

## Modeling trace gas emissions from agricultural ecosystems

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### Abstract

A computer simulation model was developed for predicting trace gas emissions from agricultural ecosystems. The denitrification-decomposition (DNDC) model consists of two components. The first component, consisting of the soil climate, crop growth, and decomposition submodels, predicts soil temperature, moisture, pH, Eh, and substrate concentration profiles based on ecological drivers (e.g., climate, soil, vegetation, and anthropogenic activity). The second component, consisting of the nitrification, denitrification, and fermentation submodels, predicts  $\text{NH}_3$ , NO,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  fluxes based on the soil environmental variables. Classical laws of physics, chemistry, or biology or empirical equations generated from laboratory observations were used in the model to parameterize each specific reaction. The entire model links trace gas emissions to basic ecological drivers. Through validation against data sets of NO,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  emissions measured at four agricultural sites, the model showed its ability to capture patterns and magnitudes of trace gas emissions.

### Introduction

In the context of global climate change, several trace gases, such as methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), nitric oxide (NO), and ammonia ( $\text{NH}_3$ ), are drawing attention because of their radiative or chemical effects in the atmosphere. Field measurement campaigns were launched for quantifying gas fluxes at site scale. Meanwhile, models were developed to extrapolate results from the site scale to the regional or global scale. Soil is one of the major sources of the four trace gases. Under cultivated conditions, agricultural soils are subject to a great deal of anthropogenic disturbance including tillage, fertilization, irrigation, manure amendment, weeding, and liming. Anthropogenic activities elevate soil trace gas emissions and, hence, play an important role in the atmospheric balance of the trace gases. Various models, such as CASA (Potter et al., 1993), CENTURY (Parton et al., 1996), ExpertN (Baldioli et al., 1994), Hole-in-the-Pipe (Firestone and Davidson, 1989), NLOOS (Riley & Matson 1989), and others were developed for scaling up gas emission estimates. Each of the models has its own strategy or philosophy. Some models tried to use the least number of input parameters and more empirical equations to capture basic

patterns of gas fluxes so that these models could be easily used at the regional or global scale. Some models tried to include more mechanisms to better track processes affecting gas production/consumption. To join the modeling efforts, a University of New Hampshire-based biogeochemical research group developed a process-oriented model to predict NO,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  emissions from agricultural ecosystems. Several papers have reported on the early development of the model, focusing only on  $\text{N}_2\text{O}$  and  $\text{CO}_2$  (Li et al., 1992a; 1994). This paper discusses the latest research progress including simulations of NO,  $\text{CH}_4$ , and  $\text{NH}_3$ .

### Model framework

Emissions of NO,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{NH}_3$  are highly variable in space and time. The challenges of modeling the trace gas emissions come from three aspects: (1) some of the gases (e.g., NO and  $\text{N}_2\text{O}$ ) have multiple sources (e.g., nitrification, denitrification, and chemo-denitrification); (2) all the gases are produced and consumed simultaneously in the soils, controlled by the kinetics of a series of geochemical or biochemical reactions; and (3) there are a large number of environmental variables driving the biogeochemical reactions.

To construct a process model of soil trace gases, all the factors including ecological drivers, soil environmental variables, and biogeochemical reactions should be integrated into one framework. To handle such a complex system, we adopted the concept of a biogeochemical field for our modeling practice. Paralleling the concept of biogeochemical cycle which describes the transport and transformation of the chemical elements, biogeochemical field answers what controls the elements' behavior. A biogeochemical field is an assembly of the spatially and temporally differentiated environmental forces that drive biogeochemical reactions in an ecosystem. For example, the biogeochemical field driving NO, N<sub>2</sub>O, CH<sub>4</sub>, and NH<sub>3</sub>-relevant reactions consists of the environmental forces deriving from soil temperature, moisture, pH, Eh, substrate concentration, and other soil environmental factors. All the soil environmental factors are further controlled by several ecological drivers including climate, soil physical properties, vegetation, and anthropogenic activity. All the impacts in the system can be categorized into two groups. The first group includes the impacts of ecological drivers on soil environmental variables; the second includes the impacts of the soil environmental variables on trace gas-related geochemical or biochemical reactions (Figure 1). The goal of our modeling efforts was to build the two groups of impacts in a model framework.

The denitrification-decomposition (DNDC) model was constructed with two components. The first component, consisting of the soil climate, crop growth and decomposition submodels, predicts soil tempera-

ture, moisture, pH, redox potential (Eh), and substrate concentration profiles based on ecological drivers (e.g., climate, soil, vegetation, and anthropogenic activity). The second component, consisting of the nitrification, denitrification and fermentation submodels, predicts NO, N<sub>2</sub>O, CH<sub>4</sub>, and NH<sub>3</sub> fluxes based on the soil environmental variables. Classical laws of physics, chemistry, or biology or empirical equations generated from laboratory observations were used in the model to parameterize each specific reaction. The entire model forms a bridge between trace gas emissions and basic ecological drivers (Figure 2).

### Linking ecological drivers to soil environmental variables

The first task in model development was to set links between ecological drivers and soil environmental variables. Usually, ecological drivers collectively affect soil environmental variables. Since the combination of ecological drivers in each ecosystem is unique, DNDC needs site-specific input data of climate, soil, vegetation, and farming practices for the simulated agricultural land. DNDC integrates the ecological drivers in the three submodels to generate their collective effects on soil temperature, moisture, pH, Eh, and substrate concentrations. The soil climate submodel calculates soil temperature, moisture, and Eh profiles by integrating air temperature, precipitation, soil thermal and hydraulic properties, and oxygen status. By integrating crop characters, climate, soil properties, and farming practices, the plant growth submodel simulates plant

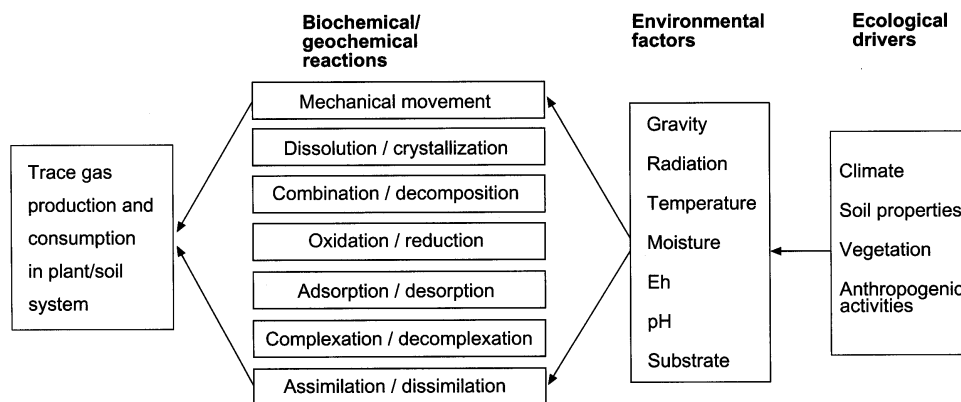


Figure 1. A biogeochemical model is a mathematical expression of biogeochemical field which consists of spatially and temporally differentiated environmental forces driving a series of biogeochemical reactions in ecosystems. Fluxes of NO, N<sub>2</sub>O, CH<sub>4</sub>, and NH<sub>3</sub> are regulated by directions and rates of the relevant biogeochemical reactions

