Assessment of Cadmium Migration into Groundwater in Mae Sot District, Tak Province using Monte Carlo Technique

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การประเมินการเคลื่อนตัวของแคดเมียมลงสู่ชั้นน้ำบาดาลบริเวณอำเภอแม่สอด จังหวัดตากโดยใช้เทคนิคมอนติคาร์โล

นายพงศธร ธัญญวัชรกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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พงศธร ธัญญวัชรกุล : การประเมินการเคลื่อนตัวของแคดเมียมลงสู่ชั้นน้ำบาดาลบริเวณอำเภอแม่สอด จังหวัดตากโดยใช้เทคนิคมอนติคาร์โล (Assessment of Cadmium Migration into Groundwater in Mae Sot District, Tak Province using Monte Carlo Technique) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ศรีเลิศ โชติพันธรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.สุรัฐ ขวัญเมือง, 79 หน้า.

แม่สอดเป็นหนึ่งในอำเภอของจังหวัดตากซึ่งประสบปัญหาการปนเปื้อนของแคดเมียมในบริเวณพื้นที่ศึกษา การได้รับแคดเมียมเข้าสู่ร่างกายในปริมาณมากส่งผลให้เกิดผลเสียต่อไตและระบบกระดูกในร่างกาย อันได้แก่ โรคไตวาย, กระดูกพรุน, กระดูกน่วม, โรคอิไต อิไต และโรคมะเร็งปอด การศึกษาในครั้งนี้มีวัตถุประสงค์เพื่อศึกษาลักษณะการดูดซึมโลหะหนักของแคดเมียมในดินบริเวณพื้นที่ศึกษา อีกทั้งนำเทคนิคมอนติคาร์โลเข้ามาประยุกต์ใช้ร่วมกับการสร้างแบบจำลองทางคณิตศาสตร์เพื่อเพิ่มประสิทธิภาพในการประเมินการเคลื่อนตัวของแคดเมียมลงสู่ชั้นน้ำบาดาล ทั้งนี้ได้มีการศึกษาการทดลองแบทช์เทียบกับไอโซเทอมแบบ ฟรุนดลิช, แลงเมียร์ และเชิงเส้น เพื่อใช้อธิบายการดูดซึมของแคดเมียมในดิน นอกจากนี้ได้มีการใช้การสกัดลำดับขั้นแบบ BCR เพื่อหาปริมาณการซึมออกของแคดเมียม (BCR1+2) เพื่อนำมาเป็นความเข้มข้นเริ่มต้นและความเข้มข้นสำหรับเปรียบเทียบผลของแบบจำลอง ในส่วนของแบบจำลองเชิงคณิศาสตร์ ได้มีการนำ โปรแกรม HYDRUS-1D มาใช้ร่วมกับเทคนิคมอนติคาร์โลผ่านโปรแกรม MATLAB ในการประเมินการเคลื่อนตัวของแคดเมียมลงสู่ชั้นน้ำบาดาล นอกจากนี้ ได้มีการใช้ Nash and Sutcliffe model efficiency (NSE) มาใช้ประเมินผลการจำลองทางคณิตศาสตร์เทียบกับความเข้มข้นแคดเมียมที่ระดับความลึกต่างๆ จากผลการทดลองแบบแบทช์ในตัวอย่างดิน พบว่าดินส่วนใหญ่สอดคล้องกับไอโซเทอมแบบฟรุนดลิช (R^2 อยู่ระหว่าง 0.957-0.984) ในขณะที่มีเพียงตัวอย่างดิน 2 ตัวอย่างที่สามารถอธิบายได้โดยไอโซเทอมของแลงเมียร์ (R^2 อยู่ระหว่าง 0.995-0.998) จากผลการสกัดความเข้มข้นของแคดเมียมในดินโดยวิธีสกัดลำดับขั้นแบบ BCR พบว่ามีเพียง 2 ตัวอย่างดิน (S4 และ S5) ที่พบความเข้มข้นของแคดเมียม ในดินที่ BCR1 และ BCR2 จากผลการประเมินการเคลื่อนตัวของแคดเมียมโดยแบบจำลองเชิงคณิตศาสตร์ที่ประยุกต์ร่วมกับเทคนิคมอนติคาร์โลพบว่า ผลการจำลองโดยประยุกต์ร่วมกับเทคนิคมอนติคาร์โล ให้ค่าความเข้มข้นของแคดเมียมน้อยกว่าความเข้มข้นของแคดเมียมในดินที่ระดับความลึกต่างๆที่ได้จากผลการทดลอง นอกจากนี้ การประเมินผลของแบบจำลองโดยใช้ NSE พบว่าแบบจำลองให้ค่า NSE ของตัวอย่างดิน S4 และ S5 เท่ากับ 0.223 และ -1.606 ตามลำดับ

สาขาวิชา การจัดการสารอันตรายและสิ่งแวดล้อม

ปีการศึกษา 2560

ลายมือชื่อนิสิต ....

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PONGSATHORN THUNYAWATCHARAKUL: Assessment of Cadmium Migration into Groundwater in Mae Sot District, Tak Province using Monte Carlo Technique. ADVISOR: ASSOC. PROF. SRILERT CHOTPANTARAT, Ph.D., CO-ADVISOR: SURAT KWANMUANG, Ph.D., 79 pp.

Mae Sot is a district in Tak province that confronts Cd contamination within the area. The target organs for Cd exposure was kidneys and skeletal system which could lead to severe health effects such as renal dysfunction, osteoporosis, bone softening, Itai-Itai disease, and lung cancer. The intention of this study was to examine the sorption behavior of nine soil samples in the study area and applied Monte Carlo technique that would increase model efficiency for Cd migration in to the soil profile. Batch adsorption experiments were performed and fitted with the adsorption isotherms as follows: Linear, Langmuir, and Freundlich isotherms. Moreover, BCR sequential extraction was used to extract bioavailable Cd (BCR1+ BCR2), which used as model initial Cd concentration and Cd concentration in soil profile. HYDRUS-1D was used as a numerical modeling instrument to simulate Cd transportation in the soil profile, and MATLAB was used for Monte Carlo application in HYDRUS-1D. Furthermore, Nash and Sutcliffe model efficiency (NSE) was used to evaluated the numerical model in this study. Batch adsorption experiment showed that seven soil samples were fitted well with Freundlich adsorption isotherm (R^2 between 0.957-0.984), while the other two soil samples (S1 and S2) were explained by Langmuir isotherm (R^2 between 0.995-0.998). However, BCR sequential extraction from soil samples showed that only 2 soil samples (S4 and S5) can be detected Cd concentration in BCR1 and BCR2 Based on the application of Monte Carlo method in HYDRUS-1D (under the non-equilibrium condition), the result showed that the simulation results are lower than the experimental data with NSE values of 0.223 and -1.606 for S4 and S5, respectively.

Field of Study:	Hazardous Substance and Environmental Management	Student's Signature	
		Advisor's Signature	
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CHAPTER 1

INTRODUCTION

1.1 Rationale

Cadmium (Cd) is a heavy metal, which generally occurs with zinc (Zn), lead (Pb), and copper (Cu) minerals. Source of Cd contamination in the environment can be caused by the natural, fuel combustion, or human activities such as mining and using fertilizers (Järup, 2003). Cd exposure leads to renal tabular dysfunction in kidney, and reduces metabolism in body, which cause kidney stone and bone softening. Moreover, Cd was categorized as carcinogen substance that cause lung cancer in human for long-term exposure (WHO, 2010). As a result, it is important to study transportation of this contaminant in order to prevent these severe effects in human health.

Heavy metal leaching to environment from mining activities is one of the major concerns from Thailand's economic development. Three decades ago, Mae sot district, Tak province, discovered the largest zinc deposit source in South East Asia in Phadaeng deposit. Zinc mining in the area was operated by the Phadaeng Industry Public Company limited that had mine production capacity up to 214,023 metric tons or around 5,550 million baht. The consequences from mining activities caused high amount of waste rocks and tailings were released into the environment (Akkajit, 2015; Akkajit and Tongcumpou, 2010).

As a result, the International Water Management Institute (IWMI) reported Mae Sot district, Tak province, as high-level Cd concentration in agricultural soils and rice grain in 1998. Cd concentration in soil varied from 0.5-284 mg kg^{-1} higher than European Union (EU) standard that allows Cd concentration in soil not exceed 1.0 - 3.0 mg kg^{-1} based on soil pH (Simmons et al., 2005). The cadmium in Mae Sot was found with Pb as solid-solution or inclusion in Hemimorphite (PCD, 2010). Cd contamination in the district comes from Mae Tao creek where the upper part of stream flows through zinc mining zone. Along with zinc mineral, Cd contaminant binds with suspended sediment and flow in to the stream where people in this site use as irrigation water for their paddy field (Kosolsaksakul et al., 2014; Simmons et al., 2005)

After Simmons investigation this field for Cd contamination in soils and rice grain, several research (Akkajit and Tongcumpou, 2010; Kosolsaksakul et al., 2014) examined factors that corresponding Cd fractionation and distribution in this area. Akkajit and Toncumpou (2010) studied fractionation of Cd for bioavailability in the contaminated sites in Mae Sot district by using BCR sequential extraction along with other related metals (Cu, Fe, Zn, Pb, and Mn). The results showed that Cd had the highest proportion in the exchangeable fraction (BCR1) as compared with other metals. Kosolsakul et al. (2014) also studied fractionation of Cd in this site by using BCR sequential extraction and Tessier sequential extraction and found that soil samples were separated into 3 classes, depending on their Cd concentrations: low, medium, and high concentration. As a result, Cd had the highest proportion in BCR1 in all ranges of Cd concentration, accounting for 67-81% of all BCR proportion. For Tessier sequential extraction, the reducible form (T2) accounting for the highest proportion for percentage of fractionation (45.2-72.4%). Moreover, the exchangeable form (T1) is lower when Cd concentration in soil is increased, whereas the reducible form (T2) is higher in samples with high Cd concentration.

As mentioned, since there are many studies that investigated the leaching and fractionation of Cd in soil samples in the site, yet sorption behavior of Cd in such soils and numerical transport modeling of Cd into the groundwater in study area are still not completely known. It is well-known that groundwater is an important resource that account for the largest proportion of freshwater compared with surface water, such as lake and stream. It is an important resource when surface water is shortage. Groundwater can be recharged from many water sources such as stream, lake, and precipitation, then recharge into the groundwater system. If recharge water contaminated with contaminants, it will eventually cause groundwater contamination. In conclusion, study of sorption behavior of Cd onto soils is a significant factor, influencing on leaching potential of Cd through the soils and then reaching through the groundwater table in the site.

For numerical modeling, HYDRUS-1D was used in order to simulate migration of Cd into groundwater system. It was designed to simulate heat movement, water flow, and solution transport based on advection-dispersion model. Moreover, the software package can simulate in saturated, unsaturated, and partial saturated. The software package consists of GUI part for input parameter and modeling part for the numerical calculation (Šimůnek et al., 2009). HYDRUS-1D has been used in many studies. For examples, van der Grift and Griffioen (2008) used HYDRUS-1D to study transportation of Cd and Zn in unsaturated zone in Kempen area, Netherland. Selle et al. (2011) applied HYDRUS-1D with Monte Carlo method in order to estimate deep percolation of irrigation water by using soil moisture parameter. Generally, numerical modeling is an instrument that designed to stimulate transportation of contaminant through soil media, but in the environment scenario, there are many parameters with many uncertainties which makes single simulation of numerical modeling would not enough to interpret the movement of contaminants. As a result, application of probabilistic method such as Monte Carlo method integrated into the numerical modeling could become an alternative way to the solve problem involving with uncertainty parameters.

1.2 Hypothesis

1. Most soil sample in the study area could be described by Freundlich isotherm

2. The Monte Carlo technique can enhance the model efficiency of the transport modeling for predicting Cd movement into groundwater

1.3 Objectives

1. to investigate Cd sorption behavior onto soils and leaching potential of Cd in soils in the study area.

2. to integrate the numerical transport modeling with Monte Carlo technique to simulate Cd movement into shallow groundwater.

1.4 Scope of study

1. Cd contaminated soils were collected from agricultural area near Mae Tao creek

2. HYDRUS-1D was used for numerical modeling, and MATLAB was used to apply Monte Carlo technique in to the model.

3. The simulation was done in unsaturated zone of soil profile.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction of Cadmium and Health effect

Cadmium (Cd) is a heavy metal that discovered by German chemist Friedrich Stormeyer in 1817. It has 48 in atomic number with oxidation number +2 that associate with occurrence of Cu, Pb, and Zn (Järup, 2003; Nordberg, 2009). Source of Cd exposure can be found in Natural and Anthropogenic source.

Natural source: volcanic eruption, rock weathering, and sediment transportation (WHO, 2010).

Anthropogenic source: Color pigment, Ni-Cd batteries, industrial emission, mining, smelting, using fertilizer, smoking cigarette (Järup, 2003).

Proportion of Cd in the earth is considered as trace element that can be found only 0.2 mg kg^{-1}. Most of Cd is found in sedimentary rock, and associate with potential zinc source like Sphalerite ($ZnCO_3$) as by-product in Zinc mineral (Traina, 1999).

Cd exposure can come from many pathways. Eating or drinking Cd contaminated crops, aquatic lives, and water cause severe effect in human body, also, inhalation of Cd fumes from non-ferrous industry or contaminated air can also lead to Cd exposure. Not only these source of inhalation can cause Cd exposure, smoking cigarette can be resulted in Cd exposure in both active and passive ways of smoking. Target organ of Cd contamination are kidney and skeletal system. Accumulation of Cd in kidney increase excretion of low molecular weight of protein in urine, and cause renal dysfunction. Moreover, it disturbs metabolism of calcium in human body that causes bone softening, osteoporosis, and Itai-Itai disease as a combination of both symptoms and renal dysfunction. Cd is not only effect on kidney and skeletal system, but International Agency for Research on Cancer (IARC) categorized Cd as a human carcinogenic substance (group I) which cause lung cancer in people who inhaled Cd fumes from non-ferrous industry and smoking cigarette (Järup, 2003; WHO, 2010).

As mentioned about the severe effects from Cd exposure, there are many regulations that comes from public agency in many countries in order to control the Cd concentration in the environment. USEPA regulated a standard for Cd level in drinking water not higher than 0.005 mg L^{-1}. The European Union regulated the acceptable level of Cd concentration in soil around 1.0-3.0 mg kg^{-1} based on soil pH. Codex Committee on Food Additives and Contaminants (CCFAC) set Cd concentration level in rice not exceed 0.2 mg kg^{-1} (Simmons et al., 2005)

2.2 Cadmium Contamination in soil and groundwater

Because of hazardous of Cd contamination, there are many researchers study about Cd contamination in the environment.

Takijima and Katsumi (1973) examined Cd concentration in soil and rice in Fukui prefecture that encountered Cd contamination problem, would cause from zinc mining in the area. The result from the investigation showed that rice grain from the agriculture area along Kuzuryu river varied from 0.02-1.82 ppm in unpolished rice product and ranged from 0.2-10.4 ppm for Cd concentration in soil content. Moreover, this study found that there is no relationship between Cd concentation in rice and the concentration in soil of the study area, also, the concentration of Cd in soil was found mostly in top soil.

Álvarez-Ayuso et al. (2013) studied Cd distribution in soil at El Losar del Barco village in Ávila, Spain, where spharlerite-bearing waste dump site was located. The soil samples were taken at different distances from the dump site and at mine process plant in the site as soil profile sampling. The result from the study showed that the highest Cd concentration was 218 mg kg^{-1} that found on surface at the ores dumb site which the concentration was influenced by the distance from the site, and the concentration from the surface soil at mine processing area was found at 11 mg kg^{-1} on surface soil with decreased in lower depth of soil profile as same as the waste dumb area.

2.3 Speciation of Cd in the environment system

Cd can have many forms in each different of environmental conditions, which its stability constants and speciation associated with thermodynamic data (Powell et al., 2011).

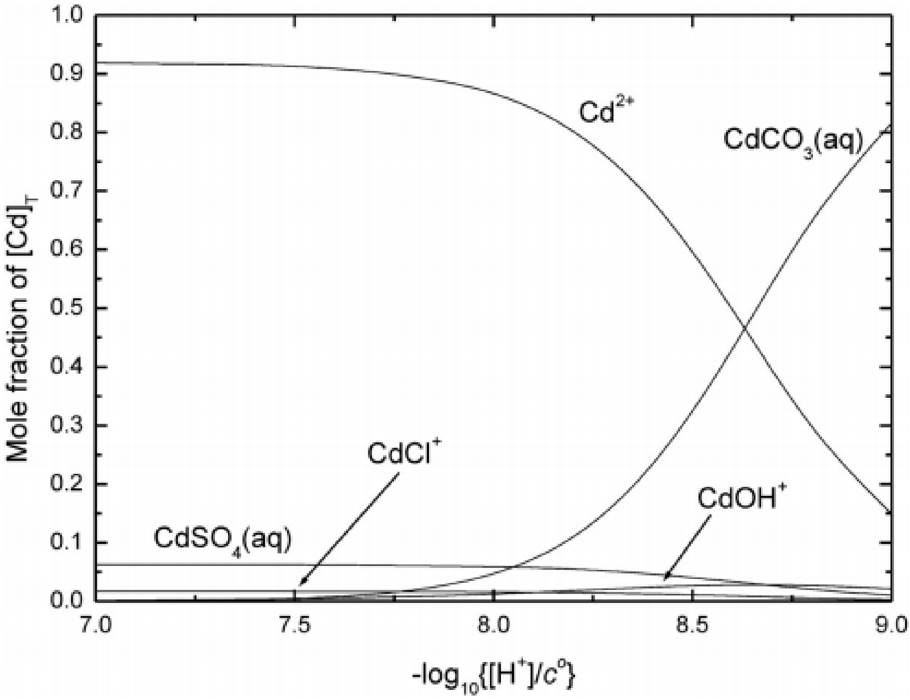


Figure 2.1 *Diagram between mole fraction and pH of dissolved Cd speciation in freshwater system with ionic strength 1.5 mM and* CO_2 *in the air that has fugacity equal to 370 µbar (Powell et al., 2011)*

Figure 2.1 shows Cd formation in equilibrium condition with atmospheric CO_2 and ionic strength equivalent to 1.5 mM in freshwater, which can be seen that the dominant species of Cd in this environmental condition is Cd^{2+} when $pH < 8.65$ and $CdCO_3$ at $pH > 8.65$. Moreover, $CdSO_4$ and $CdOH^+$ can also be found as a minor species in the condition.

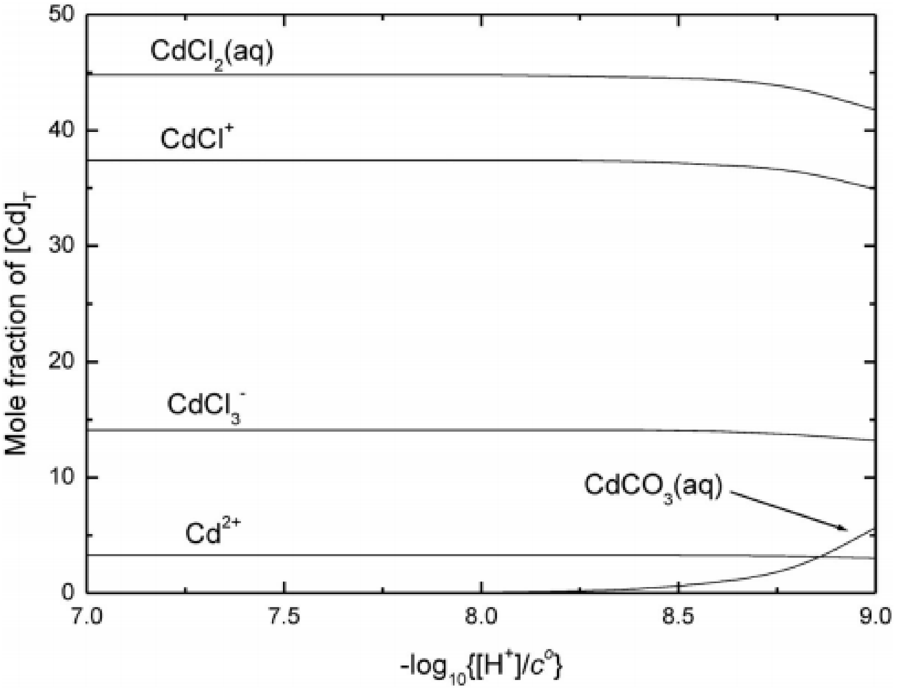


***Figure 2.2** Diagram between mole fraction and pH of dissolved Cd speciation in saltwater system with 360 μbar of CO_2 and 670 mM of ionic strength (Powell et al., 2011)*

From Figure 2.2 shows Cd species in saline water system (ionic strength = 670 mM). When pH higher than 8.5, changing of mole fractions is not influenced by pH. $CdCl_2$ is found as a dominant specie, around 44.8%, then $CdCl^+$ and $CdCl^{3-}$. In the other hand, Cd^{2+} only exist at 3% in the system, and $CdCO_3$ is highly formed when pH in the system higher than 9 as showed in Figure 2.2. Note that the above figure also includes competition of Ca^{2+} and Mg^{2+} reaction with inorganic anion.

As a result, Cd specie that dominated in freshwater condition is Cd^{2+} with low ionic strength and weak acid condition, and $CdCl_2$ and $CdCl^+$ can be found naturally in saltwater system which can be formed in neutral or weak alkaine condition.

