UNIVERSITI PUTRA MALAYSIA

EVALUATION OF A PROCESS-BASED MODEL FOR THE ESTIMATION OF NITROGEN LOSSES IN A FLOODED RICE SYSTEM

MUHAMMAD KHAIRIL FAHMIER BIN AMAT SADIKIN

EVALUATION OF A PROCESS-BASED MODEL FOR THE ESTIMATION OF NITROGEN LOSSES IN A FLOODED RICE SYSTEM

MUHAMMAD KHAIRIL FAHMIER BIN AMAT SADIKIN

184327

BACHELOR OF ENGINEERING

(AGRICULTURAL AND BIOSYSTEMS)

FACULTY OF ENGINEERING

UNIVERSITI PUTRA MALAYSIA

SERDANG, SELANGOR

2018/2019

APPROVAL SHEET

This project report here to entitle "**EVALUATION OF A PROCESS-BASED MODEL FOR THE ESTIMATION OF NITROGEN LOSSES IN A FLOODED RICE SYSTEM**" was prepared and submitted by **MUHAMMAD KHAIRIL FAHMIER BIN AMAT SADIKIN** in partial fulfilment of the requirement for the degree of Bachelor of Engineering (Agricultural and Biosystems) is hereby accepted.

Approved by:

…………………………… Date: ………………………….

(Dr. Nurulhuda binti Khairudin)

Project Supervisor

Approved by:

…………………………… Date: ………………………….

(Prof. Sr. Gs. Dr. Abdul Rashid bin Mohamed Shariff C. Eng)

Project Examiner

Approved by:

…………………………… Date: ………………………….

(Dr. Diyana binti Jamaludin)

Project Examiner

ACKNOWLEDGEMENT

Alhamdulillah. First, I would like to thank Allah S.W.T, I got an opportunity to work and finally completed my thesis. I also want to thank the individual who has helped me during this project, especially my supervisor, Dr. Nurulhuda binti Khairudin who has contributed a lot to me throughout this project in giving support, advice, suggestions and encouragements.

I would like to express a special thanks to my panel examiner, Prof. Sr. Gs. Dr. Abdul Rashid bin Mohamed Shariff C. Eng. and Dr. Diyana binti Jamaludin for their comments and suggestions to improve my project.

I want to thank my friends who has helped and supported me in order to complete this thesis. Last but not least my deepest thanks to my parents En. Amat Sadikin bin Ponidin and Pn. Holilah binti Sidek and also to my brother and sister for their support and constant encouragement especially during hard times.

TABLE OF CONTENT

Contents

ABSTRACT

Simulation of nitrogen (N) losses by using a mathematical model in flooded rice system is important for designing and developing protocols for the management of crop nutrients to ensure sustainable production. Objective for this study are to select an appropriate process-based model for simulation purpose and to test the performance of the model against secondary data sets, and a mathematical model proposed by Liang's was chosen in order to estimate N losses from urea applied in a flooded rice system. However, as a first step, the performance of this model in quantifying N losses must be evaluated. N transformations namely, urea hydrolysis, volatilization, nitrification, denitrification and N transportations like runoff, lateral seepage, vertical leaching and crop uptake were consider in this study. The secondary datasets from Xu et al., (2018) that consist of observed ammonia volatilization, ammonium (NH_4^+) left in soil solutions and nitrate (NO_3^-) left in soil solutions were used to evaluate the model's performance. This model underwent parameter calibration three times. Results showed that the observed ammonia volatilization were well predicted by this model, but not for NH_4^+ and NO_3^- left in soil solutions. The model simulation values were not exactly same as the observation values for NH_4^+ left in soil solutions and NO_3^- left in soil solutions. The performance of this model in identifying NH_4^+ and NO_3^- beneath soil surface is still poor.

ABSTRAK

Simulasi kehilangan nitrogen (N) dengan menggunakan model matematik dalam sistem berasap banjir adalah penting untuk mereka bentuk dan membangunkan protokol untuk pengurusan nutrien tanaman untuk memastikan pengeluaran mapan. Objektif kajian ini adalah untuk memilih model berasaskan proses yang sesuai untuk tujuan simulasi dan menguji prestasi model terhadap set data sekunder, dan model matematik yang dicadangkan oleh Liang telah dipilih untuk menganggarkan kerugian N dari urea yang digunakan dalam banjir sistem beras. Walau bagaimanapun, sebagai langkah pertama, prestasi model ini dalam mengira kerugian N mesti dinilai. Transformasi N iaitu, urea hidrolisis, volatilisasi, nitrifikasi, denitrifikasi dan pengangkutan N seperti larian, rembesan sisi, peleburan menegak dan pengambilan tanaman dipertimbangkan dalam kajian ini. Data sekunder dari Xu et al., (2018) yang terdiri daripada volatilisasi ammonia yang diperhatikan, ammonium (NH_4^+) yang tersisa dalam penyelesaian tanah dan nitrat (NO_3^-) yang tersisa dalam penyelesaian tanah digunakan untuk menilai prestasi model. Model ini menjalani penentukuran parameter tiga kali. Keputusan menunjukkan bahawa volatilisasi ammonia yang diperhatikan telah diramalkan dengan baik oleh model ini, tetapi bukan untuk penyelesaian tanah di NH_4^+ dan NO_3^-. Nilai simulasi model tidak sama dengan nilai pemerhatian untuk NH_4^+ tinggal dalam penyelesaian tanah dan NO_3^- tinggal dalam penyelesaian tanah. Prestasi model ini dalam mengenalpasti NH_4^+ dan NO_3^- di bawah permukaan tanah masih lemah.

.

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

N	Nitrogen
NH_4^+	Ammonium
NO_3^-	Nitrate
$CO(NH_2)_2$	Urea
O_2	Oxygen
NH_2	Amides
NH_3	Ammonia
N_2O	Nitrous oxide
N_2	Dinitrogen
CO_2	Carbon dioxide
CH_4	Methane
NO_2	Nitrogen dioxide
DAT	Days after transplant
MD	Mean of difference
R^2	Coefficient of determination
EF	Modelling efficiency

CHAPTER 1

INTRODUCTION

1.1 Overview

Rice is the main source of food and calories for over half of the world's population. In 2012, rice was harvested about 156 million ha in worldwide, and about more than half of the worldwide harvested region were in Asia and South East Asia, respectively (FAQ, 2013). Asian countries manage nearly 90% of the total rice production and consumption; while Africa and Latin America consume and produce the remaining 10% (Hossain et al., 2004).

Rice growing is one of the aspect economic and political factors of the South East Asian national objectives (Kamaruddin et al., 2013). In South East Asia, rice crops on the harvested area are mainly grown by smallholder farmers which are generally less than 4 ha per farmer. (Kamaruddin et al., 2013).

Some of the yield losses occurred because of insufficient of nitrogen (N). Therefore, nitrogen (N) is one of the important fertilizer nutrients that is needed for rice crops (Makino, 2011).

However, half of the total N applied on the field is not absorbed, and it is proved that nitrogen fertilizers has been utilized and absorbed by crops inefficiently (Dobermann and Cassman 2002). Volatilization of ammonia, denitrification, leaching, and runoff losses are the main reasons for the low efficiency of nitrogen by crops (Cho et al., 2003). The emissions of nitrous and nitric oxide and ammonia cause of air pollution (Azam et al., 2002). Nitrous oxide absorbs infrared radiation which helps to warm the area and deplete the ozone layer (Bohlool et al., 1992). Nitric oxide and ammonia deposition in earth-based or aquatic environment can cause acidification and eutrophication. Nitrate leaching leads to toxicity to soil water (Shrestha and Ladha 1998).

Therefore, N losses from fertilized and flooded rice system must be minimized in order to reduce production costs and negative environmental effects. In the last 30 years, process-based N dynamics models have been developed as an alternative way to simulate the N dynamic of flooded soil systems (Rao et al., 1984). Soil-plant system models can be used to simulate sufficient N supply for optimal cultivation as well as to minimize N losses.

1.2 Problem statement

Nitrogen (N) is an important nutrient rice plants, because serious insufficiency of N in rice plants will reduce the yield. Different mechanisms of N losses are from N transformations and N transportations process including ammonia volatilization, denitrification, nitrate leaching, lateral seepage and surface runoff. These losses could lead to environmental problem such as air, aquatic systems and groundwater pollution. It is important to estimate the losses of nitrogen. The N losses can be estimated by a various techniques. Some of the methods are by field measurements and simulations of nitrogen losses model. But, the field measurements are more laborious, costly, and time consuming compared to simulations of models. So, a simulation of the nitrogen model is a suitable method to estimate N losses.

Next, the yield progress of the crops should also need to increase in a way that meets the needs of the growing population. Therefore, in order to meet demand and help of growing population and as well as to lower the poverty of farmers, it is important to increase the yield of rice crops. Therefore, a lot of factors affecting the output of rice crops. Traditional method and simulation of crop model method might be a solution in order to examine the field management in rice crops. But, a simulation of the nitrogen model might be the best method. Crops models simulations are useful for investigating the effects of domain management at low cost, labour and time on yield and the environment. However, the evaluation of the performance of the crops models must be done first in order to improve the accuracy in the simulations.

The advantages of simulations of model method are, by using a simulation we can study the behaviour of the N losses in the system without building it. Unexpected phenomenon and behaviour also can be predicted by using simulations of the model. However, the models that have been developed must be tested and evaluated with data sets in order to increase the confidence in the simultions.

1.3 Objectives

The main objective of this study is to evaluate the performance of a model for simulation of N losses in a fertilised and flooded rice system. The specific objectives are:

1. To select an appropriate process-based model.
2. To programme and simulate the model using Rsoftware.
3. To test model performance against secondary data sets.

1.4 Scope of research

The scope of this project is focused on evaluating the performance of the selected model against secondary data sets.

CHAPTER 2

LITERATURE REVIEW

2.1 Sources of nitrogen in flooded rice system

As a Nitrogen source, rice crops commonly prefer ammonium than nitrate. Rice seedlings absorb faster on NH_4^+ compared to NO_3^- if both NH_4^+ and NO_3^- are present. Ammonium sulphate and urea ($CO(NH_2)_2$) are examples of ammonium based fertilizers that are commonly used in rice farming practices in recent years. Urea ($CO(NH_2)_2$; 460 g N kg^{-1}) is still the primary market source of N (Soares et al., 2012). Therefore, in models that simulate N dynamics and losses on fertilized and flooded rice systems, urea hydrolysis concept is relevant (Table 2.1). Organic fertilizers are also usually used. The biological process known as the ammonification process (N mineralization) converts organic N to ammonium (NH_4^+). The rate of ammonification is slower in a flooded rice system than an upland agricultural field because oxygen (O_2) is deficit in a flooded paddy field; however, a low level of O_2 also limits nitrification as well as N immobilization, resulting in the accumulation of NH_4^+ in soil.

Table 2.1 Some of the N dynamics models with types of fertilizer and method of application (adopted from Nurulhuda et al., 2017).

Model	**Inorganic fertiliser type**			**Fertiliser application method in a rice field**	
	Urea	**NH_4^+ based**	**NO_3^- based**	**Broadcasted into floodwater**	**Incorporated into flooded soil**
NFLOOD v. 1	-	√	-	√	√
NFLOOD v. 2	-	√	-	-	√
J-M’s	-	√	-	√	-
S-K’s	√	-	-	√	√

CERES-Rice	√	√	√	√	√
Chowdary’s	√	-	-	√	-
Nakasone’s	-	-	√	√ (mixed in water)	-
Yoshinaga’s	-	√		√	-
DNDC-Rice	√	√	√	-	√
K-K’s	-	-	-	-	-
Liang’s	√	-	-	√	-
RICEWNB	N fertiliser type not specified			-	√
RIWER	√	-	-	√	√
APSIM-Oryza[c]	√	√	√	√	√

[c] If floodwater is absent, APSIM-Oryza by default incorporates applied N into the top soil layer

2.2 Characteristics of a flooded rice system

There are 3 separate soil layers: plough, hard pan, and subsoil layers (Figure 2.1), which are mainly determined by the prevailing oxidation or redox potential in a flooded soil system, making a flooded rice system dynamic and composite soil water system. Hard pan is located between the plough and subsoil layers, and is found between 0.10 m to 0.30 m from the soil surface (Aimrun and Amin, 2009).

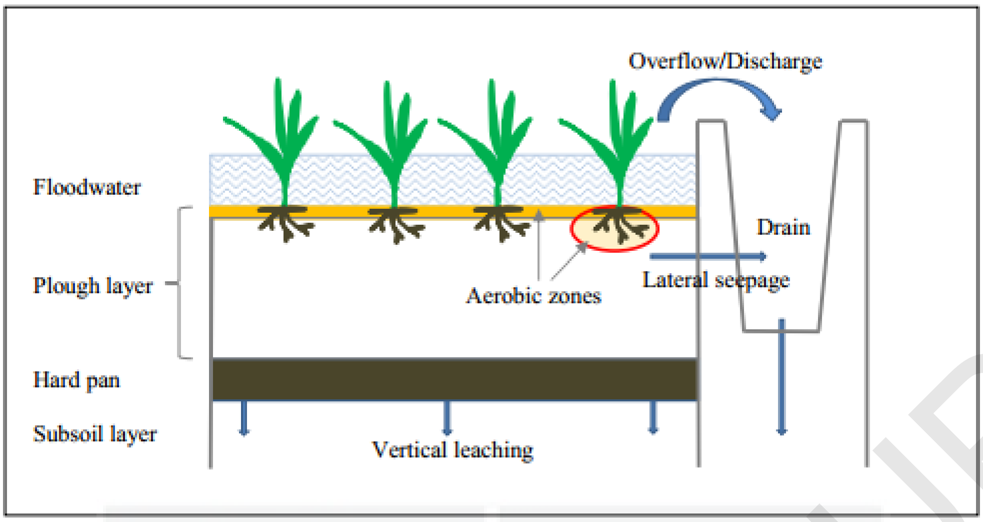


Figure 2.1 Shows the general characteristic of flooded rice system (Nurulhuda et al., 2017).

