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# A process-oriented model of $N_2O$ and NO emissions from forest soils: 1. Model development

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**Abstract.** To predict emissions of nitrous oxide ($N_2O$) and nitric oxide (NO) from forest soils, we have developed a process-oriented model by integrating several new features with three existing models, PnET, Denitrification-Decomposition (DNDC), and a nitrification model. In the new model, two components were established to predict (1) the effects of ecological drivers (e.g., climate, soil, vegetation, and anthropogenic activity) on soil environmental factors (e.g., temperature, moisture, pH, redox potential, and substrates concentrations), and (2) effects of the soil environmental factors on the biochemical or geochemical reactions which govern NO and $N_2O$ production and consumption. The first component consists of three submodels for predicting soil climate, forest growth, and turnover of soil organic matter. The second component contains two submodels for nitrification and denitrification. A kinetic scheme, a so-called "anaerobic balloon," was developed to calculate the anaerobic status of the soil and divide the soil into aerobic and anaerobic fractions. Nitrification is only allowed to occur in the aerobic fraction, while denitrification occurs only in the anaerobic fraction. The size of the anaerobic balloon is defined by the simulated oxygen partial pressure which is calculated based on oxygen diffusion and consumption rates in the soil. As the balloon swells or shrinks, the model dynamically allocates substrates (e.g., dissolved organic carbon, ammonium, nitrate, etc.) into the aerobic and anaerobic fractions. With this approach, the model is able to predict both nitrification and denitrification in the same soil at the same time. This feature is important for soils where aerobic and anaerobic microsites often exist simultaneously. With the kinetic framework as well as its interacting functions, the PnET-N-DNDC model links ecological drivers to trace gas emissions. Tests for validating the new model are published in a companion paper [*Stange et al.*, this issue].

## 1. Introduction

Forest ecosystems cover approximately 1/3 of the Earth's land surface [*Potter et al.*, 1996]. Emissions of nitrogen trace gases from forest soils have been identified as an important source for atmospheric nitrous oxide ($N_2O$) and nitric oxide (NO). The *Intergovernmental Panel on Climate Change (IPCC)* [1992] estimates that $N_2O$ emissions from tropical and temperate forests range from 2.4 -5.7 Tg N $yr^{-1}$. *Lee et al.* [1997] estimate that NO emissions from forest soils are approximately 3.6 Tg N $yr^{-1}$, representing 33% of all NO emissions from soils worldwide [*IPCC*, 1992]. These estimates have a high degree of uncertainty due to the spatial and temporal variation of gas flux rates. During the last 2 decades, numerous laboratory and field studies were conducted to measure soil NO and $N_2O$ emissions from various ecosystems including forests [e.g., *Keller et al.*, 1986, 1988; *Bowden et al.*, 1991; *Papen et al.*, 1993; *Butterbach-Bahl et al.*, 1997, 1998]. In particular, the utilization of a series of advanced techniques, such as automated chambers [e.g., *Butterbach-Bahl et al.*, 1997; *Crill et al.*, 1999], $^{15}N$ tracers [*Mosier and Schimel*, 1993; *Davidson et al.*, 1991; *Hart et al.*, 1994; *Stark and Hart*, 1997], inhibitors (e.g., acetylene, nitrapyrin, oxygen, etc.) [*Hynes and Knowles*, 1978; *Davidson et al., 1986*; *Robertson and Tiedje*, 1987], and barometric process separation method [*Ingwersen et al.*, 1999], has produced sound data sets which not only revealed the magnitude of the fluxes, but also enabled to analyze the mechanisms of production and consumption of NO and $N_2O$. On the basis of field and laboratory observations, process models have been developed. The "Hole-in-the Pipe" model, developed by *Firestone and Davidson* [1989], has now been applied to predicting NO and $N_2O$ emissions from tropical forests [*Davidson et al.*, 1998]. The model calculates the sum of NO and $N_2O$ emissions as a fraction of soil N mineralization rates, and $NO/N_2O$ ratio based on soil moisture. The concept of a leaky pipe has also been adopted by several other models. In the Carnegie-Ames-Stanford approach (CASA) model, the primary controlling factors are gross rates of N mineralization and soil moisture. The total potential loss of N as $N_2O$ and NO is set as a constant fraction (1%) of mineralized N. The relative proportions of N trace gas emission ($NO:N_2O:N_2$) are a function of soil moisture [*Potter et al.*, 1993]. In the new version of the CENTURY model [*Parton et al.*, 1996], nitrification rate is calculated based on decomposition rate, and nitrification-induced $N_2O$ flux is a fraction of the nitrification rate. Denitrification rate is a function of soil $NO_3^-$ content, soil respiration, and soil moisture. The $N_2O/N_2$ ratio is calculated with an empirical equation developed based on the 5-day experiment



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performed by *Weier et al.* [1993]. All the three models predict trace gas fluxes as fractions of rates of either mineralization or nitrification with little consideration of the kinetics of the relevant biochemical reactions. In fact, it is the kinetics of production, consumption, and diffusion of NO and $N_2O$ in the sequential reactions which brings about the characteristic variation of the gas fluxes in space and time. Therefore lack of these key features could make a model less process-driven and hence less applicable across climate zones, soil types, or ecosystems. In order to derive a widely applicable N model we have developed a new model which attempts to capture the biochemical kinetics of nitrification and denitrification. This paper reports the construction of the PnET-N-DNDC model, which was based on a series of hypotheses and results generated from various field and laboratory observations.

## 2. Hypotheses for Modeling NO and $N_2O$ Emissions

Emissions of NO and $N_2O$ have been observed from various soils. On the basis of field measurements or laboratory incubation studies, researchers have concluded that production and consumption of NO and $N_2O$ in soils are mainly due to activity of soil microbes [e.g., *Firestone et al.*, 1980; *Anderson and Levine*, 1986; *Davidson et al.*, 1986; *Tiedje et al.*, 1984], although chemical decomposition of nitrite has conditional contributions to soil NO production [e.g., *Van Cleemput and Baert*, 1984; *Chalk and Smith*, 1983]. The challenges of modeling NO and $N_2O$ emissions attribute to three reasons: (1) NO or $N_2O$ is a multisource gas. There are at least three sources, namely, nitrification, denitrification, and chemodenitrification. The three reactions are so different in their thermodynamics and kinetics that, when they are mixed together, the pattern of NO or $N_2O$ fluxes is unavoidably complex. (2) Each of the reactions is driven by a number of forces including soil environmental factors (e.g., temperature, moisture, pH, Eh, and substrate concentration) and ecological drivers (e.g., climate, soil physical properties, vegetation, and anthropogenic activity). Any change in the combination of the forces will alter the magnitude and/or pattern of NO or $N_2O$ fluxes. (3) NO or $N_2O$ is an intermediate or byproduct of nitrification and denitrification. It means that the fluxes of NO or $N_2O$ are determined by the kinetics of production, consumption, and diffusion of the gases in the sequential biochemical reactions. To handle such a complex system, we adopted the concept of biogeochemical field to back our modeling effort. Paralleling the concept of biogeochemical cycle which describes transport and transformation of the chemical elements, the biogeochemical field answers what controls the elements' behaviors in ecosystems. A biogeochemical field is an assembly of forces regulating the concerned biochemical or geochemical reactions in a specific ecosystem. The soil NO and $N_2O$ emissions from an ecosystem must be controlled by a series of reactions driven by the forces (Figure 1). To link the driving forces to NO and $N_2O$ emissions, we constructed the PnET-N-DNDC model with two components to link the ecological drivers to the soil environmental factors, and the soil environmental factors to the relevant reactions, respectively.

A crucial environmental factor which influences microbial production of gaseous N-products is the aeration status of soils. By use of specific inhibitors or $^{15}N$-labeled substrates, many researchers have observed the effects of soil aeration status on N-turnover during nitrification and denitrification [e.g., *Rosswall*, 1982; *Stevens et al.*, 1997] and on the production of N-trace gases ($N_2O$, NO) during these processes [e.g., *Anderson and Levine*, 1986]. Simulation of soil redox potential is inherently important for a process model of NO and $N_2O$ emissions. Currently, most of the trace gas models (e.g., CASA, CENTURY, DNDC, etc.) only use

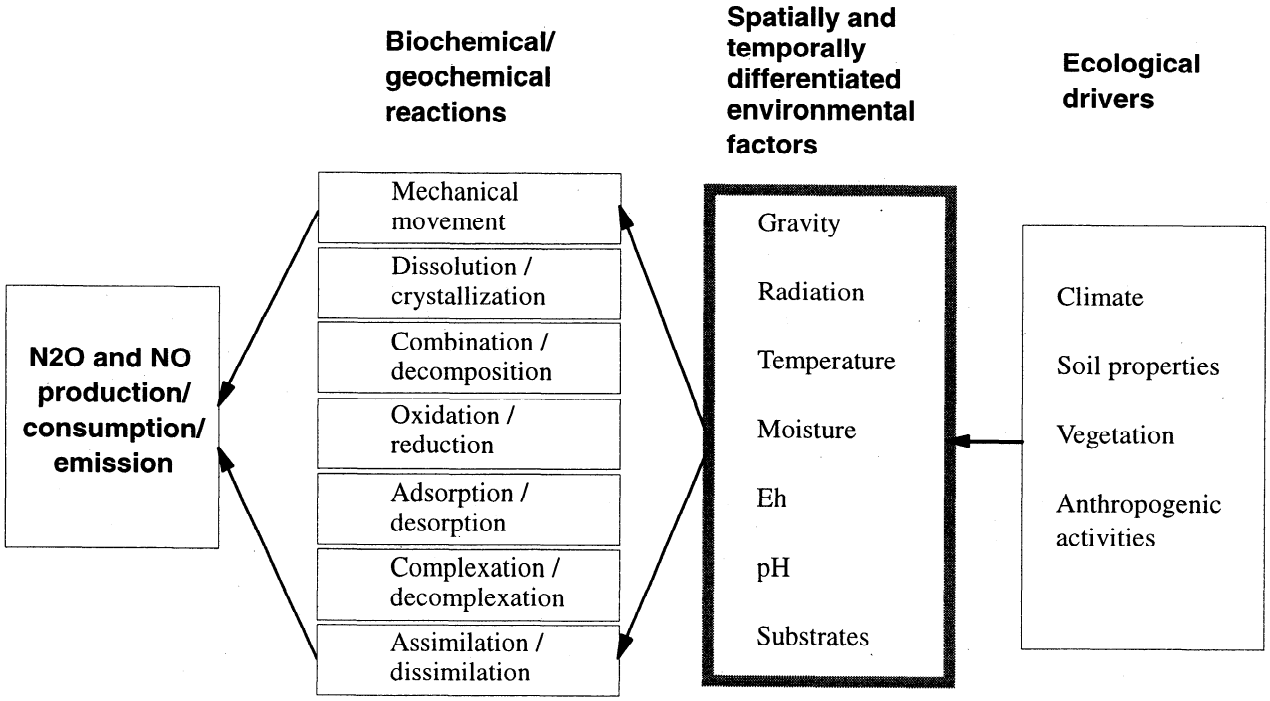


**Figure 1.** A biogeochemical field is an assembly of forces controlling concerned biochemical or geochemical reactions in a specific ecosystem. The ecological drivers control spatial and temporal variations of the environmental factors, and the latter regulate all of the relevant geochemical and/or biochemical reactions. A biogeochemical model is to integrate the links among the ecological drivers, the environmental factors, and the biogeochemical reactions. The PnET-N-DNDC model was developed based on this biogeochemical concept.