2.4 Cadmium Adsorption in Soil

Type of Cd adsorption can be separated in to two types (Christensen and Haung, 1999)

1. Non-specific sorption – The sorption type allows Cd ions attach to the negative charge site of adsorbent by electrostatic force (McBride, 1989). As a result, Cd ions can be replaced by other cation which makes Cd become more exchangeable, more potential of Cd leaching (Loganathan et al., 2012).

2. Specific sorption – Cd has chemical bounding with negative and neutral charge site of adsorbent. As a result, it causes inner-sphere complex form of Cd ions to the adsorbent that makes this type of sorption becomes more difficult to leaching than non-specific sorption type (Loganathan et al., 2012).

Moreover, Cd can become an organic ligand complex forms or precipitate in the soil as $Cd_3(PO_4)_2$, $CdCO_3$, $Cd(OH)_2$, and CdS forms(Christensen and Haung, 1999; Loganathan et al., 2012).

2.5 Factor that control Cd adsorption

Because the result from adsorption can prevent Cd leaching into the groundwater system and allows for more bioavailability, understanding factors that influence soil adsorption becomes important. There is many researches that study for the factors that control Cd adsorption.

Wang et al. (2004) studied sorption behavior of Cd in montmorillonite that affected by glyphosate. The result from this study shows that glyphosate, which has functional group $-PO_3$ and –COOH, decreases adsorption of montmorillonite when pH is over than 6.7 and it has small effect when pH is lower than 6.7.

Li et al. (2011) investigated the effect of temperature on Carbendazim and Cd in soil. The result shows that the rate of adsorption becomes increased when the temperature and concentration of Cd are increased.

Tahervand and Jalali (2016) studied adsorption and desorption of heavy metal (Fe, Ni, and Cd) by various soil pH in 4 types of calcareous soil samples that have different soil properties in Hamerdan, Iran. As a result, the adsorption behavior of soils depends on pH and type of heavy metal. Ni and Cd have the same trend of sorption behavior compare with sorption behavior of Fe. Moreover, the selectivity of heavy metal adsorption and desorption in soil depend on pH, $CaCO_3$, OM, and nature of metal.

The higher proportion of OM leads to higher adsorption rate of Cd and Ni, and higher $CaCO_3$ in soil sample causes higher adsorption rate of Fe than OM.

Waleeithikul and Chotpantarat (2016) studied Cd sorption behavior of soil in Mae Sot, Tak province, by using batch adsorption experiment. The result from experiment show that sorption behavior in Mae Sot fitted well with Freundlich isotherm. Moreover, adsorption rate of Cd in this study area is higher than desorption rate (>75% adsorption).

In conclusion, the factor that control sorption behavior in soil is pH, organic matter (OM), clay content, and temperature. Thus, all of the studies point to the same conclusion that pH is one of an important factor that control adsorption reate of heavy metal in soil.

2.6 General information of study area

Study area is located in Mae Sot district, Tak province that can be divided into 4 sub-district; Tha Sai Luat, Mae Ku, Mae Tao, and Phra That Pha Daeng. The study area has 2 stream Mae Tao creek and Mae Ku creek that suffering from Cd contamination in agricultural soils. The study area has mountain area on the east side of the area and flat plain in the middle and the west side. Also, has mining area on the east side as shown in Figure 2.3

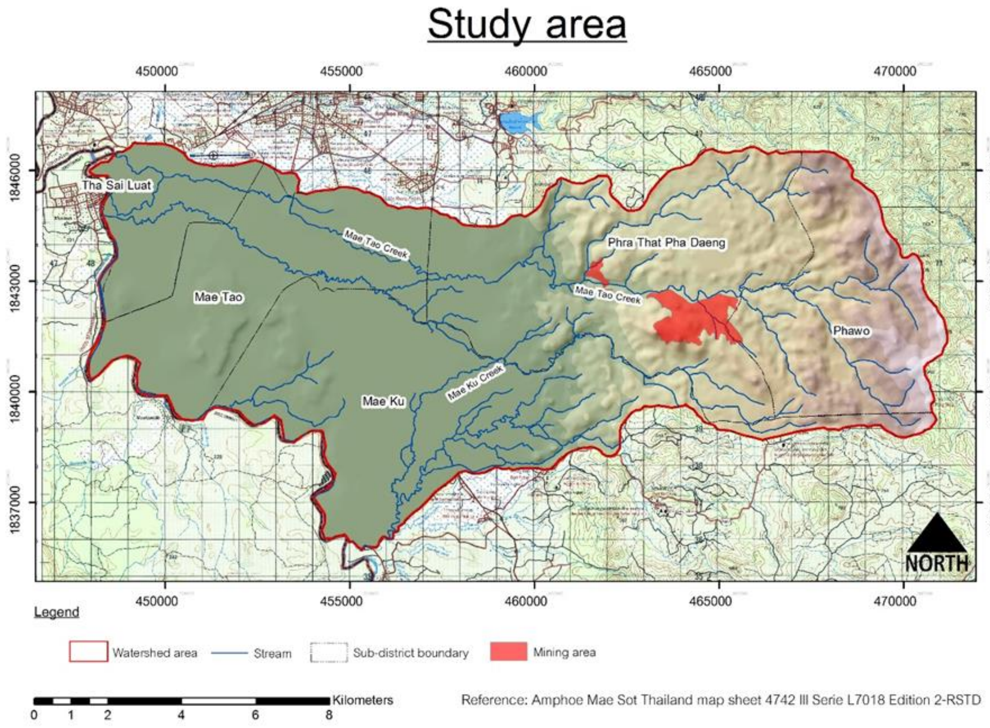
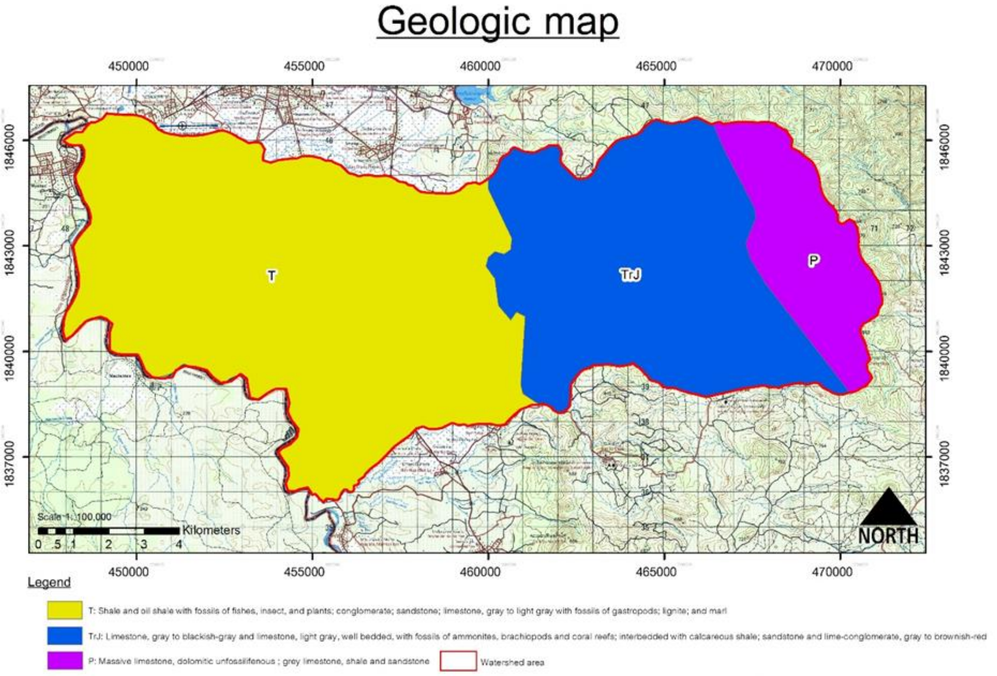


Figure 2.3 *Study area map in Mae Sot, Tak province*

2.6.1 Geology and mining

Doi Phadaeng is grouped in Upper-Jurassic age rocks, consisting of dark gray limestone and light gray bedded limestone with fossils of ammonites, brachiopods, and coral reefs, inter-bedded with calcareous shale, sandstone, and red lime-conglomerate as shown in Figure 2.4 Zinc ores in Phadaeng are found in fault plains, pores, and fractures in sandstone and dolomitic limestone as secondary minerals in form of zinc silicate, carbonate, and oxide, e.g. hemimotphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$], smithsonite ($ZnCO_3$), hydrozincite [$2ZnCO_3.3Zn(OH)_2$], and loseyite [$Mn(Zn)_7(OH)_{10}(CO_3)_2$] (Akkajit and Tongcumpou, 2010).



Reference: Amphoe Mae Sot Thailand map sheet 4742 III Serie L7018 Edition 2-RSTD

Figure 2.4 *Geologic map of study area*

2.6.2 Soil in study area

The soil in the study area can be separated in to 8 types based on USDA soil texture clasification as shown in Table 2.1 and Figure 2.5.

Table 2.1 *Soil types classification based on USDA soil classification and proportion of each soil types in the study area*

Soil texture*	**Percentage in the study area** (%)
Loam, Silt loam, Silty clay loam	2.81
Silty clay	6.23
Sandy loam, loamy sand	10.92
Clay	4.67
Sandy loam, sandy clay loam	14.45
Clay loam, Silty clay loam	19.97
Clay loam	0.91
Sandy loam	1.41

*Note: Rockland and Slope complex will not include in the calculation

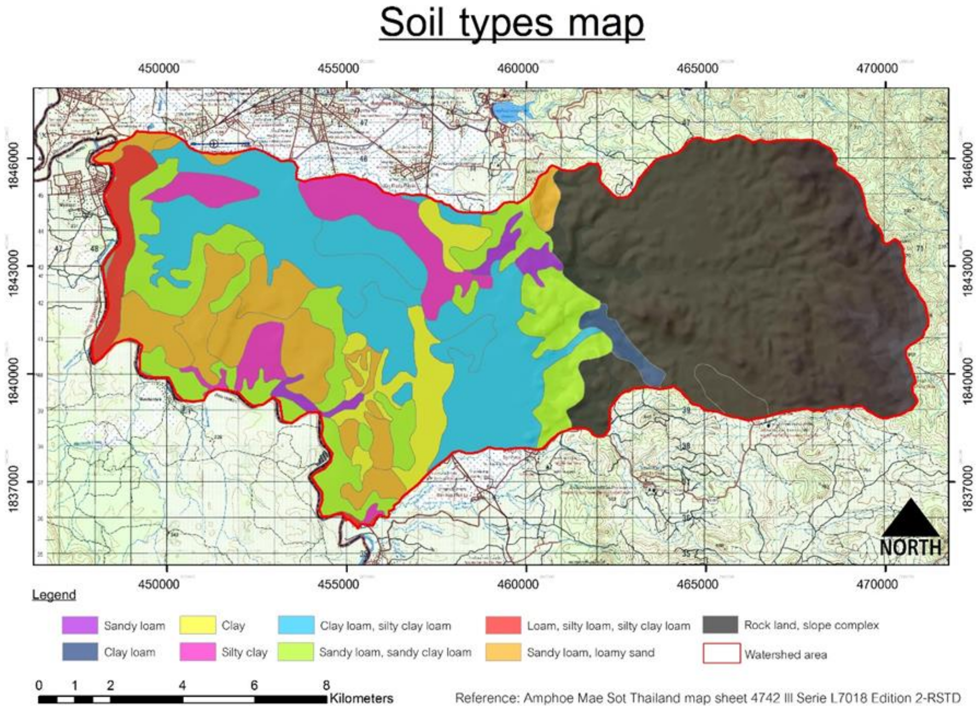


Figure 2.5 *Soil map of the study area*

2.6.3 Background of heavy metal contamination

Mae Sot is an area that suffering from Cd contamination in agricultural soil. The contamination was reported around 1998-2003 by the collaboration project between International Water Management Institute (IWMI) and Department of Agricultural (DOA). They found high concentration of Cd in rice field and rice grain which lead many researchers come to investigate Cd contamination and other heavy metals in this Mae Tao creek and the adjacent area, mostly focus on soil contamination.

Typically, background concentration of Cd in Thailand varied from 0.002-0.141 mg kg^{-1}, but in the previous studies in Mae Sot district show that Cd level in this region exceed many standards that regulated to control Cd concentration, for example European Union regulated Cd concentration level in soil 1.0-3.0 mg kg^{-1} base on soil pH. As a result, it caused severe damage to rice that was grown in this study area (Kosolsaksakul et al., 2014; Simmons et al., 2005) Simmons et al. (2005) investigated Cd concentration in rice field and rice grain in Phra That Pha Daeng sub-district. The preliminary study was performed in Ban Pha Te that close to the Zn mining area. Soil samples were collected from 159 fields at 0-30 cm. depth from surface. Moreover, rice grains were collected from 90 fields in order to analyze for Cd and Zn concentrations. The Cd and Zn concentration were ranged from 3.4-284 mg kg^{-1} and 197-8036 mg kg^{-1} respectively, and also found that the Cd concentration had a strong relationship with Zn concentration. The Cd concentration in rice grain is ranged from 0.1-4.4 mg kg^{-1} which exceed the Codex Committee on Food Additives and Contaminants (CCCAC) that allow not over than 0.2 mg kg^{-1}.

An extensive study was performed in 2001-2002 when soil samples and rice samples were collected from 334 and 434 fields respectively in Mae Tao creek. The result from the investigation showed that Cd and Zn concentration ranged from 0.5-218 mg kg^{-1} and 700-1718 mg kg^{-1} respectively, and Cd concentration still has strong relationship with Zn concentration. Cd concentration in rice grains varied from less than 0.05 to 7.7 mg kg^{-1}, 85% of samples exceed CCFAC Cd concentration in rice. Furthermore, the investigation of Cd concentration from 15 soil profiles show that 80% Cd and Zn concentration are mostly accumulated in upper soil, at 0-30 cm. depth from the surface, that support an idea that Cd come from irrigation water that comes from Mae Tao creek (Simmons et al., 2005).

Because of Cd contamination problem, bioavailability of Cd and other metals in the study area is a necessary factor in order to know the available capacity for plant in order to remediate the contaminant along Mae Tao creek. Akkajit and Tongcumpou (2010) studied concentration and fractionation of Cd and other related metal (Cu, Fe, Mn, Pb, and Zn) for bioavailability by using the Community Bureau of Reference (BCR) sequential extraction. Then, the relationship between parameters, pH, organic matter, oxidation-reduction potential, and other metals concentration were analyzed by using Principle Component Analysis (PCA).

The result of the study shows that total concentration of Cu, Fe, Zn, Cd, Pb, and Mn ranged from 5.0-27.5 mg kg^{-1}, 3473 - 17,963 mg kg^{-1}, 26.12 - 3138 mg kg^{-1}, 0.73-172.7

mg kg^{-1}, 6.4 - 160.3 mg kg^{-1}, 65.27 - 1222 mg kg^{-1} respectively. From the result, the concentration level of other referred metals except Zn and Cd were ranged in acceptable level. The result of BCR that used to analyze bioavailability of soil on the site showed that soil samples had the highest proportion in BCR1 (25-30%), Similar to Cd, Zn, and Mn which also had high amount of BCR2, (reducible fraction). As a result, Zn, Mn, and Cd had proportion of BCR1 and BCR2 (exchangeable and reducible form) more than 40%. On the other hand, Cu and Fe were associated with other phases more than BCR1 and BCR2. For the Principle Component analysis in the study, it showed that soil properties (pH, ORP, and OM) had low relationship with bioavailability of Cd, but the relationship with Cd bioavailability and Cd concentration were strong, same as Zn and Pb in both total and available metals.

Kosolsaksakul et al. (2014) studied factors that control Cd plant uptake and Cd partition in soil. The result from this studied showed that soil samples had Cd concentration ranged from 2.5-2.86 mg kg^{-1}, lower than Cd concentration from Simmons et al. (2005) that cover Ban Pa Te, near zinc mining area. The concentration of Cd was found from 0-40 cm. from surface. Moreover, Cd concentration can be divided in to 3 group, low concentration (< 10 mg kg^{-1}), medium concentration (10-50 mg kg^{-1}), and high concentration (> 50 mg kg^{-1}). Soil samples that extracted by using BCR and Tessier sequential extraction. In BCR sequential extraction, the soil samples had highest proportion in BCR1 (67%-84%). Soil samples in Tessier sequential extraction can be separated in easily soluble phase (T1) and carbonate soluble phase (T2). The Cd proportion Tessier sequential extraction possible shifted to T2 more when Cd concentration in soil is higher, from 45% to 75% in T2 from medium-concentration soil sample to high-concentration soil sample.

In conclusion, from overall that mentioned, Cd contamination in paddy soils come from irrigation water that received from Mae Tao creek. The highest concentration from the studies located in Ban Pa Te which is 200 mg kg^{-1}, whereas Ban Mae Tao Mai had 80 mg kg^{-1} Cd concentration (Akkajit and Tongcumpou, 2010; Kosolsaksakul et al., 2014; Simmons et al., 2005). Many results from BCR sequential extraction showed that most of Cd had potential to leach out from the soils because of high proportion in exchangeable fraction (BCR1), from 30-80% (Akkajit and Tongcumpou, 2010; Kosolsaksakul et al., 2014).

CHAPTER 3
METHODOLOGY

3.1 Data Preparation and Field Observation

3.1.1 Data Preparation

The information in the study area was collected in order to assign soil sampling points in the study area. All of detail of the information that used to create sampling spots are shown on the Table 3.1.

Table 3.1 *Input information for sampling spots assignment*

Data	Type	Source
Topographic Map	Raster	Royal Thai Survey Department (2006) with 1:50,000 map scale
Stream	Shapefile	Land Development Department
Soil type	Shapefile	Land Development Department
Cadmium Contamination Map	Shapefile	Modified from Akkajit and Tongcumpou (2010)

3.1.2 Field Observation

After all of information were collected and sampling spots were assigned, field observation was done to collect the 9 soil samples for the experiments. Type of soil sampling in this study can be divided in to 3 types of the soil sampling, consisting of bulk soil sampling, soil core sampling and soil profile sampling.

1) **Bulk soil sampling** – Based on Land Development Department (LDD) soil sampling method, the interested sampling spot was separated into 4 sub-sampling spots, on the center, north, south, east, and west direction. All four sub-sampling spots were far from the center spot around 10 meter. Take out

the organic matter from the soil surface (15 cm. from surface). Dig the sub-sampling in to V-shape that had 30 cm. depth from surface. Then, dug out both side of the V-shape hole in each spot and mix it together for 1 kg. The soil sample is a representative soil of the interested spot.

2) **Soil core sample** – This sample type was performed in order to preserve soil formation in the sampling spot to analyze hydraulic conductivity of the soil. The first 15 cm. of soil was dug out in order to clear top organic matter, then the soil ring was hammered down until the soil ring was filled, around 5.5 cm legth of core sampling. Dug the soil ring up and wiped out the excess soil surface without damage to any soil structure.

3) **Soil profile sampling** - This type of soil sample was done in order to cross-check the calculated result from the numerical modeling. Soil samples were taken by using a hand auger from 0-5, 5-10, 10-20, 20-30, 30-40, 40-60, 60-80, 80-100 cm from soil surface. All of the samples were analyzed by using BCR sequential extraction to get Cd content in those specific depth for a model validation.

The sampling spot in the study area was shown in Figure 3.1 which had 2 types of soil sampling; bulk soil sampling and soil core sampling in each spots, only red spots in the map were included soil profile sampling.

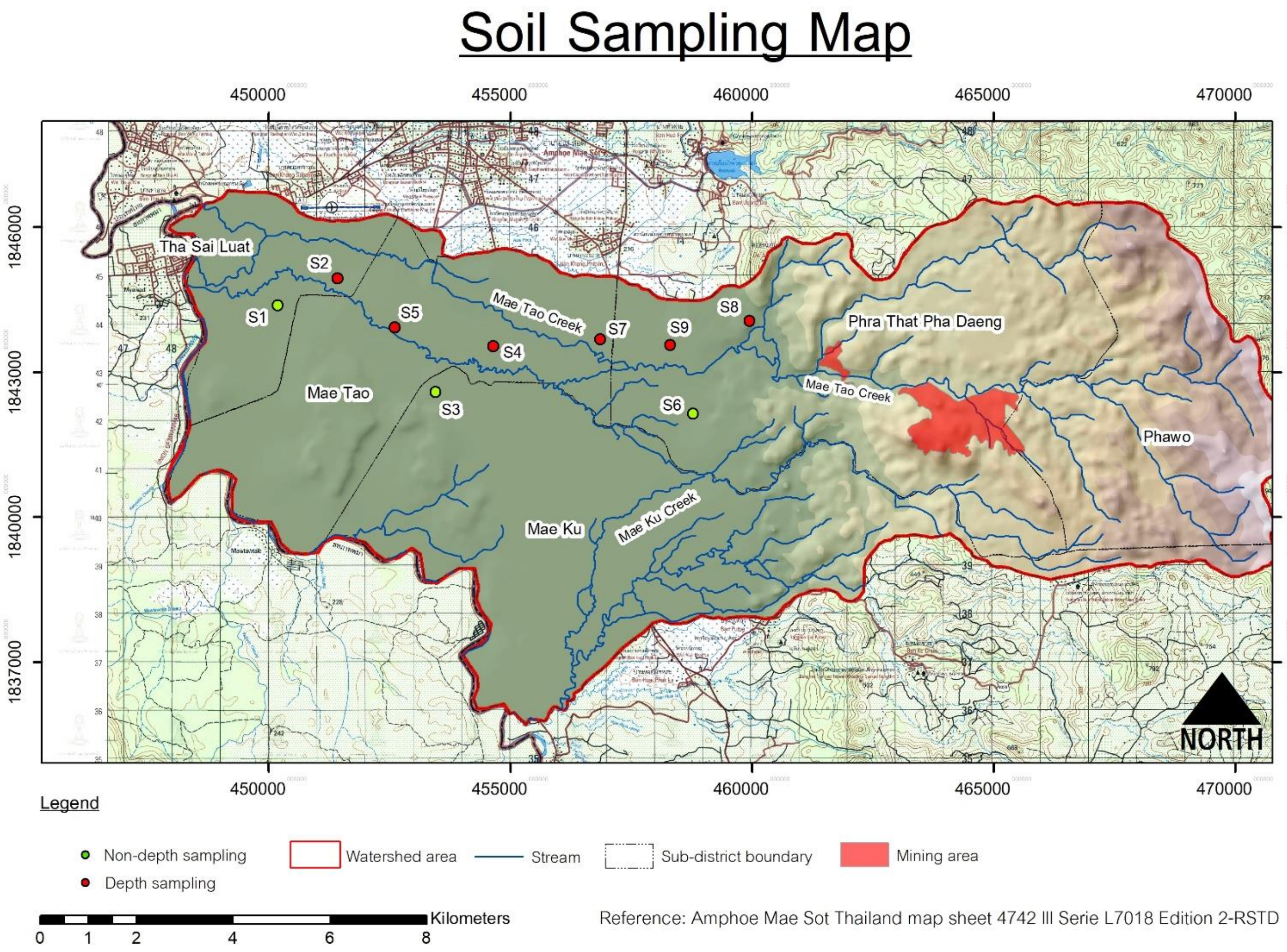


Figure 3.1 *Study area and sampling spots*

3.2 Soil Analysis

3.2.1 Soil preparation

After all samples were collected, except soil in core sampling, soil samples were grinded through 2 mm sieve and dry in the oven at 60^{o} C around 6 days in order to maintain some organic matter in the sample, which may lose from high temperature dry. As a result, lower than 2 mm of soil grain was used for the sorption and BCR sequential extraction experiments.

