ความเป็นไปและการเคลื่อนที่ของคาร์โบฟูรานหลังการใช้ในนาข้าว โดยแบบจำลอง Root Zone Water Quality Model (RZWQM)

นางสาวดาวฉาย จันทร์เพ็ญ

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FATE AND TRANSPORT OF CARBOFURAN UNDER APPLICATION
IN RICE FIELD BY APPLICATION OF
ROOT ZONE WATER QUALITY MODEL (RZWQM)

Miss Daochai Janpen

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2009

Thesis Title	Fate and transport of carbofuran under application in rice field by application of Root Zone Water Quality Model (RZWQM)
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Field of Study	Environmental Management
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นางสาวดาวฉาย จันทร์เพ็ญ : ความเป็นไปและการเคลื่อนที่ของคาร์โบฟูรานหลังการใช้ในนาข้าว โดยแบบจำลอง Root Zone Water Quality Model (RZWQM). (Fate and transport of carbofuran under application in rice field by Root Zone Water Quality Model) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: อ.ดร. พิเชฐ ชัยวิวัฒน์วรกุล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร. อลิศรา เรืองแสง, 131 หน้า.

พื้นที่ในจังหวัดขอนแก่นเป็นพื้นที่เกี่ยวข้องกับการทำเกษตรกรรมเป็นส่วนใหญ่ โดยในการปลูกพืชนี้มักจะมีการใช้ปุ๋ยและยาฆ่าแมลงเป็นจำนวนมาก ก่อให้เกิดผลกระทบต่อสิ่งแวดล้อมรวมถึงสิ่งมีชีวิตต่างๆ คาร์โบฟูรานเป็นยาฆ่าแมลงที่มีความเป็นพิษสูงซึ่งนิยมใช้ในกลุ่มของเกษตรกร โดยชาวนาใช้สำหรับควบคุมแมลงและศัตรูอื่นๆที่มาทำลายข้าว งานวิจัยนี้เป็นการศึกษาความเป็นไปและการเคลื่อนที่ของยาฆ่าแมลงชนิดนี้หลังจากการใช้อย่างต่อเนื่องยาวนานเป็นระยะเวลาสิบปีในนาข้าวโดยใช้แบบจำลอง Root Zone Water Quality Model (RZWQM) จากการจำลองพบว่า ปริมาณของคาร์โบฟูรานที่ตกค้างอยู่ในดินในปีที่สิบเท่ากับ 32.80 กิโลกรัมต่อเฮกตาร์ โดยปัจจัยสำคัญที่มีผลต่อการย่อยสลายของคาร์โบฟูรานในดินคือการย่อยสลายบริเวณใต้ผิวดิน โดยสิ่งมีชีวิตแบบมีอากาศและจากสิ่งไม่มีชีวิตในชั้นดิน นอกจากนี้ยังมีปัจจัยอื่นๆ ได้แก่ จำนวนครั้งที่ใช้คาร์โบฟูรานในแต่ปี ความสามารถในการไหลของน้ำในดินซึ่งจะขึ้นอยู่กับชนิดของดินและปริมาณของน้ำในนาข้าว ในส่วนของการเคลื่อนที่ของยาฆ่าแมลงชนิดนี้ในดิน งานวิจัยพบว่าน้ำเป็นปัจจัยหลักที่ทำให้คาร์โบฟูรานสามารถเคลื่อนที่ได้อย่างรวดเร็วในชั้นดิน

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต Daochai Janpen
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5187532420 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS : CARBOFURAN / DEGRADATION / KHON KAEN PROVINCE / RICE FIELD / ROOT ZONE WATER QUALITY MODEL (RZWQM)

DAOCHAI JANPEN : FATE AND TRANSPORT OF CARBOFURAN UNDER APPLICATION IN RICE FIELD BY ROOT ZONE WATER QUALITY MODEL (RZWQM). THESIS ADVISOR : PICHET CHAIWIWATWORAKUL, Ph.D., THESIS CO-ADVISOR : ASSOCIATE PROFESSOR ALISSARA REUNGSANG, Ph.D., 131 pp.

Most of the land in Khon Kaen Province, located in Northeast Thailand, is used for agricultural purposes and, therefore, contains fertilizers and pesticides. These additives may have harmful impacts on ecosystems and human health. One of the widely used pesticides is carbofuran. It is used to control soil-dwelling and foliar-feeding insects e.g. boll weevils, mosquitoes, and white grubs. This study illustrates the fate and transport of carbofuran in rice field using the Root Zone Water Quality Model (RZWQM). The concentrations of the pesticide under several different agricultural management scenarios were determined. In ten years simulation from 1999 to 2008, the overestimated concentration of residual carbofuran was equal to 32.80 kg/ha at the end of year 2008. Using a sensitivity analysis, it was determined that soil subsurface aerobic and abiotic system significantly have impact on dissipation/degradation of carbofuran in soil. Other parameters, which have effects on carbofuran concentration in soil, include the number of pesticide applications, soil hydraulics, and type and amount of water source. The pesticide can rapidly transport into soil profile that mainly caused by water leaching.

Field of Study : Environmental Management Student's Signature Daochai Janpen
Academic Year : 2009 Advisor's Signature R. C.
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ACKNOWLEDGEMENTS

I would like to express my greatest appreciation to my advisor Dr. Pichet Chaiwiwatworakul for his kindness and for providing me an opportunity to be his advisee. I owe him my deepest gratitude for his valuable guidance, encouragement, and support throughout my research.

I would like to express my deep and sincere gratitude to my co-advisor Associate Professor Dr. Alissara Reungsang for her kindness and useful comments and suggestions throughout my study. I am also genuinely thankful to my graduate committee: Assistant Professor Dr. Manaskorn Rachakornkij, Dr. Somchai Chonwattana, and Dr. Pisut Painmanakul.

Furthermore, I would like to gratefully recognize the collaborative efforts provided by several agencies of Thailand, which are the Thai Meteorological Department, the Khon Kaen Rice Seed Center, and the Land Development Department of Thailand, and the owner of study area. My appreciation is also extended to Somporn Sanlertmongkonkun, Pensri Plangklang and Mullika Teerakun for their help and support.

This thesis would have been possible without the financial support from the National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), under the Graduate School of Chulalongkorn University.

I owe my loving thanks to my dear family and friends for their love, cheerful encouragement, and uplifting support throughout my life.

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CHAPTER I

INTRODUCTION

1.1 General introduction

It has been estimated that half of the world's population depends on wholly or partially on rice. Ninety percent of the world crop is grown and consumed in Asia, while, less quantity of rice is exported to other continents. Thailand was one of the most important rice exporters. About 30 percent of whole exported rice was from Thailand (FAO, 2003). However, rice planting is frequently associated with several types and high amount of pesticides and fertilizers that may lead to a major impact on the ecosystem and human health problems.

Carbofuran can affect on many pests. It is used to control soil-dwelling and foliar-feeding insects; for example, boll weevils, mosquitoes, alfalfa weevil, aphids, and white grubs (Trotter *et al.*, 1991). It is also very effective in the control of main paddy pests such as leafhoppers and whorl maggots (Aquino and Pathak, 1972; Venkateswarlu *et al.*, 1977). The characteristics of carbofuran is a crystalline, solid, odorless, and the color varying from colorless to gray depending on the purity. Carbofuran can reversibly inhibit acetylcholinesterase (AChE), which is in the nervous system and motor endplates of the target species. Since carbofuran is a member of carbamate group of pesticides, so it can also inhibit cholinesterase (Gupta, 1994) and impact on ingestion (Extoxnet, 2001). Due to the fact that granular carbofuran look very similar to seeds, there is mistaking of consumption by birds. Each bird was killed by only one grain of granular carbofuran due to its high toxicity. Therefore, the USEPA and FMC Corporation were in agreement to ban all granular carbofuran, and the ban was effective in 1994, while liquid form still remains in use until now. In Thailand, carbofuran was imported equal to approximately 5,000 tons in form of Furadan 3G in 2007 (FMC corporation, 2008).

Due to a high toxicity of carbofuran, the impacts of agricultural management practices from application of carbofuran in rice field were assessed in this study by mathematical models. Mathematical models was applied in order to gain a better understanding of fate and transport of pesticides or other chemicals in the applied area and to predict future conditions under the changes of agricultural management. Root Zone Water Quality Model (RZWQM) is one of the inclusive agricultural systems models. It is made up of six main components that are physical, soil chemical, nutrient, crop production, pesticide, and management processes (Hanson *et al.*, 1998).

In this study, RZWQM was used to predict behavior of carbofuran after the application in rice field under normal condition and various agricultural management practices and rice soil condition.

1.2 Objectives

1. To illustrate fate and transport of carbofuran under long term application in rice field
2. To identify the processes and parameters that play significant role in the carbofuran fate and transport in rice field
3. To predict potential of carbofuran accumulated in rice field using the validated model

1.3 Scopes

1. Laboratory scale data from Khon Kaen University and other data from several departments of Thailand (e.g. the Thai Meteorological Department, the Khonkaen Rice Seed Center, and Land Development Department) were used for simulating fate and transport of carbofuran in rice field.
2. Fate and transport of carbofuran in rice field was simulated by using the most suitable pesticide transport model.

3. Sensitivity analysis was conducted to identify the effects of model parameters on the processes.

4. The RZWQM was verified with observation data to make sure that the acceptable results would be obtained.

5. The validated RZWQM was used to predict fate and transport of carbofuran under long term application and other different scenarios.

    - Agricultural management practices are changed e.g. rice is cultivated four times per year.
    - Soil condition are changed e.g. pH and macropore size.

1.4 Hypothesis

Long term application of carbofuran has impact on its accumulation in rice field.

1.5 Expected outcome

Conditions of fate and transport of carbofuran, which simulated by RZWQM, could lead to further studies such as agricultural management and risk assessment due to carbofuran accumulated under long term application in rice field.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Carbofuran

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) is a broad-spectrum systematic carbamate insecticide, nematicide, and acaricide. Trotter *et al.* (1991) listed the products, which contain carbofuran, as Furadan, Curaterr, Yaltox, Bay 70143, Carbodan and ENT 27164.

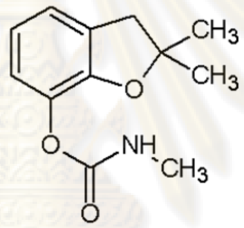

Figure 2-1 Structure of carbofuran

2.1.1 Properties of carbofuran

Carbofuran has a molecular weight of 221.26 and a melting point of 150-152°C. In general, carbofuran is degraded quickly under alkaline conditions and is stable under neutral or acidic conditions (Anon, 1971). The characteristics of carbofuran are crystalline, solid, and odorless; in addition, it varies in color from colorless to gray depending on its purity. Furthermore, Cal/EPA (2000) stated that carbofuran is degraded at temperatures higher than 130°C, and it can support combustion if ignited. The other properties of carbofuran are shown in Table 2-1.

Table 2-1 Physical-chemical properties of carbofuran

Physical-Chemical Properties	
Molecular weight	221.26
Molecular formula[1]	$C_{12}H_{15}NO_3$
Melting point [2]	150-152 °C
Water solubility [3]	351 ppm (25°C)
Vapor pressure [4]	6×10^{-7} mm Hg (25°C)
Octanol-water partition coefficient (K_{ow}) [3]	17 for 1 mg l^{-1} (20°C) 26 for 10 mg l^{-1} (20°C)
Henry's Law constant [1]	3.9×10^{-9} atm m3/mol
Hydrolysis half-lives (days) [3]	27.7 (pH 7, 25°C); 2.73 (pH 8, 25°C); 0.54 (pH 9, 25°C)
Aqueous photolysis half-life (days) [3]	7.95×10^{3} (pH 7, 28°C)
Soil photolysis half-life (days) [3]	138 (27°C, pH 5.7, sandy-loam, 2.1% organic carbon, 21% moisture)
Aerobic degradation half-life (days)[3]	22 (25°C, pH 5.7, sandy-loam, 2.1% organic carbon, 21% moisture)
Anaerobic degradation half-life (days) [3]	30.0 (25°C, pH 5.7, sandy-loam, 2.1% organic carbon, 21% moisture)
Field dissipation half-life (days) [3]	13.0 (pH 7.3, sandy-loam, 0.38% organic carbon)

Table 2-1 Physical-chemical properties of carbofuran (cont.)

Physical-Chemical Properties	
Adsorption coefficient (*Koc*) [5]	22

[1] Howard (1991)

[2] Lewis (1996)

[3] DPR Ecotox Database (2002)

[4] Alvarez (1989)

[5] Extoxnet (2001)

2.1.2 Mode of action

Carbofuran can reversibly inhibit acetylcholinesterase (AChE), which is in the nervous system and motor endplates of the target species. Since carbofuran is a member of the carbamate group of pesticides, it can also inhibit cholinesterase (Gupta, 1994) and impact on ingestion (Extoxnet, 1996).

2.1.3 Health effects

For acute toxicity, carbofuran is highly toxic when it is inhaled or ingested, and moderately toxic by dermal adsorption (Baron, 1991). The oral LD_{50} for rats, mammalian, and dogs are 5, 2, and 19 mg/kg day, respectively. Dermal LD_{50} for rabbits is 885 mg/kg day, and inhalation LC_{50} in guinea pigs, rats, and dogs are 43 mg/m^3 day, 85 mg/l day, and 52 mg/l day, respectively (EPA, 2006). With regard to chronic toxicity, the ability of pups to survive was reduced by a daily feeding of 100 ppm of carbofuran to pregnant rats, and the lowest amount of pesticide that leads to teratogenic effects in mice is 210 µg/kg day (EPA, 2006). The symptoms of carbofuran poisoning in humans consist of vomiting, abdominal cramps, diarrhea, sweating, nausea, weakness, imbalance, blurred vision, breathing difficulty, increased blood pressure, and incontinence. In addition, the respiration system can fail and bring about death (Extoxnet, 1993).

2.1.4 Environmental fate of carbofuran

In order to enhance agricultural productivity, carbofuran and other pesticides are used extensively, and this leads to their contamination of the environment. Mora *et al*. (1996) stated that carbofuran is moderately persistent in the environment. Its half-life is 26-110 days in soil, depending upon the pH, soil type, temperature, moisture content and microorganisms present. Achik and Sciavon (1989) examined the extent of the adsorption capacity of carbofuran on soil. They concluded that the climatic conditions, which are the nature, quantity, and frequency of precipitation, are highly related to carbofuran's persistence in a treated area. In addition, carbofuran is stable in acidic and neutral conditions, whereas it hydrolyses under alkaline conditions. Moreover, toxic fumes may be released when there is a thermal breakdown (WHO, 1996a, 1996b).

Air

Duel *et al*. (1979) states that the properties of carbofuran, which are low vapor pressure and low Henry's Law constant, cause it to have a low tendency to volatilize from water or moist soils. However, when carbofuran is in the air, there is vapor-phase photooxidation from its reaction with hydroxyl radicals. Carbofuran's half-life under this reaction is about 4.6 hours in the atmosphere (Howard, 1991).

Water

The major degradation pathway of carbofuran in water and sediment is base-catalyzed hydrolysis to form carbofuran phenol (Yu *et al*., 1974; Seiber *et al*., 1978; Brahmaprakash *et al*., 1987; Talebi and Walker, 1993). In addition, the aqueous hydrolysis rate of carbofuran increases when pH increases.

Seiber et al. (1978) proved that the hydrolysis of carbofuran at pH 10 was more than 700 times higher than at pH 7, which can be expressed with half-lives at 1.2 hours and 864 hours for pH 10 and pH 7, respectively.

For another degradation pathway, i.e., photolysis, is less important when compared with the hydrolysis of carbofuran. The photolysis rate of carbofuran decreases when the amount of dissolved organic matter (DOM) increases.

Soil

Cohen (1996) states that carbofuran is quite mobile in soil and surface runoff due to its high water solubility (351 ppm at 25°C) and low adsorption coefficient (K_{oc} = 22). However, carbofuran could be less mobile in clay soil owing to the presence of organic matter (Kumari *et al*., 1988).

Getzin (1972) found that the degradation rate of carbofuran in alkaline soil (pH 7.9) is higher than it is in acidic and neutral soils (pH 4.3-6.8) by about 7 to 10 times. In conclusion, in alkaline soil, hydrolysis is the main process of degradation, while in acidic and neutral soils, microbial and chemical mechanisms play more significant roles in carbofuran degradation (Getzin, 1973).

Li and Wong (1980) state that the degradation rate of carbofuran in rice fileds is greater when the moisture content in soil is higher. Moreover, Lalah and Wandiga (1996) conclude that the dissipation of carbofuran under flooded conditions tends to be more rapid than it is under non-flooded conditions.

Shelton and Parkin (1991) studied the effects of soil moisture content on the sorption and biodegradation of carbofuran in soil. Carbofuran (Carbonyl-14C) was added to soil samples with different moisture contents, and the release of $^{14}CO_2$ was determined. The results indicate that soil moisture content does not only activate the population of microorganisms, but it also increases the biodegradation of carbofuran owing to desorption.

On account of the low vapor pressure and low Henry's Law constant of carbofuran, volatilization is an insignificant dissipation route for carbofuran. In addition, Lalah *et al*. (1996) reported that the carbofuran volatilization rate under flooded soil conditions is higher than it is under non-flooded soil conditions, and they attribute this to carbofuran's co-evaporation with water on the surface soil.

Biota

Since carbofuran is highly toxic, a bird can be killed by only one grain of its granular form. Many birds mistakenly consume granular carbofuran as it looks very similar to seeds.

Eisler (1985) states that although carbofuran can interrupt the metabolism of lipids and enzymes in fish, the effects are reversible constituting in no visible permanent damage. In addition, Evert (2002) reports that carbofuran has high water solubility and low K_{ow}, so it does not tend to bioaccumulate to a large extent in any biota.

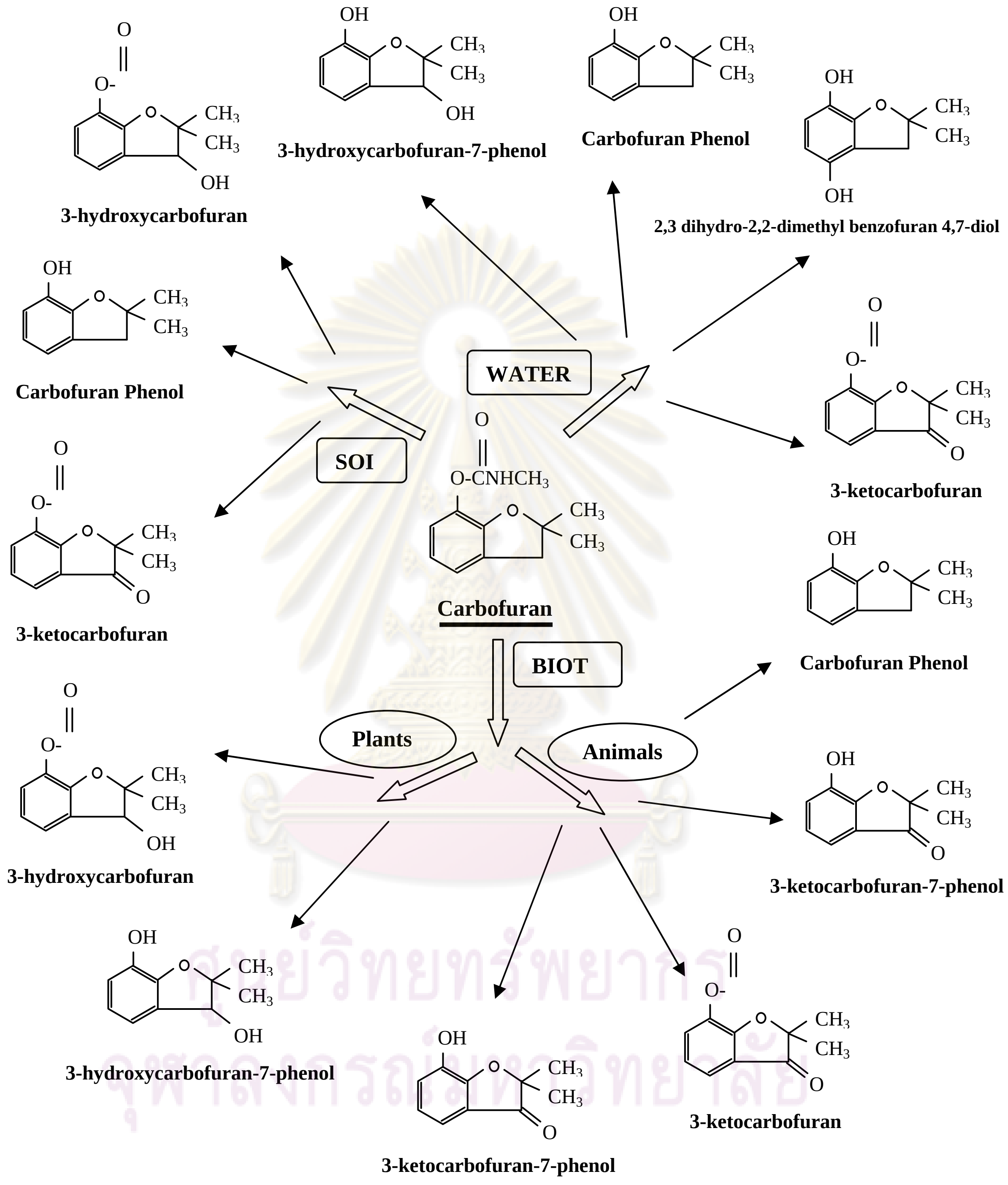

Figure 2-2 Environmental fate of carbofuran (Evert, 2002)

2.1.5 Regulatory history

Carbofuran was first registered in the United States in 1969 (EPA, 2006). In 1991, the Environmental Protection Agency (EPA) and the technical registrant cooperated to ban the use of the granular form of carbofuran in ecologically responsive areas that are not associated with human health concerns, and it took effect on September 1, 1994 (Extoxnet, 1996). At last, on November 18, 2009, the United States Environmental Protection Agency banned carbofuran's registration and application (EPA, 2009). The maximum contaminant level goal (MCLG) and the maximum contaminant level (MCL) for carbofuran concentrations in drinking water are set at 40 ppb. Adhering to this level should not lead to health effects (EPA, 2006).

2.1.6 Carbofuran in Thailand

The Ministry of Agriculture and Cooperatives of Thailand (1989) announced that carbofuran is a pesticide with high toxicity (LD_{50} < 30 mg/kg), and its concentration cannot exceed 0.05 ppm in water. Anat Thapinta and Hudak (2000) addressed pesticide use, environmental problems, and regulations in Thailand. They state that in 1985 and 1987, the concentration of carbofuran in water samples from main rivers in Thailand had been 0.01-1.37 ppb, which was not more than the standard. In addition, they also report that the carbofuran concentration in soil and in various vegetables was 45.10-8418.50 ppb in 1996 and 0.03-0.50 ppm in 1987-1989. In 2007, around 5,000 tons of carbofuran was imported in form of Furadan 3G (FMC corporation, 2008). Examples of the maximum residue limit (MRL) of carbofuran in livestock and food products are expressed in Table 2-2 in accordance with the Thai Agricultural Commodity and Food Standard (2006).

Table 2-2 MRL of carbofuran in livestock and food products

Product	The Maximum Residue Limit (MRL) (mg/kg-product)
Fowl meat	0.08
Gizzard	0.08
Egg	0.1
Milk	0.05
Rice	0.1
Banana	0.1
Sweet corn	0.1

2.2 Pesticide fate and transport model

- **An ecosystem model**

Yu *et al.* (1974) studied the fate of carbofuran in a model ecosystem by using ring-^{14}C- and labeled carbofuran. They state that carbofuran was highly toxic to crabs, snails, and clams. It was found that no parent carbofuran was found in living organisms. Nevertheless, large amounts of the parent carbofuran were found in crabs that had died almost immediately after a pesticide application.

- **A rice-fish model**

Jayaraman *et al.* (1989) used a rice-fish model ecosystem to investigate the fate of carbofuran. The results showed that 3-hydroxy carbofuran was present in rice leaves and carbofuran fixed in the soil transferred to the leaves even during the graining and harvesting stages. With regard to the fate of carbofuran in soil, they found that carbofuran disappears rapidly, and soil operates as a reservoir for the pesticide. Carbofuran in water is found in low concentrations due to some degradation of carbofuran in water because of metabolites (Nurnsri Tayaputch *et al.*, 1986). In addition, they found that in the Nurnsri Tayaputch *et al.* study there was no bioaccumulation in fish; however, some metabolites of carbofuran were found. This shows that the fish could degrade the parent carbofuran.

- **The Behavior Assessment Model (BAM) and Groundwater-potential Model (GWP)**

Yen *et al.* (1997) used the Behavior Assessment Model (BAM) and Groundwater-Potential Model (GWP) to assess the possible contamination of carbofuran in groundwater. They concluded that carbofuran can contaminate groundwater. They also studied two subtropical soils at different moisture contents and soil temperatures to determine the dissipation coefficient of carbofuran by resolving the degradation and adsorption. The results show that the carbofuran residue in soil tends to be lower when the moisture content is higher. Moreover, increasing of the soil temperature and moisture content increased the dissipation rate of carbofuran in soil, and the kinetics of the dissipation followed first-order kinetics.

- **A level IV fugacity model**

Paraiba *et al.* (2007) studied the fate of carbofuran in irrigated rice by using a level IV fugacity model. The researchers found that level IV fugacity models underestimate the concentration of carbofuran in water and slightly underestimate the concentration of carbofuran in soil. In addition, they concluded where the concentrations of carbofuran were higher: water > soil > rice plants > air.

2.3 Root Zone Water Quality Model (RZWQM)

2.3.1 Significant processes in the RZWQM using time-scale based calculations

Hanson *et al.* (1998) summarized the relative flow of information among all the major components of the model. The processes in the RZWQM are calculated at different time scales, which are sub-hourly and daily intervals (Figure 2-3).

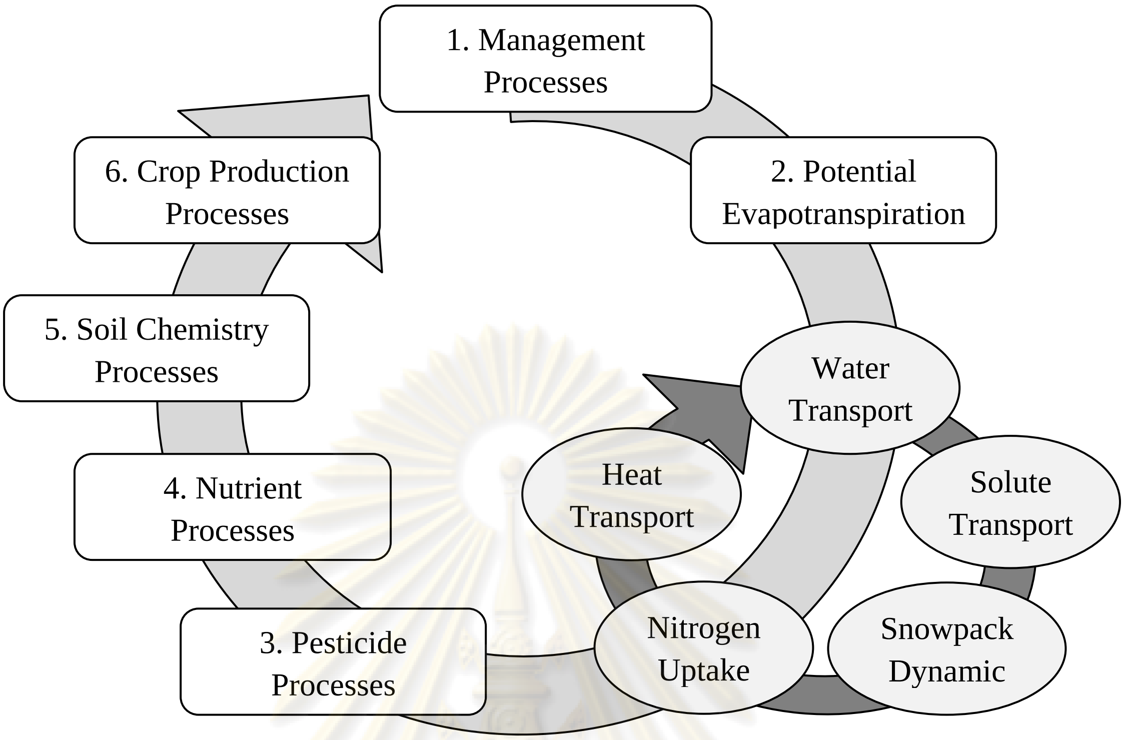

Figure 2-3 Processes in Root Zone Water Quality Model (Ahuja *et al.*, 2000)

As seen in Figure 2-3, the daily time loop consists of the following seven processes:

- Management processes - the effects of chemicals, manure, irrigation water and tillage on the system
- Potential evapotranspiration - evaporation and transpiration fluxes that are related to the soil surface and plant root, respectively
- Fate and transport processes - water, chemical, and heat transport
- Pesticide processes - degradation of pesticide on the surface of plants and residue as well as within soil horizons
- Nutrient processes – the carbon and nitrogen cycle
- Soil chemistry system - typically equilibrium equations
- Crop production and harvesting processes

All processes are calculated daily (the larger loop) except the fate and transport processes, which are estimated in sub-hourly (the smaller loop).