Aimrun and Amin (2009) explained that the hard pan has the lowest penetrability. Furthermore, the hard pan can also restricts the growth beyond the layer of rice roots (Aimrun and Amin, 2009). Formation of hard pan in flooded soil system will be in two ways, compaction physique caused by the repeated plough layer puddling, which is then accompanied by utilization of heavy machinery or chemical precipitation (Sharma and De Datta, 1986).

In flooded rice system, the overall percolation rates are site specific, ranging from 1 mm day^{-1} to as high as 30 mm day^{-1} (Aimrun et al., 2010). In addition, lateral seepage in flooded rice systems is also reported through an adjacent bund (Liang et al., 2014).

Penetration of oxygen (O_2) in flooded rice system is reported only in the upper 1 mm to 6 mm of the plough layer (Liesack et al., 2000). Besides, small scale O_2 consuming zones are made inside the rhizosphere in the plough layer, because of active release of O_2 by rice roots (Liesack et al., 2000).

2.3 Nitrogen cycle in flooded rice system

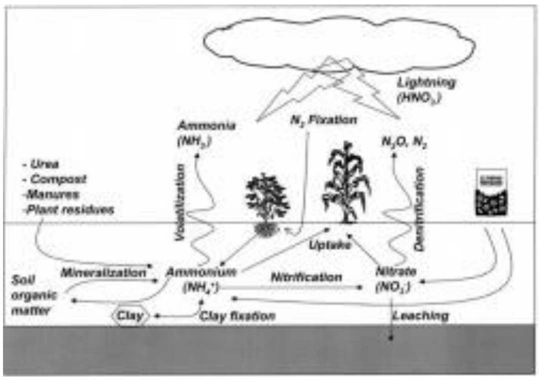


Figure 2.2 N cycle in upland soils (Espinoza et al., 1914)

N exists in different forms and modification in soils continuously between different forms. N exists in inorganic forms as well as organic forms. Generally, the N cycle as shown in Fig. 2.2 is showed the paths of N transform into different forms follow through the ecosystem. Amide (NH_2) is one of the organic materials that accounts for more than 90% of the total N in environment (Espinoza et 81., 1914).

Rice crop cultivation absorbs N in the form of dissolved ammonium (NH_4^+) or nitrate (NO_3^-) that are found in the root zone of rice crops (Brady and Weil, 2008). Moreover, the NH_4^+ or NO_3^- may undertake other pathways or losses such as NH_3 volatilisation, instantaneous nitrification and denitrification, leaching, dissimilatory NO_3^- reduction to NH_4^+, and immobilisation of N (Reddy, 1982).

NH_3 volatilisation in flooded rice system is said to happen on the floodwater surface of the flooded rice scheme. Nitrification is oxidation of NH_4^+ to NO_3^-, and, consequently, it passes off in any of the three aerobic zones in flooded rice system (Reddy, I982, Rao et al., I984). Denitritication is reduction of NO_3 that resulted in N_2O as an intermediate product, and N_2 as the final product, and consequently takes place within the anaerobic plough layer (Reddy, I982). Dissimilatory NO_3^- reduction to NH_4^+ also occur in the anaerobic plough layer, and the amount of NO_3^- available for denitrification also can be described by this process (Buresh and Patrick, 1978, Yin et al., 2002). In addition, anaerobic NH_4^+ oxidation (Anammox), where NO_3^- and NH_4^+ are directly transformed into N_2, was recently reported in flooded rice systems (Zhu et al., 2011).

NH_4^+ and NO_3^- transportation between floodwater and soil takes place by diffusion or mass transfer with percolated water (Reddy, 1982). Unlike the positively charged NH_4^+, which may attach to the negatively charged clay particles, the negatively charged NO_3^- is susceptible to leaching (Reddy, I982).

2.4 Nitrogen dynamics model

Nitrogen (N) fertilizer is used to enhance grain production in flooded rice systems but all N is not consumed through rice (Fageria et al., 20l4). Thus, N losses from fertilized and flooded rice systems should be minimized to reduce cost and adverse environmental results. To estimate N dynamics, a number of semi physical N dynamics model have been introduced for the purpose of simulating N dynamics in flooded soil systems.

The CERES models function to simulates rice plant growth and development (including grain production), and N dynamics in a flooded soil system by involving phenology, growth, soil water and nitrogen (N) balance in this model. The CERES model restricts output by using data on soil water and nitrogen dynamics for simulating crop (Svensson, 2012). In more than one site or for more than one season, experimental data only is needed in The CERES-Rice model for calibrated and evaluated purposes (Bouman and Van Laar, 2006).

The Chowdary’s model is a model to simulate seasonal N losses in a fertilised and flooded rice system. It comprises all important N cycle process for urea in the flooded fields, namely urea hydrolysis, volatilization, nitrification, mineralisation, immobilization, denitrifcation, uptake and leaching. Some of the parameters are required to offer an acceptable quantifying mechanism for anaerobic N processes in flooded rice fields.

Yoshinaga's is a model to simulate inorganic N dynamics in the flooded rice system. The DNDC (DeNitrification–DeComposition)-Rice model is the best model to simulate the N content of the rice field. This is because the DNDC model is based on the process of calculating greenhouse gas emissions from the rice field. DNDC model, is a model designed to simulate emissions from agricultural and forest ecosystems of trace gasses like CO_2, methane (CH_4), N_2O, NO, and NH_3 (Li et al. 2004). Original DNDC model has been modified and updated into a DNDC-Rice model in order to enable the researchers to continuously submerged simulation of CH_4 release from paddy fields (Fumoto et al. 2008, 2017). Liang's(Liang et al.,2007) model is to predict the seasonal N losses including NO_3^- leaching, horizontal seepage, NH_3 volatilization and denifitrication in a fertilised and flooded rice system.

APSIM is a model that simulates cropping systems through a combinations of biophysical and management modules. This model was developed to simulate soil water, C, N and P dynamics and their interaction in crop systems. Basically, APSIM model is incapable to simulate process associated with the long-term flooded and saturated soil environment. Therefore the ORYZA2000 model (Bouman and van Laar, 2006) has been integrated into APSIM structure model and validated through some research in order to overcome this problem (Zhang et al., 2006).

2.5 Expanding the use of nitrogen dynamics model in a flooded rice system

N transportation and translation operations are complex and difficult to interpret depending on the active nature of paddy fields. Thus, it would be very important to have a fully calibrated and mathematical model to describe these procedures. Although many researchers have successfully assessed the N cycle in paddy fields in recent years with numerical models, but it still face a challenge in terms of their overall complexity. According to Jeon (2004), some models only focus on N uptake and fate in floodwater, but Chowdary (2004) explained that most of the model more focusing on N transport in the soils or describe N cycle in soils. Although a lot of experimental data has been provided, but it is important to model N cycling in flooded soils in order to obtain an estimated and accurate result (Chowdary et al., 2004). In 1984, Rao's (1984) set up a NFLOOD model to explain N dynamics in flooded soils without considering the plant uptake. However, the Rao's model has been modified by Chowdary by combining soil-water and N balance, yet there is no observation of N loss via subsurface lateral seepage. The three-dimensional FEMWATER model developed by Chen and Liu (2002) to simulate a lateral seepage process in a terraced paddy field and found that the deficiency of N or other nutrient modules combined in the model can cause the significant lateral seepage at the boundary of the field.

For simulating of N behaviour in soil-plants system, a lot of advanced numerical models were developed. These models, however, unable to explain and relate all major processes and ingredients of N-transformation, and there was much lack of discontinuous fertilizer input. The transformations of N were commonly considered to adopt kinetics of the first order and a lumped parameter model for the assessment of nitrate leaching was developed by Ling and Aly (1998). Although this model takes into account water and fertilizer applications, plant absorption, weather and different processes of N transformation, its application is limited to the unsaturated zone. Certain models comparatively simple are available for predicting N fertilizer movement and making regional estimates of nitrate leaching in several field soils (Magesan et al., 1999).

A modelling approach can be employed to estimate the effects of various agriculture management practices on N loss from paddy fields in different scheme simulations and predictions for a long period of time. Modelling study helps in terms of getting more accurate results and time saving compared with traditional field experiments.

CHAPTER 3

METHODOLOGY

3.1 Model selection

Model from Liang et al., (2007) was selected in this study because this model was developed to simulate N losses which is suitable for objective of this study. Liang's model has two main components. The first component is pathway of N-transportations namely surface runoff, lateral seepage, vertical leaching and N uptake by rice plants. The second main component is pathway of N-transformations in flooded rice system. The N transformations are urea hydrolysis, ammonia volatilization, nitrification and denitrification. The conceptual model is given in Figure. 3.1

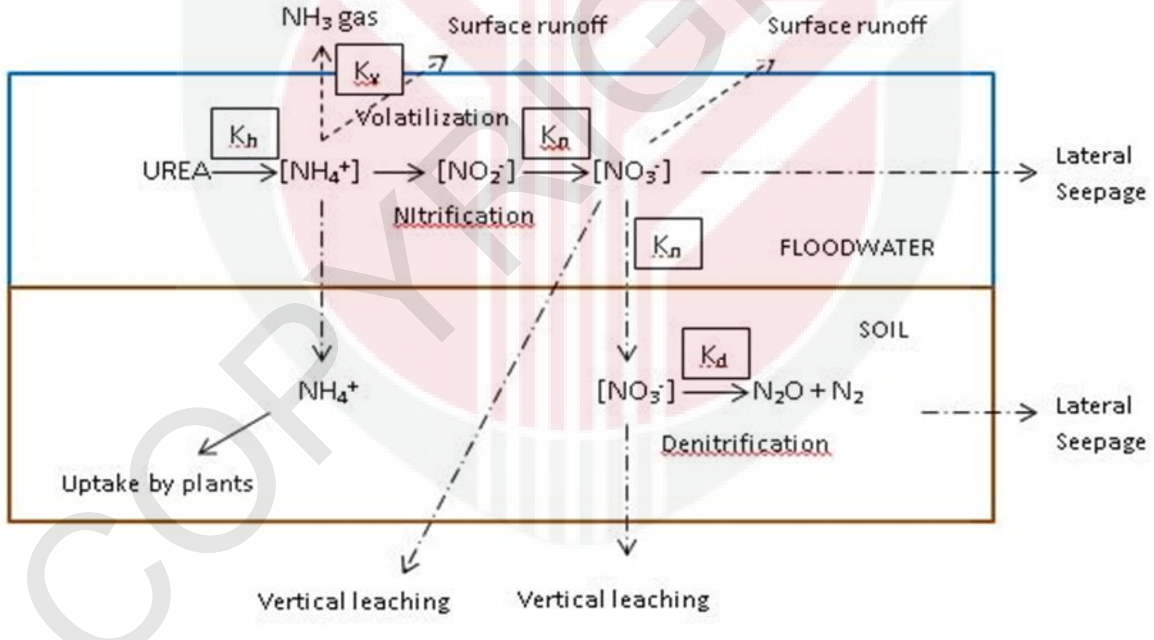


Figure 3.1 Nitrogen transportations and transformation in flooded rice system.

3.2 Model development

The conceptual model developed by Liang's was translated into mathematical equations. Then, the mathematical equations were discretized using the Euler forward scheme. Subsequently the equations were programmed and simulated in R studio software. The simulation time step is daily.

3.2.1 The N transformations

The N transformations processes are urea hydrolysis, ammonia volatilization, nitrification and denitrification. These N transformation processes happen when the urea fertilizer was applied to the floodwater system.

Where *u* is the amount of urea in the floodwater (kg N ha^{-1}) is described as follows:

$$\frac{du}{dt} = Kh \times u - SR \times u/z \tag{1}$$

Where *Kh* is the rate constant for urea hydrolysis (day^{-1}), the value of urea in surface runoff is given by, $SR \times u/z$ (kg N ha^{-1}), while z is flood water depth (m).