**Table 1.** Summary of Effects of Soil Environmental Factors on Nitrification, Denitrification, and Chemodenitrification

| Soil Factor | Nitrification | Denitrification | Chemodenitrification |
|---|---|---|---|
| Microorganism | nitrifying bacteria | denitrifying bacteria | none |
| Substrates | DOC, $NH_4^+$ | DOC, $NO_3^-$, $NO_2^-$, NO, and $N_2O$ | $NO_2^-$ |
| Temperature | optimum range: 25°-30°C | optimum range: 25°-30°C | no optimum temperature |
| Moisture | affected only when moisure is very low | favors high moisure | no significant effect |
| Eh | no significant effect until pO2 < 0.5% | crucial factor for anaerobic microsites | no direct effect |
| pH | optimum range: 7-8 | increase with increasing pH; but different denitrifiers have different sensitivities | reaction occurs only at low pH (<5) |

soil moisture as an indicator of soil aeration status. It is convenient, but not sufficient. For example, two soils with the same moisture could have very different redox potentials if they have different respiration rates. In addition, the redox potential could keep decreasing in a submerged soil although its moisture remains constant. In the new model, we developed a kinetic scheme to predict the soil aeration status for calculating nitrification and denitrification rates.

The reactions of nitrification, denitrification, and chemodenitrification are separately simulated in the model due to their inherently different mechanisms (see Table 1). Nitrifiers require aerobic conditions as they utilize the enzyme ammonia-monooxygenase, which needs molecular oxygen to oxidize ammonium ($NH_4^+$) or ammonia ($NH_3$) to hydroxylamine [*Wood*, 1987]. In contrast, anaerobic conditions favor denitrifiers as they can use nitrogen oxides as electron acceptors when oxygen is depleted in the soil [e.g., *Poth*, 1986; *Remde and Conrad*, 1990; *Kuenen and Robertson*, 1987]. Owing to the multiple enzymatic pathways of the microbes involved, it is difficult to make clear distinctions between the nitrifying and denitrifying bacteria. For example, some heterotrophic nitrifiers (e.g., *Thiosphaera pantotropha*) can simultaneously respire oxygen and nitrogen oxides which permits nitrification and denitrification to take place in the same soil at the same time [e.g., *Hutchinson and Davidson*, 1993; *Kuenen and Robertson*, 1994]. In addition, *Robertson et al.* [1988] indicates that many of the common denitrifying bacteria are also heterotrophic nitrifiers. Nitrification by heterotrophic bacteria may be responsible for all $NO_3^-$ and $NO_2^-$ production in those soils in which conditions do not favor autotrophic nitrification, for example, soils with low pH [e.g., *Lang and Jagnow*, 1986; *Papen et al.*,1993]. In spite of the complexity in categorizing the microbes, most researchers agree that (1) the dominant role of the nitrifying bacteria is to oxidize $NH_4^+$ under aerobic conditions, although other factors (e.g., soil moisture, pH, etc.) affect their activity [e.g., *Williams et al.*, 1987; *Galbally*, 1989]; and (2) the dominant role of the denitrifying bacteria is to reduce nitrogen oxides under anaerobic or semianaerobic conditions [e.g., *Tiedje et al.*, 1984; *Anderson and Levine*, 1986; *Conrad*, 1996]. Hereafter, to simplify terminology, we use "nitrifiers" to represent the nitrifying microbes, regardless whether they are heterotrophic or autotrophic, and "denitrifiers" to represent the denitrifying microbes. On the basis of observations from numerous field measurements and laboratory experiments, we composed four principles as a basis for our model development: (1) Nitrification, denitrification, and chemodenitrification are the three major reactions related to NO and/or $N_2O$ production/consumption in soils. Nitrification occurs under aerobic conditions, and denitrification occurs mainly under anaerobic conditions. Chemodenitrification occurs only in acidic soils. (2) The key factors affecting nitrification and denitrification are soil redox potential (or Eh) and the size and activity of the nitrifier and denitrifier populations in the soil. (3) Aerobic and anaerobic microsites exist simultaneously in most soils. Nitrification and denitrification occur in the aerobic and anaerobic microsites, respectively. The ratio between aerobic and anaerobic microsites is controlled by the soil redox potential. (4) Only NO is produced by chemodenitrification.

## 3. Model Framework

The new model was named PnET-N-DNDC as it was constructed by integrating a series of new developments with three existing models, namely, the Photosynthesis-Evapotranspiration (PnET) model, the Denitrification-Decomposition (DNDC) model, and the nitrification model. PnET is a forest physiology model for predicting forest photosynthesis, respiration, organic carbon production and allocation, and litter production [*Aber and Federer*, 1992]. DNDC is a soil biogeochemistry model used for predicting soil decomposition and denitrification [*Li et al.*, 1992]. The nitrification model was developed for predicting nitrifier growth/death rates, nitrification rate, and nitrification-induced NO and $N_2O$ production (F. Stange, manuscript in preparation, 1999). Observations from field and laboratory studies have shown a complex picture of soil NO and $N_2O$ emissions from multiple sources which are directly driven by a number of soil environmental factors including temperature, moisture, pH, Eh, and substrate abundance. These soil environmental factors are controlled by several ecological drivers, such as climate, soil physical properties, vegetation, and anthropogenic activities. Two components were constructed in the model to reflect the links between the ecological drivers, the soil environmental factors, and NO and $N_2O$ fluxes.

The first component contains three interacting submodels to quantify impacts of ecological drivers on the soil environmental factors. The soil climate submodel calculates soil temperature, moisture, and redox potential profiles based on daily climate data, soil physical properties, soil water status, thermal/hydraulic impacts of plants, and soil respiration. The forest growth submodel simulates forest growth driven by solar radiation, temperature, water stress, and N stress, and passes the litter production, water and N demands, and root respiration to the soil climate submodel or the decomposition submodel. The decomposition submodel tracks concentrations of substrates (e.g., dissolved organic carbon (DOC), $NH_4^+$, and $NO_3^-$) based on climate, soil properties, and management measures.

The second component, consisting of two submodels, predicts impacts of the soil environmental factors on nitrification and denitrification. The nitrification submodel predicts NO and $N_2O$

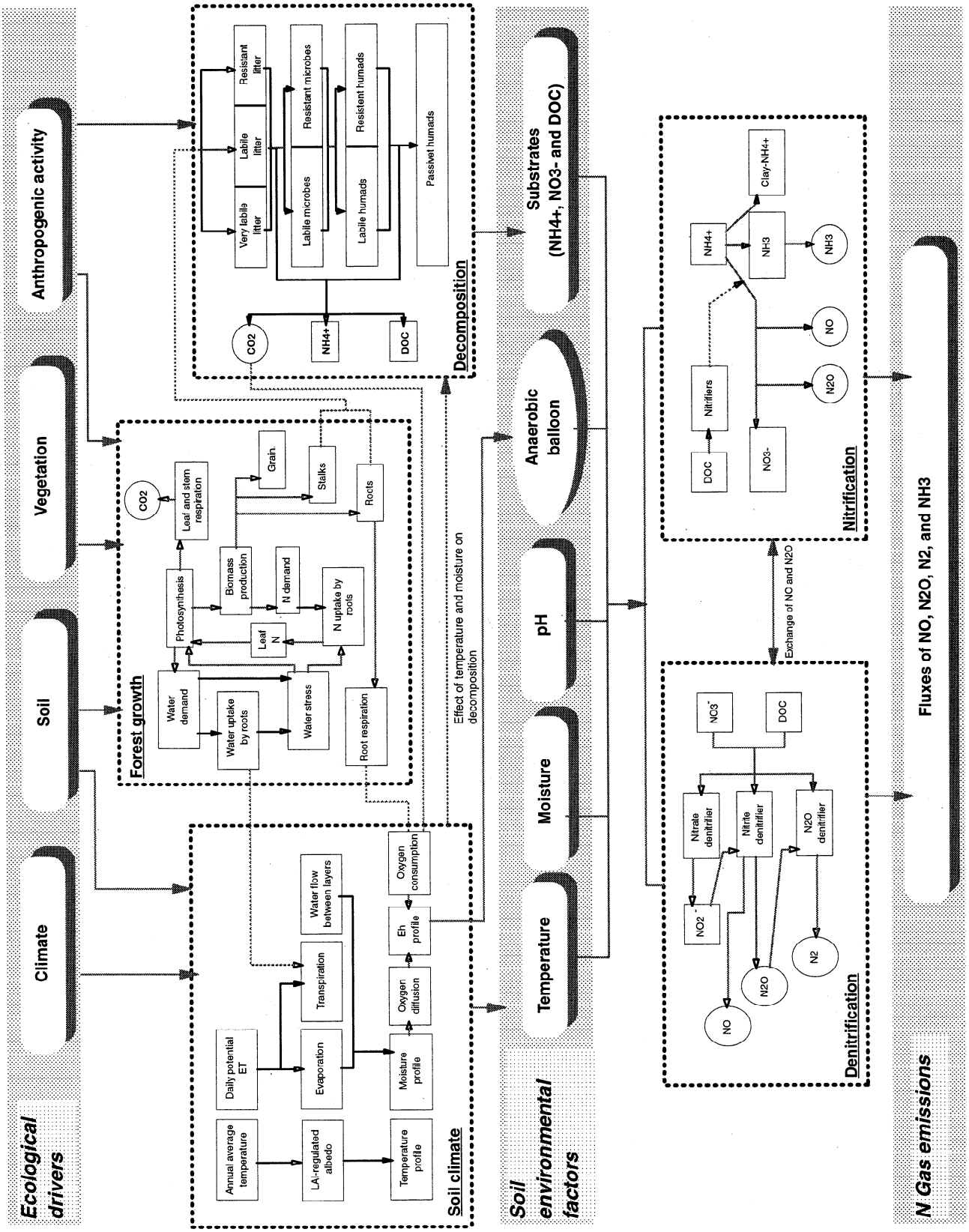
The PnET-N-DNDC Model
Ecological drivers
Climate
Soil
Vegetation
Anthropogenic activity
Soil climate
Annual average temperature
Daily potential ET
LAI-regulated albedo
Evaporation
Transpiration
Temperature profile
Moisture profile
Oxygen diffusion
Eh profile
Oxygen consumption
Water flow between layers
Forest growth
CO2
Leaf and stem respiration
Photosynthesis
Biomass production
Grain
Stalks
Roots
N demand
Leaf N
N uptake by roots
Water demand
Water uptake by roots
Water stress
Root respiration
Decomposition
Very labile litter
Labile litter
Resistant litter
Labile microbes
Resistant microbes
Labile humads
Resistent humads
Passivel humads
CO2
NH4+
DOC
Effect of temperature and moisture on decomposition
Soil environmental factors
Temperature
Moisture
pH
Anaerobic balloon
Substrates (NH4+, NO3- and DOC)
Nitrification
NH4+
Clay-NH4+
NH3
NH3
NO
N2O
Nitrifiers
DOC
NO3-
Exchange of NO and N2O
Denitrification
NO3-
DOC
Nitrate denitrifier
Nitrite denitrifier
N2O denitrifier
NO2-
NO
N2O
N2
N Gas emissions
Fluxes of NO, N2O, N2, and NH3

