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A Model of Nitrous Oxide Evolution From Soil Driven by Rainfall Events: 1. Model Structure and Sensitivity

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This paper describes a rain-event driven, process-oriented simulation model, DNDC, for the evolution of nitrous oxide (N_2O), carbon dioxide (CO_2), and dinitrogen (N_2) from agricultural soils. The model consists of three submodels: thermal-hydraulic, decomposition, and denitrification. Basic climate data drive the model to produce dynamic soil temperature and moisture profiles and shifts of aerobic-anaerobic conditions. Additional input data include soil texture and biochemical properties as well as agricultural practices. Between rainfall events the decomposition of organic matter and other oxidation reactions (including nitrification) dominate, and the levels of total organic carbon, soluble carbon, and nitrate change continuously. During rainfall events, denitrification dominates and produces N_2O and N_2. Daily emissions of N_2O and N_2 are computed during each rainfall event and cumulative emissions of the gases are determined by including nitrification N_2O emissions as well. Sensitivity analyses reveal that rainfall patterns strongly influence N_2O emissions from soils but that soluble carbon and nitrate can be limiting factors for N_2O evolution during denitrification. During a year sensitivity simulation, variations in temperature, precipitation, organic C, clay content, and pH had significant effects on denitrification rates and N_2O emissions. The responses of DNDC to changes of external parameters are consistent with field and experimental results reported in the literature.

1. INTRODUCTION

This paper reports the structure of a computer model for assessing nitrous oxide (N_2O) emissions from agricultural soils. The current atmospheric N_2O concentration is about 8% greater than in the preindustrial era and is increasing at a rate of about 0.8 ppb (0.25%) per year [*Weiss*, 1981; *Elkins and Rossen*, 1989]. Ice core measurements indicate that the concentration of atmospheric N_2O started to increase around the period 1700-1800 [*Pearman et al.*, 1986; *Khalil and Rasmussen*, 1988; *Etheridge et al.*, 1988], with a rapid concentration increase beginning about 1950 [*Intergovernmental Panel on Climate Change (IPCC)*, 1990].

Nitrous oxide is a nonreactive, long-lived, radiatively active trace gas in the troposphere. Currently, N_2O contributes approximately 5% of the global warming potential in greenhouse effect assessments [*Rodhe*, 1990]. The major sink for N_2O is photolysis in the stratosphere, leading to nitrogen oxide products which influence levels of stratospheric ozone [*Crutzen*, 1970]. Because of these important links to both climate and atmospheric chemistry the causes for the increasing atmospheric N_2O concentration are of great interest. International discussions are already in progress to develop approaches for regulating the sources of N_2O. Unfortunately, the large uncertainties present in estimates of sources of N_2O preclude the development of any detailed strategies for their mitigation.

A recent assessment of N_2O sources by the IPCC indicates that soils and agriculture fertilizers are important sources of N_2O [*IPCC*, 1990]. Nitrous oxide is primarily derived as an intermediate product of microbial denitrification and nitrification processes in soils (for reviews see *Delwiche* [1981]; *Sahrawat and Keeney* [1986]; *Seiler and Conrad* [1987]). While many laboratory and field investigations of N_2O production rates by soil microbes have been conducted, quantification of global N_2O emissions from soils has proven extremely difficult because of the heterogeneity of soil chemical, physical, and biological properties which interact to determine production and emission rates. In particular, variations in soil moisture, soil texture, and carbon and nitrogen substrates for microbial nitrification and denitrification are critical to determining N_2O emissions [e.g., *Leffelaar and Wessel*, 1988; *Tanji*, 1982; *Frissel and Van Veen*, 1981; *Batlach and Tiedje*, 1981; *Cho et al.*, 1979].

Numerous simulation models have been developed to estimate denitrification rates and processes in soils (Table 1). The early models [e.g., *Focht*, 1974; *Mehran and Tanji*, 1974] were studies of denitrification kinetics at the laboratory-incubation scale. Several of the more recent models [e.g., *Grant*, 1991; *Johnsson et al.*, 1991; *Clay et al.*, 1985; and *Molina et al.*, 1983] were designed to predict total N losses from soils on field scales, but not specifically N_2O fluxes to the atmosphere, and thus model only total denitrification ($N_2O + N_2$) in combination with various decomposition processes. Others, which focus more closely on N_2O by modeling the various steps of denitrification and microscopic processes such as substrate diffusion [e.g., *Leffelaar and Wessel*, 1988; *McConnaughey and Bouldin*, 1985], do not incorporate field scale variables such as temperature, moisture, and carbon substrate availability. *Van Veen and Frissel* [1979] model both decomposition and denitrification processes, substrate diffusion and availability,

TABLE 1. Denitrification/Decomposition Models

Reference	Model description
Focht [1974]	Denitrification kinetics independent of nitrate concentration, linear function of pH and oxygen status, exponential function of temperature. $N_2O:N_2$ ratio depends only on aeration and pH.
Mehran and Tanji [1974]	All nitrogen transformations (nitrification, denitrification, mineralization, immobilization, N plant uptake, and NH_4^+ exchange) are calculated for a single pool of each N species by first-order kinetics. No treatment of decomposition and carbon substrates.
Van Veen and Frissel [1979]	Microorganisms are central to the dynamics of N (nitrification, denitrification, mineralization and immobilization); C and N cycling are interdependent. Decay of various C and N pools by first-order or Monod kinetics; multiplicative reduction factors are used to reduce reaction rates under suboptimal environments. Denitrification model considers diffusion of O_2 and NO_3^- away from air-filled pores; only considers total denitrification.
Molina et al. [1983] and *Clay et al.* [1985]	Computes short-term dynamics of decomposition of residues and two soil carbon pools, each containing a labile and resistant component. N availability, which limits decomposition rates, results from the processes of residue decomposition, mineralization, immobilization, nitrification, and denitrification. Total denitrification fixed at a constant fraction of decomposition. Clay et al. model couples this with layered soil, soil temperature and water flow, plant growth, and tillage for field simulations.
McConnaughey and Bouldin [1985]	Model of saturated soil. Anaerobic volume and transient solute diffusion to and away from zones of N reduction are modeled. The model considers the reduction sequence: NO_3^- → NO_2^- → N_2O → N_2; transient diffusion of NO_3^-, NO_2^-, N_2O, and N_2 allowed throughout the saturated soil, while reduction of the nitrogenous species occurs only in the anaerobic region. No treatment of carbon substrate limitations.
Mosier and Parton [1985] and *Parton et al.* [1988]	Nitrification and denitrification of urea-treated and control shortgrass-prairie soils. Nitrous oxide production controlled by soil temperature, moisture, ammonium and nitrate levels.
Leffelaar and Wessel [1988]	Microbial respiration and denitrification are described for a homogeneous soil layer, in which no transport processes occur. Major processes are growth and maintenance of denitrifier biomass and reduction of NO_3^- to N_2, via NO_2^- and N_2O. Growth of biomass is calculated by a first-order rate equation in which the relative growth rate is described by a double Monod equation consisting of rate-limiting factors for C and nitrogenous substrates. The Pirt equation is used to calculate the consumption rates of substrates.
Grant [1991]	Total denitrification ($N_2O + N_2$) for agroecosystems. Couples detailed treatment of oxygen and substrate diffusion to anaerobic microsites with layered soil model of C and N dynamics in decomposition (first-order kinetics). Denitrification is controlled by temperature and oxygen concentration.
Johnsson et al. [1991]	Field scale model of total denitrification ($N_2O + N_2$), a function of potential rate, soil temperature, soil oxygen status, and nitrate availability. Potential rate, a function of soil type and cropping system. Dynamic soil temperature and moisture determined from soil type and surface. Carbon substrate assumed unlimiting.
This model	Field scale model of decomposition and denitrification, as controlled by soil climate. Daily decomposition of several soil carbon pools by first-order kinetics; rain-event-driven denitrification via growth and maintenance of individual denitrifiers. Agricultural practices, soil properties, and climate control the model. No diffusion of substrates but macroscopic flow with soil water.

and various inorganic N transformations but do not treat denitrification with enough detail to separate N_2O from N_2 production. The model of *Parton et al.*, [1988; also see *Mosier and Parton*, 1985] focuses on the relative importance of denitrification and nitrification to N_2O fluxes in grasslands and takes into account daily to seasonal variations in soil conditions but does not contain enough detail concerning substrate dynamics to be easily generalizable to a variety of agricultural ecosystems. None of these models are able to predict daily or seasonal N_2O emissions from field soils using readily available input data. In particular, none of these models can be used to study the impacts of various agricultural practices on nitrous oxide emissions.

To better understand and quantify soil sources of N_2O, we have developed a model that couples decomposition and denitrification processes, as influenced by the soil environment, to predict emissions from agricultural soils (Figure 1). The model runs on a personal computer and uses commonly available climate, soil, and agricultural practice

data as input. Our model is directed to two applications: (1) investigation of the interactions of fundamental climatic, pedologic, agronomic, and microbiological variables which influence the production and emission of nitrous oxide from agricultural soils and (2) development of an improved quantitative assessment of the large-scale emissions of nitrous oxide from agroecosystems in the United States and globally.

2. MODEL

2.1. Model Framework

Emissions of nitrous oxide and dinitrogen (N_2) from soils are not temporally continuous. On the basis of field monitoring and experimentation, pulses of N_2O and N_2 from soils are observed to follow rainfall or irrigation events [*Roulier and Fetter*, 1973; *Duxbury and McConnaughey*, 1986; *Mosier et al.*, 1986; *Sexstone et al.*, 1985; *Goodroad*
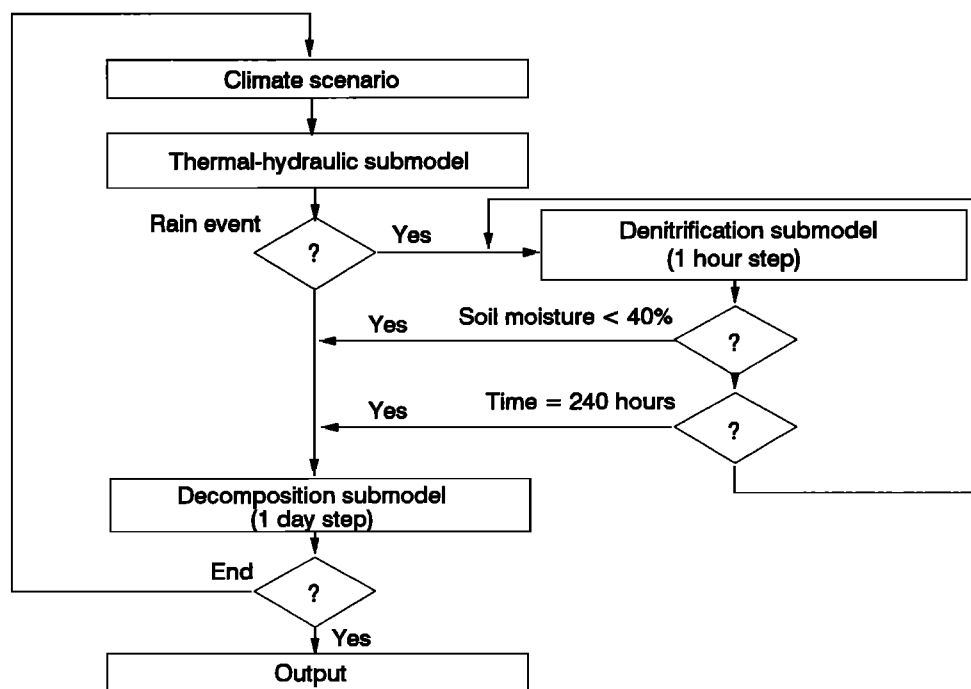
Fig. 1. Structure of DNDC model. Flow chart showing the relationship of the three submodels of thermal-hydraulic flow, decomposition, and denitrification. The thermal-hydraulic flow submodel reads daily climate data from an existing climate scenario file and calculates temperature and moisture profiles. The denitrification model starts with a rain event and continues until the soil moisture (water-filled porosity) decreases to 40%. The decomposition submodel runs continuously.

and Keeney, 1984]. The connection between emissions of N₂O and N₂ and rain events can be explained primarily through the biochemical processes related to microbial activities in soils.