3.2.2 Physiochemical of Soil

1) Hydraulic conductivity (K)

Hydraulic conductivity of soil samples was sent to analyze at Agricultural Chemistry Group, Department of Agriculture. Soil cores were filled with water around 1 week until they are saturated. Then, deionized water was filled on the top of soil core, that has tube over it, around 10 cm. height and waited until the water level goes down below 10 cm. Some sample that had high proportion of clay could take more than hour to make the water level goes down, resulting from the low hydraulic conductivity of those soils. The experiment was done in duplicate, and the results were used to determine hydraulic conductivity from below equation (Eq. 3.1)

$$K_{20} = 0.30122 \times \log \frac{h_1}{h_2} \times \left(\frac{\mu_t}{t}\right) \times 36{,}000 \qquad \text{(Eq. 3.1)}$$

Where

h_1 = initial level of water in the tube (cm.)
h_2 = final water level in the tube (cm.)
μ_t = water viscosity (mPa·s)
t = time from the initial level to final level (hr.)

2) Bulk Density

After soil cores were analyzed for hydraulic conductivity, all of samples were dried in 105 °C oven for 3 days and calculated for bulk density from the below equation (Eq. 3.2)

$$\text{Bulk Density} = \frac{(\text{Dry weight of soil core} - \text{Core weight})}{\text{Soil core volume } (100 \text{ cm}^3)} \qquad \text{(Eq. 3.2)}$$

3) Soil particle analysis

Proportion of sand silt clay in the samples were sent to analyze at Agricultural Chemistry Group, Department of Agriculture, along with soil pH and soil organic matter (OM). The Hydrometer method was used to determine the grain size of the sample.

For particle analysis part, hydrometer method was performed in order to receive proportion of sand silt and clay in soil sample. Fifty grams of soil sample that have grain size lower than 2 mm were put in to 1000 cm^3 of deionized water with 4% of sodium hexametaphosphate in 1 L cylinder. Then, the soil solution was shaken to make the solution mixed well with the soil sample and then put the 152H hydrometer into the shaken solution and recorded the measurement at 8, 15, 30 min and 1, 2, 4, 8, 16, 24, 36, 50 hr for soil particle analysis. After that, all the measurement was recorded in order to determined soil particle size (ASTM D422-63, 2007).

4) Soil Organic matter analysis

For soil organic matter analysis, soil samples were analyzed by fallowed Walkley and Black method (Walkley and Black, 1934). Ten milliliters of 1 N of Potassium Dichromate ($K_2Cr_2O_7$) and high concentration sulfuric acid 20 ml were added into 1 g of soil sample. Leave the soil solution for 30 min and filled 50 ml of deionized water in the solution, then cool the solution temperature down. Then, added 5 dropped of O-phenantholine and tritrate the solution with 0.5 N of ammonium iron (II) sulfate hexahydrate ($Fe(NH4)_2(SO_4) \cdot 6H_2O$; FAS). Finally, the organic matter in the soil was determined following Eq. 3.3.

$$\text{Organic Matter (OM)} = \frac{(B\text{-}S) \text{ x } N}{B \text{ x } W} \times 6.717 \qquad \text{(Eq. 3.3)}$$

Where B refered to FAS amout that use for Blank tritration (ml), S is FAS amount that use in sample tritation (ml), W is soil sample weight (g), and N is $K_2Cr_2O_7$ concentration (This will be used when the substance concentration not equal to 1 N).

3.2.3 Batch Adsorption Experiment

In order to understand the sorption behavior of soils in the study area, batch adsorption experiments were performed. Cd initial concentration was separated in to 3 ranges of concentration based on preliminary of soil samples. The concentration of Cd was 0-40 ppm (e.g., 0, 5, 10, 15, 20, 30, 40 ppm), 0-50 ppm (e.g., 0, 15, 25, 30, 35, 40, 50 ppm), and 0-200 ppm (e.g., 0, 25, 50, 75, 100, 150, 200 ppm) which all of the concentrations were done in triplicate. The initial concentration was applied differently based on proportion of soil particle, especially clay content, in the samples. Twenty milliliters of Cd solution were filled in 1 g of soil sample that contained in 60 ml of a polypropylene bottle. The pH of soil solution was sutained at 7 by using 0.1 M of NaOH and 0.1 M of HNO_3. Moreover, ionic strength of soil sample was adjusted to 1mM in order to make the condition as same as surface water. However, for 200 ppm initial concentration, the ionic strength raised up to 4 mM, but still in range of surface water's ionic strength (1mM to 5mM) (Aqion, 2014). After all condition were adjusted, all soil solution was shaken by the orbital shaker with 200 rpm for 24 hours, following Waleeithikul & Chotpantarat (2016). Then, soil solution was filtered with Whatman no. 42 to get rid of soil particles. As a result, only remain solution was used to analyze residue Cd concentration by using AAS (Perkin Elmer). Then, the residue concentration data were used to calculate for adsorbed Cd in soil in order to plot graph for sorption behavior analysis. The overall process of batch adsorption experiment was shown in Figure 3.2.

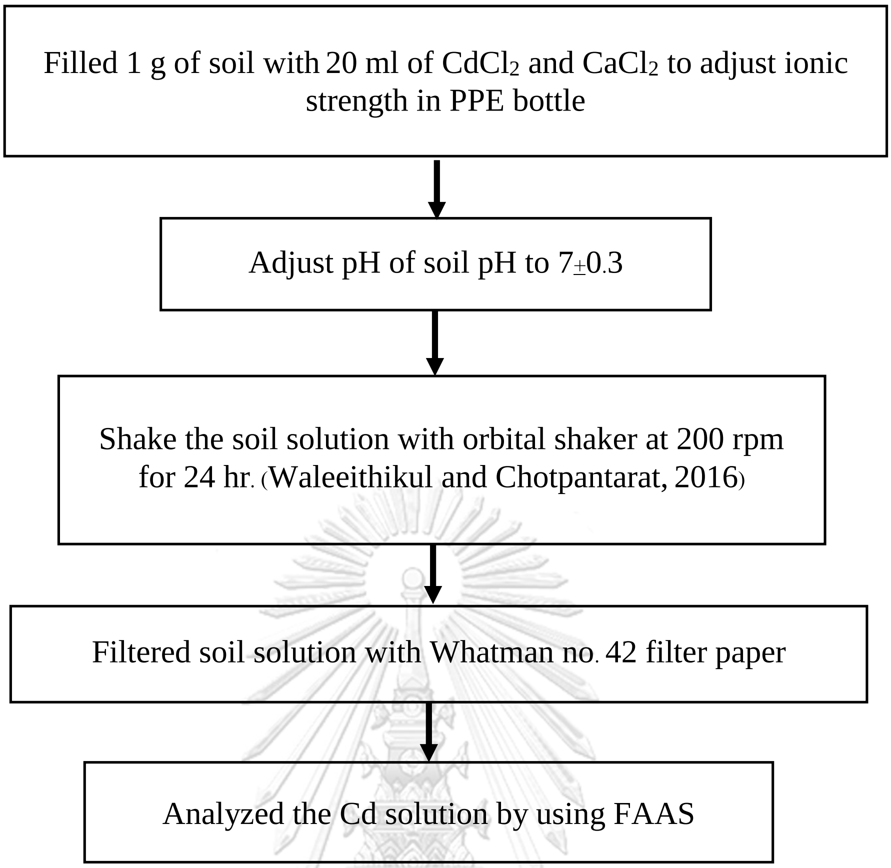


Figure 3.2 *Experimental scheme of batch adsorption experiment*

3.2.4 Sorption Behavior analysis

In order to understand sorption behavior of soil sample in the study area, adsorption isotherms were used to fitted graphs between sorbed Cd in soil (mg kg^{-1}) and residue Cd concentration in solution (mg L^{-1}). Adsorption isotherms that used in this study can be divided in to 3 types of isotherms: Linear isotherm, Freundlich isotherm, and Langmuir isotherm. For Freudlich isotherm, it used to describe sorption behavior as multilayer adsorption on heterogeneous surface, whereas Langmuir isotherm was adsorbed on homogeneous surface in monolayer form. For Linear adsorption isotherm, it is Freundlich adsorption that has Freundlich exponent (n) equal to 1 (Wikiniyadhanee, 2012). The eqution of adsorption isotherms were shown in Eq. 3.4-3.8.

1) Linear adsorption isotherm

$$Q_e = K_d C_e \qquad \text{(Eq. 3.4)}$$

Where

Q_e = sorbed Cd in soil sample (mg g^{-1})
C_e = residue Cd concentration at equilibrium (mg L^{-1})
K_d = Linear coefficient (L g^{-1})

2) Freundlich adsorption isotherm

$$Q_e = K_F C_e^{1/n} \qquad \text{(Eq. 3.5)}$$

Freundlich sorption equation in linear form

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{(Eq. 3.6)}$$

Where

Q_e = sorbed Cd in soil sample (mg g^{-1})
C_e = residue Cd concentration at equilibrium (mg L^{-1})
K_f = Freundlich coefficient (L g^{-1})
n = Freundlich adsorption exponent (-)

3) Langmuir adsorption isotherm

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad \text{(Eq. 3.7)}$$

Langmuir sorption isotherm in linear form

$$\frac{Ce}{Qe} = \frac{1}{K_L\, Q_m} + \frac{C_e}{Q_m} \qquad \text{(Eq. 3.8)}$$

Where

Q_e = sorbed Cd in soil sample (mg g^{-1})
Q_m = Maximum adsorption capacity (mg g^{-1})
C_e = residue Cd concentration at equilibrium (mg L^{-1})
K_L = Langmuir coefficient (L g^{-1})

3.2.5 Chi-Square test

Not only R^2 that be used fitted the adsorption isotherm, in order to find which isotherm could possibly explain sorption behavior of soil samples, Chi-square test, a statistical test which use to test that the observed data could be explained by the the interested hypotheses or not (Rao, 2002), were also used in this study. The equation Chi-square test are shown in Eq. 3.9.

$$\chi^2 = \sum \frac{(q-q_m)^2}{q_m} \qquad \text{(Eq. 3.9)}$$

Where

q = Cd sorbed in soil sample from the experiment at equilibrium (mg g^{-1})
q_m = Cd sorbed in soil which calculated from adsorption isotherm (mg g^{-1})

If the result from Chi-square is low, it can be interpreted that the calculated value from adsorption isotherm is fitted with experiment data, which could define as sorption behavior of the soil. In the other hand, if the Chi-square value became high, it means that the adsorption isotherm couldn't be described by that type of isotherm (Wikiniyadhanee et al., 2016).

3.2.6 PHREEQC modeling

PHREEQC is a program that written from C++ and C computer languages. The program was designed for geochemical calculations that suited for SIT models (Specific ion Interaction Theory), two ion-association aqueous models, and a Pitzer specific-ion-interaction aqueous model. This program can be used for 1) batch-reaction and 1D transport simulation with reversible and irreversible reactions 2) inverse models 3) speciation (Parkhurst and Appelo, 1999). In this study, PHREEQC was used to find the speciation of Cd and its condition in batch adsorption experiments with different initial concentration and fixed $CaCl_2$ concentration.

3.2.5 Pedotransfer function

Pedotransfer function is an empirical equation that created from available soil dataset in order to estimate parameter that difficult to obtain for input parameter in modeling (Lin et al., 2005). Typically, pedotransfer function has been developed to hydraulic properties but can apply with other parameter such as adsorption capacity or cation exchange capacity (Vogeler et al., 2011). The advantages from using pedotransfer function are lesser time-consuming and cheaper than performing the experiment, which cause more cost and time consuming than use the function (Borggaard et al., 2002).

In this study, the emphirical of pedotransfer function was applied from van der Grift and Griffioen (2008) and Beyer et al. (2009) which used to estimate Cd sorption corresponding to Cd concentration, pH, and organic matter (OM) by comparing the efficiency between two equations and the dataset in the study area in order to improve the accuracy of soil sorption estimation in the study area. The pedotransfer function of van der Grift and Griffioen (2008) and Beyer et al. (2009) were described in the following equations. For equation of Beyer et al. (2009) is showed in the below equation (Eq. 3.10)

$$\log(S) = \log(k*) - a\log(H^{+}) + b\log(OC) + n\log(C) \qquad \text{(Eq. 3.10)}$$

Where S (µg kg^{-1}) and C (µg L^{-1}) are sorbed and dissolved Cd content, $k*$ (µg^{1-n}L^{n} kg^{-1}) is intrinsic Freundlich coefficient, H^{+} refered to proton activity (mol L^{-1}), OC (%) is organic content, a (-), b (-), and n (-) are emphirical from pedotransfer function calculation.

The pedotransfer function for soil sorption estimation of van der Grift and Griffioen (2008) is showed in Eq. 3.11

$$\log[Q/C] = -4.96 + 0.36\log[\%\ \text{clay}] + 0.5\log[\%\ \text{SOM}] + 0.52\ \text{pH} \qquad \text{(Eq. 3.11)}$$

For Q is sorbed Cd in soil (mol kg^{-1}), C is Cd concentration in soil solution (mol m^{-3}), and pH (-) is a pH value from measurement.

3.2.6 Sequential extraction

A sequential extraction experiment was performed in this study to get initial Cd concentration parameter in the numerical modeling. According to the previous studies, there were many sequential extraction experiments that were studied in Mae Sot district Tak province. Akkajit and Tongcumpou (2010) studied fractionation of Cd in the study area by using BCR sequential extraction for bioavailability for Cd and other metals (Cu, Fe, Zn, Pb, and Mn), whereas Kosolsakul et al. (2014) used BCR sequential extraction and Tessier sequential extraction for soil-plant transferred factors. The result from both studies indicated that soil had the highest proportion of BCR1 in BCR sequential extraction, and T2 in Tessier sequential extraction (Akkajit and Tongcumpou, 2010; Kosolsaksakul et al., 2014). As a result, BCR1 and BCR2 were used in this study in order to receive the initial concentration parameter to estimate and concentration of Cd at the particular depth in the model validation part.

Fraction 1 - 0.25 grams of soil sample was added in 10 ml of 0.11 M acetic acid (CH_3COOH). Shake the soil samples for 16 hr by using oracle shaker, then the soil samples were separated with the solution by centrifuged soil solution at 4000 rpm for 20 min. After that, the solution was filtered by using Whatman no. 42 filter paper in order to analyzed the leached solution from the samples. For the soil residue, 20 ml of deionized water was added, shaked for 15 min, and centrifuged for 20 min to clean up the residue samples. This fraction of the sequential extraction represents Cd ion that attaches to carbonate.

Fraction 2 - The residue soil from the first fraction was added into 10 ml of 0.5 M of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), also shake for 16 hr and centrifuged 4000 rpm for 20 min and filtered for the leaching solution. In the end, BCR 2 fraction in the sequential extraction can be indicated the amount of Cd ion that bounded to Fe-Mn oxides.

After the experiment were done, all of filtered solution were analyzed for Cd concentration by using FAAS (Perkin Elmer). As a result, the overall process for BCR sequential extraction was shown in Figure 3.3

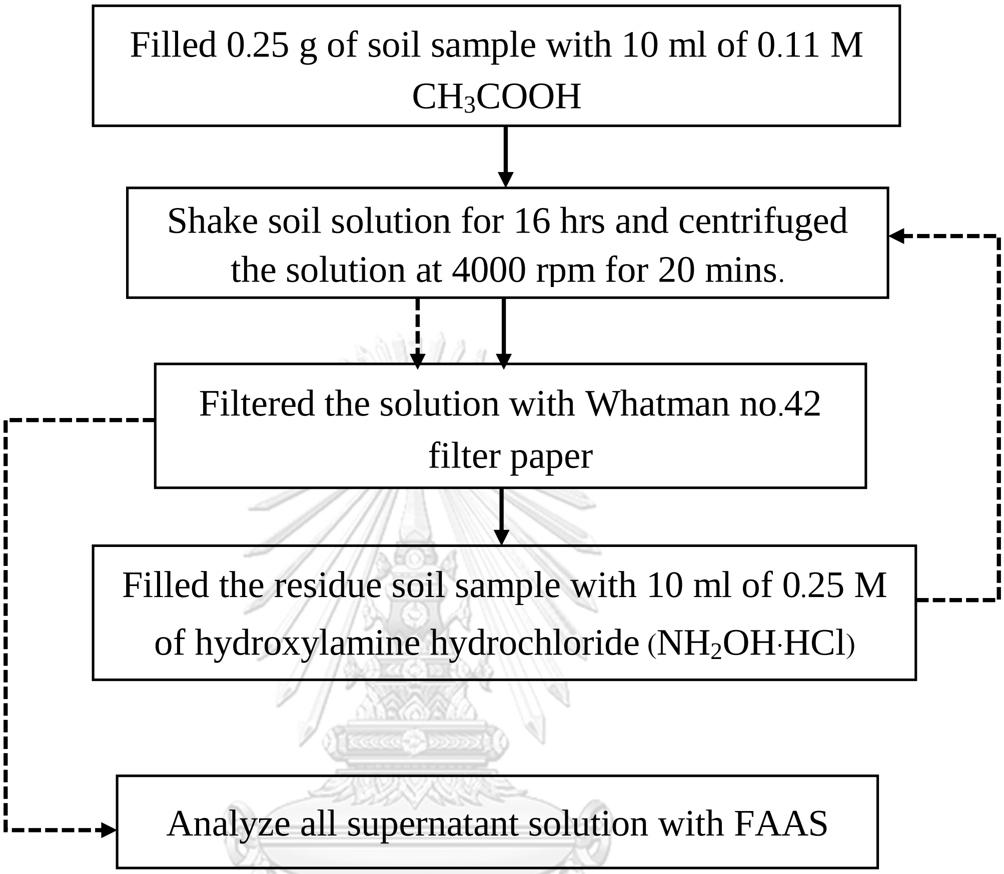


Figure 3.3 *Experimental scheme of BCR sequential extraction*

3.3 Numerical Transport Modeling

3.3.1 Transport modeling in HYDRUS-1D

HYDRUS-1D is a software package that uses to simulate transportation of water, solution, and heat. This software package can create a numerical model in saturated condition, unsaturated condition, or semi-saturated condition. The transformation equation of the software package base on advection-dispersion equation as shown in Eq. 3.12

$$\frac{\partial \theta C}{\partial t}+\rho\frac{\partial s}{\partial t}=\frac{\partial}{\partial z}\left(\theta D\frac{\partial c}{\partial z}\right)-\frac{\partial qc}{\partial z}-\phi \qquad \text{(Eq.3.12)}$$

When C and S is dissolved and adsorbed solution (mg L^{-1}), t is time (hr.), ρ is bulk density (kg L^{-1}), θ is volumetric water content, q is flow velocity (m d^{-1}), z is distance (cm), D is dispersion coefficient (m^2 s^{-1}), and ϕ is sink-source term.

3.3.2 Model Validation

After numerical modeling was finished, the BCR sequential extraction data of soils in different depth sampling were used to compare the result with the numerical simulation in order to examine the accuracy of the numerical modeling and adjust the model to make the result became more accurate.

In this study, transport condition was set as two-site model which assumes that media had 2 types of sorption: instantaneous sorption and kinetic sorption. Also, the simulation boundary began from surface level to groundwater level. Moreover, the simulation scenario was separated in to 2 parts. First, the simulation started from the beginning period of mining until the present time in order to calibrate the simulation result with the experimental data. Then other part started from the present day to the future in order to predict Cd migration until Cd reaching the groundwater level.