**Table 2.** Functions and Parameters for $O_2$ Diffusion and Volumetric Fraction of Anaerobic Microsites (ANVF)

| Equation No. | Function | Equation |
|---|---|---|
| 1 | oxygen diffusion coefficient in soil | $D_{s[L]} = D_{air}\ afps_{[L]}^{3.33} / afps_{max[L]}^{2.0}$; |
| 2 | oxygen diffusion rate affected by frost | $D_{s[L]} = D_{s[L]}\ F\_frost;\ 0 < D_{s[L]} < 1$<br>if T > 0 °C, F_frost = 1.2;<br>if T <= 0 °C, F_frost = 0.8;<br>$D_{s[L]} = D_{s[L]}\ F\_frost;\ 0 < D_{s[L]} < 1$<br>if T > 0 °C, F_frost = 1.2;<br>if T <= 0 °C, F_frost = 0.8; |
| 3 | oxygen partial pressure | $d(pO_{2[L]})/dt = (d(D_{s[L]}\ d(pO2_{[L]})/dz)/dz - R)/afps$; |
| 4 | Volumetric fraction of anaerobic microsites | $anvf_{[L]} = a\ (1-(b\ pO_{2[L]}/\ pO_{2air}))$; |

a, b, constant coefficients; afps, air-filled porosity; $afps_{max}$, porosity; anvf, volumetric fraction of anaerobic microsites; $D_{air}$, oxygen diffusion rate in the air, 0.07236 $m^2/h$ [*Beisecker*, 1994]; $D_s$, oxygen diffusion coefficient in soil; F_frost, frost factor; L, layer number; $pO_2$, oxygen partial pressure; R, oxygen consumption rate (kg C $ha^{-1}h^{-1}$); t, time (h); z, soil depth (m).

production by tracking growth and death of nitrifiers under aerobic conditions. The denitrification submodel calculates growth and death of denitrifiers, substrate consumption, and gas diffusion under anaerobic conditions. Fluxes of NO and $N_2O$ are a result of competition among the kinetics of production, consumption, and diffusion of the two gases in the soil. The five interacting submodels link the ecological drivers to the NO and $N_2O$ emissions (Figure 2). The soil climate and decomposition algorithms were adopted from the DNDC model, and the forest growth submodel was adopted from the PnET model. The structures and functions of these three submodels basically remain as they were in the parent models (further descriptions of these models are given by *Li et al.* [1992, 1994] and *Aber et al.* [1995, 1996]). In this paper, we only focus on the new features including soil aeration, NO and $N_2O$ production/consumption, and effects of forest characteristics on N-gas evolution.

## 4. An "Anaerobic Balloon"

Since nitrification and denitrification can simultaneously occur in aerobic and anaerobic microsites, respectively, in the same soil, the model must determine how to allocate substrates, such as DOC, $NH_4^+$, $NO_3^-$, etc., into the two soil fractions with different aeration status. A simple kinetic scheme was implemented to quantify the volumetric fraction of the anaerobic microsites in the soil. The scheme can be described as a dynamic "anaerobic balloon" within the soil matrix.

The size of the anaerobic balloon (i.e., volumetric fraction of the anaerobic microsites) is calculated based on soil redox potential. According to the Nernst equation, soil redox potential is determined by the product of the concentrations of all the oxidizing species versus the product of the concentrations of all the reducing species in the soil liquid phase [*Stumm and Morgan*, 1981]. The common oxidizing species in soils are oxygen, $NO_3^-$, $SO_4^{2-}$, $Fe^{3+}$, $Mn^{5+}$, $CO_2$, etc., and the common reducing species are DOC, $H_2S$, $Fe^{2+}$, $Mn^{3+}$, $H_2$, etc. Transferring an electron from a reducing species to an oxidizing species is regulated by the change in the Gibbs free energy in the system. Since oxygen possesses the lowest Gibbs free energy change to accept electrons, oxygen is usually the dominant oxidizing species in aerobic soils. Within the Eh range from 700 to 250 mV, soil redox status is dominated by the oxygen partial pressure ($pO_2$). Theoretically, other oxidizing species will not be reduced until oxygen has been depleted. Denitrifying bacteria start to use $NO_3^-$ as electron acceptor at an Eh of 350-250 mV when oxygen is close to being depleted [e.g., *Parkin and Tiedje*, 1984; *Ingwersen et al.*, 1999].

A one-dimensional soil oxygen diffusion algorithm was developed to estimate $pO_2$ in the forest soil profile. In the model, the simulated soil profile is divided into a series of horizontal layers. For each time step, oxygen fluxes between layers are determined by the gradients of soil $pO_2$. The gradient-driven equations are numerically modeled by explicit finite difference equations based on the Fick's first law. The diffusion coefficient is calculated based on the equations used by *Millington and Quirk* [1961] (see equation (1) in Table 2). Soil $pO_2$ is calculated based on the oxygen diffusion rate and consumption rate for each layer (equation (3) in Table 2). Oxygen consumption rate is the sum of soil microbial respiration and root respiration rates [e.g., *Tiedje et al.*, 1984; *Flessa and Beese*, 1995; *Sierra et al.*, 1995]. The microbial and root respiration rates are predicted by the decomposition and forest growth submodels, respectively (see Figure 2). The oxygen diffusion rate is affected by soil structure and texture. A fine-textured soil has smaller pores, and thus anoxic microsites are created at lower soil moisture contents than in a coarse-textured soil [*Parton et al.*, 1996]. Soil aggregate structure has been reported to be related to the correlation between $pO_2$ and volumetric fraction of anaerobic microsites [*Smith*, 1980, 1990]. Owing to lack of soil aggregate data for a wide variety of soils, we used soil field capacity as a substitute for the soil effective porosity for the oxygen diffusion calculation.

Many researchers have reported the effect of water logging on soil aeration status [e.g., *Smith*, 1990; *Sexstone et al.*, 1985, 1988]. During a rain event, the top layers of the soil could be temporally saturated by rainwater (e.g., several hours). This wetting could

**Figure 2.** The PnET-N-DNDC model consists of five submodels for predicting soil climate, forest growth, decomposition, nitrification, and denitrification, respectively. The first three submodels form a component to calculate soil climate/substrate profiles driven by the ecological drivers; and the last two submodels form another component to predict nitrification, denitrification, and chemodenitrification rates based on the soil environmental conditions.