By applying, the discretization method on Eq. 1, we derived the *u* as follows:

$$\frac{u_{(2)} - u_{(1)}}{\Delta t} = -Kh \times u - SR \times u/z \tag{2}$$

$$u_{(2)} = (-Kh \times u - SR \times u/z)\Delta t + u_{(1)} \tag{3}$$

From the Eqs 2 and 3, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

The UNH_4 is the amount of ammonium produced in the floodwater (kg N ha^{-1}), and is given by:

$$\frac{dUNH_4}{dt} = Kh \times u - Kv \times UNH_4 - Kn \times UNH_4 - SR \times UNH_4/z - ET \times UNH_4/z \qquad (4)$$

Where, u is the amount of urea in the floodwater (kg N ha^{-1}), while Kh, Kn, and Kv are the rate constant for urea hydrolysis (day^{-1}), ammonia volatilization (day^{-1}) and nitrification (day^{-1}) respectively. The value of NH_4^+ in surface runoff is given by, $SR \times UNH_4/z$(kg N ha^{-1}) and the rate of ammonium uptake by plants is $ET \times UNH_4/z$(kg N ha^{-1}).

By applying, the discretization method on Eq. 4, we derived the UNH_4 as follows:

$$\frac{UNH_{4(2)} - UNH_{4(1)}}{\Delta t} = Kh \times u - Kv \times UNH_4 - Kn \times UNH_4 - SR \times UNH_4/z - ET \times UNH_4/z \qquad (5)$$

$$UNH_{4(2)} = \left(Kh \times u - Kv \times UNH_4 - Kn \times UNH_4 - SR \times \frac{UNH_4}{z} - ET \times UNH_4/z \right) \Delta t + UNH_{4(1)} \qquad (6)$$

From the Eqs. 5 and 6, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

While during the volatilization process, ammonia gaseous has been produced from the part of ammonium during urea hydrolysis process.

The process of ammonia volatilization is described as follows:

$$\frac{dUNH_3}{dt} = Kv \times UNH_4 \qquad (7)$$

Where, UNH_3 is the amount of ammonia volatilization (kg N ha^{-1}). UNH_4 is the amount of ammonium in the floodwater (kg N ha^{-1}), while Kv is the rate constant for ammonia volatilization (day^{-1}).

By applying, the discretization method on Eq. 7, we derived the UNH_3 as follows:

$$\frac{UNH_{3(2)} - UNH_{3(1)}}{\Delta t} = Kv \times UNH_4 \quad (8)$$

$$UNH_{3(2)} = (Kv \times UNH_4)\Delta t + UNH_{3(1)} \quad (9)$$

From the Eqs. 8 and 9, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

Nitrification is the process of N-transformation that converts NH_4^+ to NO_3^-. The substrate for nitrification process which is NH_4^+ comes from urea hydrolysis process. Part of the nitrate produced during this process will undergoes denitrification. UNO_3 is the amount of nitrate in the floodwater (kg N ha^{-1}) is described as follows:

$$\frac{dUNO_3}{dt} = Kn \times UNH_4 - Kd \times UNO_3 - SR \times \frac{UNO_3}{z} - VL \times UNO_3/z - LS \times UNO_3/z \quad (10)$$

Where UNH_4 is the amount of ammonium produced during process urea hydrolysis (kg N ha^{-1}), while *Kh* and *Kd* are the rate constant for nitrification (mm day^{-1}) and denitrification (mm day^{-1}). The value of NO_3^- in surface runoff is given by, $SR \times UNO_3/z$(kg N ha^{-1}). The value of NO_3^- in vertical leaching is given by, $VL \times UNO_3/z$(kg N ha^{-1}) and the value of NO_3^- in lateral seepage is given by $LS \times UNO_3/z$(kg N ha^{-1}).

By applying, the discretization method on Eq. 10, we derived the UNO_3 as follows:

$$\frac{UNO_{3(2)} - UNO_{3(1)}}{\Delta t} = Kn \times UNH_4 - Kd \times UNO_3 - SR \times \frac{UNO_3}{z} - VL \times \frac{UNO_3}{z} - LS \times \frac{UNO_3}{z} \quad (11)$$

$$UNO_{3(2)} = \left(\begin{array}{c} Kn \times UNH_4 - Kd \times UNO_3 - SR \times \frac{UNO_3}{z} \\ -VL \times \frac{UNO_3}{z} - LS \times UNO_3/z \end{array} \right) \Delta t + UNH_{4(1)} \quad (12)$$

From the Eqs 11 and 12, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$

For the denitrification process, the process is described as follows:

$$\frac{dDNI}{dt} = Kd \times UNO_3 \quad (13)$$

Where, DNI is the amount of nitrate denitrified (kg N ha^{-1}), UNO$_3$ is the amount of nitrate in floodwater (kg N ha^{-1}); while *Kd* is the rate constant for denitrification (day^{-1}).

By applying, the discretization method on Eq. 13, we derived the DNI as follows:

$$\frac{DNI_{(2)} - DNI_{(1)}}{\Delta t} = Kd \times UNO_3 \tag{14}$$

$$DNI_{(2)} = (Kd \times UNO_3\ )\Delta t + DNI_{(1)} \tag{15}$$

From the Eqs 14 and 15, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

3.2.2 The N transportations

There are 3 N transportations of N losses in the model by Liang et al., (2007), which are surface runoff, lateral seepage and vertical leaching. But these 3 N transportations will relate to the amount of concentration of Urea, NH$_4$, NO$_3$. The conversion is described as follows:

$$SR \times u/z = SR \times \left(\frac{u}{10000m^2(z)} \times \frac{10000m^2}{1ha}\right)$$

This conversion might be applied to all N transportation equation including vertical leaching, N uptake by crops and lateral seepage.

The surface runoff is described as follows:

$$\frac{dSRN}{dt} = SR \times (u/z + UNH_4\ /z + UNO_3\ /z) \tag{16}$$

Where, SRN is N loss through surface runoff (kg N ha^{-1}). SR is the surface runoff (m) with given by, SR = R - BH, where R is rainfall reaching the surface (m day^{-1}) and BH as bund height (m). Where the amount of concentration of urea fertilizer is described as u/z(kg ha^{-1}/m). The amount of concentration of NH$_4$ present in the root zone is described as UNH_4/z(kg ha^{-1}/m). While, the NO$_3$ is the amount of nitrate concentration is described as UNO_3/z (kg ha^{-1}/m).

By applying, the discretization method on Eq. 16 we derived the SRN as follows:

$$\frac{SRN_{(2)} - SRN_{(1)}}{\Delta t} = SR \times (u/z + UNH_4/z + UNO_3/z) \tag{17}$$

$$SRN_{(2)} = (SR \times (u/z + UNH_4/z + UNO_3/z))\Delta t + SRN_{(1)} \tag{18}$$

From the Eqs 17 and 18, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

The vertical leaching is described as follows:

$$\frac{dVLNO_3}{dt} = VL \times UNO_3/z \tag{19}$$

Where, VLNO$_3$ is the amount of nitrate losses by a vertical leaching (kg N ha^{-1}). VL is the value of vertical leaching out of the root zone (m day^{-1}). The amount of concentration of NO$_3$ present in the root zone is described as UNO_3/z(kg ha^{-1}/m).

By applying, the discretization method on Eq. 19, we derived the VLNO as follows:

$$\frac{VLNO_{3(2)} - VLNO_{3(1)}}{\Delta t} = VL \times UNO_3/z \tag{20}$$

$$VLNO_{3(2)} = (VL \times UNO_3/z)\Delta t + VLNO_{3(1)} \tag{21}$$

From the Eqs 20 and 21, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

The lateral seepage is described as follows:

$$\frac{dLSNO_3}{dt} = LS \times UNO_3/z \tag{22}$$

While $LSNO_3$ is the amount of nitrate losses by lateral seepage (kg N ha^{-1}). LS is the lateral seepage rate (m day^{-1}), which is given by; LS = $K_1h + c$, where K_1 is the lateral seeping ratio (%), h is depth of pond water (m) and c is constant equalling to lateral seepage rate at no pond water. The NO_3 is nitrate concentration in the system is described as $UNO_3\,/z$(kg ha^{-1}/m).

By applying, the discretization method on Eq. 22, we derived the LSNO as follows:

$$\frac{LSNO_{3(2)} - LSNO_{3(1)}}{\Delta t} = LS \times UNO_3\,/z \tag{23}$$

$$LSNO_{3(2)} = (LS \times UNO_3\,/z)\Delta t + LSNO_{3(1)} \tag{24}$$

From the Eqs 23 and 24, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

While the rate of ammonium uptake by plant roots is described as follows:

$$\frac{dUTNH_4}{dt} = ET \times UNH_4\,/z \tag{25}$$

Where, $UTNH_4$ is the rate of ammonium uptake by plants from the root zone (kg N ha^{-1}), ET is the value of evapotranspiration (m day^{-1}) and is given by, ET = Kc * ET_o, where Kc is the crop coefficient and ET_o is the crop reference evapotranspiration (m day^{-1}). The concentration of NH_4 present in the root zone is described as $UNH_4\,/z$(kg ha^{-1}/m).

By applying, the discretization method on Eq. 25, we derived the LSNO as follows:

$$\frac{UTNH_{4(2)} - UTNH_{4(1)}}{\Delta t} = ET \times UNH_4\,/z \tag{26}$$

$$UTNH_{4(2)} = (ET \times UNH_4\,/z)\Delta t + UTNH_{4(1)} \tag{27}$$

From the Eqs 26 and 27, Δt is simulation time, where $\Delta t = t_{(2)} - t_{(1)} = 1$.

The values of concentration of *Urea*, NH_4 and NO_3 were converted from (kg N ha^{-1}) into (mg N L^{-1}). The conversion and derivation are described as follows:

$$NH_4 = \frac{UNH_4}{(z \times 10)} \tag{28}$$

$$NO_3 = \frac{UNO_3}{(z \times 10)} \tag{29}$$

$$Urea = \frac{u}{(z \times 10)} \tag{30}$$

where, NH_4 is the amount of concentration of ammonium present in root zone (mg N L^{-1}). UNH_4 is the amount of ammonium produced from the process urea hydrolysis (kg N ha^{-1}). While, NO_3 is the amount of nitrate concentration (mg N L^{-1}). UNO_3 is the amount of nitrate produced from the process nitrification (kg N ha^{-1}). Urea is the amount of concentration of urea fertilizer (mg N L^{-1}) and u is the amount of urea fertilizer applied on the system (kg N ha^{-1}). The z is the value of floodwater depth (m).

3.3 Simulations of model Liang et al. (2007)

The mathematical equations were then simulated using input data and parameters reported in Liang et al., (2007). The input data needed are weather, water-N management, plant growth variables and soil properties are all input data that must be supplied for simulation of the model. Daily rainfall is part of the weather data that need to consider. Water N-management schedule includes daily water depth (m), fertilizer rate (kg N ha^{-1}) and application time (day). Planting and harvesting dates and crop coefficients also need to be considering as plant growth variables input data. Soil properties, it involves saturated hydraulic conductivity (m day^{-1}).

The parameters required are includes all rate constants for N transformations process which are urea hydrolysis, ammonia volatilization, nitrification and denitrification.

Table 3.1 Range of the rate constants input parameter for different N-transformation process (Liang et al., 2007)

Input and parameters	**Values**	**Units**	**Source**
Fertilizer application rate	118 + 36 + 36 (3 splits application)	kg N ha^{-1}	Liang et al. (2007)
Pond depth(h)	50	mm	Liang et al. (2007)
Bunds height (BH)	75	mm	Liang et al. (2007)
hydraulic conductivity (K_s)	5.4	mm day^{-1}	Liang et al. (2007)
Lateral seeping ratio (K_1)	30.0	% (floodwater)	Liang et al. (2007)
Lateral seeping constant (c)	11.3	mm day^{-1}	Liang et al. (2007)
Urea hydrolysis rate (Kh)	0.576 Possible range: 0.360-0.744	day^{-1}	Liang et al. (2007)
Ammonia volatilization rate (Kv)	0.062 Possible range: 0.043-0.800	day^{-1}	Liang et al. (2007)
Nitrification rate (Kn)	0.078 Possible range: 0.020-2.000	day^{-1}	Liang et al. (2007)
Denitrification rate (Kd)	0.130 Possible range: 0.050-0.200	day^{-1}	Liang et al. (2007)
crop coefficient (K_o)	1.02	/	Assumption based on constant value for rice crops

3.4 Calibration of model using secondary datasets

The purpose of calibration is to adjust the model parameters within the expected range in order to reduce the difference between predicted and observed value. In the model described in Section 3.1, there were four parameters that needed to be calibrated. Calibration was performed manually, where each of the parameter was gradually varied individually in order to achieve EF =1, R^2 =1, MD =0 (See section 3.5 for details).

3.4.1 Description of secondary datasets

In this study, the model was calibrated using datasets from Xu et al., (2018). The secondary datasets were extracted from the experiment located at Kunshan irrigation and drainage experiment station located at Jiangsu district (31° 15’ 15’’N, 120° 57’ 43’’E) in the Tai-lake region in 2017 rice season (Xu et al., 2018). The planting date was starting from July 7 and harvested on October 30, 2017. The soil type for this area is dark yellow hydromorphic paddy soil. The fertilizer rate treatments for this system were divided into which are basal fertilizer (non-flooded stage) and top-dressing fertilizer (flooded stage). For basal fertilizer, urea was applied at amount of 150 kg ha^{-1}. While, for top-dressing fertilizer were applied in three different rates, namely tillering fertilizer (27 July, 34.5 kg N ha^{-1}), strong seedling fertilizer (7 August, 69 kg N ha^{-1}) and panicle fertilizer (29 August, 31 kg N ha^{-1}).

