CADMIUM ANALYSIS IN PIG FARM AND CANAL SYSTEM OF THE MAE KLONG RIVER

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Thesis
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Mukda Phatthanawanichchai

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CADMIUM ANALYSIS IN PIG FARM AND CANAL SYSTEM OF THE MAE KLONG RIVER

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ABSTRACT

This study aims to evaluate the accumulation of cadmium (Cd) in the Huai Rong Canal of the Mae Klong River and the large-scale pig farm in Pak Tho District, Ratchaburi Province. The Huai Rong Canal receives wastewater from several small and medium-scale pig farms situated along the canal. Samples were collected for six months from September 2005 to February 2006 at two sampling stations of Wang Manao Sub-District and Wan Dao Sub-District (Ban Khok Khi Lek), Pak Tho District, Ratchaburi Province. Four types of samples of water, sediment, aquatic plant (roots and leaves of *Ipomoea aquatica*) and aquatic animal (*Pomacea canaliculata*) were collected. For the large-scale pig farm in Pak Tor District, Ratchaburi Province, seven types of sample were collected: pig feed, sludge (dry manure), wastewater in collector tank, treated wastewater from UASB reactor, water and sediment in constructed wetlands and reused water. The samples were digested with Microwave Digestion instrument. The amount of Cd in the samples was determined by Graphite Atomic Absorption Spectrophotometer.

Cd concentrations in the Huai Rong Canal of the Mae Klong River, which receives wastewater from the small and medium-scale pig farms, can be presented in descending order as follows: *P. canaliculata* > *I. aquatica*'s root > sediment > *I. aquatica*'s leaf > water. The results also showed the bioaccumulation of Cd in snail species *P. canaliculata* on the canal sediment. For the large-scale pig farm, Cd concentrations in the wastewater treatment system can be presented in descending order as follows: wastewater in collector tank > treated wastewater from UASB reactor 1 > treated wastewater from UASB reactor 2 > water from constructed wetlands 1 > water from constructed wetlands 2 > water from constructed wetlands 3 > reused water. The results clearly showed the efficiency of wastewater treatment system in Cd reduction. In the case of solid samples, it was found that Cd concentrations in sludge (dry manure) were higher than those in feed. Cd in sediment from constructed wetlands was found in low amounts. From the results of the present study the application of dry sludge (dry manure) from pig farm on plants must be used with caution. The high Cd concentration in the sludge (dry manure) of pig farm undoubtedly comes from feed, therefore it is very important to reduce Cd concentrations in pig feed. In conclusion, the present study showed the necessity of wastewater treatment system for pig farms in Cd reduction and the need for further studies of Cd reduction in pig feed

KEY WORDS: ACCUMULATION/ CADMIUM/ PIG FARM/ *Ipomoea aquatica/ Pomacea canaliculata*

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การวิเคราะห์แคดเมียมในฟาร์มสุกรและระบบคลองของแม่น้ำแม่กลอง (CADMIUM ANALYSIS IN PIG FARM AND CANAL SYSTEM OF THE MAE KLONG RIVER

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บทคัดย่อ

การวิเคราะห์การสะสมของแคดเมียมในระบบคลองห้วยโรง แม่น้ำแม่กลอง และฟาร์มสุกรขนาดใหญ่ ในอำเภอปากท่อ จังหวัดราชบุรี คลองห้วยโรงเป็นส่วนหนึ่งของแม่น้ำแม่กลอง คลองนี้รับน้ำจากฟาร์มสุกรขนาดเล็กและขนาดกลางจำนวนมาก การศึกษาทำการเก็บตัวอย่างเป็นระยะเวลา 6 เดือน ตั้งแต่เดือนกันยายน 2548 ถึงเดือนกุมภาพันธ์ 2549 โดยมีจุดเก็บตัวอย่าง ในตำบลวังมะนาว และตำบลวันดาว (บ้านโคกขี้เหล็ก) อำเภอปากท่อ จังหวัดราชบุรีโดยทำการเก็บตัวอย่าง 4 ชนิด คือ น้ำ ดินตะกอน พืชน้ำ ได้แก่ ผักบุ้ง (*Ipomoea aquatica*) แบ่งออกเป็น ใบ และราก และสัตว์น้ำ ได้แก่ หอยเชอร์รี่ *(Pomacea canaliculata)* สำหรับฟาร์มสุกรขนาดใหญ่ ในอำเภอปากท่อ จังหวัดราชบุรี ได้ทำการเก็บตัวอย่าง 7 ชนิด คือ อาหารสุกร กากตะกอน (มูลสุกรแห้ง) น้ำเสียจากคอก น้ำเสียจากบ่อหมัก น้ำและดินตะกอนในพื้นที่ชุ่มน้ำประดิษฐ์ 3 บ่อ และน้ำที่นำกลับมาใช้ใหม่หลังการบำบัด ทำการวิเคราะห์โดยการย่อยตัวอย่างด้วยเครื่อง จากนั้นนำไปวิเคราะห์หาปริมาณแคดเมียมด้วยเครื่อง

ผลการศึกษาปริมาณแคดเมียมในตัวอย่างในคลองห้วยโรง จังหวัดราชบุรี ซึ่งส่วนใหญ่ได้รับน้ำจากฟาร์มสุกรขนาดเล็ก และขนาดกลางที่ไม่มีระบบบำบัดน้ำเสียที่มีประสิทธิภาพ ก่อนปล่อยน้ำเสีย จะพบว่าปริมาณแคดเมียมเรียงตามลำดับดังนี้ หอยเชอร์รี่ > รากฝักบุ้ง > ดินตะกอน > ใบผักบุ้ง > น้ำ จากผลการศึกษาแสดงให้เห็นถึงการสะสมของแคดเมียมในหอยเชอร์รี่ที่เป็นสิ่งมีชีวิตที่หากินบริเวณตะกอน และในฟาร์มสุกรขนาดใหญ่ซึ่งเป็นระบบปิด ในอำเภอปากท่อ จังหวัดราชบุรี แบ่งการเปรียบเทียบออกเป็น 2 ส่วนคือ ปริมาณแคดเมียมในน้ำจากระบบบำบัดแต่ละขั้นเรียงตามลำดับดังนี้ น้ำเสียจากคอก > น้ำเสียจากบ่อหมักUASB 1 > น้ำเสียจากบ่อหมักUASB 2 > น้ำในพื้นที่ชุมน้ำประดิษฐ์บ่อที่ 1 > น้ำในพื้นที่ชุ่มน้ำประดิษฐ์บ่อที่ 2 > น้ำในพื้นที่ชุ่มน้ำประดิษฐบ่อที่ 3 > น้ำที่นำกลับมาใช้ใหม่หลังการบำบัด จากผลการศึกษาแสดงให้เห็นถึงประสิทธิภาพของระบบบำบัดอย่างชัดเจน และในตัวอย่างของแข็งการศึกษาแสดงให้เห็นว่ามีปริมารแคดเมียมในกากตะกอน (มูลสุกรแห้ง)มากกว่านอาหารสุกร และมีการสะสมของแคดเมียมในดินตะกอนพื้นที่ชุ่มน้ำประดิษฐ์ด้วย จากการวิเคราะห์พบว่าน้ำเสียที่ผ่านระบบบำบัดในฟาร์มสุกรขนาดใหญ่มีปริมาณของแคดเมียมลดลงจากเดิม แต่จะมีการสะสมของแคดเมียมที่กากตะกอน(มูลสุกรแห้ง)มาก จึงต้องมีการศึกษาเพื่อลดปริมาณแคดเมียมในส่วนนี้ก่อนนำไปใช้ประโยชน์เช่น การทำเป็นปุ๋ยคอกในการทำเกษตรอินทรีย์ และจากการที่พบว่าปริมาณแคดเมียมในอาหารที่มีความเข้มข้นสูง ดังนั้นเมื่อคำนวณปริมาณการกินอาหารเปรียบเทียบกับกากตะกอน(มูลสุกรแห้ง) พบว่ามีปริมาณแคดเมียมบางส่วนที่สะสมอยู่ตัวสุกร หรือส่วนอื่นๆ ในฟาร์มสุกรที่มิได้ทำการวิเคราะห์ ดังนั้นจึงควรมีการศึกษาต่อไปโดยเฉพาะอย่างยิ่งเพื่อการลดความเข้มข้นของแคดเมียมในอาหารสุกรซึ่งเป็นแหล่งโปรตีนที่สำคัญที่สุดของคนไทยแหล่งหนึ่งและลดการปนเปื้อนของแคดเมียมในสิ่งแวดล้อม

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LIST OF ABBREVIATIONS

DO	Dissolved Oxygen
BOD	Biochemical Oxygen Demand
PO_4^{3-}	Phosphate
NO_3^-	Nitrate
TDS	Total Dissolved Solid
kg	Kilogram
mg	Milligram
μg	Microgram
g	Gram
mL	Millilitre
cm	Centimetre
nm	Nanometre
^oC	Degree Celsius
ms/cm	Millisiemen per Centimetre
mg/L	Milligram per Litre
μg/L	Microgram per Litre
mg/kg, dry weight	Milligram per Kilogram Dry Weight
ppt	Part per Thousand
ppm	Part per Million
Cd	Cadmium
Cu	Copper
Zn	Zinc

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CHAPTER I
INTRODUCTION

1.1 Background and Rational

Cadmium (Cd), one of the most toxic heavy metals to human being, can cause adverse effect to lung, kidney and resulting in emphysema, proteinurea and decalcification of bones (Adams *et al.*, 1969). Cd emissions come from two major sources i.e., natural source and anthropogenic source. Emissions occur to three major compartments of the environment, i.e, air, water and soil. Cd is a rather mobile ionic species under acidic soil conditions (Baker *et al.*, 1979) which are dominant in Thailand's agricultural land therefore one could expect Cd to be present in agricultural crops. Loads of Cd to agricultural land are from phosphate fertilizers and composted materials which are contaminated by Cd used replacing chemical fertilizers (Schouw and Tjell, 2003).

In Thailand, pork is one of the favorite meat. It produces protein that is very important substance for Thai people from the past until now. Regarding the demand of pork in Thailand and other countries and the worth from investment, more farmers decide to raise pigs. In the past, the major area of all-scale pig farms was in Nakorn Pathom Province, as a consequence the Tha Chin River has been in severe degraded water quality. Recently several pig farms have been moved to the Mae Klong River, where there are already a lot of small and medium-scale pig farms along the river course. Unfortunately, most small and medium-scale pig farms discharge wastewaters directly into the canal or the surrounding. In case that pig farms are far from water sources or lack of water, they tend not to be cleaned by water, but cleaned by manure collection for sell later. In this case, the water pollution is little. If small-scale pig farms are near water sources or rich of water resources, they tend to use water cleaning everyday that can cause a lot of water pollution. Therefore the control for the quality

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of effluent water discharged from pig farms is very importance (Chaemphuthorn, 1997). The large-scale pig farms can hardly avoid their responsibility and the government pays more attention and supports constructing wastewater system such as biogas system. Several large-scale pig farms have been succeeded in biogas production from pig manure and wastewater. Wastewater from the biogas system is air-dried on the sand bed system where sludge (dry manure) can be collected. It can be used to organic fertilizers for plants. Finally, the constructed wetlands is used before the treated wastewater from the biogas and sand bed systems is discharged into the canal. Six provinces with high pig population of Thailand are Nakorn Pathom, Ratchaburi, Chon Buri, Chachoengsao, Rayong and Nakorn Ratchasima Provinces. A survey of availability of wastewater treatment system of 100 pig farms showed that 23 % had no wastewater treatment system, 54 % ponding system and 23 % biogas system. Reported that collection water from the canals, pig farms that are located densely, highest biochemical oxygen demand (BOD) of 10,368 mg/L was found in Chachoengsao Province and lowest BOD of 890 mg/L found in Nakorn Pathom Province. The situation was more severe in the dry season due to lack of water diluting BOD (Suwathanachao, 2000). The study of pig manure and sludge (dry manure) showed the concentrations of heavy metals (copper (Cu), zinc (Zn), nickel (Ni), cadmium (Cd) and cromium (Cr)) in sludge (dry manure) were generally higher than those in pig manure (Mhowyathai and Sripanomtanakorn, 2005). Sludge (dry manure) from pig farms when used as a source of protein in pig feed (Thapjarean, 2535) and organic fertilizers in agriculture are sources of heavy metals to contamination in the environment.

Owing that water quality of the Mae Klong River has been in good condition when compared with the other rivers in Central Thailand, the major water consumption activity in the Mae Klong River is agriculture especially aquacultures of fish and shrimp. Therefore the relocation of pig farms to the Mae Klong River may be a threat to agricultural products of the area. However, this study mainly focused on cadmium concentration in the canal system of the Mae Klong River where many small and medium-scale pig farms are located and the large scale pig farm in the vicinity. In pig farms had wastewater and solid waste (sludge) with Cd can be transported to agricultural products through the canal system or organic fertilizer application.

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Therefore the present study will be very useful for future management of both types of waste from these pig farms in the Mae Klong River.

1.2 Goal and Objectives of the Study

1) To determine cadmium (Cd) contents in water, sediment, aquatic plant (*Ipomoea aquatica*) and golden apple snail (*Pomacea canaliculata*) in the Huai Rong Canal, Mae Klong River, Ratchaburi Province.

2) To determine Cd contents in the large-scale pig farm system and the wastewater treatment system.

3) To propose the scenarios for managing Cd in pig farm system.

1.3 Scope of the Study

1) Due to the unavailability of wastewater from the small and medium-scale pig farms, the cadmium (Cd) contents were determined in water, sediments, aquatic plant (*Ipomoea aquatica*) and golden apple snail (*Pomacea canaliculata*) at two sampling stations before and after the area of the small and medium-scale pig farms. All samples in the Huai Rong Canal were collected for six months during September 2005 to February 2006 representing the rainy, cool and early dry seasons.

2) For the large-scale pig farm, this study collected solid samples of feed, dry sludge from the sand bed filter, sediments from constructed wetlands and samples of wastewater in the collector tank (mixed wastewater from pigsty), treated wastewater from UASB reactor, water from constructed wetlands and reused water in large-scale pig farm. The large-scale pig farm is located in Pak Tho District, Ratchaburi Province and the samples were collected in February 2006.

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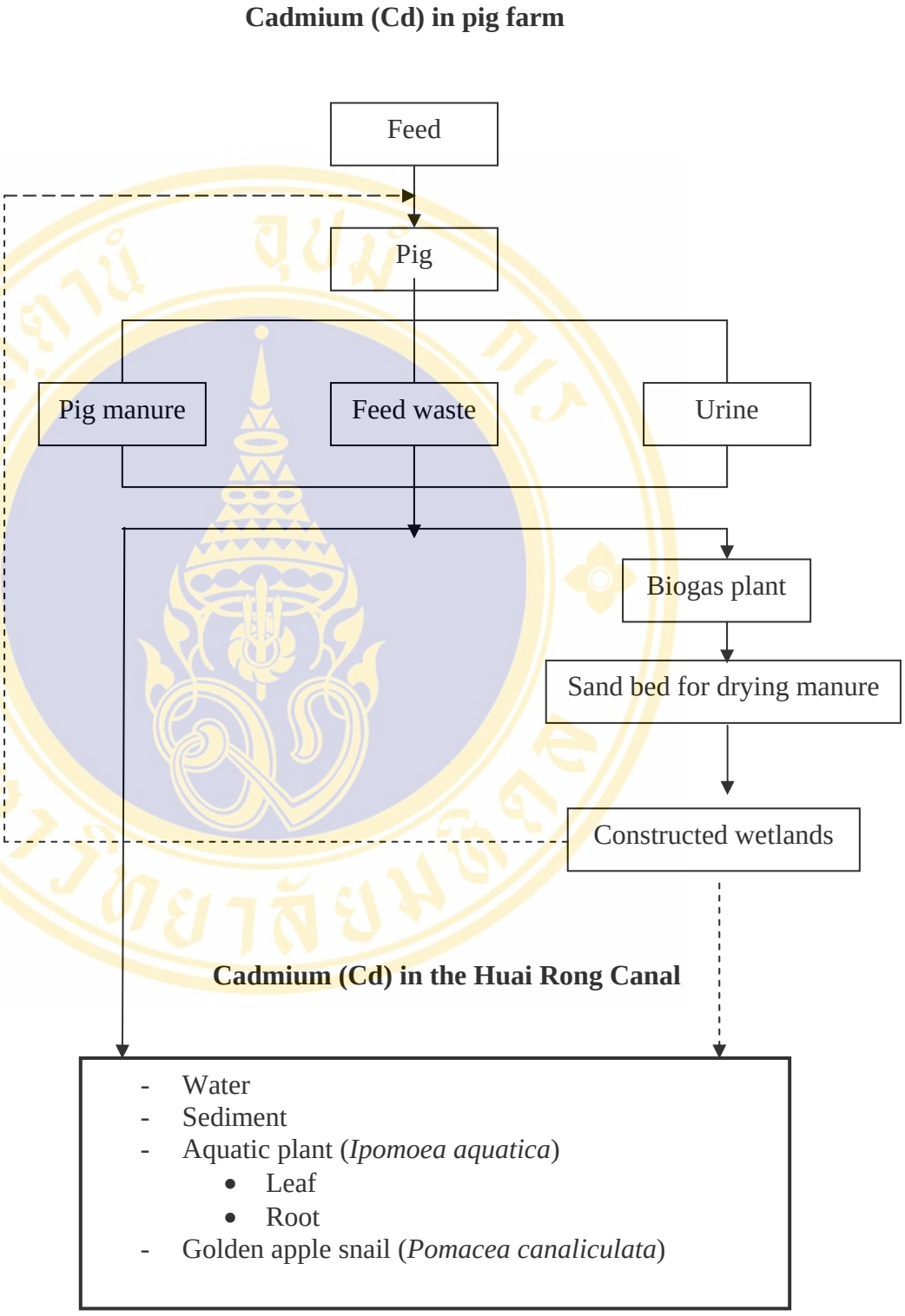
1.4 Conceptual Framework



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1.5 Operational Definitions

1.5.1 Biogas plant

A biogas plant is a system where biogas is used to generate electricity. The gas which is produced via anaerobic digestion is used to drive an electricity generator (Kottner, 2001).