# The DNDC Model

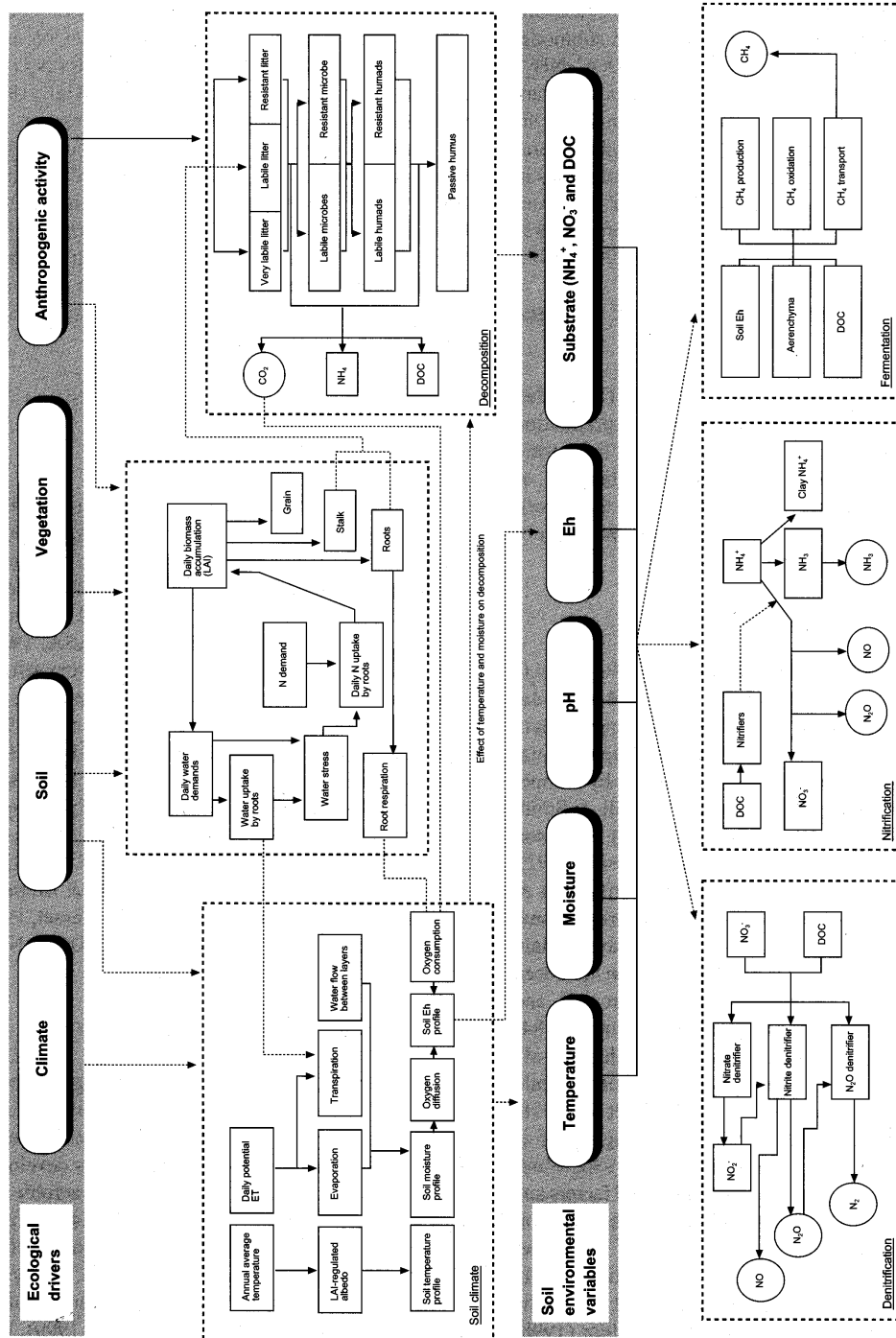


Figure 2. The DNDC model includes two components. The first component, consisting of the soil climate, plant growth, and decomposition submodels, predicts effects of climate, soil physical properties, vegetation, and anthropogenic activity on soil temperature, moisture, pH, Eh, and substrate concentration profiles. The second component, consisting of the nitrification, denitrification, and fermentation submodels, predicts NO, N<sub>2</sub>O, CH<sub>4</sub>, and NH<sub>3</sub> fluxes through simulating impacts of soil environmental conditions on the relevant geochemical and biochemical reactions

growth and its effects on soil temperature, moisture, pH, Eh, dissolved organic carbon (DOC), and available N concentrations. The decomposition submodel simulates concentrations of substrates (e.g., DOC,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ ) by integrating climate, soil properties, plant effect, and farming practices. The three submodels interact with each other to finally determine soil temperature, moisture, pH, Eh, and substrate concentrations in the soil profile at a daily time step. Most of the equations used in this component have been reported in previous papers (see details in Li et al., 1992a; 1994; 1999).

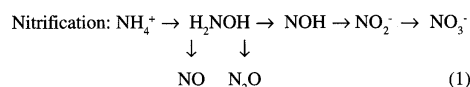
### Linking soil environmental factors to trace gases

As the second step for developing the DNDC model, we linked soil environmental variables to production and consumption rates of trace gases. The links were set up based on either the basic physical, chemical, or biological laws, or equations obtained from the experiments under controlled conditions so that the effect of each soil variable could be distinguished.

