Transport of Urea in Waterlogged Soil Column: Experimental Evidence and Modeling Approach Using WAVE Model

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The main form of nitrogen fertilizer applied to lowland rice is urea, but little is known about its transport in waterlogged soil. This study was conducted to investigate the transport of urea in waterlogged soil column using WAVE (simulation of the substances Water and Agrochemicals in the soil, crop and Vadose Environment) model which includes the parameters for urea adsorption and hydrolysis. The adsorption distribution coefficient and hydrolysis rate of urea were measured by batch experiments. A transport experiment was carried out with the soil column which was pre-incubated for 45 days under flooded condition. The urea hydrolysis rate (k) was 0.073 h^{-1}. Only 5% of the applied urea remained in soil column at 4 days after urea application. The distribution coefficient (K_d) of urea calculated from adsorption isotherm was 0.21 L kg^{-1}, so it was assumed that urea was a weak-adsorbing material. The maximum concentration of urea was appeared at the convective water front because transport of mobile and weak-adsorbing chemicals, such as urea, is dependent on water convective flow. The urea moved down to 11 cm depth only for 2 days after application, so there is a possibility that unhydrolyzed urea could move out of the root zone and not be available for crops. A simulated urea concentration distribution in waterlogged soil column using WAVE model was slightly different from the measured concentration distribution. This difference resulted from the same hydrolysis rate applied to all soil depths and overestimated hydrodynamic dispersion coefficient. In spite of these limitations, the transport of urea in waterlogged soil column could be predict with WAVE model using urea hydrolysis rate (k) and distribution coefficient (K_d) which could be measured easily from a batch experiment.

Key words : *urea, adsorption, hydrolysis, transport modeling, waterlogged soil.*

Urea is the most popular N fertilizer in rice cultivation due to its of high N content, low cost, and easy availability. In Korea, nitrogen fertilizer accounted for 50% (446,801 tons) of the total production of chemical fertilizers and 93% (415,107 tons) of the total N fertilizer consumption was in the form of urea in 1997.[1] The efficiency of urea for rice in the submerged soil is very low (20~40%), even under the best agronomic practices. Ammonium and other species derived from urea could be lost or made less available due to NH$_3$ volatilization, denitrification, leaching, ammonium fixation, and immobilization.[2] DeLanune and Patrick demonstrated that the main site of urea hydrolysis was the soil and not the floodwater.[3] The urea applied to the flooded water rapidly diffuses into the soil profile and is hydrolyzed.[4] The hydrolysis rates in submerged soils are retarded because O$_2$ is depleted. The order of hydrolysis rate was: oxidized soil>reduced soil>floodwater.[5,6] Lindau *et al.* measured urea hydrolysis rates in four rice soil suspensions.

Hydrolysis rates followed first-order kinetics. First-order hydrolysis rate coefficients ranged from 0.028 to 0.403 h^{-1}.[7] Adsorption of urea by soil was reported as early as 1940. Considering the normally rapid rate of urea hydrolysis, adsorption is not likely to influence leaching in the long term. However, for short-term leaching experiments, Broadbent *et al.* found that urea occupied an intermediate position between NO$_3^-$ and NH$_4^+$ in its susceptibility to leaching.[8] In the experiment of urea transport, it is necessary to consider the urea adsorption capacity of soils. In the laboratory, adsorption capacity is determined by either batch or column experiments.[9]

The movement of water through the soil can greatly affect the distribution of urea. Because urea is not only hydrolyzed but also adsorbed into soil, its movement in soil through water flow is complex and limited.[11] To develop proper management practices and to improve the effectiveness of urea utilization in paddy fields, understanding of urea transformation and percolation process is essential.[11] In the agricultural environment, both the development of regulations and the assessment of the agricultural chemical's long term effects would be substantially simplified by the availability of comprehensive and tested simulation models. Such models could help the decision makers to define when,

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where, and how much fertilizer to apply to the agricultural land, which require good understanding of the transfer and transformation processes of solutes as they migrate through the soil, and as such requires a good knowledge of the physical, chemical, and biological laws governing the change. Mathematical modeling is increasingly applied in the environmental studies because it allows a better insight in processes, to integrate knowledge of different discipline, to analyse complex problems in a holistic way, and to predict impacts of change on environment.