1.5.2 Constructed wetlands

A constructed wetland is an artificial marsh or swamp, created for anthropogenic discharge such as wastewater, storm water runoff or sewage treatment, and as habitat for wildlife, or for land reclamation after mining or other disturbance. Natural wetland acts as filter, removing sediments and pollutants such as heavy metal from the water, and constructed wetlands can be designed to emolate these features (Gelt, 1997).

1.5.3 Aquatic plants

In the study, type of representative aquatic plants in fresh water is *Ipomoea aquatica* (Gothberg, Greger and Bengtsson, 2002).

1.5.4 Golden apple snail

The golden apple snail (*Pomacea canaliculata*) is a large freshwater snail native to tropical and subtropical South America. The snail is found in a wide variety of habitats, including rivers, ponds, swamps, reservoirs, creeks, drainage canals and paddy fields (Hirai, 1987) and is likely to inhabit quiet waters which contain a high level of suspended matter and a high chemical Oxygen Demand (COD) (Estebenet and Martin, 2002).

1.5.5 Leaf

Leaf mean flat (usually green) organ growing from the stem, branch or roof of plant.

1.5.6 Root

Root mean a part of plant which grows in soil and absorbs food and water.

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1.5.7 Accumulation

An accumulation means the quantity of heavy metal concentrations in the samples.

1.5.8 Distribution

A distribution in this study is refered to where heavy metals are determined in two sampling stations before and after the area of the medium and small-scale pig farms.

1.6 Expected Results

The data of the accumulation of cadmium (Cd) in water, sediment, an aquatic plant (*I. aquatica*) and gloden apple snail *(P. canaliculata*) in the canal system of the Mae Klong River came from small and medium-scale pig farms that are located densely along the canal. These pig farms do not have efficiency wastewater treatment system or do not have wastewater treatment system. Also the efficiency of the wastewater treatment system of the large-scale pig farms can be evaluated. The study will show more appropriate management of both water and solid wastes from all scale pig farms.

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CHAPTER II
LITERATURE REVIEW

2.1 Water Quality Situation of the Mae Klong River

The Mae Klong River is one of the main river basins in the Chao Phraya delta. The river begins at the confluence of the Khwae Noi (Kwai Sai Yoke) and the Khwae Yai River (Kwai Si Sawasdi) in Kanchanaburi Province, pass Ratchaburi Province and empties into the Gulf of Thailand in Samut Songkhram Province.

The Mae Klong River is classified in class 3 of the Surface Water Quality Standard which dissolved oxygen (DO) is not less than 4 mg/L, biochemical oxygen demand (BOD) does not exceed 2 mg/L, pH ranged between 5-9, fecal coliform bacteria (FCB) should be less than 4,000 MPN/100mL and total coliform bacteria (TCB) should be less than 20,000 MPN/100mL (PCD, 2006). There are 10 water-quality sampling stations in the river. Water quality monitoring results during the last decade (1984–1995) are to be fair and good. The first three major polluted contributors in the Mae Klong River regarding the respective parameters are high FCB and TCB (79%), high TS (8%) and high turbidity (6%). The Mae Klong River is less polluted. The most alarming water quality problem is the low concentrations of DO during dry season in certain years. However, DO levels of almost every monitoring stations are higher than the regulated value in the established water quality standard for industrial use (not less than 4 mg/L). During 1978 to 1999, the average DO value is 6.0 mg/L and the P_{20} value during this period is 5.1 mg/L, which is within Class 3 of the Thailand's Surface Water Quality Standards. Most DO values in the river were higher than the standard values especially from Dumnensaduk District, Ratchaburi Province to Kanchanaburi Province. BOD levels were mostly below established water quality standards (not more than 2 mg/L) with average value of 1.7 mg/L and the P_{80} value of 2.3 mg/L. TCB values are found to be high with the maximum value as

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16,000,000 MPN/100 mL with the average value of 200,000 MPN/100 mL and the P_{80} value of 160,000 MPN/100 mL, which is higher than the standard value (not more than 20,000 MPN/100 mL). Average concentrations of TP, NH_3-N and NO^-_3-N in the river are 0.05, 0.14 and 0.31 mg/L, respectively. For the lower part of Mae Klong River, Average values of FCB and TCB are 44% and 43%, respectively, which are the major problem parameters of all monitoring stations during 1991 to 2000. Pollution in this section are generated mainly from domestic and industrial activities.

In summary, the Mae Klong River's water quality is still in good condition with high DO and low BOD values. However, some parts of the river especially in the urban areas, TCB and FCB are very high and sometimes higher than the values of the Thailand's Surface Water Quality Standards. During 14 years of 1985 – 1999, DO values have been slightly decreasing, while BOD values have been slightly increasing and TCB values have been extremely increasing (Menasveta and Sawangwong, 1978).

2.2 Water Quality Situation of the Huai Rong Canal

The Huai Rong Canal is a small waterway, a tributary of the Mae Klong River that is one of the main and important rivers in the central part of Thailand. The canal flows into the Rang Thap Tap, Yi San Canal and the Gulf of Thailand at Bang Tabun District, Phetchaburi Province. The water source from the canal has been used for many activities such as consumption, agriculture, aquaculture, fishing, industry, and transportation (Phangsombut, 2005).

At present, water quality of the canal is more polluted, especially in the dry season by direct and indirect discharges of industrial, agricultural, and municipal sectors. In the aspect of wastewater source discharged into the canal, the major source comes from pig farm sewage in Pak Tho District, Ratchaburi Province. There were 541,771 pigs in the district and it is one of the most populated areas of pig in Thailand (Ratchaburi Provincal Livestock Office, 2006).

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2.3 Cadmium (Cd)

2.3.1 Chemical Properties of Cd

The chemical of Cd with an atomic number of 48 and atomic mass of 112.4. The melting point is at 321°C and boiling point is at 767°C. The density is 8.7 $g.cm^{-3}$ at 20°C and the number of isotope is 15. The stable oxidation state of Cd is +2 with natural occurring isotopes as 106 (1.22%), 108 (0.88%), 110 (12.39%), 111 (12.75%), 112 (24.07%), 113 (12.26%), 114 (28.86%), and 116 (7.50%). Cd is white-bluish, malleable, lustrous, and ductile. It is dissoloved in hot HCl, H_2SO_4 and more readily in HNO_3. Some of Cd salt such as haloginated salt, sulphate and nitrate are soluble in water, while sulfide, hydroxide, and carbonates cadmium are insoluble. Cd can be oxidized in moist air at room temperature. At high temperature, the oxidation is more rapid and producing a browning cadmium oxide fume (CdO) (Lenntech Water Treatment and Air Purification Holding, 2005).

In Thailand, Cd is a rather mobile ionic species under acidic soil condition, which are dominant in lowland, one could expect it to be present in agriculture crops. Consequently, it poses the potential risk of entering human food product (Schouw and Tjell, 2003).

2.3.2 Uses of Cd

Cd has a large array of uses, and its production has grown steadily during the last forty years, even if certain applications have recently declined. Industrial Cd exposure levels in some industries were very high through the 1950's and 60's (Cherian *et al.*, 1985). In the last two decades, however, occupational exposures have dropped, following the dramatic reduction of exposure limits in most industrialized nations (Oberdorster, 1992). Many scientists and policy makers acknowledge the need to continue reducing exposures to this very toxic metal. Some jurisdictions have prohibited specific uses of Cd. Because of the wide variety of uses for Cd, only significant industrial uses of Cd are listed below in order of potential exposures, from higher to lower (Occupational Disease Panel, 1993).

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2.3.2.1 Industries

1) Nickel-cadmium battery manufacturing

Significant source of occupational exposures to Cd dusts appear to be generated at all stages in the manufacture of both industrial and household nickel-cadmium batteries, including plate-making, impregnation, plate preparation and assembly. Cd health effects may be confounded by associated exposures to nickel in this environment (Occupational Safety and Health Administration, 1992; Wittman and Hu, 2002).

2) Zinc refining/ cadmium smelting and production

Deposits of Cd occur naturally in zinc ores. Cd is so produced as a by product of zinc refining. A small amount of Cd is also recovered from cadmium-bearing scrap and waste products. Significant exposures to Cd fume and dusts as well as aerosols of cadmium sulphate are generated at several stages in Cd production (Occupational Safety and Health Administration, 1992; Wittman and Hu, 2002).

3) Cadmium-containing pigment production

Cd pigments (mainly cadmium sulfide and cadmium selenosulfide) are produced as powders, pellets, pastes and liquids and are primarily used for the colour of plastics. About 25% of worldwide production of Cd is used in pigments. High inhalation exposures may occur in calcining, crushing and milling operations especially when Cd product is present in powder form. However, wet system operations with lower inhalation exposures may be associated with increased ingestion exposure, resulting in high cadmium-blood levels even where air levels are not excessive (Tartre, 1992; Detlev *et al.*, 2003).

4) Dry colour formulating

Cd pigments possibly formulated into custom color concentrates prior to use in plastics, ceramics and specialty coatings by dry color formulators. These producers are generally very small companies, who produce custom materials in batch operations. Intermittent and highly variable exposures to Cd occur in material handling, mixing of dry pigments with other materials (blending or compounding), grinding, or cleaning (Occupational Safety and Health Administration, 1992).

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5) Cadmium-based stabilizer production

Cadmium-based stabilizers such as the barium sulfate-cadmium carboxylates (cadmium laurate or cadmium stearate) are used primarily in the production of poly-vinyl chloride (PVC). However, it has been found that other cadmium-free compounds such as calcium-zinc, barium-zinc and organo-tin stabilizers can be utilized equally well although they are not always as performance and cost-effective (Morrow, 2005).

6) Metal plating with cadmium-containing materials

Cd is highly corrosion resistant, and is widely used to plate metal parts used in general industrial hardware as well as in the automotive, electronics, marine and aerospace industries. (As much as 35% of worldwide Cd production is used in plating.) Cd plating is done by means of electroplating or mechanical plating operations. Plating may be done in independent industrial operations, or as an element of production in larger production facilities. Occupational Safety and Health Administration (OSHA) reports that at mechanical plating operations, less than 10% of the workforce is exposed to Cd, though exposures tend to be higher than those in electroplating. During electroplating, plating operators (Wittman and Hu, 2002).

7) Production of cadmium alloys

Cd is used to some copper alloys to increase the mechanical strength and wear resistance of copper wire conductors. It is also used in the production of solders, and in alloys with zinc, lead, silver or tin. Workers may be exposed to cadmium fume during melting and casting operations (Occupational Safety and Health Administration, 1992).

8) Lead smelting and refining

Lead concentrates which are processed in lead smelt and refine operations contain Cd contaminants, found naturally in the ores. Cd exposures occur in material handling, sinter plants, furnace areas, refining and casting, and maintenance operations. Workers have combined exposures to lead, Cd and other materials (Occupational Safety and Health Administration, 1992).

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9) Iron and steel production

Cd is present as a trace contaminant in the raw materials used for steelmaking. Exposures to Cd may occur during furnace operations, welding, and maintenance work on pollution control equipment (Occupational Safety and Health Administration, 1992).

10) Coal-fired electrical utilities and garbage incineration

The cinders, fly ash and flue gases produced by coal burning utilities and garbage incineration may contain problematic levels of Cd. Exposures generally occur during malfunctions, inspection and maintenance of boilers, ovens and filters, and in the transport of ash and cinders. Problematic exposures to several other metals also occur in these situations (Zwennis and Franssen, 1992).

2.3.2.2 Non - occupational exposures

Non-occupational exposures to Cd may give rise to cadmium-related disease, but, other than smoking, usually contribute relatively little to the body burden of an occupationally-exposed person (Thun, Elinder and Friberg, 1991).

1) Exposures from ambient air, water and soil

Cd levels have increased in the general environment ever since metal ores containing Cd have been refined (Elinder, 1985). In the air, Cd vapor is rapidly oxidized. Wet and dry deposition transfers Cd from the ambient air to soil, where it is absorbed by plants and enters the food chain. This process may be influenced by acidification that increases the availability of Cd in soil (Lauwerys, *et al*., 1990; World Bank, 1998).

2) Cd in food products

A major non-occupational source of Cd contains in foods as a result of uptake from the soil by plants and bioaccumulation in terrestrial and aquatic animals. The highest concentrations of Cd are found in shellfish (over 1 μg/g) and in the liver and kidneys of farm animals (0.1–1 μg/g) (World Bank, 1998). Intermediate levels may be found in grains when use of sewage sludge or phosphate fertilizers can increase Cd content of soils and through the roots of plants to edible leaves, fruits and seeds. It will also build up in animal milk and fatty tissues. Therefore, people are exposed to Cd upon consumption of Cd containing plants or animals. (Nordberg, 1988; Johnson, 1997).

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3) Cd exposures due to cigarette smoking

Cd is found in small amounts in tobacco. Although the Cd content of cigarettes which may equal or exceed that from food, cigarettes produced in Europe or the United States of America contain Cd at a concentration of 0.5–2 μg/g (dry weight) of tobacco, of which 10% can be absorbed (WHO Regional Office for Europe ,2000). Cd is absorbed much more effectively by the lung than the gut. For smokers who are not occupationally exposed to Cd, smoking is usually the main source of exposure. Cd intake from smoking can substantially increase total Cd exposure for occupationally-exposed workers (Niebohr, *et al*., 1988).

2.3.3 Effects of Cd in Environment

Naturally a very large amount of Cd is released into the environment, about 25,000 tons a year. About half of this Cd is released into rivers through weathering of rocks and some Cd is released into air through forest fires and volcanoes. The rest of the Cd is released through human activities, such as manufacturing. Higher levels of Cd found in soil or water near industrial areas or hazardous waste sites. High levels of Cd in surface soils usually result from Cd particles settling from the air. Soils near roads may contain high levels of Cd from car exhaust. Surface water also can contain low levels of dissolved Cd. Cd in water tends to sink (Illinois Department of Public Health, 2002). Another important source of Cd emission is the production of artificial phosphate fertilizers. Phosphate fertilizers are contaminated with Cd because phosphate rocks contain 2 - 170 ppm Cd. Using phosphate fertilizers can increase quantity of Cd in soil because cadmium phosphates does not dissolve easily in water. The rest of cadmium phosphates can not dissolve, so it can not be used by the plants and accumulates in soil. It was also found that rice and wheat can absorb Cd from (Sakaew, 2001). In Thailand, soil all regions have among the range of Cd contents vary from 0.001 to 0.294 ppm. Cd in soil can enter water or be taken up by plants. Fish, plants, and animals take up Cd from the environment. (Phongsakul and Autthajarusith, 1999).

Cd strongly adsorbs to organic matter in soils. When Cd is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the Cd uptake by plants. This is a potential danger to the animals

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that are dependent upon the plants for survival. Cd can accumulate in their bodies, when they eat multiple plants. Cows may have large amounts of Cd in their kidneys due to this. Earthworms and other essential soil organisms are extremely susceptive to Cd poisoning. They can die at very low concentrations and this has consequences for the soil structure. When Cd concentrations in soils are high they can influence soil processes of micro-organisms and threat the whole soil ecosystem (Lenntech Water treatment and air purification, 1998).

In aquatic ecosystems Cd can bio-accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to Cd can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to Cd poisoning than freshwater organisms (Lenntech Water treatment and air purification, 1998).

2.3.4 Effect of Cd on Human Health

Cd can enter the blood by absorption from the stomach or intestines after ingestion of food or water, or by absorption from the lungs after inhalation. Very little Cd enters the body through the skin. Usually only about 1 to 5% of what is taken in by mouth is absorbed into the blood, although about 30 to 50% of that which is inhaled is taken up into the blood. However, once Cd enters the body, it is very strongly retained; therefore, even low doses may build up significant Cd levels in the body if exposure continues for a long time (Environmental Bureau of Investigation, 1997). Cd can enter to body from food when eating food, drinking water or particles breathing in. Very little Cd enters through skin. Body rapidly takes in about one-quarter of the Cd when breathed, and about one-twentieth of the Cd eaten. The rest of the Cd is breathed out or excreted in feces. Whether do not eat foods that contain enough iron or other nutrients, likely to take up more Cd from food than usual. Cigarette smoke has Cd in it and so smokers breathe in Cd. Other people who breathe in cadmium are people who work with Cd, and people who live near hazardous waste sites or factories that release cadmium into the air. The general population and people living near hazardous waste sites may eat or drink Cd in food, dust, or water. Cd that enters body stays in liver and kidneys. Cd leaves body slowly, in urine and feces. Body keeps most Cd in a form that is not harmful, but too much Cd can overload kidneys' storage system and cause health

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damage (Habeck, 2007). The Cd Contents in the Variance Standard, presented in Tables A-1.

