Leaching potential assessment of atrazine and nitrate in sugarcane field, Suphan Buri Province

Mr. Sorranat Ratchawang

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Hazardous Substance and
Environmental Management
Inter-Department of Environmental Management
Graduate School
Chulalongkorn University
Academic Year 2018

การประเมินศักยภาพการชะละลายของอาทราซีนและไนเตรทในพื้นที่ไร่อ้อย จังหวัดสุพรรณบุรี

นายสรณัฐ ราชฉวาง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสารอันตรายและสิ่งแวดล้อม สหสาขาวิชาการจัดการสิ่งแวดล้อม
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2561

Thesis Title	Leaching potential assessment of atrazine and nitrate in sugarcane field, Suphan Buri Province
By	Mr. Sorranat Ratchawang
Field of Study	Hazardous Substance and Environmental Management
Thesis Advisor	Associate Professor Srilert Chotpantarat, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Science

.... Dean of the Graduate School
(Associate Professor Thumnoon Nhujak, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Associate Professor Ekawan Luepromchai, Ph.D.)

.... Thesis Advisor
(Associate Professor Srilert Chotpantarat, Ph.D.)

.... Examiner
(Assistant Professor Penradee Chanpiwat, Ph.D.)

.... Examiner
(Pichet Chaiwiwatworakul, Ph.D.)

.... External Examiner
(Tussanee Nettasana, Ph.D.)

สรณัฐ ราชฉวาง : การประเมินศักยภาพการชะละลายของอาทราซีนและไนเตรทในพื้นที่ไร่อ้อย จังหวัดสุพรรณบุรี. (Leaching potential assessment of atrazine and nitrate in sugarcane field, Suphan Buri Province) อ.ที่ปรึกษาหลัก : รศ. ดร.ศรีเลิศ โชติพันธรัตน์

อาทราซีนเป็นยาฆ่าแมลงที่ใช้กันอย่างแพร่หลายเพื่อควบคุมพืชใบกว้างในพืชชนิดต่างๆเช่น ข้าวและอ้อย อาทราซีนเป็นสารเคมีที่มีผลต่อระบบต่อมไร้ท่อ อีกทั้งยังมีผลต่อตับ, ระบบประสาทส่วนกลาง,ระบบภูมิคุ้มกัน และระบบหลอดเลือดหัวใจ งานวิจัยนี้ได้ทำการศึกษาในพื้นที่ปลูกอ้อยภายในอำเภออู่ทองและอำเภอสองพี่น้อง จังหวัดสุพรรณบุรี โดยทำการเก็บตัวอย่างดินและน้ำใต้ดินจากทั้งหมด 8 จุดภายในพื้นที่ศึกษา นำตัวอย่างดินมาวิเคราะห์ลักษณะการดูดซับอาทราซีด้วยวิธีแบทช์ นอกจากนี้ยังนำน้ำบาดาลมาวิเคราะห์ไนเตรทอีกด้วย โดยไนเตรทนั้นสามารถเป็นตัววัดการชะล้างของสารเคมีทางการเกษตรด้วย ในการวิเคราะห์หาการชะล้างของอาทราซีนนั้น แบบจำลอง AF/RF ถูกใช้ในการวิเคราะห์หาการชะล้างของอาทราซีน เพราะแบบจำลองชนิดนี้ใช้ตัวแปรพื้นฐานเท่านั้นในการวิเคราะห์ซึ่งเหมาะกับพื้นที่ศึกษา ซึ่งมีข้อมูลอย่างจำกัด ผลจากการทดลองแบบแบทช์นั้นพบว่า ตัวอย่างดินส่วนใหญ่สอดคล้องกับการดูดซับแบบฟรุนดลิชมากกว่าทั้งการดูดซับเชิงเส้นและแบบแลงเมียร์ โดยพบว่า K_f จากตัวอย่างทั้งหมดนั้นอยู่ในช่วง 0.28 to 0.82 ลิตร/กิโลกรัม นอกจากนี้ 1/n ยังอยู่ในช่วง 0.40 to 0.86 ไนเตรทความเข้มข้นสูงในช่วง 3.25 ถึง 71.11 มิลลิกรัมต่อลิตรยังตรวจพบในน้ำบาดาล จากการวิเคราะห์การชะล้างอาทราซีนและไนเตรทด้วยแบบจำลอง AF/RF นั้น พื้นที่ศึกษาส่วนใหญ่ถูกพบว่ามีโอกาสสูงในการชะล้างของอาทราซีนและไนเตรทจากหน้าดินสู่น้ำใต้ดิน นอกจากนี้ยังมีดินที่มีโอกาสในการชะล้างต่ำถึงปานกลางอีกด้วย การตรวจพบไนเตรทความเข้มข้นสูงในพื้นที่ตามจุดตัวอย่าง S1, S2, S4, S5 และ S6 ซึ่งถูกพิจารณาว่ามีโอกาสสูงในการชะล้างของอาทราซีนนั้นสามารถยืนยันผลการวิเคราะห์ของแบบจำลองได้ด้วยประสิทธิภาพการวิเคราะห์ 62.5%

สาขาวิชา	การจัดการสารอันตรายและสิ่งแวดล้อม	ลายมือชื่อนิสิต ....
ปีการศึกษา	2561	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5987543020 : MAJOR HAZARDOUS SUBSTANCE AND ENVIRONMENTAL MANAGEMENT
KEYWORD: Adsorption, AF/RF model, Atrazine, Groundwater, Nitrate, Suphan Buri

Sorranat Ratchawang : Leaching potential assessment of atrazine and nitrate in sugarcane field, Suphan Buri Province. Advisor: Assoc. Prof. Srilert Chotpantarat, Ph.D.

Atrazine is widely used as a herbicide to control annual broadleaf in agricultural area such as rice and sugarcane. It is considered as one of endocrine disrupting chemicals. Atrazine also affects liver, the central nervous system, immune system and cardiovascular function. The study area is sugarcane field in U-thong and Song Phi Nong district, Suphan Buri province. In this area, soil and groundwater samples were collected at eight different points distributed over the sugarcane area with different soil types. Batch adsorption experiment was carried out to evaluate the proper adsorption isotherm of each soil. Additionally, groundwater samples were analyzed for nitrate concentration. For the leaching potential assessment, AF/RF model was used because the model requires only basic parameters of the pesticide and soils. AF/RF model is tier-1 model using for defining pesticide leaching index for preliminary assessment in the area with the limited data availability. The result of batch sorption experiment indicated that soil samples were well fitted with Freundlich isotherm. K_f was found in the range of 0.284 to 0.822 L/Kg. Additionally, 1/n was reported in the ranged of 0.401 to 0.855. High nitrate concentration was also found in groundwater in the range of 3.25 to 71.11 mg/L. As a result from AF/RF model, most of the area was considered as high leaching potential for atrazine and nitrate in this study area. Moreover, there also were soil samples with low to moderate leaching potential due to the different soil types and sorption behaviors. The detected nitrate concentration conforms to the leaching potential of S1, S2, S4, S5 and S6. In the other words, the result of the leaching potential model showed 62.5% efficiency as a model performance.

Field of Study:	Hazardous Substance and Environmental Management	Student's Signature ....
Academic Year:	2018	Advisor's Signature ....

ACKNOWLEDGEMENTS

The author thankfully acknowledge the support of the Center of Excellence on Hazardous Substance Management and the International Postgraduate Programs in Environmental Management, Graduate School, Chulalongkorn University for their invaluable support in terms of facilities and scientific equipment. The author express our sincere thanks to the Grant for International Research Integration: Chula Research Scholar, Ratchadaphiseksomphot Endowment Fund (GCURS-59-06-79-01) for providing partial financial support , the Office of Higher Education Commission (OHEC) and the S&T Postgraduate Education and Research Development Office (PERDO) for the financial support of the Research Program and to the Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University for funding the Research Unit. The author also thank to Assoc. Prof. Srilert Chotpantarat, Ms.Chananya Permchati and Ms.Chantana Intim for advices and helping during laboratory work in HSM. Moreover, the author wold like to thank to Ms.Nanchaphorn Udomsri, Ms.Satika Boonkaewwan, and Mr.Pongsathorn Thunyawatcharakul for a helpful assistance during field observation.

Sorranat Ratchawang

TABLE OF CONTENTS

Page

CHAPTER 1

Introduction

1.1 Background

In Thailand, groundwater is widely used for a number of purpose, including drinking water, agricultural, municipal and industrial supplies. It has been estimated that 50% is used for drinking water, 15% for agriculture, 10% for municipal supplies, 20% for industrial supplies and 5% for other uses (Thapinta & Hudak, 2003). Pesticides are widely used in Thailand and have been detected in groundwater. The herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), which is widely used to control annual broadleaf and grass weed mostly applied in corn and sugarcane field, was found as one of the most imported herbicides in Thailand (Panuwet *et al.*, 2012).

It has been found that 0.058-0.086 μg/L of atrazine was detected in water samples collected from Chao Praya river, which is located in the central Thailand (Kruawal *et al.*, 2005). In Thailand, 1.89 μg/L of atrazine also has been found in groundwater wells in the central plain (Thapinta & Hudak, 2003). This must be considered as health concern because atrazine is an endocrine disruptor in human (Lasserre *et al.*, 2009). Monitoring and reduce atrazine leaching potential to groundwater would play an important role for protecting environment and human health.

There is a number of plants which has a problem from weed or annual broadleaf, one of them is sugarcane. Sugarcane has been planted in the most area of Suphan Buri province. It requires atrazine for protecting itself from annual broadleaf with 480-640 g/m^2 as use rate (OCSB, 2016). It has been reported that atrazine is one of the most imported herbicides (Panuwet *et al.*, 2012). Moreover, fertilizers is also used in the area for adding nutrients to the crops. Due to the intensive use of fertilizers for sugarcane or other crops, nitrate has been found in shallow well around the study area (DGR, 2009). The contamination indicates that leaching of other contaminant such as herbicide like atrazine can occur in the sugarcane area. Simulation models are the suitable tool for preventing groundwater contamination as they can predict pollution risk and enable the prevention of pollution. In case of studying for non-point source pollution, it is necessary to consider in the regional scale. To assess pesticides leaching to groundwater in regional scale, the use of simulation model integrated with a geographical information system (GIS) is very effective (de Paz & Rubio, 2006). Basically, sorption behavior play an important role in leaching potential of pesticide to groundwater. It has been reported that the lower sorption coefficient, the higher leaching potential (Chorom & Shrifi, 2010; Yao *et al.*, 2012).

There are several studies using simple models or indexes, for example Leaching index (de Paz & Rubio, 2006) and GUS (Groundwater Ubiquity Score) (Gustafson, 1989) to assess pesticide leaching in agricultural areas. One of the useful model for this regard is the AF/RF model, which is the tier 1 model based on the attenuation factor (AF) approach (Li *et al.*, 1998). This model has been used combined with a GIS to study the leaching potential of pesticides in regional scale (Hall *et al.*, 2015; Ki & Ray, 2015; Ki *et al.*, 2015), but has not been used to evaluate atrazine leaching potential in sugarcane area located in Thailand especially in Suphan Buri province.

1.2 Objectives

1.2.1 To characterize the sorption behavior of atrazine on different soil types in the study area

1.2.2 To assess the leaching potential of atrazine in the study area using the AF/RF model.

1.2.3 To evaluate the performance of the AF/RF for being applied in the future leaching potential assessment work.

1.3 Hypotheses

1.3.1 Atrazine leaching potential may be mainly influenced by properties of soils such as organic carbon, CEC, soil pH, and soil types.

1.3.2 Atrazine has high leaching potential and is considered to be a groundwater contaminant in this study area.

1.3.3 The AF/RF model has efficiency to evaluate pesticides leaching potential in the study area and can be one of the usable model for leaching assessment.

1.4 Scopes of the Study

1.4.1 The samples including soil and groundwater were collected from sugarcane field in Suphan Buri province, which is considered as the atrazine contaminated areas.

1.4.2 Sorption coefficient was estimated by the batch equilibrium method.

1.4.3 The AF/RF model was used to evaluate leaching potential of atrazine in the study area and Model performance for atrazine leaching potential was analyzed compared to atrazine contamination in the groundwater.

1.5 Expected Outcomes

1.5.1 Sorption coefficient and sorption isotherm of atrazine on different soils.

1.5.2 Leaching potential map of atrazine in sugarcane field.

CHAPTER 2

Theoretical Background and Literature Review

2.1 Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the mostly effective herbicides widely used for weed control in sugarcane, rice and other crops. It has been reported that the herbicide was detected in groundwater in the United States and Europe (Gely-Pernot *et al.*, 2017; Toccalino *et al.*, 2014), although atrazine was prohibited in the European Union in 2004 (Prado *et al.*, 2014). In Thailand, atrazine was found as one of the most imported herbicides (Panuwet *et al.*, 2012; Tawatsin, 2015) as shown in table 2.1. It was found that 0.058-0.086 µg/L of the herbicide was detected in water samples collected from the Chaopraya River, located around Bangkok, Thailand (Kruawal *et al.*, 2005). In addition, one study claimed that atrazine was found in groundwater well in Suphan Buri province, located in the central part of Thailand (1.89 µg/L as the highest concentration) (Thapinta & Hudak, 2003).

Table 2. 1 Top ten imported pesticides by active ingredient (a.i.) into Thailand (Tawatsin, 2015)

	Herbicides		**Insecticides**		**Fungicides**	
Rank	Name	a.i. (Kg)	Name	a.i. (Kg)	Name	a.i. (Kg)
1	glyphosate isopropylammonium	27,994,297	chlorpyrifos	1,193,302	mancozeb	1,513,307
2	paraquat dichloride	13,823,092	cartap hydrochloride	663,197	carbendazim	644,246
3	2,4-D sodium salt	6,361,633	carbaryl	592,587	propineb	548,961
4	2,4-D dimethyl ammonium	6,121,701	cypermethrin	504,931	captan	472,197
5	ametryn	4,621,614	carbosulfan	432,191	copper hydroxide	459,518
6	**atrazine**	**4,284,683**	isoprocarb	382,785	propiconazole	354,286
7	butachlor	2,368,861	dichlorvos	320,994	difenoconazole	347,803
8	diuron	1,776,238	chlorpyrifos+ cypermethrin	263,009	phosphonic acid	245,669
9	acetochlor	1,164,241	fenobucarb	215,289	fosetyl-aluminium	233,929
10	propanil	987,142	profenofos	189,467	metalaxyl	152,848

2.1.1 Properties and functions of atrazine

Atrazine has molecular weight of 215.7 g/mol and pKa of 1.68. It also has water solubility of 28 mg/L (Dousset *et al.*, 1994) which is moderate water solubility showing possibility to disperse through groundwater. It is also considered as having highly mobility in soils, especially in soils with low clay or organic content (OC). It has been reported to have a high potential for groundwater contamination because it is not strongly absorbed to soil particles and has lengthy soil half-life (60-100 days) although it is only moderately soluble in water (USDASCS, 1990; USEPA, 1988).

Originally, atrazine is prepared from cyanuric chloride, usually treated with ethylamine and isopropyl amine. Atrazine's function, like other triazine herbicides, is binding to the plastoquinone- binding protein in photosystem II (PS II). This can kill plant from starving and oxidative damage due to breakdown in the electron transport process (Fernández-Naveira *et al.*, 2016).

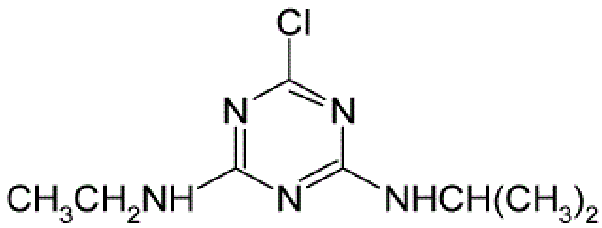


Figure 2. 1 Chemical structure of atrazine (Zarpon et al., 2006)

Chemical name: 2-chloro-4-ethylamino-6-isopropylamino-s-triazine

Molecular formula: $C_8H_{14}ClN_5$

Molecular weight: 215.7 g/mol

Water solubility: 28 mg/L

Half-life: 60-100 days

Log K_{ow}: 2.70

pK_a: 1.7

2.1.2 Toxicity of atrazine

It has been reported that atrazine is endocrine disrupting chemical (Geng *et al.*, 2013). Additionally, atrazine has been shown as a result in change or delay puberty in experimental animals (Laws *et al.*, 2003; Stoker *et al.*, 2002). The herbicide also affects liver by increasing serum lipids, liver enzymes and liver histopathology (Shirisha *et al.*, 2013). Some studies found that atrazine affects the central nervous system, immune system and cardiovascular function (Shirisha *et al.*, 2013).