Model Efficiency determination

In order to qualify that the simulated model worked properly, Nash and Sutcliffe model efficiency (NSE) (Nash and Sutcliffe, 1970) was used in this study. The equation that used to determine NSE was shown in Eq. 3.13

$$\mathrm{NSE} = 1-\frac{\sum_{i=1}^{n}(p-o)^2}{\sum_{i=1}^{n}(o-\bar{o})^2} \qquad \text{(Eq. 3.13)}$$

Where p is predicted value from the simulation, o is observed value and $\bar{o}$ is average value of all observe data.

The result from NSE could vary from $-\infty$ to 1 which all rages of ME value could be interpreted as showed in Table 3.2.

Table 3.2 Interpretation of all NSE values (Lian et al., 2007)

NSE Value	Description
1	The perfect fit between model and observed value
0.75 $\geq$	The model has a good prediction
0.36 - 0.75	Satisfactory prediction
0	The prediction as good as mean of observed value

In conclusion, for the whole process of this thesis study, all of the experimental and numerical modeling schemes were shown in Figure 3.4.

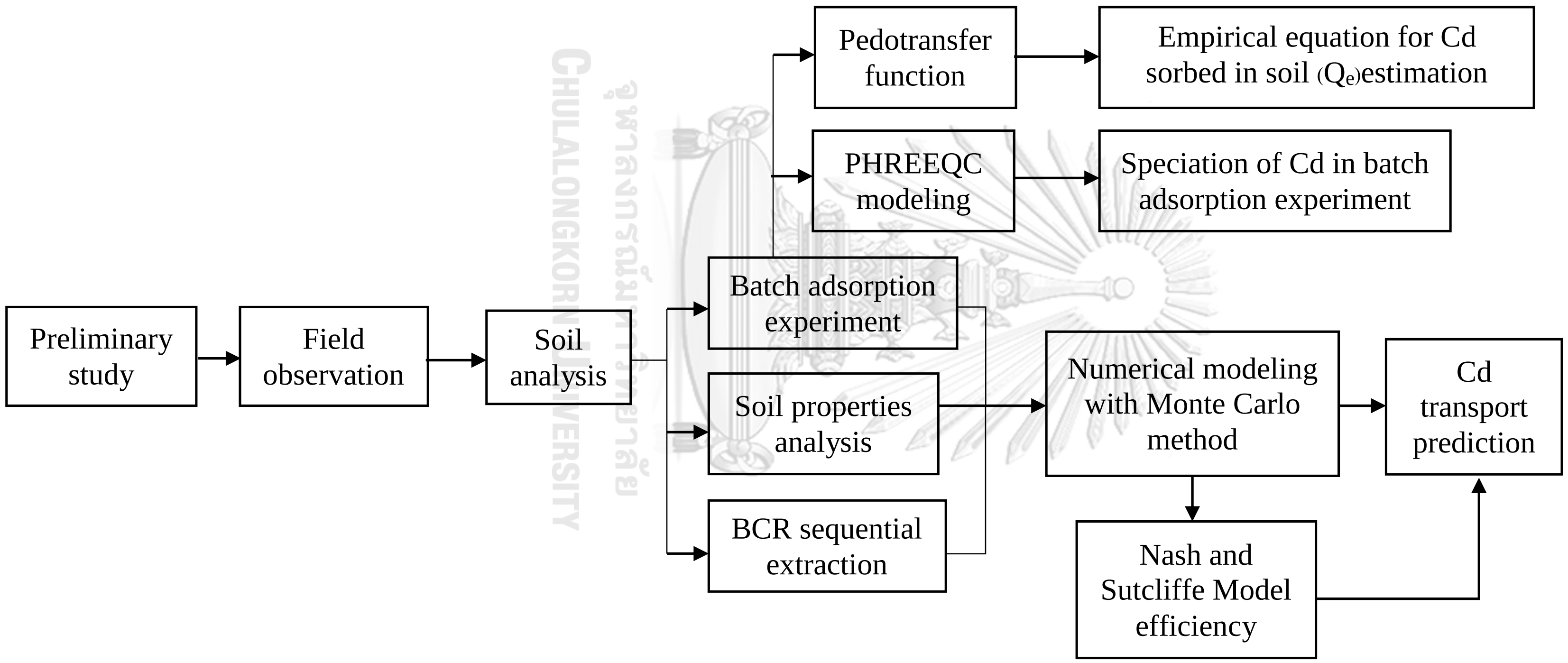


Figure 3.4 *Overall methodology scheme*

3.3.3 Introduction to Monte Carlo method

Monte Carlo is a method that uses combination of both probabilities and statistic. It can be applied in scientific research that deal with complex, time-consumed, expensive, and large dataset that inability to process by human (Anderson, 1986; Harrison, 2010). The concept of this method is using computer to repeat the experiment which result in many answers of interest based on the Law of Large Number (Kroese et al., 2014), a theorem that describes about the large number of times in the same experiment which average of these random values possible to become the expected value when it has more experiments. The result from this method can lead researcher able to do the experiment, that have complex systems, and to iterate and modify a parameter set easier. As mentioned, in order to perform Monte Carlo method, computer is necessary tool to calculate for the result because of large amount answer that unable to reach by human. Even it has many advantage using Monte Carlo method in the experiment, there are also have many disadvantages that cause from using it. First, Monte Carlo method is a combination of probability and statistics which give only the possible value from simulation, not the exact value. Second, because of the simulation, the result from Monte Carlo method require large computing resources in order to perform method. Last, like other computer programs, the program that perform Monte Carlo method is possible to have bugs. In order to fulfill the reseach gap as mentioned above, in this study, there are 3 parts as follows. Firstly, soil samples were collected from the field based on diiferent soil types. Secondly, this part consisting of 3 experiments, consisting of the physiochemical properties of soils, batch adsorption experiment and BCR sequential extraction experiment. The last part is the simulation of Cd transport by the integrated numerial modeling, HYDRUS-1D, with Monte Carlo methods. The concept of Monte Carlo technique could be explained by Figure 3.5.

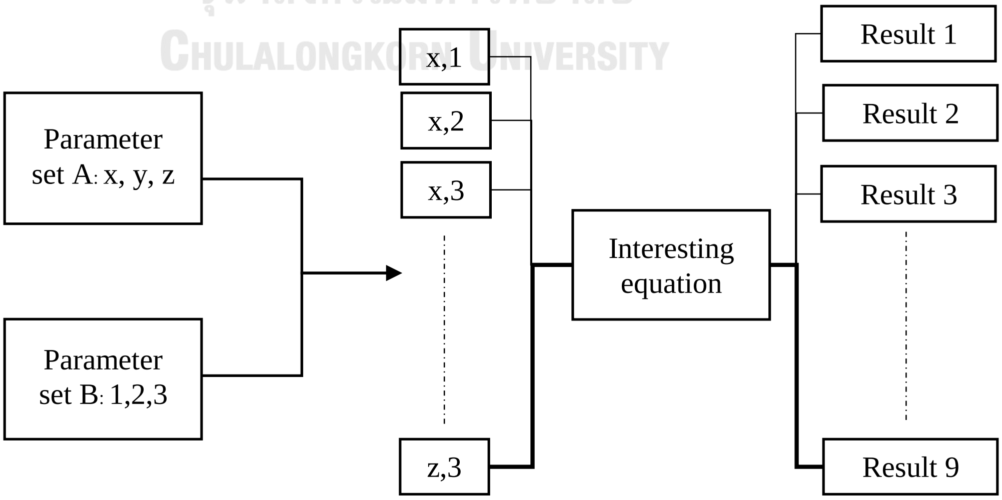


Figure 3.5 *The concept of Monte Carlo technique*

From the Figure 3.5, it showed that the result from Monte Carlo technique can produce many possibility of the results. In conclusion, it is necessary to examine average for the all possible value as a representative data of the total results.

3.3.4 Monte Carlo Simulation Scheme with HYDRUS-1D

Monte Carlo Method technique applied in HYDRUS-1D program was created from MATLAB. As mentioned previously, HYDRUS-1D is a program that use to simulate water, solution, and heat in one direction that can simulate in saturated, unsaturated, and partial saturated conditions, based on advection-dispersion equation. Software package contains 2 parts in the program, GUI part for parameter input, and modeling part that use to perform numerical simulation. Since this program can simulate for the result only one times which made this software package cannot perform multiple simulation in order to get many different results. As a result, MATLAB was used in order to make the software package able to run multiple simulation with different range of parameters.

In order to generate numerical model in HYDRUS-1D, this program will search for folders that contain at least 2 files to make HYDRUS-1D can run properly: SELECTOR.in, and PROFILE.dat. The detail of these 2 files is shown below.

SELECTOR.in - general information, time condition, water flow condition, and solution information that used to create the model.

PROFILE.dat - information about soil profile that use to modify soil profile information, containing the observed nodal information that assigned in soil profile.

Moreover, this folder also contains ADMOSPH.IN that use to adjust atmospheric information, METEO.in for meteorological data, and FIT.in for inverse modeling. When HYDRUS-1D wants to begin the numerical simulation, it locates target folder that contain interested parameter by using Level_01.dir, containing the folder destination will use for numerical simulation.

For modeling part of HYDRUS-1D, it uses DOS to perform numerical modeling, and the mentioned files, consisting of SELECTOR.in, and PROFILE.in, can be modified. As a result, MATLAB was used in order to create a function to change files' information, script file that used to random parameters, and command HYDRUS-1D to generate numerical simulation.

After the simulation was completed, all information of the simulation was contained in output file call Nod_inf.out. In this file the simulated Cd concentration level from input data was calculated and contained in each depth of soil column in the outputfile. In conclusion, all MATLAB working scheme was shown in Figure 3.6.

Summary of MATLAB process as follows:

1. create script file in MATLAB that used to operate Monte Carlo simulation on the program.
2. create function for parameters change in each Monte Carlo simulation.
3. batch file was created to performed HYDRUS-1D simulation.
4. create a cell to collected interested results.
5. create function to calculate all of the output value for the interested result

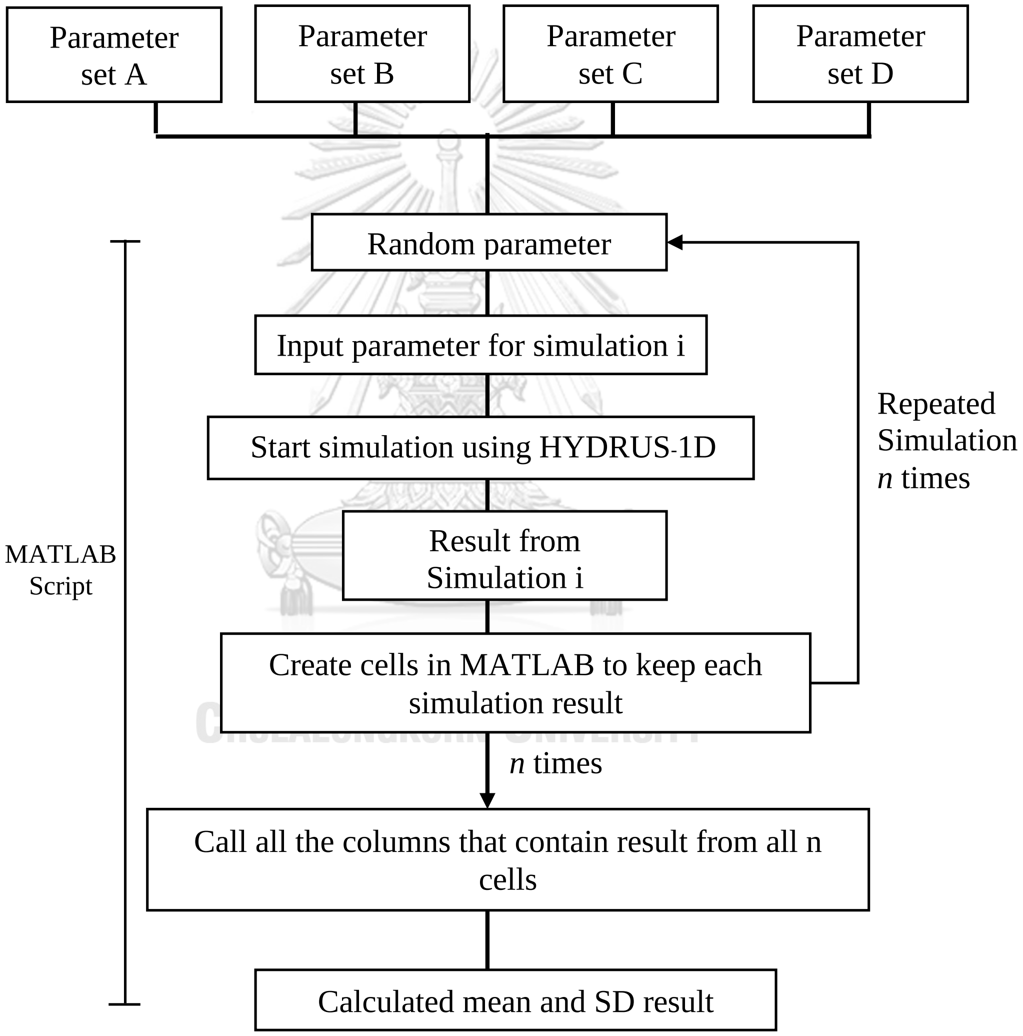


Figure 3.6 *MATLAB processing scheme*

From Figure 3.6, five thousand times of Monte Carlo method was simulated based on the acceptable range of error (Jafari et al., 2016) in oreder calculated for Cd concentration in each levels of soil profile.

3.4 Code in MATLAB to change parameters and perform Monte Carlo simulation

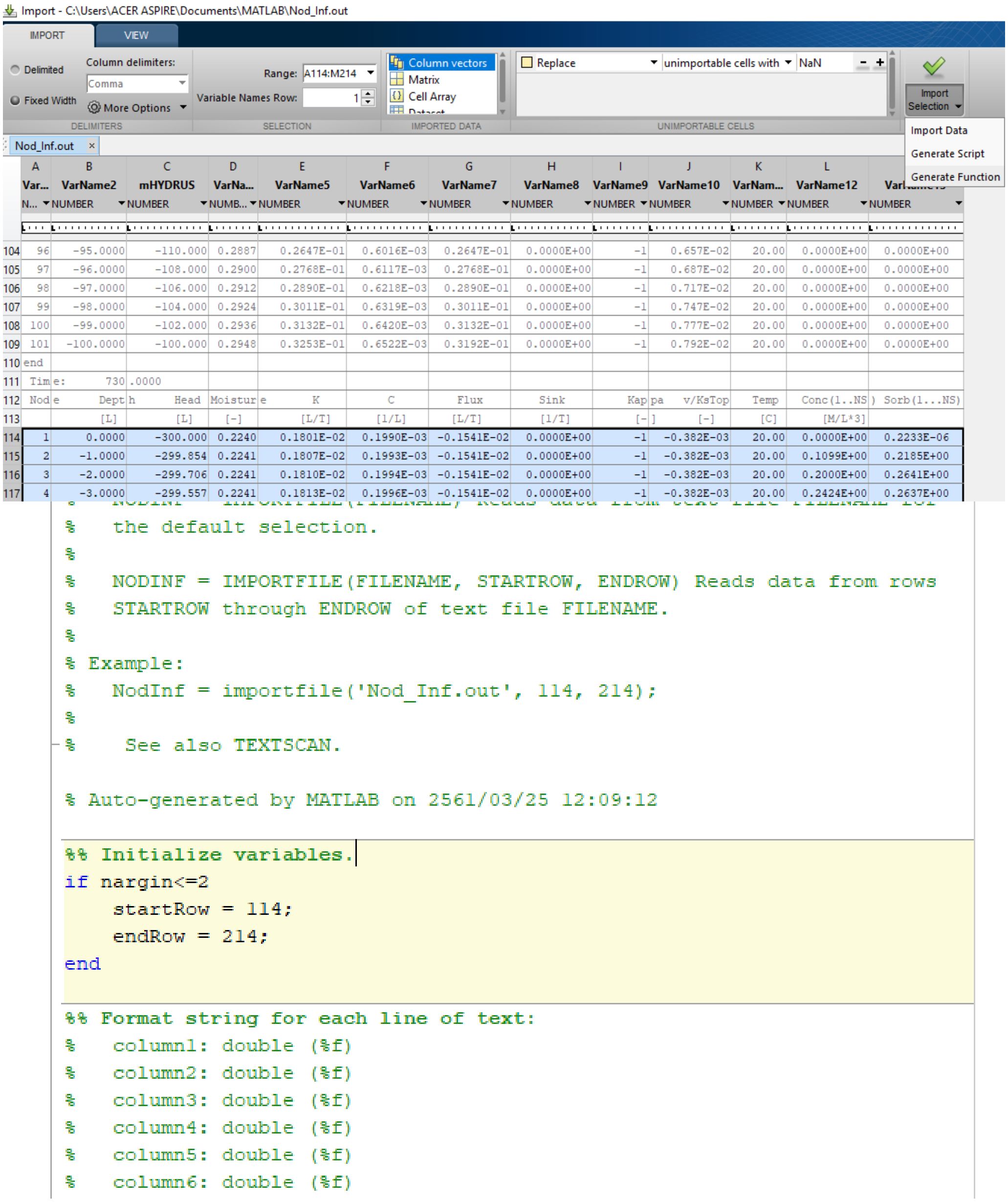
```
function Modselect(c,d,e)
%UNTITLED Summary of this function goes here
%   Detailed explanation goes here
cd 'C:\Users\Public\Documents\PC-Progress\Hydrus-1D 4.xx\Examples\Thesis project\T2ST14 Soil'
fid = fopen('Selector.in','w+');

fprintf(fid,'Pcp_File_Version=4');
fprintf(fid,'\n*** BLOCK A: BASIC INFORMATION *****************************************');
fprintf(fid,'\nHeading');
fprintf(fid,'\nWelcome to HYDRUS-1D');
fprintf(fid,'\nLUnit  TUnit  MUnit  (indicated units are obligatory for all input data)');
fprintf(fid,'\ncm');
fprintf(fid,'\ndays');
fprintf(fid,'\nmg');
fprintf(fid,'\nlWat   lChem lTemp  lSink lRoot lShort lWDep lScreen lVariabBC lEquil lInverse');
fprintf(fid,'\n t     t     f      f     f     f      f     t       f         f         f');
fprintf(fid,'\nlSnow  lHP1   lMeteo  lVapor lActiveU lFluxes lIrrig  lDummy  lDummy  lDummy');
fprintf(fid,'\n f       f       f       f       f       t       f       f       f       f');
fprintf(fid,'\nNMat    NLay  CosAlpha');
fprintf(fid,'\n  1       1       1');
fprintf(fid,'\n*** BLOCK B: WATER FLOW INFORMATION ************************************');
fprintf(fid,'\nMaxIt   TolTh   TolH       (maximum number of iterations and tolerances)');
fprintf(fid,'\n  10    0.001      1');
fprintf(fid,'\nTopInf WLayer KodTop InitCond');
fprintf(fid,'\n f     f       1       f');
fprintf(fid,'\nBotInf qGWLF FreeD SeepF KodBot DrainF  hSeep');
fprintf(fid,'\n f     f     t     f     -1      f      0');
fprintf(fid,'\n    hTabl   hTabN');
fprintf(fid,'\n    1e-006   10000');
fprintf(fid,'\n    Model   Hysteresis');
fprintf(fid,'\n      0           0');
fprintf(fid,'\n   thr     ths    Alfa      n         Ks       l');
fprintf(fid,'\n 0.0597  0.3898  0.0183  1.3953      %.3f     0.5 ',e); %change this Line
fprintf(fid,'\n*** BLOCK C: TIME INFORMATION ******************************************');
fprintf(fid,'\n        dt       dtMin       dtMax     DMul    DMul2  ItMin ItMax  MPL');
fprintf(fid,'\n      0.001      1e-005     4.99999    1.3     0.7     3     7     1');
fprintf(fid,'\n      tInit         tMax');
fprintf(fid,'\n          0           730');
fprintf(fid,'\n  lPrintD  nPrintSteps tPrintInterval lEnter');
fprintf(fid,'\n     f            1              1        t');
```

Figure 3.7 *MATLAB code for changing parameter*

3.4.1 Change input parameters in the transport numerical modeling

1. Create a function name and parameters that wanted to change.
2. Use ‘cd’ command to change your directory to the interested directory.
3. Assigned ‘fid’ by used ‘fopen’ command to open the target file
4. Copy all detail in the target file into the function
5. Fill all the lines with “fprintf (fid, ‘(information in the target file)’);” (noted: for the next line ‘\n’ is require in order to make the interested information enter down to the next line.)
6. In the line that has interested value that wanted to change, replace the target value with %f and add “fprintf (fid, ‘(information in the target file that already change interested value to %f)’, (parameter));”. Please note that you have to fill the parameter in the right sequence in function assignment in No.1 to make the function change the parameter into the exact position.

NOTE: it is important to copy all of the new detail when starting change parameter in the new soil sample because these process will rewrite everything in SELECTOR.in file in the target folder.