Kidney damage has been observed in people who are exposed to excess Cd either through air or through the diet. This kidney disease is usually not life-threatening, but it can lead to the formation of kidney stones and effects on the skeleton that are equally painful and debilitating. It may also promote hypertension and heart disease. Exposure to Cd (especially cadmium oxide) may increase the risk of lung, prostate, and kidney cancer in humans. There possibly no safe level of exposure to a cancer-causing agent. Cd also affects the bones, causing bone and joint aches and pains, a syndrome, first described in Japan, where it was termed the itai-itai ("ouch-ouch") disease. Symptoms of this disease include weak bones that lead to deformities, especially of the spine, or to more easily broken bones. It is often fatal. Cd may damage the testes (male reproductive glands) and may affect the female reproductive cycle. Cd levels in humans tend to increase with age (probably because of chronic subtle exposure), usually peaking at around age 50 and then leveling off. No Cd is present in newborns; Cd does not cross the placenta-fetal barrier nor the blood-brain barrier as lead and mercury do. Exposure during pregnancy may not be toxic to fetuses, nor does it cause the mental and brain symptoms of lead and mercury. It is a probable teratogen in humans. Cd appears to depress some immune functions, mainly by reducing host resistance to bacteria and viruses. To protect against Cd toxicity, avoid Cd exposure and intake by minimizing smoking and exposure to cigarette smoke, avoiding refined foods, shellfish, coffee, tea, and soft water and maintain good zinc levels by eating high-zinc foods, such as whole grains, legumes, and nuts (oysters are high in zinc but also high in Cd). Taking additional zinc, 15-30 mg. daily in a supplement, will offer further protection against Cd problems (Environmental Bureau of Investigation, 1997).

2.4 Pig Production

1960s and 1970s, pig production was dominated by the backyard raising of pig cross-breeds for consumption and the generation of supplementary income. The most pigs in Thailand were traditionally raised by rice farmers to consume farm by products

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and wastes and generate extra farm income. Along with buffalo, cattle and poultry, pig production was an important component in an integrated small farm cropping system where buffalo and cattle were used for draught purposes and pigs and poultry for consumption (Tisdell, Murphy and Kehren, 1997). The development of pig production from predominantly village-based to a growing commercial industry can be attributed to significant socio-economic change that has occurred in Thailand over the last few decades. This change has increased in population, tourism and income levels (following dramatic economic growth over the last 20 years) and an associated increase in demand for meat such as pork, both domestically and internationally (Murphy and Tisdell, 1995).

2.4.1 Present Situation of Pig Farm

Pig raising in Thailand has made remarkable progress for the past ten years. Majority of pig farms was small-scale, and pigs were brought up for regional consumption by the traditional raising method. From the 1990's on, this raising transferred to commercial raising and the edible pig raising industry introduced a new breed. Further, the fodder quality improvement, etc. is hastened, and the pigshed structure is also being converted to the concrete structure provided with the fodder feeding system in place of the conventional wooden type. However, majority of pig farms in Thailand are still small-scale. Table 2.1 shows the number of pig farm, total pigs and wastewater in 2008. The small-scale pig farms were counted approximately 99.3%, medium-scale pig farms were counted approximately 0.61% and large-scale pig farms were counted approximately 0.09% of all total farms (Thailand, Energy Policy and Planning Office, Ministry of Energy, 2008).

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Table 2.1: Number of pig farms, pigs and wastewater in Thailand

Pig farm Scale	Total pig farms (%)	Total pigs (%)	Total wastewater (%)
Small-scale pig farm (Total pigs: 50 to 500)	99.3	42	42
Medium-scale pig farm (Total pigs: 500 to 5,000)	0.61	18	19
Large-scale pig farm (Total pigs: 5,000 or more)	0.09	40	39
Total	100	100	100

Source: Thailand, Energy Policy and Planning Office, Ministry of Energy, 2008

Ratchaburi Province is located in the central part of Thailand. It has the largest number of pigs in Thailand. During 2006, this region had the total pigs approximately 1.36 million pigs (19.4%). It found that people in Paktor District raised pigs the most. It was about 0.54 million pigs (7.6%) from the number of raising pigs in Thailand (Ratchaburi Provincal Livestock Office, 2006). Pig raising industry scale in Ratchaburi Province was larger than any other areas in Thailand. To control the quality of effluent wastewater discharged from the pig farms, the fixed regulations are applied as shown in Table 2.2. For the time being, only the medium-scale and large-scale piggeries must follow these regulatory standards. For the small-scale pig farm, the government has not yet materialized any legal measures for regulating or supervision this discharge (Thailand, PCD, 2005).

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Table 2.2: Discharge standard from pig farms

Analysis Index	Pig farm effluent standard	
	Standard A (Large-scale pig farm)	**Standard B (Small and medium-scale pig farm)**
pH	5.5-9	5.5-9
BOD_5,mg/L	≤ 60	≤ 100
COD, mg/L	≤ 300	≤ 400
SS, mg/L	≤ 150	≤ 200
TKN, mg/L	≤ 120	≤ 200

Source: Thailand, PCD, 2005

2.4.2 Waste from Pig Farm

The primary wastes generated by pig farms are liquid organic wastes. These comprise urine, manure and spent washwaters. An 80 kg. pig will excrete approximately 3 liters of manure and urine per day; about 23 liters of water per pig are required on a daily basis. Typical waste generated at piggeries are outlined as follows (Centre for Technology and Environment Mangement, 2000).

2.4.2.1 Solid Separation

1) Pig manure

Normally, farm owners clean their farms once or twice a day which depends on their facility. A pig's weight about 80 kg. can generate manure around 1.2 kg/day. When they clean their farm, the manure will be scraped in the breeder pigsty and washed into the wastewater canal using water hose or bucket. Because manure's water content is suspended in the washing water and enters the wastewater stream. For the manure, farm owners will dry it in the sun. Then, they will

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mix it in feedstuff or use it as fertilizer. The chemical composition of sludge (dry manure) from pig farms showed in Table 2.3 (Sornkwan, 1998; Ragasilp, 2000).

Table 2.3: Chemical composition of manure and urine from pig farms (percent of dry weight)

Composition	Sludge	Urine	Total
Nitrogen (N)	0.54	1.16	1.70
Phosphorus (P)	0.59	0.08	0.67
Potassium (K)	non-detect able	non-detect able	non-detect able
Calcium (Ca)	0.82	0.01	0.83
Manganese (Mn)	0.13	0.01	0.14

Source: Ragasilp, 2000

2) Food scraps

Pig feed residue in farm (feed waste).

2.4.2.2 Wastewater

wastewater is generated from farm owner cleanings and flushing showers, spills and leaks of automatic nipple type water, pipes and hoses. Flushed manure and urine, dirt and spilled feeds find their way into the wastewater stream. Pig houses in most commercial piggeries have canals (depending on the design, some piggeries have their canals at sides, bottom, or inside the pig houses) which drains wastewater to a main canal that leads to a wastewater treatment system. In some piggeries, storm water drains to the anal and is conveyed to the wastewater treatment system. Other piggeries have separate canals for the storm water. An 80 kg. pig generates 27 to 30 L of wastewater per day. However, it could increase to 50 L if the facility does not practice good house keeping. Typical BOD for pig farms ranges from 2,500 mg/L to 9,000 mg/L (Centre for Technology and Environment Management, 2000; Ragasilp, 2000).

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2.4.3 Common Waste Management Practices

Farms usually treat their wastewater streams by direct discharge into lagoons where anaerobic, facultative, and aerobic bacteira decompose the organic material. The pond system is a good method of treatment in tropical countries where temperatures of 25 to 35 °C for sustain bacteria growth. Pond maintenance is simple, but they are prone to siltation over time. Some farms collect their organic wastes in underground or surface tanks to promote methane gas formation. Anaerobic digestion decomposes wastewater and produces methane gas in an air-free environment. However, compared to the pond system, this type of treatment requires proper design and maintenance (Sornkwan, 1998; Centre for Technology and Environment Management, 2000; Pepatung, 2002).

2.4.3.1 High-Rise Swine Housing

A system called “high-rise” provides a living area for pigs on a slatted upper floor with the manure falling through the slats onto a lower floor containing sawdust or other carbon source. With proper mixing, turning and distribution of the manure and sawdust on the lower floor, composting takes place. This system has not found wide acceptance in the swine industry due to increased cost and lack of need or incentive to manage manure as a solid (Murphy and Power, 2006).

2.4.3.2 Lagoon Aeration

An aerated lagoon is well suited for municipal and industrial wastewaters of low to medium strength. Aeration is another alternative process sometimes considered in managing swine manure in lagoons or other outside storage structures. In this process, small bubbles of air are introduced into liquid manure to stimulate the growth of aerobic bacteria. These bacteria provide high-rate degradation of organic material in the manure and less odor is emitted than with anaerobic systems. Aeration systems require significant hardware (pumps, aerators), energy inputs (usually electricity) and maintenance to keep the system operating efficiently process. Although a number of alternative management systems for swine manure are available, including several research projects that are converting manure into biological fuel, most are more costly. They also require greater inputs of management and levels of expertise. So, traditional systems (lagoon or slurry storage with land

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application) are usually most attractive to producers unless other circumstances or incentives are present (Murphy and Power, 2006; U.S. EPA., 2002)

2.4.3.3 Constructed Wetlands

Constructed wetlands are another manure management system. In a constructed wetland, liquid manure is treated aerobically (with oxygen) while aquatic plants take up some of the nutrients in the manure. Constructed wetlands can provide a high degree of treatment to manure. So far, constructed wetlands have not been used by a lot of farmers. They require a large area of ground, are expensive to construct and establish. Vegetation requires more management after storm events due to more surface area that collects rain water. Livestock producers are not allowed to release manure or wastewater into water ways, so land application is still required for water from a constructed wetland. Long-term use of wetlands with swine farms has not been well documented (Forbes, *et al.*, 2004; Pepatung, 2002).

There are numerous types and designs of constructed wetlands but these can be categorized as mainly Surface Flow or Sub-Surface Flow as shown in Figure 2.1.

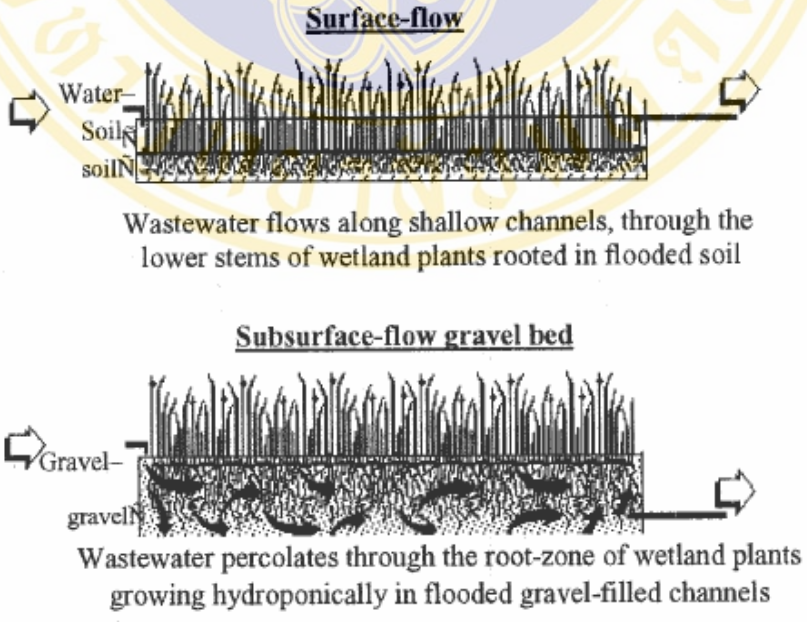

Figure 2.1: Two main types of constructed wetlands

Source: Tanner and Kloosterman, 1997

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Aquatic grass in normally defined as Vertical Flow, where water fall or cascades onto the wetland or Horizontal Flow, where it flows in level with or slightly above the surface. There are any number of variation and themes of constructed wetlands that one might use to decribe their particular design of a surface flow constructed wetlands with vertical flow inlet (Forbes, *et al.*, 2004).

2.4.3.4 Methane Digester

Methane generation through anaerobic digestion of manure is another treatment being researched. Manure is put into a closed container, where oxygen is not present and the manure is digested and methane gas is produced. This gas can be collected and burned for heat or used to generate electricity. The left over liquid has fewer odors than the original manure. The cost and labor needed for digesters has slowed implementation (Murphy and Power, 2006). Show in Figure 2.2.

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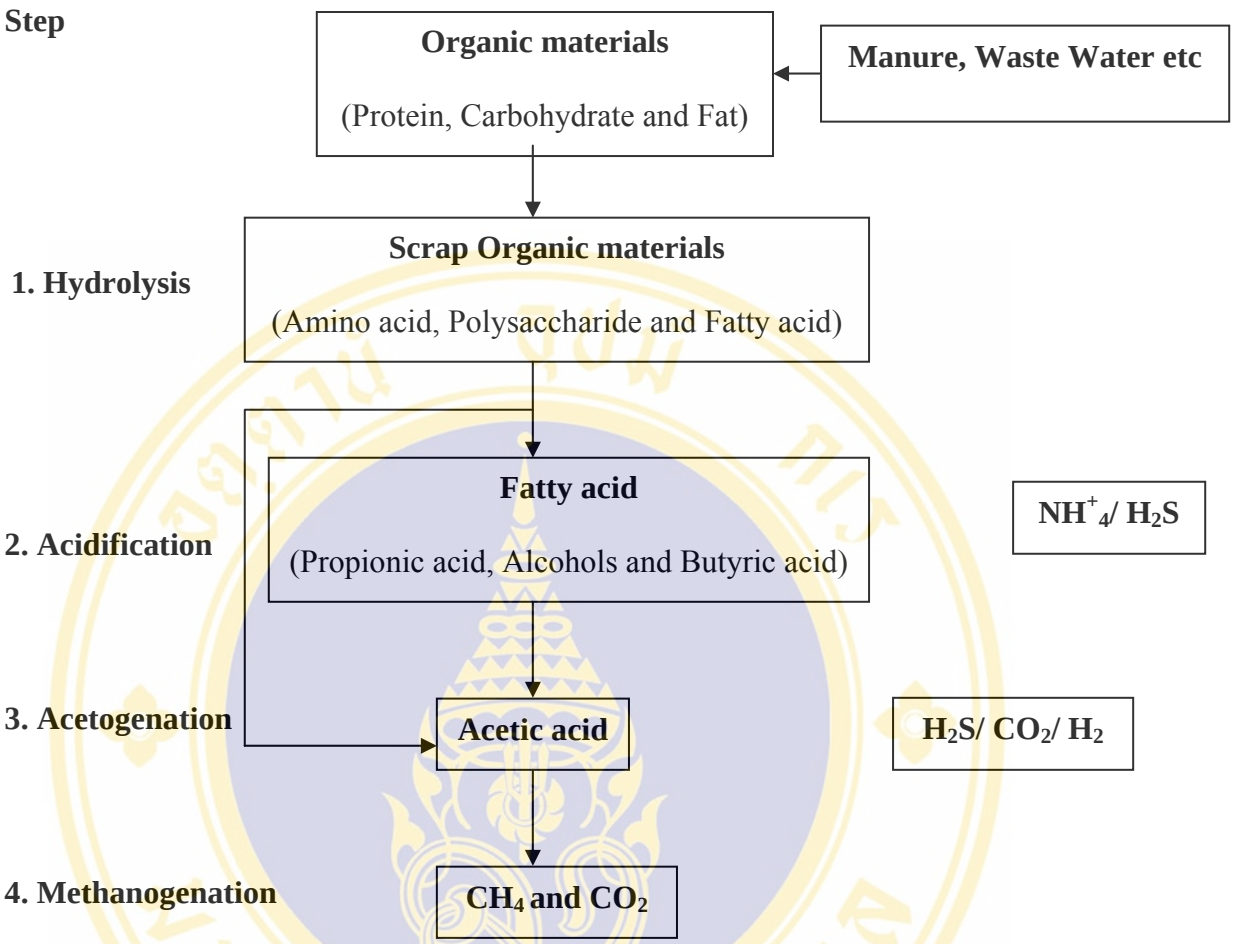

Figure 2.2: Anaerobic digestion of manure in pig farms

Source: Suwathanachao, 2000

Now a days, biogas wastewater treatments in Thailand that were recommended to use with wastewater of pig farms for energy and environment conservation are as follows.

1) Fixed Dome

Fix dome works by batch decomposition of organic matter in wastewater. This method was suitable for small pig farms that does not have much wastewater. (Thailand Energy and Environment Network, Chiang Mai University, 2003).