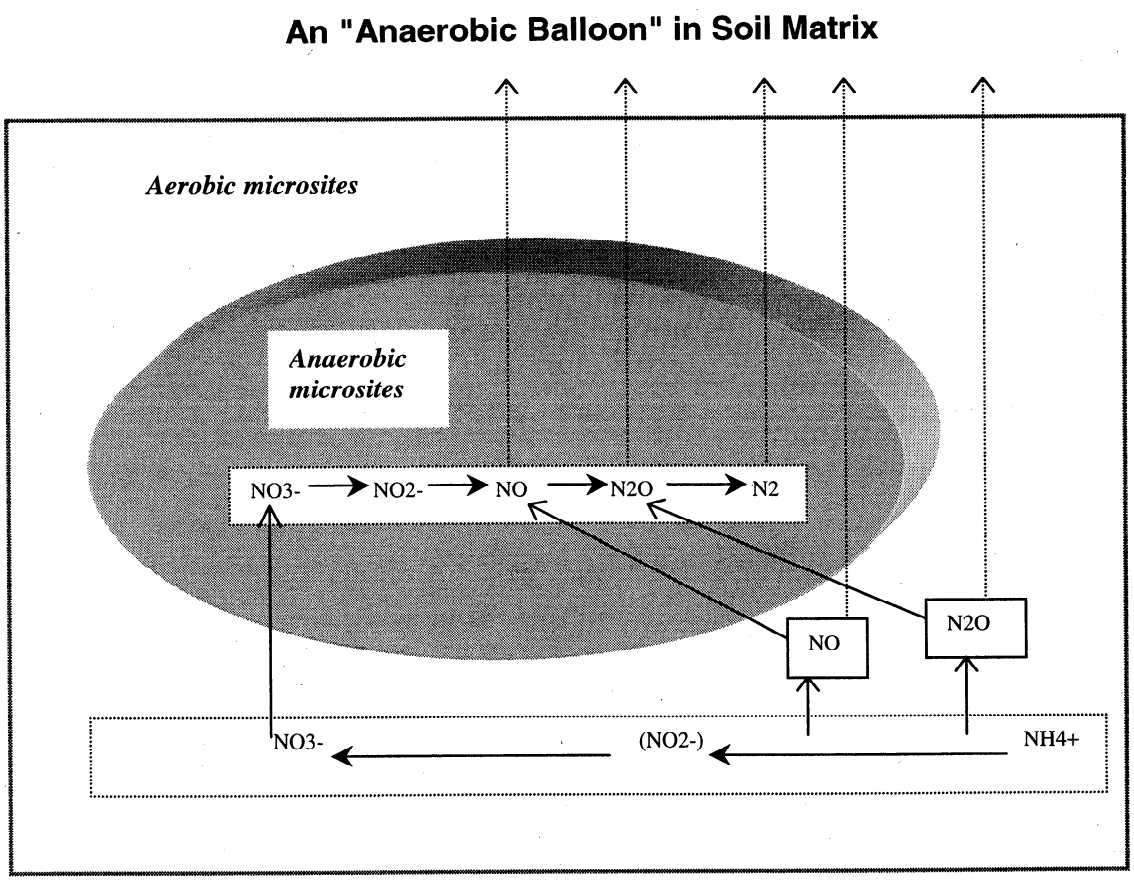


**Figure 3.** A simple kinetic scheme, "anaerobic balloon," is implemented in the PnET-N-DNDC model to quantify relative proportions of aerobic/anaerobic microsites in the soil matrix. Nitrification is allowed to occur in the aerobic fraction (out of the balloon) and denitrification in the anaerobic fraction (within the balloon). Substrates (e.g., $NH_4^+$, $NO_3^-$, DOC, etc.) as well as products (e.g., NO and $N_2O$) are allocated into the two fractions at an hourly time step.

momentarily create a low redox potential in some of the microsites and hence stimulate denitrification [e.g., *Rudaz et al.*, 1991; *Smith and Parsons*, 1985]. Following the DNDC model [*Li et al.*, 1992], we assume that all rain events are of constant intensity (0.5 cm/h) and of variable duration. At the beginning of each time step, rainfall saturates the soil layer by layer to the depth that it can fill. In the saturated layers, the oxygen diffusion rate is reduced to 1/10,000 of the diffusion rate in air (i.e., 0.07236 $m^2$/h in air [*Beisecker*, 1994]).

This switch function of soil aeration status has been confirmed by many observations [*Goreau et al.*, 1980; *Knowles*, 1982; *Stevens et al.*, 1998]. *Smith* [1980, 1990] established equations to describe the exponential increase in the volumetric fraction of anaerobic microsites with decreasing $pO_2$. A simplified linear correlation was used in our model to estimate the size of the anaerobic balloon (equation (4) in Table 2). The anaerobic balloon regulates rates of nitrification and denitrification by distributing the substrates into the aerobic and anaerobic fractions of the soil. When the anaerobic balloon swells, (1) more substrates including DOC, $NH_4^+$, $NO_3^-$, NO, and $N_2O$ will be allocated into the anaerobic microsites for denitrification, (2) less DOC and $NH_4^+$ will be left in the aerobic microsites for nitrification, and (3) the pathway for the denitrification gas products (e.g., NO and $N_2O$) to escape from the anaerobic balloon will become longer, so that the probability that the N-gases are further reduced by denitrification will increase (Figure 3). When the anaerobic balloon shrinks, all the trends will reverse. Figure 4 shows how the anaerobic volumetric fraction is affected by rainfall duration (Figure 4a), soil plus root respiration (Figure 4b), and soil texture (Figure 4c) due to their effects on oxygen diffusion and oxygen consumption.

## 5. Nitrification

Nitrification has been identified as an important source of NO and $N_2O$ in soils as demonstrated by experiments using inhibitors, the $^{15}N$-tracers, and other techniques [e.g., *Tiedje et al.*, 1984; *Anderson and Levine*, 1986; *Lipschultz et al.*, 1981; *Hooper and Terry*, 1979; *Papen et al.*, 1989]. Ammonium oxidation requires a special type of enzyme (i.e., ammonia-monooxygenase) [*Wood*, 1987], which oxidizes ammonia to hydroxylamine by utilizing molecular oxygen. Thus $NH_4^+$ concentration and $pO_2$ should be two important control factors for nitrification. However, several researchers have reported that $pO_2$ was not a crucial factor for nitrification unless $pO_2$ was very low (<0.5%) [e.g., *Anderson and Levine*, 1986; *Bollmann and Conrad*, 1998]. These observations are supported by microbiological studies. In the PnET-N-DNDC model, the anaerobic balloon is defined as a fully anaerobic area, so that nitrification is only allowed to occur outside of the balloon. In this aerobic area, nitrifier activity is controlled by several other factors but no longer by oxygen.

In addition to oxygen, temperature, moisture, pH, and substrate concentration are the major environmental factors controlling soil microbial activity. Nitrification-induced NO fluxes are highly

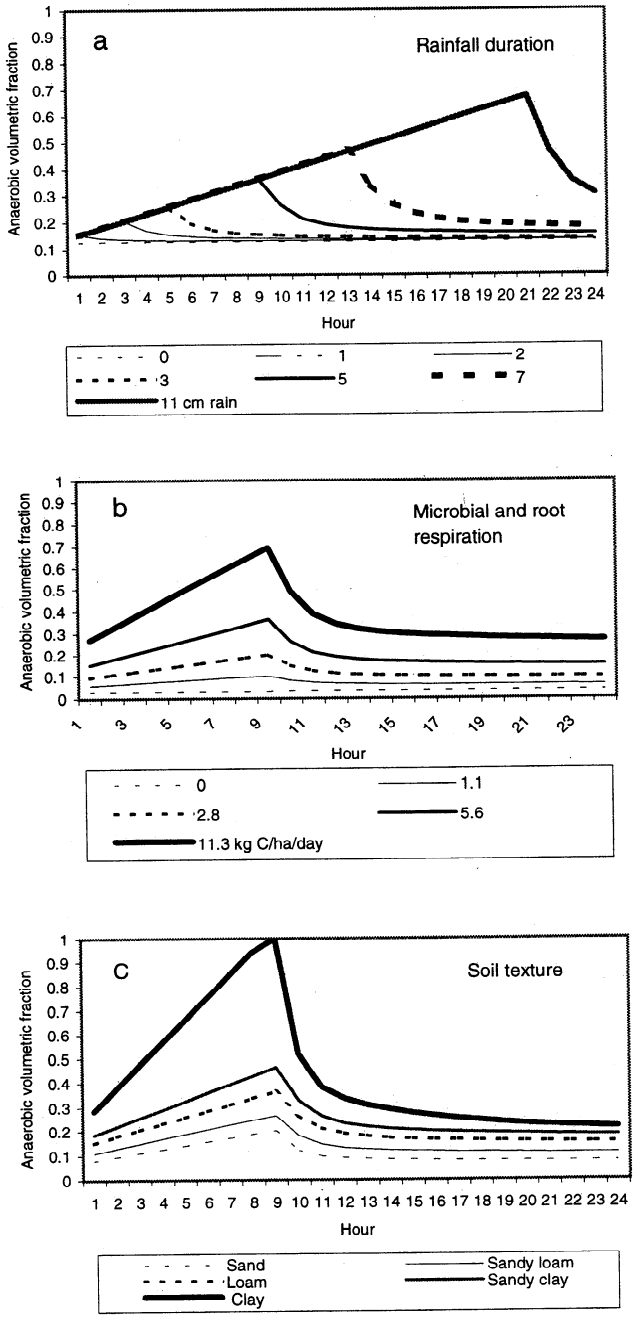


**Figure 4.** Effects of rainfall duration, soil respiration, and soil texture on soil anaerobic volumetric fraction (ANVF) during a simulated rainfall event. (a) When the rainfall lasted longer (from 1 to 11 hours), more of the soil microsites turned into anaerobic, and the anaerobic microsites sustained longer. (b) If the rainfall duration was constant (e.g., 5 hours in this case), increase in the soil (microbial plus root) respiration rate increased the anaerobic microsites. (c) Changing the soil texture from sand to clay increased the anaerobic microsites in the soil.

temperature-dependent [e.g., *Johansson*, 1984; *Slemr and Seiler*, 1991; *Valente and Thornton*, 1993]. *Ingwersen et al.* [1999] observed that nitrification rates increased with increasing temperature in the temperature range of 5°-20°C through soil incubation experiments with the samples from the Höglwald Forest in Germany. As most biological processes, nitrification exhibits a characteristic temperature optimum beyond which its activity is progressively decreased [e.g., *Saad and Conrad*, 1993]. *Williams and Fehsenfeld* [1991] found that in the temperature range of 15°-35°C, the emission of NO varies exponentially. A function with an optimum at 35°C was used in the model to calculate the impact of soil temperature on nitrifier activity (equation (5) in Table 3).

*Davidson* [1992a] has observed that NO was produced by nitrification over a wide range of soil moisture conditions from below to above field capacity. *Martin et al.* [1998] also found that soil moisture alone was a poor predictor of nitrification-induced NO emission. *Anderson and Levine* [1992] report that nitrification-induced NO emission was only slightly decreased when soil moisture exceeded field capacity. On the basis of these observations we set functions to reflect the moderate impact of soil moisture on nitrifier activity unless the soil becomes too dry (equation (6) in Table 3).