2.3.2 Description of components within the RZWQM

The RZWQM is made up of six main components, which are physical, soil chemical, nutrient, crop production, pesticide, and management processes (Hanson et al., 1998). The processes can be represented by following submodels (Malone et al., 2004a):

- Infiltration, runoff, water redistribution after infiltration, and chemical movement in the soil
- Macropore flow and chemical movement through macropores
- Evapotranspiration (ET)
- Heat transport
- Plant growth
- Organic matter/nitrogen cycling
- Soil chemistry processes
- Pesticide dissipation and degradation processes
- Chemical transfer to runoff and transport through the soil matrix
- The effects of agricultural management practices on these processes

1) Management processes

a) Timing and application methodology

The RZWQM provides for both the specific date requirement and system that deals with the cropping system. When the management process is needed to simulate a specific date, the specific date method can be used. The relative timing methods are based on the growth cycle, which comprise planting, emerging, and harvesting. During simulation, the position of pesticides or fertilizers can have direct effect on their fate; therefore, the RZWQM describes an array of application methods and consequent placements.

Summaries of timing and application methods that are included in the RZWQM are shown in Table 2-3.

Table 2-3 Summaries of timing and application options in the RZWQM (Hanson *et al.*, 1998)

Management practices	Timing options	Application options
Pesticide applications	• Plant growth cycle • Specified date	• Surface broadcast • Incorporated • Injected fumigation • Irrigation chemigated • Slow release formulations • Shielded sprayer for foliar or soil surface only
Tillage operations	• Plant growth cycle • Specified date	• 29 different implements • User specified intensity
Irrigation application	• Fixed interval • Specified dates • Root zone depletion	• Fixed amount • Varying amounts • Refill root zone
Fertilizer applications	• Plant growth cycle • Specified date • Preplant with split • Preplant split with plant demand trigger	• Surface broadcast • Incorporated • Injected NH_3-N • Irrigation fertigated • Nitrification inhibitor additives

Table 2-3 Summaries of timing and application options in the RZWQM (Hanson *et al.*, 1998) (cont.)

Management practices	Timing options	Application options
Crop planting	• Multiple year • Multi-species rotations	• 5 harvesting operations • External crop models can be fired

***b)* Tillage affects on soil properties**

The soil composition, hydraulic reaction, and combination of surface materials can be changed by tillage operations. In addition, the level of these changes depends on whether it is the primary or secondary tillage, and the type of equipments.

***c)* Surface residue decomposition**

Parr and Papendick (1978) and Bristow *et al.* (1986) stated that surface residue decreases soil-water and erosion losses, and it increases soil stability. The RZWQM not only focuses on soil-water, which is saved by limiting potential evaporation, but it also focus on the dynamics of surface-residue nitrogen.

2) Physical processes

Hydrology and heat transport processes are simulated in the physical processes component. The key physical processes are as follows:

***a)* Infiltration of water into the soil matrix**

Infiltration rates into the soil and then discrete into 1-cm increments are calculated using the Green-Ampt equation (Green and Ampt, 1991; Hachum and Alfaro, 1980) until the soil's maximum infiltration capacity is exceeded.

$$V = \frac{\overline{K}_s}{VRCF}\frac{H_c + H_o + Z_{wf}}{Z_{wf}} \qquad (2.1)$$

where V = infiltration rate at any given time (cm hr^{-1}),

$VRCF$ = viscous resistance and entrapped air correction factor,

$\overline{K}_s$ = effective average saturated hydraulic conductivity of the wetting zone (cm hr^{-1}),

H_c = capillary pressure (cm),

H_o = depth of surface ponding (cm), and

Z_{wf} = depth of the wetting front (cm).

If the infiltration rate (V) value is greater than the rainfall rate, the V value is set to be equal to the rainfall rate. Moreover, the saturated wetting front during infiltration may reach a shallow water table especially in the rainy season. Therefore, if the field is tile drained, the infiltration rate is set to the deep leakage rate plus the tile flow rate, and the tile flow is calculated by using the Hooghoudt equation (Bouwer and van Schilfgaarde, 1963; Skaggs, 1978). The 2-dimensional effects of tile drainage are determined in this equation by estimating this flux at the center point between 2 parallel drains as shown in Figure 2-4; then, the depth of the water table at the center point between the drains is estimated. The equation for flux to the drain depending on the depth of water table can be written as follows:

$$S_d(Z',t) = \frac{8K_e d_e m + 4K_e m^2}{CL^2 \Delta z} \qquad \omega > \mathrm{d} \qquad (2.2)$$

$$S_d(z',t) = 0 \qquad \omega \leq \mathrm{d} \qquad (2.3)$$

where $S_d(Z',t)$= sink term (tile drainage) (hr^{-1}),

Z' = depth of the drain (cm), user-supplied,

ω	=	distance from the water table to the bottom of the restricting layer (cm),
d	=	distance from the drain to the bottom of the restricting layer (cm),
m	=	water table height above the drain (cm),
K_e	=	effective lateral hydraulic conductivity (cm hr^{-1}), user-supplied or model calculated,
L	=	distance between drains (cm), user-supplied,
C	=	ratio of the average flux between drains to the flux midway between drains (set = 1.0),
d_e	=	equivalent depth from drain to bottom of restricting layer (cm), and
Δz	=	soil depth increment at Z' (cm).

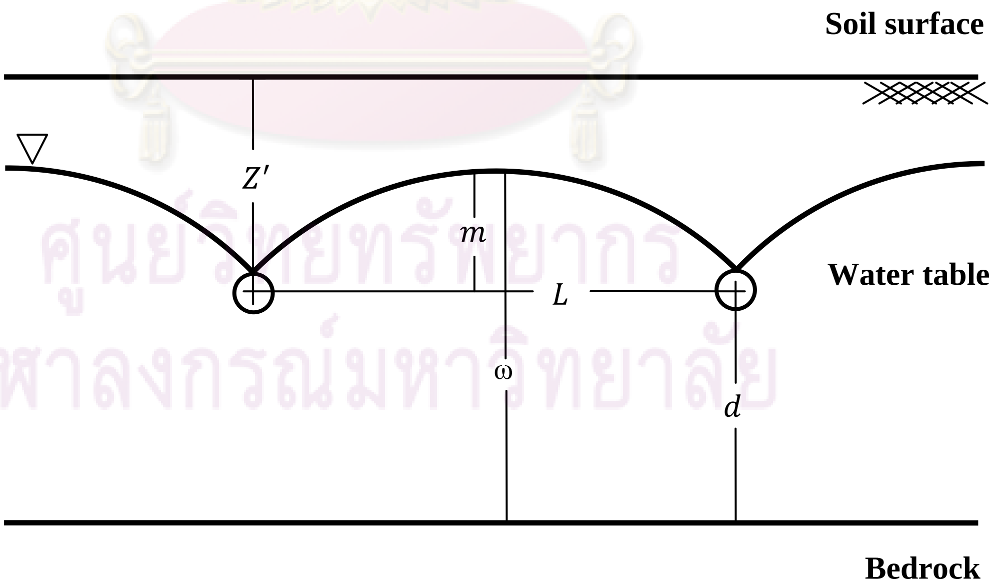

Figure 2-4 A design of a soil profile with a high water table and tile drains. The flux to the drains at the center point between the drains is simulated in

the RZWQM, and it accounts the water table depth at this point (Ahuja *et al.*, 2000).

***b)* Infiltration of surplus rainfall through macropores**

Macropores are separated from the soil matrix. A macropore is defined as a cylindrical channel or crack that has diameter greater than 0.5 mm. When there is excess rainfall that does not infiltrate into the soil matrix, the water will go to macropores. The maximum macropore infiltration rate equals the saturated hydraulic conductivity per unit area, and any extra of the excess rainfall over this maximum rate is examined as runoff. When the water enters macropore, it infiltrates in a lateral direction into the drier layers of the soil matrix below the wetting front.

Poiseuille's law and the lateral Green-Ampt equation are used to compute the maximum macropore infiltration rate (K_{mac}) and lateral water movement into the soil, respectively. Poiseuille's law is written as follows:

For cylindrical holes:

$$K_{mac} = \frac{N_p \rho g \pi r_p^4}{8\eta} = \frac{P_{mac} \rho g r_p^2}{8\eta} \tag{2.4}$$

For planner cracks:

$$K_{mac} = \frac{L_c \rho g d^3}{12\eta} = \frac{P_{mac} \rho g w^2}{12\eta} \tag{2.5}$$

where K_{mac} = the maximum macropore infiltration rate (cm hr^{-1}),

ρ = the density of water (=1.0017 g cm^{-3}),

g = the gravitational constant (=1.27 x 10^{10} cm hr^{-1}),

r_p = the radius of cylindrical holes (cm),

w = the width of planer cracks (cm),

η = the dynamic viscosity of water (=36.072 g $hr^{-1}cm^{-1}$),

N_p = the number of pores per unit area,

L_c = the total length of cracks per unit area (cm), and

P_{mac} = the continuous macroporosity as fraction of soil volume.

The radial or lateral Green-Ampt equation is shown as:

$$V_r = \frac{2\pi K_s \tau_c}{Ln\left(\frac{r_{wf}}{r_p}\right)} \tag{2.6}$$

where V_r = the transient radial infiltration rate from a cylindrical macropore (cm hr^{-1}),

K_s = saturated hydraulic conductivity (cm hr^{-1}),

τ_c = capillary drive term for the soil matrix in the depth increment in question (cm),

Ln = natural logarithm,

r_{wf} = wetted radius at any given time (cm), and

r_p = macropore radius (cm).

The amount of infiltration is used to calculate the r_{wf}. However, when r_{wf} = r_p, the Eq. (2.6) is not appropriate for the very first time step; therefore, V_r is calculated as follows:

$$V_r = 2\pi r_p \left[\frac{2K_s \tau_c(\theta_s - \theta_i)}{\frac{\Delta t_1}{2}}\right]^{1/2} \tag{2.7}$$

where $(\theta_s - \theta_i)$= the initial volumetric soil water deficit in the depth increment, and

Δt_1 = the first time step (hr).

For planer cracks, the lateral infiltration rate per unit length of the cracks uses the following equation:

$$V_r = \left[\frac{2K_s\tau_c(\theta_s - \theta_i)}{t}\right]^{1/2} \tag{2.8}$$

where t = cumulative time for lateral flow (hr).

The lateral water flow into the soil that surrounds macropores can be impeded by the lateral sorptivity reduction factor owing to an organic coating or compaction.

***c)* Transport of chemicals in soil during infiltration**

To account for the adsorption/desorption processes of chemicals, sequential partial piston displacement and mixing during infiltration is used to transport solutes within the soil matrix. During rainfall, raindrops will have an impact on the mixing of chemicals. Runoff water non-uniformly mixes with chemicals from the surface soil (top 2 cm) (Ahuja, 1990; Ahuja *et al.*, 1995). When runoff water enters macropores, the chemical in this macropore water will go into the soil matrix by lateral infiltration or leave the bottom of the root zone.

The non-uniform mixing model is used to simulate chemical transfer to the runoff and macropore flow (Malone *et al.*, 2004a). Furthermore, at the soil surface (z=0), the degree of mixing between the rainwater and soil solution is supposed to be at its maximum, and it will decrease exponentially with the depth as a function of the non-uniform mixing factor. The soil matrix is divided into the mobile (mesopore) and immobile (micropore) regions, which are treated separately from the macropore flow. In the saturated zone during rainfall or irrigation, the partial piston displacement allows for only water and chemicals to move through the mobile regions. Moreover, between mobile and immobile regions during each infiltration time step, the chemical is transferred by diffusion, and the fraction microporosity and the chemical diffusion rate in water are the only two controlling parameters that are specific to these processes.

d) **Redistribution of water and chemical after infiltration**

The soluble chemicals move with water from one depth increment to another, which includes upward movement in response to evaporation. The chemical movement is handled by starting from the bottom to the surface.

Between rainfall or irrigation events, soil water is calculated by using the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(h,z)\frac{\partial h}{\partial z} - K(h,z)\right] - S(z,t) \qquad (2.9)$$

where θ = volumetric soil water content ($cm^3\ cm^{-3}$),

t = time (hr),

z = soil depth (cm, assumed positive downward),

h = soil-water pressure head (cm),

K = hydraulic conductivity ($cm\ hr^{-1}$), a function of h, and

S = sink term for root-water uptake and tile drainage rate (hr^{-1}).

In Eq. (2.9), $h = h(z); t = 0$, and $z \geq 0$ are used as the initial condition.

***e)* Root water uptake**

A distributed sink arising from root water uptake is one of the two sink terms; the other one is the point sink arising from tile drainage. The root uptake part of the sink term is evaluated by using the approach of Nimah and Hanks (1973):

$$-S_r(z,t) = \frac{[H_r + (RRES \cdot z) - h(z,t) - s(z,t)]\, R(z) \cdot K(h)}{\Delta x \cdot \Delta z} \qquad (2.10)$$

where $S_r(z,t)$ = sink term (root uptake) (hr^{-1}),

H_r = an effective root water pressure head (cm),

$RRES$ = root resistance term and the product $(RRES \cdot z)$ accounts for gravity term and friction loss in H_r (assumed = 1.05),

$h(z,t)$ = soil-water pressure head (cm),

$s(z,t)$ = the osmotic pressure head (assumed = 0 cm),

Δx = the distance from plant roots to where $h(z,t)$ is measured (assumed = 1 cm),

Δz = soil depth increment (cm),

$R(z)$ = proportion of the total root activity in the depth increment Δz, obtained from the plant growth model, and

$K(h)$ = the hydraulic conductivity (cm hr^{-1}).

H_r is varied until potential transpiration is met in the condition that H_r does not fall below h_{min}. When H_r reaches h_{min}, this value is assumed to be steady.

***f)* Potential evaporation and transpiration**

A review of the double-layer model of Shuttleworth and Wallace (1985) or the S-W model is included in the RZWQM (Figure 2-5). The S-W model adds the partitions of evapotranspiration (ET) into soil evaporation and crop transpiration into the concept of the Penman-Monteith (P-M) model. Farahani (1994) extended this model to explain the ET processes under no-till or minimum-till practices that lead to crop residue on the soil surface. The extended S-W ET model tries to find an association between the double-layer energy combination approach of Shuttleworth and Wallace (1985) and the partial canopy resistance formulation that given by Shuttleworth and Gurney (1990) to allocate ET from a soil-residue-canopy system. The model not only describes a partially-covered soil but also estimates evaporation from the residue covered fraction of the substrate, the bare soil fraction of the substrate, and transpiration from the canopy.

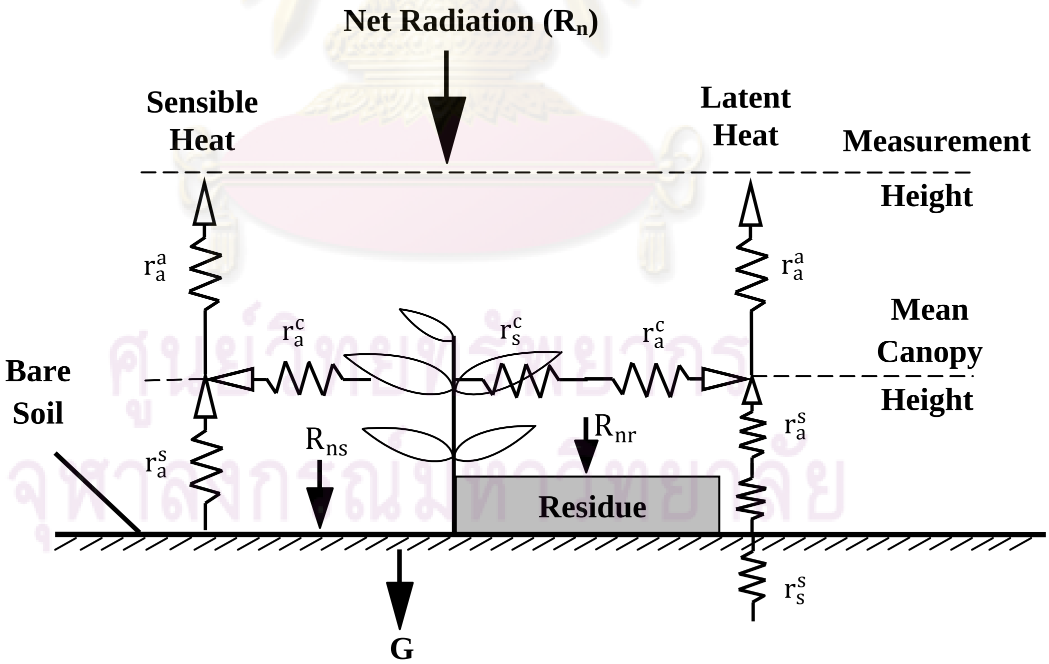

Figure 2-5 Diagram of the soil-residue-canopy system (Ahuja *et al.,* 2000)

The extend S-W ET model is divided into two layers: the soil surface and the canopy. The sum of latent heat from the canopy (λT), the bare soil

(λE_s) and residue covered (λE_r) soil areas is the total flux of the latent heat (λET) which is located above the canopy (i.e., at the measurement height), and it can be written as follows:

$$ET = T + C_s E_s + C_r E_r \tag{2.11}$$

where C_s = the fraction of a unit substrate area occupy by bare soil (decimal), and

C_r = the fraction of a unit substrate area occupy by residue (decimal).

Therefore, $C_s + C_r = 1$.

The air vapor pressure shortage at the height of the canopy air stream (VPD_o), and λT and λE_s are expressed by

$$\lambda T = \frac{\Delta[(R_n - G) - R_{nsub}] + \rho c_p (VPD_o)/\, r_a^c}{\Delta + \gamma(1 + r_s^c \,/\, r_a^c)} \tag{2.12}$$

$$\lambda E_s = \frac{\Delta(R_{ns} - G_s) + \rho c_p (VPD_o)/\, r_a^s}{\Delta + \gamma(1 + r_s^s \,/\, r_a^s)} \tag{2.13}$$

Eq. (2.13) assumes that the isothermal drying soil layer has a zero saturation deficit at the evaporating sites within the soil. Furthermore, Eq. (2.13) can be rewritten to describe λE_r if the residue covered soil areas are also assumed to be isothermal. The equation is rewritten by assigning an additional resistance to the soil vapor flux compelled by the residue:

$$\lambda E_r = \frac{\Delta(R_{nr} - G_r) + \rho c_p (VPD_o)/\, r_a^r}{\Delta + \gamma[1 + (r_s^s + r_s^r) \,/\, r_a^r]} \tag{2.14}$$

where R_n = the flux of net radiation above the canopy (W m^{-2}),

R_{nsub} = the flux of net radiation below the canopy (W m^{-2}),

R_{ns} = the flux of net radiation over bare soil (W m^{-2}),

R_{nr}	=	the flux of net radiation over residue (W m^{-2}),
G	=	the heat flux below the canopy (into the substrate),
G_s	=	the heat flux into the bare soil (W m^{-2}),
G_r	=	the heat flux into the residue (W m^{-2}),
T	=	the crop transpiration rate (kg m^{-2} s^{-1}),
E_s	=	the evaporation rate from bare soil (kg m^{-2} s^{-1}),
E_r	=	the evaporation rate from residue-covered soil (kg m^{-2} s^{-1}),
ρ	=	density of air (kg m^{-3}),
c_p	=	specific heat of air at constant pressure (J kg^{-1} K^{-1})
γ	=	the psychrometric constant (kPa K^{-1}),
Δ	=	the slope of the saturation vapor pressure versus temperature curve (kPa K^{-1}),
VPD_o	=	the vapor pressure deficit at the mean canopy height (kPa),
r_a^c	=	the bulk boundary layer resistance of the canopy elements within the canopy (s m^{-1}),
r_s^c	=	the bulk stomatal resistance of the canopy (s m^{-1}),
r_a^s	=	the aerodynamic resistance between the bare soil and mean canopy height (s m^{-1}),

r_a^r = the aerodynamic resistance between the surface cover (residue mulch^{-1}) and mean canopy height (s m^{-1}),

r_s^s = the soil surface resistance (s m^{-1}), and

r_s^r = the surface resistance of the cover (residue mulch^{-1}) (s m^{-1}).

Two assumptions are used in the derivation of Eq. (2.14). One is that the turbulent transfer coefficients and resistances of heat and water are similar, and the other is that there is no difference between the condition of the soil surface and canopy (Ahuja *et al.*, 2000). VPD_o is expressed as follows:

$$VPD_o = VPD_a + [\Delta(R_n - G) - (\Delta + \gamma)\lambda ET]r_a^a/\rho c_p \quad (2.15)$$

where VPD_a = the air saturation vapor pressure deficit at the measurement height (kPa), and

r_a^a = the aerodynamic resistance between the canopy and the measurement height (s m^{-1}).

The extended S-W ET model clearly defines a partially covered soil and predicts evaporation from the bare soil fraction and the residue covered fraction of the substrate, and transpiration from the canopy (Farahani and Ahuja, 1996). However, the RZWQM is limited to quantifing daily potential rates of bare or residue-covered soil evaporation and crop transpiration. This is because soil and canopy resistances under limiting soil water conditions are difficult to determine. The model needs estimations of the amounts of residue cover and the residue thickness; moreover, these parameters are not typically available for various tillage and residue treatments.

***g)* Heat transport and soil temperature**

Heat moves downward with infiltrated water during a rainfall or irrigation event, and it is controlled by convective-diffusive transport diffusion:

$$\frac{\partial(\rho_s C_s + \theta\rho_w C_w)T}{\partial t} = \frac{\partial}{\partial_z}\left[K_z(\theta, z)\frac{\partial T}{\partial z} - q_w(z)\rho_w C_w T\right] - q_r(z)\rho_w C_w T \qquad (2.16)$$

where $K_z(\theta, z)$= the thermal conductivity of the soil with water (W m^{-1} K^{-1}),

$q_w(z)$ = soil water flux (m s^{-1}),

$q_r(z)$ = water uptake by roots (m s^{-1}),

ρ_s = soil bulk density (kg m^{-3}),

ρ_w = density of water (kg m^{-3}),

C_s = heat capacity of soil (J m^{-3} K^{-1}),

C_w = the specific heat of water (J m^{-3} K^{-1}), and

T = the soil temperature (°C).

In addition, the temperature of the new and old water in each 1-cm increment is equilibrated at the end of the time step. The equilibration involves the heat balance equation:

$$(\theta_i\rho_w C_w + \rho_{si}C_{si})T_i^{j+1} = \Delta W_{i-1}\rho_w C_w T_{i-1}^{j+1} + [(\theta_i - \Delta W_{i-1})\rho_w C_w + \rho_{si} + C_{si}]T_i^j \qquad (2.17)$$

where θ_i = the volumetric soil water content in soil depth increment i (m^3 m^{-3}),

ρ_w = the density of water (kg m^{-3}),

C_w = the specific heat of water (J m^{-3} K^{-1}),

ρ_{si} = the soil bulk density in i (kg m^{-3}),

ΔW_{i-1} = the amount of water coming in from above during a time step (m),

C_{si} = the heat capacity of soil in i (J m^{-3} K^{-1}),

T_i^{j+1} = the new temperature in i after equilibration (°C),

T_{i-1}^{j+1} = the temperature of ΔW_{i-1}(°C), and

T_i^j = the temperature of the existing water before equilibration (°C).

For the top 1-cm increment, in which i = 1, ΔW_0 is the amount of rain or irrigation water that infiltrates at the soil surface, and T_0^{j+1} is its temperature.

3) Pesticide processes

Malone *et al.* (2004a) reported that the RZWQM may concurrently simulate the sorption of pesticide on immediate equilibrium sites, slower 'kinetic' sites, and irreversibly bound sites. In addition, a linear or Freundlich isotherm may be used for the sorption of a pesticide. Freundlich isotherm is written as follows:

$$\ln(C_s) = ln\left[K_{oc}^f F_{oc}\right] + (1/n)\ln(C_w) \tag{2.18}$$

where C_w = concentration of pesticide in soil water (μg cm^{-3}),

C_s = concentration of pesticide in soil solid phase (μg g^{-1}),

F_{oc} = Fraction of organic carbon in soil (w/w),

$(1/n)$ = a traditional way of writing the slope, and

K_{oc}^{f} = the Freundlich organic carbon sorption constant (cm^3 g^{-1}), which if n=1(the linear case), it is seen to be equal to K_{oc}, but if n>1 (n is always ≥1), $K_{oc}^{f} = K_{oc}$ only when $C_w = 1$.

With regard to the degradation and washoff of pesticides applied to plants, the RZWQM determines the pesticide degradation loss depending on the characteristics of the pesticide and the environmental conditions. In addition, pesticide degradation is determined by a first-order kinetic formulation, and the degradation coefficient is a function of temperature (Nash, 1988):

$$C = C_0 e^{-(ks+ksa+kss+kx+ko+kh+kp+kv)td'} \tag{2.19}$$

where C = the updated pesticide concentration (ppm),

C_0 = the initial pesticide concentration (ppm),

td' = time (days),

ks = lumped degradation coefficient (day^{-1}),

kv = dissipation coefficient for volatilization (day^{-1}),

kp = dissipation coefficient for photolysis (day^{-1}),

kh = dissipation coefficient for hydrolysis (day^{-1}),

ksa = dissipation coefficient for anaerobic biodegradation (day^{-1}),

kss = dissipation coefficient for aerobic biodegradation (day^{-1}),

ko = dissipation coefficient for oxidation (day^{-1}), and

kx = dissipation coefficient for complication (day^{-1}).

***a)* Degradation methods**

There are four paths in the RZWQM for simulating degradation of pesticides.

1. Using the first-order kinetic formulation with a particular lumped dissipation constant.

2. Using two dissipation rate formulations in which two separate dissipation rates are used.

    - The first rate stands for the quick dissipation period after the application until the next rainfall event.

    - The second rate is used after the rainfall event, which is normally slower.

3. Using the individual pathway method in which the users are allowed to exceed the lumped dissipation rate with individual rates as to better control the rate dominance.

4. Using a mechanism for daughter production and degradation is input data are available (Leistra, 1986).

***b)* Pesticide washoff**

The applied pesticides can be intercepted by plant leaves and the surface residue mulch layer, and these chemicals are degraded using first-order kinetics. However, they are also accessible for transport by washoff mechanisms (Willis *et al.*, 1982, 1985, 1986; McDowell *et al.*, 1985; Wauchope *et al.*, 1991). When there is rainwater or irrigation, some chemicals are mixed with the water and transported from the plant surfaces to the residue surfaces, and then go into the soil surface. The washoff equation that is used in the RZWQM is

$$P_r = P_i e^{-(kw)r} \tag{2.20}$$

where P_r = the pesticide load still remaining on the surfaces after rainfall (%),

P_i = the initial pesticide load before the rainfall (%),

kw = the rate of washoff per mm of rainfall, and

r = the amount of rainfall (mm).

Malone *et al.* (2004a) reviewed pesticide sorption and degradation in soil as shown in Figure 2-6.