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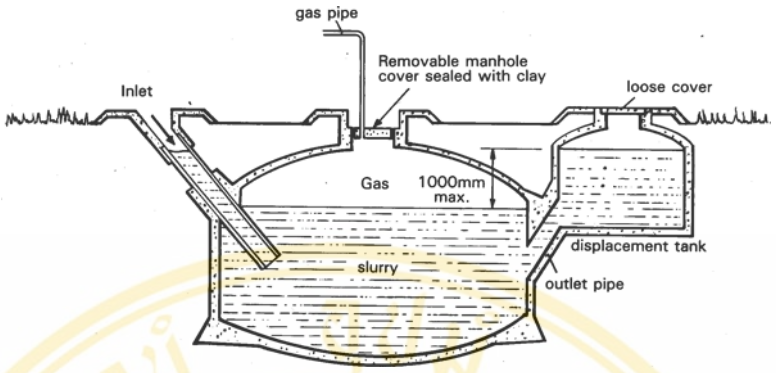

Figure 2.3: Fixed dome biogas digester

Source: SD and FAQ, 1997

2) Channel Digester + UASB

Channel Digester + UASB is composed of 2 parts that are Channel Digester and UASB. Channel Digester works together continuously with UASB. This system can support large amount of wastewater, so it is suitable for large pig farm. (Thailand Energy and Environment Network, Chiang Mai University, 2003).

2.5 Relevant Research

Aubart and Bully (1984) carried out the experiments on anaerobic digestion of rabbit wastes and pig manure mixed with rabbit wastes were made in 6-litre digesters at 37°C with manual loading once a day and mixing for 3 min each hour. The results show the optimum Total Solids (TS) content as 6% and the retention time as 7-5 days. The optimum methane yield was about 215 litres kg^{-1} VS but this is of little use for an industrial biogas plant because the wastes volume is low on a rabbit farm. A possible use of this kind of agricultural waste is in mixing rabbit wastes with pig manure to increase the pig manure VS content, which is generally low. With retention times between 15 and 10 days the methane production increases from 0·20 to 0·25 litres of methane per litre of digester per day without affecting pollution control.

Ragasilp (2000) studied the composition of pig manure in Chachoengsao Province from 3 sizes of swine farm (small, medium and large). Fermentation of pig manure and analysis in laboratory were carried out for available plant nutrients as

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nitrogen, phosphorus, potassium, calcium and magnesium. Conclusion, available plant nutrients in pig manure were quite low and non suitable for agriculture used, because difficulties for operation and management. Consideration in term of swine farm waste due to environment problem were very importance to organized which system approach by wastewater treatment system or used before drained to environment.

Suwathanachao (2000) surveyed the wastewater treatment system of 100 pig farms in six provinces with high pig population. Show that 23% did not have wastewater treatment system, 54% used ponding system and 23% used biogas wastewater treatment system. A comparative study of ponding and biogas system, each of 4 farms, revealed that the two systems could reduce organic matters measured by biochemical oxygen demand (BOD5) and chemical oxygen demand (COD) in wastewater at least 94%. An economic analysis of the two system revealed that the internal rate of return (IRR) of the ponding system was higher than the biogas system. This may be explained that the pig farms with biogas system did not take all the advantage of biogas produced from the treatment system.

Mansour and Sidky (2002) studied the distribution of some heavy metals in water and fish from Fayoum Governorate (Egypt) was studied in samples collected throughout two successive years (1997/1998 and 1998/1999). Water from Lake Qarun, a private fish farm and "Sanhour River" was found to contain heavy metals at concentration levels lower than those found in fish from the first two ecosystems. The heavy metals showed differential bioaccumulation in fish organs (e.g. flesh, head, viscera), and the accumulation pattern (as total heavy metal residues) was seasonally as follows: summer > autumn > winter > spring. Moreover, the relative accumulation of total heavy metals in the studied fish showed the following pattern: "Mousa fish" (*Solea aegyptiaca*) < "Bolti fish" (*Tilapia* sp.) < the shrimp (*Penacus* sp.) < "Bouri fish" (*Mugil* sp.). Among the analyzed metals (e.g. zinc, iron, manganese, copper, cadmium, chromium, nickel, lead, cobalt, tin), lead and cadmium were found in fish at mean concentrations above the permissible limits proposed by FAO.

Schouw and Tjell (2003) studied risk assessment of heavy metal, cadmium concentrations in the organic waste from the settlements in the Songkhla Lake Basin vary considerably depending on the origin and the possibilities of getting polluted. Apart from industrial waste the grey waste water and human excreta are the major carriers of nutrients

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out of the households, while they hold only minor concentrations of cadmium. From their results, it is safe to say that the fertilizer in use in the Songkhla Lake Basin is not usually clean, and the quality of possible alternative fertilizing materials (human excreta and grey waste water) are well above the acceptable according to European guidelines for use of waste in agriculture. Thus reuse of these wastes as fertilizer on soils will not pose a risk of contamination crops with toxic cadmium.

Bengtsson (2005) studied trace metal run-off, the differences in metal concentrations in soil water due to differences in farming practice were much less important than the inter- and intra-field differences and temporal variability. The study demonstrates that local soil characteristics, including those of the soil water chemistry, have to be considered in comparisons between farming systems with respect to element flows and balances. The cadmium and zinc concentrations in soil water showed significant differences between high concentrations in acid subsoils on one hand and lower concentrations in non-acid subsoils and topsoils on the other. The copper concentrations in soil water were quite similar in different soils. The physical and chemical soil characteristics differed in some cases among the non-acid soils. However, the differences in metal concentrations were still rather small, compared to the acid sulphate soil.

Mhowyathai and Sripanomtanakorn (2005) determined the concentration of heavy metals (copper, zinc, nickel, cadmium and chromium) in pig manure and sluge (dry manure) sample from the pig farms in Ratchaburi and Nakhon Pathom Provinces. The major heavy metal contents in pig manure and sludge were copper and zinc. In relation to some international legislation, copper and zinc contents in sludge exceed the permitted levels of the heavy metal criteria for agricultural proposes. Result from the sequential extraction study indicated that the organic and residual fraction of copper and zinc accounted the major fractions both in pig manure and sludge. The zinc fractions exhibited the higher easily mobile fraction compared with the copper fractions.

Swaddiwudhipong, et al. (2007) determined the concentration of cadmium in Mae Sot District, Tak Province, Thailand. Surveyed the 7,697 persons, only 45.6% had urinary cadmium levels < 2 μg/g creatinine. About 4.9% were between 5 and 10 μg/g creatinine and 2.3% had cadmium concentrations > 10. The urinary cadmium

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level was greater among women than men and increased with increasing age. Smokers were more likely to have high urinary cadmium than non-smokers. Persons who mainly consumed rice grown locally in the contaminated areas had higher urinary cadmium than those who did not.

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CHAPTER III
MATERIALS AND METHODS

3.1 Study Area

3.1.1 The Huai Rong Canal System

The Huai Rong Canal is a tributary of the Mae Klong River that is one of main and important river in the central part of Thailand (Phangsombut, 2005). The Huai Rong Canal (Figure 3.1) is about 2 km. long. The canal passed through areas where numerous small and medium-scale pig farms in Pak Tho District, Ratchaburi Province. The small and medium-scale pig farms activities have been suspected to dischange high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total kjedahl nitrogen (TKN) and some heavy metals including cadmium (Cd), zinc (Zn) and lead (Pb) from their wastewater.

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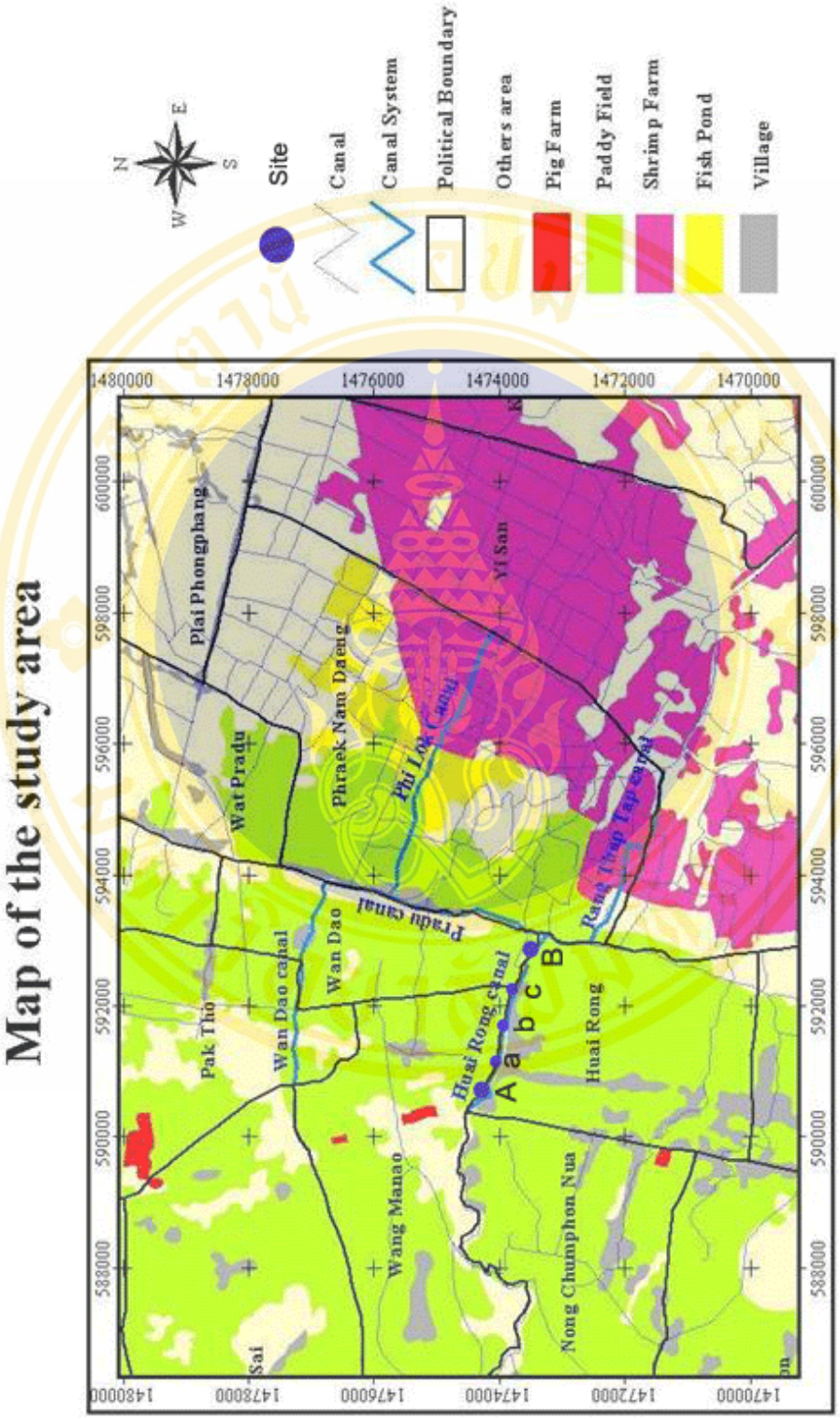

Figure 3.1: Map of the study area and sampling sites

Source: Land Development Department, 2000

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3.1.2 Large-scale Pig Farm

Large-scale pig farm in Pak Tho District, Ratchaburi Province. Large area of the province situates on bank of the Mae Klong River. The river flows through various districts in Ratchaburi Province before entering the Gulf of Thailand at Samut Songkhram Province and Bang Tabun District, Phetchaburi Province. Detail information of this large-scale pig farm follows:

- Total 15,000 pigs
- Have wastewater 300 m^3/ day
  COD = 1,800 m^3/ L
  BOD = 1,000 m^3/ L
- Have biogas wasrewater treatment system (Channel Digester + UASB) can produce biogas 1,500 m^3/ day.
- Treated wastewater to three large wetlands are simple earth excavation without lining.
- Produce sludge (dry manure) 1,000 kg/ day

3.2 Sampling Site and Parameter

3.2.1 The Huai Rong Canal System

This study have separate into sites A and B in Pak Tho District, Ratchaburi Province, are sampling sites in the freshwater part of the Huai Rong Canal. Site A (Figure 3.2) was located in Wang Manao Sub-district and site B (Figure 3.3) was located in Wan Dao Sub-district (Ban Khok Khi Lek). There shape of the canal is quite crooked, the slope of the canal forms a right angle. The bottom of the canal composes of mud. The bank is covered by not only tiny grass but also big tree. The exist on both sides of the canal with washboard road, where there are already a lot of small and medium-scale pig farms and paddy fields along the canal course. But the villages disperse among outer area. Samples were collected from each site every month from September 2005 to February 2006.

Sites a, b and c are the sites between sites A and B. Samples were collected on February 2006.

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Figure 3.2: Site A in Wang Manao Sub-district

Figure 3.3: Site B in Wan Dao Sub-district (Ban Khok Khi Lek)

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Table 3.1: Sampling sites and parameters in Huai Rong Canal

Site	Water	Sediment	Aquatic plant (Leaf/ Root)	Golden apple snail
Site A: Wang Manao Sub-District	-Water quality parameters -Heavy metals	-Heavy metals	-Heavy metals	-Heavy metals
a	-Heavy metals	-Heavy metals	-	-
b	-Heavy metals	-Heavy metals	-	-
c	-Heavy metals	-Heavy metals	-	-
Site B: Wan Dao (Ban Khok Khi Lek)	-Water quality parameters -Heavy metals	-Heavy metals	-Heavy metals	-Heavy metals

3.2.2 Large-scale Pig Farm

Large-scale pig farm used biogas system. Can reduce pollution such as; odor, surface and groundwater contamination and atmospheric emissions of methane (greenhouse gas). This farm can reduce energy cost and export electricity to the grid for sale to utility under Thailand's net metering regulations. The biogas system follows:

1. Collector tank (Figure 3.4)
2. UASB reactor (Figure 3.5)
3. Wetlands (Figure 3.6 and 3.7)
4. Reused water

Sampling site were collected on February 2006.

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Figure 3.4: Collector tank

Figure 3.5: UASB reactor

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Figure 3.6: The beginning influent of wetland

Figure 3.7: The end influent of wetland

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Table 3.2: Sampling sites and parameters in large-scale pig farm

Sampling Site	Water	Sediment
Collector tank	-Water quality parameters -Heavy metals	-
UASB reactor 1	-Water quality parameters -Heavy metals	-
UASB reactor 2	-Water quality parameters -Heavy metals	-
Wetland 1	-Water quality parameters -Heavy metals	-Heavy metals
Wetland 2	-Water quality parameters -Heavy metals	-Heavy metals
Wetland 3	-Water quality parameters -Heavy metals	-Heavy metals
Reused water	-Water quality parameters -Heavy metals	-

Table 3.3: Sources and parameters of pig feed and pig manure

Sample	source	Parameter
Feed 1	Feed in large-scale pig farm	-Heavy metals
Feed 2	Market in Pak Tor District, Ratchaburi Province	-Heavy metals
Feed 3	Market in Pak Tor District, Ratchaburi Province	-Heavy metals
Sludge	Dry sludge in large-scale pig farm	-Heavy metals

3.3 Sample Collection and Preservation

3.3.1 Water in Rang Huai Rong Canal

1) Water samples for heavy metal analysis were collected at one metre deep below surface water with water sampler. At each site the samples were collected at three sampling points in the middle and the left and right banks of the canal width. Then, the samples were stored in 100 ml polyethylene bottles.The bottles were rinsed

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twice with adequate of the sample water. To each sample bottle of 1 mL, concentrated nitric acid was added and the bottle was stored in ice box prior to analyst in the laboratory (Diagomanolin *et al.*, 2004).

2) The physico-chemical parameters for water quality were collected at the left, middle anf right of the bank in the canal. Water temperature, pH, transparency, salinity and conductivity were measured using equipments as shown in Table 3.4 in the field. Whereas the other parameters, water samples were collected using water sampler and stored in BOD glass bottles for analysis of dissolved oxygen (DO) and biochemical oxygen demand (BOD). To each sample glass bottles of 2 mL concentrated sulfuric acid was added and in 1000 ml polyethylene bottles for analysis of total dissolved solids (TDS), hardness, nitrate and total phosphorous. Preservatives were added into the bottles when necessary as shown in Table 3.4. Water samples were stored in the ice box and transferred to the laboratory.

The equipments and methods in analysis of water samplers are described in Standard Method for Examination of Water and Wastewater (APHA, 1995) and presented in Table 3.4.

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Table 3.4: Physico-chemical parameters for water quality in Huai Rong Canal

Parameters measured in the field		
Parameter	**Preservation**	**Equipment/Method**
pH	-	pH Meter
Conductivity (µmhos/cm)	-	Conductivity Meter
Salinity (ppt)	-	Conductivity Meter
Air Temperature (°C)	-	Thermometer
Water Temperature (°C)	-	DO Meter
Transparency (cm)	-	Secchi Disc
Parameters analyzed in laboratory		
Dissolved Oxygen (mg/L)	At 4º C	Azide Modification of Iodometric Method
Biochemical Oxygen Demand (mg/L)	At 4º C	Azide Modification of Iodometric Method
Total Dissolved Solid (mg/L)	At 4º C	Gravimetric Method
Hardness (mg/L)	At 4º C	EDTA Titrimetric Method
Nitrate (mg/L)	At 4º C	Bruzine Method
Total Phosphorous (mg/L)	At 4º C	Ascorbic Acid Method

3.3.2 Water in Large-scale Pig Farm

1) Water samples for heavy metal analysis were collected at one metre deep below surface water with water sampler. At each site the samples were collected at three sampling points. Then, the samples were stored in 100 ml polyethylene bottles .The bottles were rinsed twice with adequate of the sample water. To each sample bottle of 1 mL concentrated nitric acid was added and the bottle was stored in ice box prior to analyst in the laboratory (Diagomanolin *et al.*, 2004).