Import - C:\Users\ACER ASPIRE\Documents\MATLAB\Nod_Inf.out

○ Delimited
● Fixed Width
Column delimiters: Comma
More Options
Range: A114:M214
Variable Names Row: 1
Column vectors
Matrix
Cell Array
Dataset
☐ Replace unimportable cells with NaN

	A	B	C	D	E	F	G	H	I	J	K	L	
	Var...	VarName2	mHYDRUS	VarNa...	VarName5	VarName6	VarName7	VarName8	VarName9	VarName10	VarNam...	VarName12	Var
	N...	NUMBER	NUMBER	NUMB...	NUMBER	NUMBER	NUMBER	NUMBER	NUMBER	NUMBER	NUMBER	NUMBER	NUMBER
104	96	-95.0000	-110.000	0.2887	0.2647E-01	0.6016E-03	0.2647E-01	0.0000E+00	-1	0.657E-02	20.00	0.0000E+00	0.0000E+00
105	97	-96.0000	-108.000	0.2900	0.2768E-01	0.6117E-03	0.2768E-01	0.0000E+00	-1	0.687E-02	20.00	0.0000E+00	0.0000E+00
106	98	-97.0000	-106.000	0.2912	0.2890E-01	0.6218E-03	0.2890E-01	0.0000E+00	-1	0.717E-02	20.00	0.0000E+00	0.0000E+00
107	99	-98.0000	-104.000	0.2924	0.3011E-01	0.6319E-03	0.3011E-01	0.0000E+00	-1	0.747E-02	20.00	0.0000E+00	0.0000E+00
108	100	-99.0000	-102.000	0.2936	0.3132E-01	0.6420E-03	0.3132E-01	0.0000E+00	-1	0.777E-02	20.00	0.0000E+00	0.0000E+00
109	101	-100.0000	-100.000	0.2948	0.3253E-01	0.6522E-03	0.3192E-01	0.0000E+00	-1	0.792E-02	20.00	0.0000E+00	0.0000E+00
110	end												
111	Tim	e: 730	.0000										
112	Nod	e Dept	h Head	Moistur	e K	C	Flux	Sink	Kap	pa v/KsTop	Temp	Conc(1..NS	) Sorb(1...NS)
113		[L]	[L]	[-]	[L/T]	[1/L]	[L/T]	[1/T]	[-	] [-]	[C]	[M/L*3]	
114	1	0.0000	-300.000	0.2240	0.1801E-02	0.1990E-03	-0.1541E-02	0.0000E+00	-1	-0.382E-03	20.00	0.0000E+00	0.2233E-06
115	2	-1.0000	-299.854	0.2241	0.1807E-02	0.1993E-03	-0.1541E-02	0.0000E+00	-1	-0.382E-03	20.00	0.1099E+00	0.2185E+00
116	3	-2.0000	-299.706	0.2241	0.1810E-02	0.1994E-03	-0.1541E-02	0.0000E+00	-1	-0.382E-03	20.00	0.2000E+00	0.2641E+00
117	4	-3.0000	-299.557	0.2241	0.1813E-02	0.1996E-03	-0.1541E-02	0.0000E+00	-1	-0.382E-03	20.00	0.2424E+00	0.2637E+00

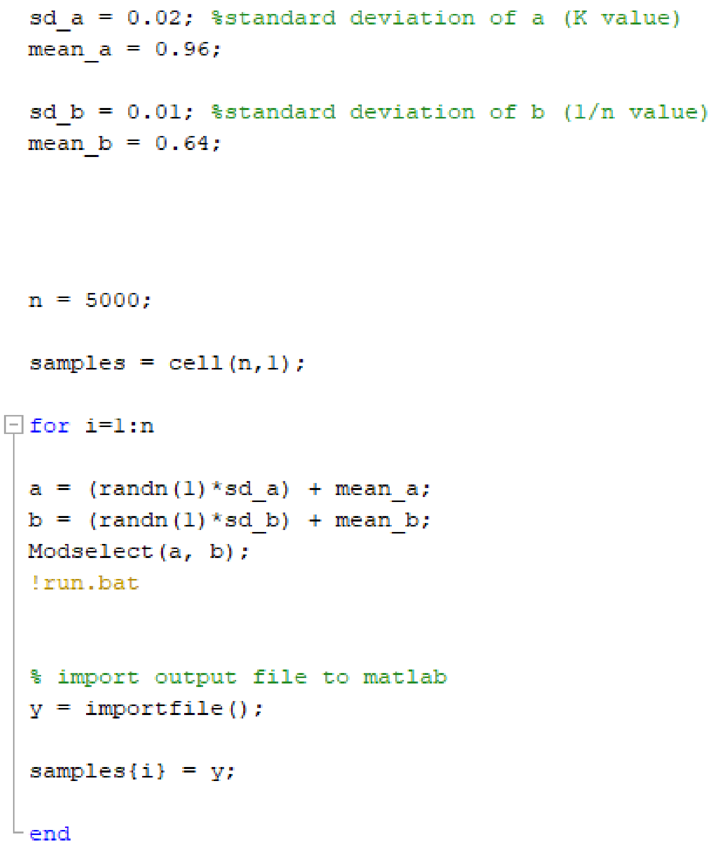
```matlab
%   the default selection.
%
%   NODINF = IMPORTFILE(FILENAME, STARTROW, ENDROW) Reads data from rows
%   STARTROW through ENDROW of text file FILENAME.
%
% Example:
%   NodInf = importfile('Nod_Inf.out', 114, 214);
%
%    See also TEXTSCAN.

% Auto-generated by MATLAB on 2561/03/25 12:09:12

%% Initialize variables.
if nargin<=2
    startRow = 114;
    endRow = 214;
end

%% Format string for each line of text:
%   column1: double (%f)
%   column2: double (%f)
%   column3: double (%f)
%   column4: double (%f)
%   column5: double (%f)
%   column6: double (%f)
```

Figure 3.8 *Text file import function*

3.4.2 Import text file to MATLAB

From Figure 3.8, this function was created by use import data in MATLAB to bring text file into the program

1. Press import data in home panel
2. Select text file that want to import in to MATLAB
3. The import GUI will appear to the screen cover the area that prefer to import in to MATLAB
4. Click import selection to set import condition as function
5. Adjust the generated function and rename the function as text file import function



```
sd_a = 0.02; %standard deviation of a (K value)
mean_a = 0.96;

sd_b = 0.01; %standard deviation of b (1/n value)
mean_b = 0.64;




n = 5000;

samples = cell(n,1);

for i=1:n

a = (randn(1)*sd_a) + mean_a;
b = (randn(1)*sd_b) + mean_b;
Modselect(a, b);
!run.bat


% import output file to matlab
y = importfile();

samples{i} = y;

end
```

Figure 3.9 *Monte Carlo script in MATLAB*

3.4.3 Monte Carlo Simulation in MATLAB

In Figure 3.9, before running MATLAB in Monte Carlo simulation, it is important to copy file H1D_CALC.EXE or H1D_CLCI.EXE, for direct simulation or inverse simulation respectively, and level_01.dir from HYDRUS folder to the operating folder to make the whole process become easier. Moreover, make sure that target folder in level_01.dir is correct in order to make the simulation work properly.

1. Generate a script and name the script to initiate Monte Carlo simulation.

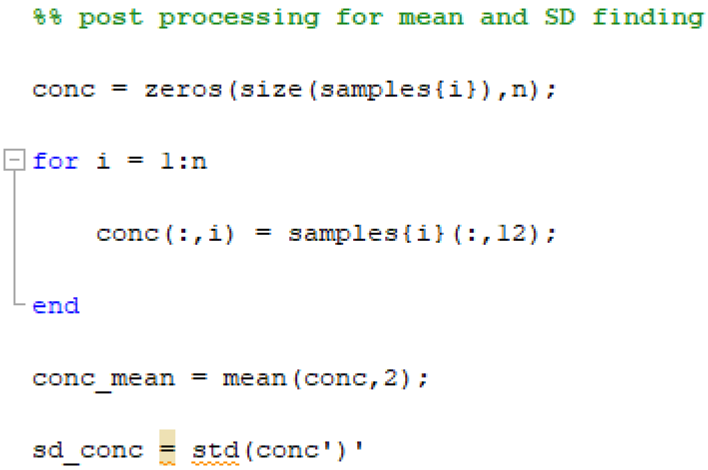
2. Set the mean and SD of all random parameters for Monte Carlo simulation.

3. Assign the running times for the Simulation in parameter n.
4. Create assigned a cell to collect all the results.
5. random parameters by using modified 'randn (1)' command, plus mean and multiply by SD to make it became the interested data set.
6. Use the function that add random parameters in to the model.
7. Run model by created batch file that use to run model (this model require enter after the simulation was finished to continue the next process, so enter command also added in this batch file) and activated by used '!' command
8. Call the result from the target folder into MATLAB
9. Put the called result in to the created cell

```
H1D_CALC<return.txt
```

Figure 3.10 *Inside batch file which used for model simulation*

In Figure 4.14, H1D_CALC was used to simulated the direct simulation of HYDRUS-1D with other command which is return.txt. In the textfile, it's contain '<0D0A>' code that is the enter button code. As a result, the batch file was created to command MATLAB to begin the simulation and press the enter in order to make the whole process of Monte Carlo simulation run continuously.



```
%% post processing for mean and SD finding

conc = zeros(size(samples{i}),n);

for i = 1:n

    conc(:,i) = samples{i}(:,12);

end

conc_mean = mean(conc,2);

sd_conc = std(conc')'
```

Figure 3.11 *MATLAB code of Average and SD calculation*

3.4.4 Created function for average and SD calculation from the result

From Figure 3.11, it is impossible to show all of the results from Monte Carlo simulation. In conclusion, mean and SD value were calculated as a representative of the interested simulation

1. Create the script for mean and SD calculation
2. Create a zero matrix as a result container by assign as same as the result roll with n column
3. Create a loop to add a specific column from 1 to n column
4. Use 'mean' command to calculate mean value, also, put 2 after interested matrix to assign the calculation direction
5. Use 'std' command to calculate SD value from dataset, it is necessary to put comma to inverse roll to column because 'std' command only calculate in the first dimension, downward direction, then use comma sign again to transform back to the same matrix

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Soil Physiochemical properties

Nine soil samples were analyzed for the proportion of soil particle, soil pH, soil organic matter (OM), cat ion exchange capacity (CEC), bulk density, and hydraulic conductivity. As a result, the physiochemical properties of soils is shown in Table 4.1.

Table 4.1 *Physiochemical properties of soil samples.*

Soil sample	Sand (%)	Silt (%)	Clay (%)	OM (%)	pH	CEC (cmol kg^{-1})	Bulk density (g cm^{-3})	Hydraulic conductivity (mm hr^{-1})
S1	62	28	10	0.37	7.0	4.11	1.622	3.616
S2	60	28	12	0.53	5.4	2.79	1.604	2.348
S3	54	15.8	30.2	1.18	4.9	9.81	1.697	6.973
S4	52.8	26	21.2	0.91	8.0	14.83	1.520	1.680
S5	49.8	26	24.2	1.6	7.6	12.23	1.417	8.000
S6	48	16	36	0.72	7.2	11.81	1.711	1.418
S7	39	28.8	32.2	1.06	7.0	16.46	1.671	0.210
S8	26.8	25.2	48	1.09	7.7	17.33	1.659	0.915
S9	16.6	25.2	58.2	2.82	5.7	21.74	1.394	0.600
Max	62	28.8	58.2	2.82	8	21.74	1.711	8
Min	16.6	15.8	10	0.37	4.9	2.79	1.394	0.21
Mean	45.44	24.33	30.22	1.14	6.72	12.35	1.59	2.86
SD	15.25	4.95	15.79	0.73	1.11	6.14	0.12	2.82

From the table 4.1, it is shown that soil types of the samples were classified from sandy loam to clay soil following USDA soil classification. Organic matter of the soil samples ranged from 0.37-2.82% which there is only one sample has organic matter higher than 2%. Soils' pH was in the range of 4.9-7.7, which most samples have pH higher than 7. Most hydraulic conductivity of soil samples is lower than 5 mm hr^{-1}, only 2 samples (S3 and S5) that higher than 5 mm hr^{-1}. There is a similarity of bulk density in each soil samples, varing from 1.394 to 1.711 g cm^{-1}, and CEC were ranged from 2.79 to 21.74 cmol kg^{-1}.

4.2 Major ion species simulation by PHREEQC

Not only using batch adsorption experiment to study sorption behavior of soil samples, this study also used PHREEQC, which is a numerical program that developed by USGS in order to investigate the major chemical species in the experiment. The result from PHREEQC found that Cd speciation simulation as batch adsorption experiment are shown in Table 4.2.

Table 4.2 *Speciation of dissolved Cd species from the batch adsorption experiment*

Initial $CdCl_2$ (mM)	**$CaCl_2$ added (mM)**	**IS (mM)**		**Cd^{2+}**	**$CdCl^+$**	**CdOHCl**	**$CdCl_2$**	**Total**
0.0842	0.3	1.14	M	7.91E-05	4.95E-06	1.97E-08	1.46E-08	
			%	93.96	5.88	0.02	0.02	99.89
0.149	0.3	1.33	M	1.39E-04	9.99E-06	3.96E-08	3.40E-08	
			%	93.13	6.71	0.03	0.02	99.89
0.187	0.3	1.43	M	1.73E-04	1.34E-05	5.29E-08	4.91E-08	
			%	92.68	7.17	0.03	0.03	99.90
0.316	0.3	1.79	M	2.88E-04	2.74E-05	1.08E-07	1.25E-07	
			%	91.14	8.67	0.03	0.04	99.88
0.521	0.3	2.35	M	4.64E-04	5.66E-05	2.22E-07	3.36E-07	
			%	88.98	10.87	0.04	0.06	99.96
0.526	0.3	1.58	M	4.84E-04	4.14E-05	1.63E-07	1.69E-07	
			%	91.96	7.86	0.03	0.03	99.89
1.587	0.3	5.03	M	1.27E-03	3.10E-04	1.18E-06	3.82E-06	
			%	80.13	19.50	0.07	0.24	99.94
1.59	0.3	5.03	M	1.27E-03	3.10E-04	1.19E-06	3.84E-06	
			%	80.12	19.51	0.07	0.24	99.95

The result from Table 4.2 showed that Cd^{2+} is the most available specie from the overall species in this study as same as Powell et al. (2011) that Cd^{2+} is the dominant Cd spicies in freshwater system that generally has a low ionic strength condition.

4.3 Batch adsorption experiment

Soil samples in the study area were analyzed for sorption behavior using batch adsorption experiment with pH 7±0.3 and 0.1-0.5 mM of ionic strength. Moreover, the initial concentrations of Cd onto soil samples were widely different, depending on the proportion of soil particle in each samples. The result from the experiment were shown in the table 4.3.

Table 4.3 *Cd adsorption and sorption percentage in soil samples*

Soil sample	Initial concentration (mg L^{-1})	Remain concentration (mg L^{-1})	Cd sorption in soil (mg g^{-1})	Percent adsorption (%)
S1	< 0.02	< 0.02	< 0.02	-
	4.67	0.196	0.089	95.803
	9.5	0.548	0.179	94.232
	13.9	1.253	0.253	90.983
	19.2	1.823	0.348	90.505
	26.5	10.86	0.313	59.019
	34.2	16.567	0.353	51.559
S2	< 0.02	< 0.02	< 0.02	-
	4.67	0.121	0.091	97.409
	9.5	0.217	0.186	97.721
	13.9	0.427	0.269	96.93
	19.2	0.664	0.371	96.543
	26.5	1.73	0.495	93.47
	34.2	13.01	0.424	61.959
S3	< 0.02	< 0.02	< 0.02	-
	12.495	0.129	0.247	98.965
	19.7	0.16	0.391	99.186
	29.85	0.189	0.593	99.368
	33.8	0.212	0.672	99.372
	37.4	0.261	0.743	99.301
	57.85	0.383	1.149	99.337
S4	< 0.02	< 0.02	< 0.02	-
	12.495	0.144	0.247	98.845
	19.7	0.404	0.386	97.951
	29.85	0.61	0.585	97.958
	33.8	0.884	0.658	97.384
	37.4	1.16	0.725	96.899
	57.85	1.902	1.119	96.712

Soil sample	Initial concentration (mg L^{-1})	Remain concentration (mg L^{-1})	Cd sorption in soil (mg g^{-1})	Percent adsorption (%)
S5	< 0.02	< 0.02	< 0.02	-
	12.495	0.122	0.247	99.026
	19.7	0.258	0.389	98.689
	29.85	0.396	0.589	98.673
	33.8	0.555	0.665	98.357
	37.4	0.764	0.733	97.956
	57.85	1.254	1.132	97.832
S6	< 0.02	< 0.02	< 0.02	-
	20.5	0.312	0.404	98.476
	39.15	1.276	0.757	96.742
	61.85	4.53	1.146	92.676
	79.1	8.4	1.414	89.381
	182.7	22.5	3.204	87.685
	291.5	43.6	4.958	85.043
S7	< 0.02	< 0.02	< 0.02	-
	20.4	0.157	0.405	99.23
	39.15	0.793	0.767	97.974
	57.7	2.75	1.099	95.234
	78.5	6.05	1.449	92.293
	181.8	15.533	3.325	91.456
	291	33.367	5.153	88.534
S8	< 0.02	< 0.02	< 0.02	-
	20.5	0.16	0.407	99.218
	39.15	0.907	0.765	97.683
	61.85	2.993	1.177	95.16
	79.1	5.533	1.471	93.005
	182.7	17.633	3.301	90.348
	291.5	31.033	5.209	89.354
S9	< 0.02	< 0.02	< 0.02	-
	20.5	0.075	0.408	99.633
	39.15	0.147	0.78	99.624
	61.85	0.403	1.229	99.349
	79.1	1.129	1.559	98.573

Soil sample	Initial concentration (mg L^{-1})	Remain concentration (mg L^{-1})	Cd sorption in soil (mg g^{-1})	Percent adsorption (%)
	182.7	6.267	3.529	96.57
	291.5	11.25	5.605	96.141

The result from batch adsorption experiment can be shown as diagrams between Cd sorbed in soil (Qe) and Cd concentration at equilibrium (Ce) were shown in Figure 4.1-4.9.

