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Research Article

Reaction Rate Constants for Urea Transformation under Flooded Conditions Using Open Static Chamber Method

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Abstract

The main form of fertilizer applied to lowland rice is urea, but very few researches are conducted on its movement and transformations under flooded soil conditions. An *in-situ* study was conducted to measure movement and transformation of urea in flooded soils. Urea transformation is difficult to model in flooded soil systems due to the complicated transformations it undergoes. An essential step in analytical modelling is the determination of model parameters such as reaction rate constants. In order to estimate the reaction rate constants, an experiment was conducted in a soil spiked with urea in chamber and the soil moisture and temperature were maintained in the field condition. In this study only ammonium volatilized is captured and analysed periodically. The nitrate content in the chamber was found out at the end of the experiment. The reaction rate constants were estimated by solving the partial differential equations representing urea reactions using risk solver platform in the MS-Excel environment. The method was found to have minimum number of observations without estimating the urea, ammonium and nitrate in soils periodically. The estimated reaction rate constant for ammonia volatilization was found to give a good estimate of volatilized ammonia with that of the observed volatilized ammonia. The estimated reaction rate constant of urea hydrolysis, distribution coefficient, volatilization, nitrification and denitrification are 0.0016 h^{-1}, 0.9, 0.0040 h^{-1}, 0.0080 h^{-1} and 0.0214 h^{-1} respectively. The reaction rate constants estimated in this study are useful for Nitrogen balance studies in flooded soils.

Keywords: Nitrogen, Nitrogen transformation, Reaction rate constants, Open static chamber

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Introduction

Nowadays the concept of *"More Fertilizer, More Yield"* sounds in the minds of the farmers and this leads to surplus use of Nitrogen (N) fertilizer for crops. It has led to an increased input of N concentration into agricultural soil – plant systems and also at the same time increased N losses into the environment. Urea is the widely used nitrogenous fertilizer. In soil, the applied urea is hydrolyzed by the enzyme urease by rhizosphere microorganisms to ammonium and nitrate which are prone to losses through volatilization, leaching and denitrification. Understanding the N cycle, N transformation and the movement of nitrogen is critical for optimum management of field conditions. So, many models have been developed to handle these problems. Models like lumped parameter model (Ling and Aly et al., 1998), analytical model (Chowdary et al., 2004) and Hydrus 1D (Young Li et al., 2015) model help to understand these N transformation and movement of nitrogen. A simple representation of urea hydrolysis assumes first order reaction kinetics and provides satisfactory results (Hongprayoon et al., 1991).

Ammonium, which can be used by plants, get leached very less because it has a positive charge and so it sticks to negatively charged clay particles. If not taken up by plants, ammonical nitrogen will be further degraded by micro-organisms to produce nitrate nitrogen, and nitrate is taken up by plants. Nitrate molecules are negatively charged. They are repelled by negatively charged clay particles, and if not taken up by plants, it will move easily with water through soil and reaches groundwater (**Figure 1**).

To estimate urea transformation parameters in a field study, inverse modelling offers a viable choice because the laboratory methods are time consuming, expensive and has practical limitations. Since N turnover is strongly affected by micro environmental conditions, additional difficulties arise from the heterogeneity of soil properties, even on very small geographical scales (Becket and Webster, 1971). Serious problems in modelling N transfer through soil – crop systems are currently posed by the lack of understanding of soil biological processes (Otter-Nacke and Kuhlmann, 1991; De Willigen, 1991), the influence of physical soil factors (Van Veen and Kuikman, 1990; Verberne et al., 1990;

Ladd et al., 1993) and the nature of decomposing substrates (Amato and Ladd, 1992; Jen-sen, 1994; Motavalli et al., 1995). The more exactly a model tries to describe the processes involved, the more complex it gets and hence, the more difficult it becomes to use.