The secondary datasets from this experiment are ammonia volatilization measurement, NH_4^+ left in soil solutions and NO_3^- left in soil solutions. Table 3.2 showed the input data supplied into the model for simulation.

Table 3.2 Input data (Xu et al., 2018)

Input data	Values	Units	Source
Fertilizer application rate (top dressing)	34.5 + 69 + 31	kg N ha^{-1}	Xu et al.,(2018)
evapotranspiration (ET$_o$)	6.55	mm	assumption based on normal value for rice plant
Depth of pond water (*h*)	30-50	mm	Xu et al.,(2018)
surface runoff rate	3	mm day^{-1}	Assumption based on climate weather at Kunshan.
Lateral seepage rate	4	mm day^{-1}	Assumption based on constant value of lateral seepage in China rice system
Vertical leaching rate	4	mm day^{-1}	Assumption based on constant value of vertical leaching in China rice system
crop coefficient (K$_o$)	1.02	/	Assumption based on constant value for rice crops

Due to lack meteorological data, most of the value such as, surface runoff rate, lateral seepage rate, and vertical leaching rate was be assume according to the constant value and based on literature review.

3.4.2 Digitization of secondary data sets

Digitization is the process of extracting data from the graph given in Xu et al.,(2018). The data that need to be extracted are ammonia volatilization measurement and nitrogen left in soil solutions at 40-50cm depth beneath soil surface in Fig (3.2)-(3.4). Digitization process was done by the freeware GetData Graph Digitizer. The values (x, y) obtained from the graph were exported into the .csv format before it was programmed into RStudio software.

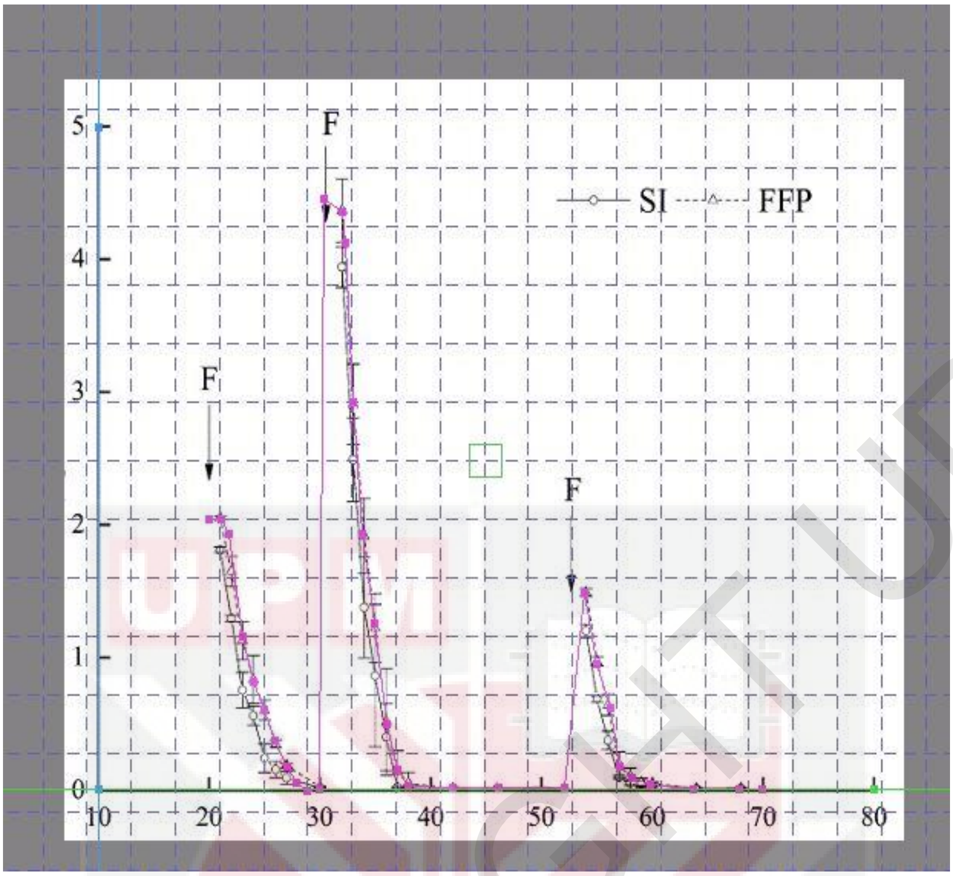


Figure 3.2 Digitization of ammonia volatilization datasets with GetData Digitizer software

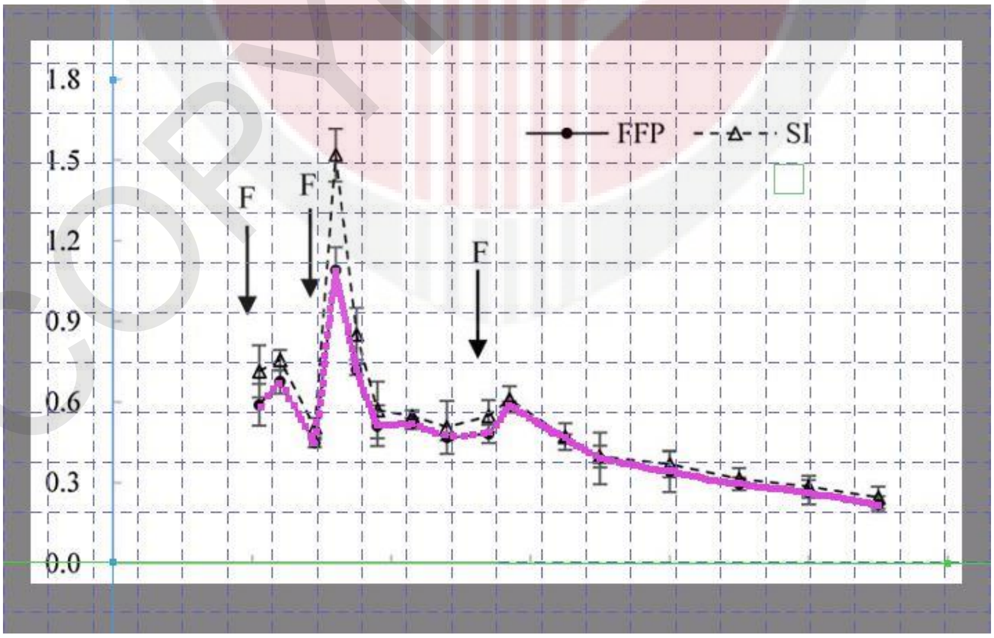


Figure 3.3 Digitization of NH_4^+ datasets with GetData Digitizer software.

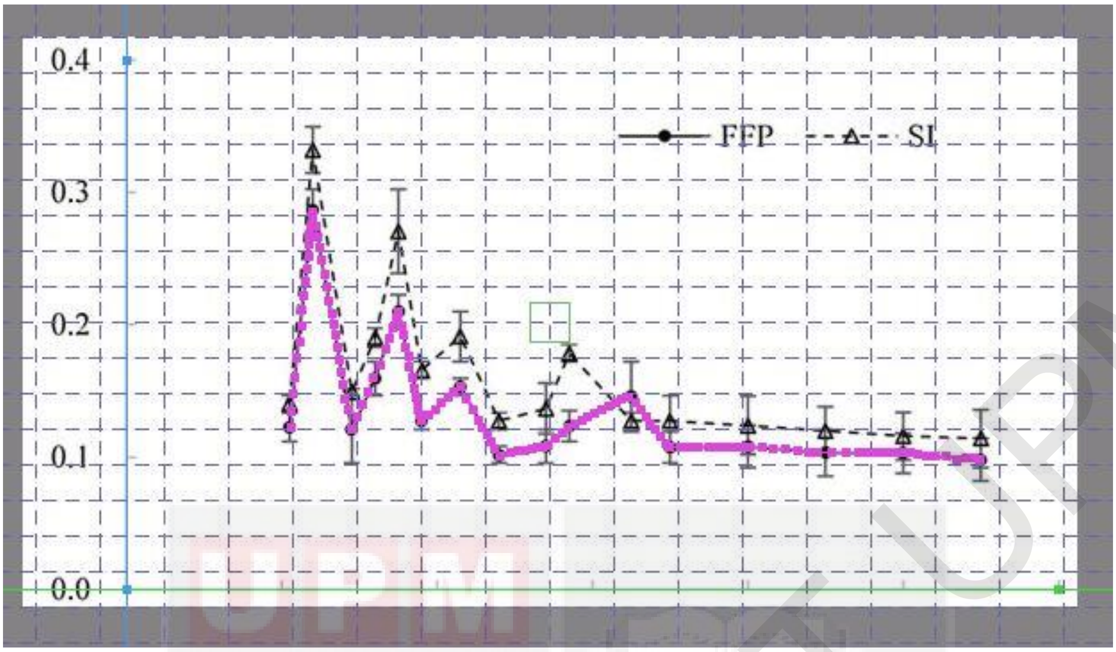


Figure 3.4 Digitization of NO_3^- datasets with GetData Digitizer software

3.5 Evaluation of the model

Performance of the selected model will be evaluated using secondary datasets. Evaluation of model was done by calculating; the mean of difference (MD), coefficient of determination (R^2), and modelling efficiency (EF). Equations for MD and R^2 are given below (Liang et al., 2007):

$$MD = \frac{1}{n}\sum_{i=1}^{n}(O_i - P_i) \tag{31}$$

O_i is the observed value at time i, while, P_i is the predicted value at time i, MD gives information on whether a model is under or over-estimating. If the MD value is equal to zero, the model is suitable for datasets.

$$R^2 = \frac{\sum_{i=1}^{n}(O_i-\bar{O})(P_i-\bar{P})^2}{\sum_{i=1}^{n}(O_i-\bar{O})^2 \sum_{i=1}^{n}(P_i-\bar{P})^2} \tag{32}$$

$\bar{O}$ is the mean of the observed values over the time period (1 – n), while $\bar{P}$ is the mean of the predicted value over the time period (1 – n). The R^2 result is describing the agreement between the predicted and observed values. If the value of R^2 equal to 1 means the model is ideal for datasets. Statistical parameter model efficiency (EF) also was been calculated and the equation is shown below (Willmott, 1981, Krause et al., 2005):

$$EF = 1 - \frac{\sum_{i=1,n}(O_i - S_i)^2}{\sum_{i=1,n}(O_i - \overline{O_\iota})^2} \tag{33}$$

$\overline{O_\iota}$ is the mean of the observed values. A value of EF = 1 indicates a perfect model. Negative values suggest that the average of the observed values is a better predictor than the model in all cases.

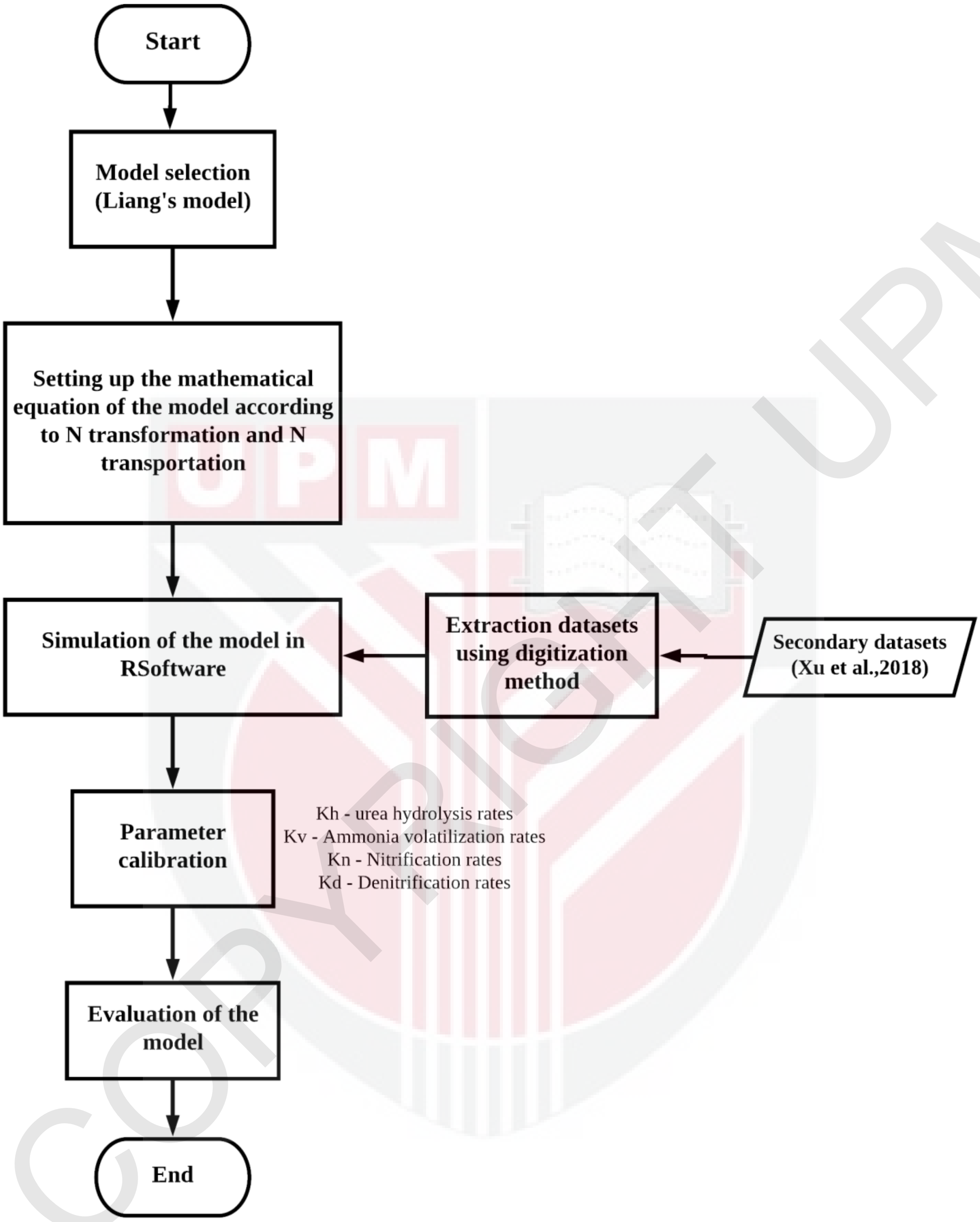


Figure 3.5 Shows the flowchart of procedures.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Parameter calibration with secondary datasets