In case of the association between atrazine and cancer, there are several studies indicating no significant correlation. There is a study evaluating the correlation between the risk of breast cancer in women living in Wisconsin and the exposure of atrazine in well water (Mcelroy *et al.*, 2007). The results indicate that there is no association between increasing of breast cancer and exposure of atrazine. Another study shows no significant association between atrazine exposure and lung, bladder, non-Hodgkin lymphoma, and prostate cancer among the participants of the Agricultural Health study (Rusiecki *et al.*, 2004). Additionally, various toxic effects of atrazine are shown in figure 2.2 (Singh *et al.*, 2017).

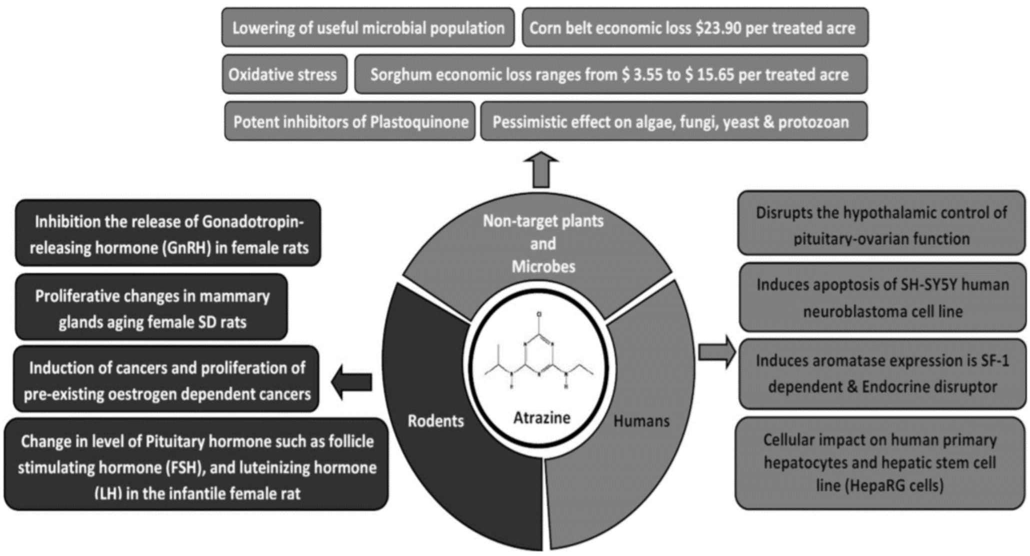


Figure 2. 2 Toxicity of atrazine (Singh et al., 2017)

2.1.3 Atrazine degradation

In the environment, atrazine can degrade to give metabolite. It has been found that degradation of atrazine can be a physicochemical and biochemical process. More than 15 metabolites of atrazine have been identified. There are 4 main metabolites including desethylatrazine, deisopropylatrazine, didealkylatrazine, and hydroxyatrazine.

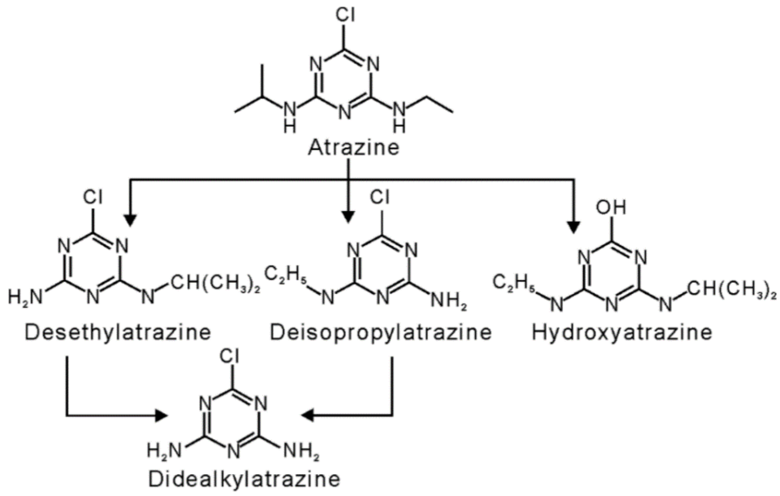


Figure 2. 3 Major degradation products of atrazine (Mudhoo & Garg, 2011)

It has been reported that hydroxyatrazine is the most important degradation product which is absorbed in soil for longer time than other metabolites. Hydroxyatrazine is also the least mobile product of atrazine. In contrast, desethylatrazine and deisopropylatrazine are reported to be the most mobile metabolite of atrazine. These metabolites are also have the same toxicity, greater water solubility and less soil interaction than atrazine which is a parent compound (Mudhoo & Garg, 2011).

2.1.4 Sorption of atrazine in soil

It has been reported that atrazine can accumulate in soil due to its low chemical reactivity, leading to groundwater vulnerability (Frank & Sirons, 1985). There are several factors affecting behavior of atrazine in environment, including sorption by soil components, sorption by plants, volatilization, biodegradation, transportation through runoff and leaching, and chemical degradation (Deng *et al.*, 2010). One of the factors, soil sorption and desorption of herbicides can affect the fate of herbicides in soil environments (Lesan & Bhandari, 2003; Wu *et al.*, 2011). Several studies claimed that the sorption and desorption of herbicides related to soil characteristics, such as clay content, ionic strength, soil pH, soil organic matter contents (McGlamery & Slife, 1966; Seol & Lee, 2000; Ureña-Amate *et al.*, 2005; Weihong *et al.*, 2009). Organic matter is frequently considered as the most important factor of sorption and desorption in soil, sediment and also solution (Lesan & Bhandari, 2003).

2.2 Nitrate

Nitrate (NO_3^-) is a chemical compound with one part nitrogen and three parts oxygen. This common form of nitrogen is usually found in water. Generally, occurring concentrations of nitrate in groundwater are naturally less than 2 mg/L originated from natural sources such as decaying plant materials, atmospheric deposition, and inorganic fertilizers. Due to the intensive agricultural practices, nitrate contamination in groundwater has been concern in many countries (Putthividhya & Pipitsombat, 2015).

The intensive application of nitrogen fertilizers is the main reason why groundwater is contaminated by nitrate around the world. In Asia, the consumption of fertilizers is increased dramatically in the last 40 years (Tirado, 2007). It is reported that contamination of nitrate in surface water and groundwater is an international problem that requires response and scientific analysis due to its effect to human health (Fewtrell, 2004). In Thailand, nitrate has been found in surface water and shallow groundwater and has been reported in Suphanburi and Kanchanaburi province. Additionally, groundwater samples from agricultural area in Chiangmai province in northern Thailand were contaminated by high concentration of nitrate (> 290 mg/L) (Putthividhya & Pipitsombat, 2015).

In this study, nitrate was used in order to compare model performance with atrazine leaching assessment due to nitrate conservative in leaching to groundwater. Although some studies have not found the correlation between nitrate concentration and concentration of pesticide in groundwater, many studies have reported that the detection of pesticides in groundwater increases with increasing of nitrate concentration. The relations observed between nitrate and pesticide concentration in groundwater do not show a sufficient basis for using nitrate as a general indicator for detection of pesticide residues in the subsurface. While pesticide can be more frequently detected in groundwater with high concentration of nitrate in some areas.

2.3 Sorption isotherm

Several studies claimed that the sorption and desorption of herbicides related to soil characteristics, such as clay content, ionic strength, soil pH, soil organic matter contents (McGlamery & Slife, 1966; Seol & Lee, 2000; Ureña-Amate *et al.*, 2005; Weihong *et al.*, 2009). Organic matter is frequently considered as the most important factor of sorption and desorption in soil, sediment and also solution (Lesan & Bhandari, 2003).

Generally, there are widely used types of sorption related to soil sorption and presented in the following:

2.3.1 Kinetic sorption

The sorption capacity can be defined using a mass equilibrium by the following equation:

$$Q_e = \frac{(C_i - C_e)V}{m}$$

where Q_e is concentration of the chemical on the solid particle (mg/g) at equilibrium, C_i is initial concentration of the chemical (mg/l), C_e is concentration of the chemical remaining in the solution at equilibrium (mg/l), and m is mass of soil (g).

2.3.1.1 The pseudo-first order

The pseudo-first order kinetic is given by the equation

$$\ln(q_e - q_t) = lnq_e - k_1 t$$

where q_e and q_t are the amounts adsorbed per unit mass at equilibrium (mg/g^{-1}) and at any time t (min), respectively, and k_1 is the pseudo-first-order sorption rate constant (min^{-1}). The values of k_1 can be obtained from the slope of the linear plot of log (q_e - q_t) and t.

2.3.1.2 The pseudo-second order

The pseudo-second order kinetics is given by the equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_e and q_t are the amounts adsorbed per unit mass at equilibrium (mg/g) and at any time t (min), and k_2 is the pseudo-second-order sorption rate constant (min^{-1}). The plot of t/q_t and t gives a straight line, which allows computation of q_e and k_2.

2.3.2 Equilibrium sorption

Equilibrium isotherms are mathematical models that used to explain the distribution of adsorbate species in solid and liquid phases (Shahmohammadi-Kalalagh, 2011). Equilibrium isotherm models which is used to describe sorption behavior are Linear, Freundlich and Langmuir equations.

2.3.2.1 Linear equation

A Linear function is easy and wildly used sorption isotherm equation.

$$Q_e = K_d \cdot C_e$$

where C_e is solution equilibrium concentration (mg/l), Q_e is the amount adsorbed chemical per mass of adsorbent (mg/g), and K_d is the linear isotherm or the distribution coefficient.

2.3.2.2 Freundlich equation

Freundlich equation is the equation based on sorption on heterogeneous surface of each chemical (Freundlich, 1906). The equation is represented as follows

$$Q_e = K_F C_e^{\frac{1}{n}}$$

This equation can be revised in linear form as

$$\log(Q_e) = \log(K_F) + \frac{1}{n}\log(C_e)$$

where, C_e is solution equilibrium concentration (mg/l), Q_e is the amount of adsorbed chemical per mass of adsorbent (mg/g), n is Freundlich equation exponent, and K_F is the Freundlich constant.

2.3.2.3 Langmuir Model

Langmuir model is the equation describing the homogenous sorption with no interact between adsorbate and surface (Langmuir, 1918). The equation may be represented as

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

Langmuir equation can be expressed in linear form as

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$$

where, Q_e is the amount of adsorbed chemical on sorbent (mg/g), C_e is the concentration of chemical at equilibrium (mg/l), Q_m is the maximum amount of adsorbed chemical per mass of sorbent (mg/g), K_L is the Langmuir constant (L/mg).

2.4 Mathematical modeling

Simulating pollutant transport in subsurface environment is useful to analyze the risk of contamination (Dusek *et al.*, 2011; Šimůnek *et al.*, 2008). Several models are able to evaluate leaching of contaminant in vadose zone such as MACRO, PRZM3, and HYDRUS (Holman *et al.*, 2004; Vanclooster *et al.*, 2000). The existing model are classified into three categories which are simple screening or tier 1, medium complexity model or tier 2, and the most complex model. Data requirement is higher for complex model than the simple one, and more precision or better performance as well (Alavi *et al.*, 2007). However, some site specific data is not available over large area which is required by some intermediate or complex model (Vanclooster *et al.*, 2000). Because of this reason, tier 1 model is used for leaching assessment in the area which has limited data available or regional scale vulnerability assessment.

Tier 1 model provide a point estimate of leaching assessment analyzed from a few properties (Hantush *et al.*, 2000). There are some tools for assessing groundwater vulnerability of pesticides by different input parameters and algorithms. Several tools are provided in order to analyze leaching assessment of pesticides such as Screening Concentration In GROund Water (SCI-GROW) (Pereira *et al.*, 2014), Windows Pesticide Screening Tool (WIN-PST) (Brown *et al.*, 2011). The results from these tools are different due to different assessment algorithms, assumptions, and data sets provided to derive them (Stackelberg *et al.*, 2012). One of the most developed model is the attenuation factor/ retardation factor (AF/RF) (de Paz & Rubio, 2006). This model has been implemented with Geographical Information System (GIS in order to study leaching potential of pesticide in a regional scale by several authors (Diaz-Diaz & Loague, 2000; Diaz-Diaz *et al.*, 1999; Shukla *et al.*, 1998).

Fate and transport of pesticide modeling is related to several sources of uncertainty (Dubus *et al.*, 2003). Many study concluded that there are large variability related with attenuation factor from uncertainties in soil, climate and pesticide properties and also land use (Loague *et al.*, 1996; Loague & Green, 1991). For accounting the uncertainties related to soil and pesticide properties, the attenuation factor was revised and the concept of reference pesticide was introduced for conducting the leaching assessments for Hawaii islands (Li *et al.*, 1998). In this study, the leaching potential of atrazine will be assessed by the AF/RF leaching evaluation tool, which is a tool based on the revised attenuation factor and has never been used in Thailand.

2.4.1 AF/RF model

The AF/RF model is a tier-1 model used to evaluate pesticides leaching potential and groundwater vulnerability (Hall *et al.*, 2015). The purpose of developing this tool was to help making decision for the Hawaii Department of Agriculture. The tool, based on the attenuation factor approach (AF) (Li *et al.*, 1998), has been implemented in the ArcGIS program (Stenemo *et al.*, 2007). AF can be defined by the equation:

$$AF = e^{\left(\frac{\ln(2)\cdot d\cdot RF\cdot \theta_{FC}}{q\cdot t_{1/2}}\right)}$$

where d is the depth to groundwater (m), θ_{FC} is the water content at field capacity, q is the water flow or recharge through the soil (m/d), k is a constant for ensuring AFR is greater than unity, and $t_{1/2}$ is the half-life of each pesticide (d). The term RF, which is known as retardation factor, can be computed by the equation:

$$RF = 1 + \frac{\rho_b \cdot f_{oc} \cdot K_{oc}}{\theta_{FC}}$$

where ρ_b is the soil bulk density (kg/m^3), f_{oc} is the fractional organic carbon content, and K_{oc} is the sorption coefficient (m^3/kg).

To assess leaching potential of pesticide, AF value is classified into five classes following (de Paz & Rubio, 2006).

2.4.2 The GUS index

The GUS index is used to assess the leaching potential of the pesticides using the sorption coefficient K_{oc} and half-life ($t_{1/2}$) of each chemicals (Gustafson, 1989). A herbicide with GUS score more than 2.8 is considered as a "leacher", while a herbicide with a value less than 1.8 is regarded as a "nonleacher" and those between 1.8 and 2.8 qualifies as a "transitional". The GUS index can be determined by the following equation:

$$GUS = \log t_{\frac{1}{2}} (4 - \log K_{oc})$$

CHAPTER 3

Methodology

3.1 The experimental framework

There are two main parts in this study, consisting of soil and groundwater analysis and pesticide leaching risk modelling. Most of the parameters required for the leaching model are provided from soil analysis and sorption experiment. Moreover, detectable concentrations of atrazine and nitrate are used to compare to the result of the model. The overall experimental framework of the current study is shown in figure 3.1.