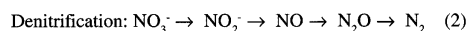
#### *NO and N<sub>2</sub>O*

Biological oxidation/reduction dominates NO and  $\text{N}_2\text{O}$  evolution in soils. Nitrification (i.e., microbial oxidation of ammonium) has been observed to be the main source of NO and  $\text{N}_2\text{O}$  under aerobic conditions (Equation 1). Based on the observations reported by Hooper & Terry (1979), Bremner et al. (1980), Chalk & Smith (1983), Tiedje (1988), Sexstone et al. (1985), Anderson & Levine (1986), Papen et al. (1982), Davidson (1992), Hutchinson & Davidson (1993), and Bollmann & Conrad (1998),  $\text{N}_2\text{O}$  or NO production is proportional to nitrification rates, although the pathways remain unknown. The factors controlling nitrification have been determined to be soil temperature, moisture, pH, and  $\text{NH}_4^+$  concentration (Johansson & Granat, 1984; Johansson, 1984; Slemr & Seiler, 1984; Williams et al., 1987; Anderson & Levine, 1987; Anderson & Poth, 1989; Valente & Thornton, 1993; Martin et al., 1998; Alexander, 1977; Saad & Conrad, 1993; Ingwersen et al., 1998; Davidson, 1992a, Bock et al., 1986; Ward, 1987). Relationships between environmental factors and nitrification rates were generalized from the observations and employed in the DNDC model. The model predicts nitrification rate by tracking nitrifier activity and  $\text{NH}_4^+$  concentration (see equations 1.1-1.6 in the Appendix). Following Blagodatsky & Richter (1998)

and Blagodatsky et al. (1998), growth and death rates of  $\text{NH}_4^+$  oxidizers are calculated based on DOC concentration, temperature, and moisture. Many observations indicated that nitrification-induced NO or  $\text{N}_2\text{O}$  was a fraction of nitrification rate (Van Niel, 1991; Baumgartner & Conrad, 1992), and the fraction was related to temperature (Johansson & Granat, 1984; Johansson, 1984; Slemr & Seiler, 1984; Williams et al., 1987; Anderson & Levine, 1987; Anderson and Poth, 1989; Slemr & Seiler, 1991; Valente & Thornton, 1993; Martin et al., 1998). DNDC calculates nitrification-induced NO or  $\text{N}_2\text{O}$  production as a function of the predicted nitrification rate and temperature (equations 1.7 and 1.8 in the Appendix).



Denitrification is another main source of  $\text{N}_2\text{O}$  and NO from soils. Denitrification includes a sequential reduction of nitrate to dinitrogen ( $\text{N}_2$ ) driven by denitrifying bacteria under anaerobic conditions (equation 2) (Firestone et al., 1980; Payne, 1981; Anderson & Levine, 1986; Poth & Focht, 1985; SSSA, 1987). Based on field and laboratory observations, denitrification rates are controlled by soil moisture and Eh (Matsubara, 1971; Payne, 1973; Payne et al., 1971; Goreau et al., 1980; Knowles, 1982; Smith, 1980, 1990; Davidson & Schimel, 1995; Stevens et al., 1998), temperature (Nömmik, 1956; Stanford, 1975; Bailey & Beauchamp, 1973; Dawson & Murphy, 1972), pH (Wijler & Delwiche, 1954; Khan & Moore, 1968; Focht, 1974; Klemmedtsoon et al., 1988; Blackmer & Bremner, 1978; Firestone et al., 1980; Leffelaar & Wessel, 1988; Ashby et al., 1998), and substrate (e.g., DOC,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , NO, and  $\text{N}_2\text{O}$ ) concentrations.



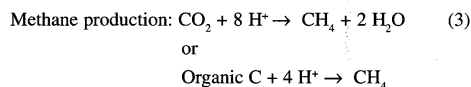
The DNDC model simulates relative growth rates of nitrate, nitrite, NO, and  $\text{N}_2\text{O}$  denitrifiers based on soil Eh, concentrations of DOC, and nitrogen oxides. A simple scheme of "anaerobic balloon" was developed in the model to divide the soil matrix into aerobic and anaerobic parts. Tracking oxygen diffusion and consumption in the soil profile, DNDC simulates swelling and shrinking of the "anaerobic balloon." Only the substrates allocated in the anaerobic part are involved in denitrification (see details in Li et al., 1999). Fol-

lowing Bader (1978), a simple function describing multinutrient-dependent growth has been set in the model to calculate relative growth rates of the denitrifiers (equations 2.1, 2.2, and 2.3 in the Appendix). Death rate of denitrifiers is simply a constant fraction of the total denitrifier biomass (equation 2.3 in the Appendix). Following Leffelaar and Wessel (1988), we assume that the relative growth rates for denitrifiers with different substrates are independent, and competition among the bacteria takes place via the common DOC substrate. The Pirt equation is used to calculate consumption rates of the substrates (equations 2.4 and 2.5 in the Appendix). Since denitrification is a typical sequential reaction, we followed the basic laws of sequential chemical kinetic reactions to calculate NO, N<sub>2</sub>O, and N<sub>2</sub> fluxes. As an intermediate of the reactions, NO or N<sub>2</sub>O flux is determined by the rates of its production, consumption, and escape from the reacting system. A simplified equation was set in DNDC to calculate diffusion rates of NO and N<sub>2</sub>O in the soil matrix. The predicted diffusion rate is a function of soil porosity, moisture, temperature, and clay content (equation 2.6 in the Appendix).

#### CH<sub>4</sub>

Methane is an end product of the biological reduction of carbon dioxide (CO<sub>2</sub>) or organic carbon under anaerobic conditions (equation 3) (Wassmann et al., 1993; Cleemput & El-Seboay, 1985; Zeikus, 1977; Yagi & Minami, 1990; Watanabe et al., 1993; Holland & Schimel, 1994; Zhou et al., 1994; Nouchi et al., 1994; Takai, 1970; Kimura et al., 1992; Kludze & DeLaune, 1995; Li et al., 1993). According to the observations obtained from field or laboratory studies, CH<sub>4</sub> fluxes were strongly controlled by soil available carbon (i.e., DOC) content (Tao et al., 1994; Shangguan, 1994; Chen et al., 1992; Cicerone et al., 1992; Cai et al., 1995; Schütz et al., 1989; Wassmann et al., 1993; De Groot & Vermoessen, 1991; Inubushi et al., 1984; Sass et al., 1991; Van Vee & Paul, 1981), soil Eh (Takai, 1956; Oremland, 1988; Schipper & Reddy, 1996; Kludze & DeLaune, 1995; Masscheleyn et al., 1993), and soil temperature (Conrad et al., 1987; Vogels et al., 1988; Conrad, 1989; Yagi et al., 1990; Parashar et al., 1993; Wang et al., 1993). The reduction of available carbon to CH<sub>4</sub> is mediated by anaerobic microbes (e.g., methanogens) that are only active when the soil redox potential is low enough (Wassmann et al., 1993; Sass et al., 1991). According to field observations by Kludze

& DeLaune (1994), Wang et al. (1993), and Masscheleyn et al. (1993), CH<sub>4</sub> production increased exponentially with decreasing Eh with a threshold range of -150 to -200 mV. Methane production increased with increasing temperature, with an optimum range of 30–40 °C. Based on the observations, DNDC calculates CH<sub>4</sub> production rate as a function of DOC content and temperature as soon as the predicted soil Eh reaches -150 mV or lower (equation 3.1 in Appendix).

