Modeling trace gas emissions from agricultural ecosystems

C.S. Li

Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, Durham, NH 03824, USA

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 NH_3, NO, N_2O, and 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, N_2O, CH_4, and 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 (CH_4), nitrous oxide (N_2O), nitric oxide (NO), and ammonia (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, N_2O, CH_4, and NH_3 emissions from agricultural ecosystems. Several papers have reported on the early development of the model, focusing only on N_2O and CO_2 (Li et al., 1992a; 1994). This paper discusses the latest research progress including simulations of NO, CH_4, and NH_3.

Model framework

Emissions of NO, N_2O, CH_4 and 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 N_2O) 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_2O, CH_4 and NH_3-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_2O, CH_4, and NH_3 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
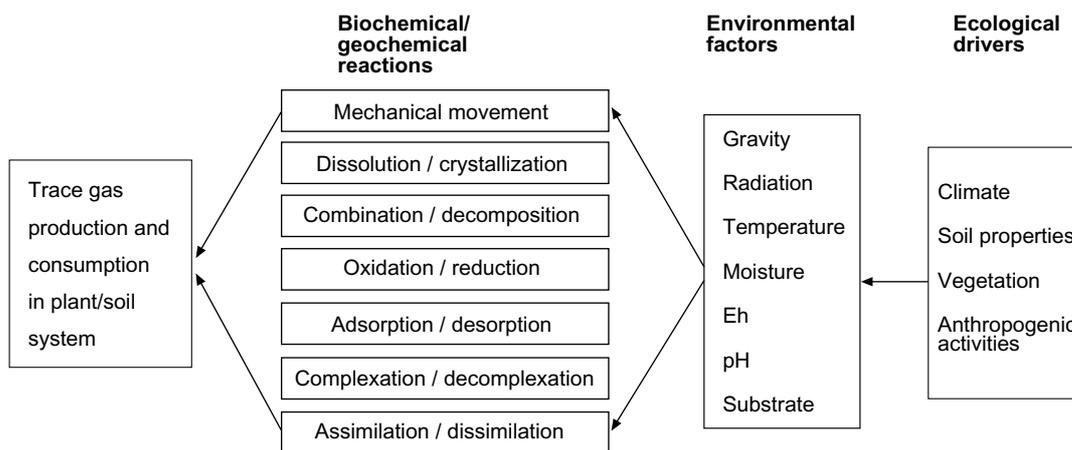
Figure 1. A biogeochemical model is a mathematical expression of biogeochemical field which consists of spatially and temporally differentiated environmental forces driving a series of biogeochemical reactions in ecosystems. Fluxes of NO, N_2O, CH_4, and NH_3 are regulated by directions and rates of the relevant biogeochemical reactions

The DNDC Model
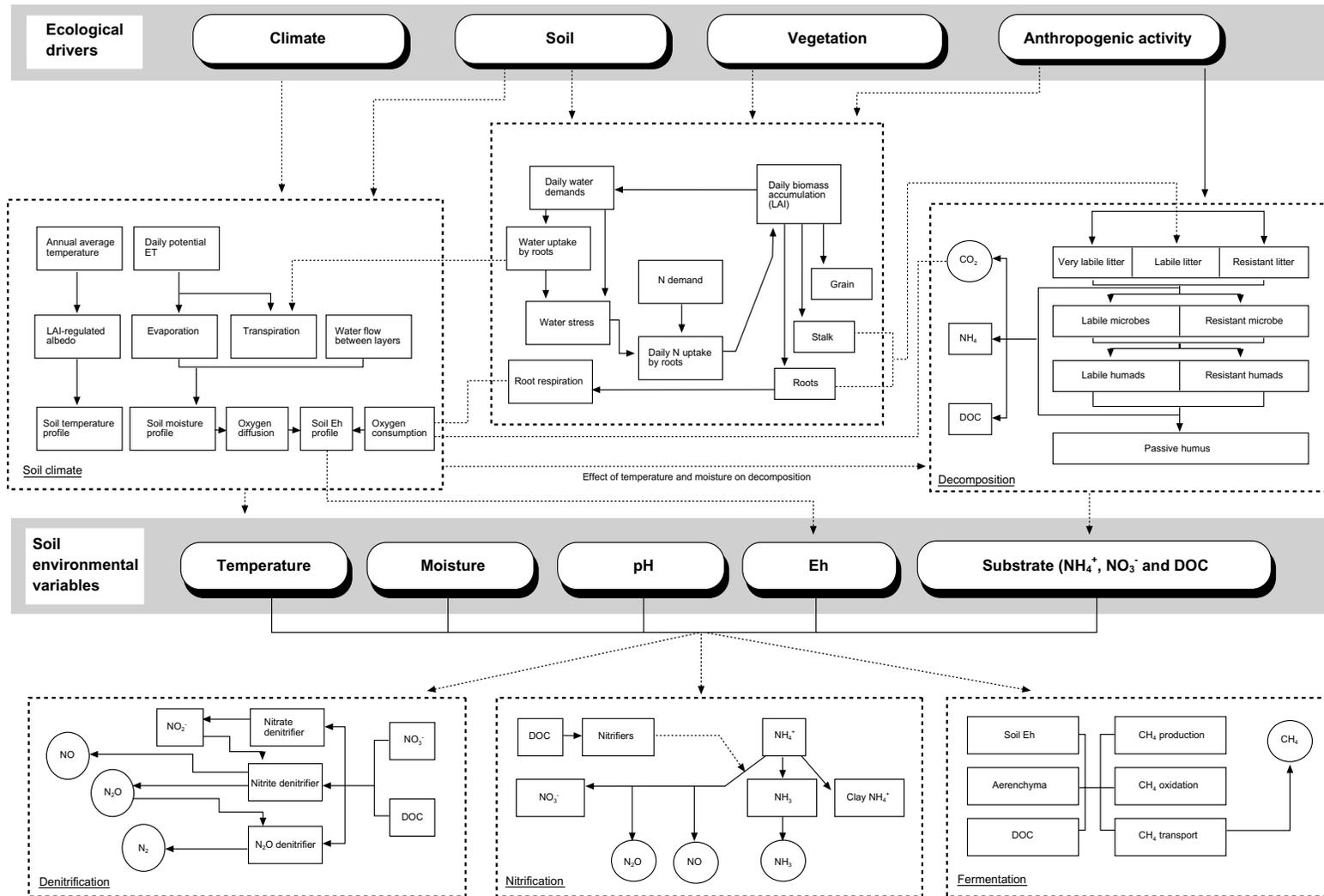
Figure 2. The DNDC model includes two components. The first component, consisting of the soil climate, plant growth, and decomposition submodels, predicts effects of climate, soil physical properties, vegetation, and anthropogenic activity on soil temperature, moisture, pH, Eh, and substrate concentration profiles. The second component, consisting of the nitrification-, denitrification, and fermentation submodels, predicts NO, N$_2$O, CH$_4$, and NH$_3$ 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, NH_4^+, and 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_2O