The objectives of this study were: (i) to measure urea adsorption distribution coefficients and hydrolysis rate constants to use as parameters for WAVE model, and (ii) to predict the distribution of urea concentration in the waterlogged soil columns with WAVE model which accounts for urea adsorption and hydrolysis.

Materials and Methods

The soil was collected at the experiment farm of the College of Agriculture and Life Sciences, SNU. The collected soil was air-dried and passed through a 2 mm sieve and used for study. The soil was a Gangseo series (Aquic Fluventic Eutrochrept). Some selected properties were presented in Table 1.

Adsorption of urea.   Soil sterilization was accomplished in an autoclave at 120°C for 1 h. Urea solutions of 50, 125, 250, 500, 750 and 1000 mg N L⁻¹ were prepared with 5 mg phenylmercuric acetate (PMA) to inhibit urease activity. A 13.3 g of sterilized soil was equilibrated with 20 ml of the above urea solutions. Each urea treatment was replicated three times. After shaking for 18 h at 25°C, the soil suspensions were centrifuged at 2400 rpm for 30 min. The supernatant was filtered and urea concentrations were determined by the diacetyl monoxime method.[12]

Hydrolysis of urea.   A 2 ml distilled water was added to 10 g soil and was incubated at 25°C for 1 day to increase microbial activity. And then, distilled water was added until soil samples were saturated. Samples were pre-incubated for 6 days at 25°C to develop reduced condition. After pre-incubation, the floodwater was removed and 10 ml of 2000 mg urea L⁻¹ solution was added. The soil samples were again incubated at 25°C for 18, 24, 39, 48, 60 and 72 h. At the end of incubation period, urea was extracted from soil by shaking for 1 h with 2 *M* KCl (1:10 soil/KCl ratio) containing 5 mg L⁻¹ of PMA. The extract solutions were filtered and analyzed for urea-N. Remaining urea concentration was determined by colorimetry as was used for adsorption experiment.
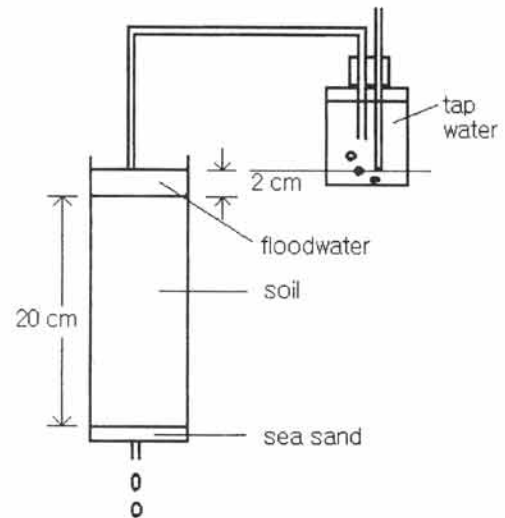

Fig. 1. Schematic diagram of the transport experiment.

Transport of urea.   An acryl column (25 cm length ×5 cm i.d.) was constructed with an 1 cm thick sea sand layer. The acryl column was uniformly packed with soil to give a 1.3 g cm⁻³ of bulk density and was saturated slowly from the bottom with tap water. A 2 cm floodwater layer was maintained (Fig. 1). The saturated soil column was incubated at 25°C for 45 days to develop a reduced condition before urea application. After pre-incubation, a percolation rate of 2.5 cm d⁻¹ was set by adjusting hydraulic head difference between floodwater and outflow. After percolation rate was adjusted, the floodwater was replaced with 350 mg N L⁻¹ of urea solution. Total amount of urea-N added to soil column was 14 mg N (equivalent to 70 kg N ha⁻¹ soil). After urea addition, the soil column was incubated for 0.5, 1, 2, 4, 6, and 12 days at 25°C. At the end of each incubation period, the floodwater was collected and urea and NH₄⁺ were determind. The soil column was sectioned into 11 layers at the depths of 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 cm. Water contents were measured in each soil layer. Urea concentration of each soil layer was determined as in adsorption experiment. The NH_4^+ and NO_3^- concentrations were determined by steam distillation procedures using MgO and Devarda's alloy.[13]

