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Environmental Fate Tracking of Manure-borne NH_3-N in Paddy Field Based on a Fugacity Model

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Fugacity 모델에 기초한 논토양에서의 액비살포에 따른 암모니아성 질소 거동추적

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Abstract

Nitrogen components in liquid manure can reduce safety and quality of environment harmfully. To minimize the environmental risks of manure, understanding fate of manure in environment is necessary. This study aimed at investigating applicability of a simplified Level Ⅲ fugacity model for simulating NH_3-N component to analyze environmental fate and transport of NH_3-N in liquid manure and to provide basis for improving management of N in the liquid manure system and for minimizing the environmental impacts of N. The model simulation conducted for four environmental compartments (air, water, soil, and rice plants) during rice-cropping to trace NH_3-N component and provided applicability of the Level Ⅲ fugacity model in studying the environmental fate of NH_3-N in manure. Most of NH_3-N was found in water body and in rice plants depending upon the physicochemical properties and proper removal processes. For more precise model results, the model is needed to modify with the detailed removal processes in each compartment and to collect proper and accurate information for input parameters. Further study should be about simulations of various N-typed fertilizers to compare with the liquid manure based on a modified and relatively simplified Level Ⅲ fugacity model.

Key words : Ammonium-Nitrogen, Fertilizer, Fugacity, Liquid manure, Livestock excretions

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1. Introduction

Since the ocean dumping of livestock's excretions has been prohibited globally in 2012, many countries are concerned about resource recovery technology from livestock excretions. One of those technologies is transformation of livestock's excretions into solid and liquid manure, which is including the same nutrients for crop production as commercial fertilizers. Before livestock manure is activated, people need to understand physical, chemical, and biological properties of manure primarily for safer and more effective management of manure. First of all, livestock manure consists of solid and liquid portions and organic and inorganic components containing feces, urine, wastewater, and runoff. For these reasons, pathogenic microorganisms and unwanted pests can live in manure environment. Common chemical compounds among 165 various compounds in manure emitted into atmosphere include Carbon dioxide (CO_2), Methane (CH_4), Ammonia (NH_3), Hydrogen sulphide and related sulphur-containing compounds (H_2S gas etc.), volatile organic acids, and nitrous oxide (N_2O) depending on the type of manure and the way it's handled.

Manure has the potential to cause environmental problems such as emissions of odorous and greenhouse gases, contaminations of surface water and groundwater sources with nutrients and pathogens, contaminations of soil as loading nutrients and accumulating salt, and so on. Unlike manure contamination from manure piles as a point source, extra attention is required over application of manure as a non-point source. To minimize the environmental risks of manure, understanding fate of manure in environment is necessary. Foul-smelling odorous gases (NH_3, N_2O, N_2, CH_4, and H_2S), mostly greenhouse gases (GHGs), are emitted from a spot into atmosphere and spread in broad space. Nitrogen components in manure can reduce safety and quality of environment harmfully. Nitrates in solution of manure runoff into surface water can cause excessive algae blooms and leaching into groundwater make it unable to drink as well as ammonia (NH_3) in manure is toxic to aquatic organisms including fish in surface water bodies.

Fate of N components in a cycle has been investigated by many researchers in experimental studies and model simulation studies related to agriculture's role in N delivery into the environment in detailed reviews (Calderon et al., 2004; Dunn et al., 2004; Hubbard et al., 2004, Kim et al, 2009). According to previous studies mentioned above, excessive nutrients, especially nitrogen (N), can cause adverse effect on growth and production of crop in soil. N components in manure can negatively impact air, surface water, groundwater, and soil. Therefore, a study is necessary to establish fate of N components in manure related to negatively impacts on environment.

A fugacity concept has been introduced by Mackay in 1972 to understand the environmental behaviors of various chemicals in multi-media, considering terms of mass transfers including diffusion, precipitation, chemical reaction, biological decomposition, leakage, ingestion and dilution of nutrients required for the growth of plants, and water variation volume within each medium (MacKay, 1991). Also, an aqui-valence concept for non-volatile compounds and ionic chemicals is introduced by Mackay and Diamond in 1989 (MacKay et al., 1994) and recently it has been studied by many researchers (Batiha et al., 2008; Csiszar et al., 2011; Gandhi et al., 2007).

Since N-nutrient in animal liquid manure consists of high soluble, non-volatile and ionic compounds, an aquivalence-based model may be proper rather than a fugacity-based model but this study uses the fugacity-based model for simplification although it has uncertainty of model formulae, input information, and so on. Thus, this study aims at investigating the applicability of the fugacity concept originated by Mackay (1991) under a steady state condition as a tool to analyze environmental fate and transport of N components in liquid manure and to provide basis for improving management of N in the liquid manure system and for minimizing the environmental impacts of N during rice-cropping. The fugacity concept has been used in steady state condition for an air-water-rice plant-soil compartment system during rice cropping, simulated for fate of ammoniacal nitrogen (NH_3-N) in manure, and evaluated its possibility during the rice cropping season. More details of model description and simulation description are in following sections.