Denitrification occurs under oxygen-deficient conditions (e.g., in wet soils following rain events), when denitrifying bacteria utilize nitrate (rather than oxygen) as an electron acceptor [e.g., *Knowles*, 1981; *Sahrawat and Keeney*, 1986; *Davidson*, 1991]. Dissolved carbon compounds (referred to below as soluble carbon) in the soil solution are the major electron donors during denitrification as carbon is converted to CO₂. Under oxic conditions, these denitrifying bacteria along with many other bacteria decompose organic residues and microbial biomass to produce soluble carbon compounds and ammonium. These two processes along with ammonia volatilization, nitrification, adsorption, and plant uptake interact to control the substrate pools for microbial activity and gaseous emissions of N₂O, N₂, and CO₂.

Because of the substantial difference in N₂O emissions between wet and dry soils, a season or year can be modeled effectively as a sequence of wet and dry periods. Soil temperature and moisture are two key factors controlling the rates of both decomposition and denitrification during these periods. Soil thermal-hydraulic flux, aerobic decomposition, and denitrification submodels of DNDC (DeNitrification and DeComposition) work together in simulating N₂O and N₂ emissions with a 1-day time step (1 hour during rain events) (Figure 1). In addition, the model calculates concentrations of nitrate, nitrite, ammonium, organic residues, microbial biomass, humads, and soluble carbon in the soil profile, as well as mineralization rates of C and N, nitrate leaching, and emissions of carbon dioxide and ammonia from the soil.

Model equations and parameters are presented in the appendices.

2.2. Submodel of Thermal-Hydraulic Flows

A one-dimensional soil heat flux and moisture flow model (Figure 2) has been designed to calculate average hourly and daily soil temperature and moisture profiles. The modeled soil is divided into a series of horizontal layers. Each layer is assumed to have a uniform temperature and moisture content, assigned to a point at the middle of the layer. For each time step, water fluxes and heat flows between layers are determined by the gradients of soil water potential and soil temperature, respectively. All values are determined per unit area in the horizontal plane. These gradient-driven equations are numerically modeled by explicit finite difference equations (see Table 2 for thermal-hydraulic model equations). Typical vertical spatial resolution is 5 cm and time steps are generally about 30 min. Rainwater is added or evapotranspired water removed at the beginning of each time step, before gradient-driven fluxes are determined. Water flow out of the bottom of the modeled profile (typically 50 cm deep) is driven by gravity drainage only [*Van Bavel and Lascano*, 1980]. Heat flux into/out of the bottom layer is determined by the gradient between the bottom layer temperature and the annual mean air temperature imposed at 500 cm depth. To run the simulation with a minimum amount of meteorological input data, the heat flux at the soil surface is simplified to a gradient driven flux between the soil surface, which is assigned a temperature equal to the mean daily air temperature, and the top soil layer temperature at a depth of several centimeters.

Data from climate scenario

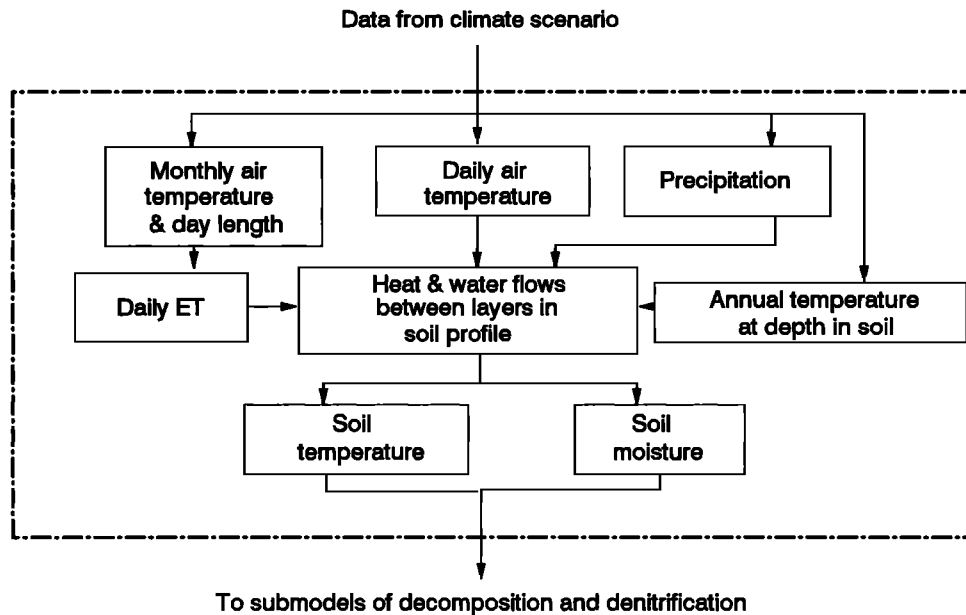To submodels of decomposition and denitrification

Fig. 2. The one-dimensional thermal-hydraulic submodel simulates soil heat flux and moisture flow and calculates hourly and daily average soil temperature and moisture profiles. The heat fluxes and moisture flows are driven by diffusion gradients (and gravity for water flow) for a layered soil profile. Soil texture controls soil hydraulic properties.

The moisture boundary condition at the soil surface has precipitation/irrigation and evapotranspiration components. Precipitation (or irrigation) events are prescribed input events. Since the goal of the DNDC model is to predict seasonal or annual N₂O emissions, the precise timing of precipitation events is not important. We assume that all rain events start at midnight, are of constant intensity (throughout an individual storm but potentially varying intensity from one storm to the next), and of variable duration. At the beginning of each time step, the rainfall for that time step

saturates the soil, layer by layer, to the depth that it can fill. Any residual rainwater (not needed to fill a layer) is uniformly distributed in the next deeper layer. At present we assume there is no surface runoff, and although evaporation of intercepted water can account for a significant fraction of rainwater, particularly for vegetation with a thick canopy [*Bras*, 1990], we do not model intercepted water.

Evapotranspiration (ET) is calculated as monthly average values using the Thornthwaite formula, in which potential ET is determined by monthly mean air temperature and then adjusted for daylight length relative to 12 hours [*Dunne and Leopold*, 1978]. If soil moisture is limiting then actual ET is less than potential ET. We follow *Sellers* [1965] in having actual ET decrease linearly from potential ET to zero as the soil water potential drops from -0.033 MPa (field capacity) to -1.5 MPa (wilting point). DNDC assumes that ET

TABLE. 2. Thermal-Hydraulic Submodel Equations

Equation	Description
$Q_{i,i+1} = -K_{i,i+1} \cdot (h_i - h_{i+1})/(z_i - z_{i+1})$	Soil water flow (layer i-1 → layer i)
$Q_b = f \cdot K_{bl}$	Soil water flow at bottom of profile
$h_i = \phi_i - z_i$	
$\phi = \phi_{sat} \cdot (\Theta_i)^{-\beta}$, if $\Theta < W_a$	Water retention relation
$\phi = -m_1 \cdot (W_a - m_2)(W_a - 1)$, if $\Theta \geq W_a$	
$q_{i,i+1} = -k_{i,i+1} \cdot (T_i - T_{i+1})/(z_i - z_{i+1})$	Soil heat flux (layer i-1 → layer i)
$q_b = k_{bl} \cdot (T_{bl} - T_{annua})/(z_{bl} - z_{deep})$	Soil heat flux at bottom of profile
$q_s = -k_1 \cdot (T_1 - T_{air})/(z_1 - 0)$	Soil heat flux at surface
$K/K_{sat} = \Theta^{(2\beta + 3)}$	Soil relative hydraulic conductivity
$k_i = (1 - n) \cdot k_{dry} + n \cdot \Theta_i \cdot k_{water}$	Soil thermal conductivity
$k_i = (1 - n) \cdot k_{om} + n \cdot \Theta_i \cdot k_{water}$	
$d\Theta_i = dt \cdot (Q_{i,i+1} - Q_{i+1,i})/(n \cdot l_i)$	Water conservation
$dT_i = dt \cdot (q_{i,i+1} - q_{i+1,i})/(C_i \cdot l_i)$	Energy conservation
$C_i = (r_{soil} \cdot c_{soil}) +$	Soil layer volumetric heat capacity
$\quad (n \cdot q_i \cdot r_{water} \cdot c_{water})$	
$E_0 = DAY_i (1.6/NM) \cdot$	Potential evapotranspiration
$\quad (10 \cdot T_a^*/I)^a$	
$E_0 = 0$, if $T_a^* \leq 0°C$	
$E = E_0$, if $\Theta > \Theta_{fc}$	Reduction of ET due to soil moisture
$E = E_0 \cdot (\Theta - \Theta_{wp})/(\Theta_{fc} - \Theta_{wp})$,	
$\quad$ if $\Theta_{fc} > \Theta > \Theta_{wp}$	
$E = 0$, if $\Theta < \Theta_{wp}$	

TABLE 3. Soil Type and Properties

Soil Type	Clay %	n %	K_{sat} cm/min	β	ϕ_{sat} cm	Θ_{fc} %	Θ_{wp} %	c J/kgK
Sand	3	39.5	1.056	4.05	3.50	32	12	2000
Loamy sand	6	41.0	0.938	4.38	1.78	30	12	2000
Sandy loam	9	43.5	0.208	4.90	7.18	45	21	2000
Silty loam	14	48.5	0.043	5.30	56.6	46	34	2000
Loam	19	45.1	0.042	5.39	14.6	55	27	2000
Snd cl loam	28	42.0	0.038	7.12	8.63	59	35	2000
Slt cl loam	34	47.7	0.010	7.75	14.6	66	40	2000
Clay loam	34	47.6	0.015	8.52	36.1	76	49	2000
Sandy clay	43	42.6	0.013	10.4	6.16	68	47	2000
Silty clay	49	49.2	0.006	10.4	17.4	75	52	2000
Clay	63	48.2	0.008	11.4	18.6	77	55	2000
Organic	6	80.0	0.010	7.75	14.6	66	40	2500

See notation section for definitions of variables. Source: Specific heats (c), *de Vries* [1975]. Θ_{fc} and Θ_{wp} calculated (see text). All other values, *Clapp and Hornberger* [1978]. Note: K_{sat} and β values for organic soil are not reported by *Clapp and Hornberger* [1978]; we chose the values for silty clay loam.

removes water from the top 20 cm of the soil; root density is assumed uniform over the top 20 cm, and root growth dynamics are modeled. For each layer, actual ET withdrawal depends on that layer's water content.

DNDC characterizes soil physical properties by soil texture (see Table 3 for soil parameters), following the work of *Clapp and Hornberger* [1978]. The soil thermal conductivity depends on soil water content and on the type of soil (mineral or organic). The soil layer net thermal conductivity for a given moisture content is an average of the thermal conductivities of the solid phase and water, weighted by their relative volumes in the soil.

Soil water tension and unsaturated hydraulic conductivity are strong functions of the soil water content. For each of these, DNDC uses the exponential formulation of *Clapp and Hornberger* [1978], with representative parameters for each of 12 soil textures.

2.3. Submodel of Decomposition

When soil is in an aerobic state, decomposition and other oxidation reactions, including nitrification, are the dominant microbial processes. Assimilation of inorganic carbon and nitrogen into microbial biomass also occurs with the decomposition of residues, microbial biomass and humads (materials partially stabilized by humification and adsorption, *McGill et al.*, [1981]). During decomposition and assimilation, organic C, soluble C, ammonium, and nitrate are produced and may accumulate. The levels of these substrates depend on the balance between the rates of mineralization (transformation of organic C or N to inorganic

C or N), assimilation, and loss (plant uptake, sorption, or volatilization).

The decomposition submodel follows that of *Molina et al.*, [1983], with three active carbon pools for the decomposition sequence (Figure 3). The soil profile is divided into horizontal layers with a typical thickness of 2 cm. Each layer is assumed to have uniform properties (temperature, moisture, substrate and microbe concentrations, etc.) and all decomposition calculations are performed layer by layer. The decomposition submodel runs in a daily time step for every day of the simulation. When a rain event occurs, the decomposition submodel pauses, and the denitrification submodel runs until the top 20 cm of the soil has an average water content of less than 40% of porosity [*Bremner and Shaw*, 1958a, b; *Nommik*, 1956], or for a maximum of 10 days by which time very little denitrification occurs in the model due to depletion of substrates. The decomposition submodel then resumes with the rainy day and the average soil climate for that rainy day.