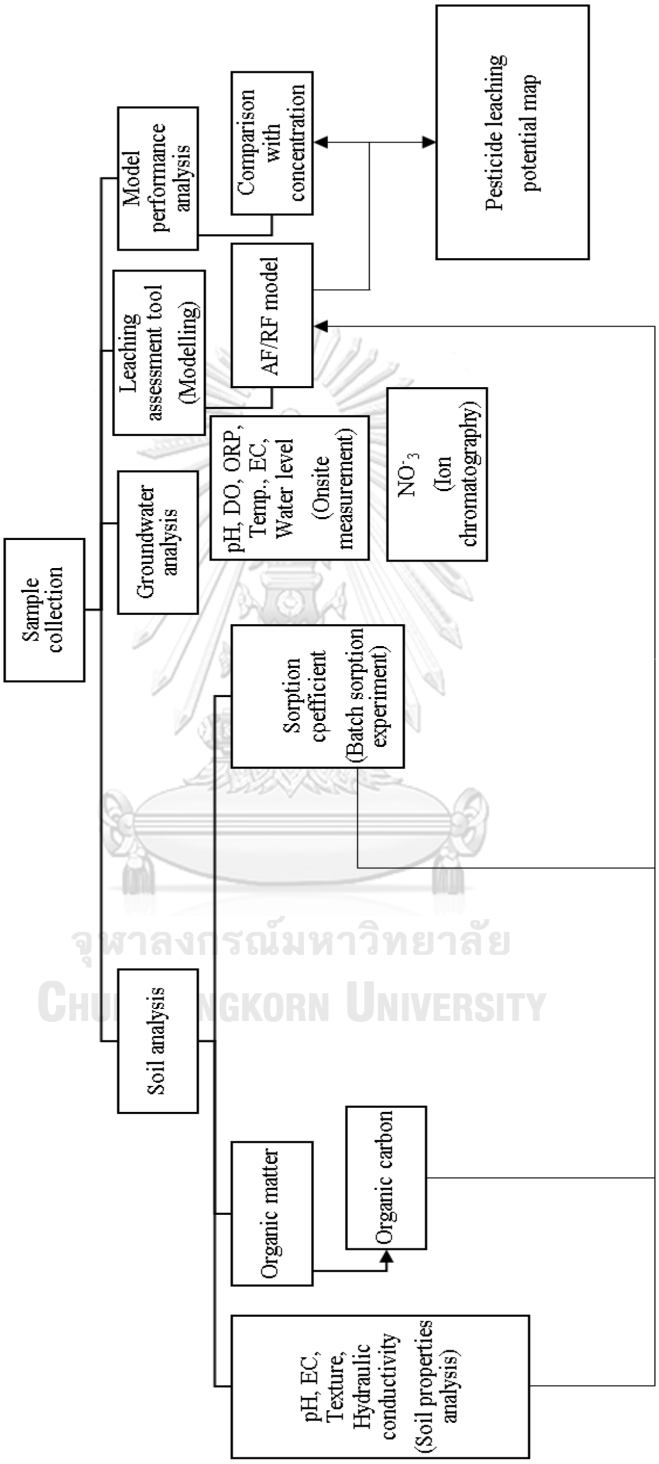

Sample collection
Soil analysis
Groundwater analysis
Leaching assessment tool (Modelling)
Model performance analysis
pH, EC, Texture, Hydraulic conductivity (Soil properties analysis)
Organic matter
Organic carbon
Sorption cpefficient (Batch sorption experiment)
pH, DO, ORP, Temp., EC, Water level (Onsite measurement)
NO_3^- (Ion chromatography)
AF/RF model
Comparison with concentration
Pesticide leaching potential map

Figure 3. 1 Study framework

3.2 Study site description

Table 3. 1 Data source for evaluating the study area

Data	Type	Source
Soil type	Shapefile	Land Development Department
Land use	Shapefile	Land Development Department
Nitrate Contamination Map	Shapefile	(DGR, 2009)

The evaluation of atrazine leaching potential of this study was performed in sugarcane field located in U-thong and Song Phi Nong district, Suphan Buri province, Thailand, which is situated in tropical zone. Topography of the province is mainly mountainous area in the west and floodplain in the east. It has been reported that the average annual precipitation and average annual temperature are 975.4 mm and 28.1ºC.

Before collecting the samples, the data will be collected and processed in ArcGIS in order to select the suitable soil and groundwater sampling points. The sources of the data was indicated in table 3.1. As a result, there were many land utilization in the area, such as active paddy field, sugarcane field, and community. Especially sugarcane, it has been considered as intensively atrazine usage for controlling weed infestation. Seventy percent of the area is used for sugarcane plantation, 29% is paddy field. Additionally, there were three soil types mainly in the study area, which are Kamphaeng Saen series, Ayutthaya series, and Saraburi series. To consider the leaching risk of atrazine in the study area, soil and groundwater were collected from 8 different sampling points located around the area of sugarcane field. These sampling points were selected according to the study of Department of Groundwater Resources. They are a wide range of nitrate concentrations and well distributed over the sugarcane area. All 8 sampling points are shown in table 3.2 and figure 3.2.

Table 3. 2 The locations of the groundwater and soil sampling points

Sample ID	Northing	Easting	Land use type
S1,W1	1557809	590867	Sugarcane field
S2,W2	1566568	588822	Sugarcane field
S3,W3	1569407	596884	Sugarcane field
S4,W4	1572767	604149	Sugarcane field
S5,W5	1572299	602557	Sugarcane field
S6,W6	1561794	597162	Sugarcane field
S7,W7	1579243	594659	Sugarcane field
S8,W8	1584274	588887	Sugarcane field

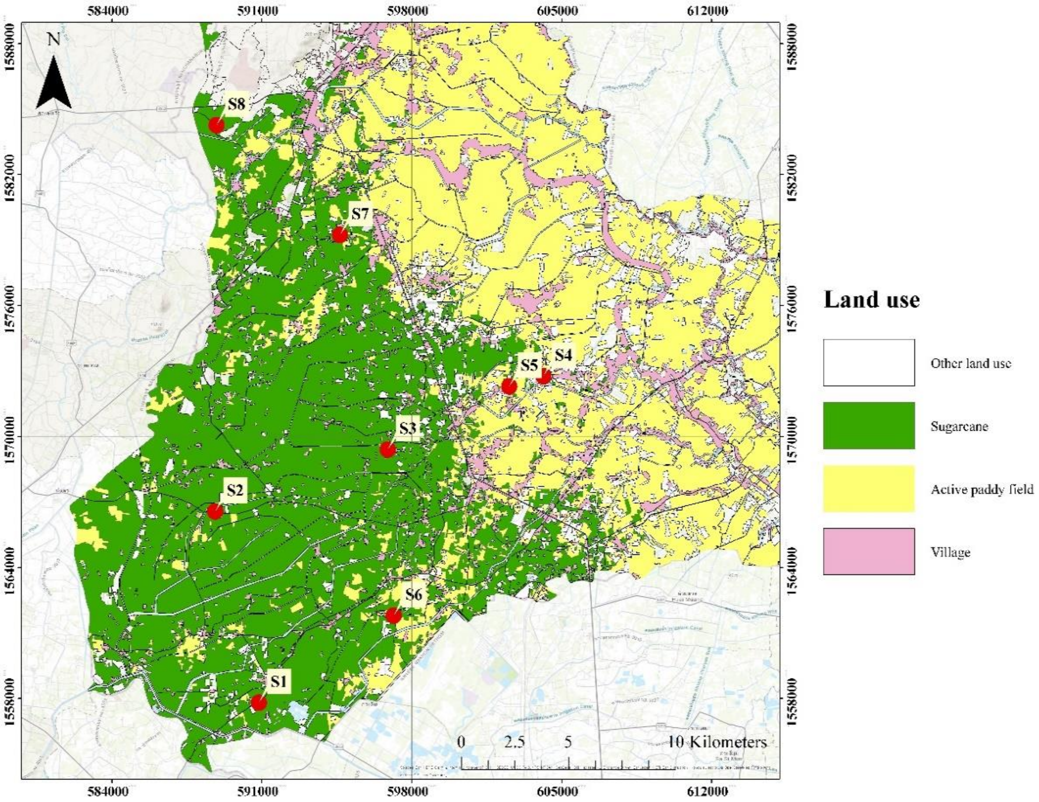


Figure 3. 2 the map showing eight soil sampling points distributed over the study area

3.3 Groundwater samples collection

In this study, groundwater samples were collected from 8 different points (same points as soil sampling points) located in U-thong and Song Phi Nong district, Suphan Buri province, Thailand. The sampling bailer with rope was dropped into shallow groundwater well until it was full. Then, the bailer was pulled from the well and poured in the bucket. Moreover, groundwater level was measured using water level meter. Rope of the meter was dropped into the well until it touched surface of the groundwater. The rope length means the depth of the groundwater well. For deep groundwater well, there was pumping system installed for groundwater consumption. Before collected, groundwater was pumped out for 15 minutes.

The parameters measured on site were pH, oxidation reduction potential (ORP), dissolved oxygen (DO), electrical conductivity (EC), and temperature. Moreover, groundwater was collected for nitrate analysis. The samples for each points were stored on ice during transportation.

3.4 Soil samples collection

Soil samples were collected from 8 different points from sugarcane field in the study area based on soil type. The samples in this study were divided into two types which are bulk soil sampling and soil core sampling.

3.4.1 Bulk soil sampling

Each soil sampling points was collected under 15 cm depth from 5 different spot around the considering sampling point. Each of sampling spot was approximately 10 m far from each other and then mixed the soil from five different spot together which was not lower than 1 kg for representing soil in the considering point.

3.4.2 Soil core sample

For this method, 15-cm-depth soil surface was firstly remove and then soil sample was collected using soil core with a total volume of 100 cm^3 and duplicated. The core was hammered down for reserving all of soil formation.

3.5 Soil preparation

After collecting soil samples, the samples were air-dried for one week and then passed through 2 mm sieve. Only soil particle ≤ 2 mm diameter was kept for further experiment as a result.

3.6 Soil analysis

3.6.1 Bulk density

Soil bulk density was determined from soil core sample conducted at Department of Agriculture, Ministry of Agriculture and Cooperative. The samples with core were firstly measured and then used for determining hydraulic conductivity. Next, soil samples with cores were oven-dried at 105°C for one day. Then, weight of the dried soil core was measured and soil bulk density was calculated by equation 3.1.

$$Bulk\ density = \frac{Weight\ of\ dry\ soil\ and\ core + Weight\ of\ core}{Soil\ core\ volume} \quad \text{(Eq. 3.1)}$$

3.6.2 Hydraulic conductivity

The experiment that was used for determining hydraulic conductivity in this study was called falling head method conducted at Department of Agriculture, Ministry of Agriculture and Cooperative. Firstly, the soil cores were filled with water until they became saturated for 3 days. Then, soil samples with core were covered by tube and filled 10 cm height with deionized water from the top of the core and triplicated. Next, hydraulic conductivity for each soil samples was calculated by equation 3.2

$$K_{20} = 0.30122 \times \log(\frac{h_1}{h_2}) \times \frac{\mu_t}{t} \times 36{,}000 \quad \text{(Eq. 3.2)}$$

where h_1 and h_2 are initial and final head of water indicated in tube (cm), μ_t is viscosity of water at the experimental temperature (mPa·s), and t is time during water head falling (hr).

Moreover, water holding capacity (θ_{FC}) can be found by this method. θ_{FC} was calculated by equation 3.3.

$$\theta_{FC} = \frac{Weight\ of\ wet\ soil\ and\ core - Weight\ of\ dry\ soil\ and\ core}{Weight\ of\ dry\ soil} \quad \text{(Eq. 3.3)}$$

3.6.3 Soil texture

For soil texture determination, hydrometer method was used for particle analysis in order to receive proportion of sand, silt and clay of soil samples.

Forty grams of a soil sample was prepared and sodium hexametaphosphate was used as a dispersant. Firstly, 40 grams of the soil sample was mixed with 250 ml of DI water and 100 ml of hexametaphosphate and then left for 12 hrs. Next, stirred the sample and then added it in 1000-ml cylinder. Deionized water was added until the volume is 1000 ml, then the cylinder will be shaken for 1 minute. Hydrometer was put into the cylinder and read at different time intervals (30 sec., 1 min., 1.5 hr., and 24 hrs.). In addition, a blank solution was prepared by adding 100 ml of hexametaphosphate in a cylinder and then DI water was added until the volume is 1000 ml.

Calculation was done as follows:

- Determined C as the concentration of soil in suspension in g/l by equation 3.4:

$$C = R \cdot R_L \qquad \text{(Eq. 3.4)}$$

where R is the hydrometer reading (g/l) and R_L is the hydrometer reading of a blank solution (without soil). Note that R and R_L will be taken at each time interval (30 sec., 1 min., 1.5 hr., and 24 hrs.)

- Determined P as the cumulative percentage for the provided time interval by equation 3.5:

$$P = \frac{C}{C_0} \times 100\% \qquad \text{(Eq. 3.5)}$$

where C_0 is a soil sample's oven dry weight.

- Determined X as the mean particle diameter in suspension (µm) at the time t (min) by equation 3.6 to 3.9:

$$X = \emptyset t^{-1/2} \quad \text{(Eq. 3.6)}$$

with

$$\emptyset = 1000 \cdot \sqrt{BL} \quad \text{(Eq. 3.7)}$$

$$B = \frac{30\eta}{g(\rho_s - \rho)} \quad \text{(Eq. 3.8)}$$

and

$$L = -0.16416(R) + 16.3 \quad \text{(Eq. 3.9)}$$

where ø is parameter of sedimentation (µm), L is effective hydrometer depth (cm), η is fluid viscosity in poise (g $cm^{-1}s^{-1}$), g is gravitational acceleration (cm^2/s), ρ_s is density of soil particle (g/cm^3), and ρ is density of solution (g/cm^3).

Then, plotted the percentage curve using hydrometer reading taken over time interval (30 s., 1 min., 1.5 hr., and 24 hrs.). The curve provides sand silt and clay percentage.

- Clay fraction

Estimated $P_{2\mu m}$ as cumulative percentage at 2µm from equation 3.10 and 3.11:

$$P_{2\mu m} = m \ln\left(\frac{2}{X_{24}}\right) + P_{24} \quad \text{(Eq. 3.10)}$$

$$m = \frac{P_{1.5} - P_{24}}{\ln(\frac{X_{1.5}}{X_{24}})} \quad \text{(Eq. 3.11)}$$

where m is slope of the percentage curve between X at 1.5 hour and 24 hours, X_{24} is mean particle diameter in suspension at 24 hours, P_{24} is cumulative percentage at 24 hours.

- Sand fraction

Calculated the 50 µm cumulative percentage using the same procedure as determining clay fraction, but using 30 sec. and 1 minute hydrometer reading.

- Silt fraction

Estimated the percent silt by equation 3.12:

$$\text{Silt percent} = 100 - (\%\ \text{sand} + \%\ \text{clay}) \quad \text{(Eq. 3.12)}$$

$$= 100 - (P_{50\mu m} + P_{2\mu m})$$

3.6.4 Soil pH

For determining soil pH, twenty grams of each soil was added into 60-ml PE bottle with 20 ml of distilled water (1:1 w/w). Then, the sample was stirred regularly for 30 minutes and left for 30 minutes until soil was settled. Next, soil pH was determined by measuring pH of water above the soil (LDD, 2010).

3.6.5 Soil organic matter

Soil samples were analyzed following Walkley and Black (1934) for determining soil organic matter. Twenty ml of high concentration sulfuric acid and ten ml of 1 N of potassium dichromate ($K_2Cr_2O_7$) were added into 1 g of soil samples. Then, fifty ml of deionized water was added in the solution after the soil solution was leaved for 30 minutes. Next, 5 drop of O-phenantholine was added and the solution was titrated with 0.5 N of ammonium iron (II) sulfate hexahydrate ($Fe(NH_4)_2(SO_4) \cdot 6H_2O$; FAS). Then, the soil organic matter can be defined by equation 3.13:

$$OM = \frac{(B-S)\times N}{B\times W} \times 6.717 \quad \text{(Eq. 3.13)}$$

where B is the amount of FAS that used for blank titration (ml), S is the amount of FAS that used for sample titration (ml), N is $K_2Cr_2O_7$ concentration, and W is weight of soil sample. Additionally, organic matter content was converted into organic carbon content by equation 3.14:

$$Organic\ matter\ (\%) = Organic\ carbon\ (\%) \times 1.72 \quad \text{(Eq. 3.14)}$$

3.7 Adsorption experiment

An atrazine adsorption ability was conducted using a batch procedure (L. Yue *et al.*, 2017). Firstly, one gram of each soil samples from the study area was put into 15-ml centrifugal tube with 10 ml of atrazine solution (in background solution of acetonitrile and 0.01 mol/l $CaCl_2$ to maintain an ionic strength). Atrazine solution was added at initial concentration of 0.5, 1, 5, 10 and 20 mg/l. Then, all tubes were sealed and shaken for 24 hours. Next, the suspensions were centrifuged at 5000 r/min for 5 minutes. A 2-ml supernatant was filtered through 0.45 µm pore size membrane and then was analyzed by HPLC. Each soil analysis was triplicated. Moreover, a blank (no soil) was prepared for each initial concentration. Atrazine loss through filtrating membrane was negligible. The amount of atrazine sorbed by soil can be calculated by equation 3.15:

$$Q_e = \frac{(C_i - C_e)V}{m} \qquad \text{(Eq. 3.15)}$$

where q_e is amount of atrazine sorbed by soil (mg/g), C_i is initial atrazine concentration (mg/l), C_e is equilibrium atrazine concentration (mg/l), V is volume of the solution (l), and m is mass of soil (g). Then, K_d or distribution coefficient was defined by equation 3.16:

$$Q_e = K_d \cdot C_e \qquad \text{(Eq. 3.16)}$$

Next, the distribution coefficient was normalize into K_{oc} by equation 3.17:

$$K_d = K_{oc} \cdot f_{oc} \qquad \text{(Eq. 3.17)}$$

where K_{oc} is sorption coefficient, and f_{oc} is fractional organic content.