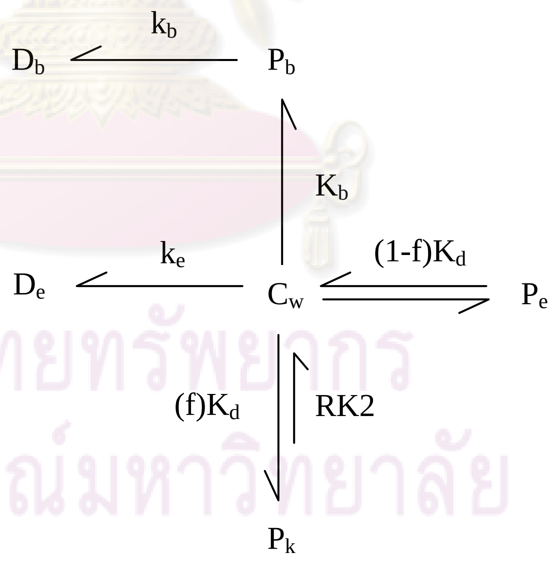

Figure 2-6 Sorption, desorption, and degradation processes in the RZWQM. Where P_b = pesticide on bound sites (µg g^{-1}), P_e = pesticide on equilibrium sites (µg g^{-1}), P_k = pesticide on kinetic sites (µg g^{-1}), C_w = pesticide in water (µg ml^{-1}), K_d = equilibrium sorption coefficient (ml g^{-1}), K_b = bound pesticide formation coefficient (ml g^{-1} day^{-1}), RK2

= desorption rate constant form kinetic sorption sites (day^{-1}), f = fraction of sorption sites that are kinetic (dimensionless), k_b = degradation coefficient of sorbed pesticide in equilibrium with water (day^{-1}), D_e = unspecified daughter product from the water phase, and D_b = unspecified degradation from the irreversibly bound sites.

4) Nutrient processes

***a)* Carbon and nitrogen pools**

Organic matter (OM) is disseminated into five pools that are as follows: (1) the slow pool and (2) fast pool for crop residue, and (3) fast pool, (4) medium pool and (5) slow pool for decaying soil OM. In addition, OM is decomposed by three microbial biomass populations that include two heterotrophs (soil fungi and facultative bacteria) and one autotroph (nitrifiers).

***b)* Fundamental process rate equations**

The basic form of the decay-rate equations for OM differ only by the values of the user-supplied rate coefficients, and the first order equations that calculates the carbon substrate source. The common rate equation, $r_{dec,i}$ (μg-C g-soil^{-1} day^{-1}) is of the following form:

$$r_{dec,i} = K_{dec,i}\, C_i \tag{2.21}$$

where i = the OM pool index, $(1 \le i \le 5)$,

C_i = the carbon substrate concentration (μg-C g-soil^{-1}), and

$K_{dec,i}$ = the first order rate coefficient (day^{-1}).

The rate coefficient is calculated by using the following:

$$K_{dec,i} = f_{aer} A_i \left(\frac{k_b T}{h_p}\right) e^{\left(\frac{E_{ai}}{R_g T}\right)} \left(\frac{O_2}{H^{kh} g_i^{kh}}\right) POP_{het} \tag{2.22}$$

where O_2 = the O_2 concentration in the soil solution (moles O_2 per liter of pore water) as controlled by temperature,

H = the hydrogen ion concentration (moles H per liter of pore water),

kh = the hydrogen ion exponent for the decay of OM,

g_i = the activity coefficient,

POP_{het} = the population of aerobic heterotrophic microbes (number organisms g soil^{-1}),

f_{aer} = the factor for the extent of aerobic conditions ($0 \leq f_{aer} \leq 1$),

k_b = the Boltzmann's constant (J °K^{-1}),

T = soil temperature index (°K),

h_b = Planck's constant (J·s),

A_i = the pool-specific rate coefficient (day^{-1} organism^{-1}), and

E_{ai} = the apparent activation energy for pool *i* (kcal mole^{-1}).

Shaffer (1985) stated that E_{ai} is computed as a function of soil salinity. Furthermore, f_{aer} is contained in order to correct the rate coefficient for O_2 depletion in the soil solution that is not comprised by temperature effects.

***c)* Nitrification**

Nitrification is a way that autotrophic bacteria convert NH_4^+ into NO_3^-, and it is calculated using zero and first order rate equations based on current NH_4^+ concentrations (moles liter-pore-water^{-1}):

$$r_{nit} = \begin{cases} -K_{nit}^{0}\,, & [NH_4^+] \geq 0.003 \text{ moles/liter pore water} \\ -K_{nit}^{1}[NH_4^+]\,, & \text{Otherwise} \end{cases} \qquad (2.23)$$

where K_{nit}^{0} = the zero order rate coefficient for nitrification (moles liter-pore-water^{-1} day^{-1}), and

K_{nit}^{1} = the first order rate coefficient for nitrification (day^{-1}).

The rate coefficients K_{nit}^{0} and K_{nit}^{1} are described as follows:

$$K_{nit}^{0} = 0.003K_{nit}^{1} = f_{aer}A_{nit}\left(\frac{k_bT}{h_p}\right)e^{\left(\frac{-E_{an}}{R_gT}\right)}\left(\frac{\sqrt{O_2}}{H^{khn}g_i^{khn}}\right)POP_{aut} \qquad (2.24)$$

where A_{nit} = the nitrification rate coefficient defined for K_{nit}^{0} (day^{-1}organism^{-1}) and K_{nit}^{1} (day^{-1} organism^{-1}),

H = the hydrogen ion concentration (moles liter-pore-water^{-1}),

khn = hydrogen ion exponent for nitrification (= 0.167 for pH ≤ 7 and =-0.333 for pH > 7),

g_i = the activity coefficient (dimensionless),

POP_{aut}= the population of autotrophic microbes (number organisms g-soil^{-1}), and

E_{an} = the apparent activation energy for nitrification (kcal mole^{-1}).

***d)* Denitrification**

Denitrification is the conversion of NO_3^- into N_2 and N_2O (r_{den}, moles NO_3^- liter-pore-water^{-1} day^{-1}):

$$r_{den} = -K_{den}[NO_3^-] \tag{2.25}$$

where r_{den} = the product of the NO_3^- concentration (moles liter-pore-water^{-1}) and the rate coefficient (t^{-1}).

K_{den} is defined by the following equation:

$$K_{den} = f_{an} A_{den} \left(\frac{k_b T}{h_p}\right) e^{\left(\frac{-E_{ad}}{R_g T}\right)} \left(\frac{C_s}{H^{khd} g_i^{khd}}\right) POP_{ana} \tag{2.26}$$

where f_{an} = the factor for anaerobic effect ($0 \leq f_{an} \leq 1$),

A_{den} = the specific denitrification rate coefficient (day^{-1} organism^{-1}),

E_{ad} = the apparent activation energy for denitrification (kcal mole^{-1}),

T = the soil temperature (°K),

H = the hydrogen ion concentration (moles liter-pore-water^{-1}),

khd = the hydrogen ion exponent for denitrification (= 0.167 for pH ≤ 7 and =-0.333 for pH > 7),

g_i = the activity coefficient (dimensionless),

POP_{ana}= the population of anaerobic microbes (number microbes g-soil^{-1}), and

C_s = the carbon substrate concentration (μg-C g-soil^{-1}).

In addition, it is simulated with respect to soil nitrates. During strong reducing conditions where there is no O_2, the model produces essentially 100% N_2 gas and no N_2O.

***e)* Growth and death of microbial biomass**

Biomass growth and death are not simulated directly. Rates of OM decay, nitrification, denitrification, and other processes assuming efficiency factors for production of biomass C are used to calculate microbial growth. The growth rate of autotrophs, which is assumed as rate of assimilation of C, is given in Eq. (2.27).

$$r_{Cass} = -a_c e_{nit} CN_8 r_{nit} \tag{2.27}$$

where r_{Cass} = autotrophic C assimilation during growth (μg-C g-soil^{-1} day^{-1}),

a_c = units conversion factor, (μg-N g-soil^{-1}) / (moles NH_4 LPW^{-1}),

e_{nit} = conversion efficiency factor,

CN_8 = C:N ratio of autotrophic biomass, and

r_{nit} = nitrification rate (moles NH_4 LPW^{-1}).

5) Soil chemical processes

In the RZWQM, the soil chemistry model includes the precipitation-dissolution of the salts, hydrolysis reactions, ion exchange, ion pairing, and redox reaction. Moreover, it examines soil pH and the solution concentrations of the major ions; generally Ca^{+2}, Mg^{+2}, Na^{+}, NH_4^{+}, Al^{+3}, HCO_3^{-}, Cl^{-}, SO_4^{-2} and NO_3^{-} are of primary importance. Lindsay (1979) informed that changes in the concentration of chemical could be calculated by using a chemical equilibrium approach.

Newton's method is used for solving equilibrium equations in order to combine simultaneous non-linear equations with mass and charge balance equations (Golden, 1965; Shaffer and Gupta, 1981). The included processes are as follows:

***a)* Ion pairing**

The significant amounts of Ca^{+2}, Mg^{+2}, Al^{+3}, and SO_4^{-2} can be occupied, so they may alter the chemical equilibrium state of the system.

***b)* The bicarbonate buffer system**

This system is a set of reactions that are involved in the dissolution and release of carbon dioxide gas (CO_2). When CO_2 in the soil reacts with soil pore water to form carbonic acid, this acid dissociates into bicarbonate and hydrogen ions. In addition, this system is significant in controlling the pH of soil-water systems.

***c)* Solid phase**

Chemical dissolution-precipitation involving calcium carbonate (lime), calcium sulfate (gypsum), and aluminum hydroxide (gibbsite), and in these cases, solubility equations are used (Shaffer *et al.*, 1992a).

The calcarious soils are often in equilibrium with calcium carbonate ($CaCO_3$ or lime), and an equation for lime solubility is used (Ahuja *et al.*, 2000).

$$(Ca^{+2})(CO_3^{-2}) - \frac{8.7 \times 10^{-9}}{\gamma_2^2} = 0.0 \tag{2.28}$$

where γ is activity coefficients for the ionic species and Equation (2.28) is the equilibrium expression for the reaction

$$\underline{CaCO_3} = Ca^{+2} + CO_3^{-2} \tag{2.29}$$

where $\underline{CaCO_3}$ is the concentration of solid phase salt, and by thermodynamic convention is taken as unity or 1.

An equation for solid phase gypsum ($\underline{CaSO_4 \times 2H_2O}$) is as follows:

$$(Ca^{+2})(SO_4^{-2}) - \frac{2.29 \times 10^{-5}}{\gamma_2^2} = 0.0 \tag{2.30}$$

Equation (2.28) represents the following reaction for the dissolution and precipitation of gypsum,

$$(\underline{CaSO_4 \times 2H_2O}) = Ca^{+2} + SO_4^{-2} \tag{2.31}$$

Acid soils are often in equilibrium with the mineral gibbsite [$Al(OH)_3$], and their solubility equation can be represented by

$$\frac{(Al^{+3})}{(H^+)^3} - \frac{1.0965 \times 10^8\ \gamma_1^3}{\gamma_3} = 0.0 \tag{2.32}$$

Equation (2.32) is the equilibrium expression for the reaction

$$\underline{AlOH_3} + 3H^+ = Al^{+3} + 3H_2O \tag{2.33}$$

By convection, in Eq. (2.32), the water concentration is set equal to 1.0.

***d)* Ion exchange**

In a soil-water system, adsorption desorption reactions are very important. Ions that absorb on clay surfaces are not available for leaching and do not directly participate in reactions in the solution phase. The major cations included in the model are Ca^{+2}, Mg^{+2}, Al^{+3}, Na^+, and NH_4^+. However, anions exchange cannot be simulated in the RZWQM (Ahuja *et al.*, 2000).

6) Crop production processes

The simulation of carbon dioxide assimilation, carbon allocation, tissue respiration, tissue loss, plant mortality, root growth, nitrogen uptake, and transpiration are specific requirements for the plant component.

***a)* Environmental fitness**

Goldberg (1989) declared that ‘environmental fitness’ is the measure of environmental appropriateness for particular species. Moreover, the current temperature, soil water availability and nutrient condition are factors that affect environmental fitness.

$$E_t^V = E_t^T min(E_t^N, E_t^W) \tag{2.34}$$

where E_t^V = fitness at time t (0…1),

E_t^T = the effect of temperature (0…1),

E_t^N = the effect of nitrogen (0…1), and

E_t^W = the effect of water on overall environmental fitness (0…1).

E_t^T, E_t^N, and E_t^W can be described using the following equations.

$$E_t^T = (A_1 {A_2}^{A_3})^z \tag{2.35}$$

$$A_1 = \frac{T_{max} - T}{T_{max} - T_{opt}} \qquad A_2 = \frac{T - T_{min}}{T_{opt} - T_{min}} \qquad A_3 = \frac{T_{opt} - T_{min}}{T_{max} - T_{opt}} \tag{2.36}$$

where T = the current temperature (soil or ambient temperature) (°C),

T_{max} = the maximum ambient temperature (°C),

T_{opt} = the optimum ambient temperature (°C),

T_{min} = the minimum ambient temperature (°C),

T = 1.328 that is default value in the RZWQM provided by Detling *et al*. (1979), and

z = shape parameter for temperature curve.

The effect of nitrogen on whole plant can be expressed as follows:

$$E_t^N = 1.0 - \frac{N_T - N}{N_T - N_L} \quad (2.37)$$

$$N_T = N_X e^{-bGS} \quad (2.38)$$

$$b = -ln\left(\frac{N_{GS=1}}{N_X}\right) \quad (2.39)$$

$$N_L = N_T \frac{N_N}{N_X e^{-b}} \quad (2.40)$$

where N_T = the target nitrogen concentration (g-N plant^{-1}),

N = the actual nitrogen concentration (g-N plant^{-1}),

N_L = the nitrogen concentration below, which the plant will not grow (g-N plant^{-1}),

N_X = the maximum percentage nitrogen of emerged plant (%),

b = the decay coefficient (dimensionless),

GS = the current growth stage at time t (0…1),

$N_{GS=1}$ = the percentage of nitrogen in the plant when the growth stage is 1.0 (%), and

N_N = the minimum whole-plant percentage nitrogen (%).

The effects of water on overall environmental fitness are described by the actual (Γ_a) and potential transpiration rates of the crop (Γ_p) (cm water day^{-1}).

$$E_t^W = 0.85\frac{\Gamma_a}{\Gamma_p} + 0.15 \tag{2.41}$$

***b)* Growth state development**

Growth state development of a plant ranges from 0 (seeds) to 1 (absolutely mature plant). Growth state (GS) is described as the relative development of the main class that is reduced by the existing environmental fitness:

$$GS = \sum_{i=1}^{t} D_j E_i^V \tag{2.42}$$

where D_j is the inverse of the minimum time required to go through the existing phenological phase j under ideal environmental conditions, and E_i^V is environmental fitness at time i.

***c)* Carbon distribution**

- Plant growth

A plant has to consume carbon and nitrogen for growth. Carbon dioxide is consequently absorbed by the plant depends on the intensity of light, canopy structure, and the current environmental stress. In addition, assimilated carbon dioxide is stored as allocable carbon.

- Photosynthesis

In the RZWQM, photosynthesis is the basis for carbon allocation. France and Thornley (1984) and Hanson (1991) have stated that this model is based on the rectangular hyperbola, and an integration of this equation is provided by Hanson (1991):

$$P_t^N = P_{max} \alpha E_t^V \int_u^d \frac{S_t}{P_{max} + \alpha S_t} dt \qquad (2.43)$$

where P_t^N = the net carbon assimilation rate (moles-C m^{-2} hr^{-1}),

P_{max} = the theoretical maximum net assimilation rate (moles-C m^{-2} day^{-1}),

u = the time at the start of the photosynthetic period or sunrise (time of day),

d = the time at the end of the photosynthetic period or sunset (time of day),

S_t = the light flux density of the canopy at time t (MJ m^{-2} day^{-1}), and

α = the light-use efficiency coefficient (dimensionless).

- Respiration

Whole-plant photorespiration rate (P_t^{Resp}) is expressed as a function of the plant weight and photosynthetic rate on the current day. Firstly, the respiration quotient of the plant (Q_{10}) can be used to determine the temperature dependent respiration parameter (γ).

$$\gamma = \frac{T_A \rho_R (Q_{10} - 1)}{10 - \rho_R (2Q_{10} + 1)} \qquad (2.44)$$

where T_A = the average daily temperature (°C),

ρ_R = the respiration coefficient (0…1), and

Q_{10} = the respiration quotient of the plant (dimensionless).

McCree (1970) proved that P_t^{Resp} can be estimated by the following equation:

$$P_t^{Resp} = \alpha P_t^N + \gamma P_t^{Bio} \quad (2.45)$$

where α = proportion of photosynthate respired for general plant maintenance (0…1), and

P_t^{Bio} = the amount of carbon in the leaves and stems (g-C plant^{-1}).

- Carbon partitioning

In a plant, carbon is distributed based on a hierarchy of demands, in which propagules get carbon first if the plant is in a reproductive growth stage, followed by the roots. After carbon is allocated to the propagules and roots, the remaining allocable carbon is divided between leaves and stems.

***d)* Nitrogen distribution**

Nitrogen uptake of plant is determined by the concentration of nitrogen in soil water that enters the plant in proportion to the root biomass present in each soil layer. Active N uptake will occur if not enough N has been brought into the plant with the water taken up by the plant. The rate of active N uptake (N_t^{Active}) is shown in Eq. (2.42), which is similar to the Michaelis-Menten substrate model.

$$N_t^{Active} = \eta_1 \times \frac{[N]}{\eta_2 + [N]} \quad (2.46)$$

where $[N]$ = the concentration of N available in the soil layer (ppm),

η_1 = the maximum proportion of N that can be removed from the soil per day (ppm), and

η_2 = the half-maximum nitrogen-uptake amount for the crop being simulated (ppm).

For nitrogen partitioning, the organ that has first access to the available N is the root. Then the N is allocated to the other plant organs. Furthermore, if the plant is in the reproductive stage, propagule N demand is met first then that of the leaves and stems, respectively.

Table 2-4 Summary of components and input parameters needed in the RZWQM (Malone *et al*., 2004a)

Processes	Modeling method	Required input
Infiltration and water redistribution between rainfall or irrigation	• Green-Ampt equation during infiltration • Richard's equation during redistribution	• Soil crust K_{sat} • Soil texture • Horizon delineation • Bulk density • Soil water retention curves or, 1/3 or 1/10 bar SWC (if available) • Initial SWC
Macropore flow	• Poiseuille's law and lateral Green-Ampt	• Lateral sorptivity reduction factor (reduces lateral water movement simulated from Green-Ampt) macroporosity • Effective soil radius • Fraction dead-end macropores • Average radius of cylindrical pores • Width, length, and depth of cracks

Table 2-4 Summary of components and input parameters needed in the RZWQM (Malone *et al*., 2004a) (cont.)

Processes	Modeling method	Required input
Evapotranspiration	• Modified Penman-Montieth	• Albedo of dry and wet soil • Albedo at crop maturity • Albedo of fresh residue • Pan coefficient (only with pan evaporation) • Dry mass of surface residue
Tile drainage	• Hooghoudt's steady state equation	• Drain depth • Drain spacing • Radius of drains • Water table leakage rate • Lateral K_{sat}
Heat transport	• Partial mixing and displacement during infiltration • Heat convective-dispersive equation during redistribution	• Soil textural class • Dry volumetric soil heat capacity • Initial soil temperature
Plant growth	• A generic plant growth model for corn and soybean	• Maximum nitrogen uptake rate • Photosynthate to respire • Specific leaf density • Plant density

Table 2-4 Summary of components and input parameters needed in the RZWQM (Malone *et al*., 2004a) (cont.)

Processes	Modeling method	Required input
		• Propagule age effect • Seed age effect • Maximum rooting depth • Minimum leaf stomatal resistance • Nitrogen sufficiency index • Luxurious nitrogen uptake factor
Organic matter/nitrogen cycling	• OMN	• Fast residue pool • Slow residue pool • Fast humus pool • Transition humus pool • Stable humus pool • Aerobic heterotrophs pool • Anaerobic heterotrophs pool • Autotrophs pool • Initial urea-nitrogen • Initial NO3-nitrogen • Initial NH4-nitrogen
Pesticide processes	• Wauchope *et al.*	• Freundlich sorption coefficient (=K_{oc} when n = 1), Freundlich exponent (1/n)

Table 2-4 Summary of components and input parameters needed in the RZWQM (Malone *et al*., 2004a) (cont.)

Processes	Modeling method	Required input
		• Parameters governing kinetic and irreversibly bound pesticide sorption • Acid/base dissociation constants • Parameters governing pesticide washoff from foliage and mulch • Pesticide half-life (foliar, residue, soil surface, and soil subsurface) • Half-life adjustment coefficient for soil depth • Half-life adjustment coefficient for soil temperature and soil water content • Metabolite (daughter) formation fraction
Chemical transport	• Non-uniform mixing model for chemical transfer to runoff • Partial displacement for matrix transport	• Non-uniform mixing factor (depend on soil type, surface roughness and cover condition) • Fraction microporosity • Diffusion rate

Table 2-4 Summary of components and input parameters needed in the RZWQM (Malone *et al*., 2004a) (cont.)

Processes	Modeling method	Required input
Agricultural management	• Bulk density re-consolidation after tillage • Soil hydraulic properties after tillage and re-consolidation • Surface residue decomposition	• Management timing - Fertilizer application date - Tillage date • Management or application type and quantity - Quantity of fertilizer surface broadcast - Chisel plow • Initial surface residue properties - C:N ratio - Dry mass of residue - Age of residue

For the case in which all input parameters cannot be achieved, Malone *et al*. (2004a) determined the minimum data requirements for the RZWQM that are shown as follows:

1. **Breakpoint rainfall**

   It is the rainfall data that reports partial description of a storm event (accumulated rain at any time) that can provide a good explanation of the storm.

2. **Daily meteorology**

   Due to outputs of the RZWQM that are mainly provided on a daily timescale, the meteorology input parameters, which include the minimum and maximum air temperatures, wind speed, solar radiation, and relative humidity, are also required on the respective timescale.

3. Site description

The location of the study area is important in the calculation of the RZWQM because different places have different conditions such as the amount of solar radiation and characteristics of soil. The minimum parameters are expressed as follows:

- Soil horizon delineation by depth
- Numerical layer depths (as generated by the RZGRID supplement program)
- Soil horizon physical properties
    - Bulk density
    - Particle size fractions for each horizon (sediment size fraction)
    - 330 or 100 cm suction water content and saturated hydraulic conductivity for each horizon (optional soil properties)
- Estimate of dry mass and age of residue on the surface
- General pesticide data (can be found in the ARS pesticide database)
    - Common name
    - Half-life
    - Partition coefficient
    - Dissipation pathway
- Specifying a crop from supplied database with regional parameters

4. Initial state

Initial state is a condition that is used at the start of simulation. Minimum data requirements about initial condition are shown as the following contents:

- Initial soil moisture contents (initial soil-horizon water content)
- Management details

- o Tillage type and timing
- o Chemical application and timing

- Initial soil temperatures
- Initial soil pH, Cation Exchange Capacity (CEC) values
- Initial nutrient model inputs
    - o Soil residue
    - o Humus
    - o Microbial populations
    - o Mineral NO_3-N, NH_4-N

When any scenario is run within the RZWQM, the model will provide the output files that are shown as the following table (Ahuja *et al.*, 2000).

Table 2-5 The RZWQM output files (Ahuja *et al.*, 2000)

File name	Output variables and description
RZWQM.OUT	Geographic information of the experimental site Soil properties by layer, summary of the initial conditions. Tabular output as requested by the user
MANAGE.OUT	Recording of management practices, such as tillage, irrigation, fertilization, and planting and harvesting. Summary of plant harvesting information
MBLWAT.OUT	Detailed water balance information.
MBLNIT.OUT	Detailed nitrogen balance information
NUPTAK.OUT	Daily nitrogen uptake by plant
NUTRI.OUT	Daily nitrogen status in organic and inorganic forms

Table 2-5 The RZWQM output files (Ahuja *et al.,* 2000) (cont.)

File name	Output variables and description
ACCWAT.OUT	Accumulated daily water storage, runoff, actual evapotranspiration, seepage, drainage, macropore flow, and infiltration
CLEACH.OUT	Chemical leaching each day out of the bottom of the soil profile
MACRO.OUT	Detailed information on chemical mass balance after each infiltration
PROFILE.OUT	Printing out important parameters associated with soil water movement
PLANT0.OUT	Daily plant biomass and nitrogen accumulation
PLANT2.OUT	Recording of plant environmental fitness parameters
PLANT3.OUT	Number of plants in each growth stage at end of each day
PLANT4.OUT	Plant height and leaf area index
PLANT5.OUT	Plant nitrogen demand and supply
PLANT.OUT	Daily nitrogen balance of the plant
PLPROD.OUT	Photosynthesis rate and corresponding plant population and LAI
PEST1P.OUT	Pesticide distribution in the soil profile each day
MBLP*.OUT	Mass balance information for each pesticide
PEST*.OUT	Total pesticide in the soil profile at the end of each day

Table 2-5 The RZWQM output files (Ahuja *et al.,* 2000) (cont.)

File name	Output variables and description
AVG6IN.OUT	Average water content, nitrate and pesticide concentrations in six inch increments
NEWINT.OUT	Recording of the system status at end of simulation runs
DAILY.PLT	All the information to generate 2-D plots of user selected variables
LAYER.PLT	All the information to generate 3-D plots of user selected variables
NUPTAK.PLT	Contains same information as NUPTAK.OUT but for plotting purpose
NUTRI.PLT	Contains same information as NUTRI.OUT but for plotting purpose

2.4 The RZWQM software interface

The program workspace and the project/scenario paradigm are shown in Figure 2-7 and Figure 2-8. A project is a structure that includes all meteorological data, analysis outputs, and individual scenarios. Each scenario within the project represents the specific inputs, which are site description, initial system state, residue state, and management practices, necessary to execute the simulation model. The scenario generates its own specific output and analysis data file.