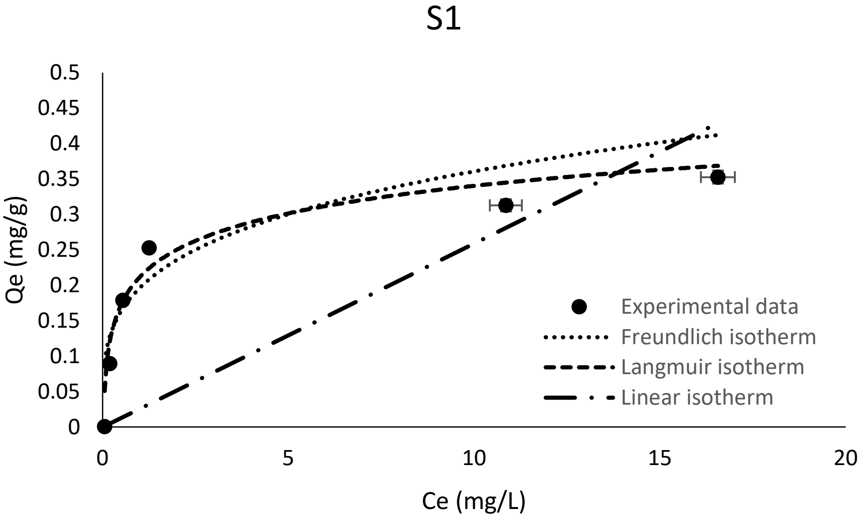


Figure 4.1 *S1 experimental data fitted with adsorption isotherms*

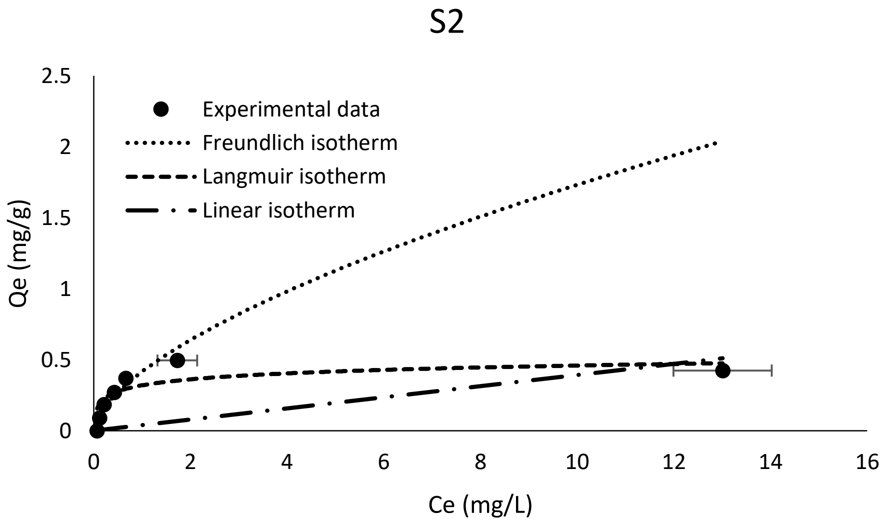


Figure 4.2 *S2 experimental data fitted with adsorption isotherms*

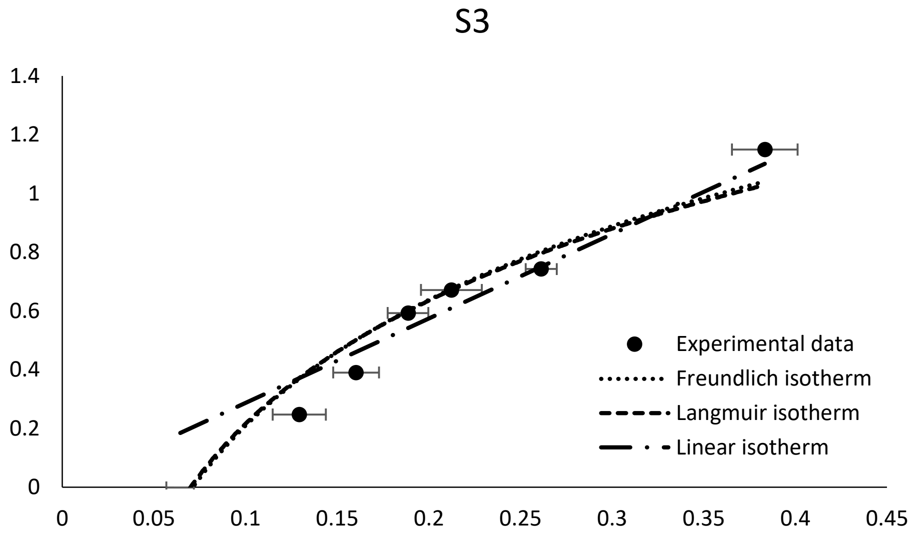


Figure 4.3 *S3 experimental data fitted with adsorption isotherms*

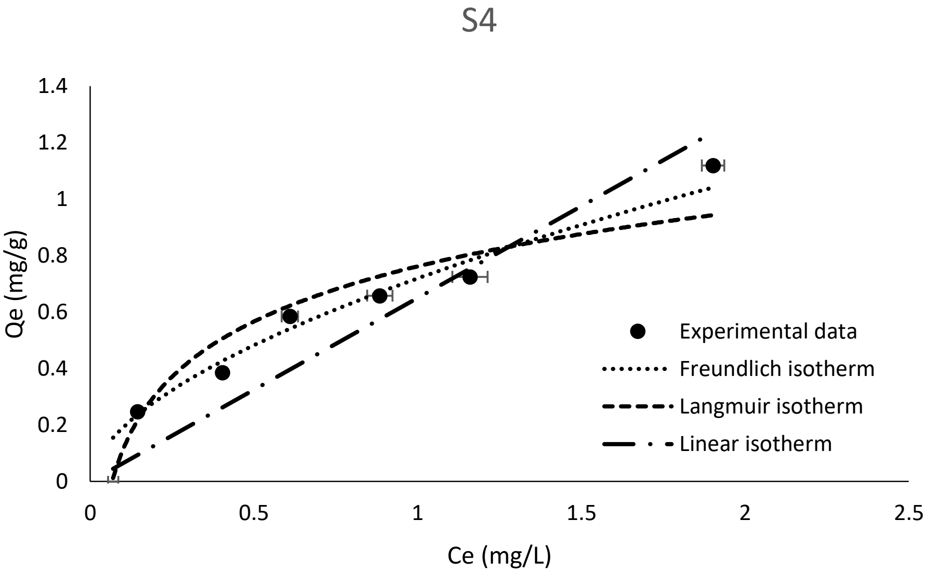


Figure 4.4 *S4 experimental data fitted with adsorption isotherms*

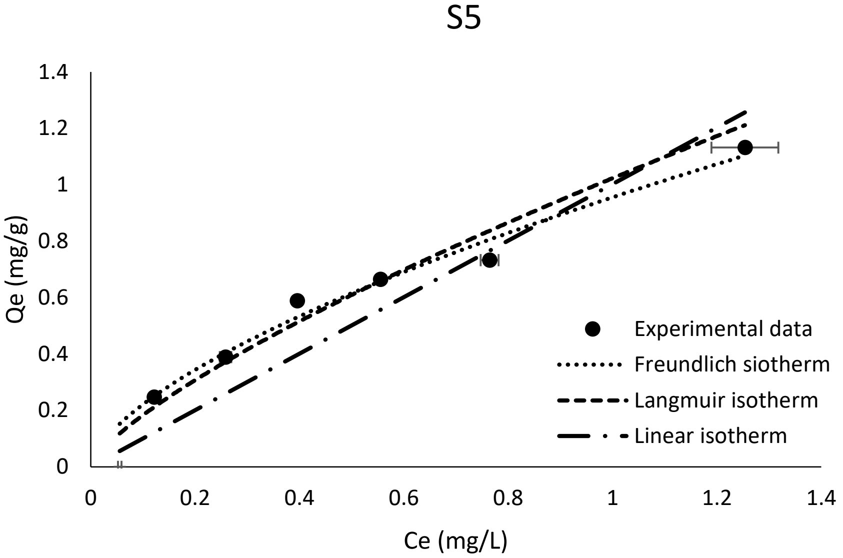


Figure 4.5 *S5 experimental data fitted with adsorption isotherms*

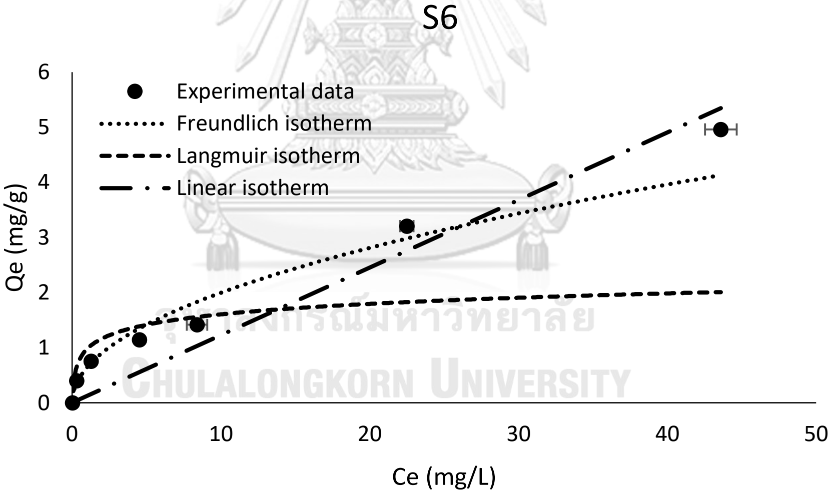


Figure 4.6 *S6 experimental data fitted with adsorption isotherms*

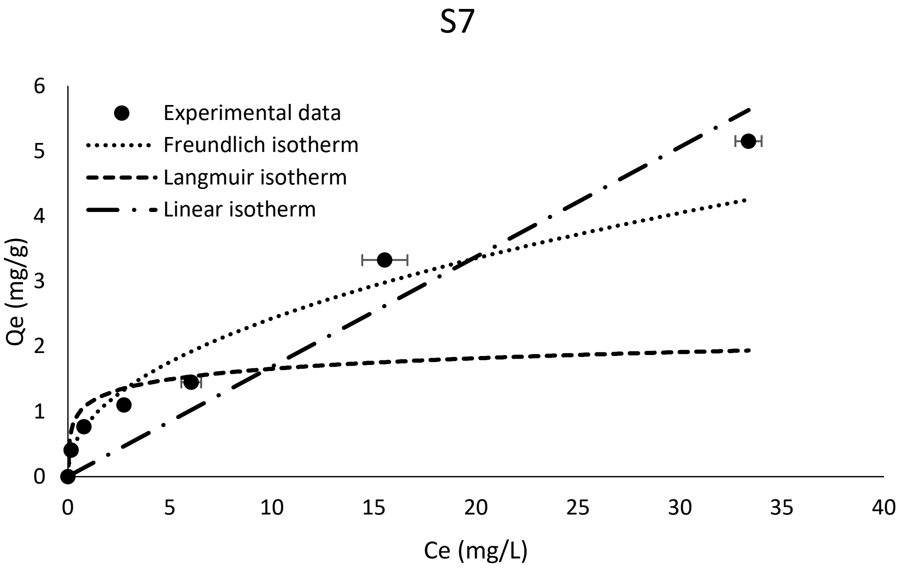


Figure 4.7 *S7 experimental data fitted with adsorption isotherms*

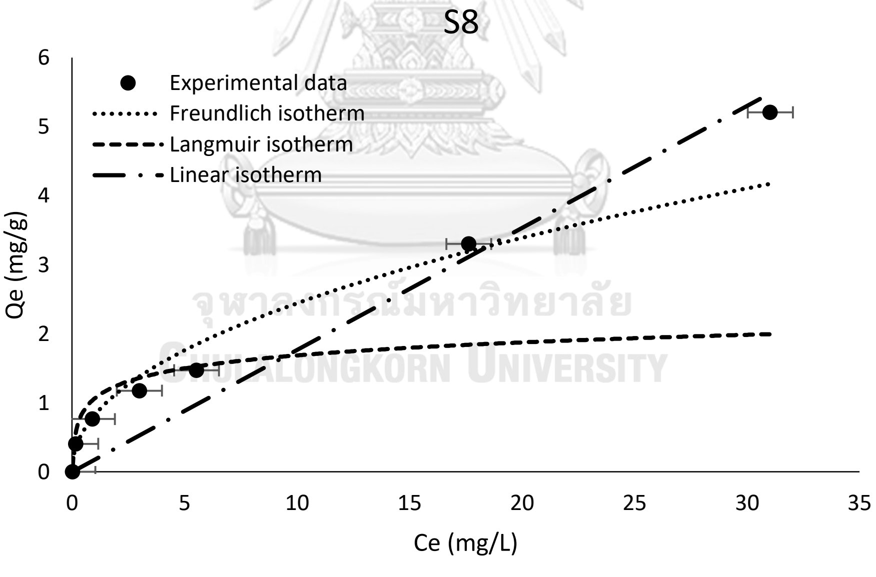


Figure 4.8 *S8 experimental data fitted with adsorption isotherms*

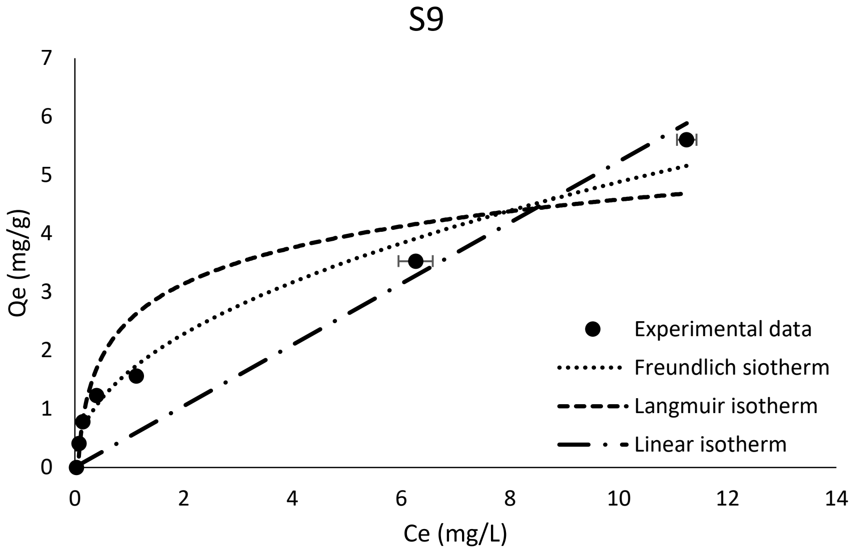


Figure 4.9 *S9 experimental data fitted with adsorption isotherms*

Table 4.4 *Isotherm parameters fitted by linear, Langmuir, and Freundlich isotherms for Cd adsorption experiments onto different soils*

Soil sample	Linear isotherm		Langmuir isotherm			Freundlich isotherm		
	K_d	R^2	K_L	Q_m	R^2	K_f	1/n	R^2
S1	0.026	n.a.	2.032	0.352	0.995	0.196	0.264	0.728
S2	0.039	n.a.	5.350	0.431	0.998	0.416	0.620	0.931
S3	2.873	0.924	n.a.	n.a.	0.902	9.025	0.914	0.979
S4	0.650	0.876	2.103	1.025	0.945	0.719	0.576	0.979
S5	1.002	0.875	1.781	1.360	0.983	0.955	0.636	0.984
S6	0.123	0.928	0.800	1.952	0.908	0.639	0.494	0.965
S7	0.169	0.909	1.724	1.838	0.883	0.831	0.466	0.958
S8	0.177	0.938	1.686	1.850	0.880	0.823	0.473	0.965
S9	0.523	0.886	1.981	3.179	0.976	1.643	0.473	0.978

n.a.: not available

From the Figure 4.1-4.9 and Table 4.4, it showed that most soils (7 soils) in the study area can be fitted well with Freundlich adsorption isotherm, but only two soil samples, S1 and S2, can be described sorption behavior of the samples by Langmuir adsorption isotherm (S1, $R^2 = 0.995$; S2, $R^2 = 0.998$). For the soil samples that fitted with Freundlich isotherm.

The result from Chi-squre test in order to assess which isotherms are appropriated to explain the soil samples was shown in table 4.5.

Table 4.5 *Chi-Square of adsorption isotherms toward soil samples*

Soil sample	Freundlich isotherm	Langmuir isotherm	Linear isotherm
S1	0.099	0.021	6.743
S2	1.311	0.081	16.363
S3	0.058	0.080	0.065
S4	0.018	0.052	0.422
S5	0.015	0.026	0.322
S6	0.315	6.123	6.670
S7	0.395	7.786	9.681
S8	0.379	7.844	8.405
S9	0.151	0.945	16.401
Min	0.015	0.021	0.065
Max	1.311	7.844	16.401
Mean	0.305	2.551	7.230
SD	0.383	3.366	5.971

The result from Table 4.5 showed that most of soil sample can be fitted well with Freundlich adsorption isotherm more than Langmuir adsorption isotherm, only S1 and S2 soil samples that had lower Chi-square values of Langmuir adsorption isotherm (0.021 and 0.081) than those of Freundlich adsorption isotherm (0.099, 1.311 respectively).

As a result, the soil sample S9 has the highest adsorption ability that can adsorb Cd at initial concentration 291 ppm and still has adsorption efficiency at 96.14% percent compared to other soil samples that has soil particle similar to that of S9. For example, as the soil sample S8 in which the proportion of soil texture is 26.8% sand, 25.2% silt, and 48% clay respectively, and has Cd adsorption capability only 89.3%. According to previous studies, the factors influencing on Cd adsorption were proportion of clay particle, soil pH and organic matters in soil. From this reason, it made S9 became the highest sorption capacity because S9 has the highest proportion of clay, account for 58.2% of total soil mass, and has the highest value in organic matter (~ 2.82 %), which increase adsorption capacity of the soil sample.

***Table 4.6** Physiochemical of Waleeithikul and Chotpantarat (2016) soil sample*

Sand (%)	Silt (%)	Clay (%)	OM (%)	pH	CEC (cmol kg^{-1})	Bulk density (g cm^{-1})	Hydraulic conductivity (cm hr^{-1})
64.5	23.2	12.3	2.61	7.8	9.21	1.313	2.367

Linear Isotherm	Langmuir Isotherm	Freundlich Isotherm
K_d = 0.650 L g^{-1}	K_L = 1.280 L g^{-1}	K_F = 0.571 L g^{-1}
	Q_m = 0.877 mg g^{-1}	1/n = 0.758
R^2 = 0.93	R^2 = 0.955	R^2 = 0.995

***Table 4.7** Adsorption isotherm of Waleeithikul and Chotpantarat (2016) soil sample*

From Table 4.6 and Table 4.7, comparing to the study of Waleeithikul and Chotpantarat (2016) which study the sorption behavior of sandy loam soil in the study area. The location of the soil sampling was located in agricultural area of Mae Tao creek in Mae Tao district near Ban Pha Te in which Simmons et al. (2005) investigated Cd contamination in soils. The soil sample consists of 64.5% sand, 23.2% silt, and 12.3% clay with pH of 7.8, organic matter of 2.61% and CEC 2.91 cmol kg^{-1}. The soil sample had similar properties to S1 and S2 soil samples in this study but has higher proportion of silt, but lower in soil OM and CEC. According to Waleeithikul and Chotpantarat study (2016), the result from their batch adsorption experiment showed that sorption behavior of the soil sample can be fitted well with Freundlich adsorption isotherm (R^2 = 0.995) with Freundlich exponent (1/n) of 0.7584 and Kf of 0.5707 L g^{-1}. In the other hand, the soil sample S1 and S2 in this study which has a similar proportion of soil particle size can be fitted well with Langmuir isotherm with Qm of 0.352 mg g^{-1} and K_L of 2.037 L g^{-1} (R^2 = 0.995). The comparison between these soil samples showed that soil sample of Waleeithikul and Chotpantarat has higher proportion of CEC than S1 and S2 soil samples, around two to four times higher, also higher in OM proportion. As a result, these two parameter made sorption behavior of Waleeithikul and Chotpantarat (2016) can be desbribed by Freundlich adsorption isotherm, whereas Langmuir adsorption isotherm can explain sorption behavior of S1 and S2 soil samples.

4.4 Pedotransfer function

There are 174 input dataset from 9 soil samples, different pH and other properties from the experiments in the multiple linear regression. The equations of pedotransfer function was shown in Table 4.6.

Table 4.8 *Coefficient result from different input for pedotransfer function*

Data input	Coefficients					R^2
	intercept	log clay	log OM	log pH	log C	
log clay OM and log pH	1.950	-0.529	1.851	-1.650	-	0.448
log OM log pH and log initial concentration (Ci)	-1.703	-	0.129	0.0520	0.956	0.990
log clay OM pH with log initial concentration (Ci)	-1.809	0.102	0.0617	0.0401	0.937	0.991
log clay OM pH with log remained concentration (Ce)	-0.870	0.660	0.539	-0.269	0.403	0.906

From the table 4.8, the set of log OM, pH and Ci can produce the empirical formula as well as the set of log clay, OM, pH, and Ci with R^2 equal to 0.990 and 0.991 as comparing to other input parameter sets. The first and the second row from Table 4.6 are the input parameters that adapted from van der grift and Griffioen (2008) and Beyer et al. (2009) which only Beyer et al. (2009) can produce the goo prediction of Qe. As a result, the pedotransferfunction for soil sorption estimation was the set of log OM, pH, and Ci since the pedotransfer function that included log clay cannot produce the better result. The empirical function of Cd sorbed in soil prediction was shown in Eq 4.1

$$\log Qe = -1.703 + 0.0520 \log (pH) + 0.129 \log (OM) + 0.956 \log (Ci) \quad \text{(Eq. 4.1)}$$

In order to cross-check the empirical formula for the sorptiom estimation, the diagram was plotted between log Qe versus log Ci was created and then compared the estimated log Qe value with observed Qe from the sorption experiment as shown in Figure 4.10.

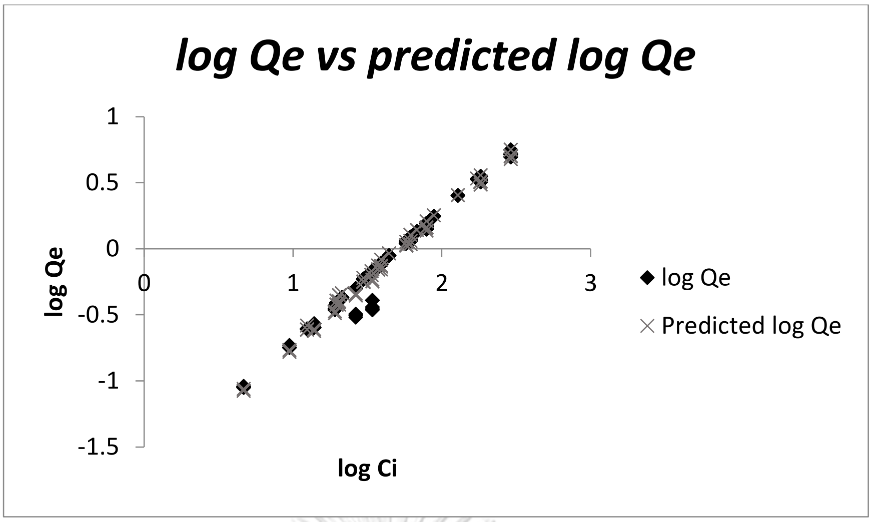


Figure 4.10 *Diagram plotting between log Qe versus predicted log Qe*

From the Figure 4.10, it showed that the predicted Qe calculated from the physico-chemical properties of the soil sample yield the result similar to Qe value from the the sorption experiment (the information of the residual error from the estimation was shown in *Appendix B,* Table B-2).

4.5 BCR sequential extraction experiment

The result from the leaching experiment which performed in order to set up the initial concentration (C_0) of the numerical modeling and model validation were shown in Table 4.6 and Table 4.7.