Modeling approach.   The Richards equation which describes soil water flow can be written as[14]:

$$C(h) \frac{\delta h}{\delta t} = \frac{\delta}{\delta z} [K(d)(\frac{\delta h}{\delta z} + 1)]$$

where, $C(h) = \frac{\delta h}{\delta h}$ is differential water capacity, θ is the volumetric water content (cm³ cm⁻³), z is the vertical coordinate (cm) defined as positive upward, t is the time (d),

Table 1. Selected properties of soil used.

pH (1:5)	CEC (cmol꜀ kg⁻¹)	O.M. (g kg⁻¹)	sand	silt	clay	Texture
			------ (%) ------			
5.0	10.4	28	52.2	28.3	19.5	sandy loam

$K(\theta)$ is the hydraulic conductivity function (cm d^{-1}) and h is the soil water pressure head (cm).

This equation was derived from combination of the Darcian water flow equation with the water mass conservation law. In saturated condition $[C(h) = 0]$, the moisture retention $[MRC = (h)]$ and hydraulic conductivity $[HCC = K(\theta)]$ or $K(h)$ functions need not be specified.

The transport of urea, obeying the advection-dispersion equation (ADE) and undergoing first-order hydrolysis with equilibrium-type adsorption by the soil matrix, may be written as[14]:

$$R\theta \frac{\delta C}{\delta t} = D\theta \frac{\delta^2 C}{\delta x^2} - v \frac{\delta C}{\delta x} - k\delta C$$

where, C represents urea concentration (mg L^{-1}), D is the hydrodynamic dispersion coefficient (cm^2 h^{-1}), v is percolation rate (cm h^{-1}), R is a retardation factor, is the volumetric water content in the soil column (cm^3 cm^{-3}), k is the first order hydrolysis rate (h^{-1}), t is time (h) and x is the spatial coordinate (cm).

The hydrodynamic dispersion coefficient D is divided into the diffusive flux and the convective flux.

$$D = D_e + D_m$$

where, D_e is the average flow velocity component by diffusive flux and D_m is the mechanical dispersion component by the convective flux

At high flow velocities, the dispersion term (D_m) is much larger than the diffusion term (D_e). That is, D_m approaches to D. The mechanical dispersion coefficient, D_m, is assumed to be proportional to the effective average macroscopic pore water velocity (V_m).

$$D_m = \lambda V_m$$

where, is the soil solute dispersivity.

The retardation factor, R, can be expressed as:

$$R = 1 + \frac{\rho}{\theta} K_d$$

where, K_d is distribution coefficient (cm^3 g^{-1}) and ρ is soil bulk density (g cm^{-3}).

Each parameter was determined as follows: C was measured through a saturated soil column experiment and k or K_d were calculated from adsorption and hydrolysis experiments. The v, θ, and ρ were adjusted to 2.5 cm d^{-1}, 54.7 cm^3 cm^{-3}, and 1.2 g cm^{-3}, respectively. The value of used for simulation was 2.1 cm which was adopted from reported result applied to sandy loam soil.[15]

WAVE (simulation of the substances Water and Agrochemicals in the soil, crop and Vadose Environment) is a one-dimensional model for the description of matter and energy flow in soil and crop systems, developed by the Institute for Land and Water Management, Belgium in 1994.

The included modules are WAT (water transport module), SOL (solute transport module), TEMP (heat transport module), NIT (nitrogen fate module), and CROP (crop growth simulation module). In simulating urea transport, WAT and SOL modules were used. Model predictions for a specific scenario require that values are specified for both the input variables and the model parameters. Input variables are those variables by which the environment affects the delineated system. Model parameters are constants in the mathematical relationships present in the model. Four files (GENDATA.IN, CLIMDATA.IN, WATDATA.IN, and SOLDATA.IN) are needed for simulation for water and solute transport.

GENDATA.IN includes information on simulation type, simulation period, soil profile development, number of soil compartments within each layer, and bulk density. The simulation type was solute model. The soil profile is divided into different soil compartments of equal size to solve the different transport equations numerically. We assumed that the soil column is composed of only one layer which has uniform soil properties. The soil column was divided into 10 compartments with uniform length, 2 cm depth, determined for easy comparison of experimental data. The simulation period was set to 20 days longer than the period of the column experiment. The date had no special meaning.