Pools of organic matter. Decomposition (as modeled in DNDC) can simultaneously occur in three organic matter pools: decomposable residues (mainly plant residues), microbial biomass, and humads; each pool has a labile and resistant component (Figure 3). The passive organic phase, or stable humus, is assumed not to interact with the active phase during the short time span of the model (about 1 year). We define soil organic carbon as the sum of microbial biomass, humads, and humus. During the decomposition process each component decomposes independently [*Hunt*, 1977; *Jenkinson*, 1977].

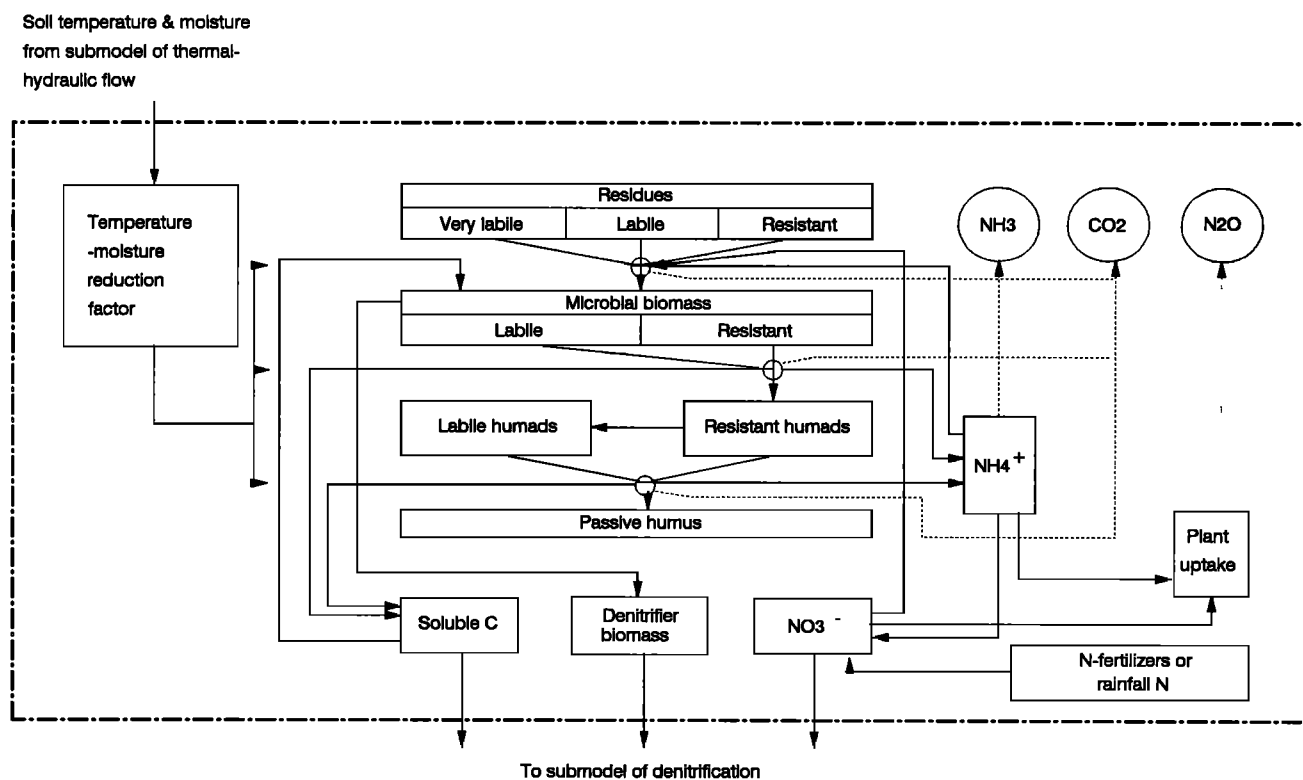*Decomposition rates.* The resistant and labile carbon pools

Fig. 3. In the decomposition submodel, organic matter consists of four pools: residue, microbial biomass, humads, and passive humus. Nonhumus pools contain labile and resistant components. Components have different temperature- and moisture-dependent decomposition rates. Pools of soluble carbon, microbial biomass, and nitrate are shared with the denitrification submodel.

TABLE 4. Decomposition Submodel Equations

Equation	Description
$dC/dt = \mu_{CLAY} \cdot \mu_{CN} \cdot \mu_{tm} \cdot (S \cdot k_1 + (1-S) \cdot k_2)$	Carbon pool decomposition rate
$R_e = B/\text{eff} = B + COP$	Biomass production and CO_2 evolution during residue decomposition
$FIXNH4 = [0.41 - 0.47 \cdot \log(NH4)] \cdot (CLAY/CLAY_{max})$	Ammonium adsorption
$\log(K_{NH4}) - \log(K_{H2O}) = \log(NH4_{aq}/NH3_{aq}) + pH$, $NH3_{aq} = 10^{\{\log(NH4_{aq}) - (\log(K_{NH4}) - \log(K_{H2O})) + pH\} \cdot (CLAY/CLAY_{max})}$	Transformation of ammonia to ammonium
$AM = 2 \cdot (NH3) \cdot (D \cdot t/3.14)^{-0.5}$	Ammonia volatilization
$dNNO = NH4(t) \cdot [1 - \exp(-K_{35} \cdot \mu_{t,a} \cdot dt)] \cdot \mu_{m,a}$	Nitrification rate
$N2O = (0.0014 \cdot NH4/30.0) \cdot (0.54 + 0.51 \cdot T)/15.8$	N_2O emitted during nitrification

(residues, microbial biomass, and humads) decompose via first-order kinetics. This formulation has been widely used to estimate mineralization potentials of soils and yield results consistent with data from incubation studies [*Molina et al.*, 1983; *Stanford and Smith*, 1972; *Smith et al.*, 1980; *Deans et al.*, 1983; *El-Haris et al.*, 1983; *Deans et al.*, 1986]. Carbon:nitrogen ratios differ significantly between residues and microbial biomass, therefore the actual decomposition rates for residues are affected by the availability of nitrogen in the soil (see Table 4 and Table 5 for decomposition equations and parameters, respectively). A reduction factor is introduced into the decomposition equation to reflect the limitations set by available N [*Molina et al.*, 1983].

For residues the specific decomposition rate (SDR) for each component was deduced from the production of carbon dioxide (CO_2) during decomposition in laboratory incubation experiments [*Gilmour et al.*, 1985]. These laboratory values of SDR are higher than field results [e.g., *Terry et al.*, 1981]. Laboratory results are based on relatively pure organic fractions, which do not exist in the field. In this study therefore we use the laboratory results, but we multiply the SDRs by a single, fixed reduction factor (0.025) to simulate all field situations. The reduction factor was determined from comparison of model runs with field-measured CO_2 emission rates on agricultural sites in Costa Rica and Germany [*Sauerbeck and Gonzalez*, 1977].

TABLE 5. Decomposition Submodel Parameters

Pool	Component	Initial Fraction	C/N	SDR 1/day
Residue	very labile	0.08[a]	2.35[a]	0.074[a]
	labile	0.32[a]	20[a]	0.074[a]
	resistant	0.60[a]	20[a]	0.02[a]
Biomass	labile	0.9[a]	8[c]	0.33[b]
	resistant	0.1[a]	8[c]	0.04[b]
Humads	labile	0.16[b]	8[d]	0.16[b]
	resistant	0.84[b]	8[d]	0.006[b]

[a]*Gilmour et al.* [1985].
[b]*Molina et al.* [1983].
[c]*Knapp et al.* [1983].
[d]*Stevenson* [1982].

The clay content of soils also affects the decomposition of organic matter; clays can adsorb organic C and shelter it from decomposition [*Bouwman*, 1990]. DNDC models this shielding effect as a multiplicative factor (0.35 to 1.67; 1.0 for loam) that decreases the decomposition rate for increasing clay contents.

Production and decomposition of microbial biomass and humads. As the residue pools decompose, the carbon released is either respired as CO_2 or incorporated into microbial biomass (Figure 3). DNDC first determines the amount of CO_2 produced. From this and a microbial efficiency value, DNDC calculates the amount of carbon incorporated into microbial biomass, with 90% going into labile biomass and 10% going into resistant biomass [*Gilmour et al.*, 1985]. Microbial efficiency, defined here as the ratio of C assimilated into microbial biomass to residue C released by decomposition, has been reported to vary between 20% and 60% [*Paul and Juma*, 1981; *Paul and Van Veen*, 1978; *Chichester et al.*, 1975; *Molina et al.*, 1983; *Gilmour et al.*, 1985]. In soils amended with easily decomposable organic material (e.g., animal wastes), the microbial population buildup is high [*Griffin and Laine*, 1983], while in unamended soils the fraction of decomposed C used for microbial growth is relatively small [*Jansson and Persson*, 1982]. This study adopts efficiency values of 60% for amended soil and 20% for unamended soil.

As microbes die and their biomass decomposes (Figure 3), 20% of the carbon is transfered to CO_2, 60% of the carbon is reincorporated into new microbial biomass, and 20% is transferred to the resistant humads pool [*Molina et al.*, 1983; *Gilmour et al.*, 1985]. The resistant humads pool can lose carbon through decomposition or via soil disturbance (see discussion of tillage effects below). As each humads pool decomposes, 40% of the carbon is transferred to the stable humus pool, 40% of the carbon is converted to CO_2 and 20% is reincorporated into microbial biomass [*Molina et al.*, 1983].

The soluble carbon pool (Figure 3) consists of the carbon from microbial biomass decomposition (60%) and humads decomposition (20%) that is recycled into microbial biomass. Thus it is not actually a carbon pool but rather an indicator of the daily rate of decomposition. When a rain event occurs, the denitrification model initiates its calculations using this soluble carbon pool as the amount of soluble carbon available in the soil.

Effect of temperature and moisture on decomposition. DNDC models the effects of soil temperature [*Nyhan*, 1976] and water content [*Clay et al.*, 1985] on microbial activity with reduction factors which retard the decomposition rate for nonoptimum conditions (Figures 4a and 4b). These relationships between microbial activity and both temperature and moisture are generally consistent with the results of other studies [e.g., *Bremner and Shaw*, 1958a, b; *Witkamp*, 1966; *Alexander*, 1971; *Myers and McGarity*, 1971; *Jager and Bruins*, 1974; *Wildung et al.*, 1975]. Since the reduction factor represents the combined effect of temperature and moisture, it is taken as the product of the two factors.