Biological oxidation/reduction dominates NO and N_2O evolution in soils. Nitrification (i.e., microbial oxidation of ammonium) has been observed to be the main source of NO and N_2O 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), N_2O 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 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; Ingwerson 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 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 NH_4^+ oxidizers are calculated based on DOC concentration, temperature, and moisture. Many observations indicated that nitrification-induced NO or N_2O 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 N_2O production as a function of the predicted nitrification rate and temperature (equations 1.7 and 1.8 in the Appendix).

$$\text{Nitrification: } NH_4^+ \rightarrow H_2NOH \rightarrow NOH \rightarrow NO_2^- \rightarrow NO_3^-$$
$$\downarrow \quad \downarrow$$
$$NO \quad N_2O \qquad (1)$$
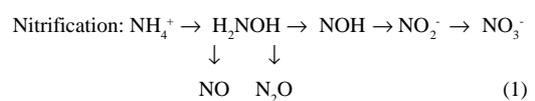
Denitrification is another main source of N_2O and NO from soils. Denitrification includes a sequential reduction of nitrate to dinitrogen (N_2) driven by denitrifying bacteria under anaerobic conditions (equation 2) (Firestone et al., 1980; Payne, 1981; Anderson & Levine, 1986; Poth & Focht, 1985; SSSA, 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; Klemedtsoon et al., 1988; Blackmer & Bremner, 1978; Firestone et al., 1980; Leffelaar & Wessel, 1988; Ashby et al., 1998), and substrate (e.g., DOC, NO_3^-, NO_2^-, NO, and N_2O) concentrations.

$$\text{Denitrification: } NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (2)$$
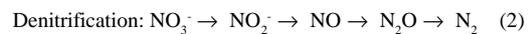
The DNDC model simulates relative growth rates of nitrate, nitrite, NO, and N_2O denitrifiers based on soil Eh, concentrations of DOC, and nitrogen oxides. A simple scheme of "anaerobic balloon" was developed in the model to divide the soil matrix into aerobic and anaerobic parts. Tracking oxygen diffusion 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_2O, and N_2 fluxes. As an intermediate of the reactions, NO or N_2O 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_2O 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_4

Methane is an end product of the biological reduction of carbon dioxide (CO_2) 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_4 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_4 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_4 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_4 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).

$$\text{Methane production: } CO_2 + 8\,H^+ \rightarrow CH_4 + 2\,H_2O \qquad (3)$$
$$\text{or}$$
$$\text{Organic C} + 4\,H^+ \rightarrow CH_4$$
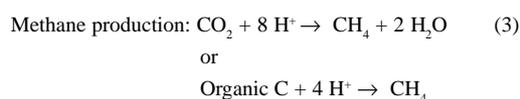
Methane is oxidized by aerobic methanotrophs in the soil. Several researchers reported that 50–80% of CH_4 produced was oxidized in the same soil (Schütz et al., 1989; Holzapfel-Pschorn et al., 1985; Sass et al., 1991; Shangguan et al., 1993; Schipper & Reddy, 1996). Researchers assumed that CH_4 produced 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_4 oxidation rate as a function of soil CH_4 concentration and Eh (equation 3.2 in the Appendix). A highly simplified scheme was employed in DNDC to model CH_4 diffusion between soil layers based on CH_4 concentration gradients, temperature, and porosity in the soil (equation 3.5 in the Appendix).

Many researchers reported that plant-mediated transport dominated CH_4 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_4 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_4 flux as a function of CH_4 concentration and plant aerenchyma (equation 3.3 in the Appendix). If the soil is unvegetated or the plant aerechyma is not well developed yet, ebullition plays a major role in CH_4 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_4 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:

$$[NH_4^+] + [OH^-] = [NH_{3\,(liquid)}] + H_2O \qquad (4)$$
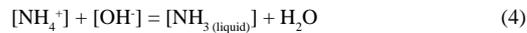
where [NH$_4^+$] is ammonium concentration, [OH$^-$] is hydroxide ion concentration, and [NH$_{3\,(liquid)}$] is ammonia concentration in soil water.

DNDC calculates NH$_{3\,(liquid)}$ 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 (μg m^{-2} s^{-1}) to air NH$_3$ concentration (μg m^{-3}). Reported velocity values range from 0.003 to 0.034 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 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$_2$O, 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$_2$O 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$_{3\,(liquid)}$/ NH$_{3\,(gas)}$ 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$_2$O, 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 CO_2, NO, N_2O, CH_4 and 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 N_2O and soil organic carbon have been published (e.g., Li et al., 1992b; Li et al., 1994; Li, 1997; Frolking, 1998). Here are reported four new cases that were examined recently for NO, N_2O, CH_4 and NH_3, respectively. The characteristics of the four agricultural sites are listed in Table 1.

NO

Fluxes of 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 kg N ha^{-1}) were applied on 1 Nov 1996. During the first 40 d following the application, high 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.

N_2O

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 (30-90 kg N ha^{-1}) were applied on 25 Nov and 6 Dec 1994 on the fertilized plot. During the two maize-growing seasons, N_2O 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 N_2O
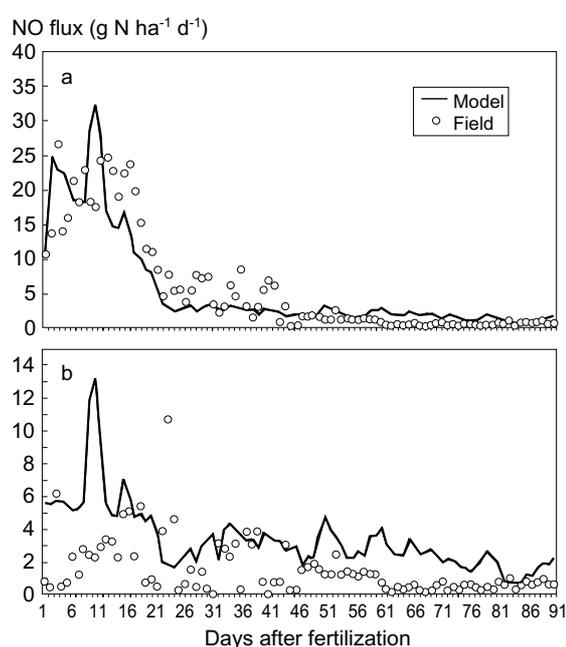
Figure 3. Measured and predicted NO fluxes from fertilized (a) and control (b) plots in a winter wheat field at Wu County, Jiangsu, China, 1 Nov 1996-9 Feb 1997