2) The chemical parameters for water quality were collected. Water were measured using equipments as shown in Table 3.5 in the field. Water samples were

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collected using water sampler and stored in BOD glass bottles for analysis of DO and BOD. To each sample glass bottles of 2 mL concentrated sulfuric acid was added. For analysis of nitrate and total phosphorous. Preservatives were added into the bottles when necessary. Water samples were stored at 4°C in the ice box and transferred to the laboratory.

The equipments and methods in analysis of water samplers are described in Standard Method for Examination of Water and Wastewater (APHA, 1995) and presented in Table 3.5.

Table 3.5: Chemical parameters for water quality in large-scale pig farm

Parameters analyzed in laboratory		
Dissolved Oxygen (mg/L)	At 4º C	Azide Modification of Iodometric Method
Biochemical Oxygen Demand (mg/L)	At 4º C	Azide Modification of Iodometric Method
Nitrate (mg/L)	At 4º C	Bruzine Method
Total Phosphorous (mg/L)	At 4º C	Ascorbic Acid Method

3.3.3 Sediment

Sediment samples were collected by using grab sampler. Each sampling site at least 1 km of sediment was collected and put in polyethylene bags that were tightly closed and kept away from sunlight (Sekhar *et al*., 2003; Kishe and Machiwa, 2003).

3.3.4 Aquatic plants

Ipomoea aquatica represented aquatic plants of the freshwater, about 10 branches (including roots and leaves) were randomly taken from the sampling sites and put into black plastic bags that were tightly closed. Figure 3.8 shows the dense clump of *Ipomoea aquatica* were taken for analysis.

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Figure 3.8: The dense clump of *Ipomoea aquatica* (freshwater plant)

3.3.5 Golden apple snail

Pomacea canaliculata were collected at sample sites in freshwater section. Because it was commonly found at studied area in fershwater section but not found in saltwater. The *P. canaliculata* samples were collected by hand-picking by the local people. Depending on size, 5-10 individuals of *P. canaliculata* were collected from each site. The *P. canaliculata* samples were kept in labelled plastic bags. The samples were immediately stored in an ice box during the transportation to the laboratory. Then they were stored in the freezer at around -20°C until dissection (Sekhar, *et a*l., 2003).

3.3.6 Feed

Feed samples were collected and put in polyethylene bags.

3.3.7 Sludge (Dry sludge)

Dry sludge samples were collected and put in polyethylene bags shown in Figure 3.9**.**

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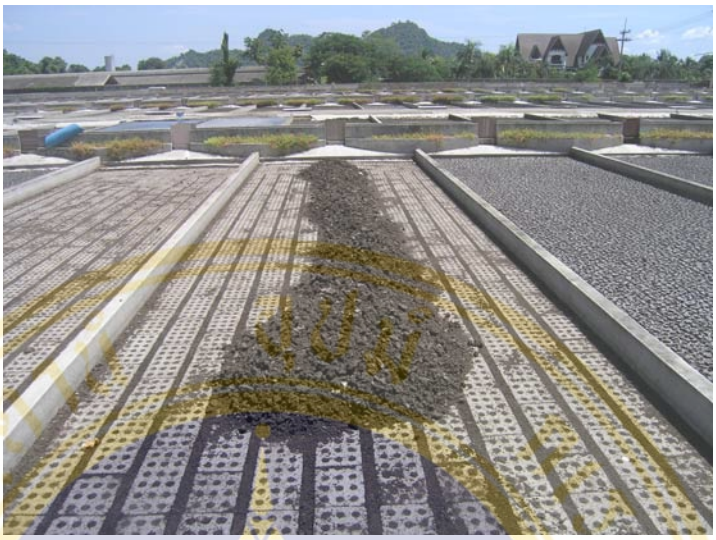

Figure 3.9: Dry manure in pig farm

3.4 Sample Preparation

3.4.1 Sediment

Samples of sediment were air-dried for 3 days and kept away from sunlight. Then, they were oven-dried at temperature 80°C for 1 day to constant weights and disaggregated and dry-sieved (Sekhar *et al*., 2003; Kishe and Machiwa, 2003).

3.4.2 Aquatic plants

Plant samples were washed thoroughly and rinsed with distilled water then divided into two sub-samples (shoot and root). The two sub-samples (Figures 3.10) were thoroughly washed again with running distilled water to remove dust particles. All plant samples were air-dried for 3 days. Then, they were oven-dried at 80°C for 1 day and milled in micro-hammer cutter to smaller particles.

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(a) Root **(b) Left**

Figure 3.10: Sub-samples of root (a) and left (b) of *Ipomoea aquatica*

3.4.3 Gloden apple snail *(Pomacea canaliculata)*

The frozen snail specimens were melted at room temperature by leaving specimens in beakers and their size were then recorded. Tissues of the snail were removed from the shell and cut into small pieces using the stainless steel knife. The samples were oven-dried at 80^0C to the constant weight. The dried tissues were ground in the baked clay mortage. The homogenized samples were kept in the plastic bags and then stored in the silica gel boxes for further analysis (Lau *et al*., 1998).

3.5 Sample Analysis

3.5.1 Sample Digestion

3.5.1.1 Water

A 10 ml of water sample was put into vessel and nitric acid (HNO_3 6 ml, 65%) was added to digest the samples (Karadede and Unlu, 2000).

3.5.1.2 Sediment

The fine fraction of dried sediment was weighed for 0.5 g (Kishe and Machiwa, 2003). and put into vessel. Nitric acid (10 ml, 65%) was added to remove organic matter in the sample.

3.5.1.3 Aquatic plants

The dried sub-samples of aquatic plants were weighed for 0.5 g and put into vessel. Nitric acid (8 ml, 65%) was added to digest the samples.

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3.5.1.4 Gloden apple snail

The dried sub-samples were weighed for 0.5 g and put into vessel. Nitric acid (8 ml, 65%) was added to digest the samples.

3.5.1.5 Feed

The dried feed was weighed for 0.5 g (Kishe and Machiwa, 2003). and put into vessel. Nitric acid (10 ml, 65%) was added to remove organic matter in the sample.

3.5.1.6 Dry sludge

The fine fraction of dried dry sludge was weighed for 0.5 g (Kishe and Machiwa, 2003). and put into vessel. Nitric acid (10 ml, 65%) was added to remove organic matter in the sample.

After completion of the microwave digestion program, the sample vessels were removed from the support module and the cover of vessel. All samples were filtered by filter paper (Whatman No.42) and transferred to 50 ml volumetric flask and then diluted to 50 ml with 1 percent of concentrated nitric acid. The samples were stored in 60 ml polyethylene bottle and kept in refrigerator until analysis.

3.5.2 Heavy Metal Analysis

The atomic absorption spectrophotometer was utilized for analyzing heavy metal that were contaminated in the water, sediment, aquatic plants, aquatic animal, feed and dry sludge. The analysis procedures are outlined below.

The glassware was cleaned by using nitric acid in order to exterminate any heavy metal on the surface. The cleaning was conducted by submerging the glassware under a solution of 10% HNO^-_3 for 15 minutes then wash with deionized water twice. This solution was poured into the glassware and shaken for a short period of time. Then clean it twice by using deionized water. The glassware should be dried prior to being used.

Heavy metals analysis in water, sediment, aquatic plants and aquatic animal, feed and dry sludge were determined in the digested solution, according to the expected concentrations Zn and Cu could be analysed by flame atomic absorbtion spectrometer (FAAS) while Cd was determined by graphite furnace atomic absorbtion spectrometer (GFAAS). GFASS was equipped with Zeeman background correction.

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The absorption lines for metals are 213.9 nm of zinc, 324.7 nm of copper and 228.8 nm of cadmium. Standards used for calibration for heavy metal determination with appropriate concentrations for each element were prepared from 1,000 ppm stock solution. The working solutions of each element were prepared by diluting the stock solution in a 50 ml volumetric flask with distilled water.

3.6 Laboratory Advance Instruments

3.6.1 Microwave Digestion System

Milestone-1200 mega microwave digestion system with MDR-technology was used in the study.

3.6.2 Graphite Furnace Atomic Absorption Spectrometer (GFAAS)

Measurements by GFAAS for heavy metals of Cd and Pb are shown in Figure 3.11 and performed using a Varian spectrAA 220Z grabhite furnace atomic absorption spectrophotometer.

Figure 3.11: Varian spectrAA 220Z graphite furnace atomic absorption spectrophotometer

3.6.3 Preparation of Reagents and Standard Solutions

All reagents are of analytical reagent grade. Distilled water were used throughout the study. All The plastics and glasswares were washed in 10 % of nitric acid for 10 minutes and rinsed with distilled water before use. Standard solutions of each metal were prepared by appropriate dilution of stock solutions of 1000 ppm J.T.

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Baker/E Merck standards and instrumental calibrated standard solutions were prepared from commercial materials

3.6.4 Atomic Absorption Detection

Metal concentrations: copper (Cu) and zinc (Zn) in the filtered digested samples were determined by flame atomic absorption spectrometer using air-acetylene flame. lead and cadmium were determined by graphite furnance atomic absorption spectrometer.

The absorption lines for metals are 213.9 nm of zinc, 324.7 nm of copper, 228.8 nm of cadmium, 248.3 nm of Iron and 217.0 nm of lead. Standard with appropriate concentrations for each element will be made from 1,000 ppm AAS stock standards.

3.7 Statistical Analysis

Statistical analysis of data will be carried out with the Excel progame to find out the mean and standard division (SD).

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CHAPTER IV
RESULTS

The results of the study are presented as follows:

1) Physico-chemical characteristics of water quality in the Huai Rong Canal system.

2) Cadmium (Cd) concentrations in the Huai Rong Canal system.

3) Accumulation of Cd in the Huai Rong Canal system.

4) Chemical characteristics of water quality in large-scale pig farm

5) Heavy metals in large-scale pig farm

6) Accumulations of Cd in large-scale pig farm

7) Sludge loading time of heavy metals in dry sludge (dry manure) from large-scale pig farm

4.1 Physico-chemical Characteristics of Water Quality in the Huai Rong Canal System

The physico-chemical parameters measured in water samples from the Huai Rong Canal were pH, temperature, dissolved oxygen (DO), biochemical oxygen demand (BOD), salinity, conductivity, transparency, hardness, total dissolved solids (TDS), phosphate (PO_4^{2-}) and nitrate (NO_3^-). The water samples were taken from two sites of the Huai Rong Canal every month during September 2005 to February 2006 (in total of 6 sampling times).

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4.1.1 Physico-chemical Characteristics of Water Quality at Site A (Wang Manao Sub-district)

The physico-chemical parameters of the water samples at site A were presented in Table 4.1.

The pH varied from 8.54 in September, being the lowest value, to 9.17 in December, being the highest value. The values in all months were within the range of the regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an ordinary treatment process and for agriculture which restricted pH values between 5 and 9 (PCD, 2006).

Temperature varied from 24.19ºC in December, being the lowest value, to 28.77ºC in September, being the highest value.

DO varied from 3.40 mg/L in October, being the lowest value, to 7.95 mg/L in December, being the highest value. Most of the DO values were accept, but exception of the DO value in September and October, were below the lowest regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an ordinary treatment process and for agriculture which restricted lowest limit at 4.00 mg/L (PCD, 2006).

BOD varied from 1.02 mg/L in November, being the lowest value, to 12.00 mg/L in January, being the highest value. The BOD values in October and November were accept, but most of the BOD values were exception and exceeded the lowest regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an ordinary treatment process and for agriculture which restricted highest limit at 2.00 mg/L (PCD, 2006).

Nitrate varied from 3.55 mg/L in February, being the lowest value, to 5.41 mg/L in December, being the highest value. Most of the nitrate values with the exception of the nitrate value in December, were below the highest regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an ordinary treatment process and for agriculture which restricted lowest limit at 5.00 mg/L (PCD, 2006).

Phosphate varied from 6.26 µg/L in November, being the lowest value, to 153.44 µg/L in January, being the highest value.

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TDS varied from 139.00 mg/L in October, being the lowest value, to 980.00 mg/L in January, being the highest value.

Conductivity varied from 0.10 ms/cm in November, being the lowest value, to 3.89 ms/cm in January, being the highest value.

Salinity varied from 0.10 ppt in November, being the lowest value, to 2.04 ppt in January, being the highest value presented in Table 4.1.

Hardness varied from 78.00 mg/L in October, being the lowest value, to 447.00 mg/L in January, being the highest value.

4.1.2 Physico-chemical Characteristics of Water Quality at Site B (Wan Dao Sub-district (Ban Khok Khi Lek))

The physico-chemical parameters of the water samples at site B were presented in Table 4.1.

pH varied from 8.45 in September, being the lowest value, to 9.43 in February, being the highest value. The values in December, January and February were higher than the range of the regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an ordinary treatment process and for agriculture which restricted pH values between 5 and 9 (PCD, 2006).

Temperature varied from 26.0°C in December, being the lowest value, to 28.9°C in September, being the high value.

DO varied from 2.13 mg/L in October, being the lowest value, to 8.35 mg/L in February, being the highest value. Most of the DO values were accepted, but the exception of the DO value in September and October, were below the lowest regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an ordinary treatment process and for agriculture which restricted lowest limit at 4.00 mg/L (PCD, 2006).

BOD varied from 0 mg/L in November, being the lowest value, to 6.20 mg/L in January, being the highest value. The BOD values in September, October and November were accepted, but in December, January and February were exception and exceeded the lowest regulated values of Thailand's Surface Water Quality Standards (1994) for Class 3 of water quality determined for consumption but passing through an

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ordinary treatment process and for agriculture which restricted highest limit at 2.00 mg/L (PCD, 2006).

Nitrate varied from 2.53 mg/L in January, being the lowest value, to 10.06 mg/L in December, being the highest value. Most of the nitrate values with the exception of the nitrate values in September, November and December, were below the highest regulated values of Thailand's Surface Water Quality Standards (1994) (PCD, 2006).

Phosphate varied from 6.06 µg/L in November, being the lowest value, to 65.00 µg/L in February, beimg the highest value.

TDS varied from 153.00 mg/L in November, being the lowest value, to 1,081 mg/L in January, being the highest value.

Conductivity varied from 0.22 ms/cm in November, being the lowest value, to 5.53 ms/cm in January, being the highest value.

Salinity varied from 0.10 ppt in November , being the lowest value, to 2.98 ppt in January, being the highest value .

Hardness varied from 65.00 mg/L in February, being the lowest value, to 560 mg/L in January, being the highest value.