2. Materials and Methods

2.1 Fugacity approach

The Level Ⅲ fugacity model (FUGⅢ) includes processes of evaporation or volatilization to atmosphere, leaching via percolating water into groundwater, advection, diffusion, and degradation (or loss). The model assumes first-order kinetics for all reactions, a linear function of all movements, and local equilibrium between compartments. FUGⅢ will estimate concentrations (C_i) of the substance (manure NH_3-N) in air, water, soil, and rice plant compartment systems as a function of fugacity f_i and fugacity capacity Z_i at the steady state condition of a mass balance equation given by $C_i=f_iZ_i$, where C_i is the concentration of chemical substance (mol/m^3), f_i is the fugacity (Pa), and Z_i is the capacity of fugacity or the proportionality constant (mol/m^3·Pa). FUGⅢ deals with the distribution in a small quantity of a chemical substance between two compartments, i and j, under constant temperature and pressure, and non-equilibrium fugacity ($f_1 \neq f_2 \neq f_3 \neq \cdots \neq f_n$) in producing constant concentration ratio between two compartments, the partition coefficient k_{ij} defined as $k_{ij} = C_i/C_j$, where, C_i and C_j are the substance concentration in each compartment i and j respectively. The substance tends to accumulate in compartments depending upon the capacity of fugacity, which describes the affinity of the substance for the compartment. Thus, the fugacity capacity of each compartment has to be defined as considering the physicochemical properties of the substance for each compartment.

2.2 Governing equation

The rice-cropping system was modeled for air (i = a = 1), water (i = w = 2), soil (i = s = 3), and rice plant (i = r = 4) compartments. Since the model assumes the mass transfer of substance occurs from air to water and rice plants, from water to air and soil, from rice plants to air and soil and from soil to water and rice plants, governing equation for the mass balance of the substance is written by Eq.1. Table 1 presents a summary of mass balance equations in each compartment.

$$E_i + Advection_i + Diffusion_{ij} - Loss_i = \frac{V_i dC_i}{dt} \quad (1)$$

Considering the steady state condition,

$$\frac{V_i dC_i}{dt} = I_i + N_i + \sum_i N_{ij} - L_i = 0 \quad (2)$$

$$N_i = Q_2(C_{i(in)} - C_{i(out)}) \quad (3)$$

$$\sum iN_{ij} = \sum iD_{ij}(f_i - f_j) \quad (4)$$

where Input term I_i is emission E_i in each compartment i, mol/hr, Advection term N_i is mass flux by advection in compartment i, mol/hr, Diffusion term N_{ij} is mass flux by diffusion in compartment i, mol/hr, where D_{ij} is related to interfacial area A_{ij}, fugacity capacity Z_i and Z_j , and mass transfer coefficient k_i and k_j in Table 2. Loss term L_i is all mass fluxes by all removal processes such as reactions, deposition, runoff, leaching, uptake, litter fall, plant growth, and so on. However the removal process in this study is considered only leaching, uptake, litter fall, and plant growth, and a removal term with the approximate value, which is added instead of the deposition and runoff processes.

The advection term considers only vertical transport in this case. The mass flux by advection in the compartment i is regarded as the linear process with a constant speed and expressed by $G_i(C_{Bi}-C_i)$, where G_i (m^3/h) is the matter flow, C_{Bi} is the concentration entering compartment i and C_i is the concentration leaving the compartment. The advection inflow ($G_{Ai}C_{Bi}$) is dealing with mass flow rate G_{Ai} and initial concentration in each compartment (C_{Bi}). Advection outflow (D_{Ai}) term is leaving from air and entering into water, leaving water and entering soil, and leaving from soil to groundwater. If i=2, dissolved components in water are leaving from water and entering into soil. The advection outflow (D_{Ai}) leaching from soil is expressed by vertical transport velocity U. The transfer coefficient by diffusion, D-value, (D_{ij}, mol/h · Pa) between two compartments i and j is estimated by the expressions as shown in Table 2. In Table 2, the substance in the compartments can be also transformed by chemical reaction, biological degradation, dilution of the rice plant growth, and water variation volume in rice fields (Hu et al., 2013) and all reactions are assumed as first-order kinetics and reaction rate coefficients λ_i are determined by the half-life of the substance in compartment i, $t^i_{1/2}$; $\lambda_i = \ln(2)/t^i_{1/2}$. The fugacity capacity and diffusivity for each one of these compartments and all removal processes are defined and summarized in Table 2. Further details for each term in Table 2 can be referred to literatures

Table 1. Mass balance equations for each compartment in the model

Mass Balance Equations [mol/hr]	
Air Compartment i = 1 $F_1 DT_1 = E_1 + Q_{A1}C_{B1} + N_{21} + N_{41}$ $DT_1 = (D_{12} + D_{14} + D_{A1} + D_{R1})$	E_i = Emissionrate of i compartment [mol/h] $Q_{Ai}C_{Bi}$ = advection inflow [mol/h] D_{Ai} = advection outflow [mol/h] N_{ij} = Diffusive flux between compartments i and j [mol/h] D_{ij} = Diffusionc oefficient between i and j [mol/h·Pa] F_i = Fugacity of compartment i [Pa] D_{Ri} = Reaction in compartment i [mol/h·Pa] D_{LF} = Litter fall [mol/h·Pa] D_{GR} = plant growth [mol/h·Pa] D_{SF} = uptake [mol/h] [mol/h·Pa] D = total dispersion coefficient in soil [mol/h·Pa] D_{others} = approximate removal by deposition and runoff (i.e.,$D_{others}=F_iR_{others}$)
Water Compartment i = 2 $F_2 DT_2 = E_2 + Q_{A2}C_{B2} + N_{12} + N_{32} + F_1 D_{A1}$ $DT_2 = D_{21} + D_{23} + D_{A2} + D_{R2}$	
Soil Compartment i = 3 $F_3 DT_3 = E_3 + Q_{A3}C_{B3} + N_{23} + F_2 D_{A2}$ $DT_3 = D_{32} + D_{A3} + D_{R3} + D_{SF}$	
Rice Plant Compartment i = 4 $F_4 DT_4 = E_4 + N_{14} + F_3 D_{SF} + F_1 D_{A1}$ $DT_4 = (D_{41} + D_{A4} + D_{R4} + D_{LF} + D_{GR} + D_{others})$	
It is assumed that rice plant growth balances litter fall, $D_{GR} = D_{LF}$.	