CLIMDATA.IN is the climate data required to solve the water flow equation. The following sequence must be followed: year, month, day, potential evapotranspiration (mm d^{-1}), precipitation (mm d^{-1}), irrigation (mm d^{-1}), interception capacity (mm), minimum and maximum temperature (°C) and global radiation (J cm^{-2} d^{-1}). The precipitation was adjusted to 25 mm daily, same as water flux. On the fifth day, 20 mm water containing urea was irrigated.

WATDATA.IN contains the input required to model soil water flow. The initial part of WATDATA.IN requires the specification of soil hydraulic parameters (MRC and HCC). In this simulation, i.e. saturated condition, MRC and HCC have no meaning. As such, we needed to set the values of these parameters for the ease of programing execution. Therefore, we set the parameters at our options except θ, 0.55 cm cm^{-3}. Saturated hydraulic conductivity (K_{sat}) of 2.5 cm d^{-1} was an input which coincided with percolation rate of the column study. The water upper boundary condition specifies a threshold pressure head value (cm) below which evaporation is limited and a maximum water depth which can be stored in the soil surface before runoff (mm) takes place. This input value was filled with WAVE manual recommendation. For bottom boundary condition, a lysimeter bottom boundary was choosed.

SOLDATA.IN contains the additional input for modeling the behaviour of solutes. Initially the solute transport parameters used in advection-dispersion equation should be specified. They were the distribution coefficient (K_d) and hydrodynamic dispersivity (λ). Other parameters

were specified based on manual for WAVE. The K_d was calculated from the adsorption isotherm batch experiment. The λ was chosen from the wide range of reported results on sandy loam soil. The irrigation containing urea was occurred once on the fifth day. The amount of added urea was equivalent to 70 kg N ha^{-1}. In the solute sink term input, urea hydrolysis was considered. It was specified from the batch incubation result and applied to all soil compartments.

Results and Discussion

Adsorption isotherm of urea. The linear adsorption model to describe the adsorption of urea into the soil is as follows[16]:

$x/m = K_d C$
where, x/m: amount of urea adsorbed at soil (mg kg^{-1})
C: equilibrium concentration of the soil solution (mg L^{-1})
K_d: distribution coeffiecient (L kg^{-1})

Distribution coefficient (K_d) describes the partitioning of the solute between solid and liquid phase and is considered analogous to the equilibrium constant. Figure 2 shows the plots of x/m against C. The slope of the straight line, 0.21 L kg^{-1}, is K_d.

For the estimation of K_d in the column experiment of urea transport, it was necessary to employ a soil/solution ratio used in the batch experiment of urea adsorption to the column experiment. However, this was not practical due to the difficulty of separation of the soil solution. In this study, the soil/solution ratio used in the batch experiment (about
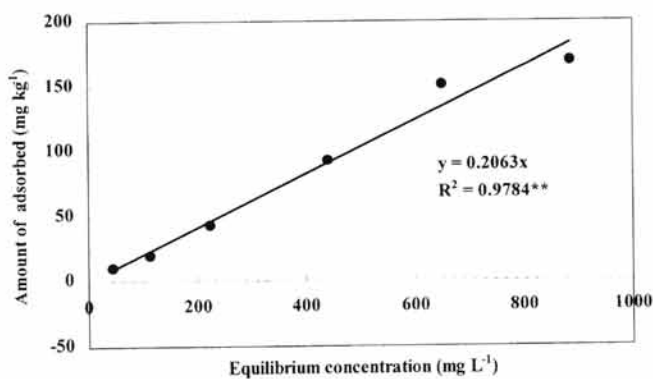
0.7) was lower than that used in the column experiment (about 2). So, a K_d value which was calculated from the batch experiment may be a little high when applied to column experiment. It was reported that K_d decreased with increasing adsorbent (soil) concentration.[9]