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Table 4.1: Physico-chemical characteristics of water quality in the Huai Rong Canal system

Site	Month	Physico-chemical Characteristics of Water Quality									
		pH	Temperature (°C)	DO mg/L	BOD mg/L	Nitrate mg/L	Phosphate mg/L	TDS mg/L	Conductivity ms/cm	Salinity ppt	Hardness mg/L
A (Wang Manao sub-district)	September	8.54	28.77	7.10	2.15	4.60	0.0031	157	0.45	0.22	82
	October	8.58	28.57	7.95	4.79	4.31	0.0037	139	0.30	0.14	78
	November	9.15	28.31	3.45	1.02	4.60	0.0036	166	0.10	0.10	99
	December	9.17	24.19	3.40	1.83	5.41	0.0021	233	0.34	0.16	106
	January	8.56	26.07	4.67	12.00	3.62	0.0015	980	3.89	2.04	447
	February	8.85	28.10	5.33	3.37	3.55	0.0011	119	0.79	0.37	82
B (Ban Khok Khi Lek)	September	8.45	28.86	6.46	1.00	6.81	0.0028	245	0.45	0.22	104
	October	8.65	28.40	6.80	1.20	4.47	0.0035	173	0.41	0.20	91
	November	8.96	27.73	2.42	0.00	5.06	0.0065	153	0.22	0.10	94
	December	9.24	26.00	2.13	5.25	10.06	0.0030	307	0.42	0.20	124
	January	9.19	26.97	4.03	6.20	4.34	0.0047	1,080	5.53	2.98	560
	February	9.43	28.84	8.35	5.47	2.53	0.0006	167	0.38	0.18	65

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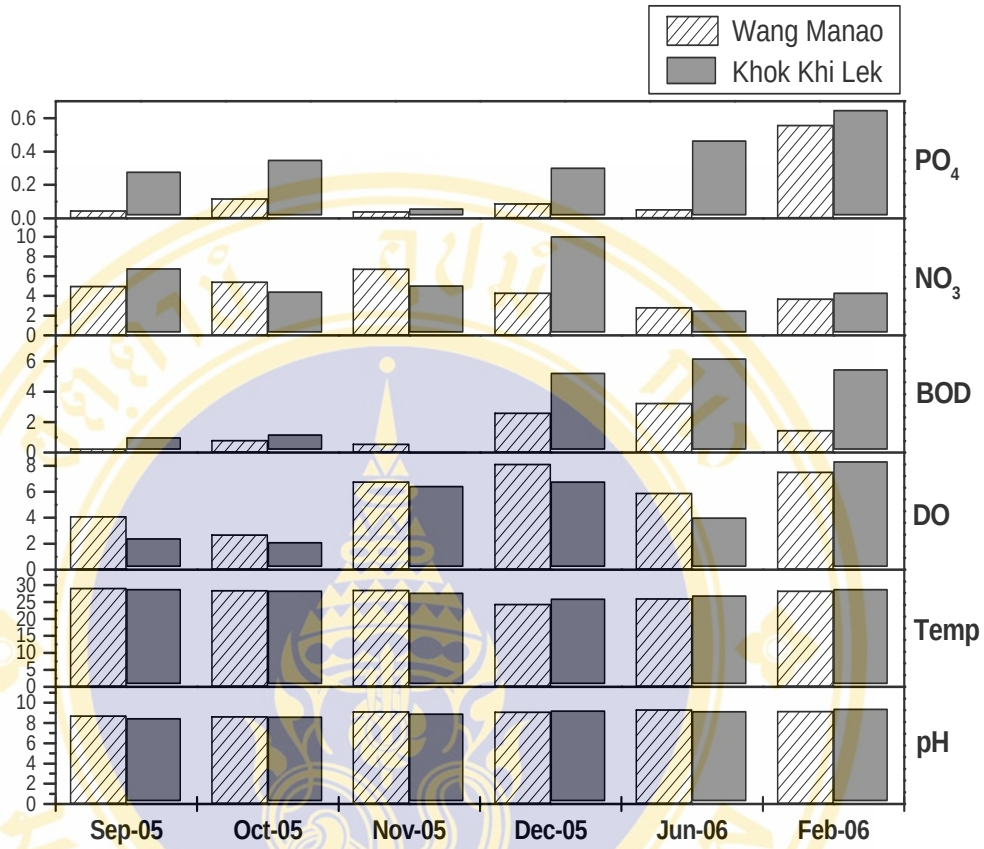

Figure 4.1 Distribution of physico-chemical characteristics of water quality in the Huai Rong Canal System

4.2 Cadmium (Cd) Concentrations in the Huai Rong Canal System

The mean concentrations of Cd in water reported as microgram of heavy metal per litre (µg/L) and in sediment, aquatic plants (in leaves and roots of *Ipomoea aquatica*) and golden apple snail (*Pomacea canaliculata*) reported as milligram of metal per kilogram dry weight (mg/kg, dry weight) of samples from the Huai Rong Canal system were carried out at two sites during September 2005 to February 2006. The results are presented in Table 4.2.

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4.2.1 Site A in Wang Manao Sub-district

4.2.1.1 Concentrations of Cd in water

The mean concentrations of Cd exhibited the lowest concentration of 0.002±0.001 µg/L in November and the highest concentration of 0.045±0.006 µg/L in October. Concentration of Cd in water at site A was below the regulated value of Thailand's Surface Water Quality standards (1994), which was restricted the highest value at 0.05 mg/L (PCD, 2006).

4.2.1.2 Concentrations of Cd in sediment

The mean concentrations of Cd exhibited the lowest concentration of 0.0015±0.0001 mg/kg dry weight in November and the highest concentration of 0.0104±0.0004 mg/kg dry weight in February. Concentrations of Cd in sediment at site A was below the regulated value of Thailand's Soil Quality Standards (1994) which was restricted the highest value at 37 mg/ kg dry weight (PCD, 2006).

4.2.1.3 Concentrations of Cd in aquatic plant (*I. aquatica*)

1) Leaf

The mean concentrations of Cd exhibited the lowest concentration of 0.003±0 mg/kg dry weight in December and the highest concentration of 0.0176±0.0017 mg/kg dry weight in February.

2) Root

The mean concentrations of Cd exhibited the lowest concentration of 0.005±0.0002 mg/kg dry weight in February and the highest concentration of 0.0084±0.0011 mg/kg dry weight in November.

4.2.1.4 Concentrations of Cd in golden apple snail (*P. canaliculata*)

The mean concentrations of Cd exhibited the lowest concentration of 0.002±0 mg/kg dry weight in January and the highest concentration of 0.0333±0.0042 mg/kg dry weight in September. The samples of golden apple snails were not found in December and February (Table 4.2). Concentrations of Cd in golden apple snail at site A was below the maximum permissible valuel of Cd at 1.0 mg/kg dry weight for bivalve molluscs suggested by European Communities (2001) (Usero et al., 2005) and the maximum value of Cd at 2.0 mg/kg dry weight for molluscs suggested by the Australia-New Zealand Food Standards Code (Usero et al., 2005).

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4.2.2 Site B in Wan Dao Sub-district (Ban Khok Khi Lek)

4.2.2.1 Concentrations of Cd in water

The mean concentrations of Cd exhibited the lowest concentration of 0.005±0.0004 µg/L in November and the highest concentration of 0.279±0 µg/L in January. Concentration of Cd in water at site A was below the regulated values of Thailand's Surface Water Quality Standards (1994), which was restricted the highest value at 0.05 mg/L (PCD, 2006).

4.2.2.2 Concentrations of Cd in sediment

The mean concentrations of Cd exhibited the lowest concentration of 0.0006±0 mg/kg dry weight in February and the highest concentration of 0.003±0.0007 mg/kg dry weight in October. Concentration of Cd in sediment at site A was below the regulated value of Thailand's Soil Quality Standards (1994) which was restricted the highest value at 37 mg/ kg dry weight (PCD, 2006).

4.2.2.3 Concentrations of Cd in aquatic plant (*I. aquatica*)

1) Leaf

The mean concentrations of Cd exhibited the lowest concentration of 0.0002±0.0004 mg/kg dry weight in December and the highest concentration of 0.0034±0.0005 mg/kg dry weight in October.

2) Root

The mean concentrations of Cd exhibited the lowest concentration of 0.0033±0.0008 mg/kg dry weight in December and the highest concentration of 0.0075±0.0014 mg/kg dry weight in September.

4.2.2.4 Concentrations of Cd in golden apple snail (*P. canaliculate*)

The mean concentrations of Cd exhibited the lowest concentration of 0.0025±0.0002 mg/kg dry weight in January and the highest concentration of 0.0788±0.0018 mg/kg dry weight in September. Concentration of Cd in golden apple snail at site A was below the maximum permissible valuel of Cd at 1.0 mg/kg dry weight for bivalve molluscs suggested by European Communities (2001) (Usero et al., 2005) and the maximum value of Cd at 2.0 mg/kg dry weight for molluscs suggested by the Australia-New Zealand Food Standards Code (Usero et al., 2005).

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Table 4.2: Concentrations of cadmium (Cd) (µg/L) at sites A and B in the Huai Rong Canal system

Month	Concentrations of Cd				
	Water (µg/L)	Sediment (mg/kg, dry weight)	Aquatic plant (*I. aquatica*) (mg/kg, dry weight)		Golden apple snail (*P. canaliculate*) (mg/kg, dry weight)
			Leaf	Root	
Site A					
September	0.035±0.007	0.0029±0.0004	0.0028±0.0011	0.0084±0.0011	0.0333±0.0042
October	0.034±0.004	0.0083±0.0013	0.0176±0.0017	0.0052±0.0004	0.0278±0.0000
November	0.002±0.001	0.0015±0.0001	0.0015±0.0003	0.0075±0.0004	0.0192±0.0038
December	0.047±0.007	0.0017±0.0009	0.0003±0.0000	0.0070±0.0006	-
January	0.045±0.006	0.0044±0.0008	0.0005±0.0000	0.0015±0.0001	0.0002±0.0000
February	0.070±0.006	0.0104±0.0004	0.0018±0.0007	0.0005±0.0002	-
Site B					
September	0.007±0.000	0.0011±0.0002	0.0028±0.0008	0.0075±0.0014	0.0788±0.0018
October	0.026±0.007	0.0008±0.0003	0.0034±0.0005	0.0057±0.0004	0.0260±0.0023
November	0.005±0.004	0.0006±0.0000	0.0011±0.0011	0.0073±0.0004	0.0147±0.0020
December	0.029±0.006	0.0022±0.0001	0.0003±0.0003	0.0053±0.0001	0.0029±0.0002
January	0.279±0.000	0.0030±0.0007	0.0002±0.0004	0.0047±0.0007	0.0025±0.0002
February	0.024±0.002	0.0029±0.0002	0.0003±0.0008	0.0033±0.0008	0.0025±0.0006

4.3 Accumulations of Cadmium (Cd) in the Huai Rong Canal System

Cd concentrations of the water and sediment samples of five sites of the Huai Rong Canal system taken in February 2006 are shown in Table 4.3.

The mean concentrations of Cd exhibited the lowest concentration of 0.0023±0 µg/L at site c and the highest concentration of 0.0042±0 µg/L at site B. Concentrations of Cd in water at all sites were below the regulated value of Thailand's Surface Water Quality Standards (1994), which was restricted the highest value at 0.05 mg/L (PCD, 2006).

The mean concentrations of Cd exhibited the lowest concentration of 0.00080±0.00005 mg/kg dry weight and the highest concentration of 0.00999±0.000194 mg/kg dry weight. Concentrations of Cd in sediment at all sites

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were below the regulated value of Thailand's Soil Quality Standards (1994) which was restricted the highest value at 37 mg/ kg dry weight (PCD, 2006).

Table 4.3: Accumulations of cadmium (Cd) (µg/L) in the Huai Rong Canal System

Sampling site	Concentration of Cd	
	Water (µg/L)	Sediment (mg/kg, dry weight)
A	0.0033±0.00014	0.00256±0.000476
a*	0.0028±0.00008	0.00153±0.000606
b*	0.0032±0.00004	0.00080±0.000050
c*	0.0023±0.00000	0.00999±0.000194
B	0.0042±0.00000	0.00250±0.000246

Remark: * a, b and c are the sites between sites A (Wang Manao Sub-district) and B (Wan Dao Sub-district)

4.4 Chemical Characteristics of Water Quality in Large-scale Pig Farm

The chemical parameters measured in water samples of large-scale pig farm in Pak Tho District, Ratchaburi Province were dissolved oxygen (DO), biochemical oxygen demand (BOD), phosphate (PO_4^{2-}) and nitrate (NO_3^-). The water samples were taken from biogas system of large-scale pig farm (in total of 7 sampling sites) in February 2006 (Table 4.4).

DO varied from 0 mg/L in collector tank, UASB reactor 1 and UASB reactor 2, being the lowest values, to 7.95 mg/L in reuse water, being the highest value.

BOD varied from 2.11 mg/L in collector tank, being the lowest value, to 17.79 mg/L in wetland 1, being the highest value. The BOD values of all sampling sites were below the regulated value of Thailand's Effluent Standard for Pig Farm (2005) for large-scale pig farm with the total pigs of more than 5,000 which was restricted the highest value at 60 mg/L (PCD, 2006).

Nitrate varied from 9.23 mg/L in reuse water, being the lowest value, to 37.99 mg/L in collector tank, being the highest value.

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Phosphate varied from 178.49 mg/L in collector tank, being the lowest value, to 244.02 µg/L in wetland 3, being the highest value.

Table 4.4: Chemical characteristics of water quality in large-scale pig farm

Sampling site	Chemical parameters			
	DO (mg/L)	BOD (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)
Collector tank	0	2.11	37.99	178.49
UASB reactor 1	0	2.75	21.15	209.59
UASB reactor 2	0	3.45	18.53	222.57
Wetland 1	0	4.70	24.95	225.61
Wetland 2	3.95	4.45	10.38	226.21
Wetland 3	16.10	3.80	11.87	244.02
Reuse water	17.79	1.90	9.23	241.93

4.5 Heavy Metals in Large-scale Pig Farm

Heavy metal concentrations measured in the biogas system of large-scale pig farm in Pak Tho District, Ratchaburi Province were Cadmium (Cd), Copper (Cu) and Zinc (Zn). The samples from 7 sampling sites were taken in February 2006. The mean concentrations of Cd in water exhibited the lowest concentration of 0.001±0.0023 µg/L in reuse water and the highest concentration of 0.245±0.0705 µg/L in collector tank**.** Concentrations of Cd in water of all sampling sites were below the regulated value of Thailand's Surface Water Quality Standards (1994), which was restricted the value at 0.05 mg/L (PCD, 2006) as shown in Table 4.5.

The mean concentrations of Cu in water exhibited the lowest concentration of 0 mg/L in reuse water and the highest concentration of 0.182±0.056 mg/L in collector tank. The highest concentrations of Cu in water of all sampling sites were above the regulated value of Thailand's Surface Water Quality Standards (1994), which was restricted the highest value at 0.1 mg/L (PCD, 2006).

The mean concentrations of Zn in water exhibited the lowest concentration of 0.033±0.023 µg/L in reuse water and the highest concentration of 0.306±0.049 µg/L in collector tank. The highest concentrations of Zn in water of all sampling sites were

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below the regulated value of Thailand's Surface Water Quality Standards (1994), which was restricted the highest value at 1.0 mg/L (PCD, 2006).

The mean concentrations of Cd in sediment exhibited the lowest concentration of 0.0010±0.0001 mg/kg dry weight in wetland 3 and the highest concentration of 0.0064±0.0013 mg/kg dry weight in wetland 1. Concentrations of Cd in sediment of all sampling sites was below the regulated value of Thailand's Soil Quality Standards (1994) which was restricted the highest value at 37 mg/ kg dry weight (PCD, 2006).

Table 4.5: Concentrations of heavy metals in large-scale pig farm

Sampling sites	Water			Sediment
	Cd (µg/L)	Cu (mg/L)	Zn (mg/L)	Cd (mg/kg dry weight)
Collector tank	0.245±0.0705	0.182±0.056	0.306±0.049	-
UASB reactor 1	0.122±0.0703	-	-	-
UASB reactor 2	0.038±0.0058	-	-	-
Wetland 1	0.041±0.0040	-	-	0.0064±0.0013
Wetland 2	0.018±0.0085	-	-	0.0015±0.0005
Wetland 3	0.002±0.0032	-	-	0.0010±0.0001
Reused water	0.001±0.0023	0.000	0.033±0.023	-

The results of Cd concentrations in pig feeds and dry sludge (dry manure) are presented in Table 4.6. When compared the three pig feeds, the mean concentrations of Cd exhibited the lowest concentrations of 0.026±0.0016 mg/kg dry weight in feed 1 and the highest concentrations of 0.151±0.0024 mg/kg dry weight in feed 2. It was also found that Cd concentrations in sludge (1.440±0.3388 mg/kg dry weight) were about 56 times higher than those in feeds 1 and 3 and about 10 times higher than those in feed 2.

The mean concentrations of Cu exhibited the lowest concentrations of 0.363±0.021 mg/kg dry weight in feed 3 and the highest concentrations of 1.326±0.230 mg/kg dry weight in feed 2. The results showed that Cu concentrations in sludge (803.7±24.74 mg/kg, dry weight) were about 2,214 times higher than those in feed 3 and about 1,272 times higher than those of feed 1 and about 606 times higher than those of feed 2.

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The mean concentrationss of Zn exhibited the lowest concentrations of 1.151±0.112 mg/kg dry weight in feed 3 and the highest concentrations of 8.110±2.303 mg/kg dry weight in feed 1. The results showed that Zn concentrations in sludge (1013.4±200.2 mg/kg dry weight) were about 880 times higher than those in feed 3, about 465 times higher than those in feed 2 and about 125 times higher than those in feed 1.

Table 4.6: Concentrations of heavy metals in pig feeds and dry sludge (dry manure)

Sample	Source	Cd (mg/kg dry weight)	Cu (mg/kg dry weight)	Zn (mg/kg dry weight)
Feed 1	Large-scale pig farm	0.026±0.0016	0.632±0.151	8.110±2.303
Feed 2	Market in Pak Tho District	0.151±0.0024	1.326±0.230	2.179±0.186
Feed 3	Market in Pak Tho District	0.036±0.1820	0.363±0.021	1.151±0.112
Dry sludge	Large-scale pig farm	1.440±0.3388	803.7±24.74	1013.4±200.2

4.6 Accumulations of Cadmium (Cd) in Large-scale Pig Farm

The accumulation of Cd in large-scale pig farm, Pak Tho District, Ratchaburi Provinces was calculated based on the following data:

-Pig feed of 5 kg/day (Jirapan, 2006).