In experiments done by *Bock et al.* [1986] and *Ward* [1987], the growth of nitrifiers was strongly affected by soil pH, with an optimum range of 7.5-8.0. Increases or decreases in pH from the optimum range reduced nitrification rates [*Ward*, 1987; *Paavolainen and Smolander*, 1998]. In our model, nitrifier activity was set as a linear function of pH within the common soil pH range (see equation (4) in Table 3).

*Blagodatsky and Richter* [1998] have developed equations to predict growth and death rates of microorganisms based on soil DOC concentration, temperature, and moisture. These equations were adopted in our model for calculating nitrifier activity (equations (1), (2), and (3) in Table 3). The initial soil nitrifier population is set as one tenth of the total soil microbial biomass based on observations obtained from the Höglwald Forest site in Germany [*Papen and von Berg*, 1998; *H. Papen and E. Zumbusch*, unpublished results, 1999].

Although nitrification has been verified to be a source of soil NO and $N_2O$, the mechanisms of production still remains unclear. *Poth and Focht* [1985] and *Firestone and Davidson* [1989] suggested that nitrification-induced $N_2O$ could be produced by either nitrifier denitrification of $NO_2^-$ under conditions of oxygen stress or chemodenitrification of nitrite produced by nitrifiers. However, oxidative production of $N_2O$ and NO during oxidation of ammonia to nitrite has to be regarded as an alternative/additional mechanism of N-trace gas production [*Hooper and Terry*, 1979; *Ritchie and Nicholas*, 1972]. Since at present the contribution of either oxidative or reductive mechanisms of $N_2O$ and NO production from nitrification cannot be quantified with certainty, we simply defined nitrification-induced NO and $N_2O$ productions as fractions of the predicted nitrification rates (functions 7 and 8 in Table 3). Only a few papers have reported the rate of NO or $N_2O$ production from nitrification. *Van Niel* [1991] and *Baumgärtner and Conrad* [1992] report that NO production was 0.1-4 % of the nitrification rates. In the model, the maximum fraction of NO loss from gross nitrification was arbitrarily set to 0.25% (equation (7) in Table 3). *Goodroad and Keeney* [1984] reported $N_2O$ losses to be in a range of 0.1-0.2% of net nitrification, whereas *Ingwersen et al.* [1999] found that $N_2O$ losses from gross nitrification were between 0.008-0.053%. On the basis of an extrapolation of data derived from experiments performed by *Ingwersen et al.* [1999], we set the maximum fraction of $N_2O$ loss from gross nitrification to 0.06% (equation (8) in Table 3).

## 6. Denitrification

Denitrification is a series of sequential reductions driven by microorganisms using N oxides as electron acceptors under anaerobic conditions [e.g., Kuenen and Robertson, 1987]. The

**Table 3.** Functions and Parameters for Nitrification

| Equation No. | Function | Equation |
|---|---|---|
| 1 | relative growth rate of nitrifiers | $\mu_g = \mu_{MAX}$ ((DOC] / (1 + [DOC]) + $F_m$ / (1 + $F_m$)); |
| 2 | relative death rate of nitrifiers | $\mu_d = a_{MAX}$ $B_n$ / (5 + [DOC])/ (1 + $F_m$); |
| 3 | net increase in nitrifiers biomass | $\mu_b$ = ($\mu_g$ - $\mu_d$) $B_n$ $F_t$ $F_m$; |
| 4 | nitrification rate | $R_n$ = $R_{max}$ [NH4] $B_n$ pH; |
| 5 | temperature factor | $F_t$ =((60-T)/ 25.78)$^{3.503}$ $e^{(3.503\ (T-34.22)/\ 25.78)}$; |
| 6 | moisture factor | if wfps > 0.05 $F_m$ = 1.01 - 0.21 wfps;<br>if wfps <= 0.05 $F_m$ = 0; |
| 7 | NO production from nitrification | NO = .0025 $R_n$ $F_t$; |
| 8 | $N_2O$ production from nitrification | $N_2O$ = 0.0006 $R_n$ $F_t$ wfps; |

$a_{MAX}$, maximum death rate for nitrifiers (1.44 1/d [from *Blagodatsky and Richter*, 1998]); $B_n$, biomass of nitrifiers (kg C/ha); [DOC], concentration of dissolved organic C (kg C/ha); $F_m$, moisture factor; $F_t$, temperature factor; [NH4], concentration of ammonium (kg N/ha); NO, NO production from nitrification; $N_2O$, $N_2O$ production from nitrification [*Ingwersen et al.*, 1999]; pH, soil pH; $R_n$, nitrification rate; $R_{max}$, maximum nitrification rate (1/h); T, soil temperature (°C); wfps, water-filled porosity; $\mu_{MAX}$, maximum growth rate for nitrifiers (4.87 1/d [from *Blagodatsky and Richter*, 1998]); $\mu_b$, net increase in nitrifiers biomass; $\mu_d$, relative death rate of nitrifiers; $\mu_g$, relative growth rate of nitrifiers.

activity of denitrifiers is driven by soil Eh, temperature, moisture, and substrates including DOC and N oxides [e.g., $NO_3^-$, $NO_2^-$, NO, and $N_2O$]. As intermediates of the processes, NO and $N_2O$ are tightly controlled by the kinetics of each step in the sequential reactions. Classical calculations for biochemical reaction kinetics were employed in the model to track the production and consumption of each reactant or product in the sequence.

Soil aeration status is a key factor regulating the denitrification sequence. The PnET-N-DNDC model defines the size of volumetric fraction of anaerobic microsites by tracking the swelling or shrinking of an anaerobic balloon (Figure 3). In the model, denitrification processes occur only within the anaerobic balloon. Even within the balloon, each step of the denitrification sequence has different kinetics and, moreover, is differently influenced by soil pH (equation (2) in Table 4).

Under anaerobic conditions, DOC (C source) and N oxides (electron acceptors) are the main substrates controlling growth of denitrifiers. According to *Bader* [1978], a simple function describing multinutrient-dependent growth has been set in the model to calculate relative growth rates (equation (1) in Table 4). Following *Leffelaar and Wessel* [1988], we assumed that relative growth rates of denitrifiers using different electron acceptors (i.e., $NO_3^-$, $NO_2^-$,

**Table 4.** Functions and Parameters for Denitrification

| Equation No. | Function | Equation |
|---|---|---|
| 1 | relative growth rate of Nox denitrifiers | $\mu_{NOx} = \mu_{NOx(max)}$ [DOC]/(Kc+[DOC]) [$No_x$]/(Kn+[$NO_x$]); |
| 2 | relative growth rate of total denitrifiers | $\mu_g = F_t$ ($\mu_{NO3}$ $F_{PH1}$+$\mu_{NO2}$ $F_{PH2}$+$\mu_{NO}$ $F_{PH2}$+$\mu_{N2O}$ $F_{PH3}$;<br>$F_t = 2^{((T-22.5)/10)}$;<br>$F_{PH1} = 1 - 1 / (1 + e^{[pH-4.25/0.5)}$;<br>$F_{PH2} = 1 - 1 / (1 + e^{[pH-5.25/1.0)}$;<br>$F_{PH3} = 1 - 1 / (1 + e^{[pH-6.25/1.5)}$; |
| 3 | denitrifier growth rate, death rate, and consumption rate of soluble carbon | $R_g = \mu_g B_d$;<br>$R_d = M_c Y_c B_d$;<br>$R_C = (\mu_g / Y_c + M_c) B_d$; |
| 4 | consumption rates of N oxides | $R_{NOx} = (\mu_{NOx}/Y_{NOx} + M_{NOx}$ [$No_x$]/[N]) $B_d$; |
| 5 | nitrogen assimiliation rate | $q_N = R_g$ /CN; |
| 6 | gas diffusion factor | $v = D_{max}$ afps (1 - anvf) $F_{clay}$ $2^{T/20}$,<br>$F_{clay}$ = 0.13 - 0.079 clay; |

afps, air-filled porosity; anvf, volumetric fraction of anaerobic microsites; $B_d$, denitrifier biomass (kg C/m$^3$); clay, clay fraction in the soil; CN, C/N ratio in denitrifiers (3.45 [*Van Verseveld and Stouthamer* 1978]); $D_c$, consumption rate of soluble carbon by denitrifiers (kg C m$^{-3}$h$^{-1}$); $D_{max}$, maximum diffusion rate in air (m$^2$/h); $D_{NOx}$, consumption rate of N oxides by denitrifiers (kg C m$^{-3}$h$^{-1}$); [DOC], soluble C concentration (kg C/m$^3$); $F_{clay}$, clay factor; $F_t$, temperature factor; $F_{PH1}$, pH factors for $NO_3^-$ denitrifiers; $F_{PH2}$, pH factors for $NO_2^-$ and NO denitrifiers; $F_{PH3}$, pH factors for $N_2O$ denitrifiers; Kc, half-saturation value of soluble carbon (0.017 kg C/m$^3$ [*Shan and Coulman*, 1978]); Kn, half-saturation value of N oxides (0.083 kg N/m$^3$ [*Shan and Coulman*, 1978]); $M_c$, maintenance coefficient on carbon (0.0076 kg N kg$^{-1}$h$^{-1}$ [*Van Verseveld et al.*, 1977]); [N], concentration of all $NO_x$ (kg N/ m$^3$); [$No_x$], concentration of for $NO_3^-$, $NO_2^-$, NO and $N_2O$ (kg N/m$^3$); pH, soil pH; $q_n$, nitrogen assimilaion rate (kg N ha$^{-1}$h$^{-1}$); T, soil temperature (°C); v, gas diffusion factor (%); $Y_c$, maximum growth rate of denitrifiers on soluble carbon (0.503 kg C/kg C [*Van Verseveld et al.*, 1977]); $M_{NOx}$, maintainance coefficient on N oxides (0.09, 0.035 and 0.079 kg N/kg/ for $NO_3^-$, $NO_2^-$ (+NO*) and $N_2O$, respectively, based on *Van Verseveld et al.* [1977]); $R_d$, denitrifier death rate; $R_g$, denitrifier growth rate; $Y_{NOx}$, maximum growth rate on N oxides (0.401, 0.428 and 0.151 kg C/kg N for $NO_3^-$, $NO_2^-$ (+NO*) and $N_2O$, respectively, based on *Van Verseveld et al.* [1977]); $\mu_g$, relative growth rate of total denitrifiers (1/h); $\mu_{NO3}$, $\mu_{NO2}$, $\mu_{NO}$, $\mu_{N2O}$, relative growth rate of $NO_3^-$-, $NO_2^-$-, NO-, and $N_2O$ denitrifiers; $\mu$NOx, relative growth rate of $NO_x$ denitrifiers (1/h); $\mu_{NOx(max)}$, maximum growth rates (0.67 1/h for $NO_3^-$, $NO_2^-$ denitrifiers, and 0.34 1/h for NO and $N_2O$ denitrifiers, based on *Hartel and Alexander* [1987]). The parameters are shared by $NO_2^-$ and NO due to the lack of data for NO.