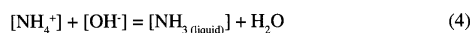


Methane is oxidized by aerobic methanotrophs in the soil. Several researchers reported that 50–80% of CH<sub>4</sub> produced was oxidized in the same soil (Schütz et al., 1989; Holzapfel-Pschorn et al., 1985; Sass et al., 1991; Shangguan et al., 1993; Schipper & Reddy, 1996). Researchers assumed that CH<sub>4</sub> produced at low Eh soil microsites could diffuse into high Eh microsites (e.g., the topsoil or the soil around roots), and hence be oxidized rapidly under higher redox conditions (DeBont et al., 1978; Holzapfel-Pschorn et al., 1985; Schütz et al., 1989; Schipper & Reddy, 1994, 1996). DNDC calculates CH<sub>4</sub> oxidation rate as a function of soil CH<sub>4</sub> concentration and Eh (equation 3.2 in the Appendix). A highly simplified scheme was employed in DNDC to model CH<sub>4</sub> diffusion between soil layers based on CH<sub>4</sub> concentration gradients, temperature, and porosity in the soil (equation 3.5 in the Appendix).

Many researchers reported that plant-mediated transport dominated CH<sub>4</sub> emissions from the soil into the atmosphere (Kludze & DeLaune, 1995; Schütz et al., 1989; Nouchi et al., 1994; Cicerone & Shetter, 1981). Linear relationships between CH<sub>4</sub> emissions and crop aboveground biomass during the growing season have been observed by Sass et al. (1990) and Whiting et al. (1991). DNDC predicts plant-transported CH<sub>4</sub> flux as a function of CH<sub>4</sub> concentration and plant aerenchyma (equation 3.3 in the Appendix). If the soil is unvegetated or the plant aerenchyma is not well developed yet, ebullition plays a major role in CH<sub>4</sub> emissions (Nouchi, 1994; Schütz et al., 1989; Chanton et al., 1989; Kelley et al., 1990; Byrnes et al., 1995). In DNDC, we assume that ebullition only occurs at the surface layer, and ebullition rate is regulated by soil CH<sub>4</sub> concentration, temperature, porosity, and plant aerenchyma (equation 3.4 in the Appendix).

$NH_3$ 

Soil  $NH_3$  concentration is directly regulated by a chemical reaction occurring in the soil liquid phase:



where  $[NH_4^+]$  is ammonium concentration,  $[OH^-]$  is hydroxide ion concentration, and  $[NH_3(\text{liquid})]$  is ammonia concentration in soil water.

DNDC calculates  $NH_3(\text{liquid})$  concentration based on  $NH_4^+$  and  $OH^-$  concentrations (equation 4.1 in the Appendix).  $NH_4^+$  concentration in the soil profile is calculated by the decomposition submodel. The submodel calculates turnover rates of soil organic matter at a daily time step (Li et al., 1992a).  $OH^-$  concentration is determined by soil pH and temperature based on Stumm and Morgan (1981). The concentration of  $NH_3$  in the soil gas phase is proportional to the  $NH_3$  concentration in the liquid phase as well as soil temperature (Glasstone, 1946; Sutton et al., 1993). We assume that daily emitted fraction of the gas phase  $NH_3$  is related to the soil air-filled porosity and clay content due to their effects on  $NH_3$  gas diffusion (equation 4.2 in the Appendix).

Based on field observations by Hooker et al. (1980) and Parton et al. (1988), ambient  $NH_3$  can be absorbed and metabolized by the plants. Plant absorption rates of  $NH_3$  have been observed to be related to  $NH_3$  concentration in the air around the leaves (Hutchinson, 1972; Hutchinson et al., 1972; Meyer, 1973; Farquhar et al., 1979, 1980; Lockyer & Whitehead, 1986), N shortage in the crops (Harper et al., 1987), leaf surface moisture (Dabney & Bouldin, 1985; Harper et al., 1987; Sutton et al., 1993), and plant-growing stage (Farquhar et al., 1979; Hooker et al., 1980; Schjorring, 1991). A linear relationship between dry  $NH_3$  deposition rates and air  $NH_3$  concentrations was observed by Hutchinson (1972), Meyer (1973), Cowling & Lockyer (1981), Aneja et al. (1986), and Sommer & Jenson (1991). Based on their observations, the concept of N deposition velocity can be represented by the ratio of  $NH_3$  absorption rate ( $\mu\text{g m}^{-2} \text{s}^{-1}$ ) to air  $NH_3$  concentration ( $\mu\text{g m}^{-3}$ ). Reported velocity values range from 0.003 to 0.034  $\text{m s}^{-1}$  (Cowling & Lockyer, 1981; Aneja et al., 1986; Sommer & Jenson, 1991) for different crops such as grass, maize, snap bean, soybean, oats, and fescue. The maximum value of the range (i.e., 0.034  $\text{m s}^{-1}$ ) was adopted in DNDC for calculating  $NH_3$  absorption rate by crops. In addition, factors such as plant N status and leaf surface moisture were also included in the calcula-

tion (equation 4.3 in the Appendix). A highly simplified scheme was included in DNDC to calculate  $NH_3$  concentrations in the air between the ground and the top of the canopy, based on the predicted soil  $NH_3$  flux, atmospheric background  $NH_3$  concentration (0.06 ppm, based on Ayers & Gras [1980] and Tsunogai & Ikeuchi [1986]), and degree of closure of the canopy. Farquhar et al. (1979) and Harper et al. (1987) observed  $NH_3$  release from the leaves during the late stages of crop growth. DNDC tracks total N content in the crops during the whole growing season (Li et al., 1994). When the model detects a decrease in the total plant N content, the reduced part will be regarded as the  $NH_3$  flux released from the plants.

The equations describing the effects of soil environmental factors on  $NO$ ,  $N_2O$ ,  $CH_4$ , and  $NH_3$  were organized into three submodels. The fermentation submodel contains all the  $CH_4$ -related equations. This submodel calculates production, oxidation, and transport of  $CH_4$  under submerged conditions. The denitrification submodel contains all the denitrification equations. This submodel calculates production, consumption, and diffusion of  $N_2O$  and  $NO$  during rainfall, irrigation, or flooding events. Nitrification-related equations are included in the nitrification submodel. As a logical extension of the  $NH_4^+ / NH_3(\text{liquid}) / NH_3(\text{gas})$  equilibrium, functions for  $NH_3$  production and volatilization are also included in the nitrification submodel. The three submodels compose the second component of the DNDC model.