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	NO	Clay loam	0.01	7.0
La Selva, Costa Rica	Maize	24.7	438.2	N_2O	Clay	0.028	6.8
Texas, USA	Rice	18.7	99.7	CH_4	Loam	0.02	6.5
Fengqiu, Henan, China	Rice	14.6	64.2	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
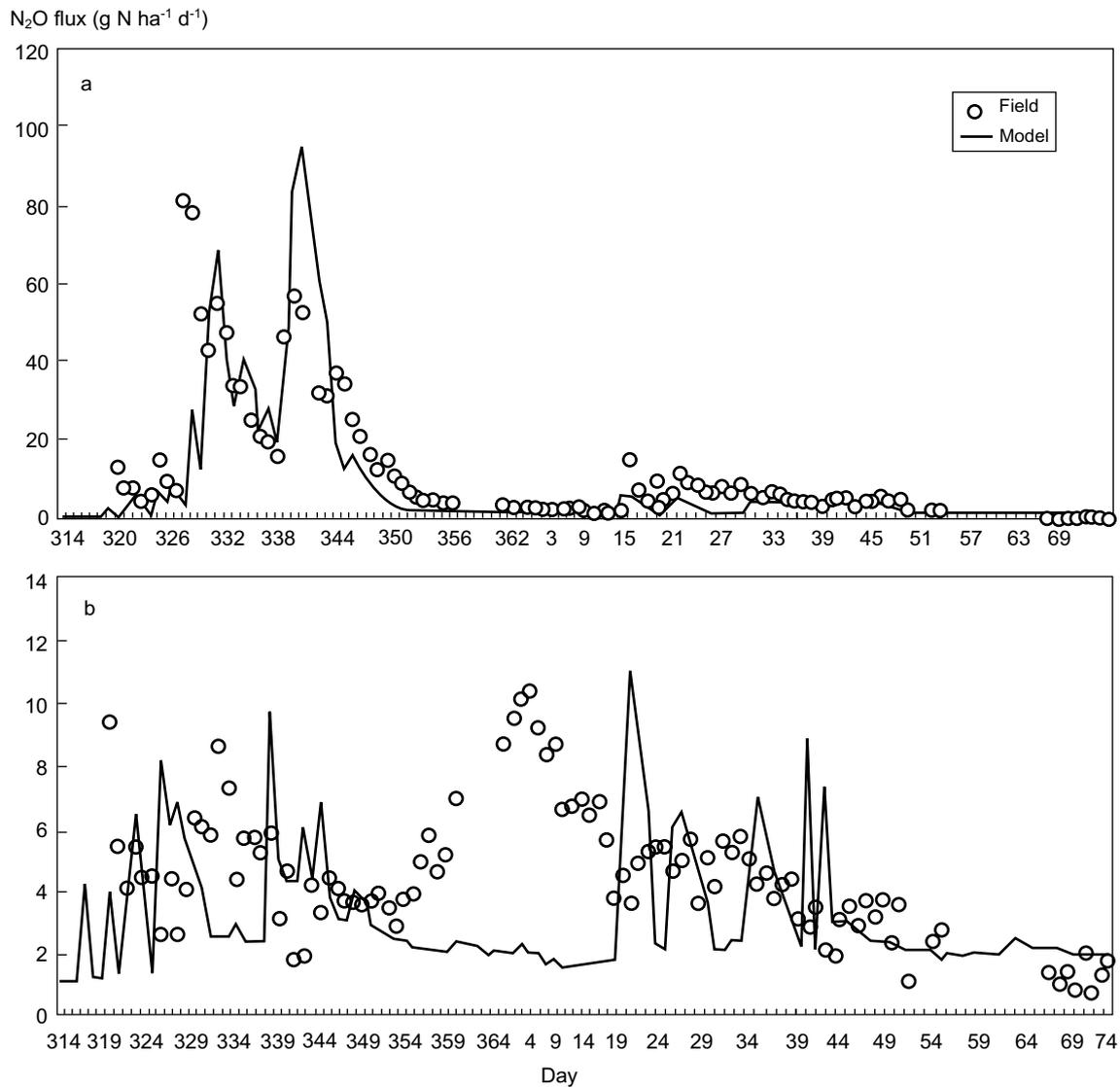
Figure 4. Measured and predicted N_2O fluxes from fertilized (a) and control (b) plots in a maize field at La Selva Biological Station in Costa Rica, November 1994-March 1995

Methane flux (kg C ha^{-1} d^{-1})
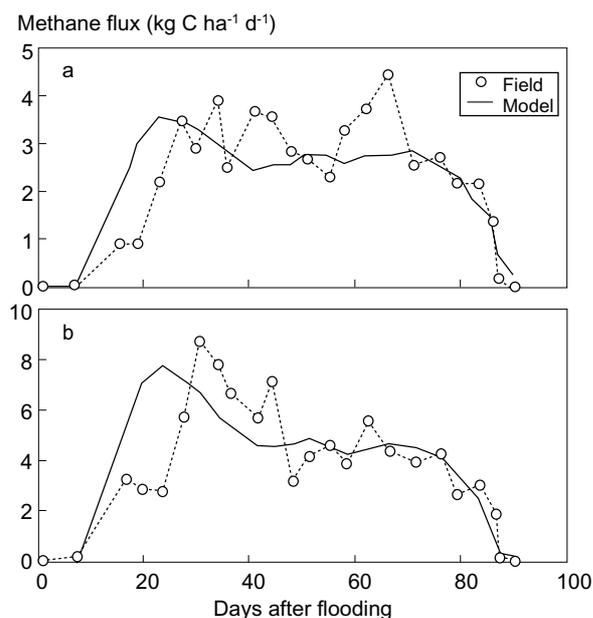
Figure 5. Measured and predicted CH$_4$ fluxes from control (a) and straw-amended (b) plots in a rice field at Texas A&M University Agricultural Center near Beaumont in Texas, USA, 1989-90

showed similar results (Figure 5). Both measured and model data showed a slight depression of 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.