NO, and $N_2O$) are independent and that competition among different denitrifier populations takes place via the common available C substrate. The Pirt equation was used to calculate consumption rates of the N-oxides (equation (4) in Table 4). Maximum growth rates and maintenance coefficients for denitrifiers were adopted from the results of Leffelaar and Wessel's incubation experiment [*Leffelaar and Wessel*, 1988]. The death rate of denitrifiers is simply a constant fraction of the total denitrifier biomass (equation (3) in Table 4).

Growth rates of denitrifiers are controlled not only by substrates but also by other soil environmental factors such as temperature and pH. On the basis of observations by, for example, *Stanford et al.* [1975], *Bailey and Beauchamp* [1973], and *Dawson and Murphy* [1972], we set a $Q_{10}$ value of 2 to calculate the impact of soil temperature on denitrification rates in the common soil temperature range (equation (2) in Table 4).

Many researchers have found that denitrification rates are highly *p*H-dependent [e.g., *Wijler and Delwiche*, 1954; *Focht*, 1974; *Firestone et al.*, 1980]. Denitrification rates increased with increasing soil pH [e.g., *Nömmik*, 1956; *Delwiche and Bryan*, 1976; *Van Cleemput and Patrick*, 1974; *Ellis et al.*, 1998] with an optimum in the range of 7.0-8.0 [*Federer and Klemedtsson*, 1988; *Yoshinari*, 1990]. In addition, pH appears to affect different denitrifiers differently. For example, at low pH (<5), most denitrification stops at $N_2O$ [e.g., *Focht*, 1974; *Leffelaar and Wessel*, 1988; *Tiedje*, 1988]. On the basis of the report by *Ashby et al.* [1998] the effects of soil pH on denitrification rates were set as Bolzman functions in the model (equation (2) in Table 4).

As gaseous intermediates, NO or $N_2O$ can be further reduced if they have not escaped from the "anaerobic balloon." Diffusion inherently plays an important role in regulating gas fluxes and $NO/N_2O/N_2$ ratio. The factors affecting NO and $N_2O$ release are the size of the anaerobic balloon, air-filled porosity, temperature, and soil adsorption coefficient [*Drury et al.*, 1992; *Davidson*, 1992a]. A highly simplified scheme was adopted in the model to quantify the gas transport factor (equation (6) in Table 4). Denitrification-induced NO or $N_2O$ emissions are the result of competition among production, consumption, and diffusion of the two gases within the anaerobic balloon.

## 7. Chemodenitrification

Many researchers have observed that chemical decomposition of nitrite plays an important role in the emission of NO from acidic soils [e.g., *Bulla et al.*, 1970; *Bremner et al.*, 1980]. It is interesting to point out that chemodenitrification seems to be only important for the production of NO, not $N_2O$ [e.g., *Blackmer and Cerrato*, 1986; *Bremner*, 1997; *Yamulki et al.*, 1997].

Soil pH has clearly proved to be an important factor for chemodenitrification since chemodenitrification occurs only when soil pH is lower than 5 [e.g., *Blackmer and Cerrato*, 1986; *McKenney et al.*, 1984, 1990; *Chalk and Smith*, 1983; *Van Cleemput and Baert*, 1984]. Since autotrophic nitrification and microbial denitrification can be reduced at low pH, chemodenitrification could become an important source of NO in acidic soils which are commonly found in many temperate forests and most of the tropical ones.

Chemodenitrification rates increase with increasing temperature up to 40°C, but not surprisingly, no temperature optimum has been found [*Van Cleemput and Baert*, 1984; *Saad and Conrad*, 1993; *Yamulki et al.*, 1997]. Chemodenitrification, the chemical decomposition of $NO_2^-$, should be directly driven by $NO_2^-$ concentrations in the soil. In fact, *Davidson*'s [1992a, b] experiments have demonstrated that the addition of $NO_2^-$ to a sterilized soil greatly increased NO emission. Davidson and his colleagues indicate that although the soil $NO_2^-$ pool usually remains small, the flux of nitrogen through this pool can be large [*Davidson et al.*, 1990]. All of this N must pass through the $NO_2^-$ pool, at least momentarily. *Davidson* [1992a] indicated that all NO emissions from the soils could be explained by chemodenitrification, if only 1% of the produced $NO_2^-$ was abiologically converted to NO. Although it is clear that $NO_2^-$ is produced by both oxidation of $NH_4$+ and reduction of $NO_3^-$, usually $NO_2^-$ is not detected in soils due to its high turnover rates. Since gross nitrification rates (200-1000 kg N $ha^{-1}yr^{-1}$) are usually higher than the denitrification rates (less than 100 kg N $ha^{-1}yr^{-1}$) in soils, we used the modeled nitrification rate rather than denitrification rate as an indicator for daily $NO_2^-$ production. In the model, chemodenitrification-induced NO production is calculated as a function of nitrification rate, soil temperature, and soil pH. The effects of soil temperature and pH on chemodenitrification were quantified based on the reports by *Yamulki et al.* [1997] and *Blackmer and Cerrato* [1986], respectively (Table 5).

Under the regulation of the "anaerobic balloon," the PnET-N-DNDC model simultaneously simulates nitrification, denitrification, and chemodenitrification at an hourly (for denitrification) or daily (for nitrification and chemodenitrification) time step. The NO or $N_2O$ produced from the three sources is joined into a common gas pool. After the diffusion calculation, part of the gases will be emitted into the air, and the remaining part will be reallocated into the new reactions of the next time step.

## 8. Effects of Forest Ecosystems

Several ecological drivers, such as climate, soil physical properties, vegetation, and anthropogenic activity, control the dynamics of soil environmental factors, and hence affect NO and $N_2O$ production/consumption in the soil. Driven by the input parameters of the ecological drivers, the PnET-N-DNDC model predicts the profiles of temperature, moisture, pH, Eh, and substrate concentration in the simulated soil. The functions linking the ecological drivers to the soil environmental dynamics include several new features developed for this model as well as the old features adopted from the parent models (i.e., PnET and DNDC). Only the new features are described in the paper.

**Table 5.** Functions and Parameters for Chemodenitrification

| Parameter | Definition |
|---|---|
| $F_t$ | temperature factor (based on *Yamulki et al.* [1997]) |
| $F_{pH}$ | pH factor (based on *Blackmer and Cerrato* [1986]) |
| $R_{chem}$ | production rate of NO from chemodenitrification, kg N $ha^{-1}d^{-1}$ |
| $R_n$ | nitrification rate, kg N $ha^{-1}d^{-1}$ |
| T | soil temperature, °C |
| pH | soil pH |
| a | constant coefficient |

Production rate of NO from chemodenitrification: $R_{chem} = a\ R_n\ F_t\ F_{pH}$; $F_t = 0.03\ T + 0.2$; $F_{pH} = 2236\ e^{(-2.5*pH)}$.

**Table 6.** Functions and Parameters for Impacts of Forest Features

| Equation No. | Function | Equation |
|---|---|---|
| 1 | effect of canopy on soil temperature | dT(soil) = -0.0037+0.2422 dT(air), coniferous forests;<br>dT(soil) = -0.0058+0.1827 dT(air), deciduous forests; |
| 2 | canopy interception of precipitation | Ri = 0.05 LAI Rp,<br>if canopy water content < canopy water capacity;<br>$C_{WC}$ = 0.2 LAI; |
| 3 | N concentration n throughfall | Nt = 0.27 + 2.7 $N_{rain}$, coniferous forests;<br>Nt = 0.20 + 1.6 $N_{rain}$, deciduous forests; |
| 4 | water-holding capacity in the litter layer | WC = $C_{org}$ / 10000; |
| 5 | partitioning of fresh litter into soil litter pools | if FL_CN < CN(vl)<br>LitterC(vl) = FL_C;<br>if CN(vl) <= FL_CN < CN(l)<br>LitterC(vl) = 1.25 P1 – 0.25 FL_C;<br>LitterC(l) = FL_C – P1;<br>LitterC(r) = 0.25 * (FL_C – P1);<br>P1=FL_C(K1–FL_CN)/(K1–CN(vl)CN(vl)/FL_CN;<br>K1 = 2 CN(l) CN(r)/(CN(l) + CN(r));<br>If CN(l) <= FL_CN < CN(r)<br>LitterC(vl)=0.25(FL_C – P2);<br>LitterC(l) = FL_C – P2;<br>LitterC(r) = 1.25 P2 – 0.25 FL_C;<br>P2=FL_C(K2-FL_CN)/(K2–CN(r)CN(r)/FL_CN;<br>K2=2CN(vl) CN(l)/(CN(vl)+CN(l));<br>If FL_CN >= CN(r)<br>LitterC(r) = FL_C; |
| 6 | microbial biomass death rate due to freezing | if T < 0°C<br>d(micro)/dt = 0.001 ASOC RBO. |

ASOC, active soil organic carbon (kg C/ha); CN(vl), C/N ratio of very labile litter pool, 10; CN(l), C/N ratio of labile litter pool, 19; CN(r), C/N ratio of resistant litter pool, 200; $C_{org}$, organic matter content in the litter layer (kg C/ha); $C_{WC}$, canopy water capacity (cm water); dT(soil), daily increase in surface soil temperature (°C); dT(air), daily increase in air temperature (°C); FL_C, fresh litter C content (kg C/ha); FL_CN, fresh litter C/N ratio; LAI, leaf area index; LitterC(vl), organic C content in very labile litter pool (kg C/ha); LitterC(l), organic C content in labile litter pool (kg C/ha); LitterC(r), organic C content in resistant litter pool (kg C/ha); micro, death rate of microbes due to freezing; $N_{rain}$, nitrogen (i.e., $NO_3^-$ and $NH_4^+$) concentration in rainfall (ppm); Nt, Nitrogen (i.e., $NO_3^-$ and $NH_4^+$) concentration in throughfall (ppm); RBO, microbial fraction of active organic carbon; Ri, interception rate (cm water/h); Rp, rainfall intensity (0.5 cm water/h, [*Li et al.*, 1992]); T, soil temperature (°C); WC, water-holding capacity of the litter layer (cm).