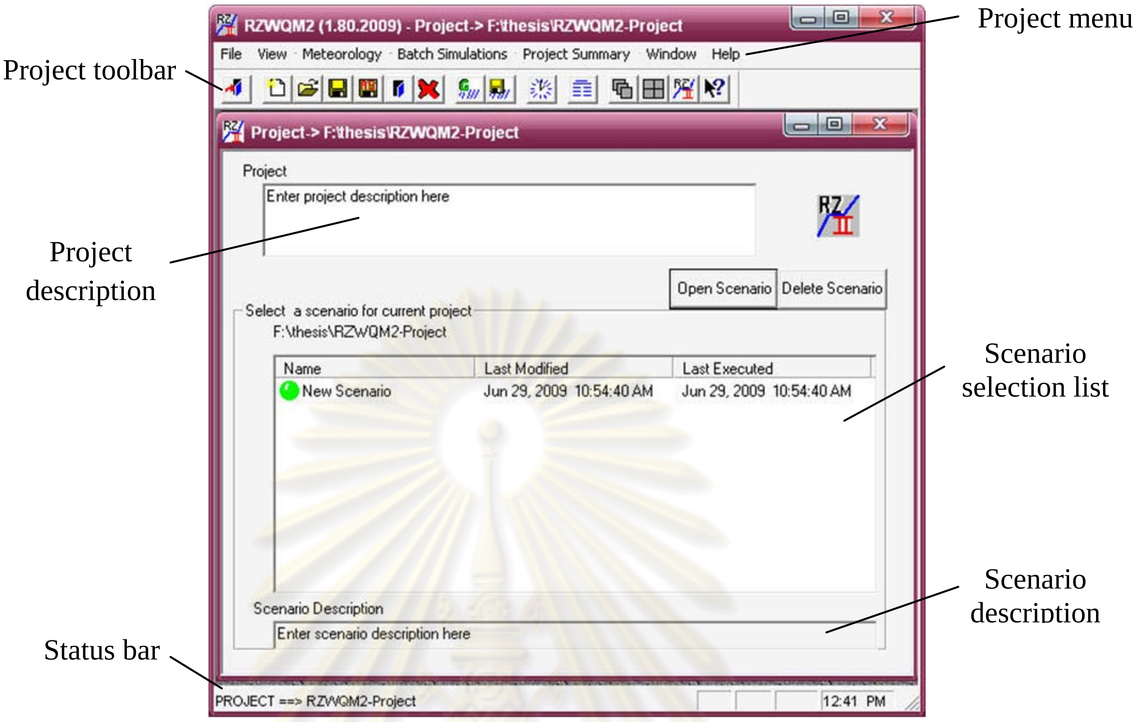

Figure 2-7 Project interface of the RZWQM

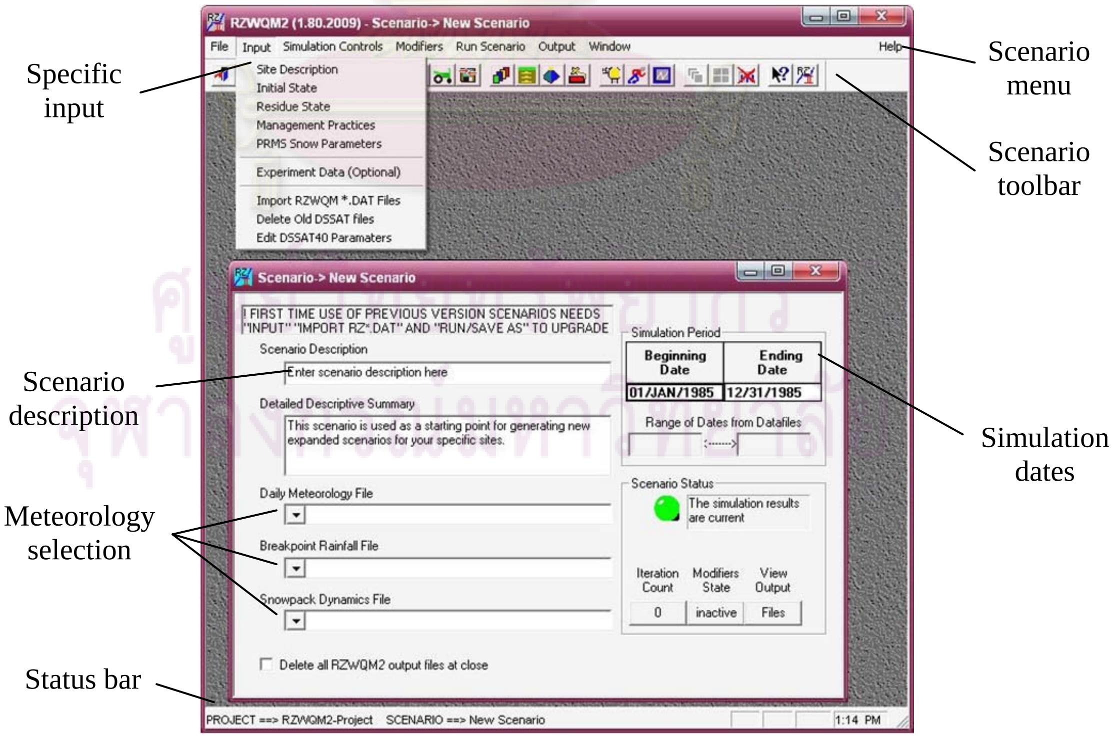

Figure 2-8 Scenario interface of the RZWQM

Normally, the RZWQM is used for determining water quality and effects from agricultural management practices on crop production and pesticide processes in wheat, soybean, and corn field. In this study, the RZWQM was used to simulate impacts of rice planting management practices and carbofuran application since rice is one of the most important agricultural product of Thailand.

CHAPTER III

METHODOLOGY

3.1 Research plan

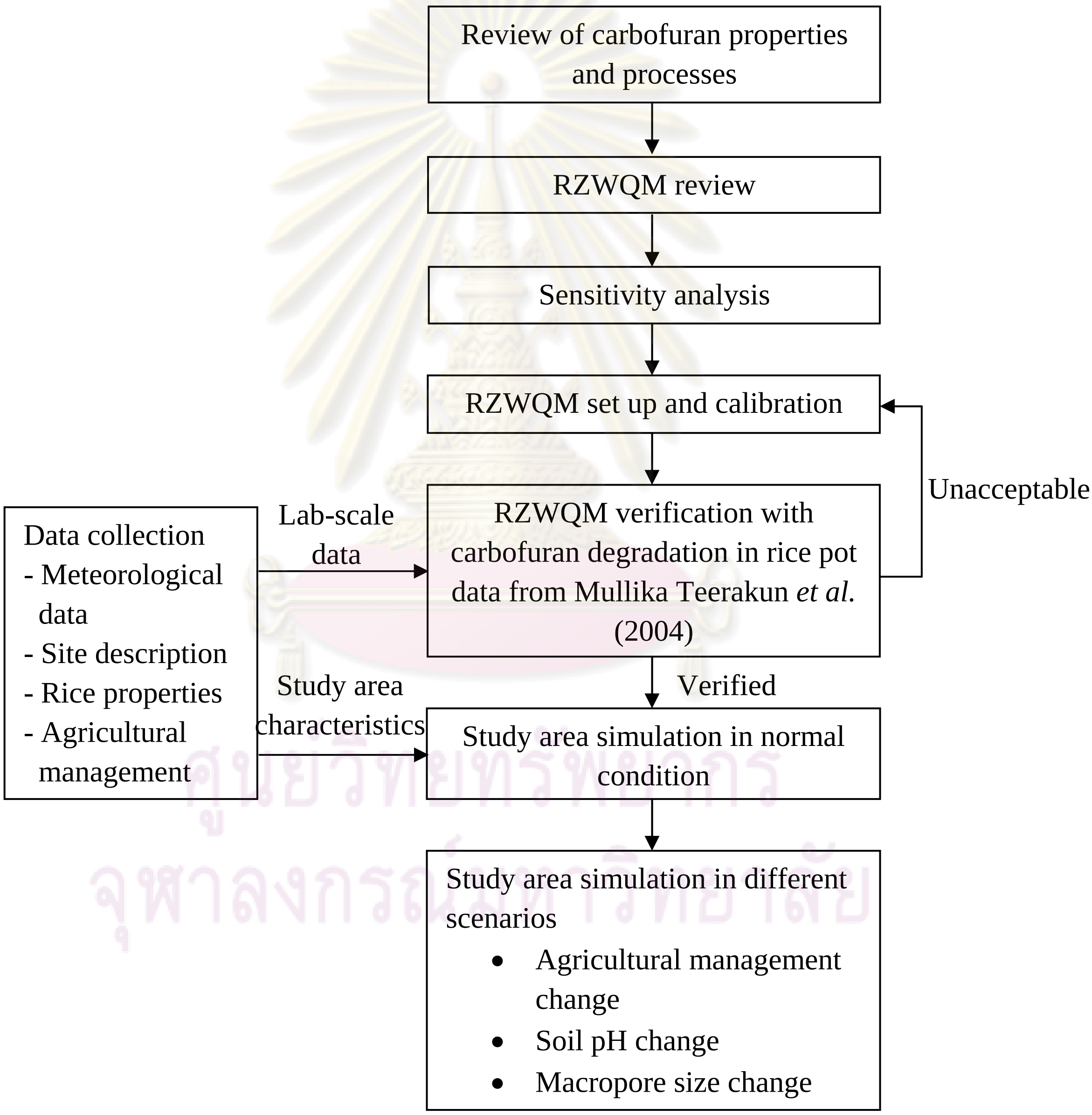

Figure 3-1 Flow diagram of research

3.2 Primary and secondary data collection

3.2.1 Breakpoint rainfall and daily meteorological data

The daily meteorology data of Khon Kaen Province were received from the Thai Meteorological Department (TMD). The meteorology station is located at 16°27'48" N, 102°47'12" E, and an elevation of 191.72 meters above sea level. The data from the TMD are breakpoint rainfall, daily minimum and maximum temperatures, daily wind run, day light hours, daily pan evaporation, and daily relative humidity (see Appendix B).

Since the RZWQM requires solar radiation in units of MJ m^{-2} day^{-1} but the TMD provides data in the unit of day light hours, derivation of the Penman-Monteith equation (Theeraphol Tungsomboun, 2006) was applied to convert the units of solar radiation as follows:

$$R_{ns} = 0.77 \times \left(0.25 + 0.50\frac{n}{N}\right) R_a \tag{3.1}$$

where R_{ns} = net shortwave radiation (MJ m^{-2} day^{-1}),

n = day light hours (hr),

N = maximum day light hours (hr), and

R_a = extraterrestrial radiation (MJ m^{-2} day^{-1}).

The R_a in Eq. (3.1) is described as follows:

$$R_a = 37.6 d_r (\omega_s \sin\varphi \sin\delta + \cos\varphi \cos\delta \sin\omega_s) \tag{3.2}$$

$$d_r = 1 + 0.033\cos(0.0172\, J) \tag{3.3}$$

where R_a = extraterrestrial radiation (MJ m^{-2} day^{-1}),

d_r = relative Earth-Sun distance,

δ	=	solar declination (rad),
φ	=	latitude (rad),
ω_s	=	sunset hour angle (rad), and
J	=	number of the day in the year.

The solar declination (δ) calculation can be achieved from the equation provided by Spencer (1971):

$$\delta = (0.006918 - 0.399912\cos r + 0.070257\sin r - 0.006758\cos 2r + 0.000907\sin 2r - 0.002697\cos 3r + 0.001480\sin 3r)(180/\pi) \quad (3.4)$$

$$r = 2\pi(J-1)/365 \quad (3.5)$$

where			
	δ	=	solar declination (degree)
	r	=	the day angle (rad), and
	J	=	number of the day in the year.

Iqbal (1983) provides a calculation of the sunset hour angle (ω_s) as follows:

$$\omega_s = \cos^{-1}(-\tan\emptyset\tan\delta) \quad (3.6)$$

where			
	ω_s	=	sunrise hour angle for a horizontal surface (degree)
	$\emptyset$	=	Geographic latitude, north positive (degree), and
	δ	=	solar declination angle(degree).

The maximum day light hours (N) in the Eq. (3.1) can be described by the Eq. (3.7) (Theeraphol Tungsomboun, 2006):

$$N = 7.64\omega_s \quad (3.7)$$

where N = the maximum day light hours (hr).

3.2.2 Site description data

Most area in Khon Kaen Province is used for agriculture, and 92.29% of rice agriculture in this province makes use of fertilizers and pesticides (Skulrat Ussanawarong *et al.*, 2007). The 0.028 ha rice field selected as the study area is located at Ban Nonmuang, Amphor Muang, Khon Kaen Province, as shown in Figure 3-2. It is located at 16°28’59.27” N, 102° 48’28.81” E, and elevation of 198 meters above sea level. Soil in this area has been classified in the Roi-Et soil series by the Land Development Department of Thailand, as sandy loam and sandy clay loam. Characteristics of the Roi-Et soil series are shown in Table 3-1.

Figure 3-2 Rice field used as the study area located in Khon Kaen Province

Table 3-1 Characteristics of the Roi-Et soil series (Kiti Malairogthsiri *et al.*, 2004)

Horizon	Depth (cm)	Soil type	pH	% sand	% silt	% clay
Ap	0-19	Sandy loam	5.2	67.9	11.6	20.5
BA	19-38	Sandy clay loam	5.5	62.8	16.2	21.0
Btg1	38-50	Sandy clay loam	5.5	65.4	9.6	25.0
Btg2	50-74	Sandy clay loam	5.0	63.2	13.3	23.0
BCg	74-93+	Sandy clay loam	5.1	65.3	14.2	20.5

A – Surface soil. It is a mineral soil layer with a highly organic matter accumulation and soil life. In addition, this layer holds iron, aluminum, organic compounds, and other soluble components.

B – Subsoil. This layer collects iron, aluminum, and organic compounds.

C – Substratum. It is a layer of separated soil parent material, and it may increase more soluble compounds that pass the B horizon.

g – gleyed soil - gray in color due to low O2 - reduction of Fe

p – plowing (only applied with the A horizon)

t – clay accumulation

Rawls *et al.* (1982) provide the typical values of the physical and hydraulic parameters of soil according to its texture, and Brakensiek *et al.* (1981) give the values for porosity distributions, residual water content, logarithm of pore size distribution index and bubbling pressure (Table 3-2).

Table 3-2 Default values of sandy loam and sandy clay loam soil used in the RZWQM (Ahuja *et al*., 2000; Brakensiek *et al*., 1981; Rawls *et al*., 1982).

Parameter	Sandy loam soil	Sandy clay loam soil
Particle density (g/cm^3)	2.650	2.650
Bulk density (g/cm^3)	1.450	1.595
Porosity	0.453	0.398
	(0.249 - 0.657)	(0.266 – 0.530)
Bubbling pressure (cm)[a]	14.660	28.080
	(3.400 – 62.200)	(5.600 – 141.500)
Pore size distribution index [a]	0.322	0.250
	(0.186 – 0.558)	(0.125 – 0.502)
2nd exponent for conductivity curve [a]	2.966	2.750
K_{sat} [a]	2.590	0.430
Residual water content [a]	0.041	0.068
	(0.000 – 0.171)	(0.000 – 0.206)
Saturated water content [a]	0.453	0.398
1/3 bar water content [a]	0.207	0.255
	(0.045 – 0.369)	(0.117 – 0.393)
1/10 bar water content [a]	0.263	0.308
15 bar water content [a]	0.095	0.148
	(0.000 – 0.223)	(0.022 – 0.274)

Table 3-2 Default values of sandy loam and sandy clay loam soil used in the RZWQM (Ahuja *et al*., 2000; Brakensiek *et al*., 1981; Rawls *et al*., 1982) (cont.)

Parameter	Sandy loam soil	Sandy clay loam soil
2nd intercept on conductivity curve [a]	7448.230	4135.810
1st exponent for conductivity curve [a]	0.000	0.000
Constant for theta curve [a]	0.000	0.000
Lateral K_{sat} to the drains (cm/hr)	14.000	14.000

[a] It is parameter used for calculating in Brooks-Corey Curve (see Appendix A)

Table 3-3 The other parameters of the site

Parameter	Value
Soil pH[1]	6.9
Crust conductivity (cm/hr)[2]	0.518
Field saturation fraction[2]	0.900
Mixing parameter (1/cm)[2]	4.400
1st horizon moisture depletion[2]	0.800
pH of rain water[6]	6.400
Albedo of dry soil[3]	0.230
Albedo of wet soil[3]	0.190
Albedo of crop at maturity[4]	0.200
Albedo of fresh residue[2]	0.800
Wind measurement height (m)[5]	10.550
Average daily sunshine fraction[2]	0.800
Average daily pan coefficient for the crop[2]	1.000

Table 3-3 The other parameters of site description (cont.)

Parameter	Value
C:N ratio of slow residue pool[2]	8.000
C:N ratio of fast residue pool[2]	80.000
C:N ratio of fast soil humus pool[2]	8.000
C:N ratio of intermediate soil humus pool[2]	10.000
C:N ratio of slow soil humus pool[2]	11.000
C:N ratio of carbon sink pool[2]	0.000
C:N ratio of aerobic heterotrophs pool[2]	8.000
C:N ratio of autotrophs pool[2]	8.000
C:N ratio of anaerobic heterotrophs pool[2]	8.000

[1]Pensri Plangklang (2008)

[2]Ahuja *et al.* (2000)

[3]JRC-IPSC and CRA-CIN (2009)

[4]Saptomo *et al.* (2004)

[5]The Thai Meteorological Department

[6]Assumption based on several literatures

Ahuja *et al.* (2000) recommended default values for the water content and soil cation exchange capacity in each soil layer (Table 3-4).

Table 3-4 Characteristics of each layer of soil

Soil layers	Depth (cm)	Volumetric water content	Temperature (°C)	Soil CEC (meq/100g)	Residual pesticide (μg/g soil)
1	0-19	0.1862	30	10.0	1.28[1]
2	19-38	0.2394	20	15.0	0.6
3	38-50	0.1405	19	15.0	0.5
4	50-74	0.1555	18	15.0	0.3
5	74-93+	0.1718	17	15.0	0.06

[1] Sureewan Sittijunda (2006)

Residual pesticide in the top layer is the amount of carbofuran directly measured in the study area. In the other layers, the amount of carbofuran is assumed based on application of carbofuran. The amount of carbofuran decreases with the increase in soil depth because the pesticide is used at the soil surface.

3.2.3 Pesticide data

The information of carbofuran required in the RZWQM is shown in the following table:

Table 3-5 Properties of carbofuran used in the RZWQM

Parameter	Value
Molecular weight (g/mole)[1]	221.26
Vapor pressure (mmHg)[2]	6×10^{-6}
Henry law's constant[3]	3.9×10^{-9}

Table 3-5 Properties of carbofuran (cont.)

Parameter	Value
Water solubility (mg/L) [1]	351
Volumetric soil water content (cc/cc)[4]	0.2
Photodegradation half-live at soil surface (days) [1]	138
Aerobic half-live at soil subsurface (days) [1]	22
Anaerobic half-live at soil subsurface (days) [1]	30
Acid dissociation (pKa)[5]	0
Base protonation (pKb) [5]	0
Frendlich isotherm (1/n) [2]	1
Adsorbed pesticide half-life (days) [1]	13
Organic-carbon sorption constant (Koc) (cc/g) [5]	22
Octanol-water partition coefficient (K_{ow}) (mg/l) [1]	17

[1]DPR Ecotox database (2002)

[2]Hornsby *et al.* (1996)

[3]Howard (1991)

[4]Ahuja *et al.* (2000)

[5]EMA pesticide properties database (2009)

3.2.4 Crop characteristics data

The rice cultivar in the study area is sticky rice strain RD6, which is one of the popular cultivar in Northeast Thailand. RD6 originates from genetic engineering using γ-rays to change the genetic of Khao Dawk Mali 105 (KDML105). The properties of RD6 are shown in Table 3-6.

Table 3-6 Properties of RD6

Parameter	Value
Length of growing season (days)[1]	180
Total seasonal nitrogen uptake rate (kg/ha)[2]	138
Maximum crop height (cm)[3]	154
Leaf area index[4]	4.2
Stover after harvest (kg/ha)[2]	1.087×10^4
C:N ratio of Stover material[5]	96.395
Max depth of roots (cm)[6]	106.1
Root biomass harvest (kg/ha)[7]	1.087×10^3
C:N ratio of root material[8]	96.395

[1]Farmer

[2]Ohnishi *et al.* (1999)

[3]Khonkaen Rice Seed Center

[4]Saptomo *et al.* (2004)

[5]Sureewan Sittijunda (2006)

[6]Fischer *et al.* (2003)

[7]Assumption from weight of Stover after harvest

[8]Assumption that it equal to C:N ratio of Stover material

3.2.5 Field management data

Most of field management data were acquired from a farmer in the study area. However, this information consists more or less of approximations; therefore, many assumptions, which are based on the life cycle and other characteristics of RD6, had been made to assign the actual month of management to input in the RZWQM. In this area, the rice field is a field where seeding rice is transplanted, also called *indirect seeding*. Since agriculture in the area mostly relies on a natural water resource, i.e., rainfall, the activities in each month are presented in Table 3-7.

Table 3-7 Step of rice planting in the study area

Month	Planting step
May	• Plough roughly for the first time in order to turn over the soil surface and destroy weeds in the field. • Plough in regular furrows for the second time to wipe out weeds and decrease soil particle size. • Rake over the soil surface and add 31.25 kg of carbofuran per ha over the soil surface. • Plant about 2.2 x 10^3 kg per ha of rice is seeds.
July	• Transplant the rice sprouts, allowing for row spacing of about 25 cm. • Add 75 kg/ha of organic fertilizer and 16 kg/ha of chemical fertilizer (16-8-8) onto the field.
August	• Add 37.50 kg/ha of chemical fertilizer (15-15-15)
September	• Add 55.15 kg/ha of organic fertilizer.
November	• Harvest

3.3 Determination of ammonium in organic fertilizer

Since different types of organic fertilizer contain dissimilar nutrient quantities but generally have the same proportion of nutrients, the ammonium concentration in the organic fertilizer applied in the study area was examined by a NH_3 probe (WTW GmbH, NH_4 500/2, Germany). The standard curve was prepared from the ammonia standard solutions (1, 10, and 100 mg-N/L). 1 g of fertilizer was weighted and 9 ml of deionized water was added. Then 100 µl of 10 M NaOH was offered and lastly, the NH_3 probe was used to measure the ammonia concentration.

3.4 Sensitivity analysis

Parameters and processes that play significant role in dissipation/degradation of carbofuran were determined by sensitivity analysis. The methodology of sensitivity analysis followed Lenhart *et al.* (2002) method. Sensitivity index (I) was calculated to express the model parameter sensitivity as shown in Eq. (3.8). It is a ratio between relative changes of model output affected from change of model parameter.

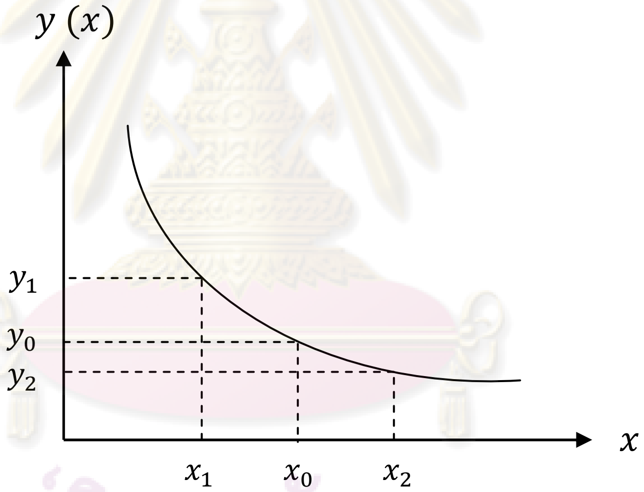

Figure 3-3 Representation of relative between output y and parameter x

$$I = \frac{(y_2 - y_1)/y_0}{2\Delta x/x_0} \tag{3.8}$$

$$x_1 = x_0 - \Delta x \tag{3.9}$$

$$x_2 = x_0 + \Delta x \tag{3.10}$$

where I = sensitivity index (dimensionless),

x_0 = initial value of parameter x,

y_0 = model output calculated with x_0,

y_1 = model output calculated with x_1, and

y_2 = model output calculated with x_2.

After sensitivity index of parameter was calculated, the parameter sensitivity was ranked into four classes as shown in Table 3-8.

Table 3-8 Sensitivity classes (Lenhart *et al.*, 2002)

Class	Sensitivity index (I)	Sensitivity
I	$0.00 \leq \lvert I \rvert < 0.05$	Small to negligible
II	$0.05 \leq \lvert I \rvert < 0.20$	Medium
III	$0.20 \leq \lvert I \rvert < 1.00$	High
IV	$\lvert I \rvert \geq 1.00$	Very high

In this research, Δx was assumed to be equal to 25 percentage of parameter x, and output y is rate constant overall of carbofuran (see Appendix C). The parameters (x) in RZWQM that were used for sensitivity analysis consists of:

- Rate constant of dissipation/degradation process that only one process was available in each time
- Soil hydraulic properties
- Microorganism population

3.5 RZWQM calibration

3.5.1 Carbofuran degradation in rice pot data from Mullika Teerakun *et al*. (2004)

Carbofuran degradation information was obtained by lab-scale studies at Khon Kaen University. Mullika Teerakun *et al.* (2004) studied the phytoremidiation ability of plants to degrade carbofuran in rice soil. Twelve species of plants were cultivated in 8 inch diameter plastic pots loaded with rice soil contained 5 mg/kg of carbofuran. The rice soil was taken from the rice field located at Ban Non-Reung, Amphur Muang, Khon Kaen Province, Thailand. All pots were watered everyday and placed alternatively in a greenhouse on a bench and then outside every two weeks. The concentration of carbofuran was calculated using a modified first-order kinetic model, which is expressed as follows:

$$C_t = C_0 e^{-kt} + Ya \tag{3.11}$$

where C_t = concentration of carbofuran as a function of time (kg/ha),

C_0 = initial concentration of carbofuran (kg/ha),

k = rate constant (day^{-1}),

t = time (days), and

Ya = asymptotic estimate of concentration of carbofuran (kg/ha).

This research concluded that carbofuran was discovered mostly in the stems and leaves, showing the ability of plants to absorb carbofuran. In addition, carbofuran accumulated well in *Helianthus annus* L. (sunflower), *Brassica* spp. (cabbage), *Oryza sativa* L. (rice), *Typha angustifolia* Linn. (cattail), and *Brasica* spp. (chinese-kale). The k and Ya values of the rice-planted soil were 0.11 and 1.06 kg/ha, respectively. Soil was categorized as loam soil, and other properties of the soil are shown in Table 3-9.

Table 3-9 Soil properties in Ban Non-Reung (Mullika Teerakun *et al*., 2004)

Property	Value
Soil type	Loam
Organic matter (%)	0.3
pH	4.95
Sand (%)	42.5
Silt (%)	32.5
Clay (%)	25.0
Bulk density (g/cm^3)	1.3
Total nitrogen (%)	0.032
C/N ratio	7.84

3.5.2 Soil properties used for model calibration

Soil density and hydraulic properties of loam soil that are used for model calibration are shown in Table 3-10.

Table 3-10 Default values of loam soil used for model calibration (Ahuja *et al*., 2000; Brakensiek *et al*., 1981; Rawls *et al*., 1982)

Parameter	Loam
Particle density (g/cm^3)	2.650
Porosity	0.463 (0.287 – 0.639)
Bubbling pressure (cm)[a]	11.2 (1.6 -76.4)
Pore size distribution index [a]	0.220 (0.137 – 0.355)
2nd exponent for conductivity curve [a]	2.411
K_{sat} [a]	1.320
Residual water content [a]	0.027 (0.000 – 0.121)
Saturated water content [a]	0.463
1/3 bar water content [a]	0.270 (0.120 – 0.420)
1/10 bar water content [a]	0.296
15 bar water content [a]	0.117 (0.021 0.213)
2nd intercept on conductivity curve [a]	805.98
1st exponent for conductivity curve [a]	0.000

Table 3-10 Default values of loam soil used for model calibration (Ahuja *et al*., 2000; Brakensiek *et al*., 1981; Rawls *et al*., 1982) (cont.)

Parameter	Loam
Constant for theta curve [a]	0.000
Lateral K_{sat} to the drains (cm/hr)	14.000
Dry volume heat capacity (J/mm^3/°C)	0.900

[a] It is a parameter used for calculating in Brooks-Corey Curve

3.5.3 Assumption for model calibration

1) Amount of irrigated water

Since there was not a certain amount of irrigated water in the Mullika Teerakun *et al.* (2004) research, the moisture holding capacity of loam soil (NDSU, 1996) was used to calculate the quantity of the water. The range of 0.17 to 0.23 cm/cm-soil was used and multiplied by soil depth (20 cm). Then 3.4 to 4.6 cm of water was applied for irrigation.

2) Crop characteristics

In the generic plant growth module, the crops provided by the RZWQM are corn, soybean, and wheat; rice parameters, however, cannot be entered. In order to solve this problem, wheat parameters were adjusted with rice properties and used as the crop in the simulation. Available parameters for rice properties, which were edited in the database, are provided in Table 3-6.

3.6 RZWQM simulation in the study area

After the result of model calibration and verification, which is degradation of carbofuran, was fitted with degradation data of Mullika Teerakun *et al.* (2004), the validated RZWQM was used to predict the meteorological data and fate and transport of carbofuran under long term application (10 years) in rice field.

3.6.1 Assumption for model simulation in the study area

Since water retention process was not included in RZWQM that different from practical rice planting, 30 cm of irrigated water was applied everyday during June to October in each year to maintain free water level above soil surface. This water amount was calculated to make it exceeded the moisture capacity of soil in the study area. Its moisture capacity is in the range of 0.11 to 0.15 cm/cm-soil (NDSU, 1996).

3.6.2 Scenario I: agricultural management practices alteration

Prices of rice on the world market have more than doubled in 2008 (BBC News, 2008; CGIAR, 2008), and there was loss from natural disaster; therefore, some farmers changed their agricultural management practices to payback. If rice was cultivated four times per year instead of one time per year, the input data that categorized in field management data was changed as shown in the following table.

Table 3-11 Step of rice planting four times per year in the study area

Month	Step of planting
January	• Rough plowing and in regular furrows • Application of carbofuran • Rice planting • Application of fertilizer
March	• Application of fertilizer
April	• Rough plowing and in regular furrows • Application of carbofuran • Rice planting • Application of fertilizer
June	• Application of fertilizer

Table 3-11 Step of rice planting four times per year in study area (cont.)