NH$_3$

At a rice field in Fengqiu County, Henan Provice, China, Cai and Zhou (1995) measured NH$_3$ fluxes from the rice soils. Ammonium bicarbonate and urea were applied at the same rate (90 kg N ha^{-1}) to two plots to test the effect of different fertilizer types on NH$_3$ emissions. Field measurements were conducted at 4-h intervals for 9 d following fertilizer applications. 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, 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 NH$_3$ fluxes observed in the field were simulated by the model (Figure 6). Simulation results showed that the applied ammonium bicarbonate immediately increased NH$_3$ concentration in the rice field water due to the equilibrium between NH$_4^+$ and NH$_3$ in the soil liquid phase. High soil pH (8.8) enhanced 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 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 NO, N$_2$O, CH$_4$, and 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^{-1}
		Control	95	0.14	0.31	kg N ha^{-1}
Maize field at La selva, Costa Rica	N$_2$O	Fertilized	125	1.25-1.40	1.17	kg N ha^{-1}
		Control	125	0.29-0.46	0.39	kg N ha^{-1}
Rice field at Texas, USA	CH$_4$	Amended with straw	90	98.9	93.8	kg C ha^{-1}
Control			90	54.7	53.9	kg C ha^{-1}
Rice field at Fengqiu County, Henan, China	NH$_3$	Fertilized with ammonium bicarbonate	9	48.3	55.2	kg N ha^{-1}
		Fertilized with urea	9	31.0	31.9	kg N ha^{-1}

NH₃ flux (kg N ha⁻¹d⁻¹)
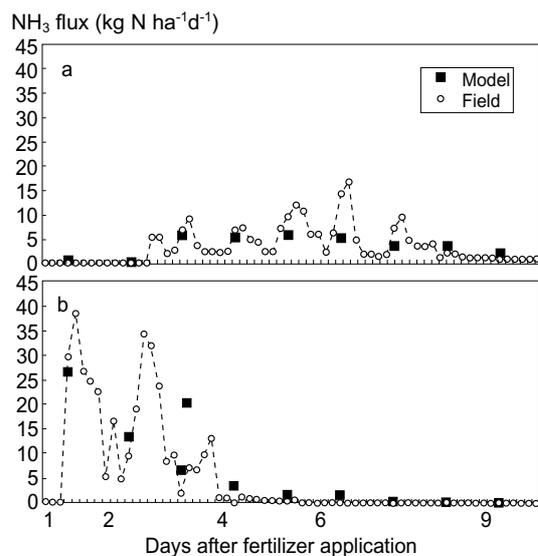
Figure 6. Measured and predicted NH₃ fluxes from urea-fertilized (a) and ammonium bicarbonate-fertilized (b) plots in a rice field at Fengqiu County, Henan, China. The NH₃ fluxes were measured in the field with 4-h intervals although DNDC only predicts daily NH₃ emissions

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 CO_2, NO, N_2O, CH_4, and 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.

Acknowledgements

References

Alexander M (1977) Introduction to Soil Microbiology. Wiley, New York

Anderson IC & Levine JS (1986) Relative rates of nitric oxide and nitrous oxide production by nitrifiers, denitrifiers, and nitrate respirers. Appl Environ Microbiol 51:938–945

Anderson IC & Levine JS (1987) Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide. J Geophys Res 92:965–976

Anderson IC & Poth MA (1989) Semiannual losses of nitrogen as NO and N_2O fron unburned and burned chaparral. Global Biogeochem Cycle 3:121–135

Aneja VP, Rogers HH & Stahel EP (1986) Dry deposition of ammonia at environmental concentrations on selected plant species. J. Air Pollut Contr Assoc 36:1338–1341

Ashby JA, Bowden WB & Murdoch PS (1998) Controls on denitrification in riparian soils in headwater catchments of a hardwood forest in the Catskill Mountains, USA. Soil Biol Biochem 30:853–864

Ayers GP & Gras JL (1980) Ammonia gas concentrations over the Southern Ocean. Nature 284:539–540

Bader FG (1978) Analysis of double-substrate limited growth. Biotechnol Bioeng 20:183–202

Bailey LD & Beauchamp EG (1973) Effects of temperature on NO_3^- and NO_2^- reduction, nitrogeneous gas production, and redox potential in a saturated soil. Can J Soil Sci 53:213–218

Baldioli M, Engel T, Klocking B, Priesack E, Schaaf T, Sperr C & Wang E (1994) xpert-N, ein Baukasten zür Simulation der Stickstoffdynamik in Boden und Pflanze. Prototyp, Benutzerhandbuch, Lehreinheit für Ackerbau und Informatik im Pflanzenbau, TU Munchen, Freising, 1–106

Baumgartner D & Conrad R (1992) Effects of soil variables and season on the production and consumption of nitric oxide in oxic soils. In: Fertility of Soils, pp 166–174, Springer-Verlag

BEARG (Beijing Environmental Assessment Research Group) (1977) Assessment of Environmental Quality in Beijing Western Suburbs. 465 p

Blackmer AM & Bremner JM (1978) Inhibitory effect on nitrate on reduction of N_2O to N_2 by soil microorganisms. Soil Biol Biochem 10:187–191

Blagodatsky SA & Richter O (1998) Microbial growth in soil and nitrogen turnover: a theoretical model considering the activity state of microorganisms. Soil Biol Biochem 30(13):1743–1755

Blagodatsky SA, Vevdokimov IV, Larionova AA & Richter J (1998) Microbial growth in soil and nitrogen turnover: model calibration with laboratory data. Soil Biol Biochem 30(13):1757–1764

Bock E, Koops HP & Harms H (1986) Cell biology of nitrifying bacteria. In: Nitrification: Special Publications of the General Microbiology. Vol. 20. Prosser JI (ed) pp 17–38, IRL Press, Oxford

Bollmann A & Conrad R (1998) Influence of O_2 availability on NO and N_2O release by nitrification and denitrification in soils. Global Change Biol 4:387–396

Bremner JM, Blackmer AM & Waring SA (1980) Formation of nitrous oxide and dinitrogen by chemical decomposition of hydroxylamine in soils. Soil Biol Biochem 12:263–269

Byrnes BH, Austin ER & Tays BK (1995) Methane emission from flooded rice soils and plants under controlled conditions. Soil Biol Biochem 27:332–339

Cai GX & Zhou ZL (1995) Gaseous loss of fertilizer nitrogen from rice fields. Acta Pedol Sin 32:128–135

Cai ZC, Yan XY, Xu H, Tsuruta H, Yagi K & Minami K (1995) Effect of nitrogen form on CH_4 emission from rice paddy field. Acta Pedol Sin 32:136–143

Chalk PM & Smith CJ (1983) Chemodinitrification. In: Freney JF & Simpson JR (eds) Gaseous Loss of Nitrogen from Plant-Soil Systems, pp 65-89, Martinus Nijhoff Publishers, The Hague

Chanton JP, Martens CS & Kelley CA (1989) Gas transport from methane-saturated tidal freshwater and wetland sediments. Limnol Oceanogr 34:807–819