Nitrogen behavior during decomposition. During the decomposition of organic matter in soils, nitrogen behavior is simulated in the following manner: (1) when organic C is oxidized to CO_2, the associated N is transformed to ammonium (NH_4^+); (2) NH_4^+ can be nitrified to nitrate or transferred to ammonia and volatilized to the air; and (3)
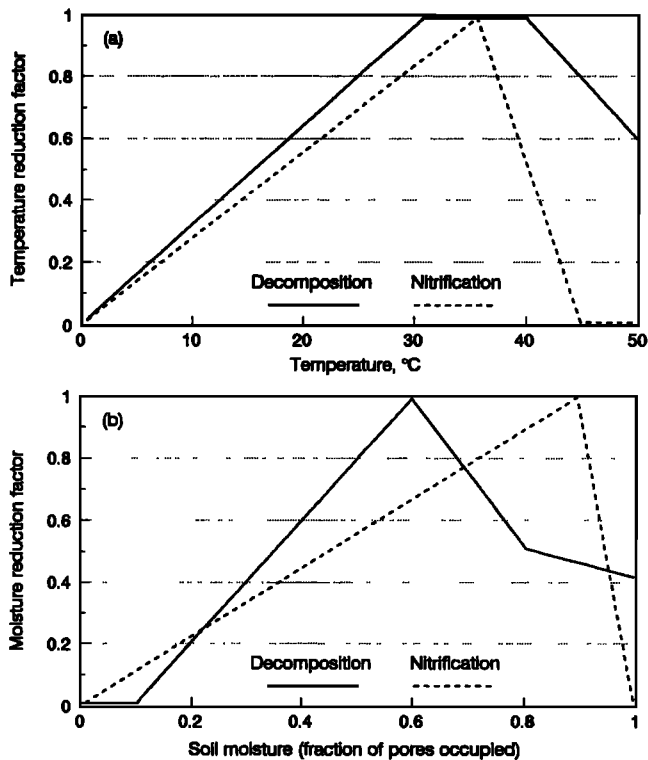
Fig. 4. Soil climate reduction factors. The dimensionless (a) temperature dependence and (b) moisture dependence reduction factors for the decomposition process (solid line) and the nitrification process (dotted line).

when organic C transfers from one pool to another, surpluses or deficits of available N can occur because of the differences in C:N ratios among different pools. If excess N is created (carbon transfer from a lower C:N pool to a higher C:N pool), the excess N is moved to the inorganic N pool. If a nitrogen deficit occurs (carbon transfer from a higher C:N pool to a lower C:N pool), the necessary nitrogen is removed from the inorganic N pool; if the pool does not contain enough N to satisfy the demand, the C transfer is reduced to an allowable level. Thus the inorganic N pool collects N (as NH_4^+ and NO_3^-) from the oxidation processes and supplies NH_4^+ and NO_3^- for assimilation, nitrification, volatilization, denitrification, or plant uptake.

Uptake of nitrate and ammonium by plants. As plants grow they take up nitrogen in the form of nitrate or ammonium. On the basis of average rates of accumulation of nitrogen in aboveground crops [Olson, 1978; Olson and Kurtz, 1982], the estimated daily uptake of N is calculated from crop type and seeding date as input data. Plant nitrogen comes from NO_3^- and NH_4^+ pools, based on their relative concentrations.

Behavior of ammonium. The major factors affecting adsorption of NH_4^+ by clay and organic matter in soil are the total available adsorption sites and the NH_4^+ concentration in the soil liquid phase [Nommik, 1965]. Since there is often a rough positive correlation between clay and organic carbon content in soils [Jones, 1972; Food and Agriculture Organization (FAO)/UNESCO, 1971-1981], clay content is chosen as an index of adsorption sites. Transformation of ammonium to ammonia is influenced by soil pH, temperature, buffer capacity [Freney et al., 1981]. Volatilization of ammonia is related to the NH_3 concentration

in the liquid phase and a diffusion coefficient [Gardner, 1965].

Effect of fertilization. Application of N fertilizers can change the N-cycle dynamics in the soil. Common N fertilizers include ammonium, nitrate, urea, and anhydrous ammonia. Nitrate fertilizer directly enters the NO_3^- pool. Urea and ammonium fertilizers transfer to nitrate through hydrolysis and/or nitrification. Anhydrous ammonia affects soil pH and transfers to ammonium.

Effect of tillage. Tillage can change the decomposition rates and the distribution of organic matter in the soil profile by physically mixing the soil and by increasing oxygen activity [Tivy, 1990]. In DNDC, when a soil is tilled there are two effects: (1) all pools of organic matter are redistributed as uniform concentrations down to the tillage depth, and (2) a fraction of the resistant humads pool is transferred into labile humads. This more rapid decomposition effect is modeled as decreasing with time after tillage. The initial transfer is 16% of the resistant humads pool, with subsequent transfers of 12%, 8%, and 4% following the next three rain events [Sorensen, 1975]. Note that without tillage there is no flow of carbon to the labile humads pool (Figure 3).

Nitrification. Under aerobic conditions, NH_4^+ can be oxidized to NO_2^- and NO_3^- by ammonium oxidizers [McGill et al., 1981; Van Veen and Frissel, 1979]. This process is called nitrification. According to a study by Watts and Hanks [1978] the potential rate of nitrification in the surface soil is related to the available NH_4^+, soil temperature, and soil moisture. DNDC models the rate as a function of these factors with an optimal rate at 35°C and soil pore moisture content of 90% (Hadas et al., [1986]; Figures 4a and 4b).

During nitrification the amount of N_2O emitted in soils correlates with the amount of nitrifiable N in soils [Parton et al., 1988, Bremner and Blackmer, 1978]. In DNDC we regard ammonium as the direct factor controlling N_2O emissions under aerobic conditions. On the basis of the data of Bremner and Blackmer [1981], N_2O emissions from nitrification processes are modeled as a function of soil temperature and soil ammonium concentration.

2.4. Submodel of Denitrification

Leffelaar and Wessel [1988] present a detailed model of denitrification processes in laboratory incubations of soil samples. Denitrification follows the reduction sequence $(NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2)$ with the rate of each process depending on the availability of the particular N oxide and all processes competing for available C. DNDC uses a similar model structure for denitrification (Figure 5), activating this submodel at every rainfall event. The soil profile is divided into horizontal layers with a typical thickness of 2 cm. Each layer is assumed to have uniform properties (temperature, moisture, substrate and microbe concentrations, etc.) and all denitrification calculations are performed layer by layer. In DNDC a rainfall event is defined as the time period from rainfall initiation to the time when relative moisture (fraction of water-occupied pores) decreases to 40%. In the model, denitrifying conditions (low oxygen availability) occur immediately upon saturation with water. During the denitrification calculation we assume that only denitrifiers are active.

Relative growth and death rates of denitrifiers. Almost all
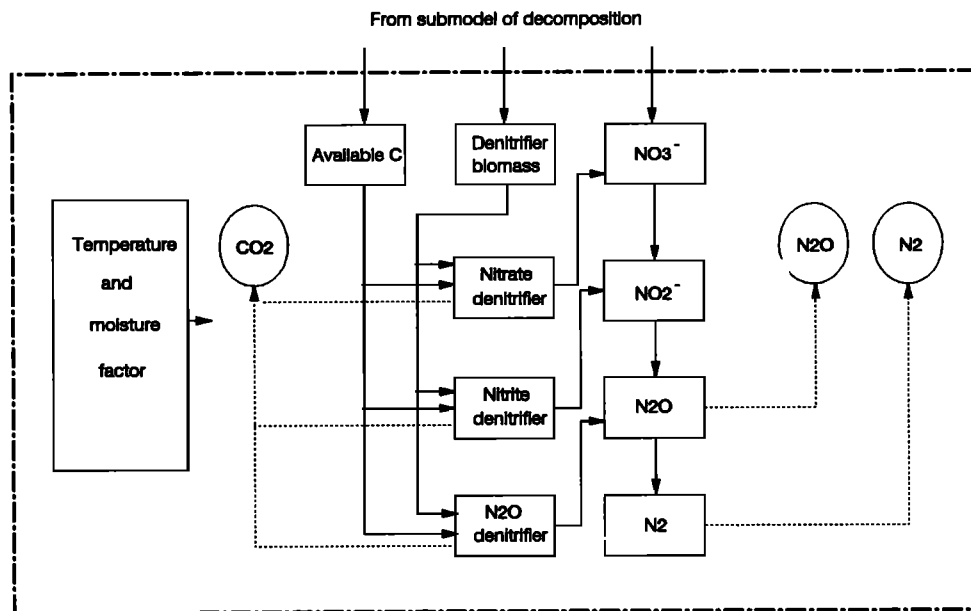
From submodel of decomposition

Fig. 5. In the denitrification submodel, initial denitrifier biomass is a fixed fraction of total microbial biomass in the decomposition submodel. Soluble carbon and nitrate from decomposition are utilized by denitrifiers as electron donor and acceptor, respectively. The evolution rates of nitrite, nitrous oxide and dinitrogen are controlled by the growth rates of the various denitrifiers, which depend on soil moisture, temperature, pH, soluble carbon, and nitrate.

denitrifiers are capable of anaerobic growth only in the presence of NO_3^-, NO_2^-, or N_2O. The growth rates of denitrifiers directly affect the reduction rates of these nitrogenous oxides. Denitrifiers are assumed to become active at the onset of a rainfall event. Tiedje [1978] and Smith and Tiedje [1979] reported a short lag period (1 to 10 hours) before denitrification began following soil wetting. Ignoring this lag time probably causes DNDC to model N_2O and N_2 production earlier than in field situations.

The growth rates of the bacteria are taken to be

TABLE 6. Denitrification Submodel Equations

Equations	Description
$\mu_{t,dn} = 2^{(T-22.5)/10}$, if $T < 60°C$	Temperature reduction factor
$\mu_{t,dn} = 0$, if $T \geq 60°C$	
$\mu_{PHNO3} = 7.14 \cdot (pH-3.8)/22.8$	pH reduction factor
$\mu_{PHNO2} = 1.0$	
$\mu_{PHN2O} = 7.22 \cdot (pH-4.4)/18.8$	
$(dB/dt)_g = u_{DN} \cdot B(t)$	Denitrifier growth rate
$u_{DN} = \mu_{t,dn} \cdot (u_{NO3} \cdot \mu_{PHNO3} +$	Relative denitrifier growth rate
$u_{NO2} \cdot \mu_{PHNO2} + u_{N2O} \cdot \mu_{PHN2O})$	
$u_{NxOy} = u_{NxOy,max} \cdot (C/(K_{c,1/2}+C)) \cdot$	Maximum denitrifier growth rate
$(NxOy/(K_{NxOy,1/2}+NxOy))$	
$(dB/dt)_d = M_c \cdot Y_c \cdot B(t)$	Denitrifier death rate
$dC_{con}/dt = (u_{DN}/Y_c + M_c) \cdot B(t)$	Consumption of soluble carbon
$dCO2/dt = dC_{con}/dt - (dB/dt)_g$	CO_2 production
$d(NxOy)/dt = (u_{NxOy}/Y_{NxOy} +$	Nitrate, nitrite, and nitrous oxide
$M_{NxOy} \cdot NxOy/N) \cdot B(t) \cdot \mu_{PHNxOy} \cdot$	consumption
$\mu_{t,dn}$	
$(dN/dt)_{ass} = (dB/dt)_g \cdot$	Nitrogen assimilation rate
$(1/CNR_{DN})$	
$P(N2) = 0.017 + ((0.025-$	N_2 emission from soil
$0.0013 \cdot AD) \cdot PA$	
$P(N2O) = (0.0006 + 0.0013 \cdot$	N_2O emission from soil
$AD) + (0.013 - 0.005 \cdot AD) \cdot PA$	

proportional to their respective biomass (Van Veen and Frissel [1981]; see Table 6 and Table 7 for denitrification submodel equations and parameters, respectively). Relative growth rates, which depend on the concentrations of carbon and electron acceptors (N oxides), are calculated with double-Monod kinetics, a simple function describing multiple-nutrient-dependent Michaelis-Menten-type growth [Bader, 1978]. Following Leffelaar and Wessel [1988] we assume that the relative growth rates for denitrifiers with different substrates are independent; competition among the bacteria takes place via the common soluble carbon substrate.

The denitrifier death rate is modeled as proportional to denitrifier biomass. The C and N from dead cells are added to the pools of immobilized C and N and no longer participate in the dynamic processes [Leffelaar and Wessel, 1988]. Since denitrifier biomass is a very small fraction of total soil biomass, this represents an insignificant loss of C and N from the soil system.

Effect of soil environment on denitrification. The effect of soil pH on denitrification has been measured by many researchers [Mueller et al., 1980; Klemedtsoon et al., 1978; Burford and Bremner, 1975; Stanford et al., 1975; Khan and Moore, 1968; Wijler and Delwiche, 1954]. On the basis of experimental studies, pH affects nitrate and nitrous oxide transformation rates differently such that at low pH (<5), most denitrification stops at N_2O [Focht, 1974; Leffelaar and Wessel, 1988]. In general, total denitrification decreases as soil pH decreases.