Table 2. Summary of Z-value and D-value used in the model

Terms	Equations
Z-value Fugacity Capacity [mol/m^3·Pa]	
Air (i=1)	$Z_a = 1/RT$
Water (i=2)	$Z_w = 1/H$; $H = (M_w V_p)/S_w$
Soil (i=3)	$Z_s = (K_{ps}\rho_s)/H$; $K_{ps} = f_{ocs} \times 0.41 \times K_{ow}$
Rice Plants (i=4)	$Z_r = (K_{pr}\rho_r)/H$; $K_{pr} = (W_p + L_p \times K_{ow}^b) \times (\rho_r/\rho_w)$
$R = 8.314 m^3 P_a mol^{(-1)} T^{(-1)}$, T= (293+25)°K, H = Henry's constant (Pa $m^3 mol^{-1}$), M_w = molar mass, V_p = vapor pressure, Sw = water solubility K_{ps} = partition coefficient for soil, K_{pr} = partition coefficient for rice plants	
D-value [mol/h·Pa]	
Advection outflow D_{Ai}	$D_{Ai} = Z_i Q_{Ai} = Z_i V_i/\tau_i$
Diffusivity in compartments between i and j, D_{ij}	$D_{12} = [\frac{1}{(k_{12} \times A_{12} \times Z_1)} + \frac{1}{(k_{22} \times A_{12} \times Z_2)}]^{(-1)}$ $D_{23} = (\frac{1}{(k_{23} \times A_{23} \times Z_2)} + \frac{Y_3}{(B_{23} \times A_{23} \times Z_2)})^{(-1)}$ $D_{14} = (\frac{1}{D_c} + \frac{1}{D_{AB-F}})^{(-1)}$
Reaction, D_{Ri}	$D_{Ri} = Z_i V_i \lambda_i = Z_i V_i \bullet (\ln(2)/\tau_{(1/2)})$
Litter fall, $D_{FS\text{-}L}$	$D_{(FS-L)} = k_{FL} V_F Z_4$, $VF = PM_F \cdot AS/\rho F$ $k_{FL} = 1/t_{(R-F)}$, $D_{GR} = D_{(FS-L)}$
Plant Growth D_{GR}	
Uptake, D_{SF}	$D_{SF} = T_r \bullet A_{14} \bullet L_A \bullet TSCF \bullet Z_2$ $TSCF = 0.784\exp[-(\log K_{OW} 1.78)^2/2.44]$
Z_i = Fugacity capacity in the compartment, i [mol/m^3·Pa] Q_{Ai} = Advection flow rate in the compartment, i [m^3/h] V_i = Volume of the compartment, i [m^3] τ_i = Residence time in the compartment, i [h] k_{12} = Air-side MTC over water, [m/h] k_{22} = Water-side MTC, [m/h] A_{ij} = Interface area between compartments i and j [m^2] $D_{AB\text{-}F}$ = Boundary layer diffusion ; Dc = Cuticle diffusion : k_{FL} = the litter fall rate *VF* = the volume of the foliage in vegetation compartment *PMF* = a vegetation specific phyto-mass per unit ground area (kg [wet weight] /m^2) Tr = Transpiration rate = 1×10^{-5} [m/h] L_A = Leaf surface area = 5 [m^2/m^2] TSCF = Transpiration stream cofactor (concentration) * MTC (mass Transfer Coefficient)	

(Cousins and Mackay, 2000; Cousins and Mackay, 2001; MacKay, 1991).

2.3 Model parameters

Nitrogen components in manure includes nitrogen gas (N_2), organic-nitrogen (Org-N), and inorganic-nitrogen such as ammoniacal nitrogen (NH_4^+-N or NH_3-N), nitrite nitrogen (NO_2^--N), and nitrate nitrogen (NO_3^--N) with changing types in the nitrogen cycle process. To understand N-balance in liquid manure, N-balance model theory for Urea has been adopted from Chowdary et al. (2004) as shown in Fig. 1.

For the model simulation, NH_3-N among N components in manure is chosen and the mechanisms of NH_3-N in manure have been applied to simulate the fate of N components in environmental media (air, water, soil, and rice plants) during rice cropping as shown in Fig. 2. As shown in Fig. 2, crops imbibe lots of nutrients from the soil. Nitrogen, mainly inorganic-N such as NH_4^+-N and NO_3^--N, is imbibed the most among those nutrients. Rice crops absorb NH_4^+-N well. It is not that the rice crops don't imbibe NO_3^--N but that NO_3^--N has less chance to get the effect as the manure because it is denitrified mostly in the rice field. Rice cropping occurs with water in the rice field and it provides the best advantage, productive stability by the water supply. In a submerged condition, root environment of the rice plant becomes a reduced state of soil.