Month	Step of planting
July	• Rough plowing and in regular furrows • Application of carbofuran • Rice planting • Application of fertilizer
September	• Application of fertilizer
October	• Rough plowing and in regular furrows • Application of carbofuran • Rice is planting • Application of fertilizer
December	• Application of fertilizer

3.6.3 Scenario II: soil pH modification

Currently, there are more city and industry growth than in the past. These activities increase the pollution in the atmosphere. Acid rain is one form of increased pollution, and when it occurs, the more acidic pH of the rain decreases soil pH, making carbofuran more stable in rice soil.

- soil pH was assumed to be equal to 4.0 for acidic soil
- soil pH was assumed to be equal to 10.0 for solving carbofuran accumulated in the applied area

3.6.4 Scenario III: change of macropore size

There is drought occurred in Thailand every year; therefore, the pore size in soil is altered. Macropore size in the rice field was supposed to be the worst case that was equivalent to 0.900 cc-macroporosity/cc-soil.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Determination of ammonium in organic fertilizer

Since there was certain concentration of ammonium in organic fertilizer, the sample was collected from the farmer to analyze the amount of ammonium. Concentration of ammonium and standard curve are shown in Table 4-1 and Figure 4-1, respectively.

Table 4-1 Concentration and conductivity of ammonium standard solutions

Concentration of ammonium (mg-N/l)	Conductivity (mV)
1	-7.3
10	-67.3
100	-126.4

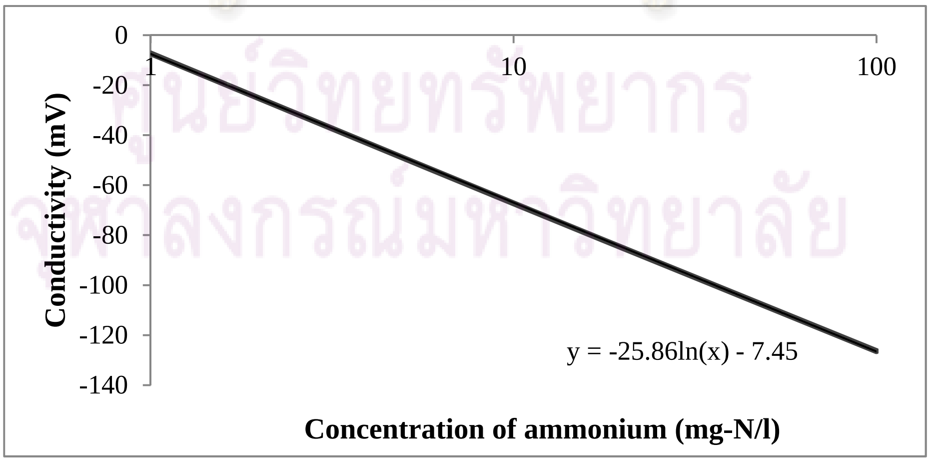

Figure 4-1 Standard curve of ammonium

In determinaing the ammonium content in organic fertilizer, the conductivity of sample solution was measured to be -123.7; therefore, the ammonium concentration was 89.6 mg-NH_4/l or 0.8064 mg- NH_4/1 g-fertilizer. In the study area, about 55.15 kg/ha of fertilizer was application, so a NH_4 application of 0.044 kg was used as the input data.

4.2 Model sensitivity

- **Dissipation/degradation processes**

The sensible dissipation/degradation processes were calculated by using Eq. (3.8). The results in Table 4-2 show that the processes, which play significant role on dissipation/degradation of carbofuran in rice field are soil surface photodegradation, soil profile lumped, soil subsurface aerobic, soil subsurface anaerobic, and soil subsurface abiotic degradation.

Table 4-2 Sensitivity of dissipation/degradation processes

Process	Sensitivity index	Sensitivity
Foliar biotic	0.00	Small to negligible
Foliar abiotic	0.00	Small to negligible
Foliar photodegradation	0.00	Small to negligible
Residue biotic	0.00	Small to negligible
Residue abiotic	0.00	Small to negligible
Residue photodegradation	0.00	Small to negligible
Soil surface biotic	0.02	Small to negligible
Soil surface volatilization	0.02	Small to negligible
Soil surface photodegradation	0.05	Medium
Soil profile lumped	0.07	Medium

Table 4-2 Sensitivity of dissipation/degradation processes (cont.)

Process	Sensitivity index	Sensitivity
Soil subsurface aerobic	0.12	Medium
Soil subsurface anaerobic	0.09	Medium
Soil subsurface abiotic	0.12	Medium

When concentration of carbofuran from each process simulation was ploted by varying day, there are only three lines since all processes that excepting soil subsurface aerobic and abiotic degradation processes gave results nearly the same values as no degradation process.

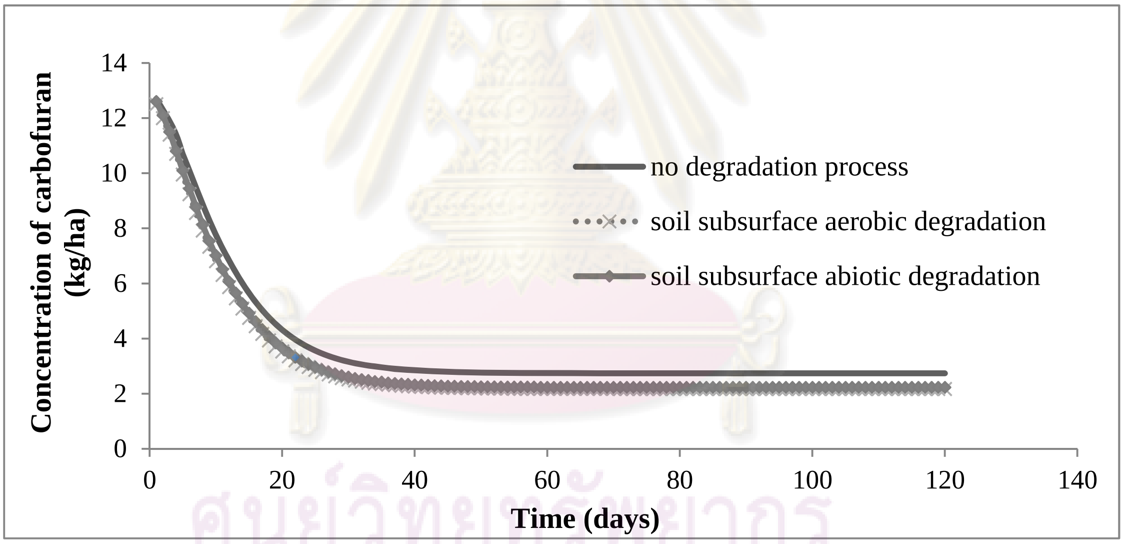

Figure 4-2 Degradation of carbofuran from soil subsurface aerobic and abiotic degradation processes

From the highest sensitivity index, the dissipation/degradation processes that had to calibrate first are soil subsurface aerobic and abiotic processes.

- **Soil hydraulic properties**

Since carbofuran fate and transport highly depends on amount of water in the system, soil hydraulic parameters used for Brook-Corey curve (see Appendix A) were analyzed. The sensitivity of each parameter is presented in Table 4-3.

Table 4-3 Sensitivity of soil hydraulic parameters

Parameter	Sensitivity index	Sensitivity
Bubbling pressure for conductivity curve (cm)	0.37	High
Bubbling pressure for theta curve (cm)	0.40	High
Pore size distribution index	0.11	Medium
2^{nd} exponent for conductivity curve	1.95	Very high
$\boldsymbol{K_{sat}}$	0.26	High
Residual water content	0.62	High
Saturated water content	0.31	High
1/3 bar water content	0.00	Small to negligible
1/10 bar water content	0.00	Small to negligible
15 bar water content	0.00	Small to negligible
2^{nd} intercept on conductivity curve	0.00	Small to negligible

Table 4-3 indicates that the most sensible soil hydraulic parameter is the 2^{nd} exponent for conductivity curve, while water content and 2^{nd} intercept on conductivity curve are not sensitive to the RZWQM simulation. Accordingly, the first parameter of soil hydraulic properties that need to consider is 2^{nd} exponent for conductivity curve. In addition, it is also found that minimum values in range of recommended information from Brakensiek *et al.* (1981) and Rawls *et al.* (1982) provided the best degradation when compared with default values (Figure 4-3).

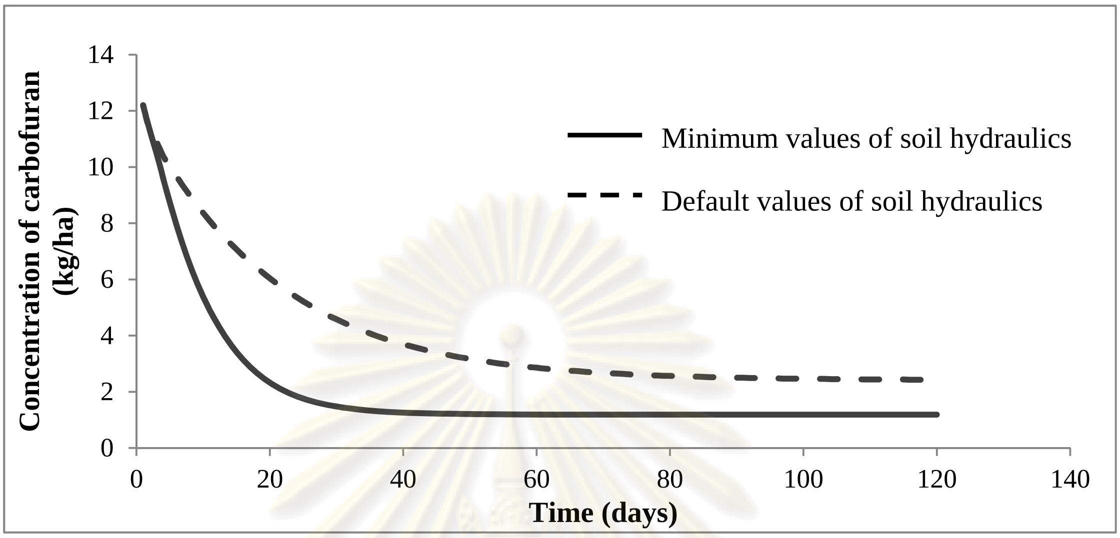

Figure 4-3 Chang of soil hydraulic parameters

- **Microorganism population**

From changing of microorganism population in the system, the output shows that microorganism and their activity have less effect on fate and transport of carbofuran in rice soil. The sensitivity index was 0.075 that lead to be classified in medium sensitivity.

Bayless *et al.* (2008) stated that in the RZWQM calculation, microorganism play significant role in nutrient process by degrading organic matter in soil. Once soil condition is changed, sorption and degradation properties of the pesticide are altered that cause high or less accumulation of the pesticide in the area. For biodegradation process, microbes have fewer effects on this pesticide process when compare with in nutrient process.

4.3 Case I: the RZWQM calibration and the study area simulation

4.3.1 Case I: the RZWQM calibration

The results of the RZWQM calibration are separated into two parts. The first part is the outputs of plant growth and soil condition. The second part is dissipation/degradation of carbofuran from the RZWQM compared with data from Mullika Teerakun *et al.* (2004) experiment.

1) Simulation of plant growth and soil condition related to the atmosphere

In Figure 4-4, at day 120, the plant height did not reach the maximum value for the reason that the length of the growing season was lower than the normal life cycle for rice (180 days). Rice growth depends on the environmental fitness of the area. It requires suitable temperature, soil water content, and soil nutrients that lead to a reduction of the soil water content and N concentration. After the lag phase (Figure 4-5), the amount of N uptake increased due to the demand of N for tillering and producing grains. Crop transpiration also has an impact on environmental fitness owing to soil water variation. The transpiration rate can be computed by the S – W model (Figure 2-5). In Figure 4-6, transpiration levels raised as the rice developed and it decreased the soil water content (Figure 4-7). Soil water appeared from infiltration during rainfall or irrigation events and redistribution between the events. Seepage, in Figure 4-8, is water that flows through soil and leaves at the bottom of the system. The seepage occurs when soil receives more water than it can hold (i.e., it exceeds its soil water capacity). However, when there were several related processes occurring concurrently with rainfall or irrigation events such as plant transpiration (Figure 4-6), seepage decreased mainly because some amount of the water was used by the plant. In Figure 4-9, the potential evapotranspiration (PET) reflects the plant transpiration and soil evaporation in the system. At day 41, the PET shows the lowest value, and it corresponds to meteorological data (Figure B-5 and B-6). that shows low evaporation and high relative humidity on that day.

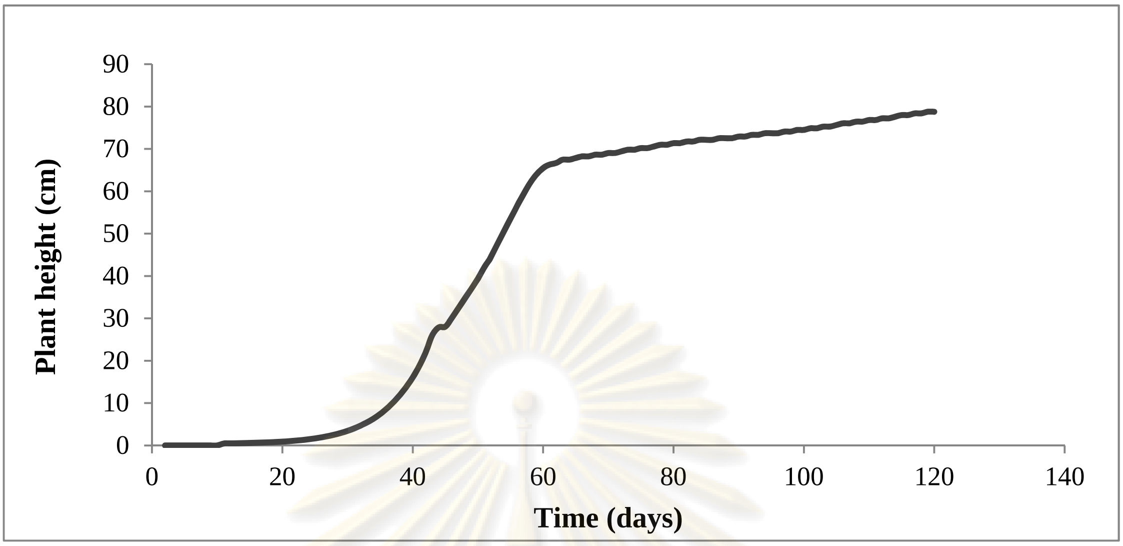

Figure 4-4 Plant height

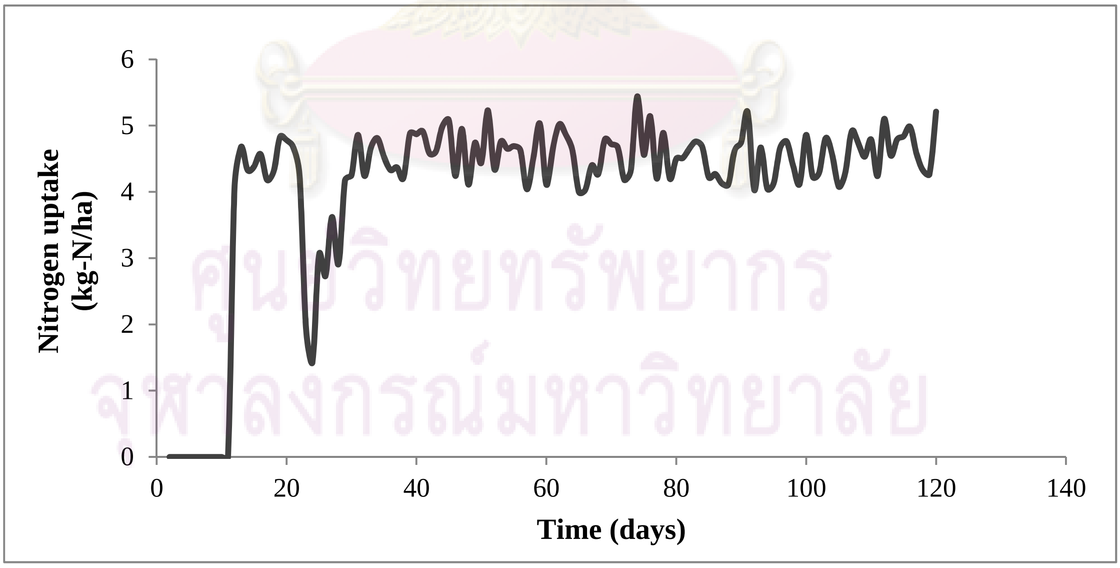

Figure 4-5 N uptake by plant

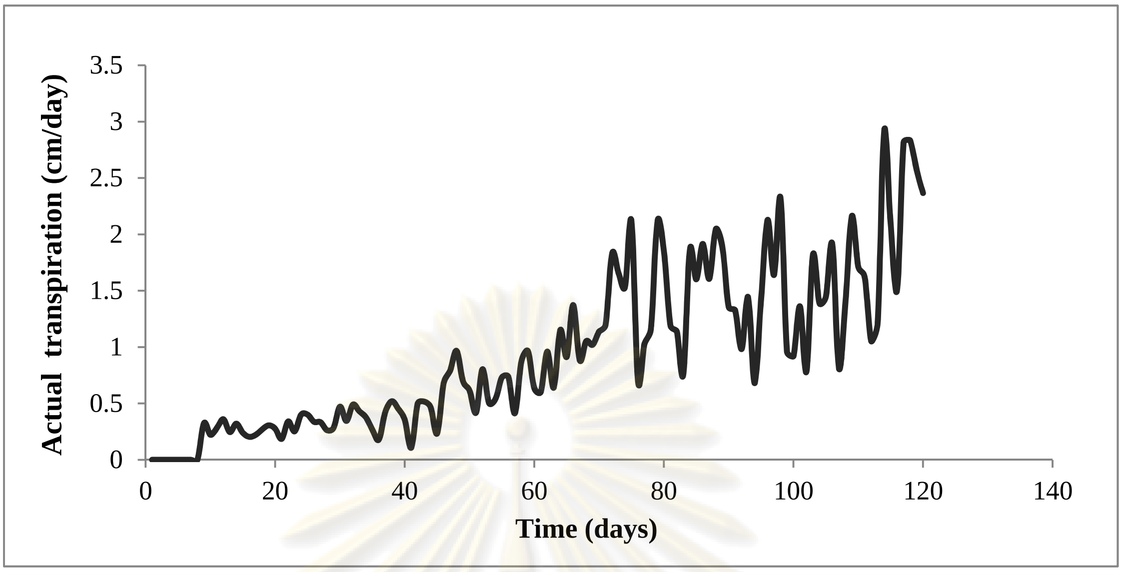

Figure 4-6 Plant transpiration

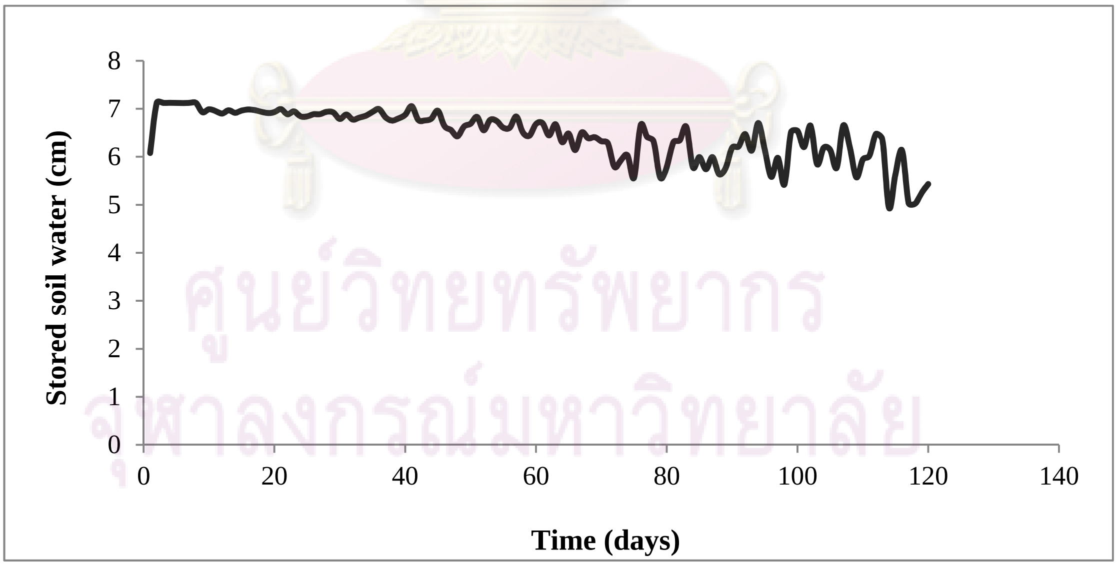

Figure 4-7 Water content in soil

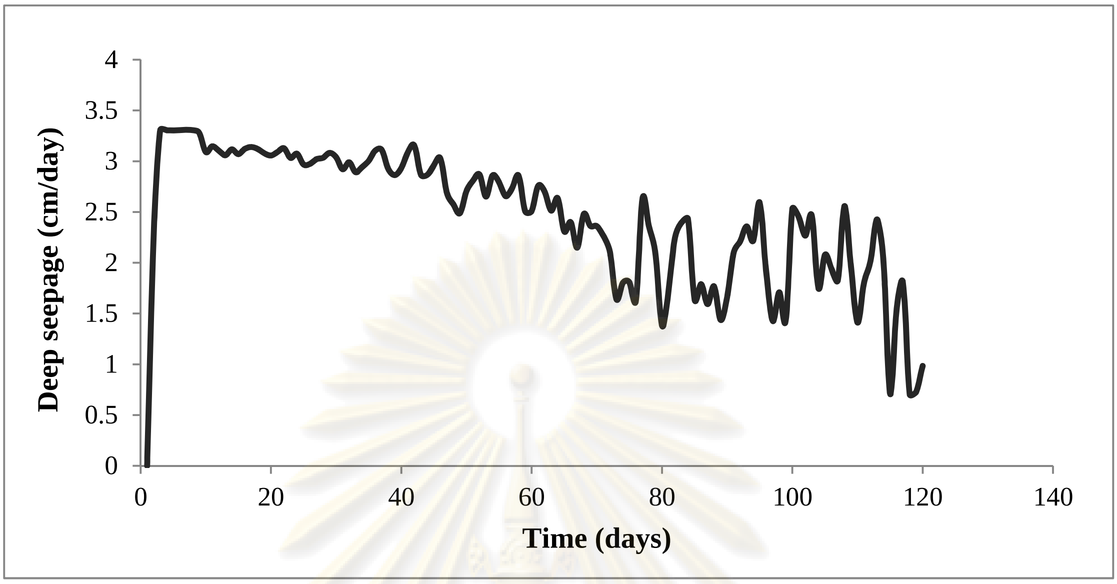

Figure 4-8 Seepage

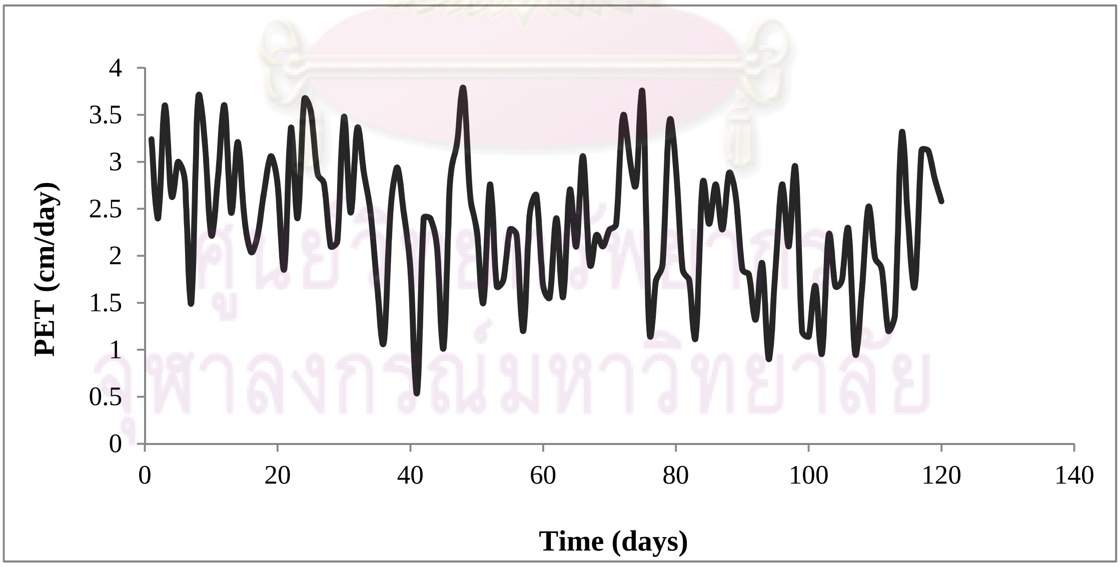

Figure 4-9 Potential evapotranspiration

The above-mentioned diagrams (Figure 4-4 to Figure 4-9) show the values in the whole soil horizon, while Figure 4-10 to Figure 4-13 show the N and water uptake of plants and the remaining water concentration in the soil layer.