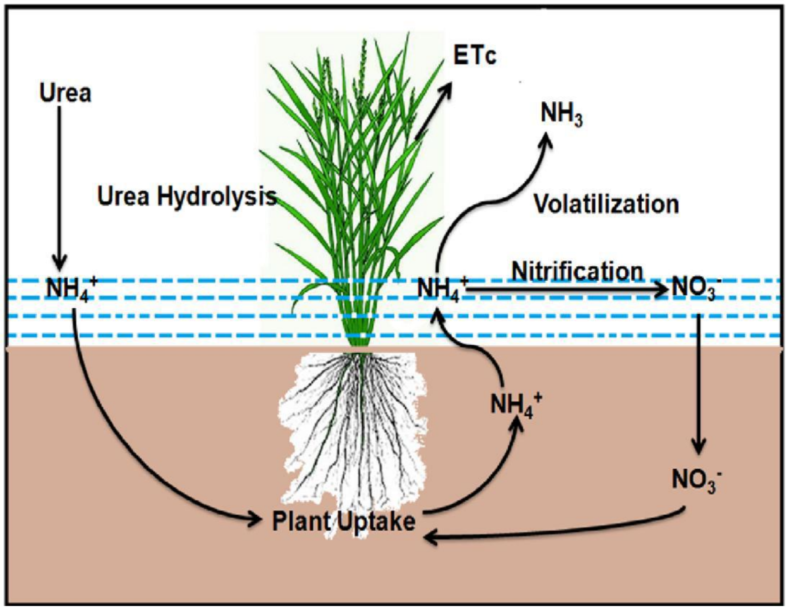

Figure 1 N transformation process

The main limitations in the use of N transformation models are inadequate representation of the coupled processes involved (Diekkruger et al., 1988) and difficulty in obtaining input parameters for the models (De Willigen P, 1991 and Schmied et al., 2000). The parameters may be obtained independently from correlations or laboratory assays, or by means of field experiments and parameter optimization using inverse simulation techniques. The application of a predictive model at a field scale and the use of inverse simulation techniques in conjunction with the field data is probably more efficient (Ritter A, 2002).

Several enclosure methods to measure NH_3–N loss using static chambers were used, as they permit monitoring of multiple treatments in the same crop season, have a low cost and require reagents and materials commonly available in laboratories worldwide (Grant *et al*., 1996). The most used static chamber was based on a semi open static design, which was developed by Nômmik (1973). It is composed of a cylinder anchor inserted into the soil connected with a chamber containing two poly foam sponges soaked in acid solution that act as an NH_3–N gas trap. Ammonia gas reacts readily with the acidic medium with the most common options being phosphoric acid (Nômmik, 1973), sulfuric acid (Sherlock *et al*., 1989) or hydrochloric acid (Janzen and McGinn, 1991). Another design is much similar to the semi open static chamber called as Open Static Chamber (OSC). In this method, a PET (Poly Ethylene Terephthalate) bottle is used by removing its bottom and placed over soil. Air movement from the soil through the bottle is facilitated through a side hole at the cap. During the travel of air, ammonia is trapped on a wick drenched with acid. Comparatively the second design is easy and of less cost.

Claudia Pozzi Jantalia et al. (2012) compared both the in-situ ammonia collection methods in the field and found that the recovery of ammonia is good in the open static chamber method.

All the reactions such as urea-to-ammonium, ammonium-to-ammonia, ammonium-to-nitrate, nitrate-to-nitrogen & nitrous oxide are coupled and consecutively happening. It is customary to represent all the reactions as partial differential equations with first order rate assumption. Finding each rate of reaction for all the reactions by estimating the quantities of each of these chemical species periodically is another big difficulty. Hence, it is customary and easy to collect and estimate only volatilized ammonia. The optimal set of reaction rate constants are found out by any suitable search procedure in which the sum of squared differences between estimated ammonia evolution and observed ammonia evolution in the field (Claudia Pozzi Jantalia et al., 2012) is minimum. Hence accurate estimation of ammonia evolution in the field is a basic need of finding reaction rate constants.

Materials and Methods

The study was conducted at the Agricultural engineering college and research institute, Kumulur, Trichy, Tamil Nadu, India. The region has a semi arid temperate climate, with a typical mean temperature of 30^0C. The experiment was conducted in the flooded field conditions applied with N fertilizer.

Open Static Chamber (OSC) method

An experimental plot of dimension 1 m × 0.75 m was used for the OSC method. Soil was collected from the experimental plot and sieved through a 2 mm sieve. Before starting the experiment, initial concentration of Ammoniacal Nitrogen (NH_4-N) and Nitrate Nitrogen (NO_3-N) were determined. This experimental setup has three parts: (1) Open Static Chamber (OSC) for volatilization (2) An acid trap for collecting emitted NH_3 and (3) Restriction for air flow.