Rate constant of urea hydrolysis. The concentrations of urea remained during incubation was shown in Table 2. Since urea hydrolysis was expected to follow the first-order kinetics, remained urea was plotted with time by a semilogarithmic scale (Fig. 3). The hydrolysis rate constant (k), the slope of straight line, was 0.0734 h^{-1} ($R^2 = 0.91**$) (Fig. 3). Lindau *et al.* reported the hydrolysis rate constants of the oxidized soils were higher than those of reduced soils.[7] In this study, rate constant was a little higher than the reported results of Lindau *et al.* This data resulted from a high redox potential of the experiment (460 mV), suggesting easy O_2 supply into the soil samples. The obtained rate constant just represents the upper oxidized layer of soil column. Saraswathi *et al.* showed that urea hydrolysis in pre-submergence soils was greatly retarded during flooding period up to 4 day. With a longer submergence time, soil E_h and urease activity decreased to a stabilized value.[17]

Concentrations of urea and NH_4^+ in soil column. The urea concentrations in soil column during incubation were presented in Fig. 4. In floodwater, the concentrations of urea were 133, 70, and 14 mg L^{-1} at 0.5, 1 and 2 days, respectively. DeLaune and Patrick reported that the main site

Fig. 2. Linear isotherm plot for urea adsorption.

Table 2. Concentration of urea remained with incubation time.

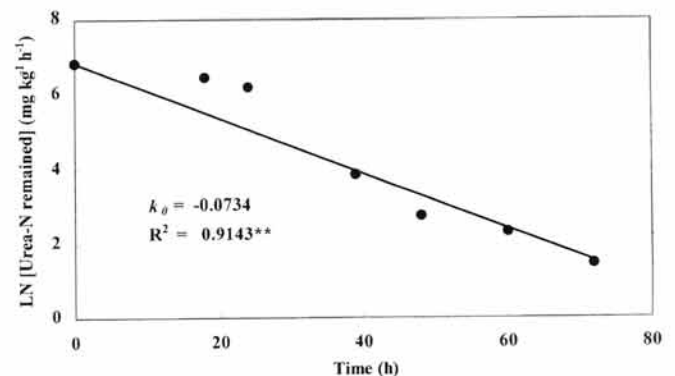| Time (h)	Urea-N Remained (mg kg^{-1})
0	933.1
18	642.9
24	494.7
39	47.7
48	15.8
60	10.2
72	4.3

Fig. 3. Semilogalithmic plot of remained urea-N with incubation time.

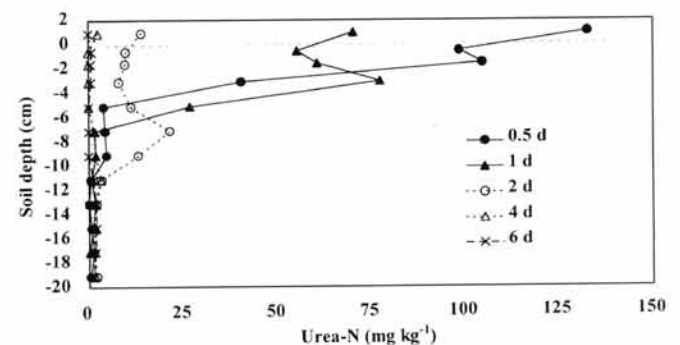
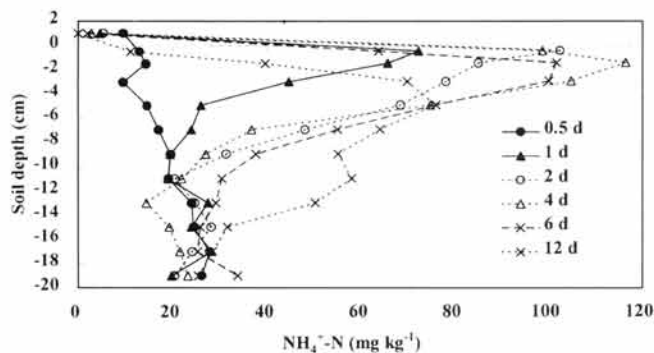Fig. 4. Urea concentrations in floodwater and soil during incubation.

Fig. 5. Ammonium-N concentrations in floodwater and soil during incubation.