Chen ZL, Gao JH, Yuan Y, Shao KS, Zhang JB, Yu ZJ & Wang BJ (1992) Study on the effects of different cultivation methods on methane emission from rice fields in Beijing. Res Environ Sci 5:1–7

Cicerone RJ, Delwiche CC, Tyler SC & Zimmerman PR (1992) Methane emission from California rice paddies with varied treatments. Global Biogeochem Cycles 6:233–248

Crill P, Keller M & Weizt A (1998) Measuring N_2O fluxes from tropical agricultural soils. Global Biogeochem Cycles (in press)

Conrad R (1989) Control methane production in terrestrial ecosystems. Exchange of trace gases between terrestrial ecosystems and atmosphere. Andereae MO & Schimel DS (eds) pp 39-58, J. Wiley & Sons, Chichester

Conrad R, Schütz H & Babbel M (1987) Temperature limitation of hydrogen turnover and methanogenesis in anoxic paddy soil. FEMS Microbiol Ecol 45:281–289

Cowling DW & Lockyer DR (1981) Increased growth of ryegrass exposed to ammonia. Nature 292:337–338

Dabney SM & Bouldin DR (1985) Fluxes of ammonia over an alfalfa field. Agron J 77:572–578

Davidson EA & Schimel JP (1995) Microbial processes of production and consumption of nitric oxide, nitrous oxide, and methane. In: Matson PA & Harriss RC (eds) Biogenic Trace Gases: Measuring Emissions from Soil and Water, pp 327–357, Cambridge University Press, Cambridge

Davidson EA (1992a) Sources of nitric oxide and nitrous oxide following wetting of dry soil. Soil Sci Soc Am J 56:95–102

Davidson EA (1992b) Pulses of nitric oxide and nitrous oxide flux following wetting of dry soil: an assessment of probable sources and importance relative to annual fluxes. Ecol Bull 42:1–7

Dawson RN & Murphy KL (1972) The temperature dependence of biological denitrification. Water Res 6:71–83

De Groot CJ, Vermoesen A & van Cleemput O (1994) Laboratory study of the emission of N_2O and CH_4 from a calcareous soil. Soil Sci 158:355–364

DeBont JAM, Lee KK & Bouldin DF (1978) Bacterial oxidation of methane in a rice paddy. Ecol Bull 26:91–96

Farquhar GD, Firth PM, Wetselaar R & Wier B (1980) On the gaseous exchange of ammonia between leaves and the environment: determination of the ammonia compensation point. Plant Physiol 66:710–714

Farquhar GD, Wetselaar R & Firth PM (1979) Ammonia volatilization from senescing leaves of maize. Science 203:1275–1258

Firestone MK, Firestone RB & Tiedje JM (1980) Nitrous oxide from soil denitrification: factors controlling its biological production. Science 208:749–751

Firestone MK & Davidson EA (1989) Microbiological basis of NO and N_2O production and consumption in soil. In: Andreae MO & Schimel DS (eds) Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, pp 7-21, John Wiley & Sons Ltd., Chichester, UK

Focht DD (1974) The effect of temperature, pH and aeration on the production of nitrous oxide and gaseous nitrogen – a zero-order kinetic model. Soil Sci 118:173–179

Frolking SE, Mosier AR, Ojima DS, Li C, Parton WJ, Potter CS, Priesack E, Stenger R, Haberbosch C, Dorsch P, Flessa H & Smith KA (1998) Comparison of N_2O emissions from soils at three temperate agricultural sites: simulations of year-round measurements by four models. Nutr Cycling Agroecosyst (in press)

Glasstone S (1946) Textbook of Physical Chemistry. 2d ed. Van Nostrand Reinhold, New York, 1320 p

Goreau TJ, Kaplan WA, Wofsy SC, McElroy MB, Valios FW & Watson SW (1980) Production of NO_2^- and N_2O by nitrifying bacteria at reduced concentrations of oxygen. Appl Environ Microbiol 40:526–532

Harper LA, Sharpe RR, Langdale GW & Giddens JE (1987) Nitrogen cycling in a wheat crop: soil. plant and aerial nitrogen transport. Agron J 79:965–973

Hartel PG & Alexander M (1987) Effect of growth of bacteria in freshly moistened soil. Soil Sci Am J 51:93-96

Holland EA & Schimel DS (1994) Ecosystem and physiological controls over methane production in northern wetlands. J Geophys Res 99:1563–1571

Holzapfel-Pschorn A, Conrad R & Seiler W (1985) Production, oxidation, and emission of methane in rice paddies. FEMS Microbiol Ecol 31:343–351

Hooker ML, Sanders DH, Peterson GA & Daigger LA (1980) Gaseous N losses from winter wheat. Agron J 72:789–792

Hooper AB & Terry KR (1979) Hydroxylamine oxidoreductase of *Nitrosomonas*: production of nitric oxide from hydroxylamine. Biochim Biophys Acta 571:12–22

Hutchinson GL & Davidson EA (1993) Processes for production and consumption of gaseous nitrogen oxides in soil. In: Harper LA, Mosier AR & Duxbury JM (eds) Agricultural Ecosystems on Trace Gases and Global Climate Change, pp 79–93

Hutchinson GL (1972) Air containing nitrogen-15 ammonia: foliar absorption by corn seedings. Science 175:759–761

Hutchinson GL, Millington RJ & Peters DB (1972) Atmospheric ammonia: absorption by plant leaves. Science 175: 771–772

Ingwerson J, Butterbach-Bahl K, Gasche R, Richter O & Papen H (1998) Barometric process separation (BaPS): new method for quantifying nitrification, denitrification, and N_2O sources in soils (submitted)

Inubushi K, Wada H & Takai Y (1984) Easily decomposable organic matter in paddy soil. IV. Relationship between reduction and organic matter decomposition. Soil Sci Plant Nutr 30:189–198

Johansson C (1984) Field measurements of emission of nitric oxide from fertilized and unfertilized forest soils in Sweden. J Atmos Chem 1:429–442

Johansson C & Granat L (1984) Emission of nitric oxide from arable land. Tellus 36B:26–37

Kelley CA, Martens CS, Chanton JP (1990) Variations in sedimentary carbon remineralization rates in the White Oak River estuary. NC Limnol Oceanogr 35:372–383

Khan MFA & Moore AW (1968) Denitrification capacity of some Alberta soils. Can J Soil Sci 48:89–91

Kimura M, Minoda T & Murase J (1993) Water-soluble organic materials in paddy soil ecosystem. II. Effects of temperature on contents of total organic materials, organic acids, and methane in leachate from submerged paddy soils amended with rice straw. Soil Sci Plant Nutr 39:713–724