3.8 Nitrate detection

Firstly, the groundwater samples collected from 8 different points in the study area were acidified by H_2SO_4 for making pH of the samples lower than 2. Then, the concentration of nitrate (NO^-_3) was measured using Ion Chromatography (IC) which has detection limit of 0.1 mg/l.

3.9 Leaching assessment modeling

Leaching potential of atrazine in the study area was analyzed using the AF/RF model, which is the tool based on the revised attenuation factor. Half-life value of atrazine, which is an input parameter of the AF/RF, is estimated from the measured K_{oc} values. Then, the model was implemented in ArcGIS. The leaching potential was classified as high, medium, moderate, low, and very low for this evaluation.

Soil (i.e. θ_{FC}, ρ_b, and f_{OC}) and recharge properties (i.e. q) were used in this assessment. In this study, the input parameters were provided by many sources shown in table 3.3.

Table 3. 3 Data requirement for the AF/RF model

Parameter	Sources
K_d	Sorption experiment (Laboratory)
f_{oc}	Derived from organic matter content (Laboratory)
d	Groundwater elevation measurement (On site measurement)
q	Hydraulic conductivity experiment (Laboratory)
θ_{FC}	Water holding capacity experiment (Laboratory)
ρ_b	Soil bulk density experiment (Laboratory)

CHAPTER 4

Results and discussion

4.1 Groundwater properties and groundwater flow

The properties of groundwater collected from eight different shallow wells with lower than 30 meter deep in the study area collected during 21st-22nd July 2018 are shown in table 4.1.

According to the Table 4.1, pH of values of groundwater samples were in the range of 7.12-7.99 indicating weakly alkaline condition since sediments are mainly weathered from limestone ((DGR, 2009)). Moreover, the another reason is possibly due to the application of alkaline pesticides such as atrazine (pKa=1.7) (Hertfordshire, 2013) , and ametryn (pKa=10.07) (Hertfordshire, 2013) in this agricultural area. As a result, groundwater had chance to be affected by leaching of these pesticides. In addition, temperatures were in a range of 28.8°C -32°C showing relatively constant across all samples. Dissolved oxygen (DO) and oxidation-reduction potential (ORP) measured on site by portable meter varied from 0.66-4.34 mg/l and 154-252.9 mV, respectively. In general, with a deep groundwater level is absent of DO (Rose & Long, 1988). However, some samples collected from shallow groundwater wells were found high DO values due to direct atmospheric oxygen diffusion. Moreover, groundwater with a pumping system affected DO values in groundwater (Bonte *et al.*, 2017). The presence of DO in groundwater indicated that DO is the primary electron acceptor for oxidation of organic compounds in groundwater (Parker *et al.*, 2012). Moreover, groundwater flow direction was derived from groundwater level measurement in this study area as shown in the Figure 4.1. In this study area, groundwater flows from the north and west (W1, W2, W3, W6, W7, and W8) to the east of the area (W4 and W5).

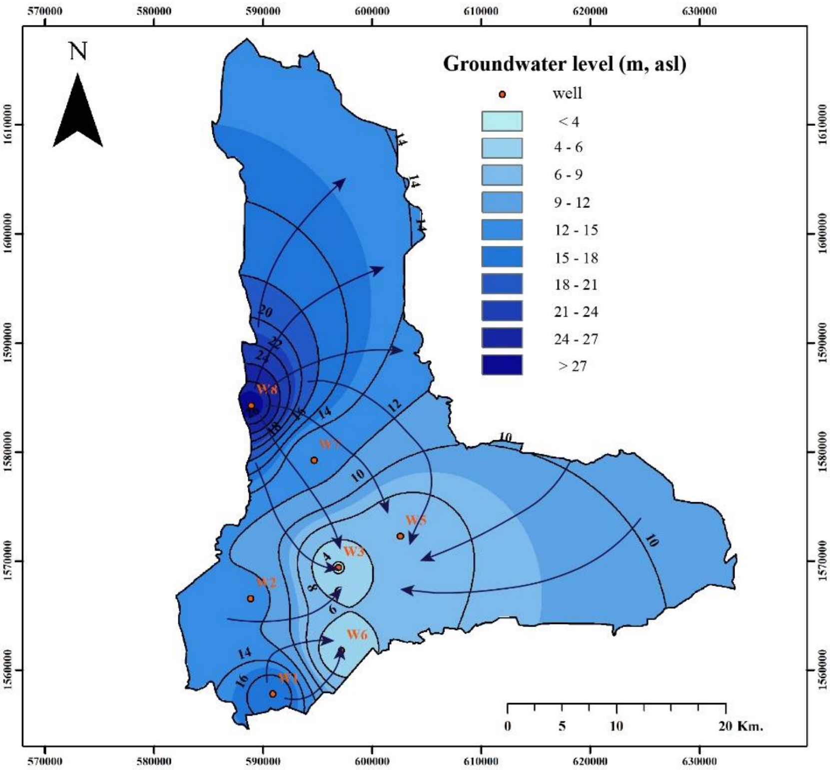


Figure 4.1 Groundwater flow direction from the groundwater level measurement during 21st-22nd July 2018

Table 4. 1 Groundwater level and on-site chemical properties of eight groundwater samples collected during 21st - 22nd July, 2018

Sample ID	pH	Depth to groundwater level (m)	Groundwater level (m, asl)	DO (mg/l)	ORP (mV)	EC (µs/cm)	Temp (°C)
W1	7.65	1.50	16.35	1.97	154.00	534.00	28.80
W2	7.72	0.50	12.66	1.65	195.40	930.00	30.10
W3	7.97	1.00	3.87	0.66	176.50	1078.00	32.00
W4	7.99	1.30	-2.10	4.34	236.30	1485.00	30.20
W5	7.12	0.65	6.42	1.63	235.10	1473.00	30.10
W6	7.80	0.90	4.01	2.90	252.90	1214.00	30.30
W7	7.23	2.50	12.25	1.96	236.00	834.00	29.90
W8	7.75	0.50	27.69	2.03	250.90	956.00	30.20
Average	7.65	1.11	10.15	2.14	217.14	1063.00	30.20
SD	0.30	0.63	8.65	1.01	34.60	302.21	0.82
Max.	7.99	2.50	27.69	4.34	252.90	1485.00	32.00
Min.	7.12	0.50	-2.10	0.66	154.00	534.00	28.80

4.2 Physico-chemical properties of soils

The physico-chemical properties of soils (i.e., pH, electro conductivity (EC), organic matter (OM), cation exchange capacity (CEC) , and soil texture) of 8 different soil samples collected from sugarcane field in the study area is indicated in Table 4.2.

As a result from Table 4.2, pH values of each soil samples were 6.80-7.90, showing weakly alkaline condition. The result was almost the same as pH of groundwater samples collected in this area because of sediments from the weather limestone and the usage of alkaline pesticide in sugarcane field in the selected area. The organic matter of the soil samples was also shown in the Table 4.2 which was in the range from 1.07 to 2.62. Only two of samples (S5 and S6) indicated OM values which were higher than 2%. Moreover, CEC values of each samples were ranged from 9.06-18.53 cmol/kg, and EC values of each samples were from 0.03-

0.309 dS/m. Furthermore, hydraulic conductivity values were in the range from 0.003 to 1.147 m/d with an average of 0.247 m/day. The hydraulic conductivity values corresponds to the soil textures (Tarboton, 2003). Hydraulic conductivity of all soil samples was lower than 1 m/d, except S8 which has 1.147 m/d. There were 4 types of soil found in the area, which were clay, clay loam, sandy clay loam, and loam (Table 4.2). According to the study of DGR (2009), soil hydraulic conductivity depends upon the soil texture in the field. DGR (2009) reported that most of the study area was covered by loam and sandy loam soils. Moreover, there was also clay soil in the area as a result from the previous study. The result can be concluded that most of this area has low water holding capacity analyzed from soil texture. Additionally, bulk density of the samples varied from 1.461-1.701 g/cm^3. Additionally, unreasonable value obtained from experiment may be an error from sampling, thus, the Neural Network Prediction (NNP) option available in HYDRUS-1D was used by assigning the values of bulk density as well as sand silt and clay percentage.

Table 4. 2 Physio-chemical properties of eight soil samples

Sample ID	pH	EC (dS/m)	OM (%)	CEC (cmol/kg)	Sand (%)	Silt (%)	Clay (%)	Bulk density (g/cm^3)	Soil type	Hydraulic conductivity (m/d)	Water holding capacity
S1	7.2	0.19	1.7	15.22	27.4	27.2	45.4	1.46	Clay	0.011	0.98
S2	7	0.08	1.15	11.14	37.4	35.2	27.4	1.54	Clay loam	0.016	0.14
S3	6.8	0.03	1.24	9.06	55.4	21.1	23.5	1.62	Sandy clay loam	0.103	0.06
S4	7.1	0.3	1.53	11.16	37.4	37	25.6	1.51	Loam	0.006*	0.96
S5	7.9	0.33	2.42	16.28	37.4	39	23.6	1.61	Loam	0.01	0.11
S6	7.2	0.1	2.62	18.53	31.4	27	41.6	1.7	Clay	0.01	0.96
S7	7.9	0.22	1.07	10.08	29.4	42.8	27.8	1.55	Clay loam	0.005*	0.09
S8	7.6	0.31	1.98	15.83	18.3	35.1	46.6	1.61	Clay	0.003*	0.06
Mean	7.34	0.2	1.71	13.41	13.73	36.36	32.68	1.57	-	0.25	0.42
SD	0.39	0.11	0.55	3.24	3.56	8.07	9.37	0.07	-	0.37	0.46
Max.	7.9	0.33	2.62	18.53	18.53	55.4	46.55	1.7	-	1.15	0.98
Min.	6.8	0.03	1.07	9.06	9.06	27.4	23.5	1.46	-	0	0.06

* Data from HYDRUS-1D

4.3 Batch adsorption experiment

Soil samples collected from the study area were analyzed for the sorption behavior using batch adsorption experiments. The results are shown in the figures 4.2-4.9.

As a result, Figures 4.2 to 4.9 and Table 4.3, it has been found that most of the soil samples can be fitted well with Freundlich isotherm. According to the result, it was found that soil sample S6 has the highest adsorption isotherm (K_d = 0.301 L/kg, K_f = 0.822 m^3/kg, and Q_M = 6.575 mg/g, indicating the highest sorption efficiency, This is because the soil sample S6 also had the highest %OM or organic matter (2.62%) which is considered as the factor influencing adsorption capacity of soil. G. Yue *et al.* (2013) also found that OM was the significant factor for adsorption of atrazine in soil in China.

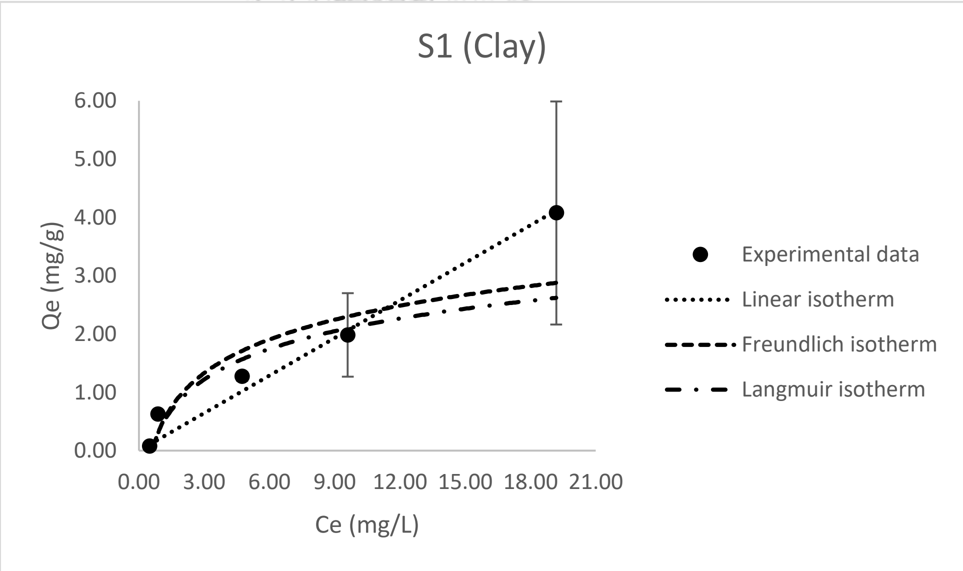


Figure 4. 2 The experimental data of soil S1 plotting with different sorption isotherms

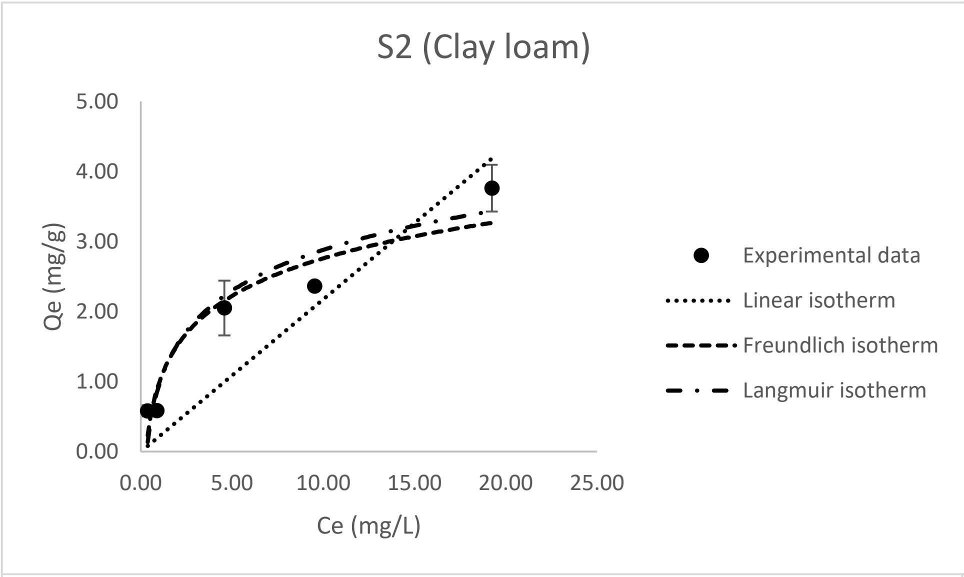


Figure 4. 3 The experimental data of soil S2 plotting with different sorption isotherms

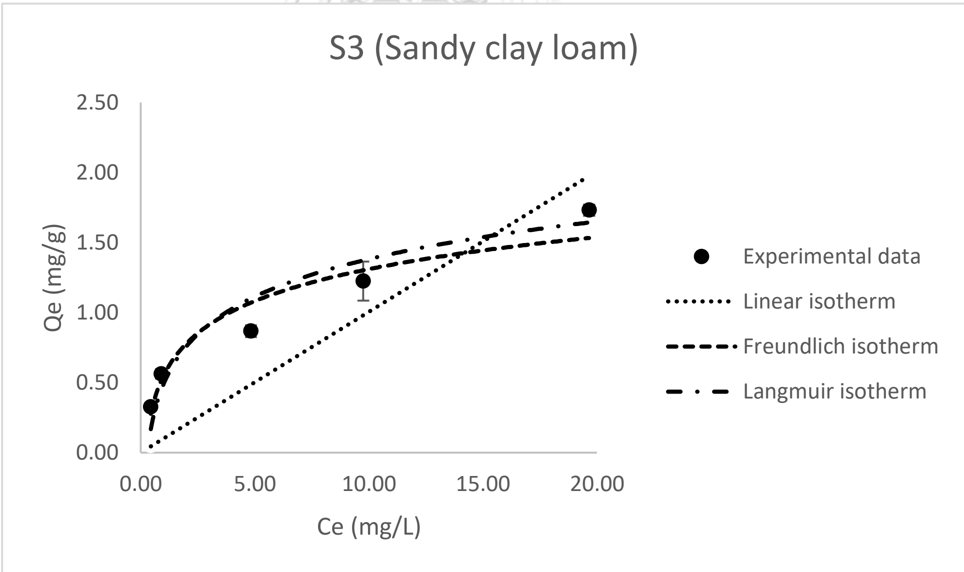


Figure 4. 4 The experimental data of soil S3 plotting with different sorption isotherms