This model was calibrated by comparing model simulated with observed data value from Xu et al.,(2018). The datasets consist of measurements of ammonia volatilization, NO_3^- left in soil solution and NH_4^+ left in soil solution at 40-50 cm depth beneath soil surface. There were some parameters that needed to be calibrated. The calibrated parameter were namely, urea hydrolysis rate (*Kh*), ammonia volatilization rate (*Kv*), nitrification rate (*Kn*), and denitrification rate (*Kd*). These parameters were calibrated three times in order to minimize the difference between simulated and observed values. The first calibration used values that were suggested by Liang et al.,(2007), while for the value for second and third guess has been set according to the possible range on Table 3.1. The value of ammonia volatilization rate (*Kv*) and nitrification rate (*Kn*) were adjusted for the second and third calibrations. Table 4.1 shows the first guess, second guess and third guess of parameters in the calibrations.

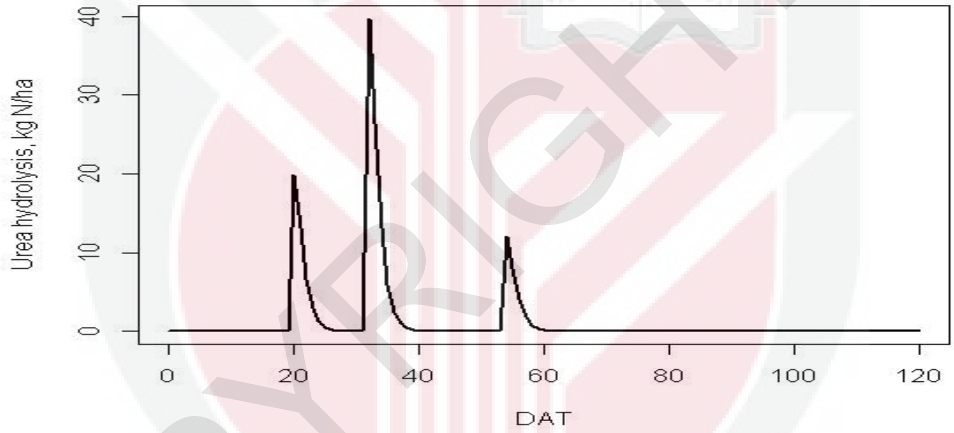
Table 4.1 Value of rate constants for calibration.

Rate of constant	First value	Second guess	Third guess
Urea hydrolysis (*Kh*)	0.576 day^{-1}	0.576 day^{-1}	0.576 day^{-1}
Volatilization rate (*Kv*)	0.062 day^{-1}	0.120 day^{-1}	0.200 day^{-1}
Nitrification rate (*Kn*)	0.078 day^{-1}	0.200 day^{-1}	0.350 day^{-1}
Denitrification rate (*Kd*)	0.130 day^{-1}	0.130 day^{-1}	0.130 day^{-1}

4.2 Simulation results for secondary datasets

The simulations for N transformations processes namely urea hydrolysis, ammonia volatilization, nitrification and denitrification and N transportations namely surface runoff, vertical leaching, lateral seepage and N uptake from crops are presented in Figs. 4.1, 4.2, 4.3 and 4.4. The results below were simulated using the third guess of parameters according to Table 4.1 and input fertilizer application rates data from Xu et al.,(2018) secondary datasets. The results just to prove that this model can simulate various N transformations and N transportations.

a)



b)

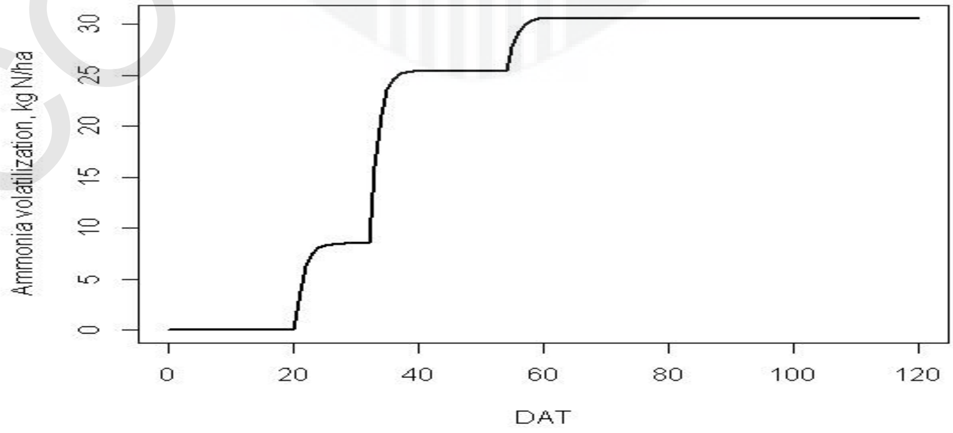
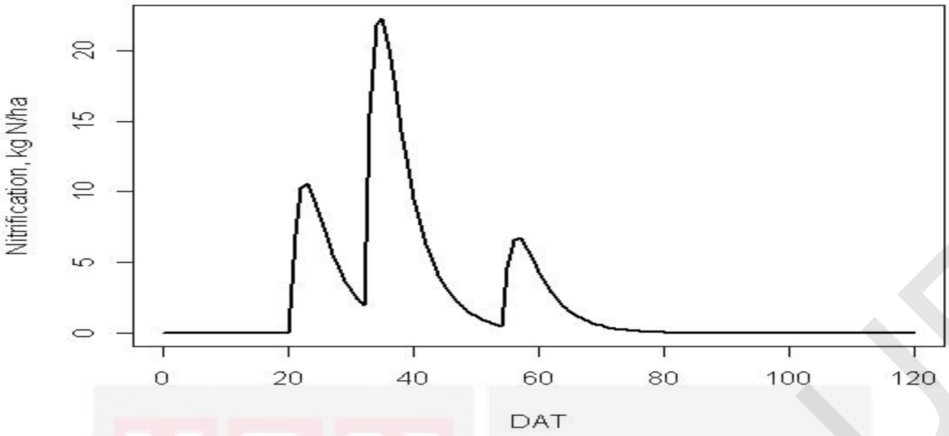


Figure 4.1 Simulated nitrogen transformation processes for third calibration. a)Urea hydrolysis, b)Ammonia volatilization.

a)



b)

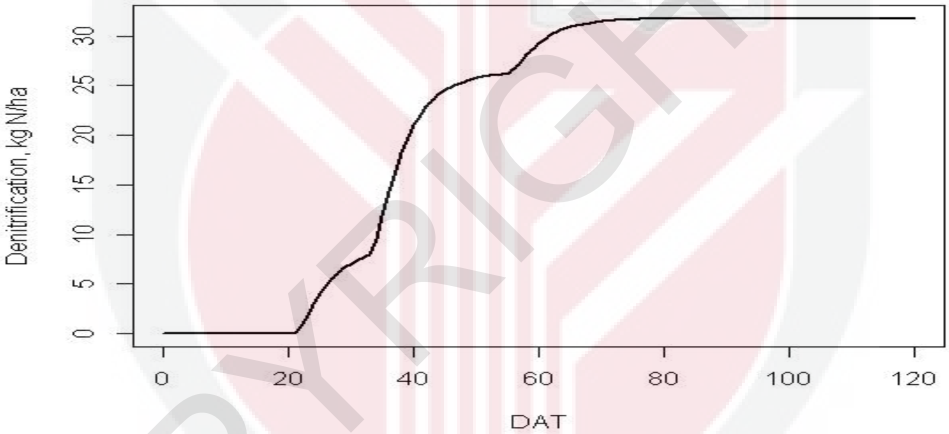


Figure 4.2 Simulated nitrogen transformation process for third calibration. a)Nitrification, b)Denitrification.

Ammonia volatilization and denitrification are considered as nitrogen loss. From Figs. 4.1 and 4.2, these processes shows almost 22% of N applied was loss from ammonia volatilization with 7.4% in 21 DAT, 11.1% in 32 DAT and 3.7% in 54 DAT and 23% of N applied was loss from denitrification process with 6.69% in 21 DAT, 12.6% in 32 DAT and 4.46% in 54 DAT. The results for N transportations namely vertical leaching, lateral seepage, surface runoff and N uptake by crops are shown in Figs. 4.3 and 4.4.

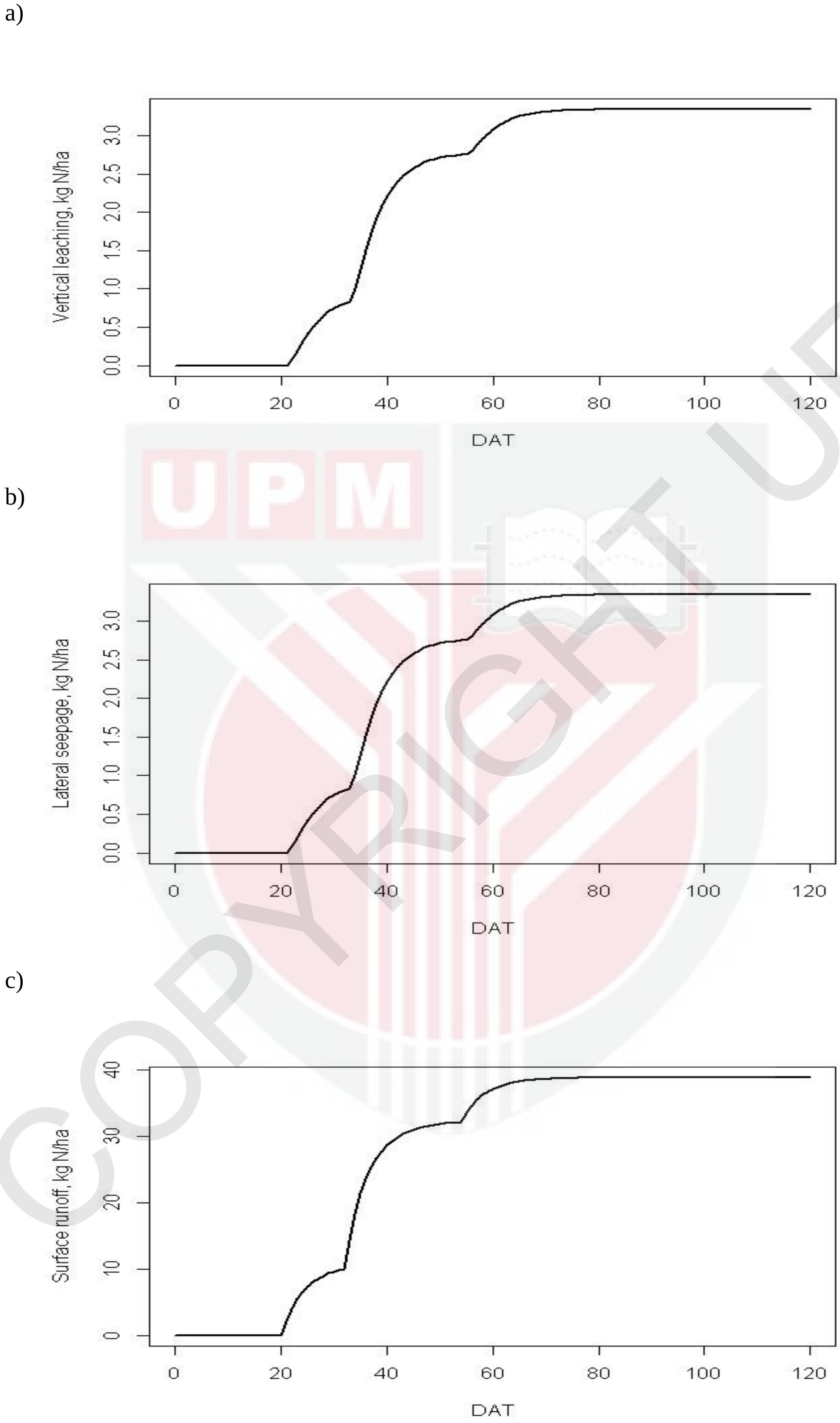


Figure 4.3 Simulated nitrogen transportations process for third calibration. a)Vertical leaching, b)lateral seepage, c)surface runoff

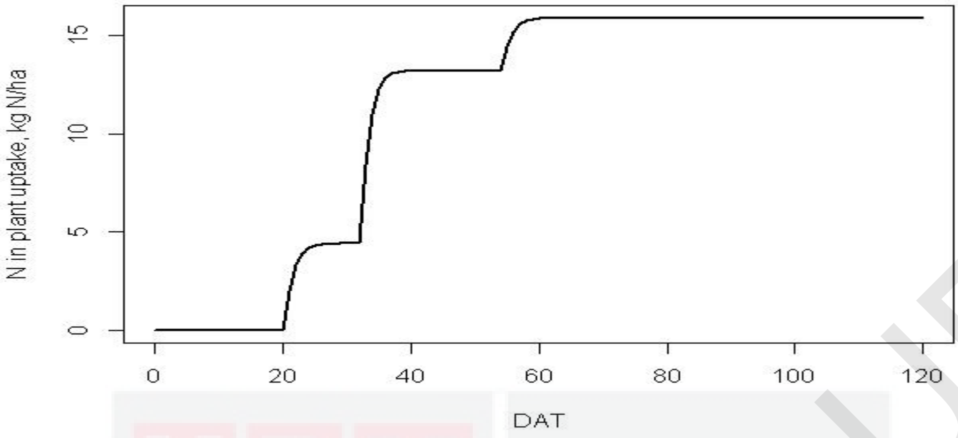


Figure 4.4 Simulated nitrogen uptake by crops for third calibration.