Passing 1-2 weeks in the submerged condition, the water body in the rice field is divided into two layers, an oxidized

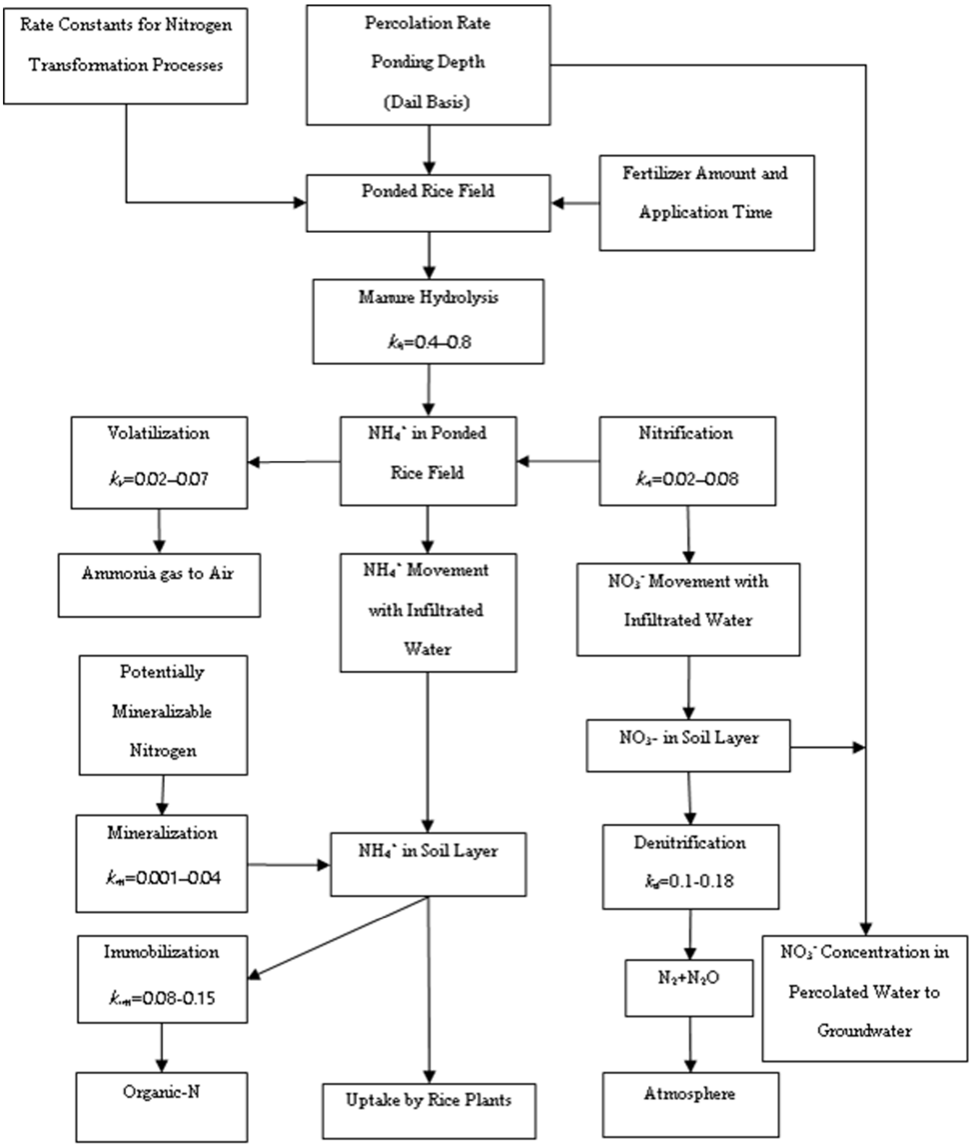

Fig. 1. Schematic representation of nitrogen balance model with reaction constants.

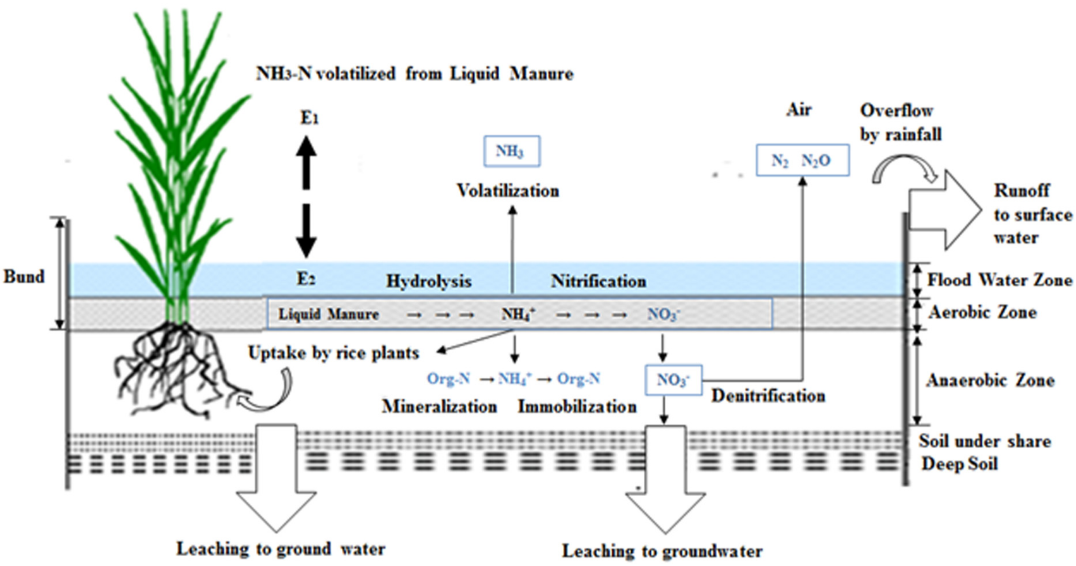

Fig. 2. Schematic representation of the N-transformations in flooded rice field.

