data file NITDENIN.DAT. For completeness, the units of the variables are given as well.

Variable in text	Name in NITDENIN.DAT	Units	Variable in text	Name in NITDENIN.DAT	Units
n_1	NitSourceParam1	$\mathrm{mmol^2\ kg^{-2}}$ (wet soil)	d_1	DenSourceParam1	$\mathrm{mol\ kg^{-1}}$ (wet soil)
n_2	NitWaterParam1	-	d_2	DenWaterParam1	-
n_3	NitWaterParam2	-	d_3	DenWaterParam2	-
n_4	NitTempParam1	-	d_4	DenTempParam1	-
n_5	NitTempParam2	-	d_5	DenTempParam2	-
n_6	NitTempParam3	-	d_6	DenTempParam3	-
n_7	NitTempParam4	-	d_7	DenTempParam4	-
n_8	NitpHParam1	-	d_8	DenElectrParam1	-
n_9	NitCECParam1	$\mathrm{mmol^2\ kg^{-2}}$ (wet soil) $\mathrm{d^{-1}}$	d_9	DenpHParam1	-
n_{10}	NitCECParam2	$\mathrm{mmol^2\ kg^{-2}}$ (wet soil) $\mathrm{d^{-1}}$	d_{10}	DenpHParam2	-
n_{11}	NitPartParam1	-	d_{11}	DenpHParam3	-
n_{12}	NitPartParam2	-	e_1	DenEmisParam4	-
n_{13}	NitPartParam3	-	e_2	DenEmisParam1	-
n_{14}	NitPartParam4	-	e_3	DenEmisParam2	-
			e_4	DenEmisParam3	$\mathrm{d^{-1}}$

12.8 Acknowledgements

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12.9 References

Bril J., H.G. van Faassen and H.Klein Gunnewiek, 1994. Modelling N_2O emission from grazed grassland. Report 24, DLO Research Institute for Agrobiology and Soil Fertility, Haren, The Netherlands, 45 p.

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