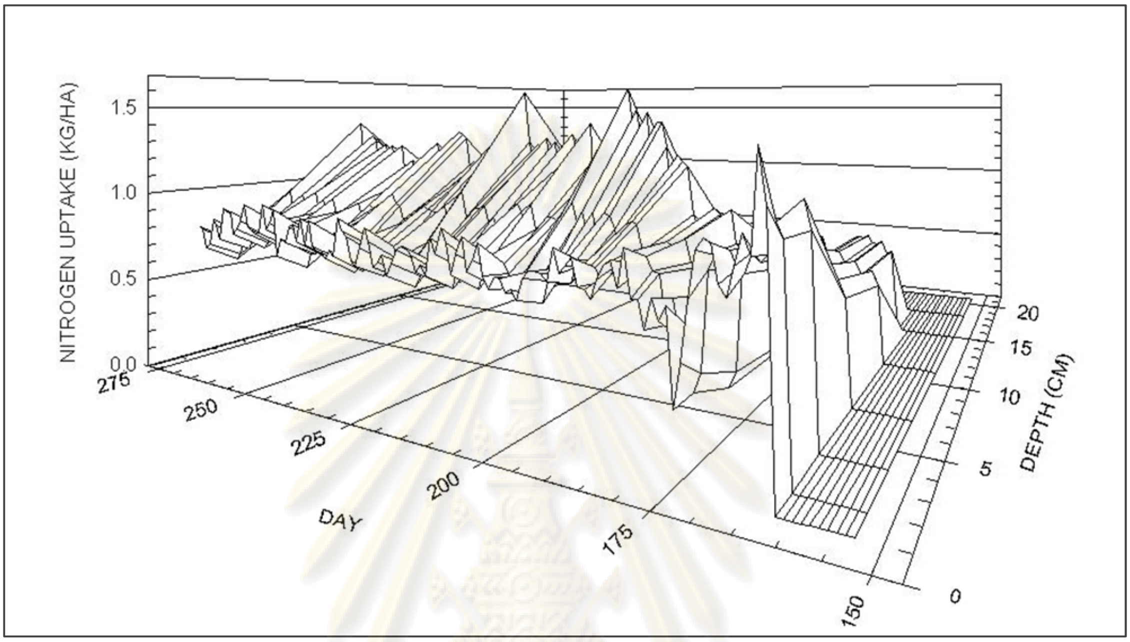

Figure 4-10 Plant N uptake in the soil layer

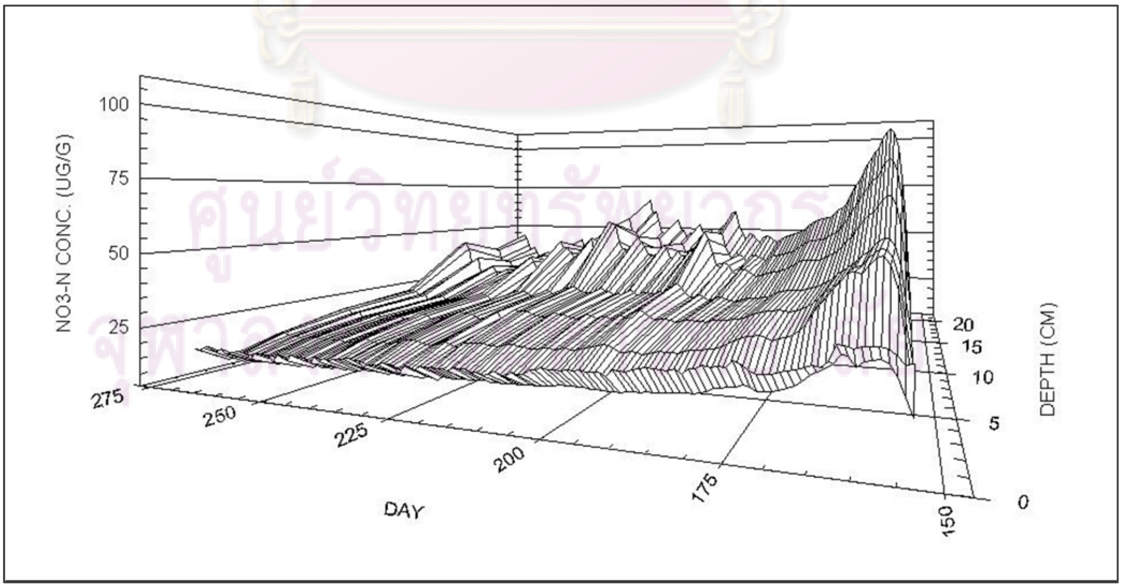

Figure 4-11 N concentration in the soil layer

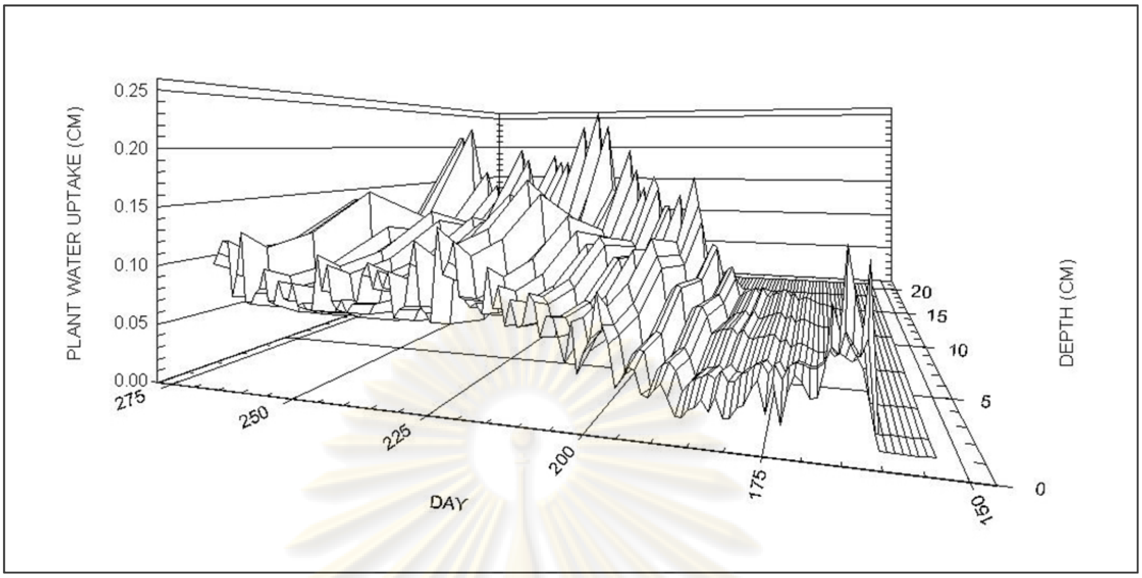

Figure 4-12 Plant water uptake in the soil layer

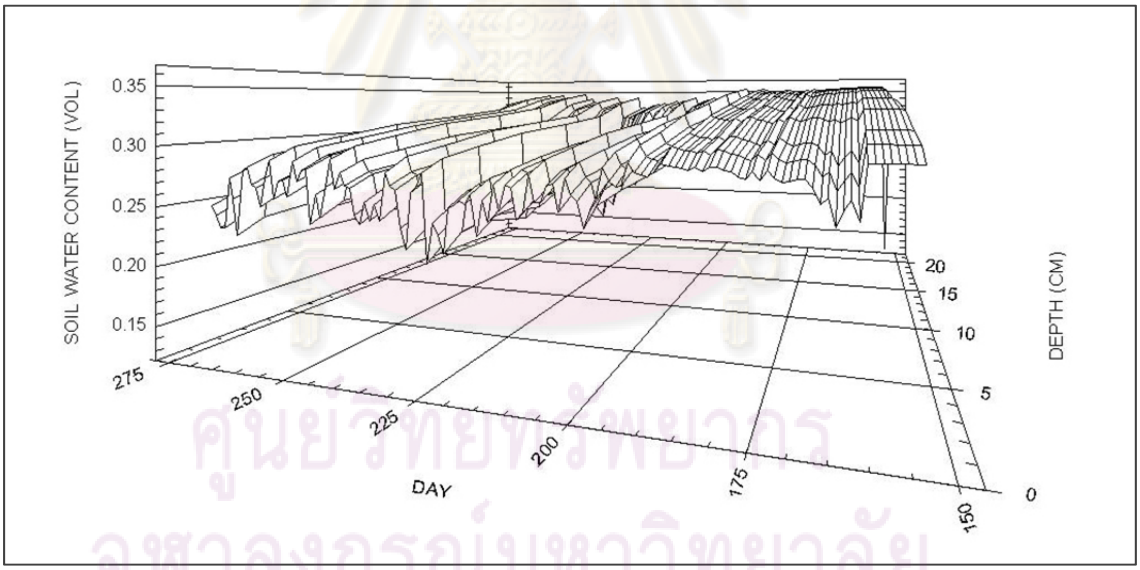

Figure 4-13 Water content in the soil layer

2) Case I: Dissipation/degradation of carbofuran

Since Mullika Teerakun *et al.* (2004) experiment focused on degradation process of carbofuran in rice soil, side effects from the pesticide washout were reduced by water recirculation. In contrast, the RZWQM cannot simulate the water recirculation process. Therefore, water leaching was diminished by using long desorption half-life and high fraction of adsorption site in model calibration as shown in Table 4-4.

Table 4-4 Desorption parameters in the RZWQM calibration for Case I

Parameter	Case I
Irrigated water (cm)	3.67
Desorption half-life (days)	140
Fraction of adsorption site	0.95

Then the rate constant for dissipation/degradation process were calibrated (Table 4-5). This table indicates that the processes, which play significant role in degradation of carbofuran, are soil subsurface aerobic degradation, soil subsurface anaerobic degradation, soil subsurface abiotic degradation, and soil profile lumped degradation. As most important degradation processes are soil subsurface processes, it may cause by properties of carbofuran. Carbofuran has high water solubility and low adsorption coefficient (Evert, 2002), so water will simply mix the pesticide from soil surface and transport into soil profile. Figure 4-14 shows concentration of carbofuran compared between Mullika Teerakun *et al.* (2004) and the RZWQM simulation.

Table 4-5 Effective k values of degradation of carbofuran for Case I

Processes of degradation	k values (day^{-1})
Soil surface biotic	0.000
Soil surface volatilization	0.000
Soil surface photodegradation	0.005
Soil profile lumped degradation	0.087
Soil subsurface aerobic dagradation	0.116
Soil subsurface anaerobic degradation	0.092
Soil subsurface abiotic degradation	0.107

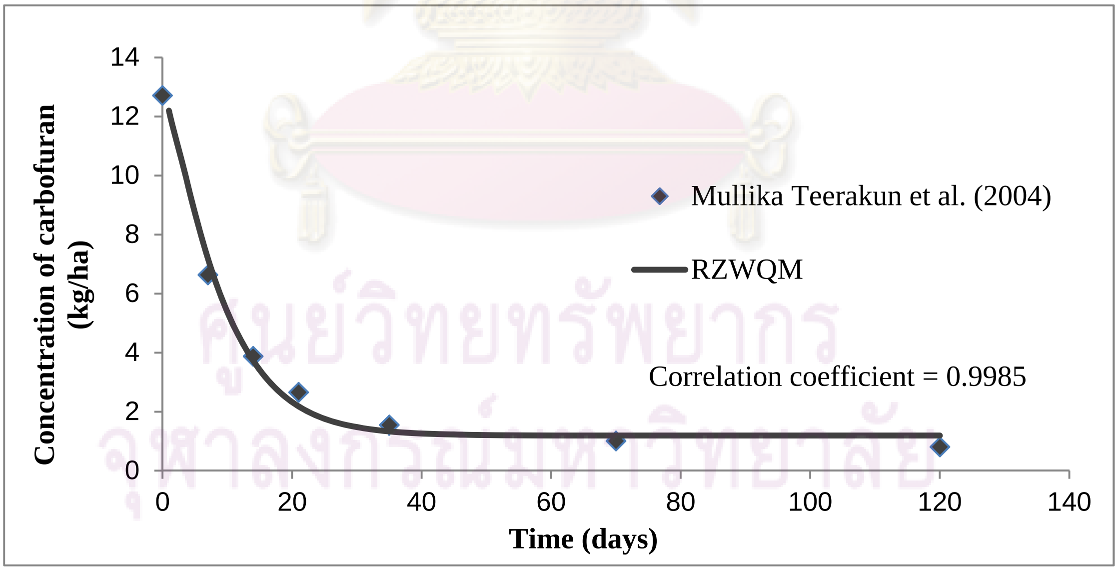

Figure 4-14 Concentration of carbofuran in rice soil (Case I)

From the modified first-order kinetic model, $C_t = C_0e^{-kt} + Ya$, rate constant (k) and residual carbofuran (Ya) were calculated. The k and Ya of Mullika Teerakun *et al.* (2004) are 0.11 and 1.06 kg/ha, and in this research are 0.12 and 1.19 kg/ha, respectively. The highest peak appeared since there was application of carbofuran in soil, and it went deeper into soil profile after the use in a few days.

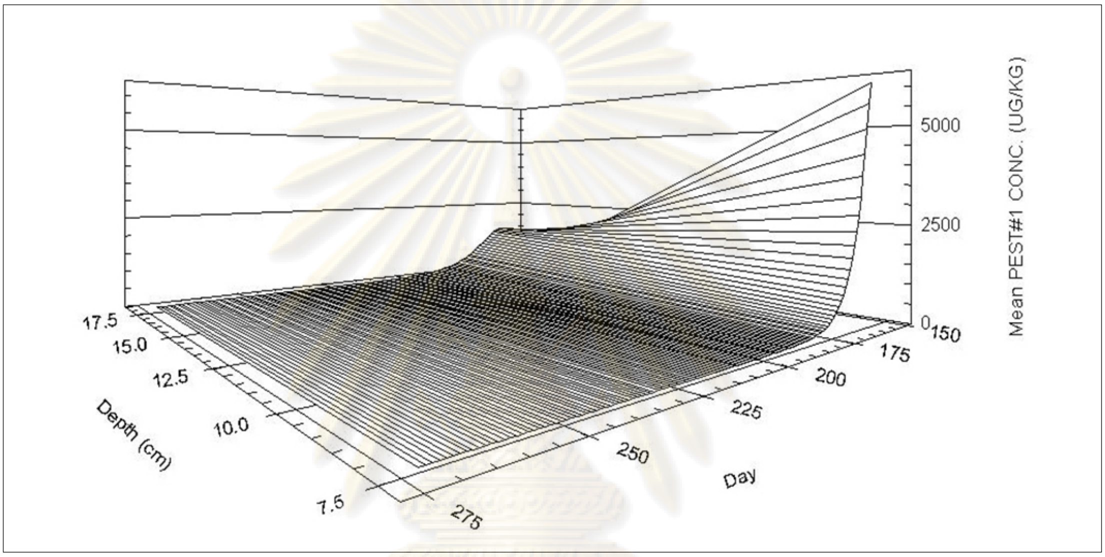

Figure 4-15 Concentration of carbofuran in soil layer

Figure 4-15 shows the output of carbofuran in soil provided by the RZWQM, and Figure 4-16 is the pesticide concentration in each soil horizon. At top soil layer, carbofuran concentration reduced in a few days that lead to increased in its amount in next layer and then decreased.

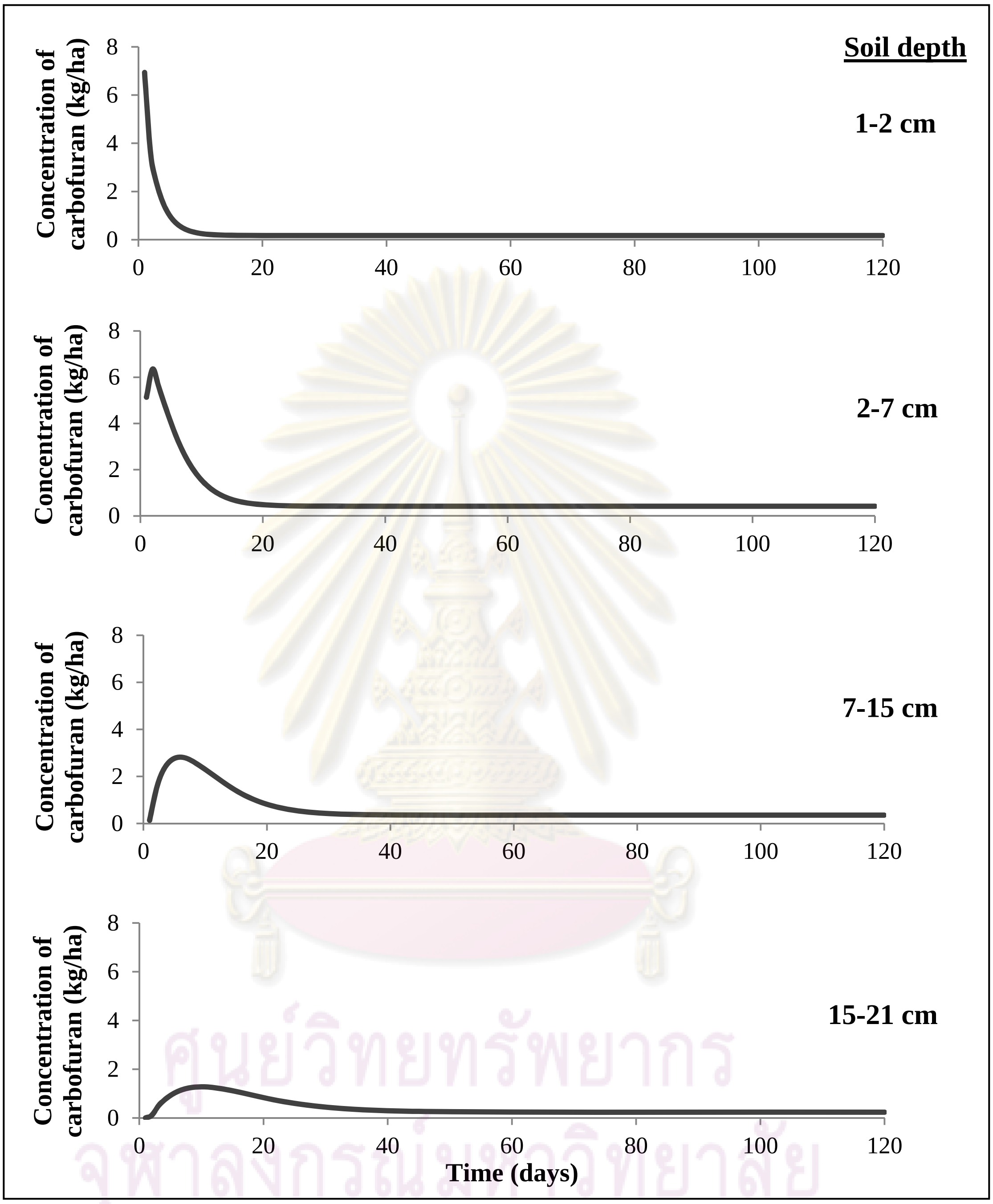

Figure 4-16 Concentration of carbofuran in soil horizon

In carbofuran dissipation, decrease of carbofuran concentration in soil is mainly caused by water leaching. This is because carbofuran has high water solubility and low adsorption coefficient. In the early stage, with high seepage (Figure 4-8), carbofuran sharply decreased, and the decreasing rate was reduced because of lower seepage. Furthermore, soil water content has effect on carbofuran in soil. Li and Wong (1980) stated that degradation rate of carbofuran is greater when water content in soil becomes higher. Figure 4-7 shows that soil contained high water content in early condition; therefore, it would result in high degradation rate of carbofuran in early stage.

When the pesticide was applied in soil, in the beginning, the highest proportion of the pesticide was appeared in kinetic pool. The rest small amount of carbofuran appeared in soil water and adsorbed pool (Figure 4-17). The pesticide residues that degraded slowly from these pools then accumulated in bound pool. Accordingly, concentration in bound pool increased as time elapses until reached steady stage and acted as residual carbofuran. Its quantity was stable since the RZWQM assumes that unbound pesticide is more degraded than bound pesticide (Malone *et al*., 2004b). This figure also illustrates that kinetic area provided the maximum dissipation rate.

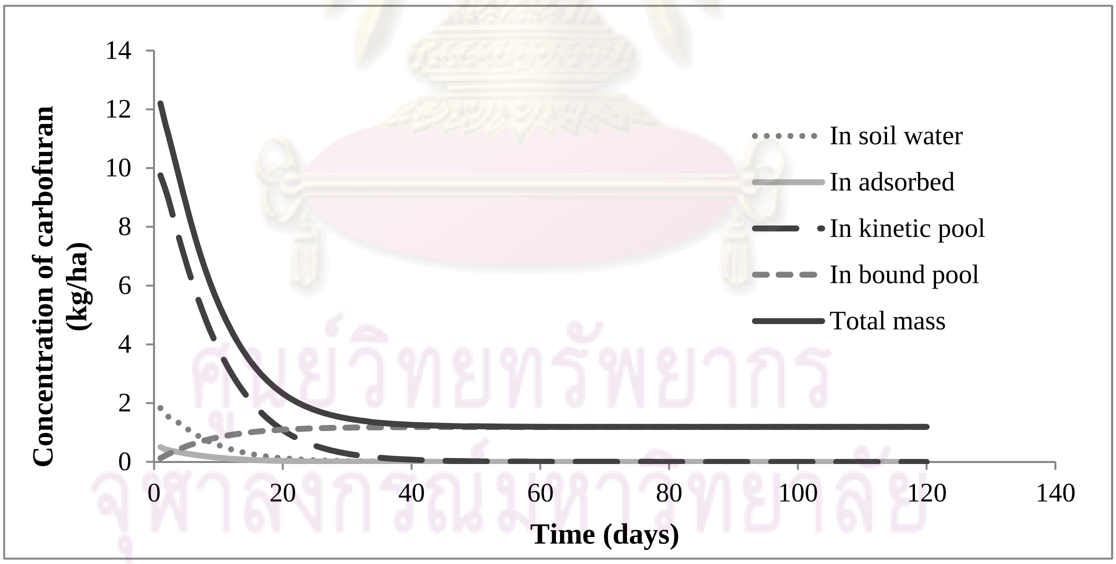

Figure 4-17 Concentration in several soil compartments

4.3.2 Case I: carbofuran degradation in the study area under normal condition

1) Simulation of soil condition related to the atmosphere

According to difference in water sources applied for rice planting between Mullika Teerakun *et al.* (2004) experiment and the study area, which are irrigated water and rain, respectively, the input parameters of water properties were not the same. This resulted in dissimilarity of soil condition such as soil pH and concentration of chemicals in soil. The examples of soil condition in the past ten year are shown in Figure 4-18 to 4-19.

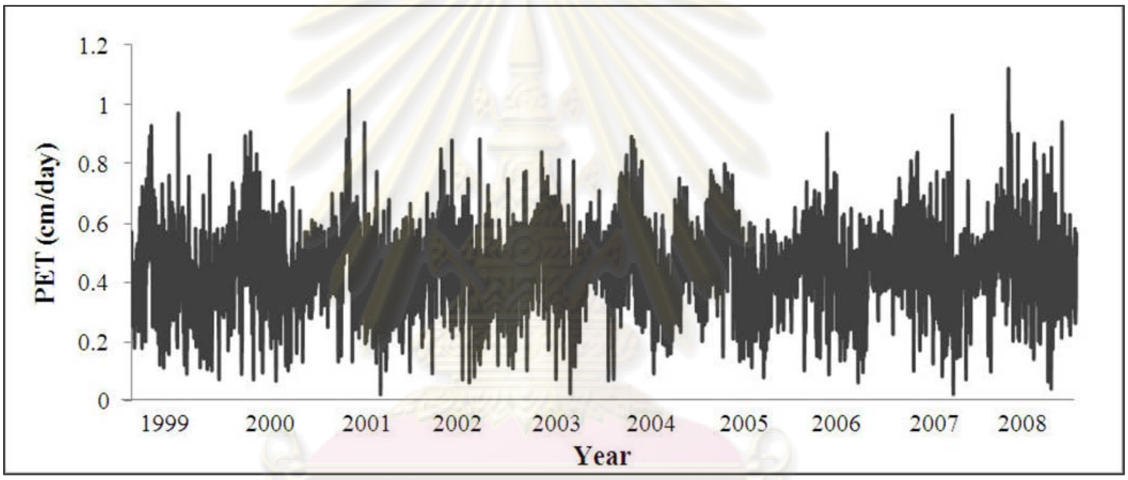

Figure 4-18 Potential evapotranspiration in the study area from the RZWQM

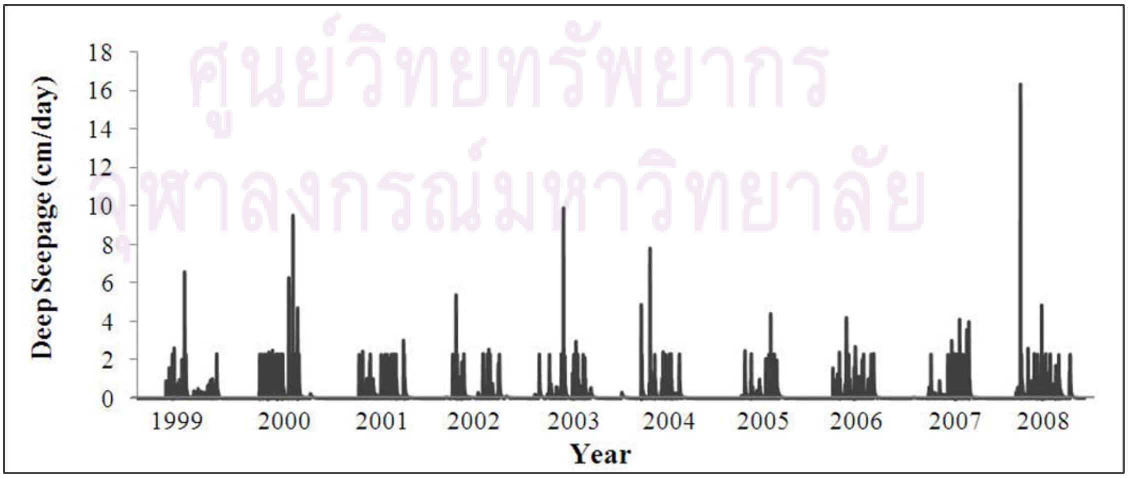

Figure 4-19 Seepage in the study area from the RZWQM

In rice field, seepage appeared due to rainfall event, and its amount depended on quantity of rain, i.e., when there was high rainfall, the high seepage level occurred. Furthermore, rice planting management also has impact on seepage such as tillage. It made more macropore in the rice field, so water can move in higher amount and deeper that lead to high seepage.

2) Case I: dissipation/degradation of carbofuran in the study area

By using long desorption half-life and high fraction of adsorption site of the pesticide, the results under long term simulation show high pesticide accumulation in the study area. The residual carbofuran at the end of year 2008 is 63.50 kg/ha (Figure 4-20).

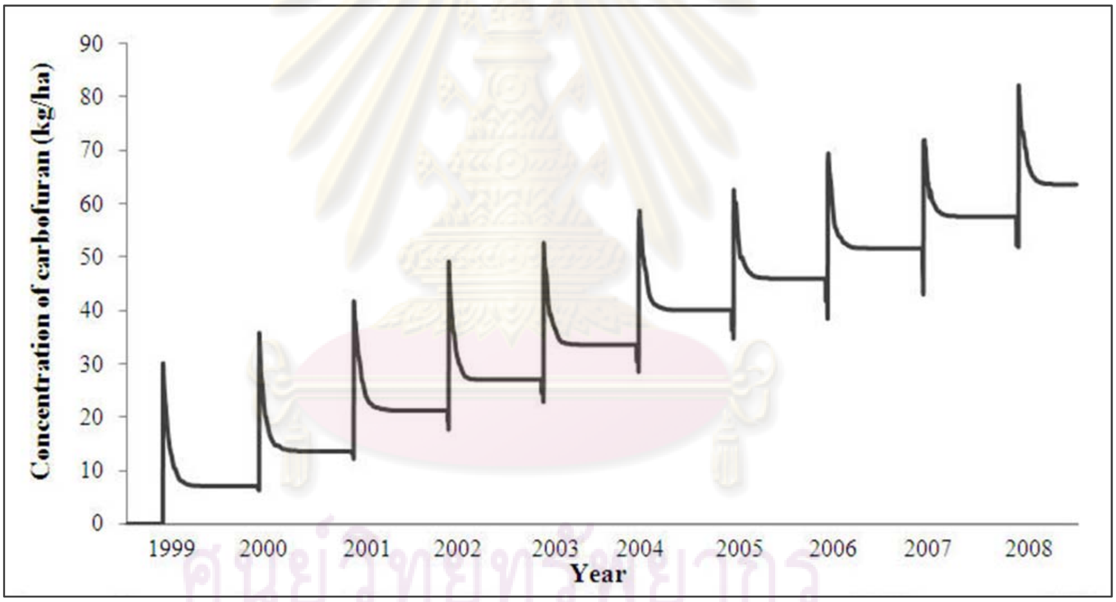

Figure 4-20 Concentration of carbofuran in the study area by using pesticide parameters in Case I

4.4 Case II: the RZWQM calibration

From considering carbofuran accumulation in the study area, the results show that there was high pesticide residue accumulated in soil, which caused by too high adsorption coefficient. Therefore, amount of irrigated water was readjusted to be equal to water demand of plant, and desorption half-life followed several literatures (Joseph *et al*., 1973; Ebleda *et al*., 1987; Pensri Plangklang, 2008). Then fraction of adsorption site and rate constants for dissipation/degradation were re-calibrated. The new values are expressed in Table 4-6 and Table 4-7.

Table 4-6 Desorption parameters in the RZWQM calibration for Case II

Parameter	Case II
Irrigated water (cm)	0.20
Desorption half-life (days)	1
Fraction of adsorption site	0.1

Table 4-7 Effective k values of degradation of carbofuran for Case II

Processes of degradation	k values (day^{-1})
Soil surface biotic	0.000
Soil surface volatilization	0.000
Soil surface photodegradation	0.005
Soil profile lumped degradation	0.069
Soil subsurface aerobic dagradation	0.115
Soil subsurface anaerobic degradation	0.023
Soil subsurface abiotic degradation	0.107

Figure 4-21 demonstrates that the verification data from the RZWQM was not fitted with Mullika Teerakun *et al.* (2004) data. Therefore, these calibrated parameters cannot be used.