Table 4.9 *Result from BCR sequential extraction for bulk soil samples*

Sample name	BCR1 (mg kg^{-1})	SD	BCR2 (mg kg^{-1})	SD
S1	< 0.02	-	< 0.02	-
S2	< 0.02	-	< 0.02	-
S3	< 0.02	-	< 0.02	-
S4	14.200	3.212	5.347	1.149
S5	3.093	0.220	1.907	0.023
S6	< 0.02	-	< 0.02	-
S7	< 0.02	-	< 0.02	-
S8	< 0.02	-	< 0.02	-
S9	< 0.02	-	< 0.02	-

Table 4.10 *Result from BCR sequential extraction for profile soil samples*

Samples	Depth (cm.)	BCR1 (mg kg^{-1})	SD	BCR2 (mg kg^{-1})	SD
S2	0-5	< 0.02	-	< 0.02	-
	5-10	< 0.02	-	< 0.02	-
	10-20	< 0.02	-	< 0.02	-
	20-30	< 0.02	-	< 0.02	-
	30-40	< 0.02	-	< 0.02	-
	40-60	< 0.02	-	< 0.02	-
S4	0-5	13.067	0.761	15.72	0.932
	5-10	17.640	0.835	12.6	0.342
	10-20	7.280	0.080	3.84	0.728
	20-30	< 0.02	-	< 0.02	-
	30-40	< 0.02	-	< 0.02	-
	40-60	< 0.02	-	< 0.02	-
S5	0-5	1.107	0.295	1.853	0.046
	5-10	1.320	0.433	2.013	0.424
	10-20	1.213	0.428	1.693	0.323
	20-30	< 0.02	-	< 0.02	-
	30-40	< 0.02	-	< 0.02	-
	40-60	< 0.02	-	< 0.02	-
S6	0-5	< 0.02	-	< 0.02	-
	5-10	< 0.02	-	< 0.02	-
	10-20	< 0.02	-	< 0.02	-
	20-30	< 0.02	-	< 0.02	-
	30-40	< 0.02	-	< 0.02	-
	40-60	< 0.02	-	< 0.02	-

Samples	Depth (cm.)	BCR1 (mg kg^{-1})	SD	BCR2 (mg kg^{-1})	SD
S7	0-5	< 0.02	-	< 0.02	-
	5-10	< 0.02	-	< 0.02	-
	10-20	< 0.02	-	< 0.02	-
	20-30	< 0.02	-	< 0.02	-
	30-40	< 0.02	-	< 0.02	-
	40-60	< 0.02	-	< 0.02	-
S9	0-5	< 0.02	-	< 0.02	-
	5-10	< 0.02	-	< 0.02	-
	10-20	< 0.02	-	< 0.02	-
	20-30	< 0.02	-	< 0.02	-
	30-40	< 0.02	-	< 0.02	-
	40-60	< 0.02	-	< 0.02	-

From both Table 4.9 and Table 4.10, only S4 and S5 soil sample that can detect the Cd concentration releasing from the soil samples. Both result showed the similarity of leaching capacity in both the previous studies of Akkajit and Tongcumpou (2010) and Kosolsaksakul et al. (2014). For the study of Akkajit and Tongcumpou (2010), the BCR2 (41.48%) was higher than BCR1 (29.9%). In the other hand, the result from the BCR sequential extraction from the study of Kosolsaksakul et al. (2014) yielded the greater proportion in BCR 1 (approx. ~ 67-84%) than that of BCR2 (approx. ~15-27%).

For the other soil samples that could not detect the Cd concentration there are two reasons that could possibly explain this scenario. For the first reason, the Cd concentration would leach deeper than the soil profile, exceeding the model boundary to the deeper profile or groundwater system. Second, bioavailability of Cd to plants in the area would cause the proportion of Cd concentration in soil become decreased since Cd can be leached out by BCR1 compared to other heavy metal (Akkajit and Tongcumpou, 2010; Ho and Evans, 2000; Tokalioglu et al., 2003)

4.6 Result from Monte Carlo Simulation

Initial conditions of soil profile simulation which applied with Monte Carlo technique for S4 and S5 soil samples were shown in Figure 4.11

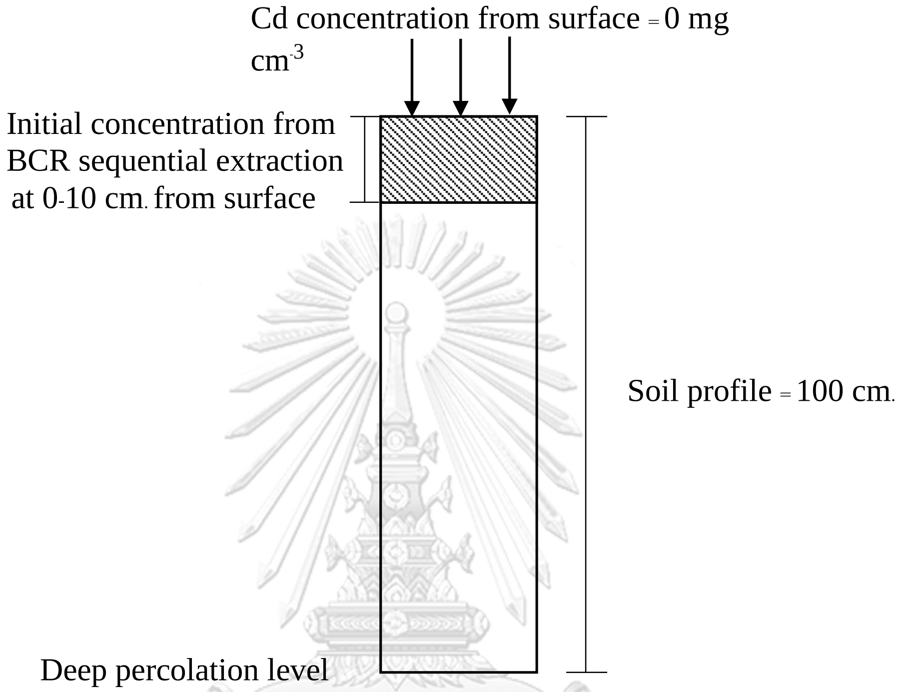


Figure 4.11 *Initial and boundary conditions of the numerical modeling*

From Figure 4.11, the initial concentration of Cd was set up in the soil since the initial condition was the 2 previous years before the present time. The initial concentration was set in the top soil layer at 0-15 cm with no input concentration on the soil surface. Then the result from Monte Carlo simulation was compared with the experimental result and 1 times simulation from HYDRUS-1D. For Monte Carlo simulation times, based on the preliminary study and Jafari et al.(Jafari et al., 2016). Five thousand rounds of Monte Carlo simulation were peformed in order to obtained Cd concentration in each soil depths. For the input parameters in HYDRUS-1D for this study were shown in table 4.11.

Table 4.11 *Input parameter for numerical modeling in HYDRUS-1D*

Parameters	Soil sample	
	S4	S5
Residual soil water content (-)	0.0597	0.068
Saturated soil water content (-)	0.3898	0.420
n in soil water retention function (-)	1.395	1.428
Alpha in soil water retention function (cm^{-1})	0.0183	0.0155
Hydraulic conductivity ($cm\ day^{-1}$)	4.03	19.20
Bulk density ($g\ cm^{-3}$)	1.52	1.42
Freundlich coefficient ($L\ g^{-1}$)	0.72±0.01	0.96±0.01
Freundlich exponent (-)	0.58±0.01	0.64±0.01
Longitudinal dispersivity (cm)	1.25	1.25
Initial concentration ($mg\ cm^{-1}$)	2.39	0.50
First order rate coefficient (day^{-1})	0.0014	0.0014
Soil adsorption fraction (-)	0.159	0.159

4.6.1 Sensitivity analysis

The result from sensitivity analysis of S4 and S5 are showed in Figure 4.12 and 4.13.

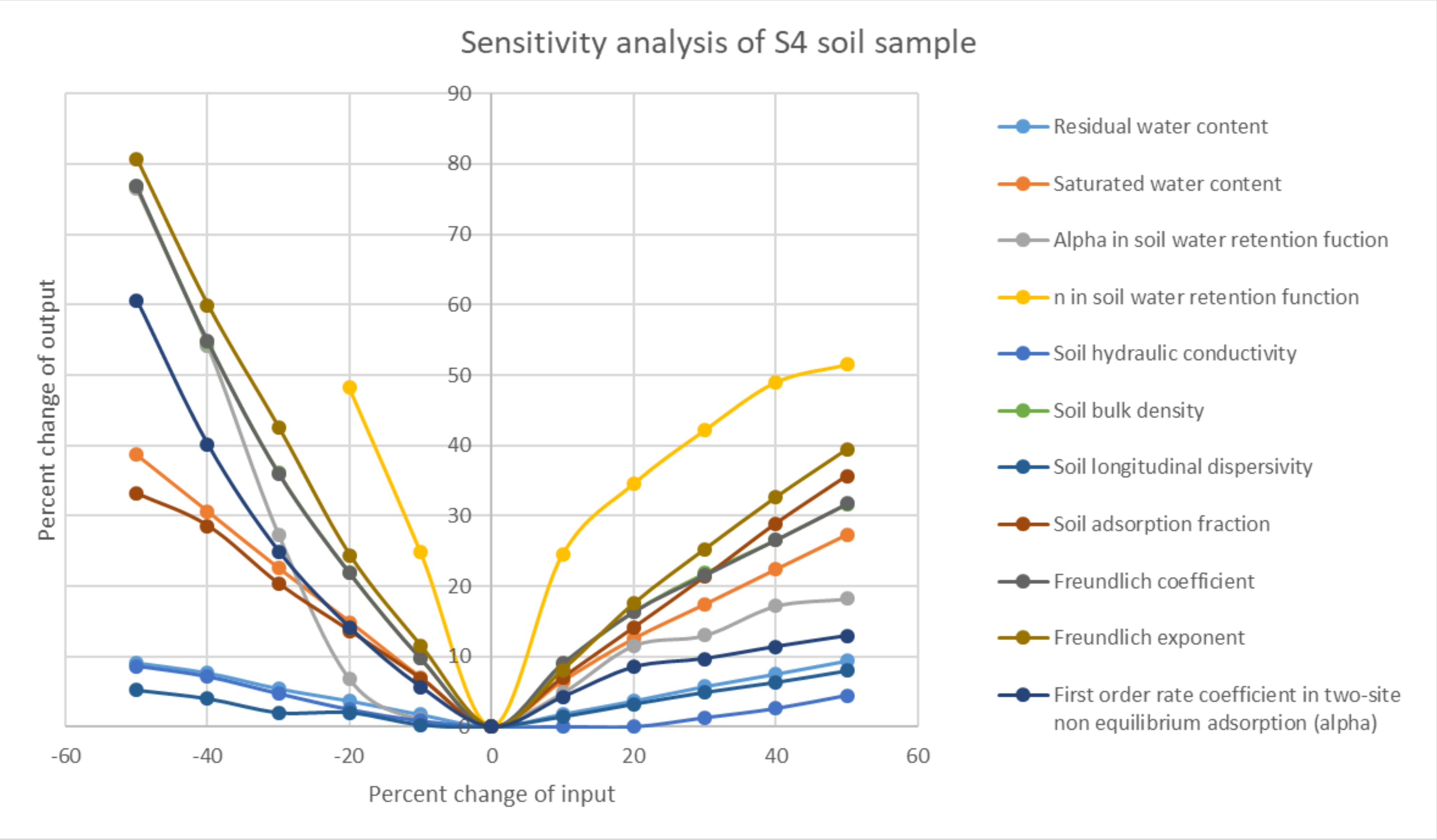


Figure 4.12 *Sensitivity analysis of S4 soil sample*

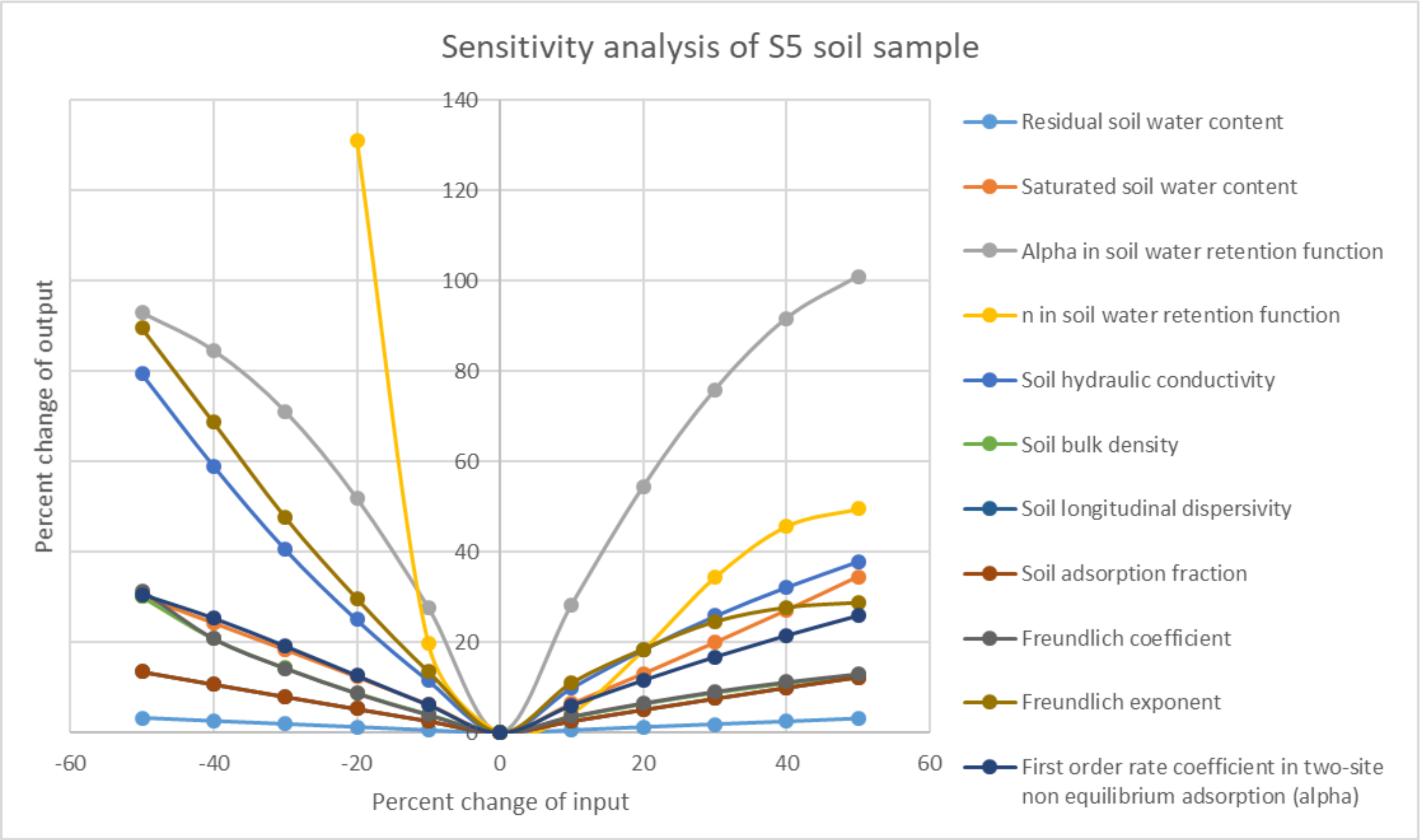


Figure 4.13 *Sensitivity analysis of S5 soil sample*

As showed in Figure 4.12 and 4.13, parameter n has the most influence in chaging of Cd concetration for both S4 and S5 soil samples. In S4 soil sample, Freundlich exponent is the next parameter that dominates the output result. For S5 soil sample, not same as S4 soil sample, alpha value (in soil water retention function) is the next parameter that influences the output result.

4.6.2 Simulation results for soil sample S4

The result from Monte Carlo simulation for S4 soil sample was shown in Figure 4.14

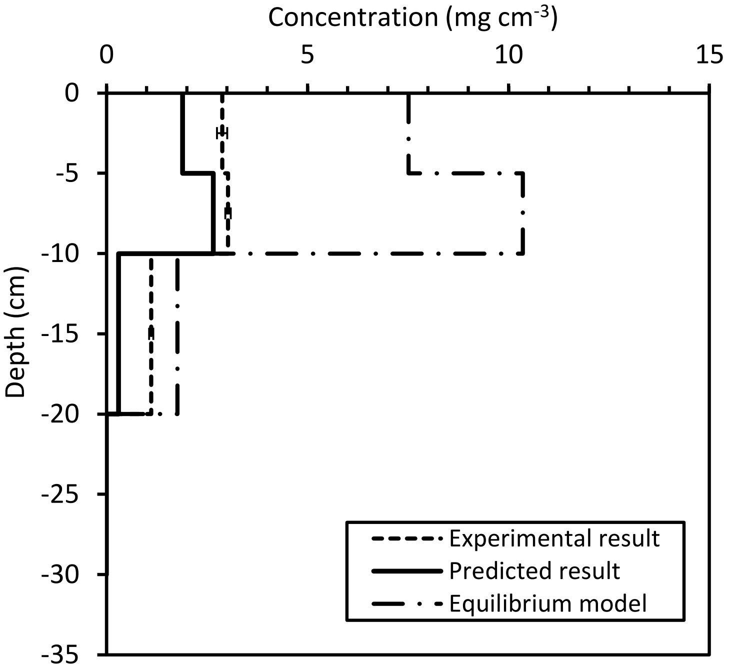


Figure 4.14 *The comparision between the numerical model applied with Monte Carlo method and the experimental result from BCR sequential extraction of S4 soil sample.*

From Figure 4.14, parameters that used to random in both soil sample were Kf and 1/n which control sorption capability of Cd. For S4 soil sample, Kf was ranged from 0.71 to 0.73 cm^3 mg^{-1} and 1/n ranged from 0.57 to 0.59. The result of the numerical modeling used compared with the experimental result showed that the numerical modeling produced the Cd concentration lower than the experimental data in every depth. By the way, using two-site model as a transport condition made the numerical modeling had the similar trend to the experimental data more than equilibrium model.

4.6.3 Simulation result for S5 soil sample

For S5 soil sample Kf and 1/n were used to random as same as S4 soil sample the parameters Kf and 1/n were varied from 0.94-0.97 cm^3 mg^{-1} and 0.62-0.65 respectively. The comparision of Monte Carlo simulation vs the experimental data and Monte Carlo simulation vs one times simulation of S5 soil sample were showed in Figure 4.15

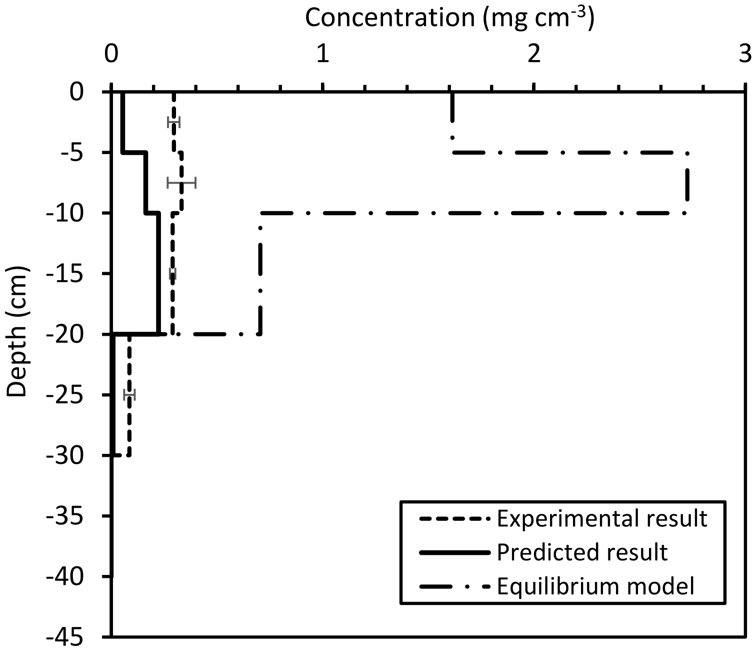


Figure 4.15 *The comparision between the numerical model applied with Monte Carlo method and the experimental result from BCR sequential extraction of S5 soil sample.*

In Figure 4.15, the result from Monte Carlo simulation in S5 had the similar result to S4 soil sample, the predicted value of Cd concentration from Mont Carlo simulation seems under estimation than the experimental value. Otherwise, the predicted Cd concentrations at below 20 cm. from soil surface approached to 0 mg cm^{-3} whereas the experimental data still had Cd concentration in this depth. As same as S4 soil sample, two-site model transport condition can describe transportation of Cd better than equilibrium model.

4.6.4 Nash and Sutcliffe model efficiency

Nash and Sutcliffe model efficiency (NSE) was calculated for both soil samples, S4 and S5. The results were shown in Table 4.12

Table 4.12 *Nash and Sutcliffe from Monte Carlo simulation*

Soil sample	NSE
S4	0.22
S5	-1.04

According from Lian et al. (2014), the model efficiency for S4 soil sample was better than the mean result of observed value but not in the satisfactory level, whereas NSE of soil sample S5 was worse than mean value of the observed. As a result, both of the numerical modeling could not be used as a representative modeling of Cd transportation in the study area.

CHAPTER 5
CONCLUSIONS AND RECOMENDATION

5.1 Conclusion

1. The soils particle in the study area can be classified into 5 types, consisting of sandy loam, sandy clay loam, sandy clay, clay loam and clay soil following USDA soil classification.

2. Sorption behavior of Cd onto soils in the study area were fitted well with Freundlich isotherm, which can be described as multi-layer adsorption. Only 2 soil samples (S1 and S2) can be fitted well with Langmuir isotherm because both soil sample has high proportion of sand and low proportion in clay, OM, and CEC compared to other soil samples.

3. the Pedotransfer function for sorbed Cd in soil (Qe) is $\log Qe = -1.703 + 0.0520 \log (pH) + 0.129 \log (OM) + 0.956 \log (Ci)$ which can produce the best result ($R^2 = 0.990$).

4. There are only 2 soil samples that can detect Cd concentration from BCR sequential extraction (soil sample S4 and S5). The other soil samples can not detect Cd concentration in BCR 1 and BCR 2 might cause from the bioavailability of Cd in soil or a long-term leaching into groundwater.

5. The numerical modeling integrated with Monte Carlo simulation caused lower estimation in both S4 and S5 soil samples. Moreover, the NSE of S4 and S5 soil samples were 0.22 and -1.04 respectively, inidicated that both numerical modeling can not be used as the representative soil to predict Cd transportation in the study area. By the way, both S4 and S5 soil sample can be used to comfirmed the transport condition of Cd are suit well with two-site adsorption model more than equilibrium model as same as Waleeithikul and Chotpantarat study (2016).

5.2 Recommendation

1. Monte Carlo method could apply with HYDRUS-PHREEQC numerical modeling to understand surface complexation of Cd.

2. The pedotransfer function should have a computeral code in order to add the estimated parameter in to the numerical model.