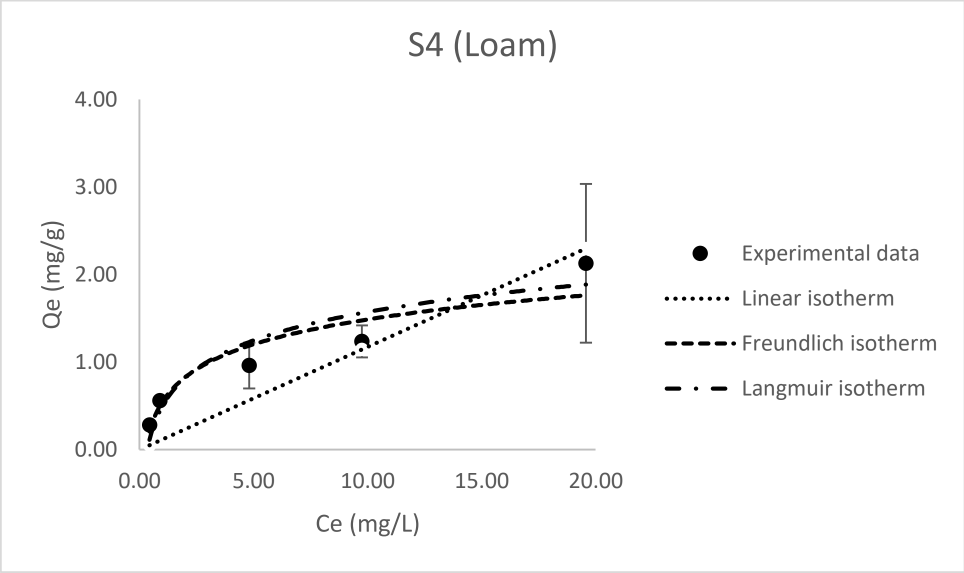


Figure 4. 5 The experimental data of soil S4 plotting with different sorption isotherms

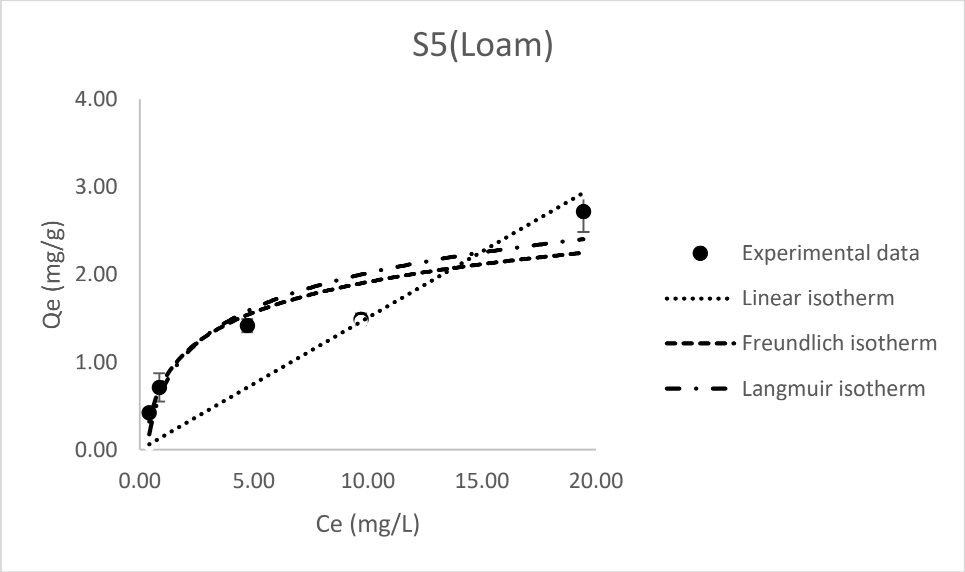


Figure 4. 6 The experimental data of soil S5 plotting with different sorption isotherms

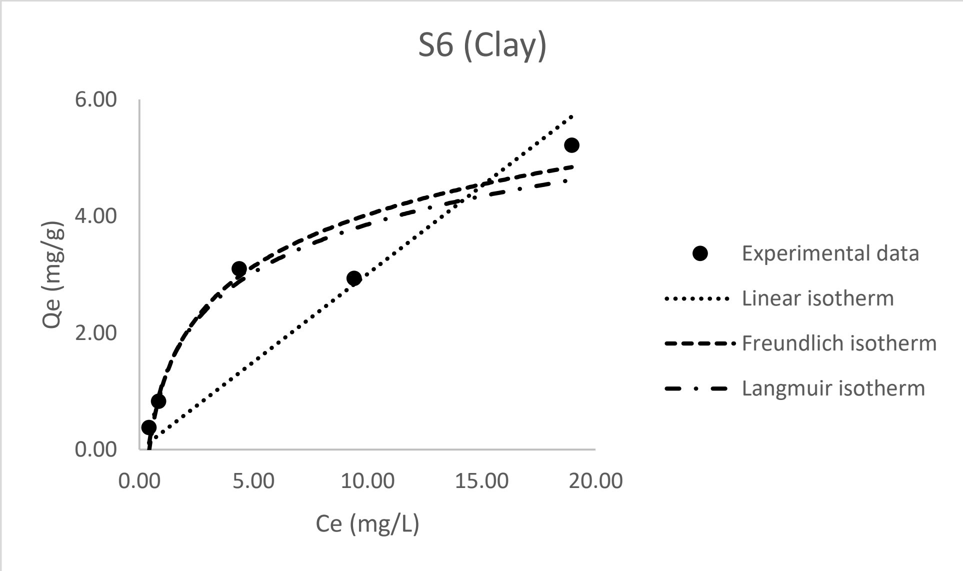


Figure 4. 7 The experimental data of soil S6 plotting with different sorption isotherms

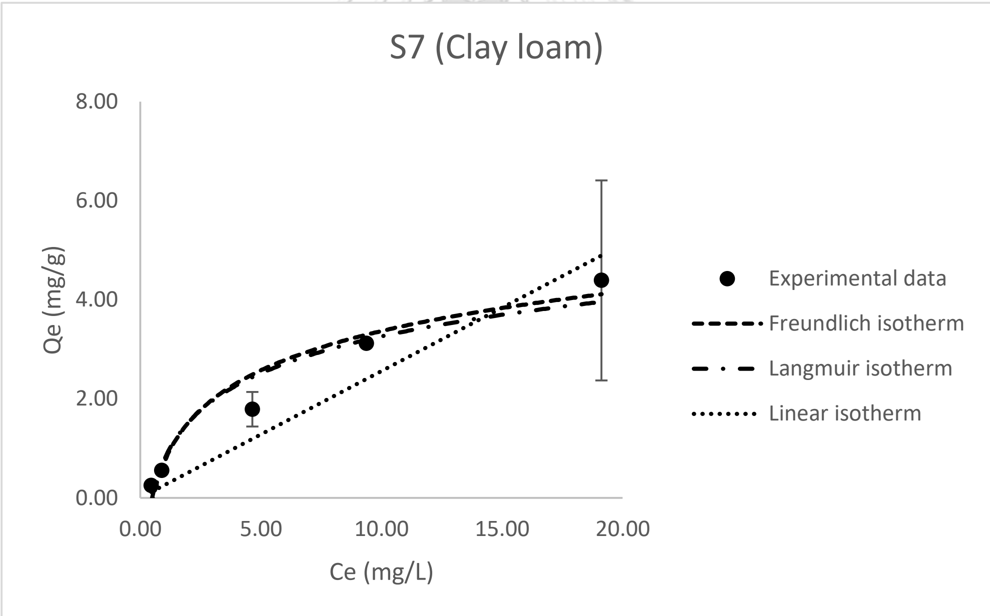


Figure 4. 8 The experimental data of soil S7 plotting with different sorption isotherms

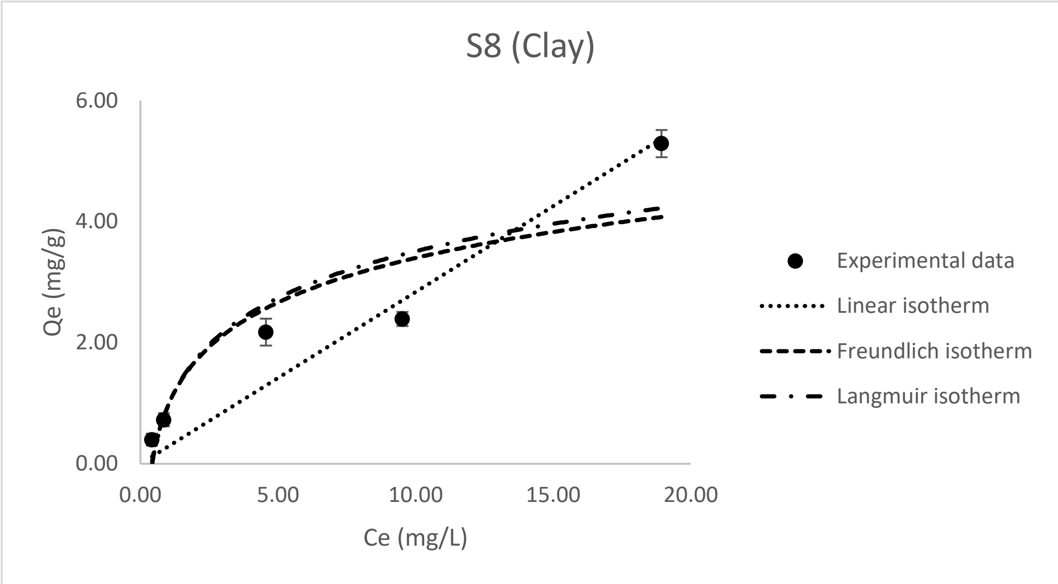


Figure 4. 9 The experimental data of soil S8 plotting with different sorption isotherms

Table 4. 3 Sorption isotherm parameters with root mean square error (RMSE) and coefficient of determination (r^2) of soil samples

Sample	Soil type	K_d (L/Kg)	r^2	RMSE	χ2	K_f (L/Kg)	1/n	r^2	RMSE	χ2	Q_M (g/Kg)	r^2	RMSE	χ^2
S1	Clay	0.171	**0.921**	0.206	2.047	0.284	0.855	0.856	0.204	0.696	7.93	0.231	0.201	1.098
S2	Clay loam	0.218	0.751	0.314	5.003	0.81	0.511	**0.959**	0.16	0.118	4.431	0.923	0.291	0.359
S3	Sandy clay loam	0.1	0.538	0.337	4.742	0.502	0.401	**0.974**	0.04	0.027	1.915	0.943	0.171	0.23
S4	Loam	0.117	0.776	0.244	3.33	0.478	0.472	**0.962**	0.123	0.07	2.411	0.86	0.167	0.294
S5	Loam	0.151	0.68	0.366	5.38	0.673	0.437	**0.963**	0.057	0.106	2.935	0.94	0.313	0.393
S6	Clay	0.301	0.749	0.872	4.284	0.822	0.656	**0.95**	0.421	0.584	6.575	0.837	0.492	0.362
S7	Clay loam	0.256	0.897	0.278	1.184	0.528	0.759	**0.989**	0.118	0.105	7.107	0.952	0.089	0.027
S8	Clay	0.284	0.921	0.288	2.243	0.736	0.633	**0.976**	0.274	0.253	6.711	0.978	0.582	0.517
Mean	-	0.2	0.779	0.363		0.604	0.59	0.954	0.175		5.002	0.833	0.288	
SD	-	0.071	0.124	0.198		0.175	0.152	0.039	0.117		2.215	0.232	0.16	
Max.	-	0.301	0.921	0.872		0.822	0.855	0.989	0.421		7.93	0.978	0.582	
Min.	-	0.1	0.538	0.206		0.284	0.401	0.856	0.04		1.915	0.231	0.089	

The isotherm results from Table 4.3 also were described by the root mean square error (RMSE) and coefficient of determination (r^2) of adsorption behavior of each soil samples. As a result, K_f was suitable for determining K_{oc}. K_f was used as K_d in the following equation (Martins *et al.*, 2018).

$$K_{oc} = K_f / f_{oc}$$

According to the K_f value derived from the Freundlich isotherm, the average value of r^2 and RMSE for 8 soils were approximately 0.954 and 0.175, respectively. Additionally, the result from Chi-square test also indicated that most of the soil samples was fitted well with Freundlich isotherm shown in Table 4.3. Only sample S6 and S7 had lower Chi-square values of Langmuir isotherm than those of Freundlich isotherm.

The measured soil properties indicated that the parameters that had high value of relation to K_d were clay content and organic matter (OM) content. The previous study claimed that the soil organic matter content (OM) played an important role for atrazine adsorption in soil and sediment (G. Yue *et al.*, 2013; L. Yue *et al.*, 2017). As a result, the soil with a high clay content expressed the high sorption coefficient. In contrast, loam and sandy clay loam soil was found to have low sorption coefficients due to low clay contents found in such soil samples (see Table 4.2).

Table 4. 4 Correlation of physico-chemical parameters of soils and sorption parameters from the batch experiment

	Sand	Silt	Clay	OM	pH	EC	CEC	1/n	$b=1/K_LQ_M$	K_d	K_f	Q_m
Sand	1											
Silt	-0.475	1										
Clay	**0.731***	-0.56	1									
OM	**0.891****	-0.264	0.415	1								
pH	0.337	-0.503	0.042	0.279	1							
EC	0.378	-0.411	0.099	0.325	0.704	1						
CEC	**0.974****	-0.508	0.661	**0.933****	0.306	0.312	1					
1/n	0.083	0.349	-0.056	0.242	0.097	-0.432	0.102	1				
$b=1/K_LQ_M$	-0.519	0.385	-0.157	-0.459	-0.294	-0.241	-0.5	0.122	1			
K_d	0.602	-0.377	0.492	0.612	0.07	-0.252	0.651	0.514	-0.509	1		
K_f	0.488	-0.663	0.607	0.246	0.006	-0.114	0.485	-0.172	-0.707	0.67	1	
Q_m	0.358	-0.522	0.603	0.073	0.328	-0.086	0.277	0.311	-0.382	0.651	0.692	1

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

Correlation of each parameters was indicated in Table 4.4. It was found that sand content had a significant relationship with CEC and organic matter of soil at a significance level of 0.01 level. As a result, clay content also had a positive relationship with K_d and K_f values. The study of Khan (2016) found a positive relationship between the sorption coefficient and clay contents as well.

Moreover, K_f from other studies indicated in Table 4.6 was in the range of 0.60 to 3.90 L/Kg. The result of K_f from this study was partly in the range of that from other sources. Additionally, 1/n of this study was also in the ranged of that from other sources which is 0.60 to 2.08.