### Input and output

Input parameters required by DNDC include daily temperature and precipitation, soil bulk density, texture, organic carbon content, pH, and farming practices (e.g., crop type and rotation, tillage, fertilization, manure amendment, irrigation, flooding, grazing, and weeding). Profiles of soil environmental variables as well as trace gas fluxes are calculated based on the input data. When DNDC is used for regional estimates of trace gas emissions, the model needs the spatially and temporally differentiated input data stored in geographic information system (GIS)-type databases in advance (Li et al., 1996). Based on the input parameters of the ecological drivers, DNDC first predicts daily soil temperature, moisture, Eh, pH, and substrate concentration, and then uses the environmental parameters to drive nitrification, denitrification,  $CH_4$  production/oxidation, and other relevant geochemical or biochemical reactions. Daily emissions of  $NO$ ,  $N_2O$ ,  $CH_4$ , and  $NH_3$  are finally calcu-

lated as their daily net fluxes. Most parts of the model run at a daily time step except the soil climate and denitrification submodels which run at an hourly time step. Output parameters from the model runs are daily soil profiles of temperature, moisture, Eh, pH, and concentrations of total soil organic carbon, nitrate, nitrite, ammonium, urea, ammonia, as well as daily fluxes of  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$ . All the daily and annual output data are recorded for future use. For the regional version of DNDC, the simulated results are recorded as geographically explicit data in a GIS database.

### Model tests

The DNDC model has been tested against several field studies. The old results related to  $\text{N}_2\text{O}$  and soil organic carbon have been published (e.g., Li et al., 1992b; Li et al., 1994; Li, 1997; Frohling, 1998). Here are reported four new cases that were examined recently for  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$ , respectively. The characteristics of the four agricultural sites are listed in Table 1.

### NO

Fluxes of  $\text{NO}$  were measured at a winter wheat field in Wu County, Jiangsu Province, China, from 1 Nov 1996 to 9 Feb 1997 by Xunhua Zheng and her colleagues (1998). Urea and farmyard manure (equivalent to  $114 \text{ kg N ha}^{-1}$ ) were applied on 1 Nov 1996. During the first 40 d following the application, high  $\text{NO}$  fluxes were observed in the fertilized plot but not in the control plot (Figure 3). Predicted results agreed with observed data and indicated that high fluxes were mainly caused by elevated nitrification rates following fertilizer application. In addition, the relatively high temperature in the early days of the experimental period also enhanced urea hydrolysis and nitrifier activity. The temperature effect can also be seen in the control plot.

### $\text{N}_2\text{O}$

Nitrous oxide was measured by Crill et al. (1998) for two plots, fertilized and unfertilized, in a maize field at La Selva Biological Station in Costa Rica from November 1994 to March 1995. Ammonium nitrate and urea ( $30\text{--}90 \text{ kg N ha}^{-1}$ ) were applied on 25 Nov and 6 Dec 1994 on the fertilized plot. During the two maize-growing seasons,  $\text{N}_2\text{O}$  fluxes were consistently low in the unfertilized plot. In contrast, in the fertilized plot, high peaks were observed immediately after fertilizer application. Simulation results agreed with observed results showing the same two high peaks as observed in the field (Figure 4), indicating that the surges of  $\text{N}_2\text{O}$

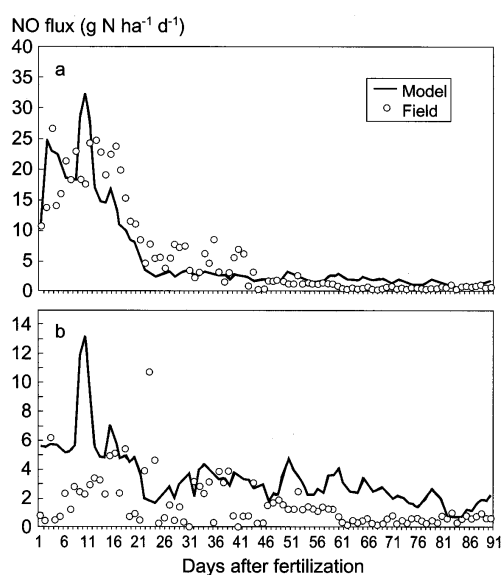


Figure 3. Measured and predicted  $\text{NO}$  fluxes from fertilized (a) and control (b) plots in a winter wheat field at Wu County, Jiangsu, China, 1 Nov 1996-9 Feb 1997

Table 1. Characteristics of four field sites for model validation tests.

Site	Crop type	Annual average temperature (°C)	Annual precipitation (cm)	Gas measured	Soil texture	Soil organic C	Soil pH
Wu, Jiangsu, China	Winter wheat	17.0	115.6	$\text{NO}$	Clay loam	0.01	7.0
La Selva, Costa Rica	Maize	24.7	438.2	$\text{N}_2\text{O}$	Clay	0.028	6.8
Texas, USA	Rice	18.7	99.7	$\text{CH}_4$	Loam	0.02	6.5
Fengqiu, Henan, China	Rice	14.6	64.2	$\text{NH}_3$	Sandy loam	0.0035	8.8

emissions were mainly caused by denitrification. Since soil temperature, moisture, and DOC did not limit denitrifier activity in the plot, additions of inorganic N immediately stimulated denitrification and  $N_2O$  emissions. Simulated results indicated that N was a limiting factor in the soil, although nitrification rates were high due to the rapid turnover of soil organic matter. The high demand of plants and soil microbes for N, as well as the strong leaching effect, did not allow  $NO_3^-$  or  $NH_4^+$  to accumulate in the topsoil.

#### $CH_4$

Ron Sass and his colleagues (1991) measured  $CH_4$  fluxes from two rice field plots, with and without straw amended, at Beaumont, Texas. The measured  $CH_4$  fluxes from the straw-amended plot were almost twice higher than that from the control plot. Field observations indicated that the higher  $CH_4$  production in the amended plot was mainly due to additional available C produced from straw decomposition. Model simulations