Klemedtsson L, Svensson B & Rosswal T (1988) A method of selective inhibition to distinguish between nitrification and denitrification as a source of nitrous oxide in soil. Biol Fertil Soils 6:112–119

Kludze HK & DeLaune RD (1995) Gaseous exchange and wetland plant response to soil redox intensity and capacity. Soil Sci Soc Am J 59:939–945

Knowles R (1982) Denirification. Microbiol Rev 46:43–70

Leffelaar PA & Wessel WW (1988) Denitrification in a homogeneous closed system: experiment and simulation. Soil Sci 146:335–349

Li C & Yu Z (1973) An environmental model and its application for an endemic human heart failure Keshan Disease in Heilongjiang Province, China. Environ Geol Health 1:9–26

Li C, Frolking S & Frolking TA (1992a) A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. J Geophys Res 97:9759–9776

Li C, Frolking S & Frolking TA (1992b) A model of nitrous oxide evolution from soil driven by rainfall events. 2. Model applications. J Geophys Res 97:9777–9783

Li C, Frolking S & Harriss R (1994) Modeling carbon bio-geochemistry in agricultural soils. Global Biogeochem Cycles 8:237–254

Li. C, Narayanan V & Harriss R (1996) Model estimates of nitrous oxide emissions from agricultural lands in the United States. Global Biogeochem Cycles 10:297–306

Li C, Frolking S, Crocker GJ, Grace RR, Klir J, Korchens M & Poulton PR (1997) Simulating trends in soil organic carbon in long-term experiments using the DNDC model. Geoderma 81:45–60

Li C, Aber J, Stange F, Butterbach-Bahl K & Papen H (1999) A process oriented model of N_2O and NO emissions from forest soils. 1. Model development. J Geophys Res (submitted)

Li DB, Zhang JW, Li WX, Yue ZT, Yu F & Gu JN (1993) Effect of agricultural methods on methane emission from rice paddies. Rural Eco-Environ 9:13–18

Lockyer DR & Whitehead DC (1986) The uptake of gaseous ammonia by the leaves of Italian Ryegrass. J Exp Bot 37:919–927

Martin RE, Scholes MC, Mosier AR, Pjima DS, Holland EA & Parton WJ (1998) Controls on annual emissions of nitric oxide from soils of the Colorado shortgrass steppe. Global Biogeochem Cycles 12:81–91

Masscheleyn PH, DeLaune RD & Patrick Jr WH (1993) Methane and nitrous oxide emission from laboratory measurements of rice soil suspension: effect of soil oxidation-reduction status. Chemosphere 26:251–260

Matsubara T (1971) Studies on denitrification. XIII. Some properties of the N_2O -anaerobically grown cell. J Biochem (Tokyo) 69:991–1001

Meyer MW (1973) Absorption and release of ammonia from and to the atmosphere by plants. Dissertation directed by J.H. Axley, University of Maryland, College Park

Nömmik H (1956) Investigations on denitrification in soil. Acta Agric Scand 6:195–228

Nouchi I, Hosono T, Aoki K & Minami K (1994) Seasonal variation in methane flux from rice paddies associated with methane concentration in soil water, rice biomass and temperature, and its modelling. Plant Soil 161:195–208

Oremland RS (1988) Biogeochemistry of methanogenic bacteria. In: Zehnder AJB (ed) Biology of Anaerobic Microorganisms. John Wiley & Sons, pp 641–705

Papen H, von Berg R, Hinkel I, Thoene B & Rennenberg H (1982) Heterotrophic nitrification by *Alcaligenes faecalis*: NO_2^-/ NO_3^-. and NO production in exponentially growing cultures. Appl Environ Microbiol 55:2068–2072

Parashar DC, Gupta PK, Rai J, Sharma RC & Singh N (1993) Effect of soil temperature on methane emission from paddy fields. Chemosphere 26:247–250

Parton WJ, Morgan JA, Altenhofen JM & Harper LA (1988) Ammonia volatilization from spring wheat plants. Agron J 80:419–425

Parton WJ, Mosier AR, Ojima DS, Valentine DW, Schimel DS, Weier K & Kulmala AE (1996) Generalized model for N_2 and N_2O production from nitrification and denitrification. Global Biogeochem Cycles 10:401–412

Payne WJ (1973) Reduction of nitrogenous oxides by microorganisms. Bacteriol Rev 37:409–452

Payne WJ (1981) The status of nitric oxide and nitrous oxide as intermediates in denitrification. In: Delwiche CC (ed) Denitrification, Nitrification and Atmospheric Nitrous Oxide, pp 85–103, Wiley, New York

Payne WJ, Riley PS & Cox CD (1971) Separate nitrite, nitric oxide, and nitrous oxide-reducing fractions from *Pseudomonas perfectomarinus*. J Bacteriol 106:356–361

Poth M & Focht DD (1985) 15-N kinetic analysis of N_2O production by *Nitrosomonas europaea*: an examination of nitrifier denitrification. Appl Environ Microbiol 49: 1134–1141

Potter CS, Randerson JT, Field CB, Matson PA, Vitousek PM, Mooney HA & Klooster SA (1993) Terrestrial ecosystem production: a process model based on global satellite and surface data. Global Biogeochem Cycles 7:811–841

Riley WJ & Matson PA (1989) The NLOSS model. 1998 Fall AGU meeting. Poster A41B-25. AGU volume 79, Number 45, 10 Nov 1998

Saad OALO & Conrad R (1993) Temperature dependence of nitrification. denitrification. and turnover of nitric oxide in different soils. Biol Fertil Soils 15:21–27

Sass RL, Fisher FM, Harcombe PA & Turner FT (1990) Methane production and emission from a Texas rice field. Global Biogeochem Cycles 4:47–68

Sass RL, Fisher FM, Harcombe PA & Turner FT (1991) Mitigation of methane emissions from rice fields: possible adverse effects of incorporated rice straw. Global Biogeochem Cycles 5: 275–287

Schütz H, Seiler W & Conrad R (1989) Processes involved in formation and emission of methane in rice paddies. Biogeochemistry 7:33–53

Schipper LA & Reddy KR (1994) Methane production and emission from four reclaimed and pristine wetlands of southeastern United States. Soil Sci Soc Am J 58:1270–1275

Schipper LA & Reddy KR (1996) Determination of methane oxidation in the rhizosphere of *Sagittaria lancifolia* using methyl fluoride. Soil Sci Soc Am J 60: 611–616