Table 3. Important parameters for the model calculation

Parameter	Symbol	Value	Unit	References
Phytomass in wet weight of foliage(rice plant)	PM_F (PM_r)	1.0	kg/m^2	MacKay, 1991
Density of foliage(rice plant)	ρ_F (ρ_r)	1030	kg/m^3	Contreras et al., 2008
Leaf area index	L	3	m^2/m^2	Larcher, 1995
Transpiration rate	T_r	10^{-4}	m^3/m$^2\cdot$h	Larcher, 1995
Total water flow rate transpired by rice plants	Q_w	8.7×10^{-5}	m^3/h	Contreras et al., 2008
Average root length of rice plants	δr	0.03	m	Contreras et al., 2008
Volumetric fraction of water in rice plants	W_p (x_w)	0.80		Contreras et al., 2008
Volumetric fraction of lipids in rice plants	L_p (x_{ls})	0.02		Contreras et al., 2008
MTC for foliage air-boundary layer diffusion	U_{AB-F}	9	m/h	Cousins and Mackay, 2001
Correction exponent for difference between plant lipids and octanol	b	0.95		
Soil density	ρ_s	1540	kg/m^3	Contreras et al., 2008
Soil organic carbon volumetric fraction	oc_s	0.17		Contreras et al., 2008
Water density	ρ_w	999.5	kg/m^3	Contreras et al., 2008
Height of water layer	δ_w	0.3	m	Contreras et al., 2008
Advection flow rate in water	G_w	1.89×10^{-5}	m^3/h	Voltolini et al., 2002
Reaction constant by Hydrology	k_h	0.744	h^{-1}	Chowdary et al., 2004
Reaction constant by Volatilization	k_v	0.06	h^{-1}	Chowdary et al., 2004
Reaction constant by Nitrification	k_n	0.08	h^{-1}	Chowdary et al., 2004
Reaction constant by Mineralization	k_m	0.002	h^{-1}	Chowdary et al., 2004
Reaction constant by Immobilization	k_{im}	0.12	h^{-1}	Chowdary et al., 2004
Reaction constant by Denitrification	k_d	0.18	h^{-1}	Chowdary et al., 2004

layer or a floodwater zone with oxygen-rich water and a reduced layer or an aerobic zone with oxygen-poor water and the soil becomes an anaerobic zone saturated with water. Sometimes, the aerobic zone is thin enough to be ignored. In Fig.1, the reactions and reaction constants or their half-life in three zones are presented when applying quick-acting nitrogen liquid manure as basic manure in the rice field. In the floodwater zone and the aerobic zone, NH_3-N(aq) in manure are transformed by hydrolysis to produce NH_4^+-N, volatilization to emit NH_3(g), and nitrification to generate NO_3^--N. The denitrification process is very important when the soil is saturated with water because the microorganisms of the denitrification process act only in waterlogged soil without oxygen in the anaerobic layer.

The reactions progressed in the saturated anaerobic zone with water include denitrifcation of NO_3^--N to produce N_2O and N_2(g) into atmosphere and leaching of NO_3^--N into groundwater, mineralization to covert Organic-N into NH_4^+-N and immobilization to reduce NH_4^+-N to form Organic-N in the soil. Also, uptake of NH_4^+-N by rice plants roots is occurred around 30-40% of N. The losses of N are mainly caused by leaching into the groundwater and by release of N_2 gas into atmosphere by the denitrification process with frequent rainfall during late springtime and early summertime. The denitrification progresses regardless of the manure and fertilizer or source of NO_3^--N such as degradation. Also, other factors of the denitrification acceleration includes crop residue to be used as a carbon source, warm soil, pH (neutral to alkalinity), and so on.

Table 3 contains significant parameters to calculate terms in mass balance equations as shown in Table 1 and Table 2. Values of parameters are taken from references marked in Table 3.

2.4 Simulation condition

Physio-chemical properties of NH_3-N in manure are important to run FUGⅢ and they are indicated in Table 4. Ammonia is in its pure gaseous state and also commercially

Table 4. Physical and chemical property of NH_3-N

Characteristic	Information	Reference
Chemical Name and synonym	Ammonia, Anhydrous ammonia, AM-FOL, Ammonia gas, Liquid ammonia, Nitro-sil, R 717	Windholz et al., 1983
Chemical formular	NH_3	
Molecular weight, M_W	17.03g mol^{-1}	LeBlanc et al., 1878
Vapor pressure, V_p	2.9 *atm* for Aqueous NH_3 (28%)	Daubert and Danner, 1989
Water solubility, S_w	0.52×10^6(20°C)gcm^{-3},mgL^{-1}	Budavari et al., 1996
$LogK_{OW}$	0.23 (estimated)	USDHHS, 2004
$LogK_{OC}$	0.155 (estimated)	USDHHS, 2004