The chamber consists of a glass bottle with an opening at bottom. The neck of the bottle is closed with a hole in the rubber cork to provide the air exit. The chamber is 160 mm in length and 110 mm in diameter. Inside the chamber, a foam is placed so that acid wets the foam by capillary rise. A stand is placed on the soil surface to support a beaker (100 ml) that contains 0.01 N Sulfuric acid solution into which the foam strip is dipped, to keep it moist during sampling period for ammonia collection.

Sampling and extraction of ammonia

On the day of sampling, the foam disc, foam strip and beaker containing 0.01N sulfuric acid solution in open static chamber is collected and replaced with new foam traps. To avoid contamination of samples, disposable hand gloves were used during sampling activities. The traps from chamber was taken out and placed immediately in a big size container (5 litres capacity) having 250 ml of 2 M KCl. The acid solution from the sample is transferred with a funnel to a 250 ml volumetric flask. The big size container and traps thoroughly rinsed two or more times with 2 M KCl solution followed by manual shaking (for 10 seconds) to extract the trapped ammonia from the foam strips and disc. An aliquot of total solution (50 ml) is filtered into glass vials, sealed and frozen until the end of analysis. Immediately after thawing, an aliquot of the solution is analyzed for ammonia concentration using distillation procedure with Bremner method.

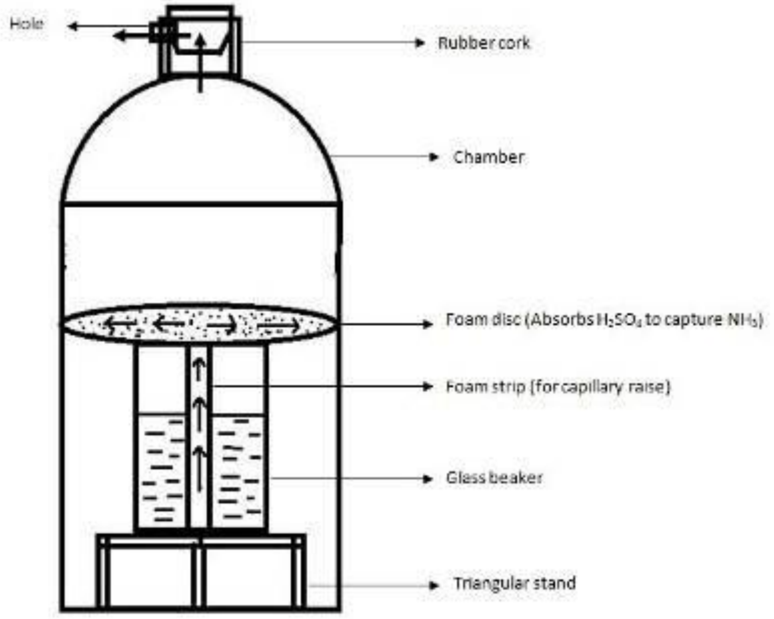

Figure 2 Open Static Chamber (OSC) method

Estimation of reaction rate constant

Following are the partial differential equations representing the transformation of urea, ammonium and nitrate with an assumption of first order reactions respectively.

For Urea

$$\frac{\partial(\theta C_1)}{\partial t} = -\mu_a \theta C_1 \tag{1}$$

For ammonium

$$\frac{\partial(\theta C_2)}{\partial t} + \rho\frac{\partial S}{\partial t} = -\mu_v\theta C_2 - \mu_n\theta C_2 + \mu_a\theta C_1 \quad (2)$$

For nitrate

$$\frac{\partial(\theta C_3)}{\partial t} = \mu_n(\theta C_2) - \mu_{dn}(\theta C_3) \quad (3)$$

Where C_i is the liquid phase concentration of the chemical species i (subscripts 1, 2, 3 represent urea, ammonium, nitrate respectively) (mg/cm^3), ρ is the bulk density of the soil (g/cm^3), θ is the moisture content of soil (cm^3/cm^3), S is the adsorbed concentration of ammonium (mg/cm^3), μ_a is the first-order reaction rate constant (1/T) representing hydrolysis of urea to ammonium, μ_v is the first-order reaction rate constant (1/T) representing volatilization of ammonium to ammonia, μ_n is the first-order reaction rate constant (1/T) representing nitrification of ammonium to nitrate and μ_{dn} is the first-order reaction rate constant (1/T) representing denitrification of nitrate to nitrous oxide.