Schjorring JK (1991) Ammonia emission from the foliage of growing plants. In: Sharkey TD, Holland EA & Mooney HA (eds) Trace Gas Emissions by Plants, pp 267–292, Academic Press, San Diego, CA

Sexstone AJ, Revsbech NP, Parking TB & Tiedie JM (1985) Direct measurement of oxygen profiles and denitrification rates in soil aggregates. Soil Sci Soc Am J 49: 645–651

272

Shah DB & Coulman GA (1978) Kinetics of nitrification and denitrification reactions. Biotechnol Bioeng 20:43-72

Shangguan XJ, Wang MX, Shen RX, Wang YS, Wassmann R, Rennenberg H, Seiler, W, Xie XL, Wang WD & Xie KH (1994) The feature of methane emission from a paddy field in the central China region. Sci Atmos Sin 18:358-365

Shangguan XJ, Wang MX, Shen RX, Wang YS, Wassmann R, Rennenberg H, Seiler, W, Xie XL, Wang WD & Xie KH (1994) The feature of methane emission from a paddy field in the central China region. Sci Atmos Sin 18:358–365

Slemr F & Seiler W (1984) Field measurements of NO and NO_2 emissions from fertilized and unfertilized soils. J Atmos Chem 2:1–24

Slemr F & Seiler W (1991) Field study of environmental variables controlling the NO and N_2O emissions from soil and of the NO and N_2O compensation points. J Geophys Res 96:13017–13031

Smith KA (1980) A model of the extent of anaerobic zones in aggregated soils and its potential application to estimates of denitrification. J Soil Sci 31:263–277

Smith KA (1990) Anaerobic zones and denitrification in soil: modelling and measurement. In: Revsbech NP & Sorensen J (eds) Denitrification in Soil and Sediment, pp 229-243, Plenum Press, New York

SSSA (Soil Science Society of America) (1987) Glossary of soil science terms. SSSA, Madison, WI, USA, 11 p

Sommer SG & Jeneson ES (1991) Foliar absorption of atmospheric ammonia by ryegrass in the field. J Environ Qual 20:153–156

Stanford G, Dzienia S & Vander Pol RA (1975) Effect of temperature on denitrification rate in soils. Soil Sci Soc Am Proc 39:867–870

Stevens RJ, Laughlin RJ & Malone JP (1998) Soil pH affects reducing nitrate to nitrous oxide and di-nitrogen. Soil Biol Biochem 30:1119–1126

Stumm W & Morgan JJ (1981) Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibia in Natural Waters. 2d ed, pp 418-503, John Wiley & Sons, New York

Sutton MA (1990) The surface/atmosphere exchange of ammonia. PhD thesis, Institute of Ecology and Resource Management, University of Edinburgh, Edinburgh

Sutton MA, Pitcairn CER & Fowler D (1993) The exchange of ammonia between the atmosphere and plant communities. In: Advances in Ecological Research. Vol. 24, pp 301-393, Academic Press Limited.

Takai Y (1970) The mechanism of methane formation in flooded paddy soil. Soil Sci Plant Nutr 16:238–244

Tao Z, Du DD, Zhou Y, Mai GX & Liu XW (1995) Effect of different agricultural methods on methane emission from rice paddy. Agro-Environ Prot 14:101–104

Tiedje JM (1988) Ecology of denitrification and dissmilatory nitrate reduction to ammonium. In: Zehnder AJB (ed) Biology of Anaerobic Microorganisms. pp 179-244, Wiley, New York

Tsunogai S & Ikeuchi K (1986) Ammonia in the atmosphere. Geochemistry J 2:157–166

Valente RJ & Thornton FC (1993) Emissions of NO from soil at a rural site in Central Tennessee. J Geophys Res 98:16745–16753

Van Cleemput O & El-Sebaag AS (1985) Gaseous hydrocarbons in soil. Adv Agron 38:181–195

Van Niel EWJ (1991) Nitrification by heterotrophic denitrifiers and its relationship to autotrophic nitrification. PhD thesis, Delft University of Technology, Delft

Van Veen JA & Paul EA (1981) Organic carbon dynamics in grassland soils. 1. Background information and computer simulation. Can J Soil Sci 61:185–201

Van Verseveld HW, Meijer EM & Stouthamer AH (1977) Energy conservation during nitrate respiration in *Paracoccus denitrificans.* Arch Microbiol 112:17-23

Van Verseveld HW & Stouthamer AH (1978) Growth yields and the efficiency of oxidative phosphorylation during autotrophic growth of *Paracoccus denitrificans* on methanol and formate. Arch Microbiol 118:21-26

Vernatski VI (1924) La Geochimie, P Revue scient

Vogels GD, Keltjens JT & van der Drift C (1988) Biochemistry of methane production. In: Zehnder AJB (ed) Biology of Anaerobic Microorganisms, pp 707-770. John Wiley & Sons, New York

Wang ZP, DeLaune RD, Masscheleyn PH & Patrick Jr WH (1993) Soil redox and pH effects on methane production in a flooded rice soil. Soil Sci Soc Am J 51:382–385

Ward BB (1987) Kinetic studies on ammonia and methane oxidation by *Nitrosococcus oceanus*. Arch Microbiol 147:126–133

Wassmann R, Papen H & Rennenberg H (1993) Methane emission from rice paddies and possible mitigation strategies. Chemosphere 26:201–217

Watanabe A, Katoh K & Kimura M (1993) Effect of rice straw application on CH_4 emission from paddy fields. I. Effect of weathering of rice straw in the field during off-crop season. Soil Sci Plant Nutr 39:701–706

Whiting GJ, Chanton JP, Barlett DS & Happell JD (1991) Relationships between CH_4 emission. biomass and CO_2 exchange in a subtropical grassland. J Geophys Res 96: 13067–13071

Wijler J & Delwiche CC (1954) Investigations on the denitrifying process in soil. Plant Soil 5:155–169

Williams EJ, Parrish DD & Fehsenfeld FC (1987) Determination of nitrogen oxide emissions from soils: results from a grassland site in Colorado, United States. J Geophys Res 92:2173–2179

Yagi K, Minami K & Breitenbeck GA (1990) Emission and production of methane from paddy fields. Transactions of the 14th International Congress of Soil Science, pp 238–243, International Society of Soil Science, Kyoto

Zeikus JG (1977) The biology of methanogenic bacteria. Bacteriol Rev 41:514–541

Zheng XH, Wang YS, Wang MX, Shen RX, Li LT & Jin JS (1998) Automated measurements of NO emissions from cropland. Environ Sci 19(2) (in press)

Zhou Y, Tao Z & Du DD (1994) Agricultural measure options for reducing methane emission from rice field. Rural Eco-Environ 10:6–8

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

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
$$Fm = 0.8 + 0.21 * (1.0 - wfps), \text{ if } wfps > 0.05;$$
$$Fm = 0, \text{ if } wfps <= 0.05;$$

Equation 1.7. Nitrification-induced NO (kg N/ha/d)
$$NO = 0.0025 * Rn * Ft;$$
Equation 1.8. Nitrification-induced N_2O (kg N/ha/d)
$$N_2O = 0.0024 * Rn;$$
DOC – Concentration of dissolved organic C, kg C/ha;
BIO – Nitrifier biomass, kg C/ha;
$[NH_4^+]$ – Concentration of ammonium, kg N/ha;
pH – Soil pH.