An exponential relationship between denitrification rate and temperature has been observed [e.g., Focht, 1974; Nommik, 1956; Dawson and Murphy, 1972]. According to Bailey and Beauchamp [1973] and Nommik [1956] the rate of denitrification is very temperature dependent in the $10°-35°C$ range, with a Q_{10} near 2.0 [Stanford et al., 1975; Knowles, 1981]. The rate continues to increase at higher temperatures, reaching a maximum at $60°-75°C$ and then falling to zero

TABLE 7. Denitrification Parameters

Parameter	Definition	Value	Unit	Source
$u_{(max,NO3)}$	Maximum growth rate of NO_3^- denitrifier	0.67	1/hour	Hartel and Alexander [1987]
$u_{(max,NO2)}$	Maximum growth rate of NO_2^- denitrifier	0.67	1/hour	Hartel and Alexander [1987]
$u_{(max,N2O)}$	Maximum growth rate of N_2O denitrifier	0.34	1/hour	Hartel and Alexander [1987]
Kc	Half-saturation value of soluble carbon	0.017	kg C/m³	Shah and Coulman [1978]
Kn	Half-saturation value of N-oxides	0.083	kg N/m³	Shah and Coulman [1978]
Mc	Maintenance coefficient on C	0.0076	kg C/kg/h	Van Verseveld et al. [1977]
$M(NO_3)$	Maintenance coefficient on nitrate	0.09	kg N/kg/h	Van Verseveld et al. [1977]
$M(NO_2)$	Maintenance coefficient on nitrite	0.035	kg N/kg/h	Van Verseveld et al. [1977]
$M(N_2O)$	Maintenance coefficient on N_2O	0.079	kg N/kg/h	Van Verseveld et al. [1977]
Yc	Maximum growth rate on soluble C	0.503	kg C/kg C	Van Verseveld et al. [1977]
$Y_{(max,NO3)}$	Maximum growth rate on nitrate	0.401	kg C/kg N	Van Verseveld et al. [1977]
$Y_{(max,NO2)}$	Maximum growth rate on nitrite	0.428	kg C/kg N	Van Verseveld et al. [1977]
$Y_{(max,N2O)}$	Maximum growth rate on N_2O	0.151	kg C/kg N	Van Verseveld et al. [1977]
R	C/N ratio in denitrifiers	3.45		Van Verseveld and Stouthamer [1978]
RBO	Ratio of microbial to total organic C	0.01-0.025		Woldendorp [1981] and Anderson and Domsch [1989]
FD	Ratio of denitrifiers to microbial biomass	0.001-0.5		Focht and Verstraete [1977]

[Keeney et al., 1979; Bremner and Shaw, 1958b]. At lower temperatures the denitrification rate decreases but is measurable down to 0°-5°C [Bailey and Beauchamp, 1973; Bremner and Shaw, 1958b; Smid and Beauchamp, 1976]. Since most parameters adopted in this study are based on a standard temperature of 22.5°C, the temperature effect factor is a standard exponential function equal to 1.0 at 22.5°C (Q_{10} = 2). This one temperature factor is applied to the activities of NO_3^-, NO_2^-, and N_2O denitrifiers.

Consumption of C, NO_3^-, NO_2^-, and N_2O; Production of CO_2. Soluble carbon can be used by bacteria as the basic material for cell synthesis and energy [Pirt, 1965]. The consumption rate of soluble carbon depends on the biomass, relative growth rate, and maintenance coefficients of the denitrifier populations. Carbon dioxide production is calculated as the difference between the total amount of carbon consumed and the amount used for cell synthesis.

Nitrate, nitrite, and nitrous oxide consumption are calculated with Pirt's equation. The maintenance coefficients must be multiplied by the relative presence of each electron acceptor in the water phase (NxOy/N), because data reported in the literature are for maintenance sufficient to support the entire denitrifier biomass, NO_3^- denitrifier + NO_2^- denitrifier + N_2O denitrifier [Leffelaar and Wessel, 1988].

On the basis of the growth rates of denitrifiers and the C:N ratio in the bacteria the assimilation of N during denitrification can be calculated. A C:N ratio (by weight) of 3.45 is used, based on the chemical composition of denitrifiers ($C_6H_{10.8}N_{1.5}O_{2.9}$), in accordance with data reported for Paracoccus denitrificans [Verseveld and Stouthamer, 1978].

Diffusion of N_2O and N_2 in soil. During rainfall events, when a soil layer is initially saturated with water, diffusion of N_2O and N_2 is neglected because of the low diffusion rates in soil water. According to the results of Letey et al., [1980] the daily emissions of N_2O or N_2, as a percentage of total N_2O or N_2, are related to the adsorption coefficients of the gases in soils and to the air-filled porosity of the soil. Based on their data, N_2 and N_2O emissions are modeled as functions of both adsorption coefficient and air-filled porosity. Since denitrification is concentrated in the surface soil in most cases, the effect of soil depth on diffusion is not considered

in this model. These emission factors are not gradient driven and will undoubtedly create some artifacts in the shape of the denitrification N_2O pulse.

3. MODEL OPERATION

Climate, soil physical and chemical properties, and land use are important factors which govern N_2O-production processes in soils. These factors comprise the input for the DNDC Model (Table 8). Daily mean air temperature and daily rainfall/irrigation data are compiled into a climate scenario. Irrigation events are considered equivalent to rainfall events. Additional input data include soil properties such as texture, initial temperature and moisture, density, pH, initial organic residue content, organic carbon and nitrate concentrations, crop type, tillage practices, amendments, and fertilizer applications.

Since denitrification mostly occurs within the top 30-75 cm for most mineral soils [Gilliam et al., 1978; Rolston et al., 1976; Khan and Moore, 1968], a typical total thickness of a modeled soil profile is 50 cm. Initially, the top 10 cm of soil is assumed to be chemically uniform. Below this level, the concentrations of organic residues, organic C and NO_3^- decrease exponentially with depth (50% every 10 cm). During rainfall events, dissolved NO_3^- and NO_2^- move down to deeper layers with the water flux. In the model, N_2O and N_2 do not move with the water flux. The thermal-hydraulic

TABLE 8. Model Input Parameters

Category	Parameter
Climate	Mean daily air temperature; rainfall events (timing, intensity, duration); NO_3^- concentration in rainwater.
Soil	Type (texture); density; pH; initial residue, organic carbon, nitrate, and ammonium contents; initial soil temperature and moisture.
Land use	Crop type; seeding and harvest time.
Agronomic practices	Tillage (timing, intensity); fertilizer application (species, amount, timing, depth); manure amendment (type, amount, timing); irrigation (amount, timing); crop rotation (crop types, rotation pattern).

submodel starts the simulation by assuming a soil with uniform temperature and water content profiles.

The model output includes daily moisture and temperature profiles, concentrations of residues, organic carbon, microbial biomass, soluble carbon, NH_4^+, NO_3^-, NO_2^-, N_2O, and N_2 in the profile, and emissions of N_2O, N_2, NH_3, and CO_2 from the soil.

4. SENSITIVITY ANALYSIS

To test the response of the sub-models and the complete model to variations of relevant parameters from baseline conditions, four sensitivity analyses were conducted: (1) the sensitivity of soil moisture to soil texture and rainfall patterns; (2) the sensitivity of decomposition to drying period duration, soil temperature, soil moisture, initial residue, and organic C; (3) the sensitivity of denitrification to soil-soluble C, nitrate, and rainfall duration; and (4) the sensitivity of total model behavior for an annual simulation to variations in soil properties, initial organic C, annual precipitation, and temperature.

In order to unravel the complex behavior of DNDC our sensitivity analyses were conducted by varying one parameter and fixing others during one cycle. This sensitivity analysis does not validate the model but demonstrates that the model behavior is consistent with its structure and assumptions, as described in section 2. Model validations against field measurements are reported in a companion paper [Li et al., this issue].

4.1. Soil Moisture and Rainfall Patterns: The Thermal-Hydraulic Submodel

The DNDC model illustrates the importance of soil moisture to both denitrification and decomposition. This section examines two tests of the sensitivity of the thermal-hydraulic submodel to soil texture and imposed precipitation/irrigation conditions, one to rainfall intervals and the other to rainfall amounts.

In the first test the thermal-hydraulic submodel was run for five different rainfall patterns spread over a 90-day period: (1) 1.25 cm of rain in 5 hours every 4 days, (2) 2.50 cm of rain in 5 hours every 8 days, (3) 3.75 cm of rain in 5 hours every 12 days, (4) 5.00 cm of rain in 5 hours every 16 days, and (5) 6.25 cm of rain in 5 hours every 20 days. The total rainfall was the same for each simulation. For each soil type the amount of time the soil was dry (water content < 40% water-filled pore space) and the amount of time the soil was wet (water content > 65% water-filled pore space) increased as the rainfall interval increased, while the time that the soil was at an intermediate water content decreased (Figure 6). Other things being equal, we would expect N_2O emissions to increase as both rainfall interval and duration increased.

Two simulation studies examined the effects of increased rain amounts for evenly spaced storms (10-day intervals): one varied rainfall intensity and the other varied rainfall duration. Both had the expected effect of increasing the amount of time the soils were quite wet (>65% pore space occupied) and decreasing the amount of time the soils were dry. For all thermal-hydraulic submodel tests, sandier soils were drier than the clayey or organic soils in any particular simulation.
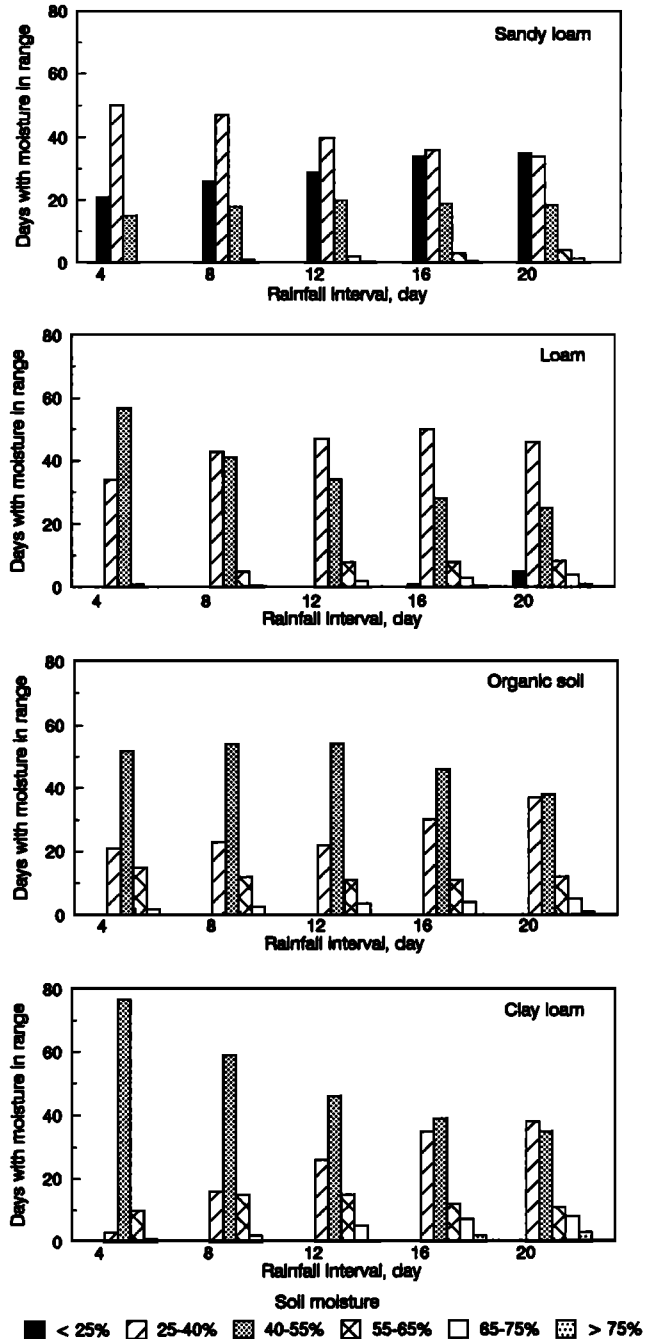

Fig. 6. Soil moisture and rainfall patterns. Soil moisture dependence on rain storm interval (days between storms) for sandy loam, loam, clay loam, and organic soils. The height of the bars represent the amount of time, in days, that the top 20 cm of the soil had an average water-filled pore space in the range indicated.