Vertical leaching (Fig. 4.3a), lateral seepage (Fig. 4.3b) and surface runoff (Fig. 4.3c) that are considered as N losses, also show cumulative trends as well as N uptake by crop (Fig. 4.4). In order to check for programming error, simulation of N balance has been done and the results for N balance are presented in Fig. 4.5.

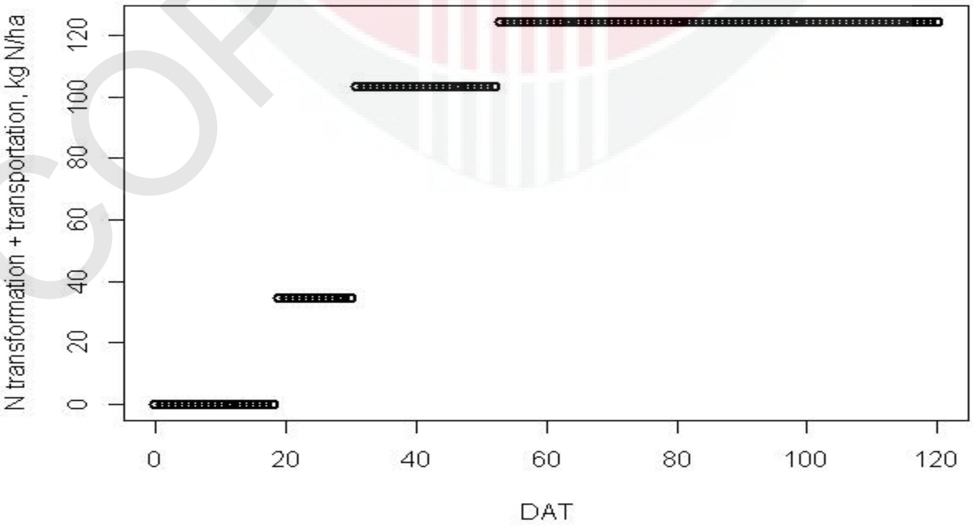


Figure 4.5 N balance for simulation of the model

The results from Fig 4.5 shows the straight line at the 34.5 kg N ha^{-1}, 103.5 kg N ha^{-1} and 134.5 kg N ha^{-1} and it proved that there is no programming and simulation error because the total amount of N transformations and transportations are equal to the total amount of N from urea applied. From Xu et al.,(2018) datasets, only ammonia volatilization, NH_4^+ left in soil solution and NO_3^- left in soil solution data were available for evaluation. The performance of the model is further evaluated with values of MD, R^2, and EF in order to determine whether this model can be acceptable or not with Xu et al.,(2018) secondary datasets. The analysis is performed on all three calibrations which are first guess, second guess and third guess according to Table 4.1. The analysis results for ammonia volatilization are presented in Table 4.2, 4.3 and 4.4. The model results of ammonia volatilization, NH_4^+ left in soil solution and NO_3^- left in soil solution compared to the observation data from Xu et al.,(2018) for all three calibrations are presented in Figs. 4.6, 4.7 and 4.8.

Table 4.2 Statistics of simulated and observed data for first calibration.

Rate of constant	Process	Observed values (kg N ha^{-1})	Simulated values (kg N ha^{-1})	MD (kg N ha^{-1})	R^2	EF
K_h = 0.576 day^{-1} K_v = 0.062 day^{-1} K_n = 0.078 day^{-1} K_d = 0.130 day^{-1}	Ammonia volatilization	31.50	23.28	-8.22	0.91	0.75
	NH_4^+ left in soil	42.22	83.52	41.3	0.36	-52.16
	NO_3^- left in soil	12.61	34.29	21.68	0.25	-222.20

Table 4.3 Statistics of simulated and observed data for second calibration.

Rate of constant	Process	Observed values (kg N ha^{-1})	Simulated values (kg N ha^{-1})	MD (kg N ha^{-1})	R^2	EF
K_h = 0.576 day^{-1} K_v = 0.120 day^{-1} K_n = 0.200 day^{-1} K_d = 0.130 day^{-1}	Ammonia volatilization	31.50	28.19	-3.31	0.93	0.92
	NH_4^+ left in soil	42.22	52.20	9.98	0.26	-63.25
	NO_3^- left in soil	12.61	54.95	42.34	0.27	-728.49

Table 4.4 Statistics of simulated and observed data for third calibration.

Rate of constant	Process	Observed values (kg N ha^{-1})	Simulated values (kg N ha^{-1})	MD (kg N ha^{-1})	R^2	EF
K_h = 0.576 day^{-1} K_v = 0.200 day^{-1} K_n = 0.350 day^{-1} K_d = 0.130 day^{-1}	Ammonia volatilization	31.50	31.76	0.26	0.85	0.65
	NH_4^+ left in soil	42.22	35.29	-6.93	0.20	-43.56
	NO_3^- left in soil	12.61	65.01	52.4	0.28	-1148.62

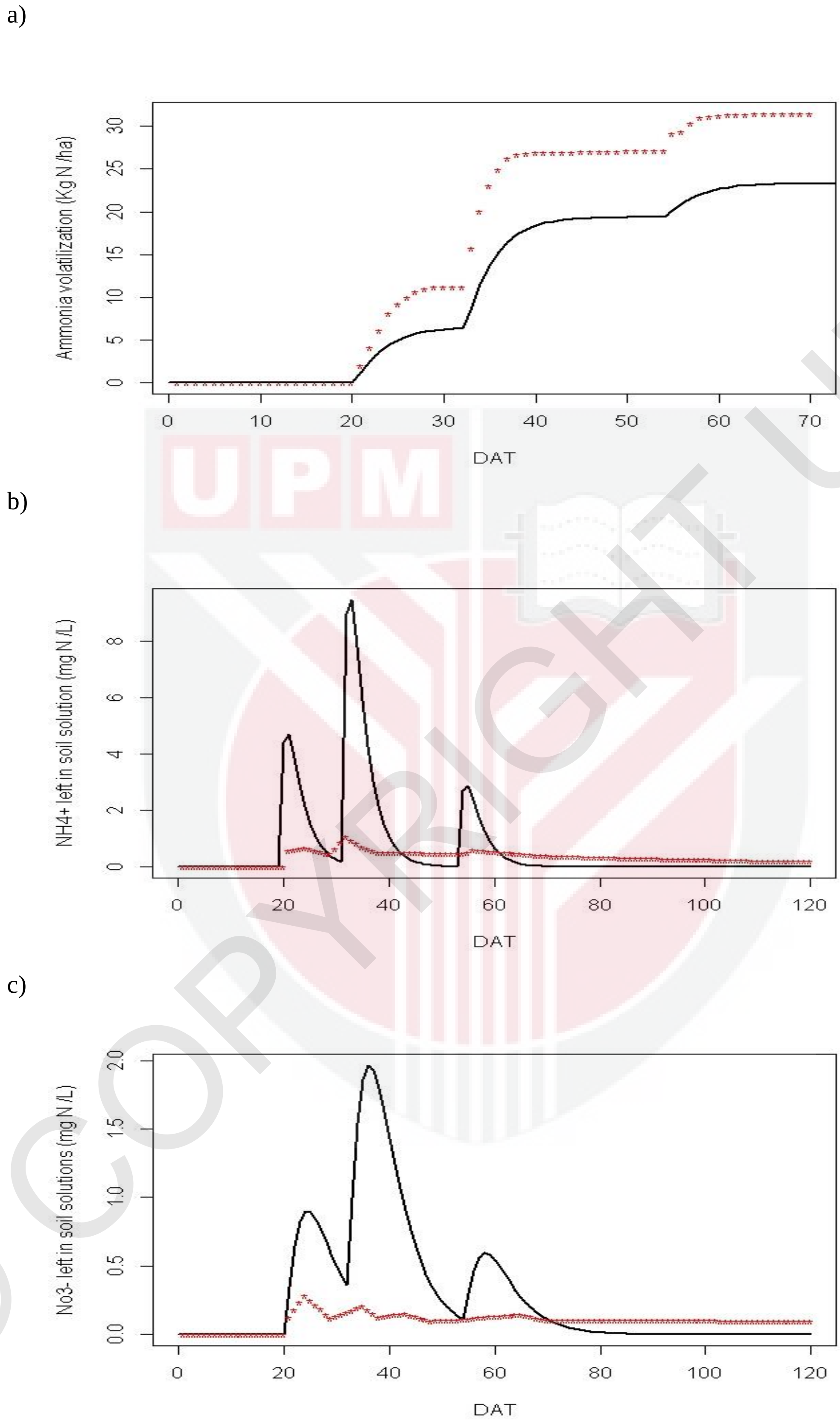


Figure 4.6 Comparison between simulated(-) and observed(*) values for first calibration a)Ammonia volatilization, b)NH_4^+ left in soil solution, c)NO_3^- left in soil solution.

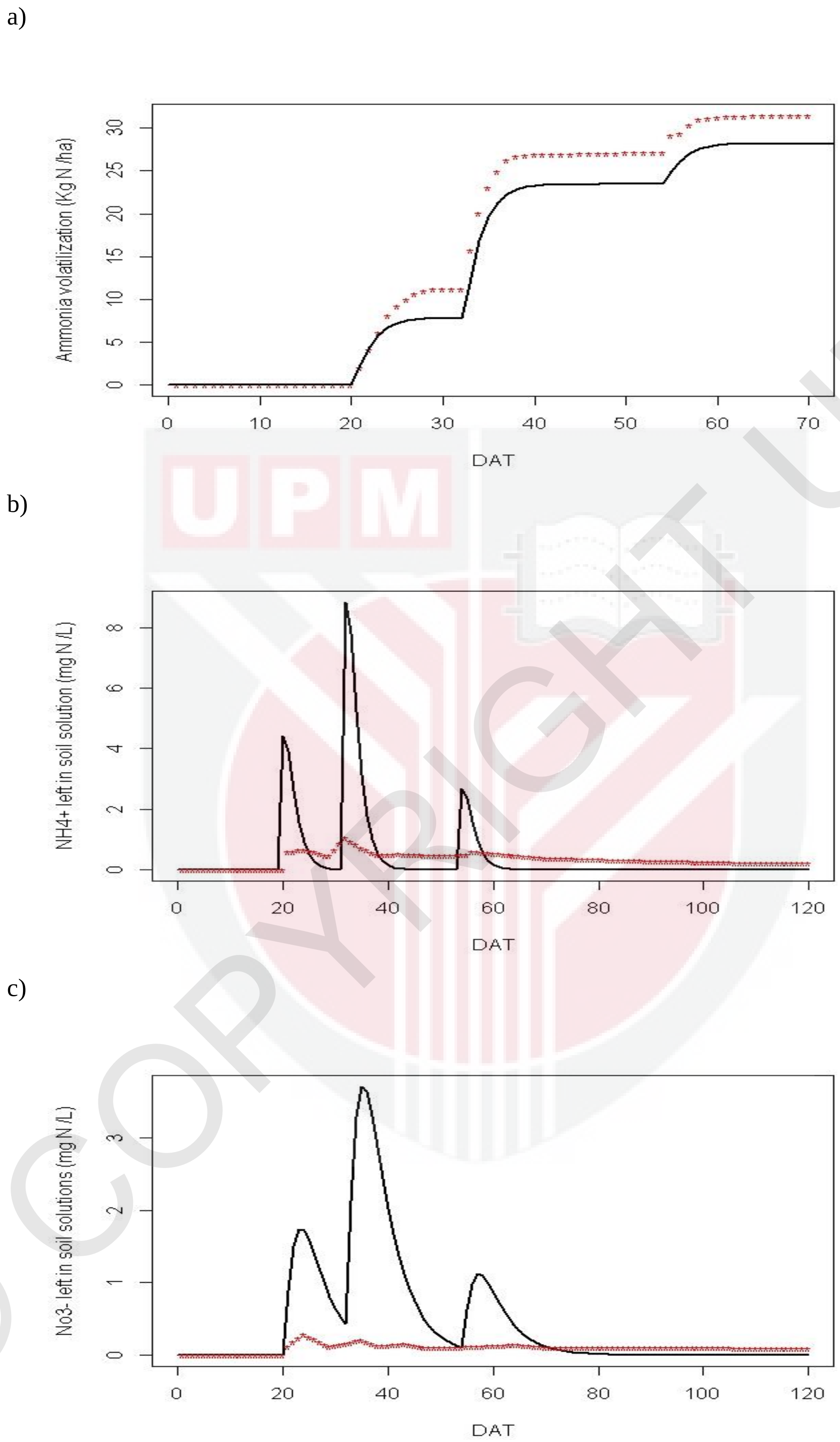


Figure 4.7 Comparison between simulated(-) and observed(*) values for second calibration a)Ammonia volatilization, b) NH_4^+ left in soil solution, c)NO_3^- left in soil solution.