Table 4. 5 Sorption coefficient of atrazine in soil from other studies

Soil	Sand	Silt	Clay	% OM	% OC	pH	K_d (L/Kg)	K_{oc} (L/Kg)	K_f (L/Kg)	1/n	Source
1	6.00	23.60	70.40	n/a	n/a	n/a	n/a	n/a	2.60	0.85	Martins et al., 2018
2	4.70	12.20	83.10	n/a	n/a	n/a	n/a	n/a	0.60	0.60	
3	12.60	43.40	43.90	n/a	n/a	n/a	n/a	n/a	3.90	0.80	
4	11.70	22.80	65.50	n/a	n/a	n/a	n/a	n/a	0.99	0.80	
5	4.70	39.20	56.10	n/a	n/a	n/a	n/a	n/a	3.30	0.86	
6	4.20	28.40	67.40	n/a	n/a	n/a	n/a	n/a	0.61	0.79	
7	67.00	30.00	3.00	n/a	0.97	8.40	2.98	n/a	3.02	2.08	
8	16.00	39.00	45.00	n/a	2.80	6.40	2.60	92.00	n/a	n/a	
9	2.00	66.00	32.00	n/a	2.40	6.30	2.80	114.00	n/a	n/a	
10	19.00	58.00	23.00	n/a	5.50	6.90	4.00	74.00	n/a	n/a	
11	11.00	62.00	27.00	n/a	2.00	6.10	2.90	146.00	n/a	n/a	
12	5.00	31.00	64.00	n/a	2.40	6.50	3.40	141.00	n/a	n/a	
13	n/a	n/a	n/a	0.65	n/a	4.30	0.51	145.00	n/a	n/a	Olivier et al., 2001
14	n/a	n/a	n/a	1.07	n/a	4.50	0.85	146.00	n/a	n/a	
15	n/a	n/a	n/a	5.15	n/a	6.30	1.69	61.00	n/a	n/a	
16	n/a	n/a	n/a	3.44	n/a	5.80	1.34	67.00	n/a	n/a	
17	n/a	n/a	n/a	4.55	n/a	5.10	2.16	81.86	n/a	n/a	Arantes et al., 2011
18	n/a	n/a	n/a	4.68	n/a	6.00	2.86	105.15	n/a	n/a	
19	n/a	n/a	n/a	3.86	n/a	5.40	3.03	135.27	n/a	n/a	
20	n/a	n/a	n/a	n/a	n/a	n/a	n/a	171.77	n/a	n/a	
21	34.12	40.20	25.68	3.23	n/a	4.19	n/a	n/a	2.09	0.64	Weber et al., 2000
22	42.09	23.92	33.99	4.19	n/a	5.21	n/a	n/a	1.86	0.58	
23	24.50	59.27	16.23	6.37	n/a	7.50	n/a	n/a	2.45	0.68	

4.4 Nitrate concentrations in groundwater

Nitrate concentrations in groundwater was also analyzed in this study. The result was shown in Figure 4.10.

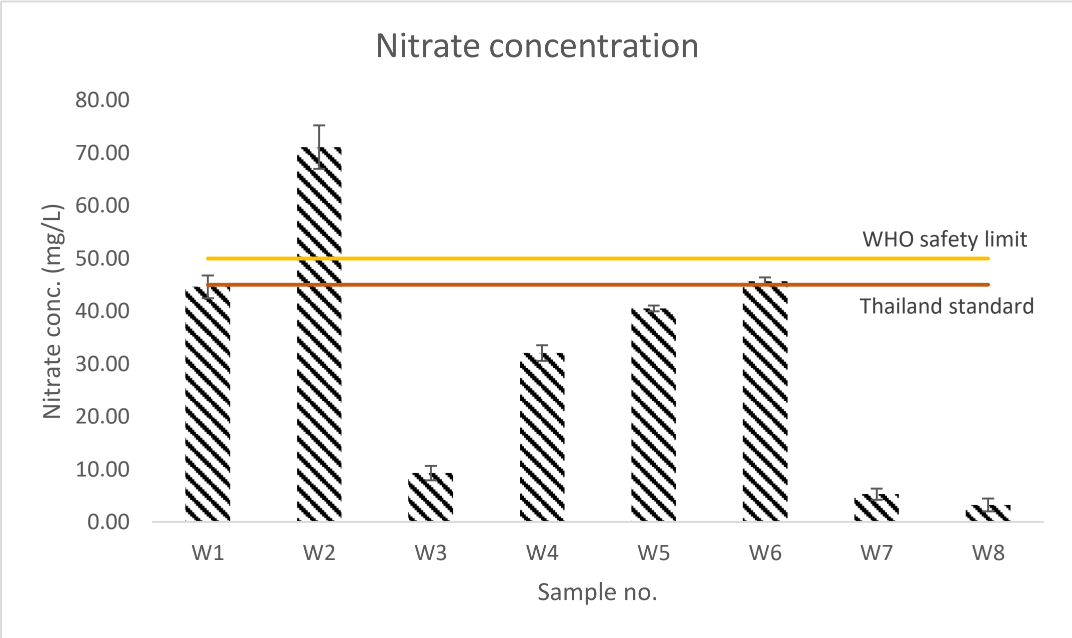


Figure 4. 10 Nitrate concentration in groundwater samples

The result was ranged from 3.250 – 71.110 mg/L with an average of 31.484 mg/L. From figure 4.12, two of samples had nitrate concentration exceeding Thai standard which is 45 mg/L. One of them had the concentration over WHO safety limit which is 50 mg/L. It has been reported that farmers in the study area usually use urea fertilizer (46-0-0), ammonium sulfate fertilizer and also organic fertilizer in rice and sugarcane field (DGR, 2009). From Table 4.11, the result of measured nitrate in this study indicated the similar trend conform the detectable nitrate concentrations reported by Department of Groundwater Resources.

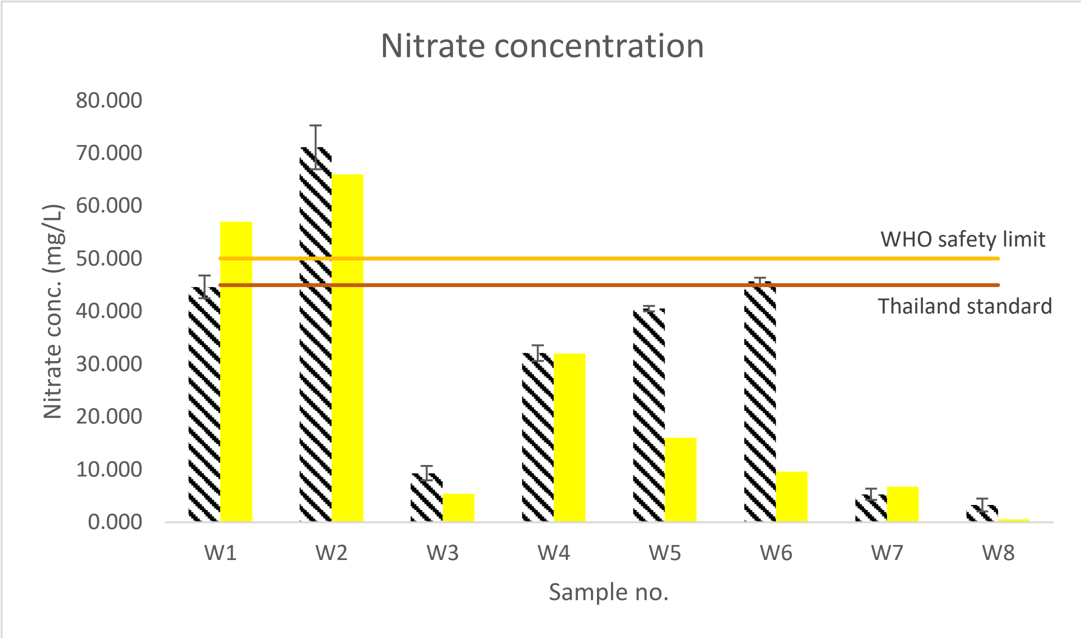


Figure 4. 11 Nitrate concentration in groundwater samples during 21st -22nd July 2018 (this study) and 2009 (DGR, 2009) in the study area

It has been reported that nitrate can be detected in the similar trend as pesticide concentrations found in groundwater table. It has been found this relation in several areas (Hallberg, 1997; Kross & Hallberg, 1990; Vonberg *et al.*, 2014). The result also showed a contrast result of detected nitrate and detected atrazine concentrations in groundwater. In other words, some groundwater samples had high nitrate concentration but had low atrazine in groundwater. It has been found that most pesticides are slow during leaching due to adsorption of soil organic matter, while nitrate was a conservative solute and not react with soil (Hallberg, 1997).

4.5 Leaching risk

The result was derived from AF/RF model. For classifying the leaching potential of atrazine, the attenuation factor was divided into 5 classes: very low (0 to 0.00001), low (0.00001 to 0.01), moderate (0.01 to 0.1), medium (0.1 to 0.25), and high (0.25 to 1) (de Paz & Rubio, 2006). It can be better presented in the form of map for large area evaluation. As a result, Figure 4.13 indicates leaching of atrazine in this study area. The leaching risk of atrazine is mostly high in the area due to their low adsorption capacity by soil (K_{oc}) which was ranged from 0.017 to

0.121 m^3/kg. The difference of this evaluation is caused by soil properties. It was found that most of soil with low water holding capacity and low organic matter content indicated high risk for applied atrazine. Moreover, soil which texture mostly was clay loam or loam also showed high leaching potential. In contrast, lower leaching potential was considered for soil with higher percentage of organic matter and water holding capacity.

This leaching evaluation map can provide an overview for estimating the pollution potential. Generally, the AF index is used to identify the area with high potential of groundwater contamination from chemicals. From the result of this evaluation, the area of high AF index should be monitored first for limiting fund of groundwater well monitoring. Chemicals with such as atrazine which had high AF index in most of the area should be analyzed more intensively.

Table 4. 6 GUS index of atrazine in soil samples

Soil	Soil type	K_{oc} (m^3/kg)	GUS
S1	Clay	17.27	4.99
S2	Clay loam	121.15	3.46
S3	Sandy clay loam	69.66	3.90
S4	Loam	53.74	4.10
S5	Loam	47.84	4.19
S6	Clay	53.94	4.10
S7	Clay loam	84.83	3.74
S8	Clay	63.95	3.97

GUS index from Table 4.6 also indicated high leaching risk of this herbicide. All soil samples indicated high potential of atrazine leaching to groundwater. The results of GUS index calculated from the parameters measured in this study were mostly in the ranged of GUS index from other sources (ranging from 3.20 to 4.10) as shown in Table 4.7.

However, the result of AF index, which considers other environmental factors, found that samples S1, S4 and S6 had low risk for leaching of atrazine. These three samples were found to have low hydraulic conductivity. This is the reason why they are low leaching potential. This parameter is one of the important parameters used to estimate the leaching potential by AF/RF model, but is not included for estimating of GUS index. Thus, in the case, AF/RF value could be applicable as a screening tool for groundwater monitoring and protection. .

Table 4.7 GUS index of atrazine from other sources

K_{oc} (L/Kg)	GUS	Sources
n/a	3.20	Hereford, 2013
147	4.10	Murray, 2009
n/a	4.06	
n/a	3.56	Lichtfouse, 2011

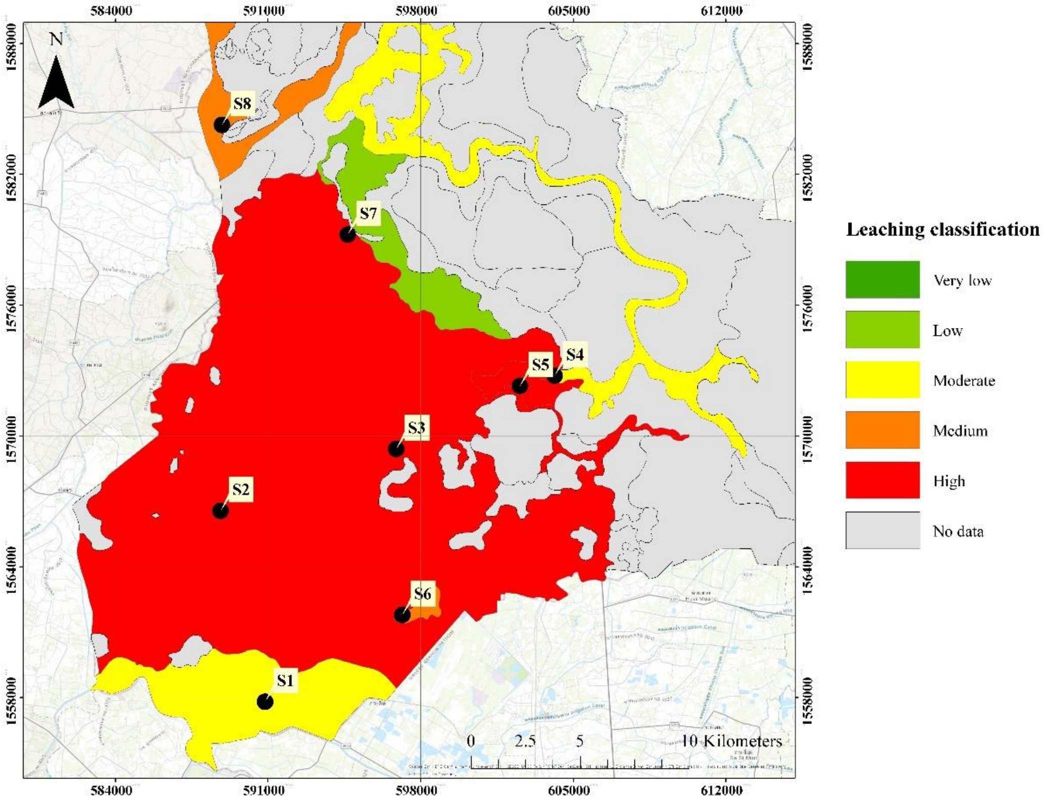


Figure 4. 12 Leaching potential map of atrazine

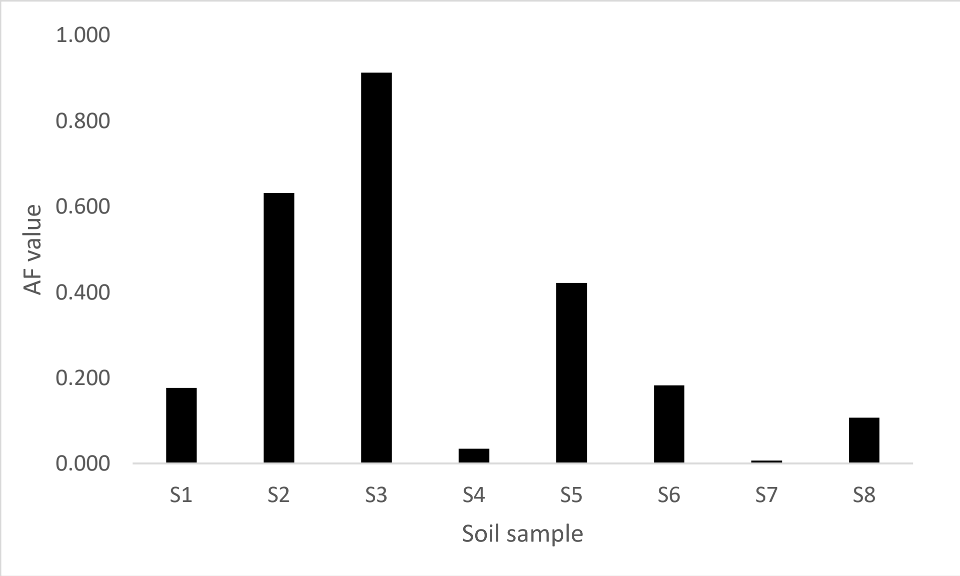


Figure 4. 13 AF value for each soil

As seen in Figure 4.13, the AF value was ranged from 0.007 to 0.913 with an average of 0.309. It has been found that soil with high water holding capacity such as S1, and S4 indicated moderate attenuation factor value. S6 which has low organic matter also showed medium AF value. It has been reported that organic matter affected AF value. Bulk density was also reported with effect to AF value (de Paz & Rubio, 2006).