4.2. Soluble Carbon and Nitrate Availability in Soil: The Decomposition Submodel

Both soluble C and NO_3^- are the products of decomposition and other oxidation reactions in soils. In DNDC the levels of the two substrates reflect the interactions of several factors, including initial organic residues, total organic carbon, soil moisture and temperature, and decomposition duration. In this section we examine the sensitivity of the decomposition submodel, which generates soluble carbon and

TABLE 9. Standard Conditions for Sensitivity Analysis of Decomposition and Denitrification Submodels

Item	Decomposition Submodel	Denitrification Submodel
Soil type	loam	loam
Soil density	1.5 g/cm³	1.5 g/cm³
Soil pH	7.0	7.0
Soil temperature	20°C	20°C
Initial residue[a]	10 g C/kg soil	
Initial organic C[b]	10 g C/kg soil	10 g C/kg soil
Initial soluble C[c]		20 mg C/kg soil
Initial nitrate	100 mg N/kg soil	100 mg N/kg soil
Initial ammonium	5 mg N/kg soil	
Dry period duration	30 days	
Rainfall intensity		0.5 cm/h
Rainfall duration		5 hours
Nitrate in rainwater		1 mg N/l

[a]Decomposable residues, including plant residues and microbial polysaccharides,
[b]Active organic carbon, including microbial biomass and humads,
[c]Water-soluble carbon.

Fig. 8. Effect of initial soil active organic C on nitrate and soluble C produced during the drying period. In the DNDC model, when initial organic carbon increases, soluble carbon increases linearly, while NO₃⁻ increases at first and then decreases because of the competition between decomposition and assimilation.

nitrate pools, to variations in parameters from standard conditions (Table 9).

Effect of initial residue and organic carbon content. As the initial organic residue content increased from 0 to 0.1 kg C/kg soil, final values (after a 30-day decomposition period) for both soluble C and NO₃⁻ increased (Figure 7). During the first two or three weeks of decomposition the very labile and labile residues rapidly decompose and produce relatively high levels of soil ammonium, which is nitrified to nitrate. The very labile residue pool has a low C:N ratio and thus introduces a lot of nitrogen into the soil. The initial organic residue pool will affect results for the first two or three dry period-rainfall cycles, but the model then equilibrates to the imposed climate scenario and initial residue pools play a less important role.

As the initial organic carbon content increased from 0 to 0.1 kg C/kg soil, the production of soluble carbon also increased (Figure 8). Nitrate levels increased up to 0.05 kg C/kg soil but then decreased slightly with further increases of organic carbon. This slight decrease in the C-rich soil is related to the high population of microbial organisms (which

follows from the higher initial organic carbon values); the microbes assimilate nitrate as it is produced by decomposition.

Effect of decomposition period duration. Under the standard conditions the soil nitrate content increased linearly as the decomposition period was extended, due to continuing nitrification of the ammonium released by decomposing organic matter. The soluble carbon level did not change since carbon decomposition and assimilation into microbial biomass reached a steady state (Figure 9).

Effect of soil climate. Soluble carbon and NO₃⁻ reached maximum values when the water-occupied fraction was fixed at about 60% of the total porosity; both wetter and drier conditions limited the production of soluble carbon and NO₃⁻ (Figure 10). As the soil temperature increased from 0° to 30°C, soluble carbon and nitrate increased. Above 40°C, soluble carbon gradually decreased and nitrate sharply decreased and then increased (Figure 11). At temperatures above 45°C (not normally found in field soils) the production of CO₂ decreased because of the depression of microbial activity. Nitrification ceases above 45°C, so no nitrate is produced, but the reduction in nitrogen assimilation due to
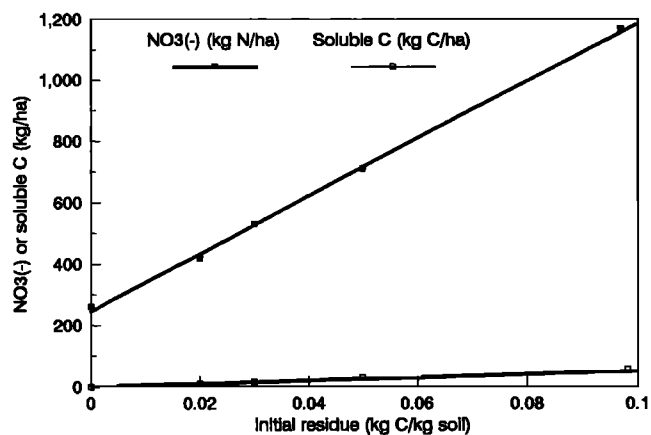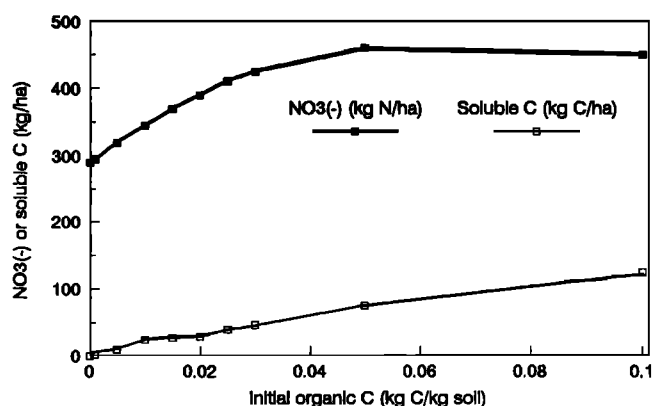

Fig. 7. Effect of initial residue content on nitrate and soluble C produced during the drying period. In the DNDC model, both soluble carbon and nitrate increase with an increase of initial residue content.
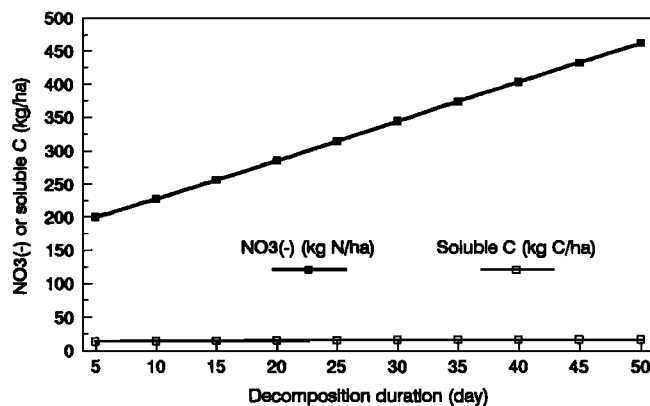

Fig. 9. Effect of decomposition duration on nitrate and soluble C produced during the drying period. In the DNDC model, nitrate increases with an increase in decomposition duration. Soluble carbon, an intermediate product during decomposition, does not change.
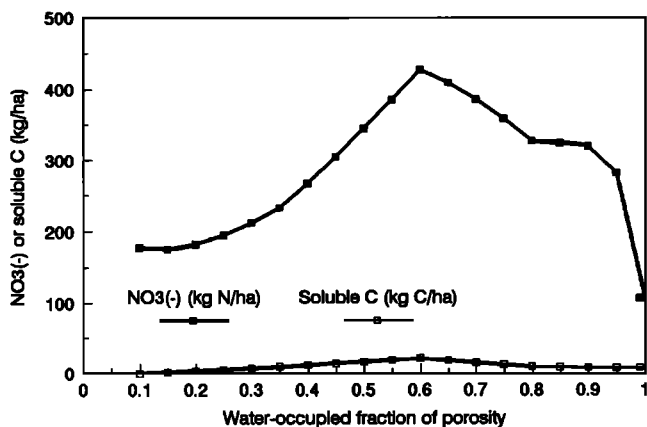
Fig. 10. Effect of soil moisture on nitrate and soluble C produced during the drying period. A soil moisture content of 60% water filled pore space is optimal for producing soluble carbon and nitrate during decomposition and nitrification process in the DNDC model.
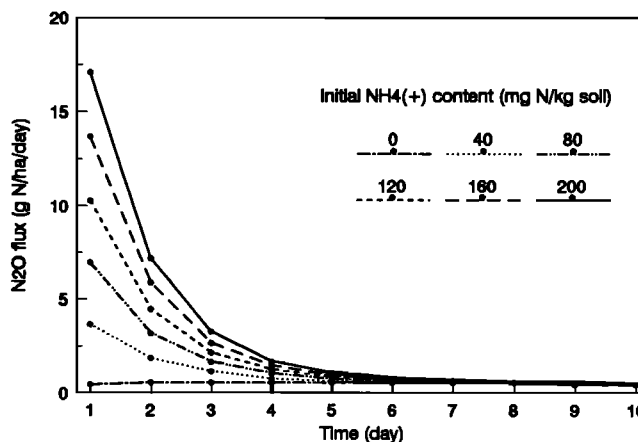

Fig. 12. Effect of initial ammonium content on N₂O flux. Initial ammonium concentration only influences the short-term evolution of N₂O in nitrification in the DNDC model. Evolved N₂O rapidly decreases over 7 days to a stable low level because NH₄⁺ is transformed into NO₃⁻.

suppressed microbial activity means that more of the initial nitrate pool remains after the 30-day decomposition period.

Effect of initial ammonium concentration on N₂O emissions. N₂O emissions from nitrification are modeled as a function of soil water ammonium concentration, soil temperature, and soil moisture. The response of the model to changes in the initial ammonium concentrations is large initially but temporary (Figure 12). Within 1 week all cases converged on a stable low level of 0.5 g N ha⁻¹ d⁻¹. This value is a function of soil temperature, moisture, and the rate of NH₄⁺ production through decomposition processes.

4.3. Emissions of N₂O During A Rainfall Event: The Denitrification Submodel

During normal model operation the denitrification submodel receives substrate status information from the decomposition submodel at the beginning of each rain event. For this sensitivity study, the denitrification model was run alone using standard conditions (Table 9).

Effect of soluble carbon and nitrate contents. Soluble C

and NO₃⁻ are the main substrates necessary to keep denitrifiers active under anaerobic conditions. As the initial value of soluble carbon increased, the rise in total denitrification (N₂O+N₂) depended on the initial content of NO₃⁻ in soils (Figure 13). For NO₃⁻ levels below about 30 mg N/kg soil and soluble carbon greater than 10 mg C/kg soil, nitrate limited total denitrification. Increasing soluble C can decrease N₂O emission because it lowers the ratio of N₂O/N₂ produced by supplying sufficient carbon substrate to complete the denitrification process (Figures 14 and 15). If the content of soluble carbon is fixed, increasing the initial NO₃⁻ content will not necessarily increase N₂O emissions (Figure 15). Thus the relationship between N₂O emission and the soluble carbon and NO₃⁻ contents in the soil appears to be quite complex. These results are consistent with numerous observations which indicate (1) water-soluble carbon is highly correlated with denitrification activity and (2) increasing carbon availability generally decreases the ratio of N₂O/N₂ [*Burford and Bremner*, 1975; *Smith and Tiedje*, 1979; *Focht and Verstraete*, 1977; *Nommik*, 1956; and *Delwiche*, 1959]. These relationships between soluble carbon and nitrate could be important for reducing N₂O emission
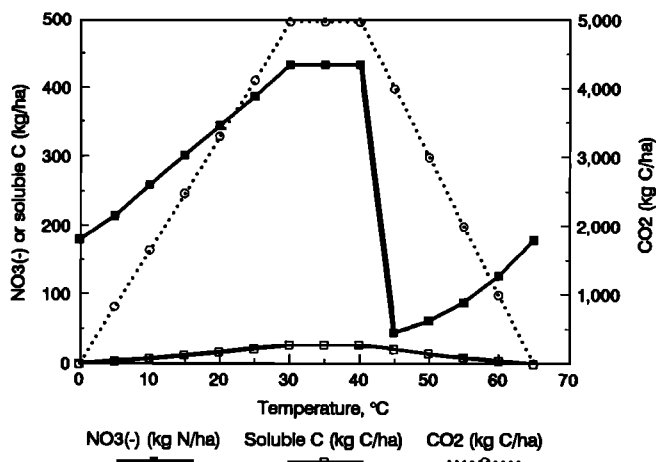