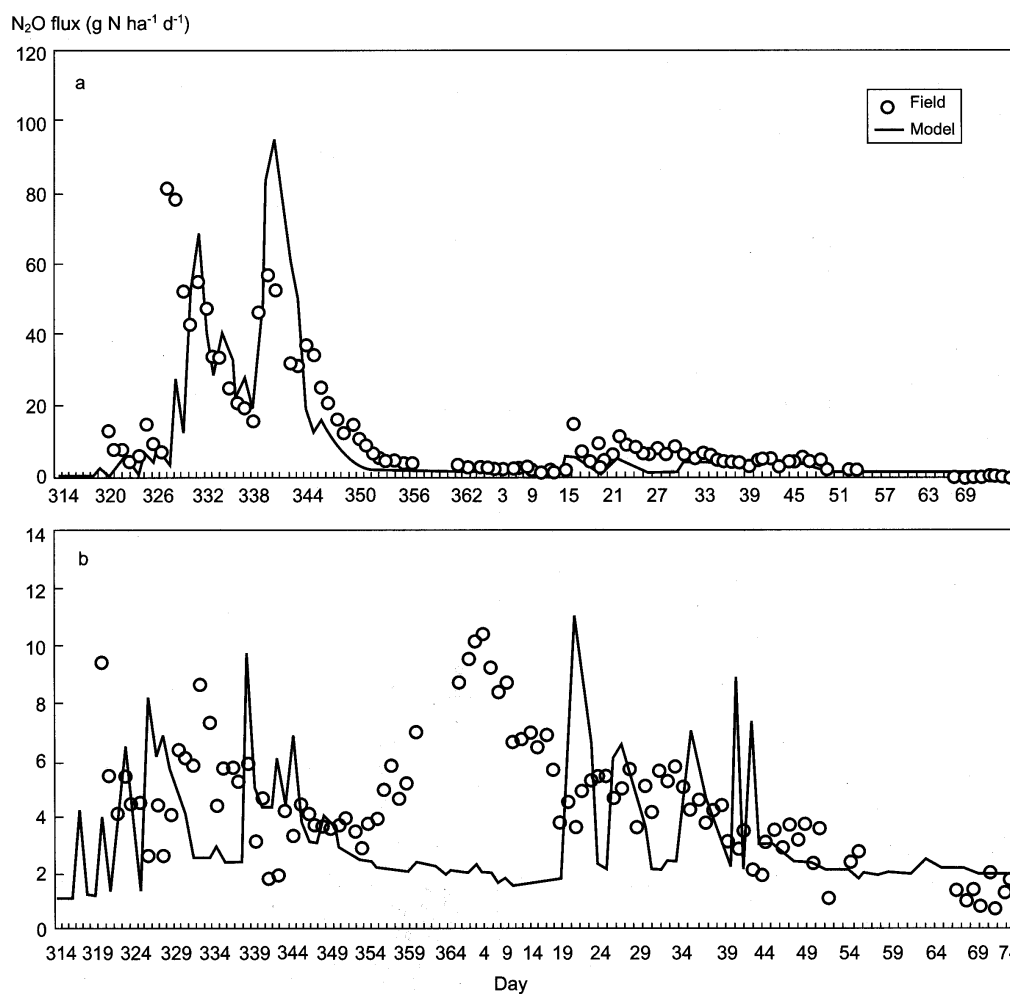


Figure 4. Measured and predicted  $N_2O$  fluxes from fertilized (a) and control (b) plots in a maize field at La Selva Biological Station in Costa Rica, November 1994–March 1995



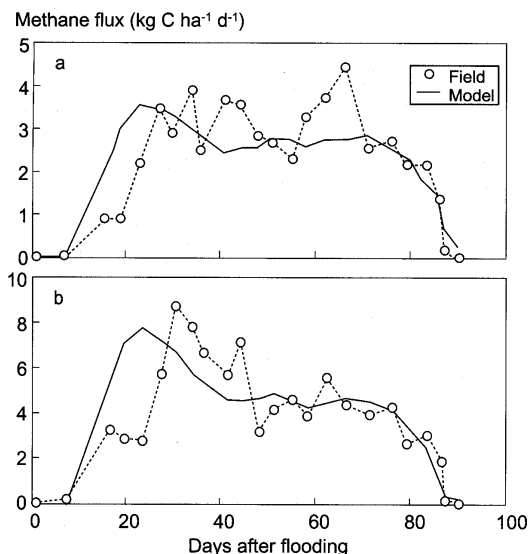


Figure 5. Measured and predicted  $\text{CH}_4$  fluxes from control (a) and straw-amended (b) plots in a rice field at Texas A&M University Agricultural Center near Beaumont in Texas, USA, 1989-90

showed similar results (Figure 5). Both measured and model data showed a slight depression of  $\text{CH}_4$  emissions in the middle of the growing season. Predicted data showed that the depression was caused by depletion of the labile straw and the undeveloped rice aerenchyma at that time.

### $\text{NH}_3$

At a rice field in Fengqiu County, Henan Province, China, Cai and Zhou (1995) measured  $\text{NH}_3$  fluxes from the rice soils. Ammonium bicarbonate and urea were applied at the same rate ( $90 \text{ kg N ha}^{-1}$ ) to two plots to test the effect of different fertilizer types on  $\text{NH}_3$  emissions. Field measurements were conducted at 4-h intervals for 9 d following fertilizer applications.  $\text{NH}_3$  fluxes measured at the ammonium bicarbonate-applied plot were initially very high, and then rapidly decreased to almost zero in the 4 d after fertilizer application. In contrast, at the urea-fertilized plot,  $\text{NH}_3$  fluxes were initially low, and gradually increased to a maximum value on the fifth day, and then decreased to a low level 8 d after application. Patterns of  $\text{NH}_3$  fluxes observed in the field were simulated by the model (Figure 6). Simulation results showed that the applied ammonium bicarbonate immediately increased  $\text{NH}_3$  concentration in the rice field water due to the equilibrium between  $\text{NH}_4^+$  and  $\text{NH}_3$  in the soil liquid phase. High soil pH (8.8) enhanced  $\text{NH}_3$  volatilization from the rice soil. In contrast, it took 4 d for the applied urea to be gradually hydrolyzed. The hydrolysis slowed down  $\text{NH}_3$  volatilization in the urea plot.

Simulated results from the four data sets showed that (1) DNDC was able to simulate the basic patterns of  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  fluxes under various farming conditions; (2) predicted total emissions during the experimental span agreed with the measurements (Table 2); and (3) measured temporal variations in gas

Table 2. Comparison between measured and predicted trace gas emissions

Site	Gas tested	Treatment	Experimental days (no.)	Total flux during experimental span		
				Measured	Predicted	Unit
Wheat field at Wu County, Jiangsu, China	NO	Fertilized	95	0.53	0.51	kg N ha <sup>-1</sup>
		Control	95	0.14	0.31	kg N ha <sup>-1</sup>
Maize field at La selva, Costa Rica	N <sub>2</sub> O	Fertilized	125	1.25-1.40	1.17	kg N ha <sup>-1</sup>
		Control	125	0.29-0.46	0.39	kg N ha <sup>-1</sup>
Rice field at Texas, USA	CH <sub>4</sub>	Amended with straw	90	98.9	93.8	kg C ha <sup>-1</sup>
Control			90	54.7	53.9	kg C ha <sup>-1</sup>
Rice field at Fengqiu County, Henan, China	NH <sub>3</sub>	Fertilized with ammonium bicarbonate	9	48.3	55.2	kg N ha <sup>-1</sup>
		Fertilized with urea	9	31.0	31.9	kg N ha <sup>-1</sup>

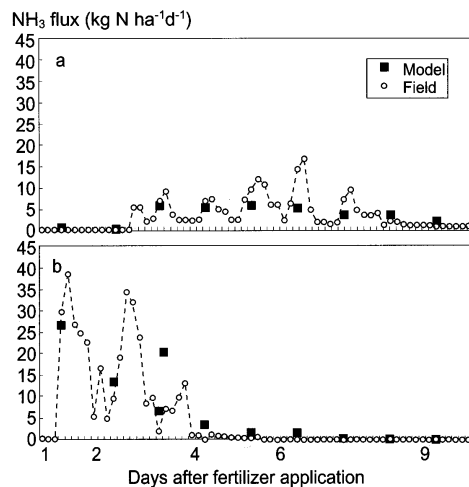


Figure 6. Measured and predicted  $\text{NH}_3$  fluxes from urea-fertilized (a) and ammonium bicarbonate-fertilized (b) plots in a rice field at Fengqiu County, Henan, China. The  $\text{NH}_3$  fluxes were measured in the field with 4-h intervals although DNDC only predicts daily  $\text{NH}_3$  emissions

fluxes can be explained with the equations built in the model.