Ammonia is subjected to cationic exchange processes that reflect the potentially strong retention of this ion by soil. The relationship between ammonium in solution (C_2) and in adsorbed state (S) is assumed as linear and the equation is as follows:

$$S = K_d C_2 \quad (4)$$

Where K_d is the distribution coefficient for ammonium (cm^3/g).

Integral equation for Equation (1) if the soil moisture content is maintained constant is as follows:

$$C_1(t) = C_1(0)e^{-\mu_a t} \quad (5)$$

Where $C_1(0)$ – initial concentration of urea and $C_1(t)$- urea concentration at any time ‘t’.

Equation (2) and (3) is solved by finite difference method explicitly with an appropriate time step. A time step of one hour was found to give satisfactory solution. The following equations are explicit forms of equation (2) and (3).

$$(\theta C_2)_{t+\Delta t} = (\theta C_2)_t + \left(\frac{\Delta t}{1+\frac{\rho K_d}{\theta}}\right)[-(\mu_v + \mu_n)(\theta C_2)_t + \mu_a\,\theta C_1(0)e^{-\mu_a t}] \quad (6)$$

$$(\theta C_3)_{t+\Delta t} = \Delta t.\mu_n(\theta C_2)_t - (\theta C_3)_t(\Delta t.\mu_{dn} - 1) \quad (7)$$

Ammonium volatilized till time ‘t’ (AV_t) from the experiment can be found out from the following equation:

$$AV(t) = \int_0^t \mu_v\,(\theta C_2)dt \quad (8)$$

Approximately, the preceding equation can be written as follows:

$$AV(t) = \textstyle\sum_0^t(\mu_v\ (\theta C_2)\Delta t \quad (9)$$

Equations (6-8) are the set of non-linear equations. They were solved using commercially available software package namely RISK SOLVER PLATFORM, which is an add-on for the MS-EXCEL. In Risk solver platform, we need to provide the range of reaction rate constants with in which search operation is to be executed. Risk solver search engine selects a set of reaction rate constants and estimate the quantities of Urea reduced, cumulative ammonium, ammonia and nitrate produced using equations (5-7 and 9) progressively for each time step. The objective function in the optimization is minimizing sum of square deviations of estimated ammonia volatilization and observed ammonia volatilization values from the field experiment. **Table 1** shows a sample of calculations done in MS-EXCEL Risk solver platform. In Table 1, sum of squared deviations between estimated ammonia evolved by equation (9) and ammonia evolved in experiment for a selected set of reaction rate constants. The risk solver platform has a facility to select an optimal set of reaction rate constant values for which the sum of squared deviation is minimum.

Results and Discussion

The experiment was carried out during the month of August 2016. During the experiment the soil temperature recorded ranges from 32°C to 35°C. The bulk density of soil is 1.63 (gm/cm^3). The soil temperature readings were recorded at 9.00 AM, 1.00 PM and 5.00 PM. **Figure 3** shows the soil temperature variation during the experiment period.

Table 1 Calculation of sum of squared deviation between simulated ammonia volatilized and experimental ammonia volatilized for OSC method