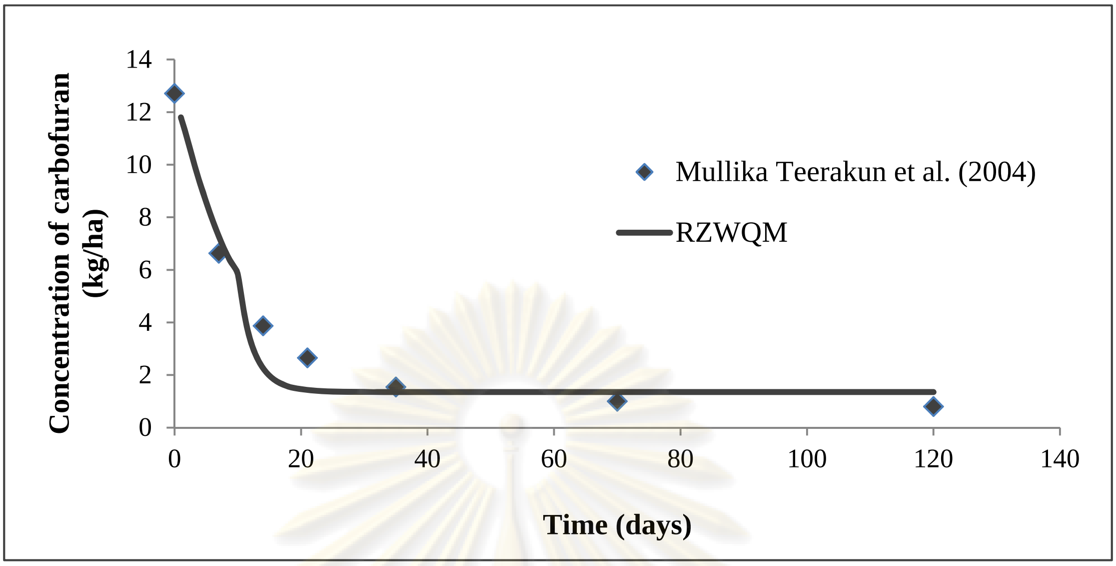

Figure 4-21 Concentration of carbofuran in rice soil (Case II)

4.5 Case III: the RZWQM calibration and the study area simulation

4.5.1 Case III: the RZWQM calibration

The third set of calibrated parameters was generated in order to compensate error from unknown certain amount of irrigated water and fraction of adsorption site. Desorption half-life was still used value from literature that was 1 day (Joseph *et al.*, 1973; Ebleda *et al.*, 1987; Pensri Plangklang, 2008), which is the same as Case II. After that, fraction of adsorption site and rate constants for dissipation/degradation were calibrated (Table 4-8 and Table 4-9).

Table 4-8 Desorption parameters in the RZWQM calibration for Case III

Parameter	Case III
Irrigated water (cm)	1.00
Desorption half-life (days)	1
Fraction of adsorption site	0.65

Table 4-9 Effective k values of degradation of carbofuran for Case III

Processes of degradation	k values (day^{-1})
Soil surface biotic	0.000
Soil surface volatilization	0.000
Soil surface photodegradation	0.005
Soil profile lumped degradation	0.086
Soil subsurface aerobic dagradation	0.099
Soil subsurface anaerobic degradation	0.072
Soil subsurface abiotic degradation	0.092

The data from the RZWQM compared with Mullika Teerakun *et al.* (2004) can acceptable with high correlation coefficient (Figure 4-22). Consequently, these calibrated pesticide parameters were then used for simulation behavior of the pesticide in the study area.

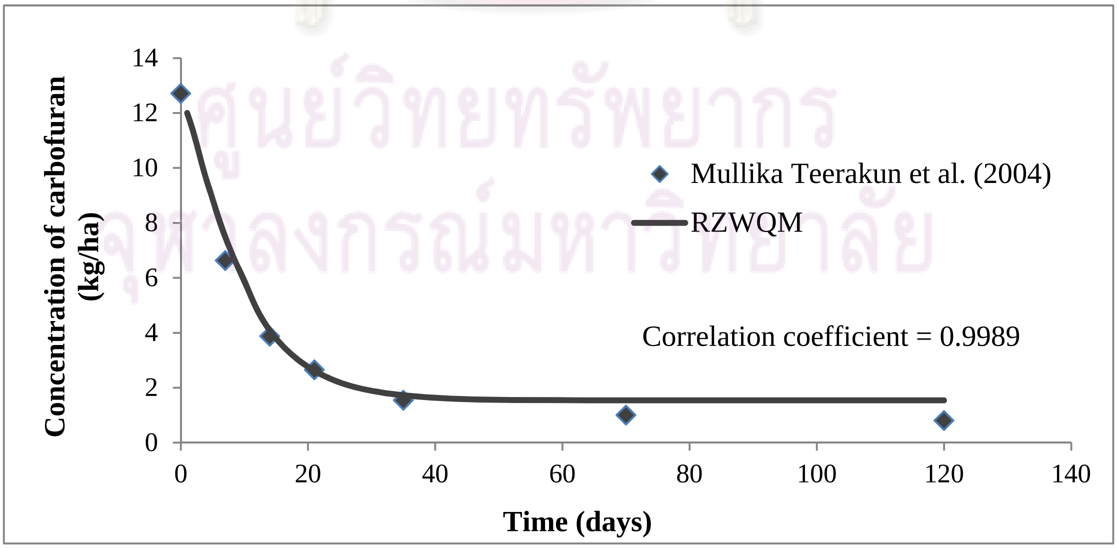

Figure 4-22 Concentration of carbofuran in rice soil (Case III)

4.5.2 Case III: Carbofuran degradation from assumption of irrigation

For carbofuran degradation simulation during ten year (since 1999 to 2008), the output showed that concentration of carbofuran of later year increased in impractical amount. This may result from the fact that the RZWQM does not include the water retention, which is a common process in rice planting. In order to solve this problem, 30 cm of irrigated water was applied everyday during June to October to keep free water level over the soil surface. Figure 4-23 demonstrates that the concentration became slightly lower after adding irrigation; therefore, irrigation addition to get flooding in paddy field is not the right way to manage flooding process because the RZWQM still cannot provide degradation of carbofuran in water flood.

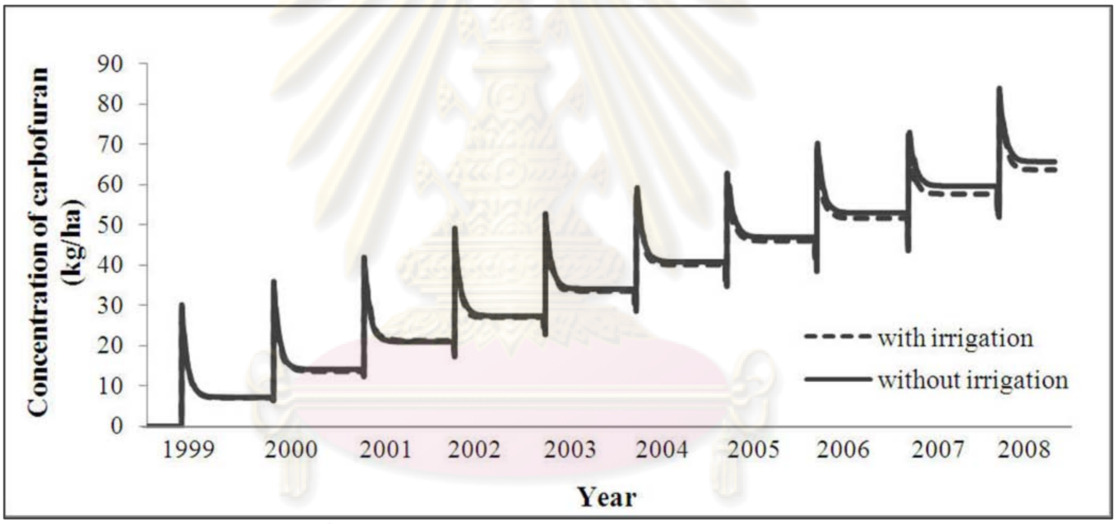

Figure 4-23 Concentration of carbofuran in the study area during 1999 to 2008

However, the irrigation was used in study area simulation to make saturated condition of soil surface that is more similar to practical situation than no irrigation.

4.5.3 Case III: carbofuran degradation in the study area under normal condition

In Case III of the RZWQM calibration, desorption half-life and fraction of adsorption site were lower than Case I due to low irrigated water. The quantity of carbofuran in soil was around a half of Case I, and the residual carbofuran in Case III is 32.8 kg/ha. The accumulated carbofuran was smaller than Case I since the pesticide could less adsorb on soil and more act as unbound form that resulted in degradation rate increasing. Figure 4-24 presents sum of carbofuran concentration in soil, while Figure 4-25 shows pesticide quantity in each soil layer.

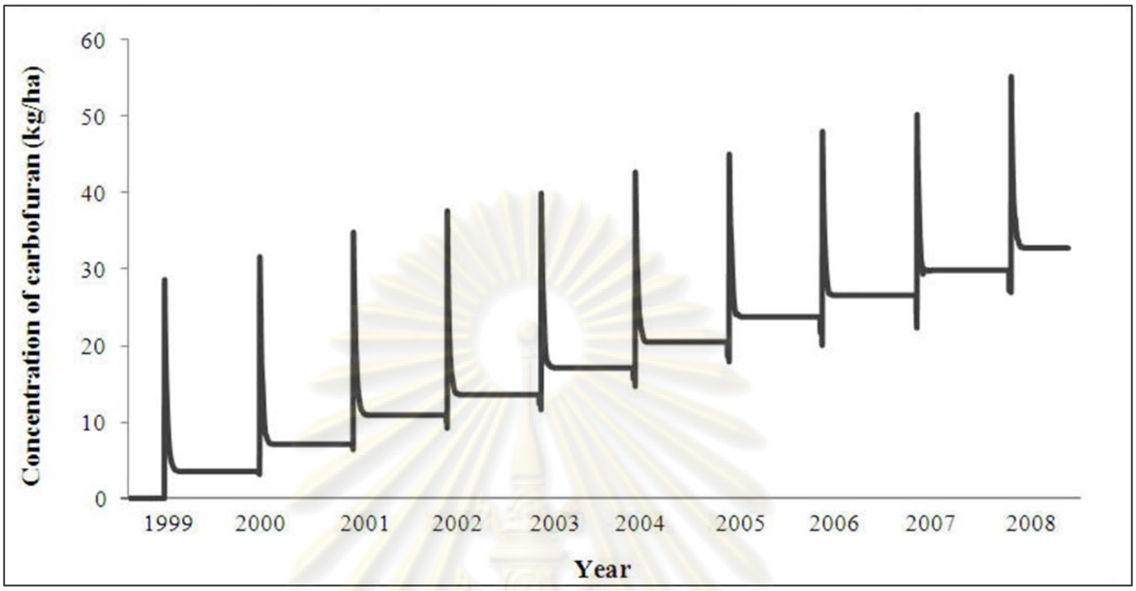

Figure 4-24 Concentration of carbofuran in the study area by using pesticide parameters in Case III

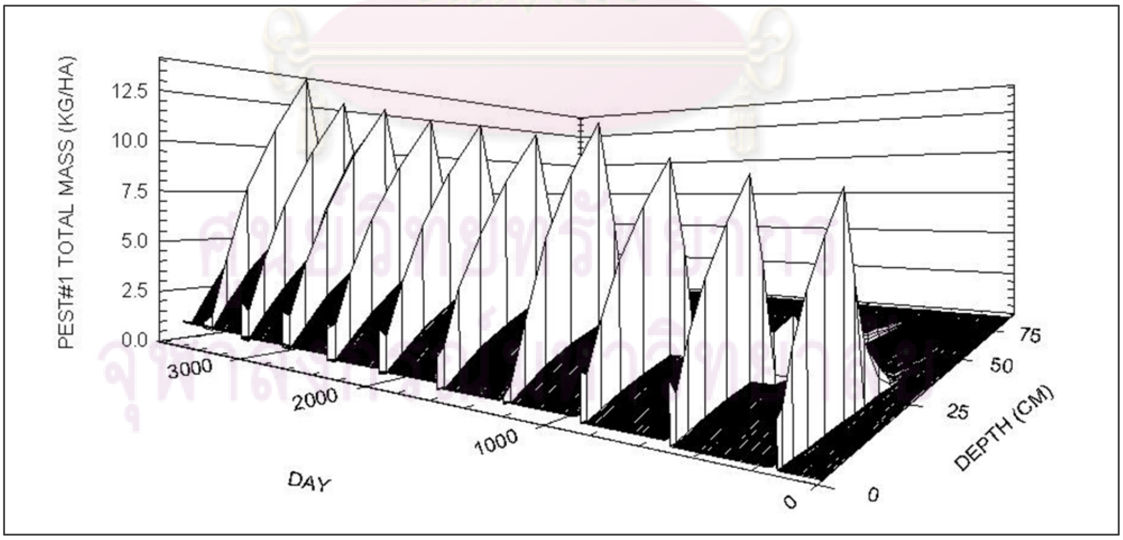

Figure 4-25 Concentration of carbofuran in soil layer during 1999 to 2008

4.5.4 Scenario I: change of agricultural management practices

The carbofuran concentration of this scenario is unrealistic. Even when rice was planted only one time per year, the study area still accumulated high concentration of the pesticide. With more frequent application of carbofuran, i.e., four times per year, the concentration at the end of the year reached 26.00 kg/ha that closed to the applied amount already (Figure 4-26).

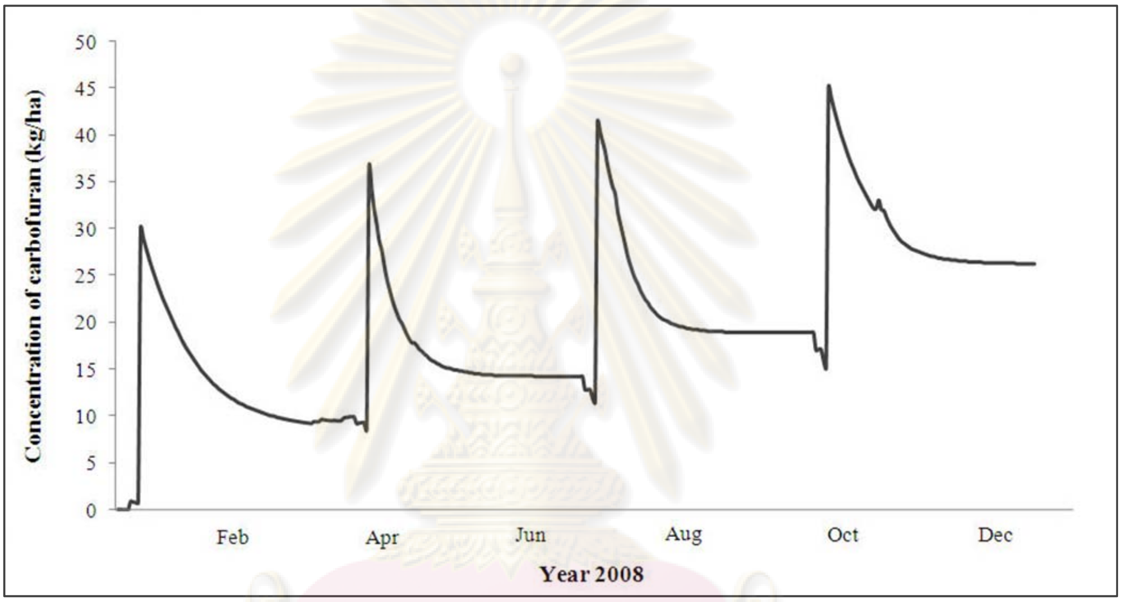

Figure 4-26 Concentration of carobofuran in the study area depended on rice planting four times per year

4.5.5 Scenario II: soil pH modification

When comparing soil pH modification scenario with normal scenario, carbofuran is more stable in acidic condition (pH 4.0) due to properties of carbofuran. The results show that pH of soil impacted on carbofuran degradation (Figure 4-27). At soil pH 10.0, degradation rate is higher than under normal and acidic condition. However, the outputs from the RZWQM are different from several literatures, which stated that carbofuran in basic soil is significantly degraded faster. The difference in the results might due to the fact that the main process of carbofuran dissipation in the RZWQM was water leaching.

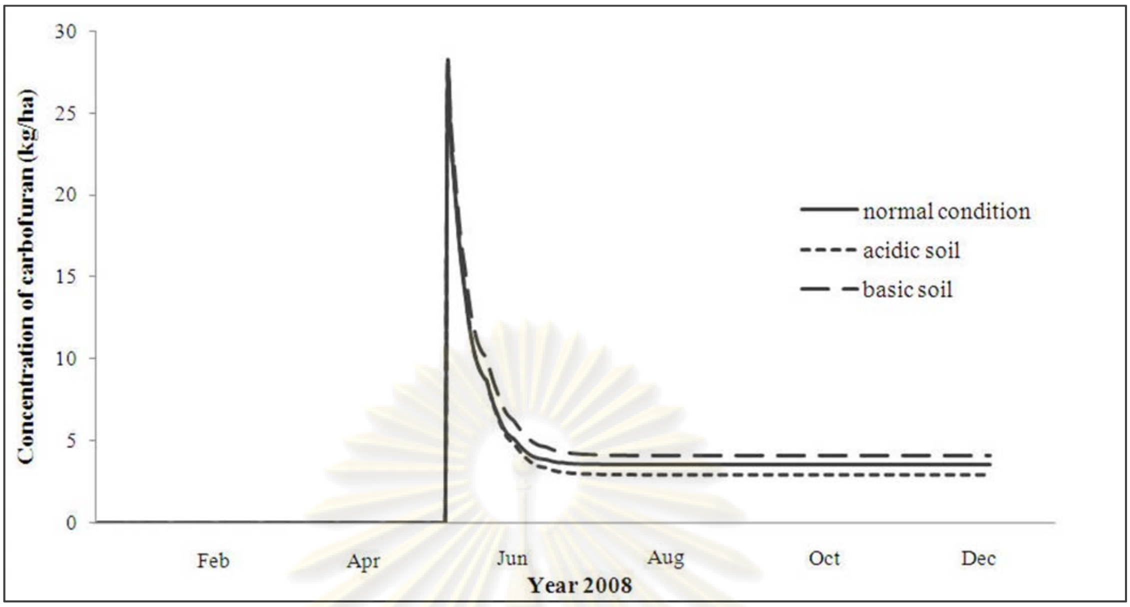

Figure 4-27 Concentration of carbofuran in soil pH modification

4.5.6 Scenario III: change in macropore size

For increase in the macropore size in the study area, water can be greater flow and carbofuran is dissolved with water, so carbofuran can be further transported into soil profile and may be leach to groundwater. Consequently, detected carbofuran in soil is lower than normal condition (Figure 4-28).

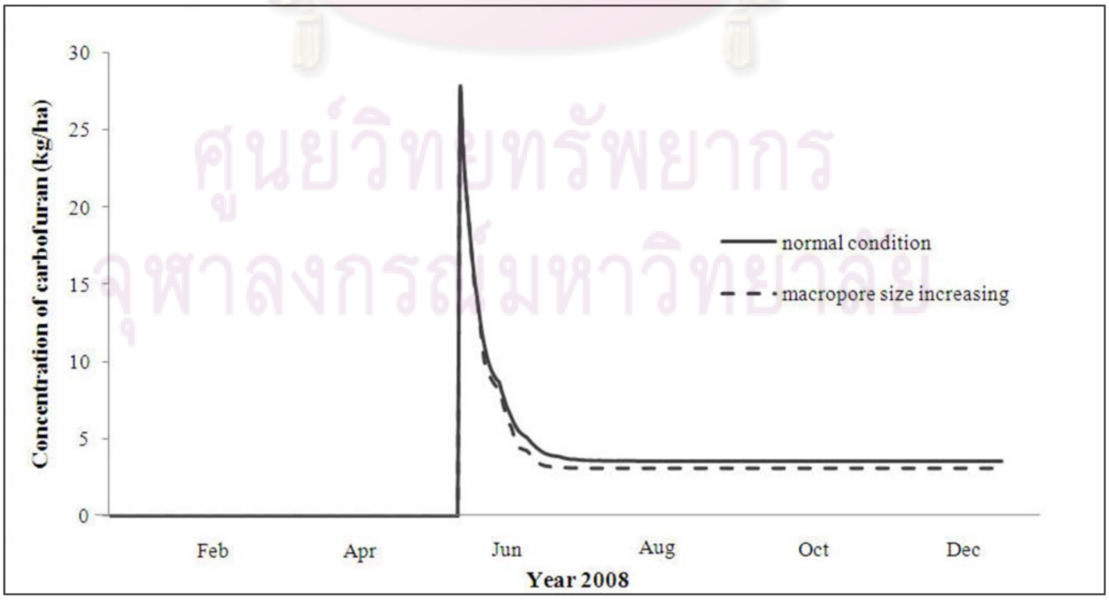

Figure 4-28 Concentration of carbofuran from changing macropore size

4.6 Factors that have impact on the RZWQM simulation in the study area

Possible factors that can make the output different from that of a real situation, in which carbofuran residue was found in very low or undetected amount, can be listed as follows:

- Dissimilar parameters between the calibration data and field simulation data

  Calibration data was taken from the Mullika Teerakun *et al.* (2004) experiment, which was a lab-scale test. Rice was planted in greenhouse bench, so its atmospheric condition is controlled and differed from that of the outside. Accordingly, the calibrated parameters may not have been correctly achieved.

- Excluded processes in the RZWQM

  - Since the major degradation pathway of carbofuran is hydrolysis, in a flood, carbofuran degrades more than the pesticide in the soil. The RZWQM does not include a calculation of pesticide degradation in a water flood; therefore, the concentration of the pesticide was higher.

  - The RZWQM has never been used to simulate rice as a crop, which is a limitation of the RZWQM. In this study, wheat was used as the representative of rice. In reality, rice will consume carbofuran residue through nutrient and water uptake.

- Sorption process in pesticide processes in the RZWQM

  The RZWQM uses Freundlich isotherm for calculating sorption process of the pesticide, so there is no upper limit of adsorption. The pesticide becomes the residues at higher concentration in soil.

- Homogeneity of application at soil surface

  Farmers may not use the same amounts of pesticides in each area. The collected soil would not be in applied district but the RZWQM assumed that quantity of pesticide is identical in whole area.

- Depth of the collected soil

  Results demonstrate that carbofuran residue was low in the top layer of soil; thereby, all of the carbofuran residue were not obtained during sample collection.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Results from simulating the influence of the atmosphere on plant growth and soil conditions related to the atmosphere show that the RZWQM can offer reasonable simulations. However, it stills certain limitations in agricultural management in rice field, which leads to errors in predicting the pesticide dissipation process. Since the RZWQM does not include water retention process, it calculates sum amount of the pesticide. In contrast, in practical rice field, some part of pesticide amount loss with drained water. Therefore, the RZWQM overestimated the accumulated carbofuran in rice field.

In the long term simulation (year 1999 to 2008), the residual carbofuran at the end of year 2008 was 32.80 kg/ha. This concentration means that there was an overestimated amount of pesticide. This impractical value may due to the fact that the RZWQM can only compute the processes occur in the root zone, while pesticide dissipation in flood water was not taken into consideration in the simulation. In addition, the RZWQM does not include the pesticide uptaken by plant process, so only water and nitrogen are consumed, whereas the pesticide is not uptaken.

In the Scenario I, which the pesticide was applied four times per year, an extreme amount of residue was found (26.00 kg/ha). The result shows that at the end of year, the concentration of carbofuran reached the applied amount. It means that there was very high accumulated carbofuran in the applied area.

In the Scenario II, the model shows that changes in soil pH have less of an effect on carbofuran fate and transport. The residue in soil at pH 4.0 and pH 10.0 were 4.10 and 2.93 kg/ha, respectively. Basic soil was able to degrade the pesticide faster than acid soil. When compared under normal conditions, in which the residue was

3.55 kg/ha, the concentration in basic soil showed insignificant dissimilarity. This dissimilar to other studies, which found that carbofuran in basic soil is notably degraded faster than acidic and neutral condition, might due to the fact that water leaching is the important process of dissipation of carbofuran in soil.

In the Scenario III, which change in macropore size, the residual carbofuran was 3.09 kg/ha. This level was lower than the concentration of the pesticide in the normal condition. When the macropore size in the field increased, more pesticide can be further transported after mixing with water and flow out to saturated zone. This saturated zone was not included in this study, so the lower concentration was detected by the RZWQM.

Subsurface soil aerobic and abiotic systems have a considerable impact on the dissipation/degradation processes of carbofuran in soil. Other parameters, impacting the carbofuran concentrations in soil, are the number of carbofuran applications, macropore size, soil hydraulics, and water source (e.g., whether it is irrigated water or rain). Carbofuran can rapidly transport into the soil profile by water leaching. For predicting the carbofuran concentrations in the different scenarios, it was found that soil pH and macropore size have less impacts on the carbofuran accumulation in an applied area when compared with the number of carbofuran applications, which plays a more significant role.

5.2 Recommendations

The high accumulation of carbofuran in soil mainly effects from number of the pesticide application. Therefore, the farmer should put the space of the pesticide application. For example, carbofuran is continuously used for two or three years, and in the next year, rice was then planted without the use of pesticide. Since carbofuran rapidly degrade in basic condition, in no rice planting period, lime or other basic chemicals should be added to adjust soil pH to be more basic condition in order to increase degradation rate of the pesticide in the rice field. However, the soil pH adjustment should beware of amount of lime application because neutral and tiny acid conditions are suitable for rice growth. If high concentration of basic condition is added, it not only impacts on rice development that will lead to gain the lower yield, but it also affects on the ecosystem in rice field. Due to the fact that behavior of carbofuran is highly depended on water movement in soil, when macropore size increases, carbofuran will further transport into deeper soil horizon by water leaching. This might contaminate to ground water and make more harm to the environment. Accordingly, contaminated carbofuran in groundwater should be constantly determined since water movement play significant role in the pesticide transport.

The results also show that the RZWQM can be used to determine the fate and transport of carbofuran in soil during one season of rice planting. However, to accurately simulate a long term rice-planting situation, other processes should be added to the RZWQM as follow:

- The addition of rice characteristics in generic plant growth processes
- Agricultural management practices of rice such as flooding process
- The simulation of pesticide dissipation in flood water processes
- Pesticide uptake by plant processes

Observation of carbofuran when applied second crop to soil that already have carbofuran would by very useful data for better calibrate model for long term application.

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APPENDICES

APENDDIX A

BROOKS-COREY CURVE

Brooks-Corey Curve

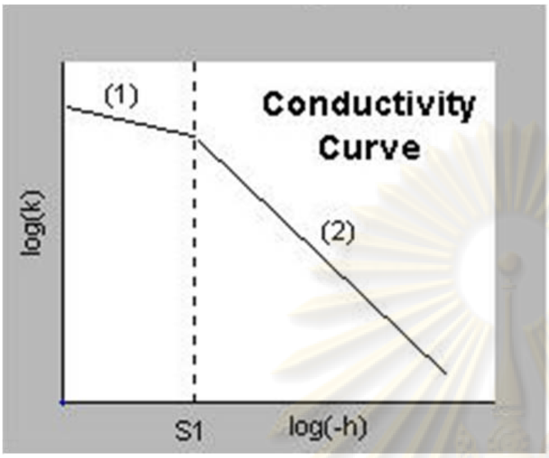

Figure A-1 Conductivity curve

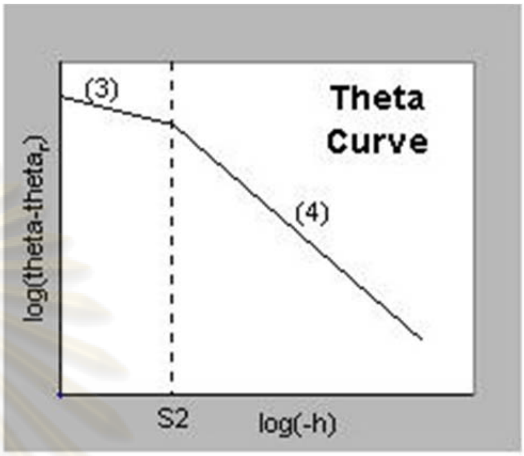

Figure A-2 Theta curve

(1) $$K(h) = C_1|h|^{-N_1}$$

(2) $$K(h) = C_2|h|^{-N_2}$$

(3) $$\theta = \theta_S - A_1|h|$$

(4) $$(\theta - \theta_r) = B|h|^{-A_2}$$

where $$B = (\theta_S - \theta_r - A_1 S_2) {S_2}^{A_2}$$

$$C_2 = C_1 (S_2)^{N_2}$$

$$N_2 = 2 + 3(A_2)$$

where	$A1$	= constant for theta curve (dimensionless),
	$A2$	= pore size distribution index (dimensionless),
	$C2$	= 2^{nd} intercept on conductivity curve (dimensionless),
	$FC13$	= 1/3 bar water content (dimensionless),
	$FC10$	= 1/10 bar water content (dimensionless),
	$FC15$	= 15 bar water content (dimensionless),
	K_{sat}	= saturated hydraulic conductivity (cm/hr),
	$N1$	= 1^{st} exponent for conductivity curve (dimensionless),
	$N2$	= 2^{nd} exponent for conductivity curve (dimensionless),
	$S1$	= bubbling pressure for conductivity curve (cm),
	$S2$	= bubbling pressure for theta curve (cm),
	θ_r	= residual water content (dimensionless), and
	θ_s	= saturated water content.