Fig. 11. Effect of soil temperature on nitrate and soluble C produced during the drying period. A soil temperature of 30°-40°C is optimal for decomposition and nitrification processes in the DNDC model.
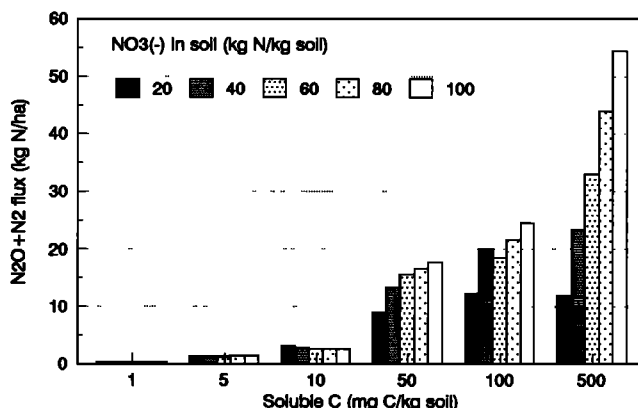

Fig. 13. Effect of soluble C and nitrate on denitrification rate. Increases in soluble carbon (1-500 mg C/kg soil) and/or nitrate (20-100 mg N/kg soil) generally cause total denitrification to increase. Either carbon or nitrate can be a limiting factor for denitrification.
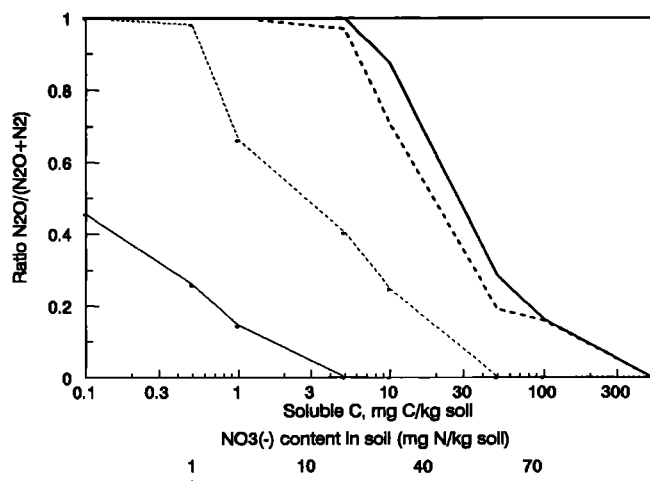
Fig. 14. Effect of soluble C and nitrate on the $N_2O/(N_2O+N_2)$ ratio. In the DNDC model, soluble carbon often limits the extent of denitrification. With increased soluble carbon, N_2 production increases and the $N_2O/(N_2O+N_2)$ ratio decreases.

from soils through changing the manner of fertilizer applications.

It is important to point out that initial values of soluble carbon and nitrate will not actually affect the model behavior significantly over a series of rain events (see Section 4.4). The denitrification submodel receives the levels of soluble carbon and nitrate as input from the decomposition submodel, and so these become internal variables after a couple of rain events. The sensitivity study, however, does demonstrate the interaction between these two pools.

Effect of rainfall duration. As rainfall duration increased from 1 to 10 hours, N_2O and N_2O+N_2 emissions increased in a near linear fashion (Figure 16). This was due to the increased volume and duration of anaerobic (denitrifying) conditions in the soil. Under field conditions this continuous increase in denitrification emissions with rainfall duration may not always occur. In this simulation, initial levels of soluble carbon and nitrate were relatively high insuring ample denitrification substrates when the rainfall occurred.

4.4. Annual N₂O Emissions: The DNDC Model

The complete DNDC model was tested for its sensitivity to various climate and soil parameters over a 1-year simulation. A set of standard climate/soil conditions was developed, based on the climate and soils of Iowa [*United States Department of Agriculture (USDA)* 1989, 1967]. In order to determine the effects of different climate or soil properties on annual emissions of N_2O, annual simulations were conducted by varying each parameter by ±20% while holding the others fixed (Table 10). The results of this analysis show that the sensitivities of total denitrification (N_2O+N_2), N_2O emissions, and CO_2 emissions to the climate/soil parameters are quite different (Figure 17). None of these sensitivity studies test the model sensitivity to different agricultural practices.

Annual total denitrification. Variations in annual precipitation had the greatest effect on the annual total denitrification (see Figure 17a); when annual precipitation was increased by 20%, total denitrification increased by more than 50%. Higher precipitation keeps the surface soil under anaerobic conditions for a longer time, enhancing denitrification. Soil pH had the second largest effect. When soil pH was reduced from 6.0 to 4.8, the annual denitrification rate decreased by 40%; denitrifiers are very sensitive to a low pH environment. When the mean annual temperature or initial total organic C were increased by 20%, total denitrification also increased by about 20%. Higher temperatures stimulate denitrifier and decomposition activity; higher organic C provides more substrates (soluble C and nitrate) to support the growth of denitrifiers. Changes in soil density, clay content, rainfall nitrate, initial soil nitrate, and initial soil ammonium had slight to no effect on total denitrification. Rainfall nitrate at these levels (0.8-1.2 mg N/L) is a small nitrate source (6 kg N/ha/yr) relative to modeled nitrification at this site (286 kg N/ha/yr).

Annual N₂O emission. Because the ratio of N_2O production to total denitrification (N_2O+N_2) depends on many factors, the behavior of the annual N_2O emissions is different from that of total denitrification (Figure 17b). Soil texture (clay content) and density had the greatest effect on N_2O emissions. When soil clay content was decreased by 20%, the annual
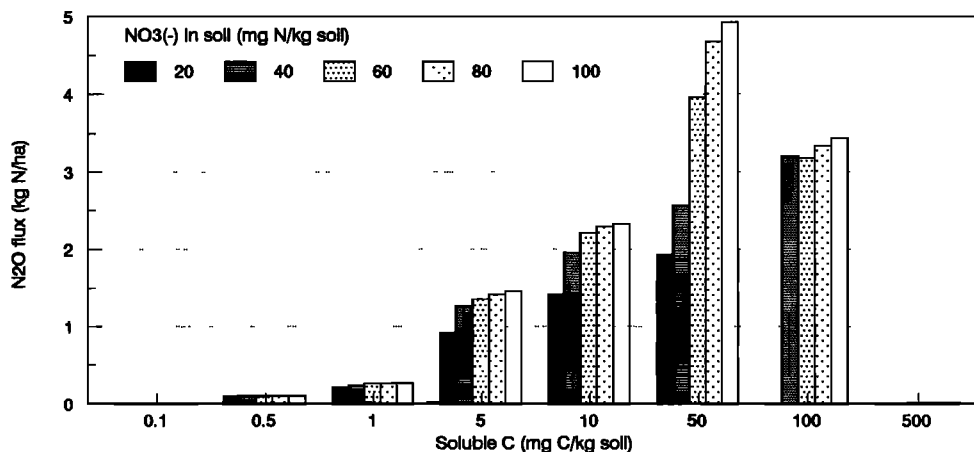

Fig. 15. Effect of soluble C and nitrate on N_2O emission. Changes in the modeled N_2O emission rates due to increasing soil nitrate content depend on the level of soluble carbon in the soil.
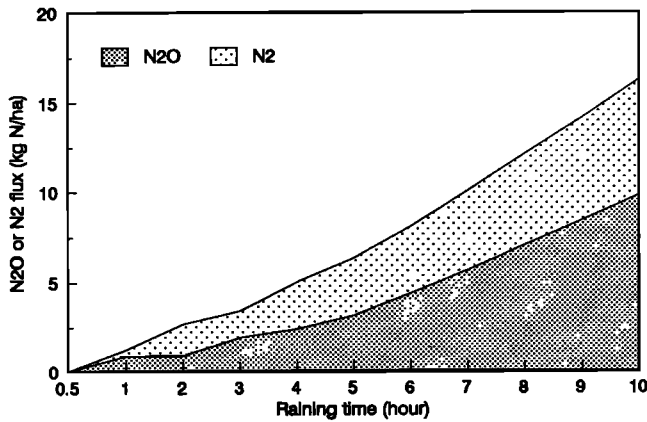
Fig. 16. Effect of rainfall duration on N_2O and N_2 flux. Modeled N_2O and N_2 emissions increase linearly with an increase in rainfall duration when carbon and nitrate substrates do not limit denitrification.

N_2O emissions increased by more than 40%. This phenomenon is due to the stronger adsorption by clays of N_2O than of N_2; the model clay content was changed without changing the soil hydraulic properties, so soil moisture changes had no effect here. Since we defined soil organic C as kg C per kg soil, an increase in soil density automatically causes an increase in organic C. An increase in organic C will increase the microbial biomass which tends to increase N_2O production more than N_2 production because of the time constraints set by various wet periods. Thus the $N_2O/(N_2O+N_2)$ ratio generally rises.

In the same vein an increase in annual precipitation greatly increased annual N_2 emission but slightly reduced N_2O emission (Figure 17); anaerobic conditions last longer, allowing denitrification processes to continue more toward completion (N_2 rather than N_2O). When soil temperature was increased by 20%, the annual N_2O emissions increased by 14% because of enhanced microbial activity. Annual N_2O emissions decreased slightly with either an increase or a decrease in soil pH reflecting the optimal pH range for N_2O production. Nitrate concentration in rainfall, initial soil nitrate, and initial ammonium had little to no effect on annual N_2O emissions.

Annual CO_2 emission. Total organic C strongly influenced annual CO_2 emissions (Figure 17c) because the soil microbial

TABLE 10. Standard Conditions and Variations for
Sensitivity Analysis on DNDC Model

Item	Condition		
	Standard	Variation	Unit
Annual rainfall events[a]	24	29 - 21	
Annual precipitation	82.5	99.1 - 66.0	cm
Annual average temperature	9.1	10.9 - 7.3	°C
Nitrate content in rain	1.0	1.2 - 0.8	mg N/l
Soil clay content	34%	40% - 27%	
Soil density	1.4	1.68 - 1.12	g/cm³
Soil pH	6.0	7.2 - 4.8	
Initial total organic C[b]	0.03	0.036-0.024	g C/kg
Initial soil nitrate	10	12 - 8	mg N/kg
Initial soil ammonium	10	12 - 8	mg N/kg

[a]Heavy and intermediate rainfalls,
[b]Including plant residues, microbial polysaccharide, and other organic matter.

pool size varies directly with total organic carbon. The same effect occurs with a change in soil density (g soil/cm³). Soil clay content showed a large inverse effect on annual CO_2 emission; clays can adsorb organic C and shield it from decomposition. When soil temperature was increased (decreased) by 20%, annual CO_2 emissions increased (decreased) by 13%, reflecting the general dependence of microbial activity on temperature. An increase in annual precipitation had a negative impact on annual CO_2 emissions. Rates of decomposition are slowed with the increased frequency/duration of anaerobic conditions. Soil pH, nitrate
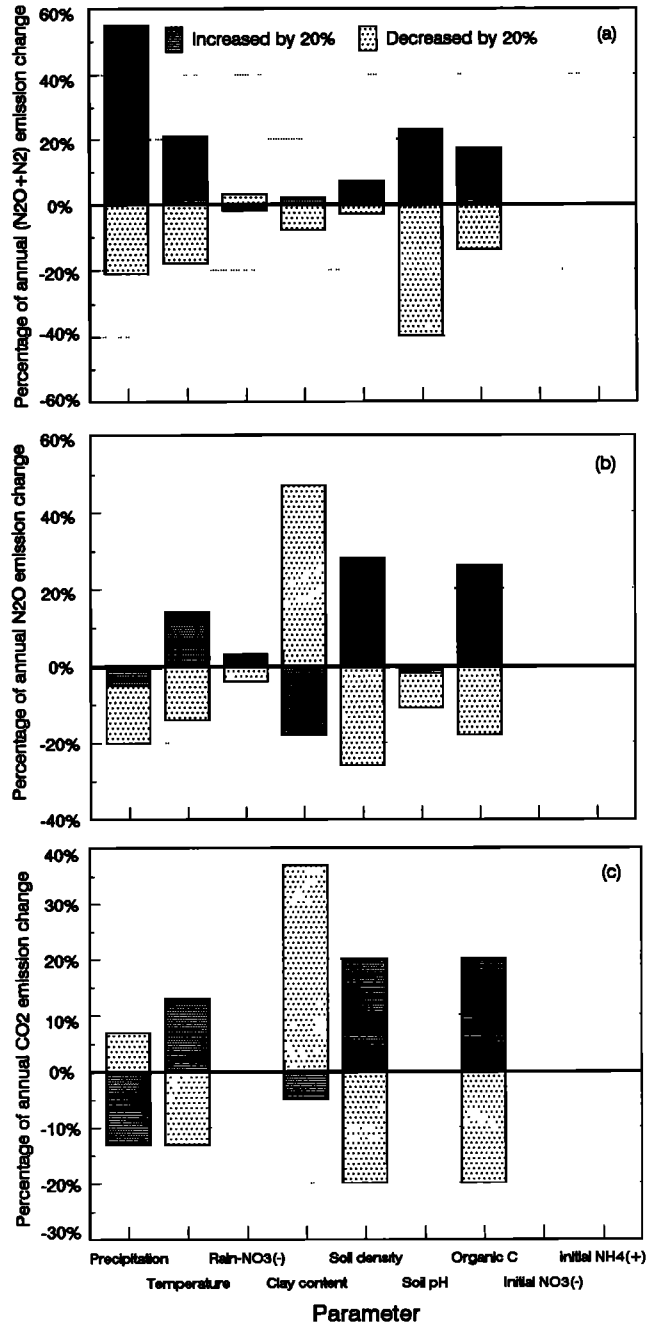