Time (h)	**Urea (θC_1) (mgN/cm^3 of soil)**	**Ammonium (θC_2) (mgN/cm^3 of soil)**	**Nitrate (θC_3) (mgN/cm^3 of soil)**	**Estimated Ammonia Volatilized (mgN/cm^3 of soil)**	**Experimental Ammonia Volatilized (mgN/cm^3 of soil)**	**Squared deviation (mgN/cm^3 of soil)**
	Eq. (5)	Eq. (6)	Eq.(7)	Eq.(8)	-	(Cl.(5)-(6))^2
0.0	0.0443	0	0	0	0	0
1	0.0442	6.904×10^{-5}	5.533×10^{-7}	3.147×10^{-7}	-	-
…..	-	-	-	-	-	-
17	0.0431	0.0010	7.870×10^{-5}	4.477×10^{-5}	-	-
18	0.0430	0.0011	8.757×10^{-5}	4.981×10^{-5}	0.0002	4.417×10^{-8}
19	0.0429	0.0011	9.686×10^{-5}	5.510×10^{-5}	-	-
…	-	-	-	-	-	-
53	0.0406	0.0025	0.0005	0.0003	-	-
54	0.0406	0.0026	0.0006	0.0003	0.00079	1.834×10^{-7}
55	0.0405	0.0026	0.0006	0.0004	-	-
…	-	-	-	-	-	-
166	0.0339	0.0041	0.0039	0.0022	-	-
167	0.0338	0.0041	0.0039	0.0022	0.0027	2.015×10^{-7}
168	0.0338	0.0042	0.0040	0.0023	-	-
…	-	-	-	-	-	-
449	0.0215	0.0031	0.0124	0.0070	-	-
450	0.0214	0.0032	0.0124	0.0071	0.0066	2.573×10^{-7}
451	0.0213	0.0033	0.0125	0.0071	-	-
…	-	-	-	-	-	-
642	0.0158	0.0022	0.0165	0.0094	-	-
643	0.0157	0.0023	0.0166	0.0094	0.01	2.640×10^{-7}
Sum of squared deviations						1.378×10^{-7}

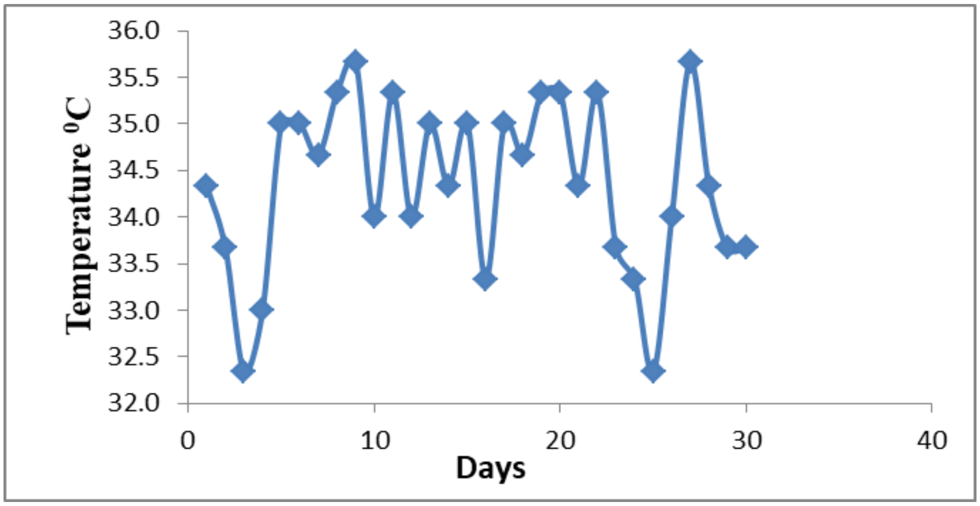

Figure 3 Variation of soil temperature during experimental periods

The initial concentration of Ammonical Nitrogen and Nitrate Nitrogen is 0.0102 mg N/cm^3 and 0.0098 mg N/cm^3 and final concentration of Ammonical Nitrogen and Nitrate Nitrogen is 0.0214 mg N/cm^3 and 0.0108 mg N/cm^3 was measured for OSC method. **Figure 4** shows the quantity of ammonia volatilized over the period of time by taking observations in the field with two experimental setups.

Figure 5 shows the estimated quantities of Urea reduced, cumulative ammonium, ammonia and nitrate. The value of estimated and experimental volatilized ammonia matches well.

Table 2 shows the reaction rate constant values for N transformation processes Obtained using optimization through Risk solver platform using the procedure discussed with Table 1.

The present research revealed that the proposed experimentation in the field and optimization frame work for computing urea reaction rate constants methodology is very versatile and can easily be adopted by the researchers.