APENDDIX B

METEOROLOGICAL DATA DURING 1999 TO 2008

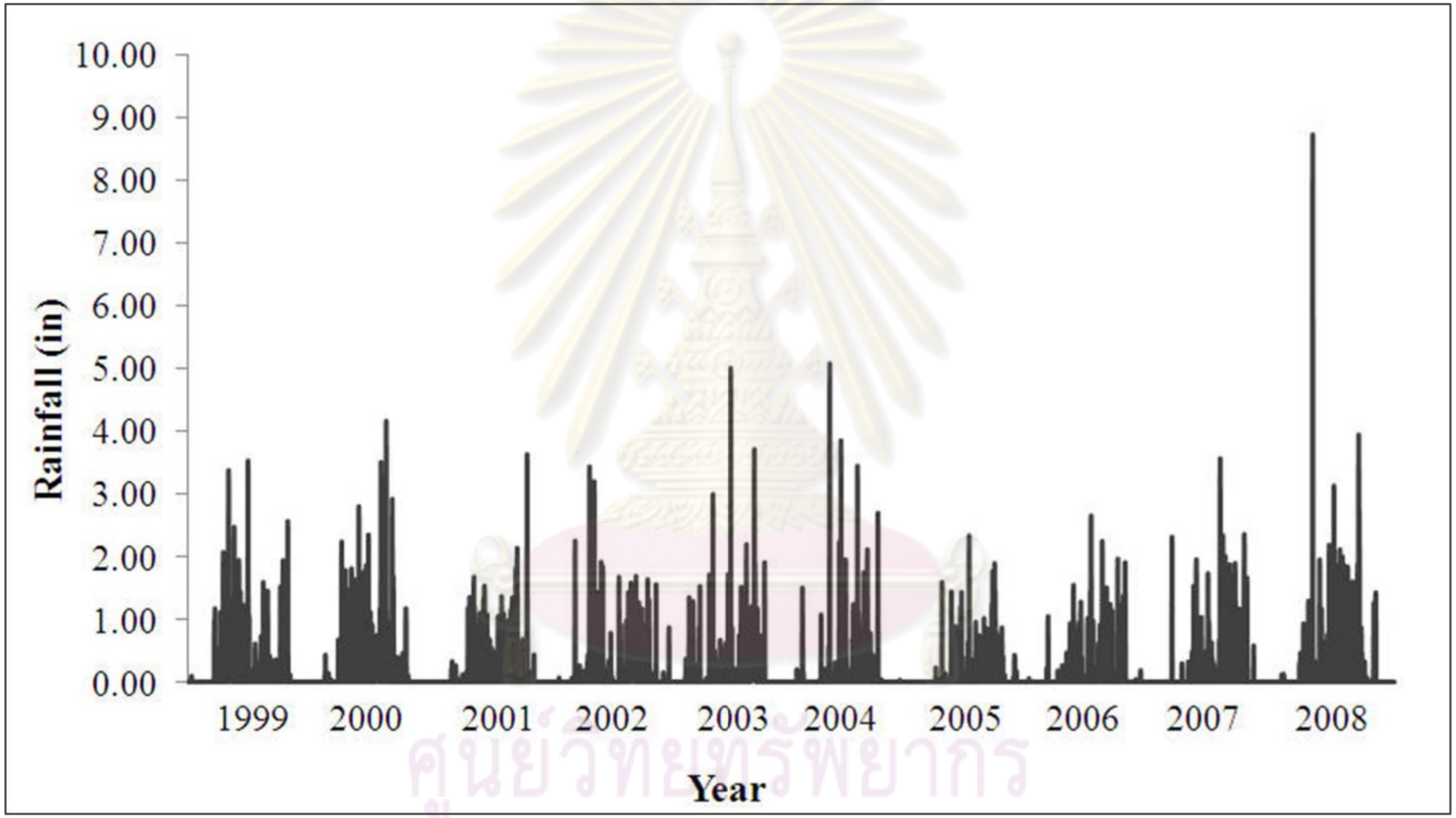

Figure B-1 Breakpoint rainfall

122

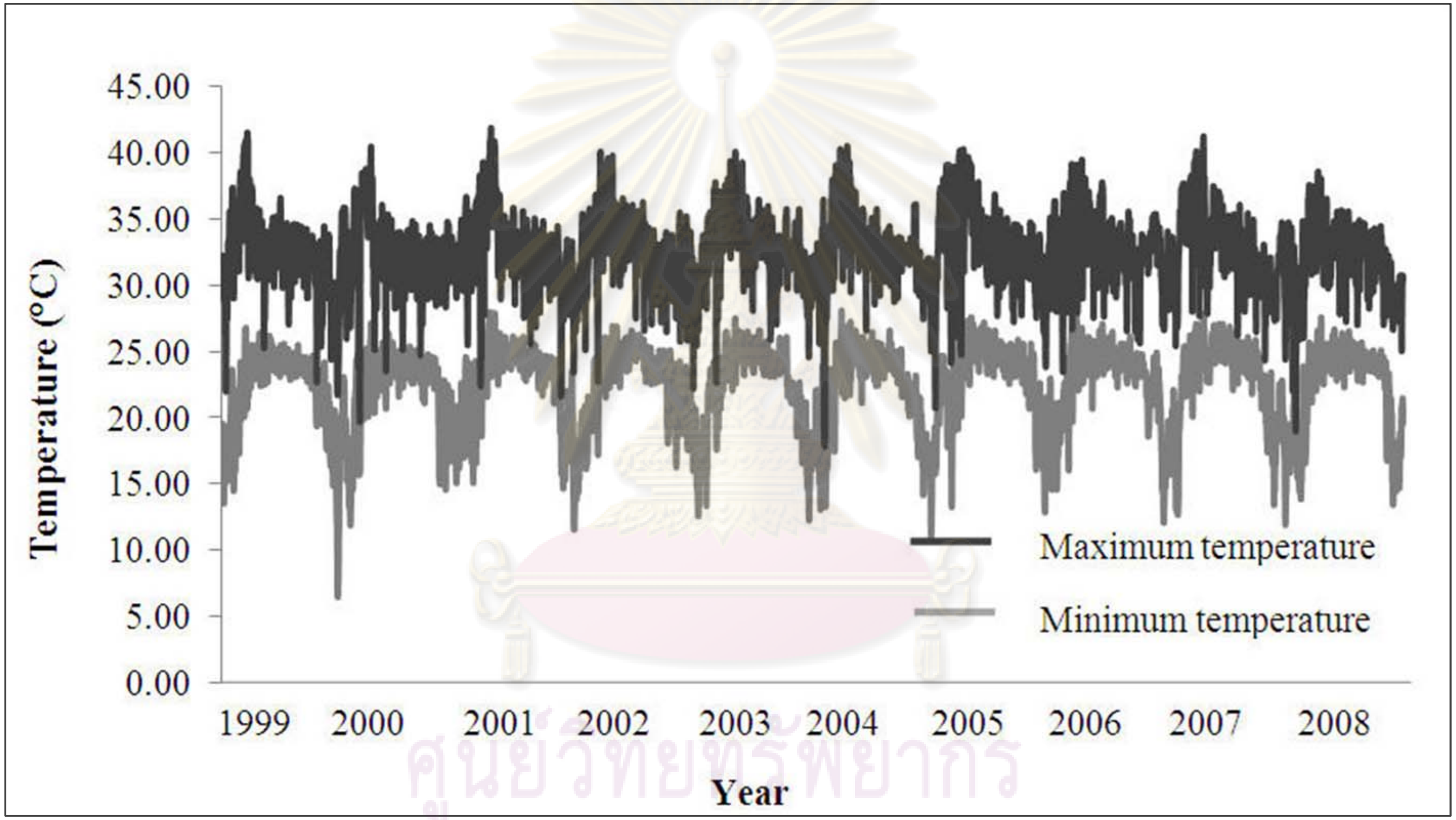

Figure B-2 Minimum and maximum temperature

123

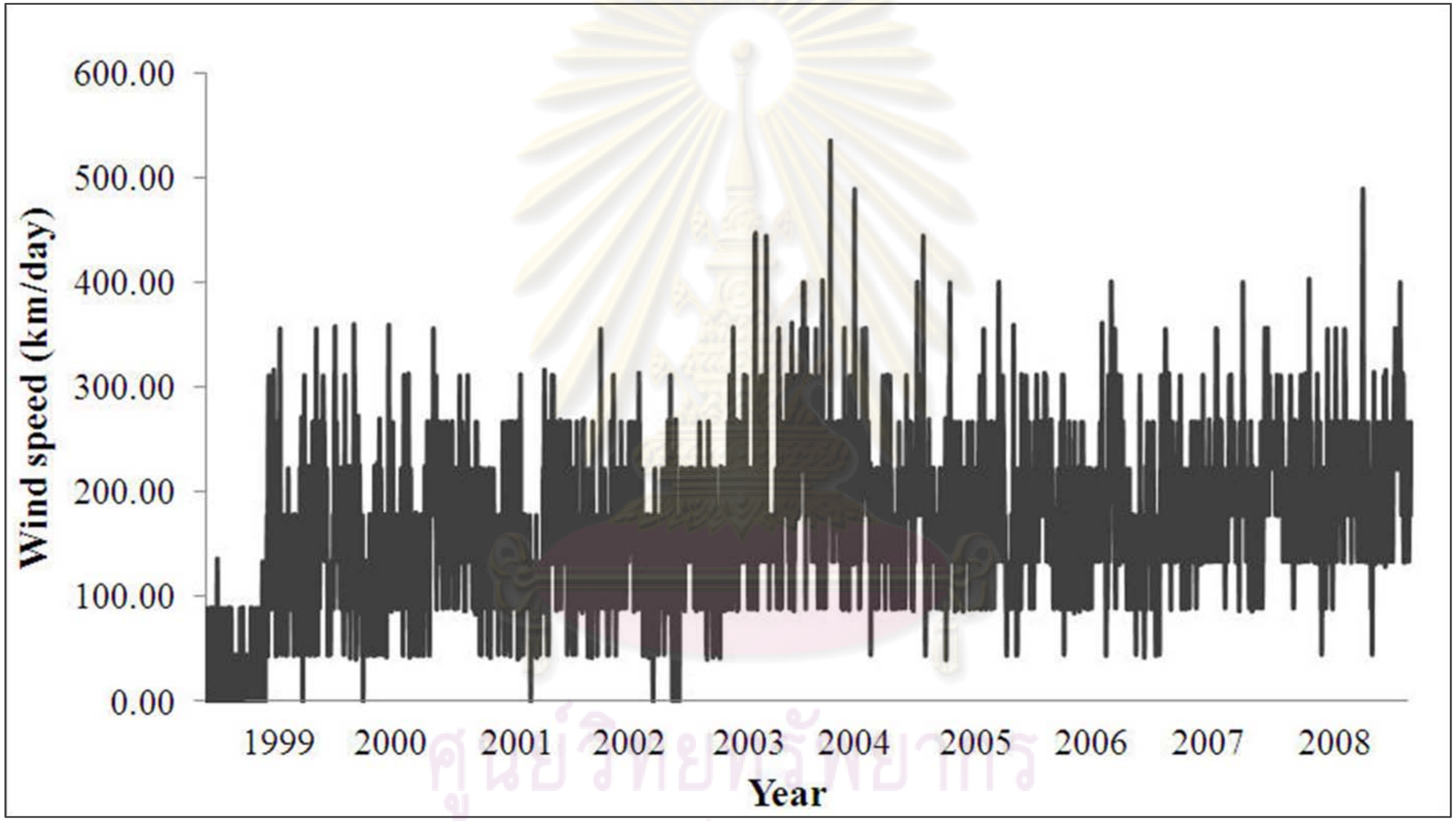

Figure B-3 Wind speed

124

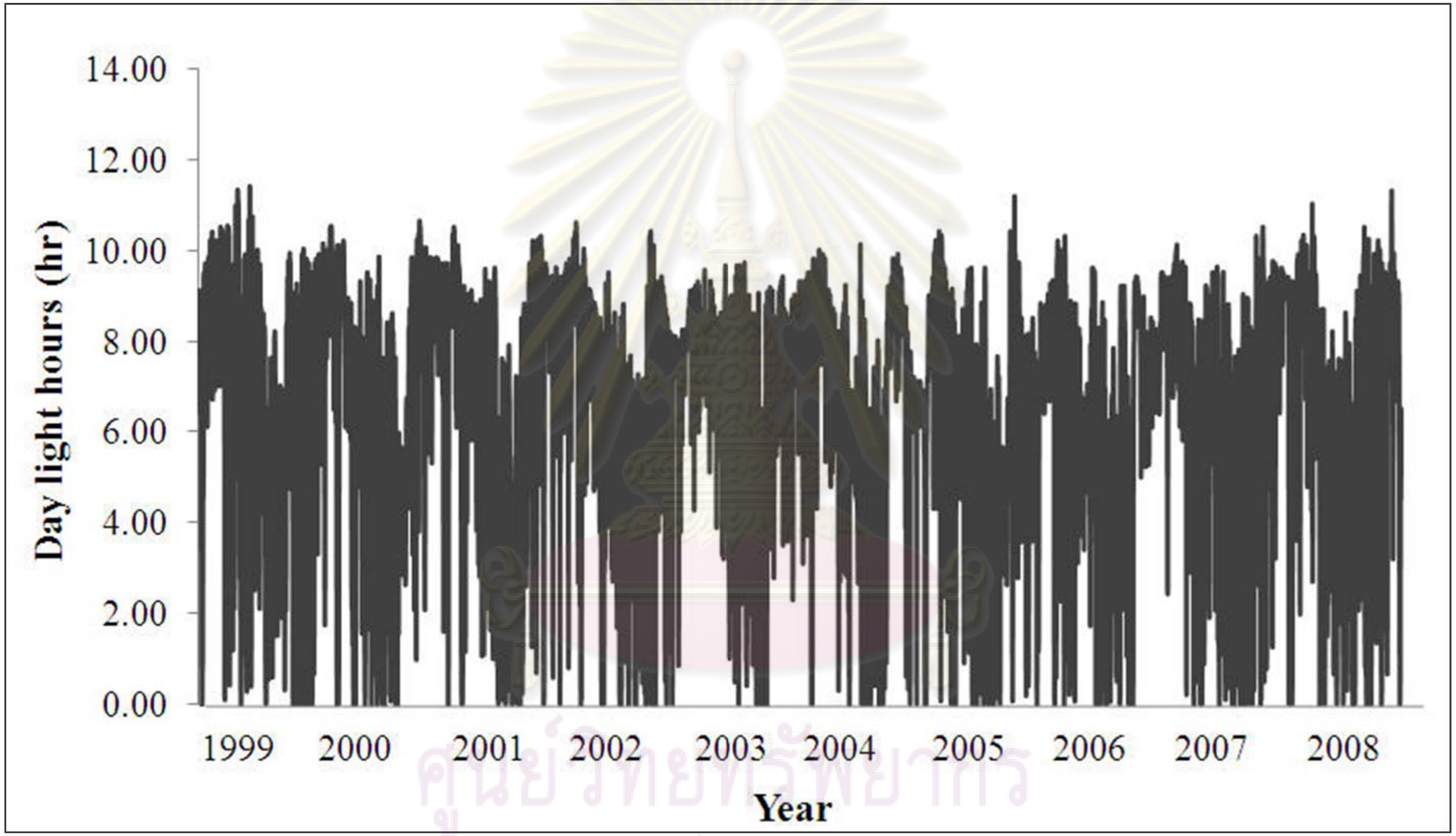

Figure B-4 Day light hours

125

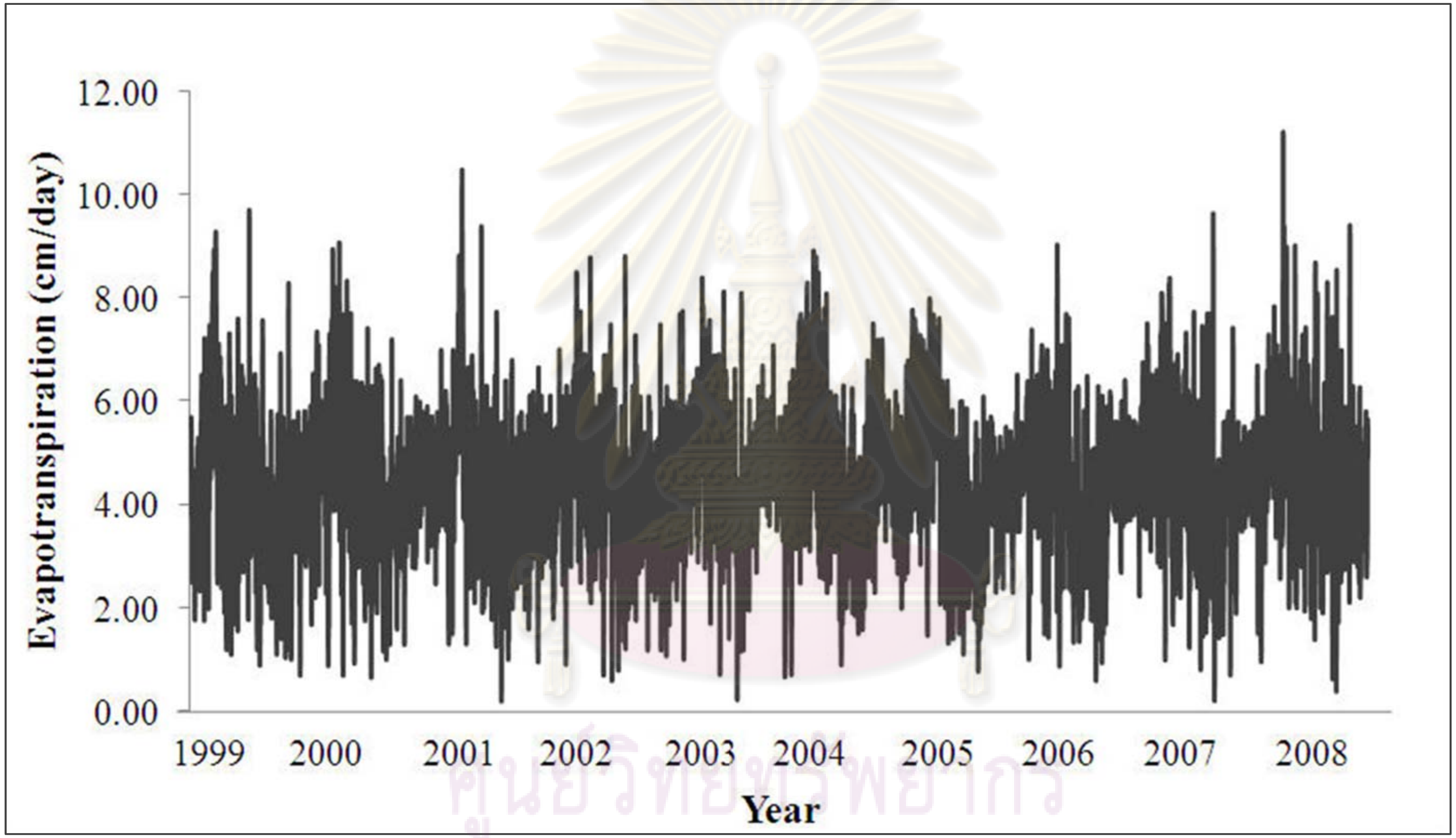

Figure B-5 Evapotranspiration

126

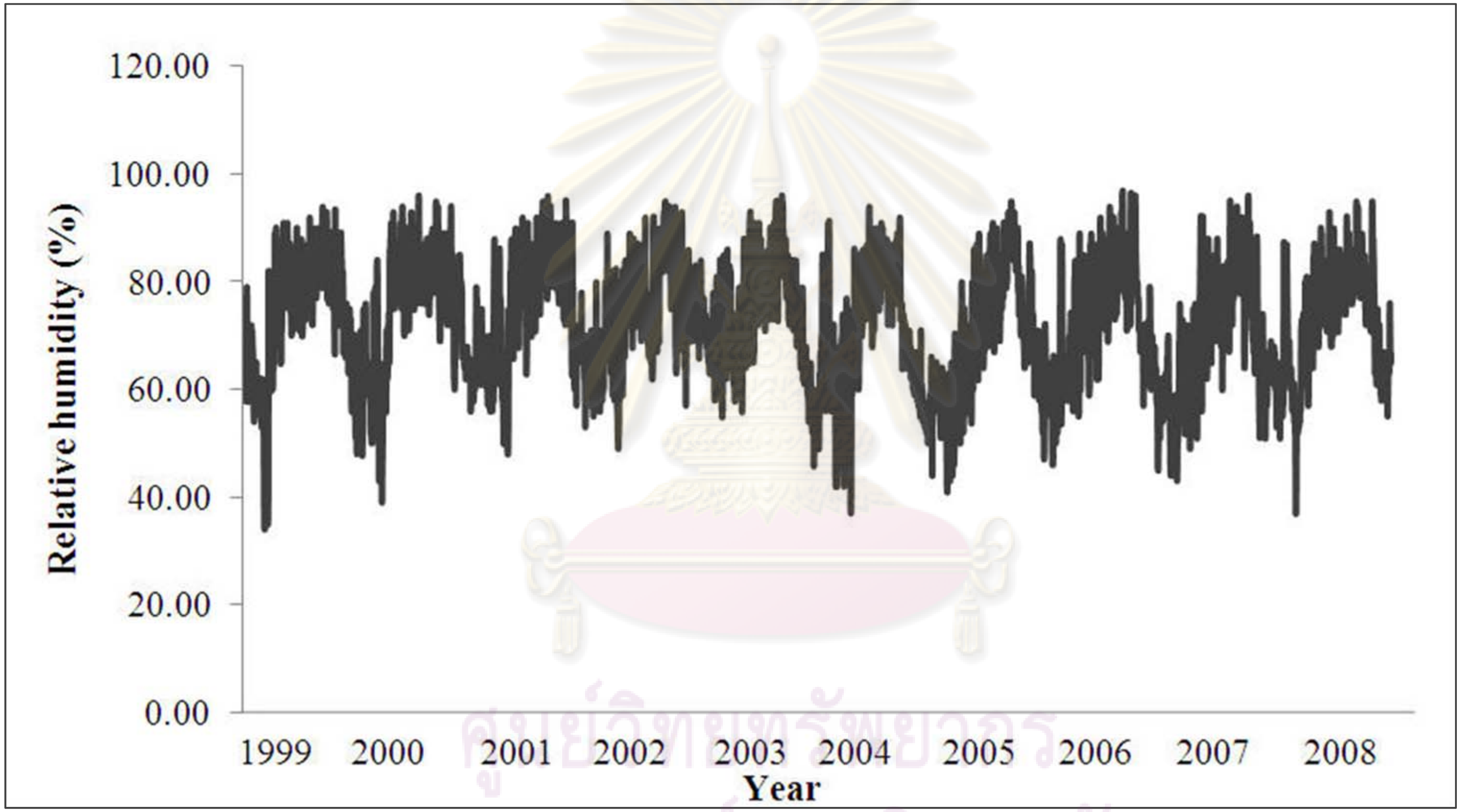

Figure B-6 Relative humidity

127

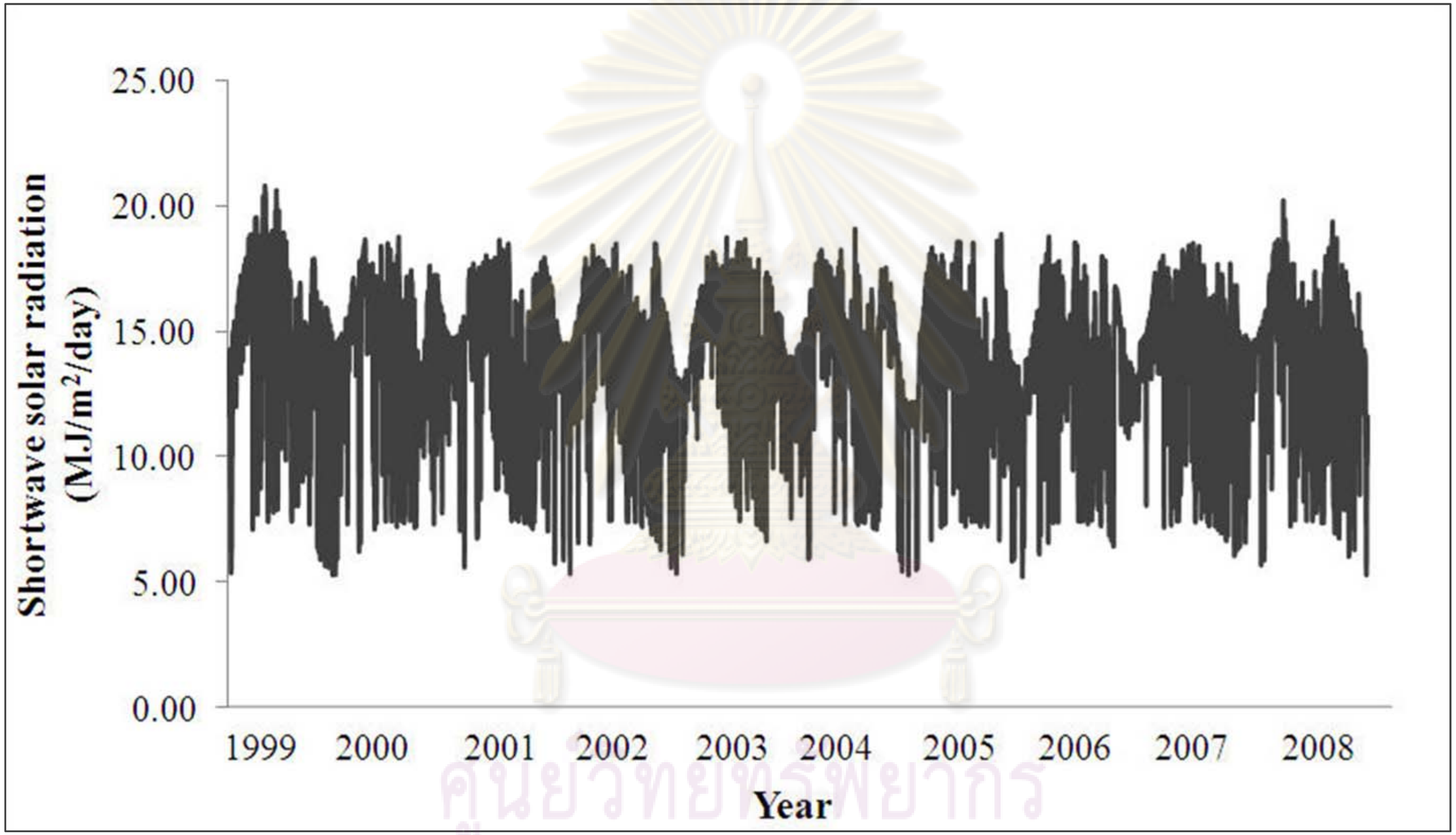

Figure B-7 Net shortwave solar radiation

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APENDDIX C

SENSITIVITY ANALYSIS

Table C-1 Parameters used in sensitivity analysis

Parameters	Value		
	x_1	x_0	x_2
Rate constant of dissipation/degradation processes	0.0825	0.1100	0.1375
$\boldsymbol{S1}$ and $\boldsymbol{S2}$	8.4	11.200	14
$\boldsymbol{A2}$	0.165	0.220	0.275
$\boldsymbol{N2}$	2.535	2.600	2.665
$\boldsymbol{K_{sat}}$	1.5	2.000	2.5
$\boldsymbol{\theta_r}$	0.0203	0.027	0.0338
$\boldsymbol{\theta_s}$	0.375	0.500	0.625
$\boldsymbol{FC13}$	0.2025	0.270	0.3375
$\boldsymbol{FC10}$	0.2625	0.350	0.4375
$\boldsymbol{FC15}$	0.0878	0.117	0.1463
$\boldsymbol{C2}$	3.75	5.000	6.25
Microorganism populations (orgs/g-soil)	7.5×10^6	1×10^7	1.25×10^7

BIOGRAPHY

Miss Daochai Janpen was born on Apirl 5th, 1986 in Bangkok. She obtained her B.Sc. degree in Microbiology from Chulalongkorn University in 2007. After that, she applied to study in the Master's degree of international program in Environmental and Hazardous Waste Management, Chulalongkorn University in May 2008 to May 2010.