### 8.1. Forest Canopy and N Deposition

Forest canopies have a huge effect on the climate of the stand (e.g., temperature, precipitation, soil moisture) and on atmospheric N-deposition. Forest canopies affect soil temperature due to shading. To account for this effect, an empirical equation was derived from measured air and soil temperatures at the Höglwald Forest in Germany [*Butterbach-Bahl et al.*, 1997] (equation (1) in Table 6). Moreover, forest canopies intercept precipitation and hence alter dynamics of the soil moisture regime. Referring to *Rutter et al.* [1971], a highly simplified function was developed to calculate canopy interception of rainfall. Maximum canopy water holding capacity is calculated based on the canopy biomass. In the simulations, a fraction, as a function of the canopy biomass, of the precipitation is intercepted by the canopy at an hourly time step until the water content in the canopy reaches its capacity (equation (2) in Table 6). Forest canopies enhance dry deposition of N from the atmosphere. Part of this N accumulates on the surface of leaves and will be transferred to the soil with the throughfall during rainfall events. Therefore N concentration in the throughfall is often higher than in the bulk precipitation. Results of the Experimental Manipulation of Forest Ecosystems in Europe (EXMAN) project and results reported by others [*Hornung et al.*, 1995] showed that N concentrations in the throughfall were positively correlated to the N concentrations in the precipitation. We deduced equations from the EXMAN data set [*Beier and Rasmussen*, 1993] to calculate total N deposition ($NO_3^- + NH_4^+$) using inorganic N concentrations in precipitation (equation (3) in Table 6). On the basis of the reports from *Wright et al.* [1995], wet N deposits range from 0.74 to more than 30 kg N $ha^{-1}yr^{-1}$ for areas in northern Europe and the United States. Since atmospheric N deposition can be a main source of N in the unfertilized forest ecosystems, changes in the magnitude of N deposition affect soil N dynamics and, in consequence, the magnitude of NO and $N_2O$ emissions. These calculations are in agreement with results reported by many researchers who described a strong positive relationship between the atmospheric N input and NO and $N_2O$ emissions from the forest soils [*Butterbach-Bahl et al.*, 1998; *McNulty et al.*, 1990; *Castro et al.*, 1993; *Bowden et al.*, 1991].

### 8.2. Forest Floor

In temperate forests, forest floors usually contain abundant organic matter (approximately 15-150 t $ha^{-1}$ [e.g., *Prichett*, 1979]). The high organic matter contents make the forest floor distinguished from the mineral layers with its special structure, aeration, water holding capacity, and microbial activity. The turnover of this organic matter provides favorable conditions for nitrification, denitrification, and chemodenitrification. In fact, the forest floor itself has been found to be a major source of N-trace gas emissions [e.g., *Borken and Brumme*, 1997; *Papen and Butterbach-Bahl*, 1999; *Pluth and Nömmik*, 1981].

In this model, the forest floor is treated as a special soil layer which is located on the top of the soil profile and is characterized by its specific organic matter content, porosity, and pH. N-trace gas

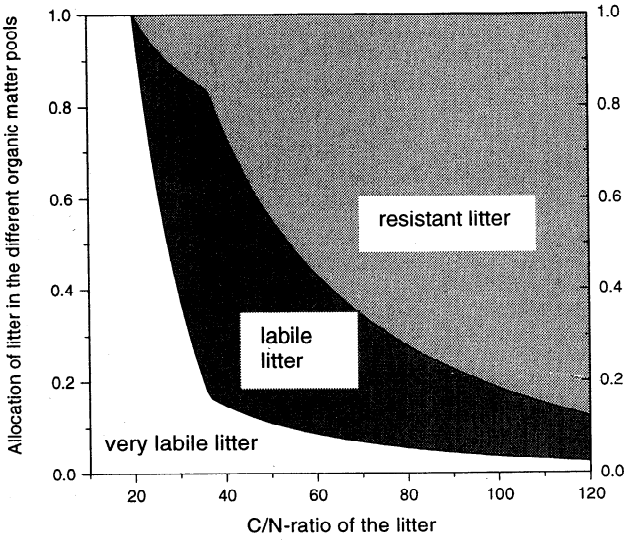


**Figure 5.** Partitioning of fresh litter into very labile, labile, and resistant litter pools of the soil is calculated based on the input litter C/N ratio.

emissions from the forest floor are affected mainly by two functions:

1. By temporally holding water, the forest floor alters the soil moisture regime. Given that every kilogram of organic matter holds 5 kg of water, 1 cm of water can be held in a forest floor containing 10,000 kg C $ha^{-1}$. Owing to water interception and evaporation in the forest floor, the moisture regime of the mineral soil is significantly altered, and hence all relevant biogeochemical reactions are affected.

2. Through the turnover of organic matter, the forest floor provides DOC, $NH_4^+$, and $NO_3^-$ as substrates for nitrification, denitrification, or chemodenitrification occurring in both the forest floor and the mineral soil. Especially during rainfall events, leaching can take the DOC and $NO_3^-$ accumulated in the forest floor during the drying period into the mineral soil layers to stimulate denitrification [*Skiba et al.*, 1992; *Smith and Parsons*, 1985].

In the model, content of soil organic matter is related to litter quantity and quality. The forest growth submodel predicts litter production and litter C/N ratio. After litter fall, the decomposition submodel allocates the fresh litter into the very labile, labile, and resistant litter pools based on the litter C/N ratio (see equation (5) in Table 6 and Figure 5). If the fresh litter has a low C/N ratio, larger fractions of the litter will be partitioned into the more labile pools. The decomposition rate of each litter pool is calculated separately based on its specific decomposition rate, temperature, and soil moisture [*Li et al.*, 1992]. Lower litter C/N ratio will lead to a faster bulk decomposition rate. This algorithm is supported by the laboratory studies by *Prescott* [1996]. Since the quantity and quality of the litter vary from forest type to forest type (Table 7), the quantity and quality of the litter layer in different types of forests can be different even they share similar climate conditions. On the basis of mechanism the PnET-N-DNDC model calculates initial organic matter contents in the forest floor as default values, though we encourage the users to use their measured data to reduce the site-specific uncertainties. The maximum water-holding capacity of the forest floor is calculated based on the organic matter content in the floor (equation (4) in Table 6).

### 8.3. Soil Fertility

The fertility of the forest soil controls the availability of nitrogen and carbon in the soil, and hence affects NO and $N_2O$ emissions. Competition between plants and microbes can become a limiting factor for N-gas production, especially in poor soils [e.g., *Jones and Richards*, 1977; *Binkley and Hart*, 1989]. Competition of nitrifying organisms with plant uptake and microbial N immobilization has been observed to be responsible for the low rates of net nitrification in the Harvard Forest soils in the United States [*Bowden et al.*, 1991]. Some researchers have observed that the presence of plants lowered denitrification by depleting the N pool [*Bowden et al.*, 1991]. Many researchers have noted rapid increases in net nitrification following cutting of forests [e.g., *Likens et al.*, 1969; *Vitousek et al.*, 1982; *Montagnini and Buschbacher*, 1988; *Fisk and Fahey*, 1990]. Forest age and vitality is also a factor to consider in determining the nutrient requirements of a forest [*Prichett*, 1979]. An aggrading forest will readily take up additional N inputs compared to a steady state forest with slower growth and therefore lower nutrient requirements [*Vitousek and Reiners*, 1975; *Bormann and Likens*, 1979]. The significant differences in soil organic matter contents as well as in NO and $N_2O$ emissions between two adjacent forest stands (spruce and beech) have been observed by the researchers [*Rothe*, 1998; *Butterbach-Bahl et al.*, 1997; *Papen and Butterbach-Bahl*, 1999; *Gasche and Papen*, 1999] in the Höglwald Forest in Germany. Since the two stands have similar climate, soil texture, and forest age, the researchers hypothesized that the difference in the gas emissions was mainly due to the different soil fertility driven by the litter quantity and quality [*Stange et al.*, this issue]. The PnET-N-DNDC model simulates forest N uptake with the algorithms adopted from the PnET model [*Aber et al.*, 1995, 1996] in conjunction with other functions of soil chemistry.

Preforest land use history also affects soil fertility. *Magill et al.* [1997] suggest that land use history could be critical in determining

**Table 7.** Characteristics of Modeled Mature Forests

| Forest Type | Leaf-N, % | Leaf C/N | Wood C/N | Litter C/N in the Forest Floor | Leaf Retention, year |
|---|---|---|---|---|---|
| Pine | 1.3 | 35 | 200 | 70 | 2.25 |
| Spruce | 1.2 | 37 | 200 | 74 | 4 |
| Fir | 1.1 | 43 | 300 | 86 | 4 |
| Hemlock | 1.1 | 42 | 350 | 84 | 4 |
| Hardwoods | 2.2 | 20 | 200 | 40 | 1 |
| Oak | 2.0 | 23 | 150 | 46 | 1 |
| Birch | 2.2 | 21 | 180 | 42 | 1 |
| Beech | 2.7 | 16 | 200 | 32 | 1 |

Based on *Aber and Federer* [1992], *Aber et al.* [1995], *Stump and Binkley* [1992], and *Cortez et al.* [1996].