2. Denitrification

Equation 2.1. Relative growth rate of NOx denitrifiers (1/h)
$$GR_{NOx} = GR_{NOx}(_{max}) * [C / (Kc + C)] * [NOx / (Kn + NOx)];$$

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/m³/h)
Growth rate : $(dBIO/dt)_g = GR * BIO(t);$
Death rate: $(dBIO/dt)_d = Mc * Yc * BIO(t);$
Carbon consumption rate: $dC/dt = (GR / Yc + Mc) * BIO(t);$

Equation 2.4. Consumption rates of N oxides (kg N/m³/h)
$$d(Nox)/dt = (GR_{NOx} / Y_{NOx} + M_{NOx} * NOx / N) * BIO(t);$$

Equation 2.5. Nitrogen assimilation rate (kg N/m³/h)
$$(dN/dt)_a = (dBIO/dt)_g / CN;$$

Equation 2.6. NO, N_2O and N_2 diffusion rates (%)
NO and N_2O: diffuse = (0.0006+0.0013*AD)+(0.013-0.005*AD)*PA*(1-anvf);
N_2: diffuse 0 0.017+((0.025-0.0013*AD)*PA*(1-anvf);
$GR_{NO_{3(max)}}$ – Maximum growth rate of NO_3^- denitrifiers, 0.67 1/h (Hartel & Alexander, 1987);
$GR_{NO_{2(max)}}$ – Maximum growth rate of NO_2^- denitrifiers, 0.67 1/h (Hartel & Alexander, 1987);
$GR_{NO_{(max)}}$ – Maximum growth rate of NO denitrifiers, 0.34 1/h (Hartel & Alexander, 1987);
$GR_{N_2O_{(max)}}$ – Maximum growth rate of N_2O denitrifiers, 0.34 1/h (Hartel & Alexander, 1987);
Kc – Half-saturation value of soluble carbon, 0.017 kg C/m³ (Shah & Coulman, 1978);
Kn – Half-saturation value of N oxides, 0.083 kg N/m³ (Shah & Coulman, 1978);
C - Soluble C concentration, kg C/m³ (calculated by DNDC);

NO_x - Concentration of NO_3^-, NO_2^-, NO or N_2O, kg N/m³ (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 /m³ (calculated by DNDC);
Mc   – Maintainance 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);
$M_{(NO_3)}, M_{(NO_2)}, M_{(N_2O)}, M_{(NO)}$– Maintainance 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$_4$ Production and Oxidation
Equation 3.1. CH_4 production rate (kg C/ha/d)
   $CH_4p = a * AC * Ft$;
   $Ft = b * e^{(0.2424 * T)}$; (factor of temperature)

Equation 3.2. CH_4 oxidation rate (kg C/ha/d)
   $CH_4o = CH_4[l] * e^{(8.6711 * Eh[l] / 1000)}$;

Equation 3.3. CH_4 flux through plant aerenchyma (kg C/ha/d)
   $CH_{4(aere)} = 0.5 * CH_4[l] * AERE$;
   $AERE = -0.0009*PGI^5+0.0047*PGI^4 -0.883*PGI^3+1.9863*PGI^2-0.3795*PGI+0.0251$;
   PGI = (days since planting) / (season days); (plant growth index)
Function 3.4. CH_4 flux through ebullition (kg C/ha/d)
   $CH_{4(ebullition)} = 0.025 * CH_4[l] * PORO * Ft * (1 - AERE)$;
   $Ft = -0.1687*(0.1*T[l])^3 +1.167*(0.1*T[l])^2 -2.0303*(0.1*T[l])+1.042$;
Function 3.5. CH_4 diffusion rate (kg C/ha/d)
   $Rd = 0.01 * (CH_4[l] - CH_4[l+1]) * T[l] * PORO$;
AC – Available C concentration, kg C/ha;
T – soil temperature, °C;
l – soil layer number;
AERE – plant aerenchyma;
FloodDay – flooding days;
PORO – soil porosity;
$CH_4[l]$ – CH_4 concentration at layer l, kg C/ha.

4. NH$_3$ Volatilization
Equation 4.1. NH_3 concentration in liquid phase (mol/l)
   $[NH3(l)] = [NH_4^+][OH^-] / Ka$;
   $NH_4^+/NH3$ equilibrium constatnt: $Ka = (1.416 + 0.01357 * T) * 10^{-5}$;
   $[OH^-] = Kw / [H^+]$, mol/l;
   $[H^+] = 10^{-pH}$, mol/l;
   $Kw = 10^{(0.08946 + 0.03605 * T)} * 10^{-15}$; (water dissociation constant)

Equation 4.2. NH_3 concentration in gas phase and flux (kg N/ha)
   $NH_3(g) = [NH_3(l)] * (T/T_0)^2$;
   $Flux(NH_3) = NH_3(g) * AFPS * (1-Clay)$, kg N/ha/d;

Equation 4.3. NH_3 deposit (kg N/ha/d)
   $Vg = MaxVg * F(plant-N) * F(lsm)$;
   $F(plant-N) = Plant-N(act) / Plant-N(opt)$;
   $F(lsm) = LSM(act) / LSM(max)$;
   $PlantUp(NH_3) = Vg * Air(NH_3) * LAI * 0.864$;
   $Air(NH_3) = Base(NH_3) + Flux(NH_3) * 10^9 / V(canopy) * LAI / (LAI + k2) * k3$;
   $V(canopy) = Height * 10000$;
T_0 – reference temperature, 45°C;
T   – soil temperature, °C;
PH   – soil pH;
AFPS   – soil air-filled porosity;
Clay   – soil clay content;

MaxVg   – maximum NH_3 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_3)   – background NH_3 concentration, 0.06 ug/m^3;
V(canopy)   – volume of the room from ground to the top of canopy, m^3/ha;
Height   – maximum height of plant, m;
LAI   – crop leaf area index;
MaxLAI   – maximum crop leaf area index;
K2, k3   – constant coefficients;