## Discussion

The DNDC model reported in this paper is the result of a 10-yr effort to predict trace gas emissions from agricultural ecosystems. By linking ecological drivers to soil environmental variables, and further, to trace gas-related biogeochemical reactions, DNDC acts as a bridge between ecological drivers and the chemical elements' behavior. During development of the model, we made every effort to incorporate the basic mechanisms or processes into the model, although gaps still exist in almost every component of the model. For example, the highly simplified diffusion equations could have brought large uncertainties to the simulated results. Nevertheless, we hope that we have established a useful tool that can be used not only for synthesizing existing observations obtained by hundreds of researchers during the last several decades but also for testing new hypotheses for future studies. In comparison with other models focusing on a couple of trace gases, DNDC

has the advantage of predicting  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  simultaneously. This feature could be valuable in assessing the net effect of the changing climate or alternative agricultural management on either the atmosphere or agriculture. Linked to GIS databases of climate, soil, vegetation, and farming practices, DNDC is ready for regional estimation of trace gas emissions.

Methodology development is also one of the motivations for this modeling effort. Since V.I. Vernatski initiated the concept of biogeochemistry in his famous book *La Geochimie* in 1924, 75 yr have passed. During the first 50 yr of this time period, biogeochemistry, as a scientific discipline, did not develop very fast due to the lack of social demands. Only during the last two decades, when global climate change provided new challenges to the scientific community, did people rediscover the potential of biogeochemistry in integrating the macro processes occurring at the ecosystem level with the micro processes at the molecular or atomic scale. To meet the new demand, we need to develop new methodologies based on biogeochemical concepts or principles. The modeling effort reported in this paper is a continuation of our long-term biogeochemical studies. The strategy and methodologies used in this modeling study have been successfully used in several ecological studies including human health (Li & Yu, 1973) and environmental pollution (BEARG, 1997). The author hopes this paper will fuel more interest in the methodology studies in this interdisciplinary realm.

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**Appendix: Equations and parameters****1. Nitrification**

Equation 1.1. Relative growth rate of nitrifiers

$$dG/dt = 0.0166 * (DOC / (1.0 + DOC) + Fm / (1.0 + Fm));$$

Equation 1.2. Relative death rate of nitrifiers

$$dD/dt = 0.008 * BIO * 1.0 / (1.0 + DOC) / (1.0 + Fm);$$

Equation 1.3. Net increase in nitrifier biomass

$$dBIO/dt = (dG/dt - dD/dt) * BIO * Ft * Fm;$$

$$BIO = \int^{24} dBIO/dt;$$

Equation 1.4. Nitrification rate

$$Rn = [NH_4^+] * (0.005 * BIO) * pH, \text{ (kg N/ha/day)};$$

Equation 1.5. Temperature factor

$$Ft = 3.503^{(60.0-T)/(60.0-34.22)} * e^{3.503 * (T-34.22)/(60.0-34.22)};$$

Equation 1.6. Moisture factor

$$Fm = 0.8 + 0.21 * (1.0 - wfps), \text{ if } wfps > 0.05;$$

$$Fm = 0, \text{ if } wfps \leq 0.05;$$

Equation 1.7. Nitrification-induced NO (kg N/ha/d)

$$NO = 0.0025 * Rn * Ft;$$

Equation 1.8. Nitrification-induced N<sub>2</sub>O (kg N/ha/d)

$$N_2O = 0.0024 * Rn;$$

DOC – Concentration of dissolved organic C, kg C/ha;  
BIO – Nitrifier biomass, kg C/ha;  
[NH<sub>4</sub><sup>+</sup>] – Concentration of ammonium, kg N/ha;

pH – Soil pH.

**2. Denitrification**Equation 2.1. Relative growth rate of NO<sub>x</sub> denitrifiers (1/h)

$$GR_{NO_x} = GR_{NO_x(max)} * [C / (Kc + C)] * [NO_x / (Kn + NO_x)];$$

Equation 2.2. Relative growth rate of total denitrifiers (1/h)

$$GR = Ft * (GR_{NO_3} * PH1 + GR_{NO_2} * PH2 + GR_{NO} * PH3 + GR_{N_2O} * PH4);$$

$$Ft = a * 2^{(T - 22.5) / 10.0};$$

Equation 2.3. Denitrifier growth/death and consumption of soluble carbon (kg C/m<sup>3</sup>/h)

$$\text{Growth rate: } (dBIO/dt)_g = GR * BIO(t);$$

$$\text{Death rate: } (dBIO/dt)_d = Mc * Yc * BIO(t);$$

$$\text{Carbon consumption rate: } dC/dt = (GR / Yc + Mc) * BIO(t);$$

Equation 2.4. Consumption rates of N oxides (kg N/m<sup>3</sup>/h)

$$d(NO_x)/dt = (GR_{NO_x} / Y_{NO_x} + M_{NO_x} * NO_x / N) * BIO(t);$$

Equation 2.5. Nitrogen assimilation rate (kg N/m<sup>3</sup>/h)

$$(dN/dt)_a = (dBIO/dt)_g / CN;$$

Equation 2.6. NO, N<sub>2</sub>O and N<sub>2</sub> diffusion rates (%)

$$\text{NO and N}_2\text{O: diffuse} = (0.0006 + 0.0013 * AD) + (0.013 - 0.005 * AD) * PA * (1 - anv);$$

$$\text{N}_2: \text{diffuse} = 0.017 + (0.025 - 0.0013 * AD) * PA * (1 - anv);$$

GR<sub>NO<sub>3</sub>(max)</sub> – Maximum growth rate of NO<sub>3</sub><sup>-</sup> denitrifiers, 0.67 1/h (Hartel & Alexander, 1987);GR<sub>NO<sub>2</sub>(max)</sub> – Maximum growth rate of NO<sub>2</sub><sup>-</sup> denitrifiers, 0.67 1/h (Hartel & Alexander, 1987);GR<sub>NO(max)</sub> – Maximum growth rate of NO denitrifiers, 0.34 1/h (Hartel & Alexander, 1987);GR<sub>N<sub>2</sub>O(max)</sub> – Maximum growth rate of N<sub>2</sub>O denitrifiers, 0.34 1/h (Hartel & Alexander, 1987);Kc – Half-saturation value of soluble carbon, 0.017 kg C/m<sup>3</sup> (Shah & Coulman, 1978);Kn – Half-saturation value of N oxides, 0.083 kg N/m<sup>3</sup> (Shah & Coulman, 1978);C – Soluble C concentration, kg C/m<sup>3</sup> (calculated by DNDC);