**Table 8.** Input Parameters

| Parameter | Unit | Default Value |
|---|---|---|
| Climate | | |
| Daily maximum and minimum air temperature | °C | none |
| Daily precipitation | cm/d | none |
| Photosynthesis actively radiation (PAR)* | μmol $m^{-2}$ $s^{-1}$ | |
| Atmospheric N deposition | ppm | none |
| Soil | | |
| Organic C content at litter layer† | kg C/ha | |
| Organic C content at top of mineral soil | kg C/kg soil | none |
| Bulk density of mineral soil | g/$cm^3$ | none |
| pH at litter layer | | none |
| pH at mineral soil | | none |
| Texture of mineral soil | | none |
| Clay fraction in mineral soil | | 0-1 |
| Vegetation | | |
| Forest type‡ | | |
| Forest age | year | none |

*Default daily PAR values are calculated based on latitude, day length, horizontal potential insolation, potential insolation, declination of the Sun, radius vector of the Sun, solar constant, and a default cloud index 0.5. The users are encouraged to use their measured PAR as the default data will cause discrepancies for the simulated results.

†Default annually litter accumulation rate is calculated by an empirical equation ($dL/dt = (5700 - 80 \text{ latitude}) - L / 10^{[-0.8 + 0.04 \text{ latitude}]}$), developed based on data of *Olson* [1963] and *Bray and Gorham* [1964].

‡Pine, spruce, fir, hemlock, mixed hardwoods, oak, birch, and beech.

current N status of soils and forests. Land use history is recorded in the quantity and quality of soil organic matter (SOM). Rather than distinguish moder, mor, or mull, we characterize SOM in forest soils based on amounts and C/N ratios of the organic matter (see details given by *Li et al.* [1992, 1994]). Initial pool sizes of organic matter in the soil profile are required as input parameters (Table 8).

### 8.4. Soil Freezing/Thawing

The effects of soil freezing/thawing on NO or $N_2O$ emissions have been reported by many researchers [e.g., *Anderson and Levine*, 1992; *Martin et al.*, 1998; *Papen and Butterbach-Bahl*, 1999]. There are several hypotheses for this phenomenon, including soil Eh depression due to limitation of $O_2$-diffusion in the frozen soil, an increase in DOC due to microorganisms dying of the cold, an increase in $NH_4^+$ and $NO_3^-$ concentration due to the fractionation of soil water during the freezing process, and stimulation of favorable conditions for denitrification by the thawing water [e.g., *Christensen and Tiedje*, 1990; *Röver et al.*, 1998; *Papen and Butterbach-Bahl*, 1999]. To simulate the effects of soil freezing and thawing on NO and $N_2O$ emissions, we implemented four mechanisms in the model. If the soil temperature is below 0°C, (1) a constant fraction of the soil microorganisms will die and will be added to the labile humads pool (equation (6) in Table 6); (2) the oxygen diffusion rate in the soil will decrease due to the frozen surface (equation (2) in Table 2); (3) the NO and $N_2O$ produced will be confined to the soil until the time of thaw; and (4) the thawing water flux will be equivalent to a rainfall to affect the soil biogeochemical processes based on the model's routines. Figure 6 shows how the PnET-N-DNDC model simulates effects of freezing/thawing on N gas emissions. The mechanisms implemented in the model are preliminary and may not be sufficient to explain the high fluxes of $N_2O$ from the frozen soils during the freezing period. Modifications in this part will be expected in the future.

### 8.5. Forest Management

The PnET-N-DNDC model simulates the effects of forest management on the soil environmental factors including N-substrates concentrations and soil pH. In the model, fertilization with four types of fertilizers including ammonium, nitrate, urea, and anhydrous ammonia is parameterized. The simulated application methods include surface application and injection of fertilizers into the soil. By application of ammonium, nitrate, or anhydrous ammonia to the soil, the nitrogen is directly allocated into the corresponding inorganic N pools, whereas in the case of urea application the model will first simulate the hydrolysis of urea. The model also predicts the effects of liming on soil pH, and hence on a series of pH-driven reactions including nitrification, denitrification, and chemodenitrification. The effects of removing litter mass on soil C and N dynamics can be predicted by resetting organic matter content in the forest floor.

## 9. Discussion

Development of the PnET-N-DNDC model was an attempt of our long-term studies on biogeochemistry. On the basis of biogeochemical principles we tried to integrate the mechanisms obtained by numerous researchers into a general model framework. A series of tests were conducted to find the strengths and weaknesses of the new model (see details given by *Stange et al.* [this issue]). The tests revealed that implementation of the anaerobic balloon significantly improved predictions of NO and $N_2O$ emissions from the forest soils by (1) separating the soil matrix into aerobic and anaerobic fractions, (2) allocating the substrates into the fractions with different aeration, and (3) allowing the intermediates (e.g., NO and $N_2O$) to transfer between the aerobic and anaerobic microsites. Since nitrification and denitrification are typically sequential oxidation-reduction processes, the scheme of

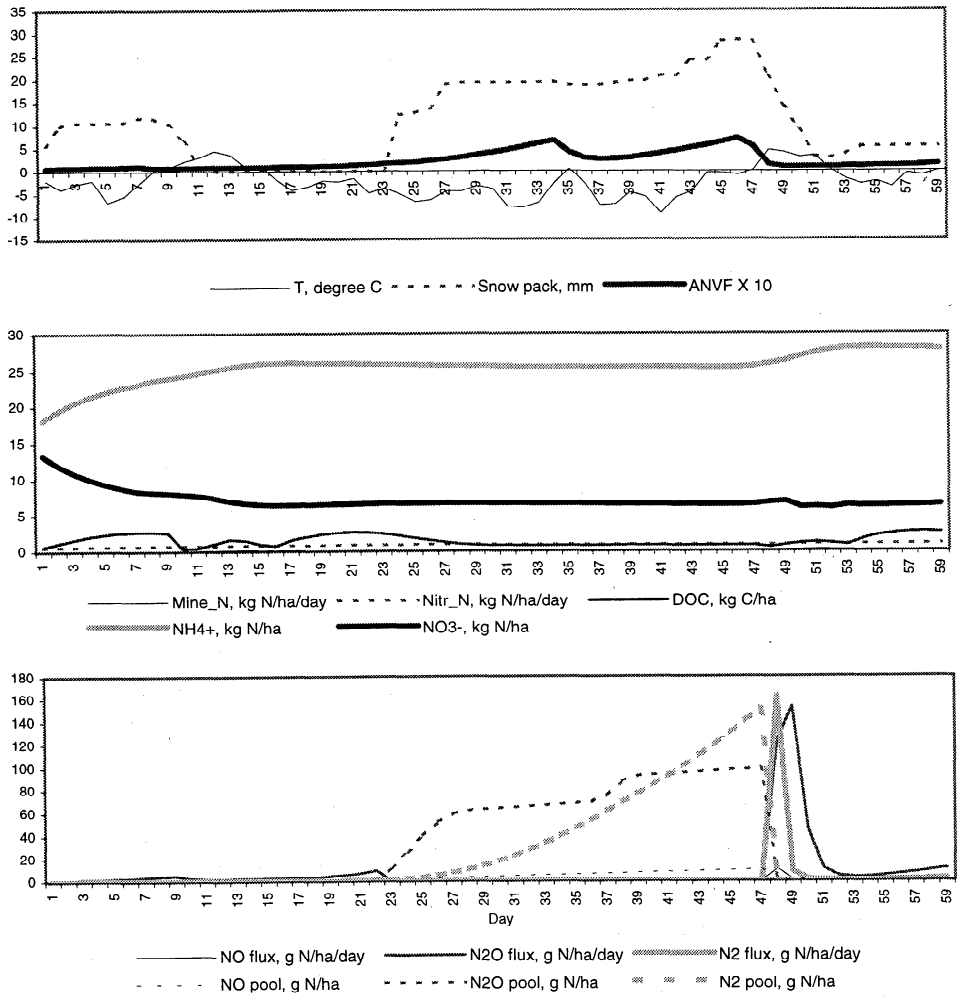


**Figure 6.** Model-simulated effects of soil freezing/thawing on NO and $N_2O$ emissions. During most time of the simulated period of 60 days, the temperatures were lower than 0°C. During the continuous freezing period from day 15 to day 47, the soil mineralization and nitrification rates were minimized due to the cold and try soil conditions, and the soil $NO_3^-$, $NH_4^+$, and DOC concentrations did not vary dramatically either. Only the soil anaerobic volumetric fraction (ANVF) gradually increased due to the frozen surface which blocked the way of oxygen diffusion from the atmosphere to the soil profile. Meanwhile, nitrification- and/or denitrification-induced NO, $N_2O$, and $N_2$ were accumulated in the soil profile. On day 47 when the thawing started, the confined gases, combining with the gases induced by the thawing water flux, were released to form a pulse of emission.

a dynamic anaerobic balloon could become a general approach for the studies on soil N in various ecosystems. Actually, we recently tested the anaerobic balloon by embedding it in an agroecosystem model, DNDC. Compared to the original version of DNDC, this improved version showed a better agreement between modeled and measured $N_2O$ emissions for several agricultural sites worldwide (C. Li et al., unpublished results, 1999). In addition, our tests also showed that the anaerobic balloon played a unique role in predicting trace gas emissions from the submerged soils such as rice paddies. In comparison with the moisture-driving algorithms, application of the anaerobic balloon could provide more precise predictions of trace gas emissions under a wider scope of climate-soil conditions. Although the PnET-N-DNDC model has not been tested for tropical forests, we assume there are strong potentials for applying the model to predict N dynamics in the tropical forest soils. To approach this goal, we may have to face the challenges of integrating the special litterfall pattern, rapid turnover rates of organic matter, highly aggregated soils, and other specific tropical features into the model.

Weaknesses remain in this model. For example, we know little of the pathways by which NO and $N_2O$ are formed during nitrification. The production of nitrification-induced NO or $N_2O$ had to be set as an arbitrary fraction of the nitrification rate based on very limited observations. In addition, NO or $N_2O$ uptake by soils has been reported by several researchers [e.g., *Bowden et al.*, 1991; *Butterbach-Bahl et al.*, 1998; *Papke and Papen*, 1998], but we are not able to parameterize this process due to lack of understanding of the mechanisms. Quantifying and characterizing soil organic matter dynamics is also a limiting factor. Many former studies [e.g., *Li et al.*, 1996] indicate that SOM is one of the most sensitive factors affecting the soil N dynamics including nitrogenous gas fluxes. Characterization of soil organic matter should therefore become an important issue in the future studies.

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