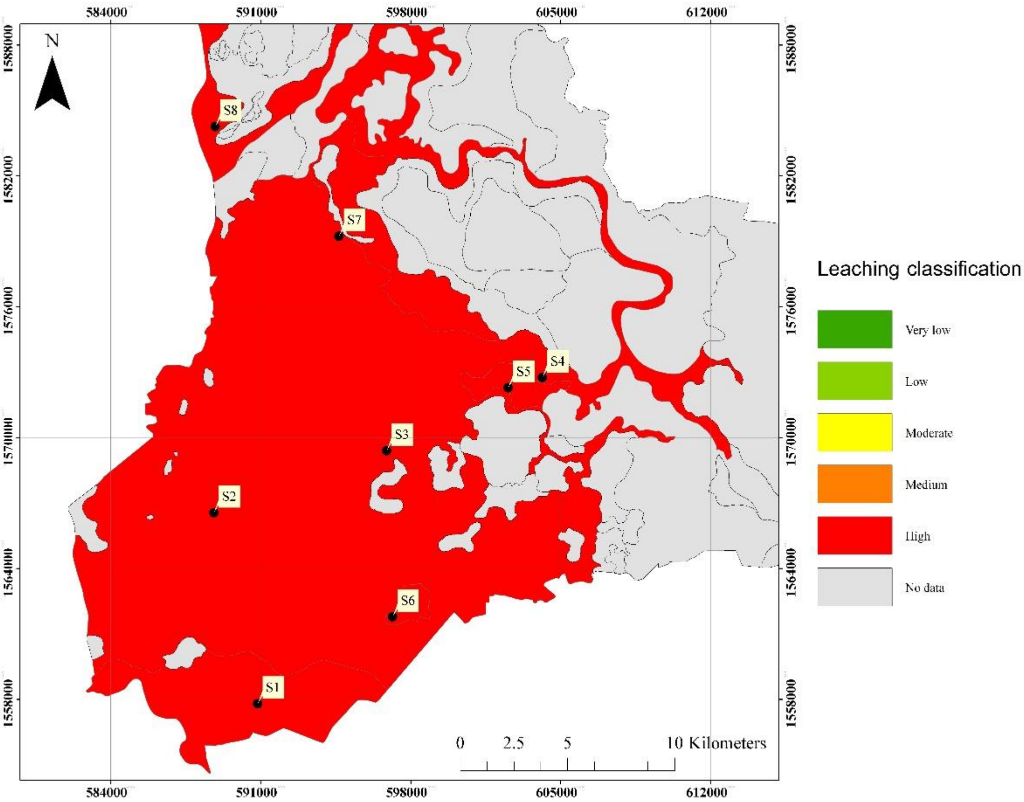


Figure 4. 14 Leaching potential map of nitrate

Leaching potential of nitrate was also evaluated in this study area due to the usage of nitrogen fertilizer in the area.

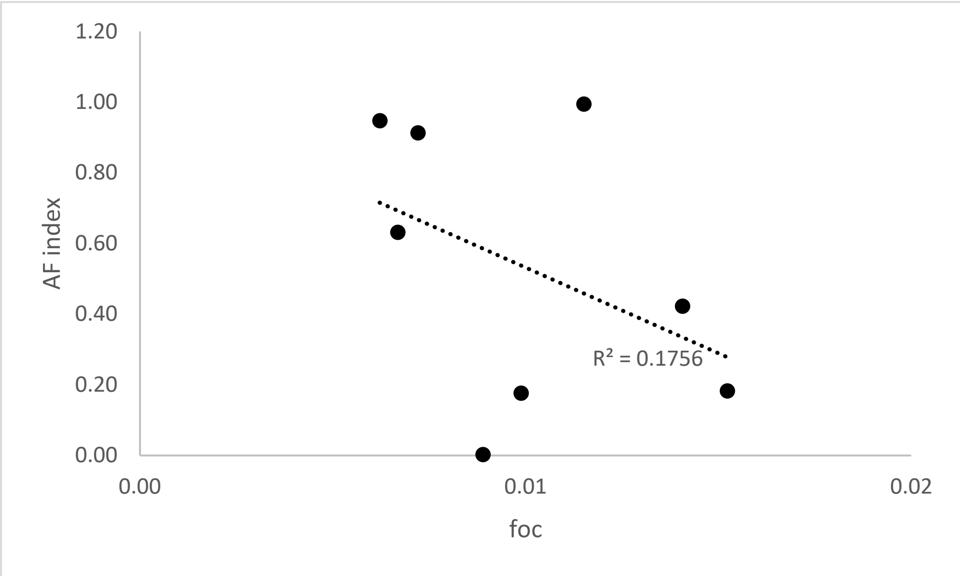


Figure 4. 15 Relation between AF value and f_{oc} of soil samples

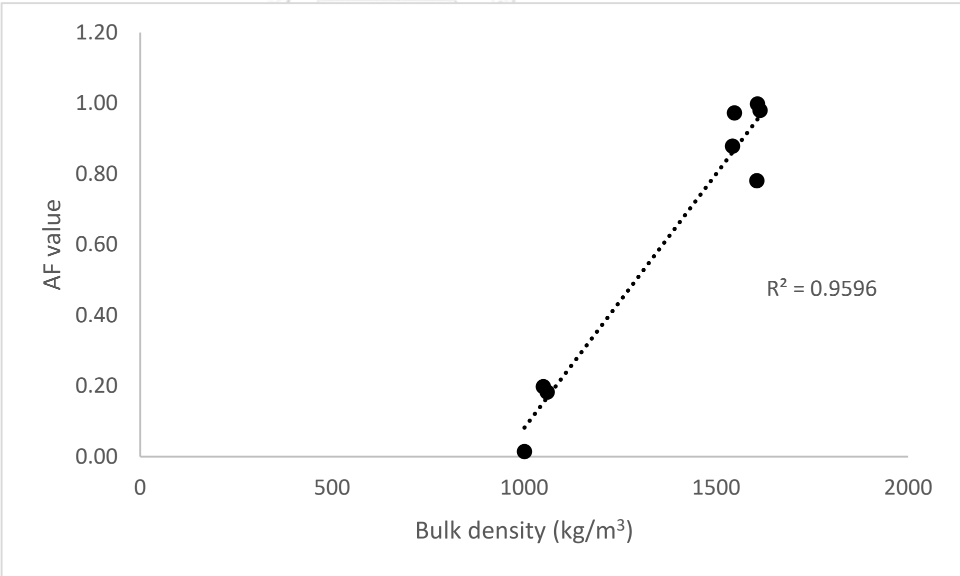


Figure 4. 16 Relation between AF value and bulk density of soil samples

In this study, organic carbon and bulk density were found to have effect to AF value. From Figure 4.15 and Figure 4.16, AF value was increased when f_{oc} was decreased. The soil with a high organic carbon generally has high sorption capacity, causing low leaching of pesticide from soil surface to groundwater; thus AF value was low. Moreover, the bulk density also had strong relationship with AF value in this study. It has also been reported that f_{oc} were found to have the most effect to the leaching potential analysis, using the Partial Rank Correlation Coefficient Analysis (PRCC) (D'Alessio *et al.*, 2018).

4.6 Comparison of concentration and values of AF

For evaluating model performance, the result of the leaching model was compared with nitrate concentration in groundwater. As a result, from Figure 4.17, it was found that three (S2, S5, and S6) of six samples which had high AF values compared to other samples were contaminated by high concentration of nitrate. Moreover, sample (S4) with low AF values was contaminated by lower concentration of nitrate. However, the values of AF of samples S3, S7 and S8 appeared to be not conformed to the nitrate concentrations since the other factors not concerning in this model, such as the horizontal hydraulic conductivity in aquifer. Moreover, the half-life value is one of the main factors, which use the average value from the previous study. However, the result can be concluded that this model could be used as a screening tool for evaluating the leaching potential of pesticide in the study area with 62.5% efficiency.

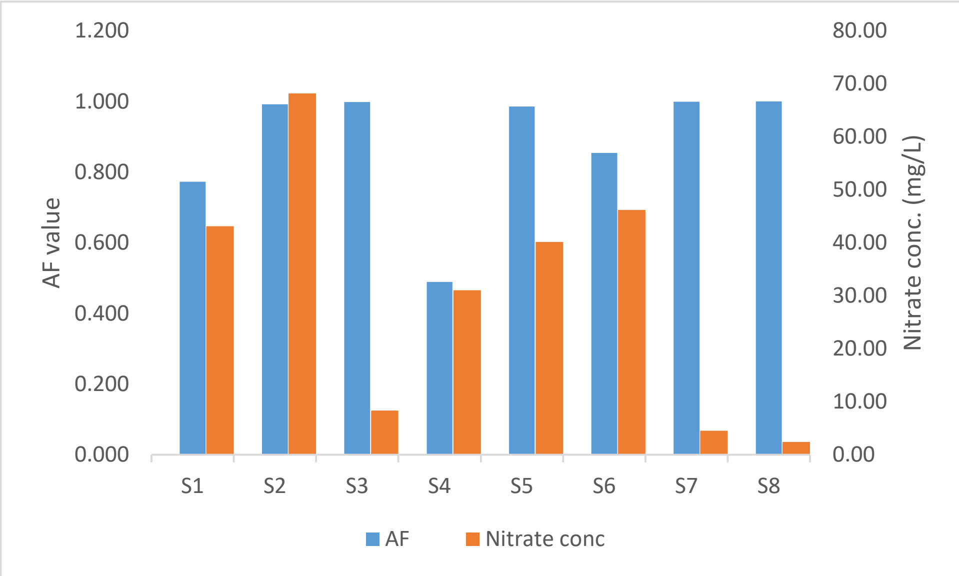


Figure 4. 17 Comparison of AF value and nitrate concentration in groundwater

Chapter 5

Conclusions and recommendations

5.1 Conclusions

In this study, soil and groundwater samples were collected in sugarcane field in U-thong and Song Phi Nong district, Suphan Buri province, Thailand. Soil samples collected in the area of study were identified by different adsorption isotherms. Adsorption behavior of most of the samples can be well explained by Freundlich isotherm. Nitrate in groundwater was also analyzed in this study. The result reported that groundwater with high nitrate concentration had the same trend to detected nitrate in this area reported by Department of Groundwater Resources.

Leaching potential of atrazine and nitrate was also evaluated in this study. The result from leaching assessment by AF/RF model also reported that soil with low sorption coefficient was also found to have high leaching risk. Most of the leaching risk evaluation of nitrate was confirmed with nitrate detection in groundwater in the study site. This evaluation can also help risk management, groundwater resource planning and protection of health risks related to groundwater expose to pesticide contaminated groundwater.

5.2 Recommendations

The limitation of AF/RF model is the factor that not used for evaluating the leaching of pesticide including seasonal effect or application periods. For result with more reliable, more complex model should be used to assess pesticide leaching in the area of study. The AF/RF model is only used for basic evaluation in wide area because this model requires only basic parameters of soil and pesticide properties. Moreover, there is bioactivity in soil. This activity is not included in the model, making the result overestimated.

Pesticide half-life should be tested by the experiment. This study used half-life from other sources due to limitation of time. Moreover, infiltration rate should be tested for getting more reliable recharge rate than getting from soil core sample.

REFERENCES

Alavi, G., Dusek, J., Vogel, T., Green, R., & Ray, C. (2007). Evaluation of dual-permeability models for chemical leaching assessment to assist pesticide regulation in Hawaii. *Vadose Zone Journal, 6*(4), 735-745.

Bonte, M., Wols, B., Maas, K., & Stuyfzand, P. (2017). Sources of dissolved oxygen in monitoring and pumping wells. *Hydrogeology Journal, 25*(1), 55-66.

Brown, J., Bach, L., Aldous, A., Wyers, A., & DeGagné, J. (2011). Groundwater-dependent ecosystems in Oregon: an assessment of their distribution and associated threats. *Frontiers in Ecology and the Environment, 9*(2), 97-102.

Chorom, M., & Shrifi, S. (2010). *Increase sorption endosulfan by soil amendments and its effects on retention and leaching from soil.* Paper presented at the 19th World Congress of Soil Science.

D'Alessio, M., Wang, T., Swift, C. E., Shanmungam, M. S., & Ray, C. (2018). A Tier-I leaching risk assessment of three anticoagulant compounds in the forested areas of Hawai'i. *Science of The Total Environment, 630*, 889-902.

de Paz, J. M., & Rubio, J. L. (2006). Application of a GIS-AF/RF model to assess the risk of herbicide leaching in a citrus-growing area of the Valencia Community, Spain. *Sci Total Environ, 371*(1-3), 44-54. doi:10.1016/j.scitotenv.2006.07.018

Deng, J., Jiang, X., Hu, W., & Hu, L. (2010). Quantifying hysteresis of atrazine desorption from a sandy loam soil. *Journal of Environmental Sciences, 22*(12), 1923-1929. doi:10.1016/S1001-0742(09)60340-5

DGR. (2009). *The assessment of agricultural pollutants in groundwater and guildline design for groundwater remediation in Kanchanaburi and Suphanburi provinces project* Retrieved from Bangkok: http://www.dgr.go.th/project_kpn/file/2551/04.pdf

Diaz-Diaz, R., & Loague, K. (2000). Regional-scale leaching assessments for Tenerife: effect of data uncertainties. *Journal of environmental quality, 29*(3), 835-847.

Diaz-Diaz, R., Loague, K., & Notario, J. S. (1999). An assessment of agrochemical leaching potentials for Tenerife. *Journal of contaminant hydrology, 36*(1-2), 1-30.

Dousset, S., Mouvet, C., & Schiavon, M. (1994). Sorption of terbuthylazine and atrazine in relation to the physico-chemical properties of three soils. *Chemosphere, 28*(3), 467-476. doi:https://doi.org/10.1016/0045-6535(94)90291-7

Dubus, I. G., Brown, C. D., & Beulke, S. (2003). Sources of uncertainty in pesticide fate modelling. *Science of The Total Environment, 317*(1-3), 53-72.

Dusek, J., Dohnal, M., Vogel, T., & Ray, C. (2011). Field leaching of pesticides at five test sites in Hawaii: modeling flow and transport. *Pest management science, 67*(12), 1571-1582.

Fernández-Naveira, A., Rioboo, C., Cid, A., & Herrero, C. (2016). Atrazine induced changes in elemental and biochemical composition and nitrate reductase activity in Chlamydomonas reinhardtii. *European Journal of Phycology, 51*(3), 338-345.

Fewtrell, L. (2004). Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environmental health perspectives, 112*(14), 1371.

Frank, R., & Sirons, G. J. (1985). Dissipation of atrazine residues from soils. *Bulletin of environmental contamination and toxicology, 34*(1), 541-548.

Freundlich, H. (1906). Über die absorption in lösungen. *Über Die Adsorption in Lösungen*, 385-470.

Gely-Pernot, A., Saci, S., Kernanec, P. Y., Hao, C., Giton, F., Kervarrec, C., . . . Smagulova, F. (2017). Embryonic exposure to the widely-used herbicide atrazine disrupts meiosis and normal follicle formation in female mice. *Sci Rep, 7*(1), 3526. doi:10.1038/s41598-017-03738-1

Geng, Y., Ma, J., Jia, R., Xue, L.-q., Tao, C.-j., Li, C.-j., . . . Lin, Y. (2013). Impact of Long-Term Atrazine Use on Groundwater Safety in Jilin Province, China. *Journal of Integrative Agriculture*, *12*(2), 305-313. doi:https://doi.org/10.1016/S2095-3119(13)60229-4

Gustafson, D. I. (1989). Groundwater ubiquity score: A simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry, 8*(4), 339-357. doi:10.1002/etc.5620080411

Hall, K. E., Ray, C., Ki, S. J., Spokas, K. A., & Koskinen, W. C. (2015). Pesticide sorption and leaching potential on three Hawaiian soils. *J Environ Manage, 159*, 227-234. doi:10.1016/j.jenvman.2015.04.046

Hallberg, G. (1997). Pesticides in Ground Water; Distribution, Trends, and Governing Factors. *Ground Water*, *35*(5), 920-922.

Hantush, M., Marino, M., & Islam, M. (2000). Models for leaching of pesticides in soils and groundwater. *Journal of Hydrology*, *227*(1-4), 66-83.

Hertfordshire, U. (2013). The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU). *University of Hertfordshire, 2006–2013*.

Holman, I. P., Dubus, I. G., Hollis, J., & Brown, C. D. (2004). Using a linked soil model emulator and unsaturated zone leaching model to account for preferential flow when assessing the spatially distributed risk of pesticide leaching to groundwater in England and Wales. *Science of The Total Environment, 318*(1-3), 73-88.

Khan, S. U. (2016). *Pesticides in the soil environment*: Elsevier.

Ki, S. J., & Ray, C. (2015). A GIS-assisted regional screening tool to evaluate the leaching potential of volatile and non-volatile pesticides. *Journal of Hydrology, 522*, 163-173. doi:10.1016/j.jhydrol.2014.12.024

Ki, S. J., Ray, C., & Hantush, M. M. (2015). Applying a statewide geospatial leaching tool for assessing soil vulnerability ratings for agrochemicals across the contiguous United States. *Water Res, 77*, 107-118. doi:10.1016/j.watres.2015.03.009

Kross, B., & Hallberg, G. R. (1990). The Iowa state-wide rural well-water survey water-quality data: Initial analysis.