Fig. 6. Predicted (Mo) and measured (Me) urea concentrations on the 1st and 2nd day after incubation.

of urea hydrolysis was the soil and not the floodwater.[3] In soil, the highest urea concentration was observed at 1-2 cm depth. The applied urea moved down to the 2-4 cm depth on 0.5 day. This result showed that percolation rate mainly affected urea distribution in soil column because little portion of applied urea was adsorbed into soil particle. Since the percolation rate was 2.5 cm d^{-1}, it took 0.5 day for water to percolate about 1.3 cm. Therefore, we found the highest concentration of urea transported by convective flow at 1-2 cm depth. The urea at 2-4 cm depth may have been dispersed from the upper part of the soil. On the 1st and 2nd days, the highest concentrations of urea were observed at 2-4 and 6-8 cm depth, respectively. On the 2nd day, urea moved downward to 11 cm. On the 4th day, 95% of the applied urea was hydrolyzed. Most of the applied urea were hydrolyzed to NH_4^+ then absorbed by the plant. Urea hydrolysis rate was largely dependent on the soil environment such as temperature.[18] When the urea was applied as a basal fertilizer in spring, the urea hydrolysis rate was relatively small due to low temperature on seedling period, so unhydrolyzed urea could move out of root zone and were not available for crops.[19]

The concentrations of NH_4^+ in the soil column during incubation were presented in Fig. 5. In floodwater, NH_4^+ concentrations decreased with increasing incubation time. The concentrations were 9.5 and 2.0 mg L^{-1} on the 0.5 and 6th days, respectively. On the 12th day, NH_4^+ was not detected in floodwater. Unlike urea, NH_4^+ did not move to downward easily. On 2nd day, the highest concentration of NH_4^+ was observed at 0-1 cm depth, but 6-8 cm for urea. Even on the 6th day, the highest concentration was shown at 1-2 cm depth, which may be due to high adsorption capacity of NH_4^+ into the soil. The total amount of NH_4^+ in soil during incubation was greatly increased from 218.9 mg kg^{-1} on the 0.5 day to 536.2 mg kg^{-1} on the 2nd day due to NH_4^+ produced from hydrolysis of appled urea. The broadcasting urea was hydrolyzed to NH_4^+. So, it is very important to reduce the NH_4^+ loss by management of irrigation water, timing/method of application, and inhibitions of urea hydrolysis and algal proliferation.[20]

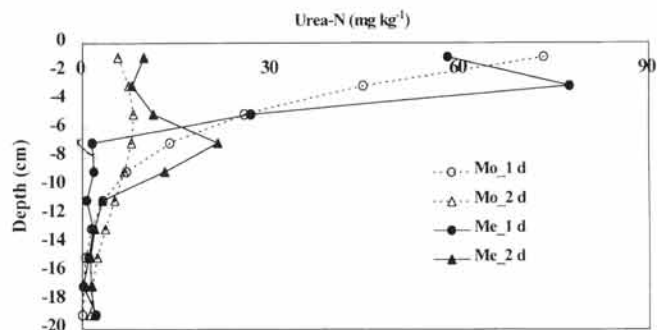**Modeling of transport of urea.** Figure 6 showed the measured values (Me) of urea concentration in the soil

column and the predicted values (Mo) using WAVE model. Because WAVE cannot consider floodwater, the urea concentration in floodwater was omitted. The predicted values were not consistent with the measured values. The total amount of remained urea by prediction was smaller than the value by measurement. The urea hydrolysis rate calculated from the column experiment (0.029 h^{-1}) was smaller than that from the batch experiment (0.073 h^{-1}). This indicated that the urea hydrolysis rate was underestimated in WAVE model. It is necessary to determine the hydrolysis rate of each soil layer with different redox potentials. The urease activity of the upper soil layer with oxidizing condition would be higher than that of the lower soil layer. At lower depth of soil column (below 10 cm), the predicted urea concentrations were higher than the measured values. This result was thought to be related with the hydrodynamic dispersion coefficient because we used the estimated value (5.25 cm[2] d^{-1}) for simulation. Even though there was some difference between the predicted value and the measured value, particularly in the upper layers of the soil column (above 4 cm), the trends of urea concentartion distribution in the soil column obtained from WAVE model was very similar to that obtained from the measurement. The estimation of urea concentration in the waterlogged soil column was possible with urea hydrolysis rate (k) and distribution coefficient (K_d) which could be measured easily from the batch experiment.

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