Fig. 17. Sensitivity of N_2O+N_2, N_2O and CO_2 emissions to increasing or decreasing input parameters by 20% in a loam soil in Iowa, USA. Changes in environmental parameter values (±20% from standard conditions; see Table 4) cause variations in (a) annual total denitrification ($N_2O + N_2$) flux, (b) annual N_2O flux, and (c) annual CO_2 flux.

content in rainfall, initial soil nitrate, and initial ammonium all had little or no effect on annual CO_2 emissions.

5. SUMMARY AND CONCLUSIONS

This paper describes a process-oriented rain-event model of soil nitrogen and carbon biogeochemistry that has been developed to predict N_2O emissions from agricultural soils over a growing season. A soil thermal-hydraulic model propagates a surface climate (daily mean air temperature and precipitation/irrigation) into the soil to determine soil temperature and moisture profiles. A decomposition submodel tracks the soluble carbon and nitrogen pools in the soil as plant residues decompose and soil microbes grow and die. A rain-event-initiated denitrification submodel calculates N_2O and N_2 production while the soil is wet during and following rain/irrigation events. The model allows for cropping, fertilizer and organic matter additions, and soil tillage so that agricultural practices can be simulated.

We performed a series of sensitivity studies of the total model and the three submodels to determine the factors which have strong effects on the behavior of DNDC and its three submodels (Table 11). Although the specific sensitivities depended on somewhat arbitrary standard conditions and variations, we feel that the model behavior (for N_2O evolution, total denitrification, and CO_2 emissions) is representative of what is (or would be) observed in the field. What these sensitivity studies do not portray are the impacts of agricultural land use practices and the interactions of the various processes as several factors change at once, as would happen when comparing different agroecosystems. Only through studying the complex interactions among soil climate, decomposition and denitrification processes, and agronomic practices can a complete picture of agroecosystem scale

nitrous oxide fluxes begin to emerge. A companion paper reports the comparison of DNDC simulations to field studies [Li et al., this issue].

Since most fundamental biogeochemical processes have been included in DNDC, it can potentially serve not only for estimating N_2O emissions but also for other processes related to mass exchange between soil systems and the atmosphere, such as fertilizer efficiency, carbon balance in soils, CH_4 and CO_2 emissions, nitrogen leaching, and groundwater pollution.

NOTATION

Thermal-Hydraulic Submodel Variables

a ET parameter ($= 0.49 + 0.079 \cdot I - 7.71e \cdot 5 \cdot I^2 + 6.75e \cdot 7 \cdot I^3$).

c_x specific heat of material x, J kg^{-1} $°C^{-1}$.

DAY_1 1/12 of the day's hours of daylight.

$d\Theta_i$ change in the water content of soil layer i.

dt time step length, s.

dT_i change in temperature of soil layer.

E actual ET, cm d^{-1}.

f drainage factor (f is presently fixed at 1.0).

h_i hydraulic head for level i, cm.

I ET parameter $\{=\Sigma_{n-1}^{12} (T_n^*/5)^{1.5}\}$, °C.

k_{dry} mineral soil thermal conductivity (0.029), J cm s^{-1} $°C^{-1}$.

k_i total soil thermal conductivity of layer i, J cm s^{-1} $°C^{-1}$.

$k_{i,i-1}$ average thermal conductivity of layers i and i-1, J cm s^{-1} $°C^{-1}$.

k_{om} organic matter thermal conductivity (0.0025), J cm s^{-1} $°C^{-1}$.

k_{water} water thermal conductivity (0.0057), J cm s^{-1} $°C^{-1}$.

$K_{i,i-1}$ average hydraulic conductivity of layers i and i-1, cm s^{-1}.

K_{sat} saturated hydraulic conductivity, cm s^{-1}.

l_i thickness of layer i, cm.

m_1 parameter $\{=y_o(1-W_o)^2 - y_o \cdot \beta / [W_o \cdot (1-W_o)]\}$, cm.

m_2 parameter $\{=2 \cdot W_o - 1 - y_o \cdot \beta / (m_1 \cdot W_o)\}$.

n soil porosity.

NM number of days in the month.

$q_{i,i-1}$ heat flux from layer i-1 down to layer i, J s^{-1}.

$Q_{i,i-1}$ flow of water per unit area from layer i-1 down to layer i, cm s^{-1}.

t time, s.

T_i temperature for level i, °C.

T_{mean} mean annual air temperature, °C.

T_n^* mean monthly air temperature of month n, °C.

W_o water content where retention curve has inflection (0.92).

z_{deep} depth where temperature variation assumed negligible (500), cm.

z_i depth of layer i (positive down from surface), cm.

β soil water parameter (range = 4 to 11.4).

σ material density, kg m^{-3}.

Θ_i layer i water content (fraction pore volume occupied).

Θ_{fc} soil water content at field capacity.

Θ_{wp} soil water content at the plant wilting point.

ϕ_{sat} water tension parameter, cm.

ϕ_o soil water tension at the inflection point, cm.

Decomposition Submodel Variables

AM accumulated NH_3 loss at time t, mol cm^{-2}.

B total microbial biomass produced, kg C.

$CLAY$ soil clay fractional content.

$CLAY_{max}$ maximum clay fraction in model soils (0.63).

COP CO_2 respired during residue decomposition, kg C.

CP C produced by potential residue decomposition, kg C ha^{-1} d^{-1}.

D diffusion coefficient (0.025), cm^2 d^{-1}.

$dNNO$ $NH4^+$ converted to NO_3^-, kg N ha^{-1} d^{-1}.

eff microbial efficiency for decomposing residues.

$FIXNH4$ proportion of adsorbed NH_4^+.

k_1 specific decomposition rate (SDR) of labile fraction, d^{-1}.

k_r SDR of the resistant fraction, d^{-1}.

K_{NH4} dissociation constant for NH_4^+:NH_3 equilibrium.

K_{H2O} dissociation constant for H^+:OH^- equilibrium.

TABLE 11. Highly Sensitive Factors Affecting DNDC Model and Submodels

Model	Item	Highly Sensitive Factors
DNDC model	N_2O	(1) Soil clay content
		(2) Soil organic C
		(3) Mean annual temperature
	N_2O+N_2	(1) Annual precipitation
		(2) Soil pH
		(3) Mean annual temperature
		(4) Soil organic C
	CO_2	(1) Soil organic C
		(2) Soil clay content
		(3) Mean annual temperature
		(4) Annual precipitation
Thermal-hydraulic submodel	Soil moisture	(1) Rainfall patterns
		(2) Soil texture
Decomposition submodel	Soluble C	(1) Initial organic C
		(2) Soil temperature
		(3) Soil moisture
		(4) Dry period duration
	Nitrate	(1) Initial organic C
		(2) Dry duration
		(3) Soil temperature
		(4) Soil moisture
Denitrification submodel	N_2O	(1) Precipitation
		(2) Soil soluble C
		(3) Soil nitrate
		(4) Soil texture

K_{3s} nitrification rate at 35°C (25), mg kg^{-1} soil d^{-1}.

$NH3$ NH₃ concentration in liquid phase, mol cm^{-3}.

$NH3_m$ NH₃ concentration in liquid phase, mol L^{-1}.

$NH4$ NH₄$^+$ concentration in the soil liquid, g N kg-1 soil.

$NH4_m$ NH₄$^+$ concentration in liquid phase, mol L^{-1}.

$NH4(t)$ available NH₄$^+$ at time t, kg N ha^{-1}.

NP N produced by potential residue decomposition per day plus free NH₄$^+$ and NO₃$^-$ in soil, kg N ha^{-1}.

$N2O$ daily emission of N₂O, ng N g^{-1} soil d^{-1}.

pH soil pH.

R_c total decomposed residue C, kg C.

S labile fraction of organic C compounds in the pool.

t time, d.

μ_{tm} combined temperature and moisture reduction factor.

μ_{CLAY} clay content reduction factor {=log(.14/CLAY) + 1}.

μ_{CN} C:N ratio reduction factor {=0.2 + 7.2/(CP/NP)}.

$\mu_{m,n}$ moisture reduction factor for nitrification.

$\mu_{t,n}$ temperature reduction factor for nitrification.

Denitrification Submodel Variables

AD adsorption factor depending on clay content in the soil {range = 0-2}.

AM accumulated NH₃ loss at time t, mol/cm².

B total biomass of the denitrifier, kg C ha^{-1}.

$(dB/dt)_g$ potential growth rate of denitrifier biomass, kg C ha^{-1} d^{-1}.

$(dB/dt)_d$ death rate of denitrifier biomass, kg C ha^{-1} h^{-1}.

C mineralized carbon concentration in the soil, kg C ha^{-1}.

C_{con} consumed soluble C, kg C ha^{-1}.

$C_{con,t}$ total consumption of soluble C, kg C ha^{-1}.

CNR_{DN} C/N ratio in denitrifiers (3.45).

$CO2$ CO₂ production, kg C ha^{-1}.

$K_{c,1/2}$ half-saturation value of soluble C, kg C m^{-3}.

$K_{N\pi Oy,1/2}$ half-saturation value of NO₃$^-$, NO₂$^-$, or N₂O, kg N m^{-3}.

M_c maintenance coefficient of carbon, kg C kg^{-1} C h^{-1}.

$M_{N\pi Oy}$ maintenance coefficient of NO₃$^-$, NO₂$^-$,or N₂O, kg N kg^{-1} h^{-1}.

N total nitrogen as NO₃$^-$, NO₂$^-$,and N₂O, kg N ha^{-1}.

$(dN/dt)_{asm}$ nitrogen assimilation rate by denitrifiers, kg N ha^{-1} d^{-1}.

$NxOy$ concentration of NO₃$^-$, NO₂$^-$, or N₂O in soil water, kg N ha^{-1}.

$P(N2O)$ imitted fraction of the total N₂O evolved in a day.

$P(N2)$ emitted fraction of the total N₂ evolved in a day.

PA air-filled fraction of the total porosity.

PH soil pH.

t time, d.

T temperature, °C

u_{DN} relative growth rate of the denitrifiers.

$u_{N\pi Oy}$ relative growth rate of NO₃$^-$, NO₂$^-$, or N₂O denitrifiers.

$u_{N\pi Oy,max}$ maximum growth rate of NO₃$^-$, NO₂$^-$, or N₂O denitrifiers.

Y_c maximum growth yield on soluble carbon, kg C kg^{-1} C.

$Y_{N\pi Oy}$ maximum growth yield on NO₃$^-$, NO₂$^-$,or N₂O, kg C kg^{-1} N.

$\mu_{PHN\pi Oy}$ soil pH reduction factor.

$\mu_{t,da}$ soil temperature reduction factor.

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