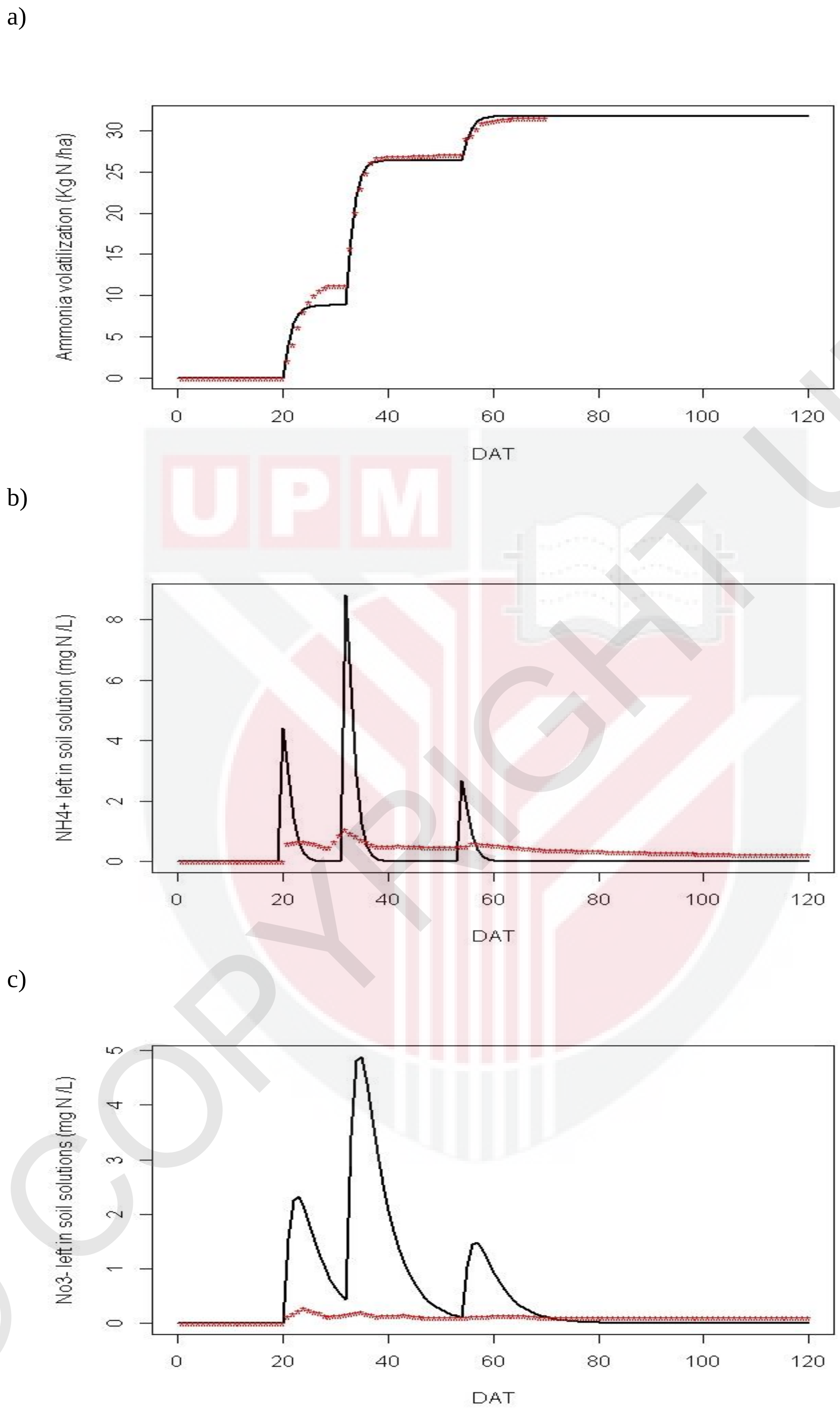


Figure 4.8 Comparison between simulated(-) and observed(*) values for third calibration a)Ammonia volatilization, b) NH_4^+ left in soil solution, c)NO_3^- left in soil solution.

4.3 Discussion on model performance

Figs. 4.6, 4.7 and 4.8, it shows a good fit and same pattern between simulated and observed values of ammonia volatilization from Xu et al.,(2018) datasets for all three calibrations. This result also have been proved by calculating MD, R^2 and EF. The values of MD for ammonia volatilization between simulated and observed values for all three calibrations were -8.22, -3.31 and 0.26, respectively. From the analysis result of MD, its shows that the model is under-estimating for first and second calibration and over estimating for third calibration. While the value of R^2 for ammonia volatilization between simulated and observed value for all three calibration were 0.91, 0.93 and 0.85 respectively. The R^2 value for ammonia volatilization between simulated and observed for all three calibrations were close to 1 indicates that this model gives a good agreement between the simulated and observed values. The analysis result of EF for ammonia volatilization were 0.75, 0.92 and 0.65 for all three calibrations, and its shows that this model are able to simulate ammonia volatilization from Xu et al.,(2018) datasets.

While, the result for NH_4^+ and NO_3^- left in soil solutions shows that observed and simulation values might have a same pattern for certain days after transplant (DAT) but did not show a good fit and a big gap between observed and simulated value. The MD values for NH_4^+ left in soil solution were 41.3, 9.98 and -6.93, while for NO_3^- left in soil solutions were 21.68, 42.34 and 52.4 respectively. The R^2 values for NH_4^+ left in soil solution were 0.36, 0.26 and 0.20, while, NO_3^- left in soil solutions were 0.25, 0.27 and 0.28. The values of R^2 for NH_4^+ left in soil solutions and NO_3^- left in soil solutions between observed and predicted values indicates that this model did not gives a good agreement between the simulated and observed values for NH_4^+ left in soil solutions and NO_3^- left in soil solutions. The EF values for $NH4^+$ left in soil solution and NO_3^- left in soil solutions between simulated and observed values also did not gives a satisfactory results. From the analysis, its shows that this model performance for simulating NH_4^+ left in soil solution and NO_3^- left in soil solutions is still poor. It is due to lack of meteorological data provided from Xu et al.,(2018) datasets. It is difficult to estimates the percolation, evapotranspiration and leaching rates for this process due to lack of meteorological data. Percolation, evapotranspiration and leaching rates is very important in order to determine the amount of NH_4^+ and NO_3^- penetrates and diffuse into the root zone. So the meteorological data from secondary datasets is important for this model in order to simulate N transformation and N transportation process more clearly.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, based on this study, Liang's model performance in quantifying N losses against secondary datasets from Xu et al.,(2018) has provided positive feedback on the simulation of ammonia volatilization. It clearly shows a close agreement and good fit between simulation and observation values, but performance of this model in quantifying NH_4^+ in left in soil solutions and NO_3^- in left in soil solutions at 40-50 cm beneath soil surface did not gives a satisfy results because of the performance of the model is not fit with the observation values. There were huge errors between simulated and observation values for NH_4^+ in left in soil solutions and NO_3^- in left in soil solutions after calibrations. The lack of input data from secondary datasets could be one of the challenges during calibration in order to produce a good quality of results. Futhermore, it is difficult to get suitable secondary data for calibration.

This model also should undergo some improvement in quantifying N losses below soil surface by clearly define and explain the percolation and diffusion process from floodwater zone to below soil surface. Selection of secondary datasets also must be considered in this study. It is because, this model is very dependent on meteorological data on that location in order to simulate N transportation such as surface runoff and N uptake by crops. So, the selected datasets should have enough meteorological data such as precipitation, infiltration and other else.

REFERENCES

Aimrun, W., Amin, M.S.M., Gholizadeh, A., 2010. Spatial Variability of Irrigation Water Percolation Rates and Its Relation to Rice Productivity Smart Farming Technology Laboratory , Institute of Advanced Technology , Department of Biology and Agricultural Engineering , Faculty of Engineering , *Paddy Water Environ,* 7,pp. 51–55.

Amin, W.A.Æ.M.S.M., 2009. Pedo-transfer function for saturated hydraulic conductivity of lowland paddy soils. *Paddy and Water Environment,* pp.217–225.

Antonopoulos, V.Z., 2010. Modelling of water and nitrogen balances in the ponded water and soil profile of rice fields in Northern Greece. *Agric. Water Manag*. 98, 321–330.

Azam, F., Müller, C., Weiske, A., Benckise, G. and Ottow, J. C.G. 2002. Nitrification and denitrification as sources of atmospheric nitrous oxide: Role of oxidizable carbon and applied nitrogen. *Biol. Fertil. Soils*, 35: 54–61.

Bohlool, B. B., Ladha, J. K., Garrity, D. P. and George, T. 1992. Biological nitrogen fixation for sustainable agriculture: A perspective. *Plant Soil*, 141: 1–11.

Bouman, B.A.M., 2006. Description and evaluation of the rice growth model ORYZA2000 under nitrogen-limited conditions. *Agricultural systems,* 87(3),pp. 249–273.

Cassman, K.G., Walters, D.T., 2002. Agroecosystems , nitrogen-use efficiency and nitrogen management. *AMBIO: J Hum Environ,* 31, pp. 132-140

Cho 2003 Cho, J. Y. 2003. Seasonal runoff estimation of N and P in a paddy field of central Korea. *Nutrient Cycling in Agroecosystems*, 65: 43–52.

Chowdary, V.M., Rao, N.H., Sarma, P.B.S., 2004. A coupled soil water and nitrogen balance model for flooded rice fields in India. *Agric Ecosyst Environ,* 103, pp. 425–441.

Conference, F.A.O.R., 2004. FAO RICE CONFERENCE Rome, Italy, 12-13 February 2004

LONG-TERM PROSPECTS FOR THE GLOBAL RICE ECONOMY 12–13.

Espinoza, L., Slaton, N., Daniels, M., 1914. *The Nitrogen and Phosphorous Cycle in Soils*.University of Arkansas, United States Department of Agriculture and County Governments Cooperating.

Hayashi, K., Nishimura, S., Yagi, K., Hayashi, K., Nishimura, S., Yagi, K., 2006. Ammonia volatilization from the surface of a Japanese paddy field during rice cultivation. *Soil Sci Plant Nutr,* 52, pp. 545-555.

Kamaruddin, R., Ali, J., Saad, N.M., Farmer, P., 2013. Happiness and its Influencing Factors among Paddy Farmers in Granary Area of MADA. *World Appl Sci J,* 28, pp. 91–99.

Katayanagi, N., Fumoto, T., Hayano, M., Shirato, Y., Takata, Y., Leon, A., Yagi, K., 2017. Science of the Total Environment Estimation of total CH 4 emission from Japanese rice paddies using a new estimation method based on the DNDC-Rice simulation model. *Sci. Total Environ*. 601–602, 346–355.

Li, C., Mosier, A., Wassmann, R., Cai, Z., Zheng, X., Huang, Y., Tsuruta, H., Boonjawat, J., Lantin, R., 2004. Modeling greenhouse gas emissions from rice-based production systems : Sensitivity and upscaling. *Glob Biogeochem Cycl,* 18, pp. 1–19.

Liang, X.Q., Chen, Y.X., Li, H., Tian, G.M., Ni, W.Z., He, M.M., Zhang, Z.J., 2007. Modeling transport and fate of nitrogen from urea applied to a near-trench paddy field. *Environ Pollut*, 150, pp. 313-320.

Liesack, W., Schnell, S., Revsbech, N.P., 2000. Microbiology of flooded rice paddies. *FEMS Microbiol Rev,* 24, pp. 639-645.

Ling, G., Aly, I.E., 1998. A lumped parameter model for nitrogen transformation in the saturated zone. *Water Resources Research,* 34,pp. 203–212.

Makino, A., 2011. Photosynthesis , Grain Yield , and Nitrogen Utilization. *Photosynthesis and Yield,* 155,pp. 125–129.

Nurulhuda, K., Gaydon, D.S., Jing, Q., Zakaria, M.P., Struik, P.C., Keesman, K.J., 2017. Nitrogen dynamics in flooded soil systems : an overview on concepts and performance of models.

Nurulhuda, K., Struik, P.C., Keesman, K.J., 2017. Set-membership estimation from poor quality data sets : Modelling ammonia volatilisation in flooded rice systems. *Environ. Model. Softw*. 88, 138–150.