Table 5. Important input variables for the model simulation

Parameter	Symbol	Value	Unit
Area of plantation	A_r	100×42	m^2
Amount Liquid Manure (NH_3-N)	P_d	1.01×10^2	mol m^{-2}
Volume of Air	V_a	100×42×8	m^3
Volume of water	V_w	100×42×0.2	m^3
Volume of Soil	V_s	100×42×0.5	m^3
Volume of Rice plants	V_r	1400(A) × 0.12(H)	m^3
Average residence time of rice-cropping	τ_r	240	hrs

or commonly available in an aqueous solution about 28–30% NH_3, which is almost saturated in water (Weast et al., 1988). Liquid manure used in this study contains 0.19% total nitrogen (TN) and 29.8% aqueous NH_3-N of TN and 15.6% gaseous NH_3 of TN. The temperature for simulation was 25ºC (298ºK). Also Table 4 and Table 5 present important input parameters for the model simulation. Table 5 includes major parameters to run the simulation.

3. Results and Discussion

After a certain amount of liquid manure (1.01×10^2 mol as NH_3-N/$m^{2)}$ was sprayed under specific conditions as shown in Table 4 and 5, the model simulation was conducted for 10 days and the model results were analyzed and discussed in this section.

3.1 Fugacity Capacity

The model simulation estimated capacity of fugacity Z_i, fugacity F_i for non-equilibrium each other (i.e., $F_1 \neq F_2 \neq F_3 \neq F_4$), and concentration C_i in each compartment i (i = 1 ~ 4 for air, water, soil, and rice plants). Capacity of fugacity in each compartment, Z_i, was calculated as a function of partition coefficient between compartments i and j, and physicochemical property of the substance NH_3 and compartments (air, water, soil and rice plants). Z_i is not time dependent so Z_i of NH_3 for each compartment is constant with time changes. Z_1 is valued as 4.04×10^{-4} mol/m^3·Pa for air, Z_2 is 1.04×10^{-1} mol/m^3·Pa for water, Z_3 is 1.894×10^{-2} mol/m^3·Pa for soil, and Z_4 is 9.19×10^{-2} mol/m^3·Pa for rice plants. As shown in Fig. 3, water compartment (Z_2) took 48.3%, next was the rice plant compartment (Z_4) with 42.7%, soil compartment had little about 8.8% (Z_3), and the minimum value was found in the air compartment (Z_1) less than 0.2%.

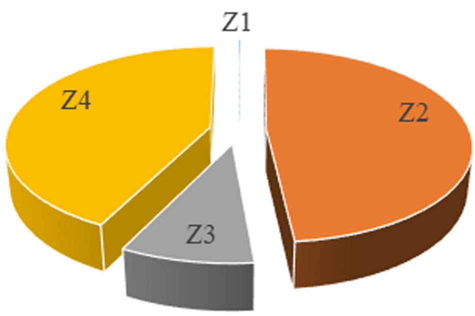

Fig. 3. Content of fugacity capacity Z_i in each compartment resulted from the model simulation. The values of Z_i are 0.2% for air Z1, 48.3% for water Z2, 8.8% for soil Z3 and 42.7% for rice plant Z4.

3.2 Variation of Fugacity and Concentration

During all simulations, the same amount of emission was used but emission rates were different depending upon different detention times. Fugacity and concentration for all compartments except the rice plant compartment were decreased linearly with the detention time change in the log-log graph but those for the rice plant compartment were performed nonlinearly in the log-log graph. Fig. 4 and Fig. 5 present the log-log graph between fugacity and different detention times in (a) and between concentration and different detention times in (b). The detention times were applied from 1 hour to 20 days with one time emission of manure initially. Fig. 4 is the case that the value of other removal term is same as that of uptake from soil, R_{others} = RSF, and Fig. 5 is the case that the removal term for the rice plant compartment is ignored, R_{others} = 0. In Fig. 4(a) and Fig. 5(a), fugacity values from the highest to the lowest were found in air, water, soil, and rice plant compartment orderly until 2 days and 1 day respectively. After that day, fugacity in soil (F3) was lower than fugacity in rice plant (F4).

Unlike the fugacity, the highest concentration was determined in water, next was in soil and rice plant, and air detected the lowest values in Fig. 4(b) and Fig. 5(b). Concentrations between soil and rice plants were exchanged after 0.15 days and the concentration in rice plants was greater than the concentration in the soil and closed to the concentration of water with time increase, and the most concentration of NH_3 was remained in the water compartment in Fig. 4(b) but in Fig. 5(b) the rice plants took NH_3-N mostly after 7 days. As shown in Fig. 4 and Fig. 5, changes of fugacity and concentration in the rice plants were depending on the removal term considerably.