-Total pig number of 15,000 (Energy Policy and Planning Office, 2008)

-Total dry sludge 1,000 kg/day (Energy Policy and Planning Office, 2008)

-Cd concentration in feed of 0.026 mg/kg dw/day as shown in Table 4.6

-Cd concentration in sludge of 1.440 mg/kg dw/day as shown in Table 4.6

Total feed used = 15,000 pigs x 5 kg/day

= 75,000 kg/day

Total Cd concentration in feed = 0.026 mg/kg dw/day x 75,000 kg/day

= 1,950 mg/kg dw/day

Total Cd concentration in sludge = 1.44 mg/kg dw/day x 1,000 kg/day

= 1,440 mg/kg dw/day

So, Cd amount accumulated in the large-scale pig farm is as follows:

= Total Cd amount in feed - Total Cd amount in sludge

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= 1,950 mg/kg dw/day - 1,440 mg/kg dw/day

= 510 mg/kg dw/day

4.7 Sludge Loading Time of Heavy Metals in Dry Sludge (Dry Manure) from Large-scale Pig Farm

Heavy metals from pig farms can disperse to environment by utilization of sludge as feed and fertilizer that has important nutrients for plants as presented in Table 2.3. Sludge loading time represents the time limit (in year) for application of the dry manure in agriculture by heavy metal contents in soil. Calculation of sludge loading time can be carried out as described by Mhowyathai and Sripanomtanakorn (1995). Concentrations of heavy metals in dry sludge (dry manure) for calculating limitation as fertilizers depend on plant-available nitrogen from the relation of equations (1) and (2).

$$\mathbf{S_N = U_N / N_p} \quad (1)$$

whereas S_N = Annual sludge loading, ton/(ha-year)

U_N = Crop N uptake, kg N/(ha-year)

N_p = Plant-available N in sludge, kg N/dry ton

$$\mathbf{N_p = NO_3\text{-}N + K_v (NH_4\text{-}N) + f_v (ON)} \quad (2)$$

whereas NO_3 = Nitrate in sludge, kg N/dry ton

K_v = Volatilization factor

NH_4^+ = Ammonia N in sludge, kg N/dry ton

f_v = Mineralization factor for first year

ON = Organic N in sludge, kg N/dry ton

And sludge loading time that was limited by heavy metal contents accumulated in soil can be determined by equation (3).

$$\mathbf{T_N = C_{limit} / S_N \times C_{heavy\ metal}} \quad (3)$$

whereas T_N = Time of sludge loading, year

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C_{limit} = Cumulative pollutant loading limits, kg/ha

S_N = Calculated from equation (1)

$C_{heavy\ metal}$ = Heavy metal concentration in sludge, kg/ton

Qualifications of sludge used in equation 1 are presented in Table A-2 of Appendix. Calculation of plant-available N in sludge is determined using values suggested in Mhowyathai and Sripanomtanakorn (1995) which are as follows: Total N = 21.3 kg/ton, NH_4^+ = 1.29 kg/ton and $NO_2^- + NO_3^-$ = 0.039 kg/ton. From Table 4.6, heavy metal contents are converted from mg/kg dw into kg/ton dw and the results obtained are as follows: Cu = 0.803 kg/ton, Zn = 1.013 kg/ton, Cd = 0.0014 kg/ton. The additional parameters are K_v = 0.5 (surface application), U_N = 300 kg N/(ha-year) and f_v = 0.35 (estimated from the research that determined f_v value of wastewater sludge from anaerobic decomposition in Thailand with the range of 0.27-0.42 (Sripanomtanakorn and Polprasert, 2002)). Culmulative pollutant loading limits according to US. EPA as presented in Table A-2 of Appendix are used in the calculation of equation (3).

The results from equation (3) showed that time of sludge loading are as follows: T_{Cu} = 47.79 year, T_{Zn} = 70.71 year, and T_{Cd} = 712.98 year. Therefore Cu content determined the safe period for application of sludge to crop is 47.79 years.

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CHAPTER V
DISCUSSIONS

5.1 Water Quality of the Huai Rong Canal System

The Huai Rong, Pradu and Rang Thap Tap Canals are the connection of the canal system of Ratchaburi and Samut Songkhram Provinces. The Huai Rong Canal is a canal in Ratchaburi Province that flows into the Pradu Canal. The Rang Thap Tap Canal is a small waterway that branches out from the Pradu Canal, a tributary of the Mae Klong River. The Pradu Canal flows into the Yi San Canal and the latter ends up at the Gulf of Thailand at Ban Tabun District, Phetchaburi Province. The results indicated that monthly variation influencing on the physico-chemical characteristics of water quality of the Huai Rong Canal during September 2005 to February 2006 of sites A (Wang Manao Sub-district, Pak Tho District, Ratchaburi Province) and B (Wan Dao Sub-district, Pak Tho District, Ratchaburi Province). The six-month period of sample collection can be categorised based on the classification of Thailand Meteorological Department (2007) as follows: mid May to mid October being the rainy season, mid October to mid February being the cool season and mid February to mid May being the dry season. Therefore in the present study, only two seasons are covered, i.e., September and October as the rainy season and Nonember to February as the cool season.

Site A, observed in Wang Manao Sub-district received major pollution from pig farms and paddy fields. It was found that water temperature values in both the rainy and warm seasons were higher than those in the cool season (Table 4.1). The pH values varied from 8.54 to 9.17 representing rather high alkalinity in the canal water and this may be due to the major rock type in Ratchaburi Province which is limestone rock. The study of Jantarawattana (2006) in the Huai Rong Canal during June 2004 to April 2005 found pH values of the canal water varying from 7.29 to 7.81.

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Roachanakanan (2005) carried out the study in the Haui Rong Canal during March to July 2005 found pH values varying from 6.76 (March) to 8.16 (July). The only pH values in November and December were higher than the regulated values Class 3 (5.0 to 9.0) for Surface Water Quality Standards (PCD, 2006) and the US. EPA criteria (6.5 to 9.0) for freshwater life (US. EPA, 1986 cited by Rios-Arana et al., 2003). The dissolved oxygen (DO) values varied from 3.40 to 7.95 mg/L. Only the DO values of November and December (the cool season) were below the minimum requirement for Class 3 of the Surface Water Quality Standards (4.00 mg/L: PCD, 2006). Low DO values in the cool and early warm seasons (3.45, 3.40 and 4.67 in November, December and January, respectively) when compared with those in the rainy season (7.10 and 7.95 in September and October, respectively) indicated the low turbulence which causes less oxygen dissolved in water (Jayaprakash et al., 2005). The biochemical oxygen demand (BOD) values of water samples from site A varying from 1.02 to 12.00 mg/L. The phosphate values varied from 0.0011 to 0.0037 mg/L. The nitrate values varied from 3.55 to 5.41 mg/L. In December, the nitrate value at site A (5.41 mg/L) was higher than the regulated value for Class 3 of the Surface Water Quality Standards (not more than 5.0 mg/L: PCD, 2006). In December paddy field farmers (paddy field was the major activity in the area around the Huai Rong Canal) discharged wastewaters from the fields into the canal before harvesting the rice grains (Jantarawattana, 2006). The wastewater from the paddy fields was the nitrogen enrichment water. The hardness values of site A varied from 78 to 447 mg/L as $CaCO_3$, alkalinity levels increased in December and reached the highest in January (the cool season) (more than 300 mg/L as $CaCO_3$ as very hard water level: Malee (2002)). In the rainy season, the hardness values (99 to 106 mg/L as $CaCO_3$) were lower than 300 mg/L as $CaCO_3$ therefore it can be categorised as moderately hard water level (75 to 150 mg/L as $CaCO_3$: Malee (2002)). The conductivity values varied from 0.10 to 3.89 ms/cm. The high conductivity value was in January while the values in other months were low (lower than 1 mS/cm). Similarly, the high salinity value (2.04 ppt) was in January while the values in other months were low (lower than 0.5 ppt). The total dissolved solids (TDS) of water samples at site A varied from 139 to 980 mg/L. TDS values increased in the cool season (January) (more than 500 mg/L) and were slightly low in the warm and rainy seasons. The relationship of water quality

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parameters of TDS, conductivity, salinity and hardness can be clearly observed as shown in Table 4.1.

Site B, observed in Wan Dao Sub-district received major pollution from pig farms and paddy fields. It was found that water temperature values in both the rainy and warm seasons were higher than those in the cool season (Table 4.1). The pH values varied from 8.45 to 9.43 representing rather high alkalinity in the canal water and this may be due to the major rock type in Ratchaburi Province which is limestone rock. The study of Jantarawattana (2006) in the Huai Rong Canal during June 2004 to April 2005 found pH values of the canal water varying from 7.29 to 7.81. Roachanakanan (2005) carried out the study in the Haui Rong Canal during March to July 2005 found pH values varying from 6.76 (March) to 8.16 (July). The only pH values in December, January and February were higher than the regulated values Class 3 (5.0 to 9.0) for Surface Water Quality Standards (PCD, 2006) and the US. EPA criteria (6.5 to 9.0) for freshwater life (US. EPA, 1986 cited by Rios-Arana et al., 2003). The dissolved oxygen (DO) values varied from 2.13 to 8.35 mg/L. Only the DO values of November and December (the cool season) were below the minimum requirement for Class 3 of the Surface Water Quality Standards (4.00 mg/L: PCD, 2006). Low DO values in the cool and early warm seasons (2.42, 2.13 and 4.03 in November, December and January, respectively) when compared with those in the rainy season (6.46 and 6.80 in September and October, respectively) indicated the low turbulence which causes less oxygen dissolved in water (Jayaprakash et al., 2005). The biochemical oxygen demand (BOD) values of water samples from site B varying from 0 to 6.20 mg/L. The phosphate values varied from 0.0006 to 0.0065 mg/L. The nitrate values varied from 2.53 to 10.06 mg/L. In September, November and December the nitrate value at site B (6.81, 5.06 and 10.06 mg/L, respectively) was higher than the regulated value for Class 3 of the Surface Water Quality Standards (not more than 5.0 mg/L: PCD, 2006). In December paddy field farmers (paddy field was the major activity in the area around the Huai Rong Canal) discharged wastewaters from the fields into the canal before harvesting the rice grains (Jantarawattana, 2006). The wastewater from the paddy fields was the nitrogen enrichment water. The hardness values of site B varied from 65 to 560 mg/L as $CaCO_3$, alkalinity levels increased in December and reached the highest in January (the cool season) (more than 300 mg/L

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as $CaCO_3$ as very hard water level: Malee (2002)). In the rainy season, the hardness values (94 to 124 mg/L as $CaCO_3$) were lower than 300 mg/L as $CaCO_3$ therefore it can be categorised as moderately hard water level (75 to 150 mg/L as $CaCO_3$: Malee (2002)). The conductivity values varied from 0.22 to 5.53 ms/cm. The high conductivity value was in January while the values in other months were low (lower than 1 mS/cm). Similarly, the high salinity value (2.98 ppt) was in January while the values in other months were low (lower than 0.5 ppt). The total dissolved solids (TDS) of water samples at site B varied from 153 to 1,080 mg/L. TDS values increased in the cool season (January) (more than 500 mg/L) and were slightly low in the warm and rainy seasons. The relationship of water quality parameters of TDS, conductivity, salinity and hardness can be clearly observed as shown in Table 4.1.

5.2 Cadmium (Cd) Concentrations in the Huai Rong Canal System

In the study area of the Huai Rong Canal System of the Mae Klong River, Ratchaburi Province at sites A and B, the major contributors to water pollution were from small- and medium-scale pig farms and paddy fields. Although there were households of local community scattered in the study area however the present study did not take into account of domestic wastewater. The local people normally discharged wastewater into the soil and due that the soil type in the area is sand clay soil that has pH of 7 to 8 (Land Development Department, 2000), Cd precipitation and accumulation are well developed in this kind of soil (Schouw and Tjell, 2003).

The results showed that high concentrations of Cd in water and sediment of sites A and B were found in the cool and early warm seasons whereas high concentrations of Cd in *I. aquatica* and *P. canaliculate* were found in the rainy season (Table 4.2). From the results as shown in Table 4, it was found that pH values were alkaline therefore Cd can not be in water and precipitate into the sediment (Baker et al. 1979). Cd starts precipitating from water and accumulate in sediments (Baker et al., 1979). As the consequence, concentrations of Cd in sediment (0.0006±0 to 0.0104±0.0004 mg/kg dry weight). And the data expressed the concentration of Cd in aquatic plant (*I. aquatica*) (0.0002±0.0004 to 0.0176±0.0017 mg/kg dry weight) and golden apple snail (*P. canaliculate*) (0.0002±0 to 0.0788±0.0018 mg/kg dry weight). The tendency for

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maximum concentration of Cd during the early warm to rainy seasons, due to the increased physiological activity of aquatic life for the duration of the mating period and the warm season when feeding and exchange processes mark a maximum, conform with the studied at the Topolitsa Dam, situated on the Topolnitsa River in Southern Bulgaria. It encompassed the seasons winter, spring and summer of 2000. A seasonal variation of the content of Cd in two studied species of fish (*Perca fluviatilis* and *Alburnus alburnua*). The contents of Cd by seasons increase in the order winter< spring< autumn< summer (Velcheva, 2002). In the present studied the highest Cd value in aquatic life was found in the dry season however the different findings in other seasons were suggested.

When comparing the concentrations of Cd in four samples during the study period from September 2005 to February 2006, it can be presented as the followings:

Golden apple snail (*P. canaliculata*)> Root of *I. aquatica*> Sediment> Leaf of *I. aquatica*

The present result shows that Cd concentrations in *P. canaliculata* were the highest (0.0002 to 0.0788 mg/kg dry weight), followed by root of *I. aquatica* (0.0005 to 0.0084 mg/kg dry weight), sediment (0.0006 to 0.0104 mg/kg dry weight), leaf of *I. aquatica* (0.0002 to 0.0176 mg/kg dry weight), and water were the lowest (0.002 to 0.279µg/L). The correlation showed that sediments accumulated Cd from the water in canal and roots of *I. aquatica* uptake the heavy metals from waters and subsequently translocate to leafs of the plants to grow up. Most of Cd concentrations in golden apple snail *(P. canaliculata*) correlated to those in sediment more than in water and aquatic plant. This result support that the most concentration of Cd are in golden apple snail *(P. canaliculata*) and root of *I. aquatica*.

When comparing, concentrations of Cd in *P. canaliculata*, present studied were lower than Pollution Control Departmaent (PCD, 2006) and the regulated value of Waste and Hazardous Substance Management Bureau (Sakeaw, 2001), presented in Table 5.1.

In sediment, concentrations of Cd were lower than the regulated value of Soil Quality Standards (PCD, 2006), Environmental Protection Agency (ATSDR, 2000), Computer Environmental Legislative Data System (ATSDR, 2000) and higher than in Australia (Thailand, Fish Inspection and Quality Control Division, 2007) and when

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comparing the value from the same area of studied, they were similar, the canal system of Mae Klong River, Thailand (Jantarawattana, 2006) presented in Table 5.1.

The concentrations of Cd in *I. aquatica* (leaf and root), present studied were lower than Pollution Control Department (PCD, 2006) and when comparing the value from the same area of studied, they were similar, the canal system of Mae Klong River, Thailand (Jantarawattana, 2006) presented in Table 5.1. But when comparing value had higher than the canal near Vipavadee Rangsit Road, Thailand (Chavengsuksopak, 1990) The study of bioaccumulation and detection of trace level of Cd in aquatic systems by *Eichhornia crassipes*'s roots have high concentrate of Cd more than tops, comformation with present study is the *Ipomoea aquatica*' roots that have high concentrate of Cd more than leaf (Wolvertan and McDonald, 1978) that conform with the result, Cd accumulation to root of *I. aquatica* was higher than leaf of *I. aquatica* because *E. crassipes* and *I. aquatica* were the plant that live in freshwater and float on water as well.

The concentrations of Cd in water, present study are lower than the regulated value of Surface Water Quality Standards (PCD, 2006), Environmental Protection Agency (ATSDR, 2000), Computer Environmental Legislative Data System (ATSDR, 2000) and when comparing the value from the same area of study, they had a little hight valure than the canal system of the Mae Klong River (Jantarawattana, 2006) presented in Table 5.1.

In Table 5.1, Cd concentrations in water, sediments, aquatic plant (*I. aquatica*) and golden apple snail (*P. canaliculate*) in the Huai Rong Canal, the Mae Klong River, Ratchaburi Province are comparable with those found in the previous studies and the Surface Water Quality Standards, Thailand and other standards.

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Table 5.1: Concentrations of cadmium (µg/L) in the Huai Rong Canal of Thailand and other literature values

Reference	Concentrations of cadmium				
	Water (µg/L)	Sediment (mg/kg dw)	Aquatic plant (mg/kg dw)		Aquatic animal (mg/kg dw)
			I. aquatica		
			Leaf	Root	*P. canaliculata*
Present Study	0.002-0.445	0.006-0.135	0.019-1.757	0.051-0.841	0.015-7.875
Pollution Control Department[a]	0.5** (mg/L) 0.05*** (mg/L)	< 37	0.2 ppm		1 ppm
The canal system of Ratchaburi and Samut Songkhram Provinces, Thailand[b]	ND-0.139	0-0.091	ND-0.097		-
The canal near Vipavadee Rangsit Road, Thailand[c]	-	-	ND-0.0038		-
Mae Sot District, Tak Province, Thailand[d]	-	0.3-326	-		-

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Table 5.1: Concentrations of cadmium (µg/L) in the Huai Rong Canal of Thailand and other literature values (continuous)

Reference	Concentrations of cadmium				
	Water (µg/L)	Sediment (mg/kg dw)	Aquatic plant (mg/kg dw)		Aquatic animal (mg/kg dw)
			I. aquatica		
			Leaf	Root	*P. canaliculata*
Present Study	0.002-0.445	0.006-0.135	0.019-1.757	0.051-0.841	0.015-7.875
Waste and Hazardous Substance Management Bureau [e]	50	-	-		1 ppm
Environmental Protection Agency [f]	< 3.9	< 0.8	-		-
Computer-Environmental Legislative Data System [g]	< 10	< 15	-		-
In Australia [h]	2	0.04-2.0 ppm	-		-

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Remarks:

a PCD, 2006

b Jantarawattana, 2006

c Chavengsuksopak, 1990

d Swaddiwudipong *et al.*, 2004

e Sakeaw, 2001

f ATSDR, 2000

g ATSDR, 2000

h Thailand, Fish Inspection and Quality Control Division, 2007

* water hardness not more than 100 mg/L as $CaCO_3$

** water hardness more than 100 mg/L as $CaCO_3$

The present result shows that Cd concentrations in water, sediment, aquatic plant (*I. aquatica*) and aquatic animal (*P. canaliculata*) were below the lowest regulated value of the U. S. Environmental Protection Agency, 2000. In the future of Huai Rong Canal, small and medium-scale pig farms may increase and discharged more wastewater to canal. If the wastewater management systems are not going to improve, accumulation of Cd in aquatic life will increase and effect ecology system.