Shrestha, R. K. and Ladha, J. K. 1998. Nitrate in groundwater and integration of nitrogen-catch crop in rice-sweet pepper cropping system. *Soil Sci. Soc. Am. J.*, 62: 1610–1619.

Soares, J.R., Cantarella, H., Leite, M., Menegale, D.C., 2012. Soil Biology & Biochemistry Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors. *Soil Biol. Biochem,* 52,pp. 82–89.

Xinqiang, L., Junli, Y., Miaomiao, H., Hua, L., Liang, L., Guangming, T., 2014. Geoderma Modeling the fate of fertilizer N in paddy rice systems receiving manure and urea. *Geoderma* 228–229, 54–61.

Xu, J., Liu, B., Wang, H., Liu, W., Li, Y., Dai, Y., Lu, T., 2019. Ammonia volatilization and nitrogen leaching following top-dressing of urea from water-saving irrigated rice field: impact of two-split surge irrigation. *Paddy Water Environ.* 17, 45–51.

APPENDIX

Source Code

```
t <-seq(0,120) #planting days
dt= 1
kh= 0.576  #0.576          #0.360-0.744
kv= 0.062  #0.120  #0.200   #0.043-0.800
kn= 0.078  #0.200  #0.350   #0.020-2.000
kd= 0.130  #0.130          #0.050-0.200

u = 0        #initial value of urea
unh4 = 0      #initial value of ammonium produced
unh3loss = 0  #initial value of ammonia volatilized
uno3 = 0      #initial value of nitrate
uni = 0       #initial value of dinitrogen

srurea = 0    #initial value of surface runoff from urea
srnh4 = 0     #initial value of surface runoff from ammonium
srno3 = 0     #initial value of surface runoff from nitrate
srn = 0       #initial value of total surface runoff
utnh4 = 0     #initial value of N uptake by crops
vlno3 = 0     #initial value of vertical leaching
lsno3 = 0     #initial value of lateral seepage


nh4=0        #initial value of ammonium concentration
no3=0        #initial value of nitrate concentration

sr = 3/1000   #surface runoff rate (m/day)
et = 5/1000   #evapotranspiration rate (m/day)
vl = 4/1000   #vertical leaching rate (m/day)
ls = 4/1000   #lateral seepage rate (m/day)

z=0.05       #depth of floodwater(m)


urea = u/(z * 10)   #initial value of urea concentration

for (k in c(1:20)){
  (u[k+1]<- (-kh * u[k] - sr * u[k]/z) * dt + u[k]) #kg N/ha
  (urea[k+1]<-(u[k]/(z * 10))) #mg N/L
  (srurea[k+1]<-(sr * u[k]/z) * dt + srurea[k]) #kg N/ha

  (unh4[k+1]<- (kh * u[k] - kv * unh4[k] - kn * unh4[k] - (sr * unh4[k]/z) - (et * unh4[k]/z)) *
dt + unh4[k]) #kg N/ha
  (srnh4[k+1]<-(sr * unh4[k]/z) * dt + srnh4[k]) #kg N/ha
  (utnh4[k+1]<-(et * unh4[k]/z) * dt + utnh4[k]) #kg N/ha
  (nh4[k+1]<-(unh4[k+1]/(0.45 * 10))) #mg N/L

  (unh3loss[k+1]<-(kv * unh4[k])*dt + unh3loss[k]) #kg N/ha
```

```
  (uno3[k+1]<-(kn * unh4[k] - kd * uno3[k] - sr * uno3[k]/z - vl * uno3[k]/z - ls * uno3[k]/z)
* dt + uno3[k]) #kg N/ha
  (srno3[k+1]<-(sr * uno3[k]/z) * dt + srno3[k]) #kg N/ha
  (no3[k+1]<-(uno3[k+1]/(0.45 * 10))) #mg N/L

  (uni[k+1]<-(kd * uno3[k])*dt + uni[k]) #kg N/ha
  (vlno3[k+1]<-(vl * uno3[k]/z) * dt + vlno3[k]) #kg N/ha
  (lsno3[k+1]<-(ls * uno3[k]/z) * dt + lsno3[k]) #kg N/ha

  (srn[k+1]<-srurea[k] + srnh4[k] + srno3[k]) #kg N/ha
}

u[20]=u[19]+34.5   #First application of urea fertilizer (34.5 kg N/ha)

for (k in c(20:32)){
  (u[k+1]<- (-kh * u[k] - sr * u[k]/z) * dt + u[k]) #kg N/ha
  (urea[k+1]<-(u[k]/(z * 10))) #mg N/L
  (srurea[k+1]<-(sr * u[k]/z) * dt + srurea[k]) #kg N/ha

  (unh4[k+1]<- (kh * u[k] - kv * unh4[k] - kn * unh4[k] - (sr * unh4[k]/z) - (et * unh4[k]/z)) *
dt + unh4[k]) #kg N/ha
  (srnh4[k+1]<-(sr * unh4[k]/z) * dt + srnh4[k]) #kg N/ha
  (utnh4[k+1]<-(et * unh4[k]/z) * dt + utnh4[k]) #kg N/ha
  (nh4[k+1]<-(unh4[k+1]/(0.45 * 10))) #mg N/L

  (unh3loss[k+1]<-(kv * unh4[k])*dt + unh3loss[k]) #kg N/ha

  (uno3[k+1]<-(kn * unh4[k] - kd * uno3[k] - sr * uno3[k]/z - vl * uno3[k]/z - ls * uno3[k]/z)
* dt + uno3[k]) #kg N/ha
  (srno3[k+1]<-(sr * uno3[k]/z) * dt + srno3[k]) #kg N/ha
  (no3[k+1]<-(uno3[k+1]/(0.45 * 10))) #mg N/L

  (uni[k+1]<-(kd * uno3[k])*dt + uni[k]) #kg N/ha
  (vlno3[k+1]<-(vl * uno3[k]/z) * dt + vlno3[k]) #kg N/ha
  (lsno3[k+1]<-(ls * uno3[k]/z) * dt + lsno3[k]) #kg N/ha

  (srn[k+1]<-srurea[k] + srnh4[k] + srno3[k]) #kg N/ha

}

u[32]=u[31]+69  #Second application of urea fertilizer (69 kg N/ha)

for (k in c(32:54)){
  (u[k+1]<- (-kh * u[k] - sr * u[k]/z) * dt + u[k]) #kg N/ha
  (urea[k+1]<-(u[k]/(z * 10))) #mg N/L
  (srurea[k+1]<-(sr * u[k]/z) * dt + srurea[k]) #kg N/ha

  (unh4[k+1]<- (kh * u[k] - kv * unh4[k] - kn * unh4[k] - (sr * unh4[k]/z) - (et * unh4[k]/z)) *
dt + unh4[k]) #kg N/ha
  (srnh4[k+1]<-(sr * unh4[k]/z) * dt + srnh4[k]) #kg N/ha
```

```
  (utnh4[k+1]<-(et * unh4[k]/z) * dt + utnh4[k]) #kg N/ha
  (nh4[k+1]<-(unh4[k+1]/(0.45 * 10))) #mg N/L

  (unh3loss[k+1]<-(kv * unh4[k])*dt + unh3loss[k]) #kg N/ha

  (uno3[k+1]<-(kn * unh4[k] - kd * uno3[k] - sr * uno3[k]/z - vl * uno3[k]/z - ls * uno3[k]/z)
* dt + uno3[k]) #kg N/ha
  (srno3[k+1]<-(sr * uno3[k]/z) * dt + srno3[k]) #kg N/ha
  (no3[k+1]<-(uno3[k+1]/(0.45 * 10))) #mg N/L

  (uni[k+1]<-(kd * uno3[k])*dt + uni[k]) #kg N/ha
  (vlno3[k+1]<-(vl * uno3[k]/z) * dt + vlno3[k]) #kg N/ha
  (lsno3[k+1]<-(ls * uno3[k]/z) * dt + lsno3[k]) #kg N/ha

  (srn[k+1]<-srurea[k] + srnh4[k] + srno3[k]) #kg N/ha

}

u[54]=u[53]+21 #Third application of urea fertilizer (21 kg N/ha)

for (k in c(54:120)){
  (u[k+1]<- (-kh * u[k] - sr * u[k]/z) * dt + u[k]) #kg N/ha
  (urea[k+1]<-(u[k]/(z * 10))) #mg N/L
  (srurea[k+1]<-(sr * u[k]/z) * dt + srurea[k]) #kg N/ha

  (unh4[k+1]<- (kh * u[k] - kv * unh4[k] - kn * unh4[k] - (sr * unh4[k]/z) - (et * unh4[k]/z)) *
dt + unh4[k]) #kg N/ha
  (srnh4[k+1]<-(sr * unh4[k]/z) * dt + srnh4[k]) #kg N/ha
  (utnh4[k+1]<-(et * unh4[k]/z) * dt + utnh4[k]) #kg N/ha
  (nh4[k+1]<-(unh4[k+1]/(0.45 * 10))) #mg N/L

  (unh3loss[k+1]<-(kv * unh4[k])*dt + unh3loss[k]) #kg N/ha

  (uno3[k+1]<-(kn * unh4[k] - kd * uno3[k] - sr * uno3[k]/z - vl * uno3[k]/z - ls * uno3[k]/z)
* dt + uno3[k]) #kg N/ha
  (srno3[k+1]<-(sr * uno3[k]/z) * dt + srno3[k]) #kg N/ha
  (no3[k+1]<-(uno3[k+1]/(0.45 * 10))) #mg N/L

  (uni[k+1]<-(kd * uno3[k])*dt + uni[k]) #kg N/ha
  (vlno3[k+1]<-(vl * uno3[k]/z) * dt + vlno3[k]) #kg N/ha
  (lsno3[k+1]<-(ls * uno3[k]/z) * dt + lsno3[k]) #kg N/ha

  (srn[k+1]<-srurea[k] + srnh4[k] + srno3[k]) #kg N/ha

}

transform = u + unh4 + unh3loss + uno3 + uni                #Total N transformation (kg N/ha)
transport = srurea + srnh4 + utnh4 + srno3 + vlno3 + lsno3   #Total N transporation (kg N/ha)
check = transform + transport
```

```
par(mfrow = c(4,4))  #To display more than 1 graph
plot(u~t,xlab = "DAT", ylab ="u, kg N/ha",type="l",lwd="2")
plot(unh4~t,xlab = "DAT", ylab ="Urea hydrolysis, kg N/ha",type="l",lwd="2")
plot(unh3loss~t,xlab = "DAT", ylab ="Ammonia volatilization, kg N/ha",type="l",lwd="2")
plot(uno3~t,xlab = "DAT", ylab ="Nitrification, kg N/ha",type="l",lwd="2")
plot(uni~t,xlab = "DAT", ylab ="Denitrification, kg N/ha",type="l",lwd="2")
plot(utnh4~t,xlab = "DAT", ylab ="N in plant uptake, kg N/ha",type="l",lwd="2")
plot(vlno3~t,xlab = "DAT", ylab ="Vertical leaching, kg N/ha",type="l",lwd="2")
plot(lsno3~t,xlab = "DAT", ylab ="Lateral seepage, kg N/ha",type="l",lwd="2")
plot(srn~t,xlab = "DAT", ylab ="Surface runoff, kg N/ha",type="l",lwd="2")


nh4obs = read.csv("nh4+.csv");          #Observed datasets for Nh4+ left in soil solutions
avobs = read.csv("acummulatedav.csv");  #Observed datasets for ammonia volatilization
no3obs = read.csv("no3-.csv");          #Observed datasets for NO3- left in soil solutions


#compare simulated and observed
plot(nh4~t,font.lab=2,cex.lab=1.5,font=2,xlab = "Days after transplant" , ylab = "NH4+ left
in soil solution (mg N /L)" ,type="l", col="black", lty=1, lwd = "2")

points(nh4obs, col="red", pch="*")
lines(nh4obs, col="red",lty=2)

plot(avobs,font.lab=2,cex.lab=1.5,xlab = "Days after transplant",font=2 , ylab = "Ammonia
volatilization (Kg N /ha)" ,type="p" , pch="*", col="red", lty=2)

points(avobs, col="red", pch="*")
lines(unh3loss~t, col="black",lty=1, lwd = "2")

plot(no3~t,font.lab=2,cex.lab=1.5,font=2,xlab = "Days after transplant" , ylab = "No3- left in
soil solutions (mg N /L)" ,type="l", col="black", lty=1, lwd = "2")

points(no3obs, col="red", pch="*")
lines(no3obs, col="red",lty=2)

plot(check~t ,font.lab=2 ,xlab = "DAT", ylab ="N transformation + transportation, kg
N/ha",type="p",lwd="2")
axis(2,las=2, font=2)

#To display data in table
u <- data.frame(t,u)
unh4 <- data.frame(t,unh4)
unh3loss <- data.frame(t,unh3loss)
uno3 <- data.frame(t,uno3)
uni <- data.frame(t,uni)
utnh4 <- data.frame(t,utnh4)
vlno3 <- data.frame(t,vlno3)
lsno3 <- data.frame(t,lsno3)
nh4 <- data.frame(t,nh4)
```

```
no3 <- data.frame(t,no3)
check <- data.frame(t,check)
```