Kruawal, K., Sacher, F., Werner, A., Müller, J., & Knepper, T. P. (2005). Chemical water quality in Thailand and its impacts on the drinking water production in Thailand. *Science of The Total Environment, 340*(1), 57-70. doi:https://doi.org/10.1016/j.scitotenv.2004.08.008

Lasserre, J.-P., Fack, F., Revets, D., Planchon, S., Renaut, J., Hoffmann, L., . . . Bohn, T. (2009). Effects of the endocrine disruptors atrazine and PCB 153 on the protein expression of MCF-7 human cells. *Journal of proteome research, 8*(12), 5485-5496.

Laws, S. C., Ferrell, J. M., Stoker, T. E., & Cooper, R. L. (2003). Pubertal development in female Wistar rats following exposure to propazine and atrazine biotransformation by-products, diamino-S-chlorotriazine and hydroxyatrazine. *Toxicological sciences, 76*(1), 190-200.

LDD. (2010). *Procedure Manual of Soil chemical Analysis process*. Retrieved from http://www.ldd.go.th/ldd_en/

Lesan, H. M., & Bhandari, A. (2003). Atrazine sorption on surface soils: Time-dependent phase distribution and apparent desorption hysteresis. *Water Research, 37*(7), 1644-1654. doi:10.1016/S0043-1354(02)00497-9

Li, Z., Yost, R., & Green, R. (1998). Incorporating uncertainty in a chemical leaching assessment. *Journal of contaminant hydrology, 29*(4), 285-299.

Loague, K., Bernknopf, R., Green, R., & Giambelluca, T. (1996). Uncertainty of groundwater vulnerability assessments for agricultural regions in Hawaii. *Journal of environmental quality, 25*(3), 475-490.

Loague, K., & Green, R. E. (1991). Statistical and graphical methods for evaluating solute transport models: overview and application. *Journal of contaminant hydrology, 7*(1-2), 51-73.

Martins, E. C., Bohone, J. B., & Abate, G. (2018). Sorption and desorption of atrazine on soils: The effect of different soil fractions. *Geoderma, 322*, 131-139.

Mcelroy, J. A., Gangnon, R. E., Newcomb, P. A., Kanarek, M. S., Anderson, H. A., Brook, J. V., . . . Remington, P. L. (2007). Risk of breast cancer for women living in rural areas from adult exposure to atrazine from well water in Wisconsin. *Journal of Exposure Science and Environmental Epidemiology, 17*(2), 207.

McGlamery, M. D., & Slife, F. (1966). The adsorption and desorption of atrazine as affected by pH, temperature, and concentration. *Weeds, 14*(3), 237-239.

Mudhoo, A., & Garg, V. (2011). Sorption, transport and transformation of atrazine in soils, minerals and composts: a review. *Pedosphere, 21*(1), 11-25.

OCSB. (2016). *Sugarcane management*. Retrieved from www.ocsb.go.th/upload/journal/fileupload/144-4003.pdf

Panuwet, P., Siriwong, W., Prapamontol, T., Ryan, P. B., Fiedler, N., Robson, M. G., & Barr, D. B. (2012). Agricultural Pesticide Management in Thailand: Situation and Population Health Risk. *Environ Sci Policy, 17*, 72-81. doi:10.1016/j.envsci.2011.12.005

Parker, S. R., Gammons, C. H., Smith, M. G., & Poulson, S. R. (2012). Behavior of stable isotopes of dissolved oxygen, dissolved inorganic carbon and nitrate in groundwater at a former wood treatment facility containing hydrocarbon contamination. *Applied geochemistry, 27*(6), 1101-1110.

Pereira, A. S., Cerejeira, M. J., & Daam, M. A. (2014). Comparing ecotoxicological standards of plant protection products potentially toxic to groundwater life with their measured and modelled concentrations. *Ecotoxicology and Environmental Safety, 102*, 152-159.

Prado, B., Fuentes, M., Verhulst, N., Govaerts, B., De Leon, F., & Zamora, O. (2014). Fate of atrazine in a soil under different agronomic management practices. *J Environ Sci Health B, 49*(11), 844-855. doi:10.1080/03601234.2014.938555

Putthividhya, A., & Pipitsombat, R. (2015). GIS-based and laboratory-scaled leaching assessment of agricultural contamination in heavily cultivated area of Thailand. *Environmental Earth Sciences, 73*(8), 3975-3986.

Rose, S., & Long, A. (1988). Monitoring dissolved oxygen in ground water: some basic considerations. *Groundwater Monitoring & Remediation, 8*(1), 93-97.

Rusiecki, J. A., De Roos, A., Lee, W. J., Dosemeci, M., Lubin, J. H., Hoppin, J. A., . . . Alavanja, M. C. R. (2004). Cancer Incidence Among Pesticide Applicators Exposed to Atrazine in the Agricultural Health Study. *JNCI: Journal of the National Cancer Institute, 96*(18), 1375-1382. doi:10.1093/jnci/djh264

Seol, Y., & Lee, L. S. (2000). Effect of dissolved organic matter in treated effluents on sorption of atrazine and prometryn by soils. *Soil Science Society of America Journal, 64*(6), 1976-1983.

Shahmohammadi-Kalalagh, S. (2011). Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by kaolinite. *Caspian Journal of Environmental Sciences, 9*(2), 243-255.

Shirisha, K., Salma, B. B., & Mastan, M. (2013). Protective Effect of Andrographis paniculata Against Atrazine Induced Renotoxicity in Albino Rats. *IOSR Journal of Pharmacy, 10*, 17-21.

Shukla, S., Mostaghimi, S., Shanholtz, V., & Collins, M. (1998). A GIS-based modeling approach for evaluating groundwater vulnerability to pesticides. *Journal of the American Water Resources Association (USA)*.

Šimůnek, J., van Genuchten, M. T., & Šejna, M. (2008). Development and applications of the HYDRUS and STANMOD software packages and related codes. *Vadose Zone Journal, 7*(2), 587-600.

Singh, S., Kumar, V., Chauhan, A., Datta, S., Wani, A. B., Singh, N., & Singh, J. (2017). Toxicity, degradation and analysis of the herbicide atrazine. *Environmental Chemistry Letters*, 1-27.

Stackelberg, P. E., Barbash, J. E., Gilliom, R. J., Stone, W. W., & Wolock, D. M. (2012). Regression models for estimating concentrations of atrazine plus deethylatrazine in shallow groundwater in agricultural areas of the United States. *Journal of environmental quality, 41*(2), 479-494.

Stenemo, F., Ray, C., Yost, R., & Matsuda, S. (2007). A screening tool for vulnerability assessment of pesticide leaching to groundwater for the islands of Hawaii, USA. *Pest Manag Sci, 63*(4), 404-411. doi:10.1002/ps.1345

Stoker, T., Guidici, D., Laws, S., & Cooper, R. (2002). The effects of atrazine metabolites on puberty and thyroid function in the male Wistar rat. *Toxicological sciences, 67*(2), 198-206.

Tarboton, D. G. (2003). Rainfall-runoff processes. *Utah State University*.

Tawatsin, A. (2015). Pesticides used in Thailand and toxic effects to human health. *Medical Research Archives*(3).

Thapinta, A., & Hudak, P. F. (2003). Use of geographic information systems for assessing groundwater pollution potential by pesticides in Central Thailand. *Environment International, 29*(1), 87-93. doi:10.1016/s0160-4120(02)00149-6

Tirado, R. (2007). Nitrates in drinking water in the Philippines and Thailand. *Greenpeace Research Laboratories Technical Note, 11*, 2007.

Toccalino, P. L., Gilliom, R. J., Lindsey, B. D., & Rupert, M. G. (2014). Pesticides in groundwater of the United States: decadal-scale changes, 1993-2011. *Ground Water, 52 Suppl 1*, 112-125. doi:10.1111/gwat.12176

Ureña-Amate, M., Socías-Viciana, M., González-Pradas, E., & Saifi, M. (2005). Effects of ionic strength and temperature on adsorption of atrazine by a heat treated kerolite. *Chemosphere, 59*(1), 69-74.

USDASCS. (1990). *SCS/ARS/CES Pesticide Properties Database: Version 2.0 (Summary)*. Retrieved from Syracuse, New York:

USEPA. (1988). *Atrazine: Health Advisory*. Retrieved from Washington, DC:

Vanclooster, M., Boesten, J., Trevisan, M., Brown, C., Capri, E., Eklo, O., . . . Van der Linden, A. (2000). A European test of pesticide-leaching models: methodology and major recommendations. *Agricultural water management, 44*(1-3), 1-19.

Vonberg, D., Vanderborght, J., Cremer, N., Pütz, T., Herbst, M., & Vereecken, H. (2014). 20 years of long-term atrazine monitoring in a shallow aquifer in western Germany. *Water Research, 50*, 294-306.

Walkley, A., & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil science, 37*(1), 29-38.

Weihong, W., Haizhen, W., Jianming, X., & Zhengmiao, X. (2009). Adsorption characteristic of bensulfuron-methyl at variable added Pb2+ concentrations on paddy soils. *Journal of Environmental Sciences, 21*(8), 1129-1134.

Wu, C., Zhang, S., Nie, G., Zhang, Z., & Wang, J. (2011). Adsorption and desorption of herbicide monosulfuron-ester in Chinese soils. *Journal of Environmental Sciences, 23*(9), 1524-1532. doi:10.1016/S1001-0742(10)60583-9

Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A. R. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere, 89*(11), 1467-1471.

Yue, G., Jing, M., Ran, J., XUE, L.-q., TAO, C.-j., LI, C.-j., & Yan, L. (2013). Impact of long-term atrazine use on groundwater safety in Jilin Province, China. *Journal of Integrative Agriculture, 12*(2), 305-313.

Yue, L., Ge, C., Feng, D., Yu, H., Deng, H., & Fu, B. (2017). Adsorption–desorption behavior of atrazine on agricultural soils in China. *Journal of Environmental Sciences, 57*, 180-189.

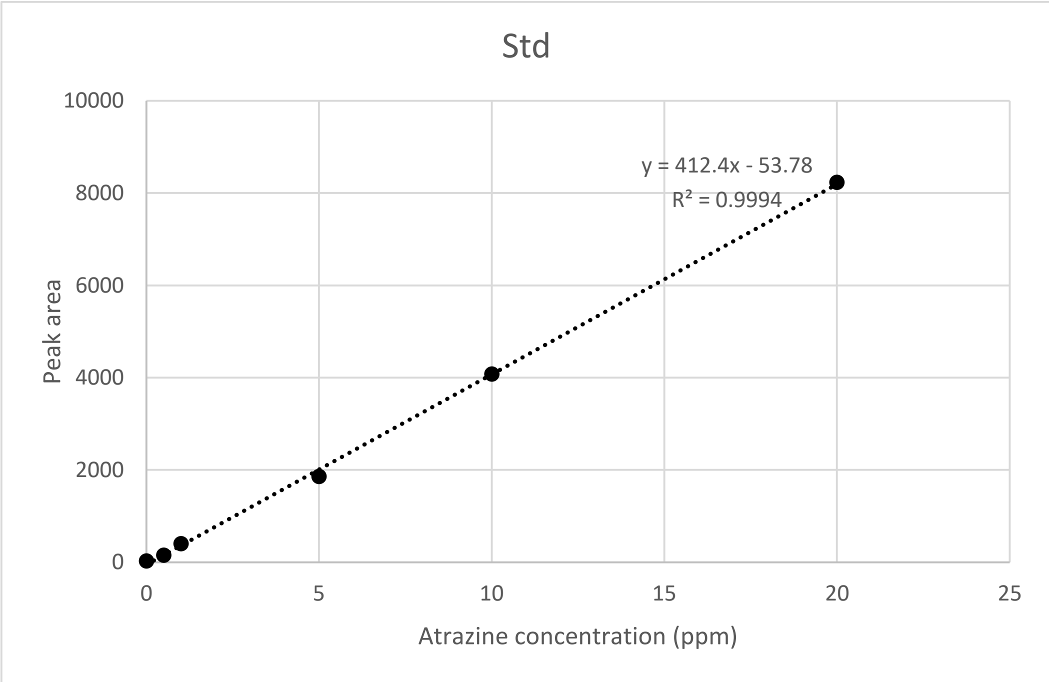
Appendix

A-1 Raw data derived from the batch adsorption experiment

Sample	Initial conc. (mg/l)	Ce 1 (mg/l)	Q1 (mg/g)	Ce 2 (mg/l)	Q2 (mg/g)	Ce 3 (mg/l)	Q3 (mg/g)	%RSD
S1	0.5	0.48	0.08	0.49	0.05	0.48	0.10	0.97
	1	0.90	0.51	0.89	0.57	0.88	0.62	1.32
	5	4.75	1.27	4.73	1.37	4.76	1.22	0.31
	10	9.60	1.98	9.54	2.28	9.82	0.92	1.48
	20	19.18	4.08	19.12	4.39	19.81	0.93	1.97
S2	0.5	0.38	0.59	0.40	0.50	0.37	0.66	4.17
	1	0.88	0.59	0.89	0.57	0.88	0.61	0.52
	5	4.60	2.02	4.66	1.68	4.51	2.46	1.71
	10	9.52	2.38	9.53	2.34	9.53	2.37	0.04
	20	19.30	3.51	19.17	4.14	19.27	3.63	0.35
S3	0.5	0.43	0.33	0.43	0.34	0.44	0.32	0.57
	1	0.89	0.53	0.88	0.59	0.89	0.56	0.77
	5	4.84	0.82	4.82	0.90	4.82	0.88	0.17
	10	9.79	1.06	9.74	1.32	9.74	1.29	0.29
	20	19.65	1.77	19.66	1.70	19.66	1.72	0.04
S4	0.5	0.44	0.28	0.44	0.28	0.44	0.29	0.08
	1	0.89	0.54	0.89	0.56	0.88	0.58	0.53
	5	4.86	0.68	4.80	1.00	4.76	1.20	1.09
	10	9.74	1.31	9.73	1.37	9.79	1.03	0.37
	20	19.69	1.55	19.37	3.17	19.67	1.66	0.93
S5	0.5	0.41	0.43	0.42	0.41	0.42	0.42	0.61
	1	0.86	0.71	0.83	0.87	0.89	0.55	3.73
	5	4.72	1.39	4.70	1.50	4.73	1.35	0.32
	10	9.69	1.55	9.70	1.49	9.72	1.42	0.14
	20	19.41	2.97	19.50	2.50	19.46	2.68	0.24
S6	0.5	0.43	0.35	0.42	0.40	0.42	0.39	1.20
	1	0.84	0.81	0.82	0.88	0.84	0.80	1.04
	5	4.36	3.18	4.39	3.04	4.39	3.07	0.33
	10	9.42	2.90	9.42	2.92	9.40	2.98	0.09
	20	18.96	5.21	18.98	5.12	18.93	5.33	0.11
S7	0.5	0.45	0.23	0.46	0.22	0.44	0.29	1.72
	1	0.90	0.51	0.88	0.60	0.89	0.55	0.97
	5	4.72	1.39	4.59	2.04	4.61	1.94	1.51
	10	9.37	3.16	9.38	3.08	9.38	3.12	0.08
	20	18.67	6.64	19.45	2.73	19.24	3.80	2.11
S8	0.5	0.43	0.36	0.40	0.51	0.43	0.33	4.60
	1	0.88	0.62	0.83	0.84	0.86	0.72	2.57

5	4.60	2.01	4.58	2.09	4.51	2.43	0.97
10	9.50	2.51	9.52	2.38	9.54	2.28	0.25
20	18.99	5.04	18.93	5.35	18.90	5.48	0.24

A-2 Standard curve for batch adsorption experiment



A-3 Nitrate concentration detected in groundwater samples

Sample	Nitrate (mg/L)		Mean	SD
	Rep1	Rep2		
1	43.110	46.150	44.630	2.150
2	68.190	74.030	71.110	4.130
3	8.340	10.250	9.295	1.351
4	31.030	33.110	32.070	1.471
5	40.150	40.890	40.520	0.523
6	46.190	45.220	45.705	0.686
7	4.530	6.050	5.290	1.075
8	2.390	4.110	3.250	1.216

A-4 Soil and groundwater sampling site located around sugarcane field, U-thong and Song Pee Nong district, Suphan Buri province

VITA

NAME	Sorranat Ratchawang
DATE OF BIRTH	3 March 1994
PLACE OF BIRTH	Lamphun
INSTITUTIONS ATTENDED	International Programs in Hazardous Substance and Environmental Management
HOME ADDRESS	53/1 Wiangyong sub-district, Muang district Lamphun