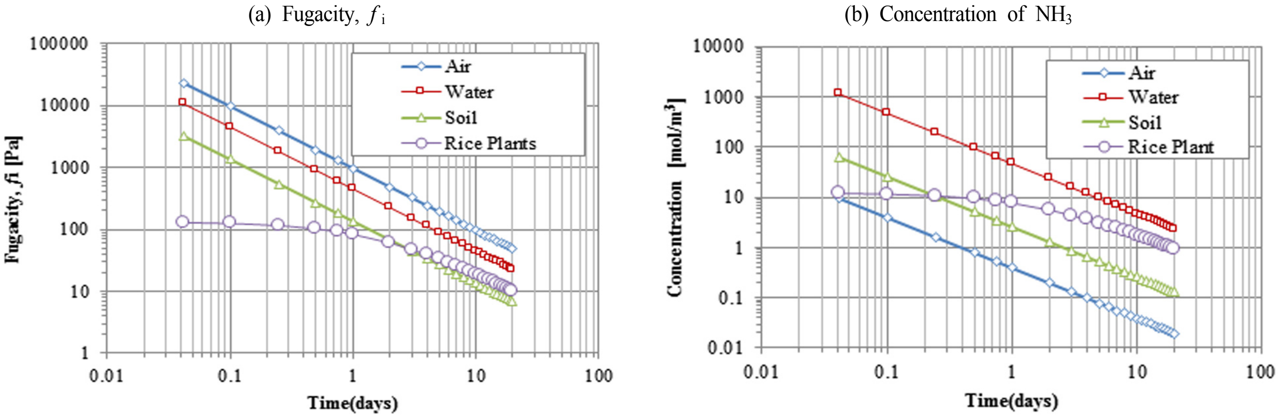

Fig. 4. Changes of Fugacity and concentration in each compartment for different detention times from 1hour to 20 days.

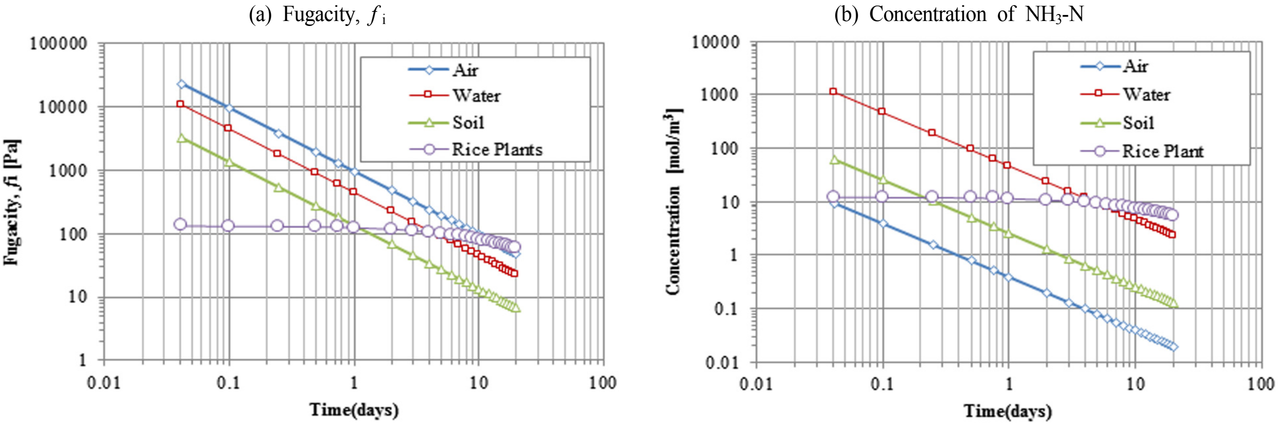

Fig. 5. Changes of Fugacity and concentration in each compartment for different detention times from 1hour to 20 days when the removal process in the rice plants was ignored.

3.3 Mass Balance

Fig. 6 shows the mass balance with values for all processes of the model equation graphically. Units of all values in Fig. 6 were [mol/hr] and the values between gain and loss for each compartment were matched well. In the compartment of air, the gain was from emission and diffusion from water to air,

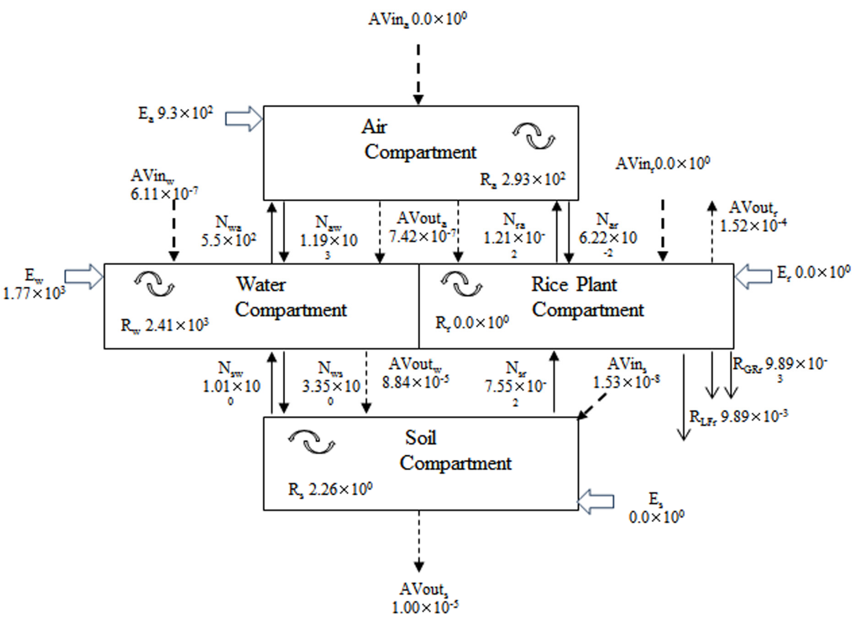

Fig. 6. Graphical representation of mass balance (mol/hr) in and between compartments.

and the loss was caused by the diffusion from air to water and transformation in the compartment. The water compartment was mostly affected by emission and diffusion from air to water for the gain and by transformation and diffusion from water to air for the loss. The mass in the soil compartment was balanced with the gain from diffusion from water to soil and the loss from transformation and diffusion from soil to water. The rice plants were gained by uptake of NH_3-N from the soil and lost by diffusion from rice plants to air and by removal processes. The removal processes in the rice plants were not described in details but assumed the same value of uptake from soil.