5.3 Cadmium (Cd) Accumulation in the Huai Rong Canal System

During the study accumulations of Cd from the water and the sediment samples were taken from five sites and collected on February 2006. can be presented as the followings:

5.3.1 Accumulation of Cd in water

The results showed that Cd were accumulated at five sites, have the nearly equal value because in this canal had the high pH values (pH 8.45 to 9.43 in September 2005 to February 2006) Cd start precipitating from water and accumulated in sediments, so these values could not determine the accumulations of Cd.

5.3.2 Accumulation of Cd in sediment

b < B < a < A < c.

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*a, b and c are the sites between A (Wang Manao Sub-district) and B (Wan Dao Sub-district)

The results showed that Cd were intensely accumulated at site c because this site have a lot of medium and small-scale pig farms were here, while they were slightly accumulated at site b.

Then there were the Cd analysis from the quality of water treatment system of the large-sacle pig farm in order to compare the Cd concentration of small and medium-scale pig farms that do not have proper wastewater treatment system. By using the Cd concentration analysis from the Huai Rong Canal to represent in comparing.

5.4 Water Quality in the Large-scale Pig Farm

The results influenced on the chemical characteristics of water quality in large-scale pig farm system are presented as followings:

Reuse water> Wetland 3> Wetland 2> Wetland 1> UASB reactor 2> UASB reactor 1> Collector tank

The reuse water had the highest DO value (17.79 mg/L) and the lowest BOD value (1.90 mg/L). In collector tank, UASB reactor 1 and UASB reactor 2 had the lowest DO value (0 mg/L) and the BOD value ranged from (2.11-4.7 mg/L). The quantity of the water will be better respectively from these steps of wastewater treatment, but in wetland had BOD value higher than collector tank and UASB reactor because algae in wetland used a lot of oxygen at noon, so BOD value from sampling at wetland was higher. The quantity of the water will be better respectively from these steps of wastewater treatment.

5.5 Heavy Metal Concentrations in the Large-scale Pig Farm

Comparing the concentrations of Cadmium (Cd), Copper (Cu) and Zn (Zinc) were taken from seven sites in biogas wastewater treatment system in large-scale pig system farm are presentd as followings:

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Collector tank> UASB reactor1> UASB reactor2> Wetland 1> Wetland 2> Wetland 3> Reused water

The collector tank had the highest concentration of Cd (0.245 µg/L), Cu (0.182 mg/L) and Zn (0.306 mg/L) values, when flow the wastewater to biogas wastewater treatment system (UASB reactor 1, UASB reactor 2, Wetland 1, Wetland 2 and Wetland 3, respectively). The resued water had the lowest concentration of Cd (0.001 µg/L), Cu (0 mg/L) and Zn (0.033 mg/L). In this result the biogas wastewater treatment system could reduce Cd 99.59 %, Cu 100 % and Zn 89.22 %.

When comparing the concentrations of Cd in wetland (water and sediment). The sediment had the highest concentration of Cd, because the pH value of water in wetland had 5.5-9 so Cd precipitation and accumulation are well in this kind of sediment and it was up to wetland, if wetland had been use for a long time, accumulation of Cd would be high.

5.6 Accumulations of Cadmium (Cd) in Large-scale Pig Farm

Comparing the concentrations of the Cd were taken from feed and sludge (warm manure), large-scale pig farm, Pak Tho District, Ratchaburi Province. Total concentrations of Cd accumulation content in this large-scale pig farm had 510 mg/kg dw/day (total concentration of Cd in feed - total concentration of Cd in sludge). May remain in pig body, wastewater treatment system and sediment of wetland. From the experiment, It was found that high concentration of Cd content are from sediment of wetland (0.0010-0.0064 mg/kg, warm weight).

5.7 Sludge Using Rate for Fertilizers

Concentrations of Cd, Cu and Zn in manure and sludge of the large-scale pig farm in the present study are lower than those studied by Mhowyathai and Sripanomtanakorn (2005) from 13 pig farms in Ratchaburi and Nakhon Pathom Provinces (Table 5.2). All heavy metal concentrations when comparing the are lower than the value from () and the values were within the range of the regulated values of

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quality concentration limits of United States of America, Germany and France (Mhowyathai and Sripanomtanakorn, 2005).

Table 5.2: Characteristics of manure and sludge of large-scale pig farms and literature

Parameter	Present Study (mg/kg dry weight)		Mhowyathai and Sripanomtanakorn, 2005 (mg/kg dry weight)		US. EPA [a]	Germany [b]	France [c]
	Manure	Sludge	Manure	Sludge			
pH	-	-	7.80	7.17	-	-	-
Organic C (%)	-	-	37.92	27.45	-	-	-
TS (%)	-	-	84.13	91.00	-	-	-
Total N (%)	-	-	2.76	2.13	-	-	-
NH_4^+ (mg/kg)	-	-	1357.80	1289.20	-	-	-
NO_2^- + NO_3^- (mg/kg)	-	-	53.80	39.20	-	-	-
Cu (mg/kg)	18.20	803.70	219.20	1260.80	1500	1200	1500
Zn (mg/kg)	30.60	1013.40	736.30	4477.30	2800	3000	3000
Cd (mg/kg)	0.025	1.44	2.90	4.40	39	20	40
T_{Cu} (year)		47.79					
T_{Zn} (year)		70.71					
T_{Cd} (year)		712.98					

Source: Mhowyathai and Sripanomtanakorn, 2005

Remarks: a United State Environmental Protection Agency, 1995
b Smith, 1996
c Smith, 1996

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To determine the time for safe using sludge that is about 48 years Using sludge before this time may cause concentration of Zn accumulation in soil that is harmful to the plant (Mhowyathai and Sripanomtanakorn, 2005).

Comparing between Cd contents in the water in the Huai Rong Canal and the large-scale pig farms, small and medium-scale pig farms the Huai Rong Canal, Site A (Wang Manao Sub-district) and site B (Wan Dao Sub-district) were the sites to represent as the Huai Rong Canal which had concentration of Cd in the water higher than reused water from the large-scale pig farm as presented in Table 5.3.

Table 5.3: Concentrations of cadmium (Cd) (µg/L) in the Huai Rong Canal and large-scale pig farm

Sampling site	Concentration of Cd (µg/L)
1. Water from the Huai Rong Canal	
• Wang Manao Sub-district	0.106
• Wan Dao Sub-district (Ban Kho Khi Lek)	0.062
2. Water from large-scale pig farm	
• Collector tank	0.245
• UASB reactor 1	0.122
• UASB reactor 2	0.038
• Wetland 1	0.041
• Wetland 2	0.018
• Wetland 3	0.002
• Reuse water	0.001

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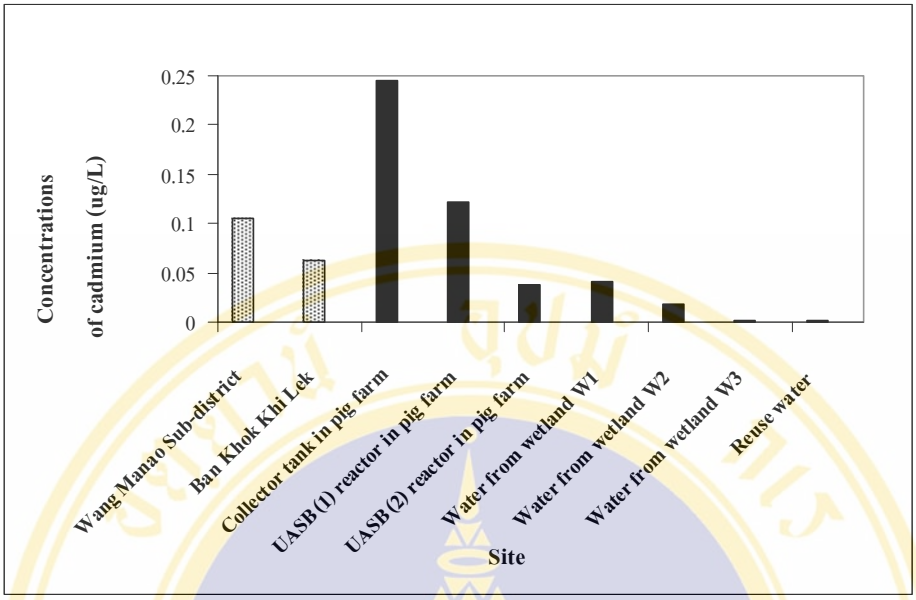

Figure 5.1 Concentrations of cadmium (Cd) (µg/L) in the Huai Rong Canal and large-scale pig farm

Comparing resued water from large-scale pig farm had concentrations of Cd 0.001 µg/L with water from site A (Wang Manao Sub-distract) concentrations of Cd 0.039 µg/L and water from site B (Wan Dao Sub-district) concentrations of Cd 0.062 µg/L. In this result the biogas wastewater treatment system could reduce Cd 97.44 % when comparing with water from site A (Wang Manao Sub-distract) and 98.39 % and when comparing with water from site B (Wan Dao Sub-district).

Thus, the government and the pig farm owners should cooperate to each other, the government has to control the quantity and the quality of wastwater from the pig farms. For the small and medium-scale pig farms, owners should provide the standard and efficiency water treatment system in order to reserve the environment in the future.

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CHAPTER VI
CONCLUSIONS/ RECOMMENDATION

6.1 Conclusions

According to the objectives of the present study the following conclusions can be made as follows.

1. To determine cadmium (Cd) from small and medium-scale pig farms of the Huai Rong Canal, the Mae Klong River, Ratchaburi Province in every month during September 2005 to February 2006 (in total of 6 sampling times) of sites A (Wang Manao Sub-District) and B (Wan Dao Sub-District).

1.1. The physico-chemical characteristics of water quality in the rainy season were due to the higher turbulence in the canal water, more oxygen circulation to increase oxygen solubility in the water (hight dissolved oxygen (DO)). In the dry season, water quality was the worst because there was wastewater discharged from a lot of small-and medium-scale pig farms into the canal. High biochemical oxygen demand (BOD) caused by discharged wastewater contained high organic matters determined during the dry season was due to the low turbulence (less DO for microorganism). However, the water quality of the canal system was in Class 3 (agriculture uses) of the Surface Water Quality Standards (PCD, 2006).

1.2. In case of average concentrations of Cd in water, sediment, aquatic plant (*Ipomoea aquatica*) and golden apple snail (*Pomacea canaliculata*), it was found that the concentrations of Cd in water and sediment were highest in the dry season as a consequence of the low turbulence in the canal. Also due to water pH values as alkaline in this season, Cd starts precipitating from water and accumulates in sediments. High Cd concentrations in aquatic plant (*I. aquatica*) and golden apple snail (*P. canaliculate*) were found during in the early dry to rainy seasons.

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2. To determine Cd contents in large-scale pig farm**,** Pak Tor District, Ratchaburi Province in February 2006.

2.1. It was found that the physico-chemical characteristics of wastewater from large-scale pig farm was improved continuously after passing through each step of biogas wastewater treatment system operated in the farm studied.

2.2. The average concentrations of Cd content reduced after passing through each step of biogas wastewater treatment system. When compared Cd content in feed with that in sludge, Cd content in sludge was much higher than that in feed.

3. It was concluded that Cd contents of the Huai Rong Canal from small- and medium-scale pig farms were about 38 to 61% which are higher than Cd content from large-scale pig farm. The large-scale pig farm is a close system and has biogas wastewater treatment system that helps increasing water quality and reducing Cd in the wastewater. The major source of Cd is from pig feed depending on formular of various feed production.

6.2 Recommendations

6.2.1 Recommendation for Applications

As it was found that the wastewater treatment system of the large-scale pig farm can reduce amount of Cd dramatically therefore it should promote for small-and medium-scale pig farms. The suitable management, appropriate technology and support by government using both laws and initial fund should be made for small-and medium-scale pig farms which have less fund, lack of technology and land to construct wastewater treatment system. As mentioned above about the Cd contamination in different feed formula, therefore feed quality control is needed before distribution to farmers.

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6.2.2 Recommendation for Further Study

1. Cd concentration in different pig organs should be further carried out to demostrate the location of Cd accumulation.

2. High Cd content in pig manure can be a problem in utilisation as feed or fertilizer therefore the study should be carried out to identify the appropriate method to reduce Cd content and the suitable amount of application of pig manure with different Cd contents which can be met the safe limits.

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APPENDIX

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Table A-1: Cadmium Contents in the Variance Standard

Source/ Authority	Quantity
Canadian Water Quality Guidelines	
Drinking water	0.005 mg/L
Protection of freshwater aquatic life	0.0002-0.0018 mg/L depending on hardness (under review)
Irrigation	0.01 mg/L
Livestock watering	0.02 mg/L
Ontario Water Quality Objectives	
Protection of freshwater aquatic life	0.0002 mg/L
Interim Objective under development	0.0001 mg/L Hardness 0-100 mg/L $CaCO_3$ 0.0005 mg/L Hardness >100 mg/L $CaCO_3$

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Source/ Authority	Quantity
U.S. EPA	
Interim Maximum Contaminant (MCL)	0.005 mg/L (5 µg/L)
Proposed Maximum Contaminant Level Goal (MCLG)	0.005 mg/L
No cadmium allowed in pesticides	
U.S. Food and Drug Administration (FDA)	
Food colors maximum	0.015 mg/L
The Occupational Safety and Health Administration (OSHA)	
Workplace air	100 mg cadmium/m^3 air as cadmium fumes 200 mg cadmium/m^3 air as cadmium dust
Legal airborne permissible exposure limit (PEL)	0.2 mg/m^3averaged over an 8 hour work shift 0.6 mg/m^3 not to be exceeded during any (15 minute) work period

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Source/ Authority	**Quantity**
OSHA	is planning to limit all cadmium compounds to either 1 or 5 mg/cubic meter.
ACGIH	
Recommended airborne exposure limit	0.05 mg/m3 for cadmium dust averaged over an 8 hour work shift
A concentration of 0.001 mg/l in freshwater hardness above 100 mg/L $CaCO_3$ is considered harmful to aquatic life.	
LC50 values	
Rainbow trout	0.0036 mg/L
Daphnia magna	0.056 mg/L
Fathead minnow	0.030 mg/L

Source: Environmental Bureau of Investigation (EBI), 1997

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Table2: Physico-chemical Characteristics of manure and sludge in large-scale pig farms to compare international legislation high quality concentration limits (mg/kg) of United States of America, Germany and France

Parameter		Manure	Sludge	US. EPA				Germany	France
				Ceiling concentration limits (mg/kg)	Cumulative loading limits (ka/ha)	'High quality' concentration limits (mg/kg)	Annual loading limits (kg/ha-year)		
pH	Rang	6.59-8.93	6.23-7.48	-	-	-	-	-	-
	Mean	7.80	7.17						
Organic (C%)	Rang	36.82-39.48	19.63-31.70	-	-	-	-	-	-
	Mean	37.92	27.45						
TS (%)	Rang	71.35-91.15	86.35-91.90	-	-	-	-	-	-
	Mean	84.13	91.00						
Total N (%)	Rang	1.63-4.21	0.98-2.35	-	-	-	-	-	-
	Mean	2.76	2.13						
NH_4^+	Rang	599-4,591	416-4,205	-	-	-	-	-	-
(mg/kg)	Mean	1357.80	1,289.20						
$NO_2^- + NO_3^-$	Rang	4-124	15-77	-	-	-	-	-	-
(mg/kg)	Mean	53.80	39.20						
Cu (mg/kg)	Rang	133-391	746-1,769	4,300	1,500	1,500	75	1,200	1,500
	Mean	219.2	1260.8						
Zn (mg/kg)	Rang	663-888	2,650-6,864	7,500	2,800	2,800	140	3,000	3,000
	Mean	736.3	4,477.30						
Ni (mg/kg)	Rang	15-25	25-39	420	420	420	21	200	200
	Mean	19.0	30.10						
Cd (mg/kg)	Rang	1-4	3-8	85	39	39	1.6	20	40
	Mean	2.9	4.4						
Cr (mg/kg)	Rang	13-22	11-50	3,000	3,000	1,200	150	1,200	1,000
	Mea	16.9	30.9						

Source: Mhowyathai and Sripanomtanakorn, 1995

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