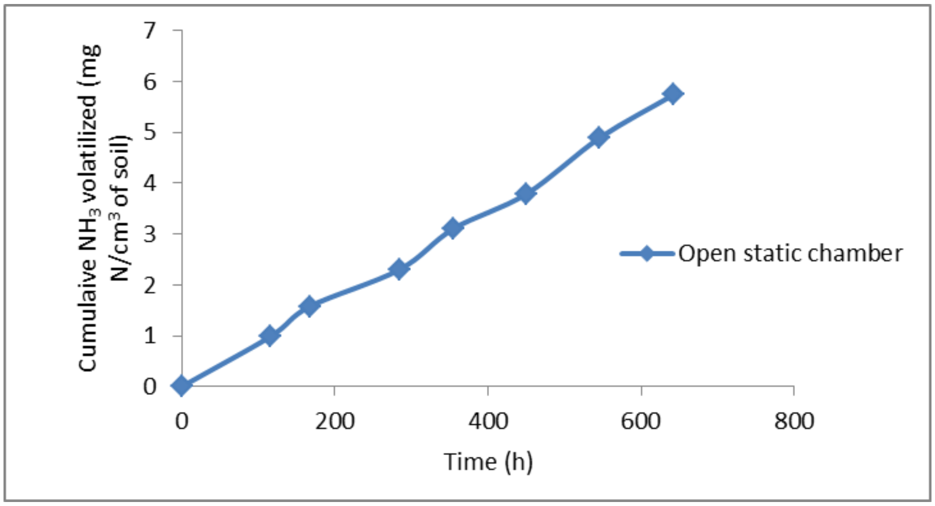

Figure 4 Quantity of ammonia volatilized over period of time using OSC method

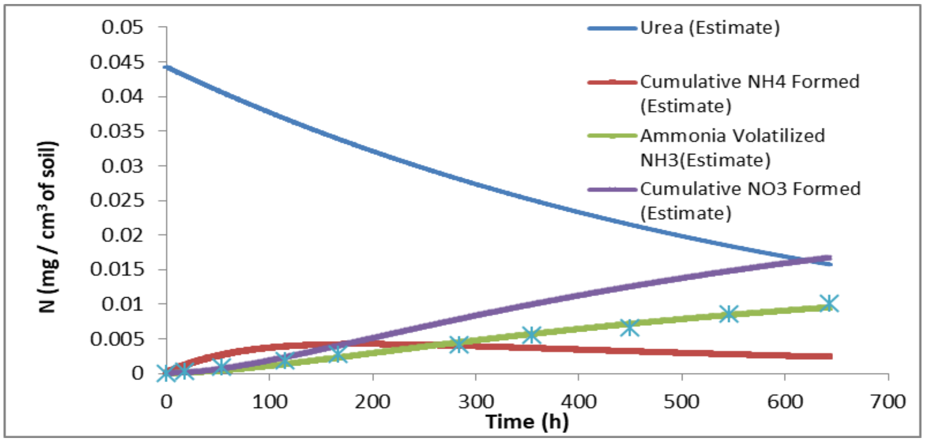

Figure 5 Evolution of the Different Nitrogen Forms

Table 2 Estimated values of reaction rate constants

N transformation processes	Urea hydrolysis (μ_a) (h^{-1})	Ammonia Volatilization (μ_v) (h^{-1})	Nitrification (μ_n) (h^{-1})	Denitrification (μ_{dn}) (h^{-1})
Estimated values	0.0016	0.0040	0.0080	0.0214
Range (Chowdary et al.,2004)	0.0036 - 0.18	0.0017 - 0.0087	0.0140 – 1.1000	0.02- 0.08

Conclusion

Urea reaction process in the soil is very complicated. But estimation of reaction rate constants is essential to do nitrogen balance studies. The usefulness of the laboratory estimation methods is very limited due to the fact that the real field situations cannot be simulated in the lab. With minimum number of observation in the field four reaction rate constants for urea hydrolysis, ammonia volatilization, nitrification and denitrification were found out by devising optimization method using risk solver platform in MS-Excel environment. The estimated reaction rate constant of urea hydrolysis, distribution coefficient, volatilization, nitrification and denitrification are 0.0016 h^{-1}, 0.90, 0.0040 h^{-1}, 0.0080 h^{-1} and 0.0214 h^{-1} respectively for the present study. The estimated values are lying within the ranges reported in the literature.

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