3. In this study, only ion-exchange sorption was considered which didn't include chemosorption and inner surface complexation Cd adsorption. As a result, Cd concentration from the numerical modeling could inaccurate from miscalculation of those factors

4. Seasoning concentration should be included for the Cd concentration, applied with Monte Carlo method to make the numerical model become the representative of Cd transport of the soil sample, and more of hydraulic conductivity data should do in triplicate sampling in order to increase the efficiency of Monte Carlo method.

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APPENDIX A

Table A-1 *Location and land use of sampling sites*

Soil sample	X	Y	Elevation (m)	Description
S1	450188	1844385	209	Harvested sugarcane field
S2	451425	1844944	209	Sugarcane field
S3	453450	1842591	229	Plowing agricultural area
S4	454646	1843538	221	Harvested sugarcane field
S5	452607	1843926	209	Agricultural area
S6	458786	1842137	241	Paddy field
S7	456864	1843681	223	Harvested corn field
S8	459954	1844060	261	Teak wood
S9	458308	1843564	245	Sugarcane field

Table A-2 *Soil properties of the study area*

Soil sample	Sand (%)	Silt (%)	Clay (%)	OM (%)	pH	CEC (cmol$_c$/kg)	BD (g/cm^3)	HC (mm/hr)	porosity
S1	62	28	10	0.37	7	4.11	1.622	3.616	0.390
S2	60	28	12	0.53	5.4	2.79	1.604	2.348	0.397
S3	54	15.8	30.2	1.18	4.9	9.81	1.697	6.973	0.362
S4	52.8	26	21.2	0.91	8	14.83	1.520	1.68	0.429
S5	49.8	26	24.2	1.6	7.6	12.23	1.417	8	0.467
S6	48	16	36	0.72	7.2	11.81	1.7109	1.418	0.357
S7	39	28.8	32.2	1.06	7	16.46	1.671	0.21	0.372
S8	26.8	25.2	48	1.09	7.7	17.33	1.6587	0.915	0.376
S9	16.6	25.2	58.2	2.82	5.7	21.74	1.3939	0.6	0.476

APPENDIX B

Table B-1 *Dataset for pedotransfer function in the study area*

Kf ($L\ g^{-1}$)	1/n (-)	Clay (%)	OM (%)	pH (-)	Remained concentration ($mg\ L^{-1}$)	Sorbed Cd in soil ($mg\ g^{-1}$)	initial concentration ($mg\ L^{-1}$)
0.648	0.929	24.2	1.60	7.6	0.118	0.248	12.495
0.648	0.929	24.2	1.60	7.6	0.268	0.389	19.700
0.648	0.929	24.2	1.60	7.6	0.393	0.589	29.850
0.648	0.929	24.2	1.60	7.6	0.558	0.665	33.800
0.648	0.929	24.2	1.60	7.6	0.757	0.733	37.400
0.648	0.929	24.2	1.60	7.6	1.324	1.131	57.850
0.667	0.944	24.2	1.60	7.6	0.123	0.247	12.495
0.667	0.944	24.2	1.60	7.6	0.246	0.389	19.700
0.667	0.944	24.2	1.60	7.6	0.392	0.589	29.850
0.667	0.944	24.2	1.60	7.6	0.549	0.665	33.800
0.667	0.944	24.2	1.60	7.6	0.752	0.733	37.400
0.667	0.944	24.2	1.60	7.6	1.198	1.133	57.850
0.642	0.936	24.2	1.60	7.6	0.124	0.247	12.495
0.642	0.936	24.2	1.60	7.6	0.261	0.389	19.700
0.642	0.936	24.2	1.60	7.6	0.403	0.589	29.850
0.642	0.936	24.2	1.60	7.6	0.559	0.665	33.800
0.642	0.936	24.2	1.60	7.6	0.784	0.732	37.400
0.642	0.936	24.2	1.60	7.6	1.240	1.132	57.850
0.711	0.554	21.2	0.91	8	0.144	0.247	12.495
0.711	0.554	21.2	0.91	8	0.390	0.386	19.700
0.711	0.554	21.2	0.91	8	0.597	0.585	29.850
0.711	0.554	21.2	0.91	8	0.842	0.659	33.800
0.711	0.554	21.2	0.91	8	1.107	0.726	37.400
0.711	0.554	21.2	0.91	8	1.868	1.120	57.850
0.688	0.545	21.2	0.91	8	0.147	0.247	12.495
0.688	0.545	21.2	0.91	8	0.406	0.386	19.700
0.688	0.545	21.2	0.91	8	0.638	0.584	29.850
0.688	0.545	21.2	0.91	8	0.894	0.658	33.800
0.688	0.545	21.2	0.91	8	1.158	0.725	37.400
0.688	0.545	21.2	0.91	8	1.902	1.119	57.850
0.680	0.524	21.2	0.91	8	0.142	0.247	12.495
0.680	0.524	21.2	0.91	8	0.415	0.386	19.700
0.680	0.524	21.2	0.91	8	0.594	0.585	29.850
0.680	0.524	21.2	0.91	8	0.917	0.658	33.800
0.680	0.524	21.2	0.91	8	1.214	0.724	37.400

Kf (L g^{-1})	1/n (-)	Clay (%)	OM (%)	pH (-)	Remained concentration (mg L^{-1})	Sorbed Cd in soil (mg g^{-1})	initial concentration (mg L^{-1})
0.680	0.524	21.2	0.91	8	1.936	1.118	57.850
17.370	2.544	30.2	1.18	4.9	0.129	0.247	12.495
17.370	2.544	30.2	1.18	4.9	0.166	0.391	19.700
17.370	2.544	30.2	1.18	4.9	0.190	0.593	29.850
17.370	2.544	30.2	1.18	4.9	0.228	0.671	33.800
17.370	2.544	30.2	1.18	4.9	0.253	0.743	37.400
17.370	2.544	30.2	1.18	4.9	0.379	1.149	57.850
8.084	2.016	30.2	1.18	4.9	0.115	0.248	12.495
8.084	2.016	30.2	1.18	4.9	0.146	0.391	19.700
8.084	2.016	30.2	1.18	4.9	0.199	0.593	29.850
8.084	2.016	30.2	1.18	4.9	0.195	0.672	33.800
8.084	2.016	30.2	1.18	4.9	0.270	0.743	37.400
8.084	2.016	30.2	1.18	4.9	0.403	1.149	57.850
27.346	2.824	30.2	1.18	4.9	0.144	0.247	12.495
27.346	2.824	30.2	1.18	4.9	0.169	0.391	19.700
27.346	2.824	30.2	1.18	4.9	0.177	0.593	29.850
27.346	2.824	30.2	1.18	4.9	0.214	0.672	33.800
27.346	2.824	30.2	1.18	4.9	0.261	0.743	37.400
27.346	2.824	30.2	1.18	4.9	0.368	1.150	57.850
1.588	0.430	58.2	2.82	5.7	0.067	0.409	20.500
1.588	0.430	58.2	2.82	5.7	0.127	0.780	39.150
1.588	0.430	58.2	2.82	5.7	0.412	1.229	61.850
1.588	0.430	58.2	2.82	5.7	1.182	1.558	79.100
1.588	0.430	58.2	2.82	5.7	6.620	3.522	182.700
1.588	0.430	58.2	2.82	5.7	11.050	5.609	291.500
1.577	0.464	58.2	2.82	5.7	0.086	0.408	20.500
1.577	0.464	58.2	2.82	5.7	0.153	0.780	39.150
1.577	0.464	58.2	2.82	5.7	0.416	1.229	61.850
1.577	0.464	58.2	2.82	5.7	1.138	1.559	79.100
1.577	0.464	58.2	2.82	5.7	6.160	3.531	182.700
1.577	0.464	58.2	2.82	5.7	11.300	5.604	291.500
1.617	0.460	58.2	2.82	5.7	0.073	0.409	20.500
1.617	0.460	58.2	2.82	5.7	0.162	0.780	39.150
1.617	0.460	58.2	2.82	5.7	0.380	1.229	61.850
1.617	0.460	58.2	2.82	5.7	1.067	1.561	79.100
1.617	0.460	58.2	2.82	5.7	6.020	3.534	182.700

Kf (L g^{-1})	1/n (-)	Clay (%)	OM (%)	pH (-)	Remained concentration (mg L^{-1})	Sorbed Cd in soil (mg g^{-1})	initial concentration (mg L^{-1})
1.617	0.460	58.2	2.82	5.7	11.400	5.602	291.500
0.809	0.429	32.2	1.06	7	0.169	0.405	20.400
0.809	0.429	32.2	1.06	7	0.822	0.767	39.150
0.809	0.429	32.2	1.06	7	2.720	1.100	57.700
0.809	0.429	32.2	1.06	7	5.900	1.452	78.500
0.809	0.429	32.2	1.06	7	16.700	3.302	181.800
0.809	0.429	32.2	1.06	7	32.900	5.162	291.000
0.841	0.420	32.2	1.06	7	0.144	0.405	20.400
0.841	0.420	32.2	1.06	7	0.769	0.768	39.150
0.841	0.420	32.2	1.06	7	2.730	1.099	57.700
0.841	0.420	32.2	1.06	7	5.650	1.457	78.500
0.841	0.420	32.2	1.06	7	15.400	3.328	181.800
0.841	0.420	32.2	1.06	7	34.100	5.138	291.000
0.821	0.423	32.2	1.06	7	0.158	0.405	20.400
0.821	0.423	32.2	1.06	7	0.789	0.767	39.150
0.821	0.423	32.2	1.06	7	2.800	1.098	57.700
0.821	0.423	32.2	1.06	7	6.600	1.438	78.500
0.821	0.423	32.2	1.06	7	14.500	3.346	181.800
0.821	0.423	32.2	1.06	7	33.100	5.158	291.000
2.231	0.357	56.0	2.54	6.4	0.014	0.428	21.425
2.231	0.357	56.0	2.54	6.4	0.068	0.887	44.415
2.231	0.357	56.0	2.54	6.4	0.146	1.358	68.050
2.231	0.357	56.0	2.54	6.4	0.502	1.766	88.820
2.231	0.357	56.0	2.54	6.4	1.944	2.531	128.500
2.231	0.357	56.0	2.54	6.4	5.030	3.369	173.500
2.133	0.346	56.0	2.54	6.4	0.015	0.428	21.425
2.133	0.346	56.0	2.54	6.4	0.049	0.887	44.415
2.133	0.346	56.0	2.54	6.4	0.198	1.357	68.050
2.133	0.346	56.0	2.54	6.4	0.805	1.760	88.820
2.133	0.346	56.0	2.54	6.4	1.659	2.537	128.500
2.133	0.346	56.0	2.54	6.4	4.530	3.379	173.500
2.196	0.313	56.0	2.54	6.4	0.034	0.428	21.425
2.196	0.313	56.0	2.54	6.4	0.067	0.887	44.415
2.196	0.313	56.0	2.54	6.4	0.182	1.357	68.050
2.196	0.313	56.0	2.54	6.4	0.421	1.768	88.820
2.196	0.313	56.0	2.54	6.4	1.826	2.533	128.500

Kf (L g^{-1})	1/n (-)	Clay (%)	OM (%)	pH (-)	Remained concentration (mg L^{-1})	Sorbed Cd in soil (mg g^{-1})	initial concentration (mg L^{-1})
2.196	0.313	56.0	2.54	6.4	4.680	3.376	173.500
0.597	0.484	36.0	0.72	7.2	0.304	0.404	20.500
0.597	0.484	36.0	0.72	7.2	1.301	0.757	39.150
0.597	0.484	36.0	0.72	7.2	4.490	1.147	61.850
0.597	0.484	36.0	0.72	7.2	9.000	1.402	79.100
0.597	0.484	36.0	0.72	7.2	22.400	3.206	182.700
0.597	0.484	36.0	0.72	7.2	42.400	4.982	291.500
0.606	0.487	36.0	0.72	7.2	0.319	0.404	20.500
0.606	0.487	36.0	0.72	7.2	1.253	0.758	39.150
0.606	0.487	36.0	0.72	7.2	4.700	1.143	61.850
0.606	0.487	36.0	0.72	7.2	7.650	1.429	79.100
0.606	0.487	36.0	0.72	7.2	23.000	3.194	182.700
0.606	0.487	36.0	0.72	7.2	44.000	4.950	291.500
0.604	0.487	36.0	0.72	7.2	0.314	0.404	20.500
0.604	0.487	36.0	0.72	7.2	1.273	0.758	39.150
0.604	0.487	36.0	0.72	7.2	4.400	1.149	61.850
0.604	0.487	36.0	0.72	7.2	8.550	1.411	79.100
0.604	0.487	36.0	0.72	7.2	22.100	3.212	182.700
0.604	0.487	36.0	0.72	7.2	44.400	4.942	291.500
0.772	0.459	48.0	1.09	7.7	0.171	0.407	20.500
0.772	0.459	48.0	1.09	7.7	0.810	0.767	39.150
0.772	0.459	48.0	1.09	7.7	3.030	1.176	61.850
0.772	0.459	48.0	1.09	7.7	5.050	1.481	79.100
0.772	0.459	48.0	1.09	7.7	19.100	3.272	182.700
0.772	0.459	48.0	1.09	7.7	32.100	5.188	291.500
0.730	0.511	48.0	1.09	7.7	0.140	0.407	20.500
0.730	0.511	48.0	1.09	7.7	0.945	0.764	39.150
0.730	0.511	48.0	1.09	7.7	2.910	1.179	61.850
0.730	0.511	48.0	1.09	7.7	4.700	1.488	79.100
0.730	0.511	48.0	1.09	7.7	16.900	3.316	182.700
0.730	0.511	48.0	1.09	7.7	32.300	5.184	291.500
0.709	0.487	48.0	1.09	7.7	0.170	0.407	20.500
0.709	0.487	48.0	1.09	7.7	0.966	0.764	39.150
0.709	0.487	48.0	1.09	7.7	3.040	1.176	61.850
0.709	0.487	48.0	1.09	7.7	6.850	1.445	79.100
0.709	0.487	48.0	1.09	7.7	16.900	3.316	182.700

Kf (L g^{-1})	1/n (-)	Clay (%)	OM (%)	pH (-)	Remained concentration (mg L^{-1})	Sorbed Cd in soil (mg g^{-1})	initial concentration (mg L^{-1})
0.709	0.487	48.0	1.09	7.7	28.700	5.256	291.500
0.798	0.556	10.0	0.37	7	0.212	0.089	4.670
0.798	0.556	10.0	0.37	7	0.521	0.180	9.500
0.798	0.556	10.0	0.37	7	1.316	0.252	13.900
0.798	0.556	10.0	0.37	7	1.965	0.345	19.200
0.798	0.556	10.0	0.37	7	10.450	0.321	26.500
0.798	0.556	10.0	0.37	7	16.950	0.345	34.200
0.644	0.593	10.0	0.37	7	0.199	0.089	4.670
0.644	0.593	10.0	0.37	7	0.557	0.179	9.500
0.644	0.593	10.0	0.37	7	1.205	0.254	13.900
0.644	0.593	10.0	0.37	7	1.917	0.346	19.200
0.644	0.593	10.0	0.37	7	11.310	0.304	26.500
0.644	0.593	10.0	0.37	7	16.690	0.350	34.200
0.568	0.664	10.0	0.37	7	0.177	0.090	4.670
0.568	0.664	10.0	0.37	7	0.566	0.179	9.500
0.568	0.664	10.0	0.37	7	1.239	0.253	13.900
0.568	0.664	10.0	0.37	7	1.587	0.352	19.200
0.568	0.664	10.0	0.37	7	10.820	0.314	26.500
0.568	0.664	10.0	0.37	7	16.060	0.363	34.200
0.741	0.970	12.0	0.53	5.4	0.115	0.091	4.670
0.741	0.970	12.0	0.53	5.4	0.215	0.186	9.500
0.741	0.970	12.0	0.53	5.4	0.372	0.271	13.900
0.741	0.970	12.0	0.53	5.4	0.653	0.371	19.200
0.741	0.970	12.0	0.53	5.4	1.513	0.500	26.500
0.741	0.970	12.0	0.53	5.4	13.880	0.406	34.200
0.872	0.878	12.0	0.53	5.4	0.115	0.091	4.670
0.872	0.878	12.0	0.53	5.4	0.215	0.186	9.500
0.872	0.878	12.0	0.53	5.4	0.372	0.271	13.900
0.872	0.878	12.0	0.53	5.4	0.653	0.371	19.200
0.872	0.878	12.0	0.53	5.4	1.513	0.500	26.500
0.872	0.878	12.0	0.53	5.4	13.880	0.406	34.200

Table B-2 *The residual error of Figure 4.10*

Observation	Predicted log Qe	Residuals
1	-0.582	-0.024
2	-0.393	-0.017
3	-0.221	-0.009
4	-0.169	-0.008
5	-0.127	-0.008
6	0.054	-0.001
7	-0.582	-0.024
8	-0.393	-0.017
9	-0.221	-0.009
10	-0.169	-0.008
11	-0.127	-0.008
12	0.054	0.000
13	-0.582	-0.024
14	-0.393	-0.017
15	-0.221	-0.009
16	-0.169	-0.008
17	-0.127	-0.008
18	0.054	0.000
19	-0.613	0.005
20	-0.424	0.010
21	-0.251	0.018
22	-0.200	0.019
23	-0.158	0.018
24	0.024	0.026
25	-0.613	0.005
26	-0.424	0.010
27	-0.251	0.018
28	-0.200	0.018
29	-0.158	0.018
30	0.024	0.025
31	-0.613	0.005
32	-0.424	0.010
33	-0.251	0.018
34	-0.200	0.018
35	-0.158	0.017
36	0.024	0.025

Observation	Predicted log Qe	Residuals
37	-0.609	0.002
38	-0.420	0.012
39	-0.248	0.021
40	-0.196	0.023
41	-0.154	0.025
42	0.027	0.033
43	-0.609	0.003
44	-0.420	0.012
45	-0.248	0.021
46	-0.196	0.024
47	-0.154	0.025
48	0.027	0.033
49	-0.609	0.002
50	-0.420	0.012
51	-0.248	0.021
52	-0.196	0.023
53	-0.154	0.025
54	0.027	0.034
55	-0.352	-0.037
56	-0.083	-0.025
57	0.107	-0.017
58	0.209	-0.016
59	0.556	-0.010
60	0.750	-0.002
61	-0.352	-0.037
62	-0.083	-0.025
63	0.107	-0.017
64	0.209	-0.016
65	0.556	-0.009
66	0.750	-0.002
67	-0.352	-0.037
68	-0.083	-0.025
69	0.107	-0.017
70	0.209	-0.016
71	0.556	-0.008
72	0.750	-0.002
73	-0.404	0.011

Observation	Predicted log Qe	Residuals
74	-0.133	0.018
75	0.028	0.013
76	0.156	0.006
77	0.504	0.014
78	0.700	0.013
79	-0.404	0.011
80	-0.133	0.018
81	0.028	0.013
82	0.156	0.008
83	0.504	0.018
84	0.700	0.011
85	-0.404	0.011
86	-0.133	0.018
87	0.028	0.013
88	0.156	0.002
89	0.504	0.020
90	0.700	0.013
91	-0.337	-0.032
92	-0.034	-0.018
93	0.143	-0.010
94	0.254	-0.007
95	0.407	-0.004
96	0.532	-0.004
97	-0.337	-0.032
98	-0.034	-0.018
99	0.143	-0.011
100	0.254	-0.008
101	0.407	-0.003
102	0.532	-0.003
103	-0.337	-0.032
104	-0.034	-0.018
105	0.143	-0.011
106	0.254	-0.006
107	0.407	-0.003
108	0.532	-0.003
109	-0.423	0.029
110	-0.154	0.033

Observation	Predicted log Qe	Residuals
111	0.036	0.024
112	0.138	0.009
113	0.486	0.020
114	0.679	0.018
115	-0.423	0.029
116	-0.154	0.034
117	0.036	0.022
118	0.138	0.017
119	0.486	0.019
120	0.679	0.015
121	-0.423	0.029
122	-0.154	0.033
123	0.036	0.024
124	0.138	0.012
125	0.486	0.021
126	0.679	0.014
127	-0.398	0.007
128	-0.129	0.014
129	0.061	0.010
130	0.163	0.008
131	0.510	0.005
132	0.704	0.011
133	-0.398	0.008
134	-0.129	0.012
135	0.061	0.011
136	0.163	0.010
137	0.510	0.010
138	0.704	0.011
139	-0.398	0.007
140	-0.129	0.012
141	0.061	0.010
142	0.163	-0.003
143	0.510	0.010
144	0.704	0.016
145	-1.075	0.025
146	-0.780	0.034
147	-0.622	0.023

Observation	Predicted log Qe	Residuals
148	-0.488	0.025
149	-0.354	-0.140
150	-0.248	-0.214
151	-1.075	0.026
152	-0.780	0.032
153	-0.622	0.026
154	-0.488	0.026
155	-0.354	-0.164
156	-0.248	-0.208
157	-1.075	0.028
158	-0.780	0.032
159	-0.622	0.025
160	-0.488	0.034
161	-0.354	-0.150
162	-0.248	-0.192
163	-1.060	0.020
164	-0.765	0.034
165	-0.607	0.040
166	-0.473	0.043
167	-0.340	0.038
168	-0.234	-0.157
169	-1.060	0.020
170	-0.765	0.034
171	-0.607	0.040
172	-0.473	0.043
173	-0.340	0.038
174	-0.234	-0.157

VITA

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