The analysis of mass balance using Level III shown in Figure 6 can yield considerably realistic results. It can scientifically identify, quantify, and diagnose the fate of nutrients in agricultural land, the description of fate mechanism, and the analysis of mass balance, thereby preventing the excessive use of liquid manure, and inducing natural-friendly agriculture. Based on the model studying, the fate of nutrients in liquid manure in the environmental media can be understood. It can be applied to create accurate inventory for liquid manure, to control total amount of nutrients for plant growth, to quantify and minimize the nonpoint pollutants, and to quantify the pollution load affected on water quality adversely.

4. Conclusions

A series of model simulation using the fugacity concept under a steady state condition was carried out to analyze environmental fate and transport of N components in liquid manure and to provide basis for improving management of N in the liquid manure system for minimizing the environmental impacts of N during rice-cropping. Findings of the model simulation are as in the following:

1. Model sensitivity was depending on input parameters and physicochemical properties of NH_3-N in manure, which were used to calculate capacity of fugacity, Z_i and partition coefficients for each compartment. Z_i was not time dependent and had each constant value for each compartment. For NH_3-N, most of Z_i were distributed in the water body and the rice plants.
2. Fugacity and concentration for air, water, and soil were decreased linearly with time change in the log-log graph but those in rice plants were performed nonlinearly.
3. Most of NH_3-N was remained in the water body when the removal processes (deposition and runoff) in the rice plants were considered approximately, while the rice plants took NH_3-N when the removal processes are ignored.
4. The mass balance of N or N-budget among the compartments is produced by the Level Ⅲ fugacity model.

The present study has the following limitations: the model calibration by the actual observation data is not performed and the residual amount and nitrogen type change by the soil layer are not described, and the model simulation is considered as continuous emission input unlike intermittent actual emission input. Therefore, more specific and ongoing modeling and monitoring studies are required to quantify the impact of liquid manure as a non-point pollutant on water quality. Based on the simulation results, the further study is required to describe more precise removal process in the Level Ⅲ fugacity model with proper values of input parameters, to simulate the model for various N-typed fertilizers, to compare simulation results between the liquid manure and various N-typed fertilizers, and to evaluate the model with observation data of N components.

요약

액비(분뇨)에 포함된 질소성분은 환경의 질을 악화시키고 안정성을 감소시킬 수 있다. 액비로 인한 환경적 위해성을 최소화하기 위해서는 환경 매체 내에서의 액비의 거동을 이해할 필요가 있다. 액비에 포함된 암모니아성 질소(NH_3-N)의 환경 내 거동과 이송을 분석하고, 액비시스템에서 질소(N)관리의 개선을 위한 기반을 제공하며 질소의 환경에 미치는 악영향을 최소화하기 위해서, 본 연구는 단순화된 Level III fugacity 모델의 적용 가능성을 조사하는 것을 목적으로 하였다. 벼 재배 기간 중 4개의 환경구획(공기, 물, 토양 및 벼)에서 암모니아성 질소(NH_3-N) 성분을 축적하기 위해 정상상태의 fugacity 개념을 이용한 모델의 모의 실험을 실시하였으며 그 결과 Level III fugacity 모델의 적용 가능성을 검증하였다. 모델 결과, 대부분의 암모니아성 질소(NH_3-N)는 논물(수체)과 벼(식물)에 분포하였으며 공기와 논물 그리고 토양에 대한 로그-로그 그래프선상에서 fugacity와 농도는 시간에 따라 선형적으로 감소한 반면에 벼(식물)에서의 변화는 비선형적으로 나타났다. 제거과정의 민감성을 살펴본 결과 제거과정(침적과 유출)이 고려된 경우 대부분의 암모니아성 질소는 논물에 분포하였으며 제거과정이 무시된 경우에는 벼(식물)가 암모니아성 질소를 흡수하는 것으로 나타났다. 또한 질소의 물질수지에 따라 각 구획별로 질소가 분포됨을 알 수 있었다. 본 연구는 실제 관측 자료에 의한 모델 보정을 수행하지 않고 토양층에 의한 잔류량 및 질소 형태의 변화를 기술하지 않았으며 모델 시뮬레이션은 간헐적인 실제 배출량 입력과 달리 연속 배출량으로 간주하였다 . 그러므로 수질에 대한 비점 오염원으로서의 액비의 영향을 정량화하기 위해서는 보다 구체적이고 지속적인 모델링 및 모니터링 연구가 필요하다. 향후 연구의 Level Ⅲ fugacity 모델에서는 더 정확한 제거 과정을 기술하고, 입력 변수의 적절한 값을 적용하여 다양한 N 형 비료에 대한 모델 시뮬레이션을 실시하고, 액비와 다양한 N 형 비료를 사용하여 얻은 N 성분의 관측 자료를 이용하여 모델을 평가할 것이다.

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