$NO_x$  - Concentration of  $NO_3^-$ ,  $NO_2^-$ , NO or  $N_2O$ , kg N/m<sup>3</sup> (calculated by DNDC);  
 PH1, PH2, PH3 = a \* (soil pH - b), a=0.4, and b=2.5, 3.0, or 3.5, respectively; factors of impact of pH on  $NO_3^-$ ,  $NO_2^-$ , and NO and  $N_2O$  denitrifiers (Focht, 1974);  
 BIO(t) - Denitrifier biomass at time t, kg C /m<sup>3</sup> (calculated by DNDC);  
 Mc - Maintenance coefficient on carbon, 0.0076 kg C /kg/h (Van Verseveld et al., 1977);  
 Yc - Maximum growth rate on soluble carbon, 0.503 kg C /kg C (Van Verseveld et al., 1977);  
 $Y_{NO_3^-}$ ,  $Y_{NO_2^-}$ ,  $Y_{NO}$ ,  $Y_{N_2O}$  - Maximum growth rate on  $NO_3^-$ ,  $NO_2^-$ , NO and  $N_2O$ , respectively, 0.401, 0.428, 0.151, 0.151 kg C /kg N (Van Verseveld et al., 1977);  
 $M_{(NO_3^-)}$ ,  $M_{(NO_2^-)}$ ,  $M_{(N_2O)}$ ,  $M_{(NO)}$  - Maintenance coefficient on  $NO_3^-$ ,  $NO_2^-$ ,  $N_2O$  and NO, respectively, 0.09, 0.035, 0.079, 0.079 kg N /kg/h (Van Verseveld et al., 1977);  
 CN - C/N in denitrifiers, 3.45 (Van Verseveld & Stouthamer, 1978).

### 3. CH<sub>4</sub> Production and Oxidation

Equation 3.1. CH<sub>4</sub> production rate (kg C/ha/d)

$$CH_{4p} = a * AC * Ft;$$

$$Ft = b * e^{(0.2424 * T)}; \text{ (factor of temperature)}$$

Equation 3.2. CH<sub>4</sub> oxidation rate (kg C/ha/d)

$$CH_{4o} = CH_{4l} * e^{(8.6711 * Eh_l / 1000)};$$

Equation 3.3. CH<sub>4</sub> flux through plant aerenchyma (kg C/ha/d)

$$CH_{4(aere)} = 0.5 * CH_{4l} * AERE;$$

$$AERE = -0.0009 * PGI^5 + 0.0047 * PGI^4 - 0.883 * PGI^3 + 1.9863 * PGI^2 - 0.3795 * PGI + 0.0251;$$

$$PGI = (\text{days since planting}) / (\text{season days}); \text{ (plant growth index)}$$

Function 3.4. CH<sub>4</sub> flux through ebullition (kg C/ha/d)

$$CH_{4(ebullition)} = 0.025 * CH_{4l} * PORO * Ft * (1 - AERE);$$

$$Ft = -0.1687 * (0.1 * T[l])^3 + 1.167 * (0.1 * T[l])^2 - 2.0303 * (0.1 * T[l]) + 1.042;$$

Function 3.5. CH<sub>4</sub> diffusion rate (kg C/ha/d)

$$Rd = 0.01 * (CH_{4l} - CH_{4l+1}) * T[l] * PORO;$$

AC - Available C concentration, kg C/ha;

T - soil temperature, °C;

l - soil layer number;

AERE - plant aerenchyma;

FloodDay - flooding days;

PORO - soil porosity;

CH<sub>4</sub>[l] - CH<sub>4</sub> concentration at layer l, kg C/ha.

### 4. NH<sub>3</sub> Volatilization

Equation 4.1. NH<sub>3</sub> concentration in liquid phase (mol/l)

$$[NH_3(l)] = [NH_4^+] [OH^-] / Ka;$$

$$NH_4^+ / NH_3 \text{ equilibrium constant: } Ka = (1.416 + 0.01357 * T) * 10^{-5};$$

$$[OH^-] = Kw / [H^+], \text{ mol/l};$$

$$[H^+] = 10^{-pH}, \text{ mol/l};$$

$$Kw = 10^{(0.08946 + 0.03605 * T)} * 10^{-15}; \text{ (water dissociation constant)}$$

Equation 4.2. NH<sub>3</sub> concentration in gas phase and flux (kg N/ha)

$$NH_{3(g)} = [NH_3(l)] * (T/T_0)^2;$$

$$\text{Flux}(NH_3) = NH_{3(g)} * AFPS * (1 - \text{Clay}), \text{ kg N/ha/d};$$

Equation 4.3. NH<sub>3</sub> deposit (kg N/ha/d)

$$Vg = \text{MaxVg} * F(\text{plant-N}) * F(\text{lsm});$$

$$F(\text{plant-N}) = \text{Plant-N}(\text{act}) / \text{Plant-N}(\text{opt});$$

$$F(\text{lsm}) = \text{LSM}(\text{act}) / \text{LSM}(\text{max});$$

$$\text{PlantUp}(NH_3) = Vg * \text{Air}(NH_3) * \text{LAI} * 0.864;$$

$$\text{Air}(NH_3) = \text{Base}(NH_3) + \text{Flux}(NH_3) * 10^9 / V(\text{canopy}) * \text{LAI} / (\text{LAI} + k2) * k3;$$

$$V(\text{canopy}) = \text{Height} * 10000;$$

T<sub>0</sub> - reference temperature, 45°C;

T - soil temperature, °C;

PH - soil pH;

AFPS - soil air-filled porosity;

Clay - soil clay content;

MaxVg	- maximum NH <sub>3</sub> deposit velocity, 0.05 m/s;
Plant-N(act)	- crop N content, kg N/ha;
Plant-N(opt)	- crop optimum N content, kg N/ha;
LSM(act)	- water content on leaf surface, cm;
LSM(max)	- maximum water content on leaf surface, cm;
Base(NH <sub>3</sub> )	- background NH <sub>3</sub> concentration, 0.06 ug/m <sup>3</sup> ;
V(canopy)	- volume of the room from ground to the top of canopy, m <sup>3</sup> /ha;
Height	- maximum height of plant, m;
LAI	- crop leaf area index;
MaxLAI	- maximum crop leaf area index;
K2, k3	- constant coefficients;