ACCUMULATION AND DISTRIBUTION OF HEAVY METALS IN WATER, SEDIMENT, *Pomacea canaliculata* AND SOME FISH SPECIES IN THE PHI LOK CANAL SYSTEM, SAMUT SONGKHRAM PROVINCE

WALAIPORN LOSUSSACHAN

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Walaiporn Lososussachan

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ABSTRACT

Heavy metal contamination in aquatic ecosystems is a significant problem in rural areas of Thailand where the sources of metal contamination are various activities, i.e., agriculture, aquaculture and agro-industry. The Phi Lok canal system, Phraek Nam Daeng district, Samut Songkhram province, Thailand has intensive activities especially paddy fields, fish raising ponds and agro-industrial factories. These activities have inevitably increased the levels of heavy metals in the water of the Phi Lok canal and affected the ecological systems of the area. The aim of this study is to determine the accumulation of heavy metals (Cd, Cu, Fe, Pb and Zn) in water, sediment and selected tissues of aquatic organisms, i.e., *Pomacea canaliculata* and some fish species in seasonal variation. The distribution of the metals at the five sampling stations was observed. The samples were collected every two months from June 2004 to April 2005. Moreover, the study also investigated the effect of seasonal variation on physico-chemical parameters of the water quality. A microwave digestion system was used to prepare the samples for analysis. The metal analyses of samples were carried out by using Atomic Absorption Spectrophotometer (AAS).

The results showed that the sequence of total average heavy metal concentrations in the samples was Fe > Zn > Cu > Pb > Zn. Heavy metal contents among all the media was found in descending order as follows: sediment> mollusc> fish> water. The concentrations of all heavy metals in the sediment found at site A that the major land use was pig farms was the highest, whereas at site B that the major land use was fish raising ponds was the lowest. The highest concentrations in aquatic animals were found at site A, whereas the lowest concentrations were found at site D that the major land use was shrimp farms. The highest concentrations of all heavy metals in water were found at site E that the major land use was shrimp farms, whereas the lowest concentrations were found at site A. Measuring by the seasonal variation, heavy metal concentrations in water was found in descending order as follows: cold> rainy> hot whereas those in sediment and mollosc were found as follows: rainy> cold>hot. Also physico-chemical parameters of water quality were found in descending order as follows: hot> cold>rainy. Accumulation of the heavy metals in aquatic animals correlated to those in both sediment and water depending on type of heavy metals and habitat, feeding behavior and desorption mechanism of the animals.

However, the none of the heavy metals exceeded the acceptable values for human consumption designated by various health organizations.

KEY WORDS: ACCUMULATION/ DISTRIBUTION/ HEAVY METALS/ *Pomacea canaliculata*/ SAMUT SONGKHRAM PROVINCE

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บทคัดย่อ

การปนเปื้อนโลหะหนักในระบบนิเวศน้ำเป็นปัญหาสำคัญอย่างหนึ่งของพื้นที่ในชนบทของประเทศไทย ซึ่งแหล่งที่มาของโลหะหนักมาจากหลายกิจกรรมไม่ว่าจะเป็นการเกษตรกรรม การเพาะเลี้ยงสัตว์น้ำ รวมถึงอุตสาหกรรมเกษตร คลองผีหลอกในตำบลแพรกหนามแดง จังหวัดสมุทรสงครามเป็นพื้นที่ที่มีการปลูกข้าว การเพาะเลี้ยงปลา และอุตสาหกรรมเกษตรอยู่อย่างหนาแน่น ซึ่งกิจกรรมเหล่านี้จะทำให้การสะสมโลหะหนักในคลองผีหลอกเพิ่มมากขึ้นและส่งผลกระทบต่อระบบนิเวศในพื้นที่ วัตถุประสงค์ของการศึกษาเพื่อตรวจวัดการสะสมของโลหะหนัก 5 ชนิด ได้แก่ แคดเมียม ทองแดง เหล็ก ตะกั่ว และ สังกะสี ในน้ำ ดินตะกอน และสัตว์น้ำซึ่งได้แก่ หอยเชอร์รี่ และปลาบางชนิดในช่วงฤดูกาลที่แตกต่างกัน และศึกษาการกระจายของโลหะหนักใน 5 จุดเก็บตัวอย่างตลอดลำคลองผีหลอก โดยทำการเก็บตัวอย่างทุก 2 เดือน ตั้งแต่เดือนมิถุนายน 2547 ถึงเมษายน 2548 ย่อยสลายตัวอย่างดินตะกอน น้ำ และสัตว์น้ำ ในระบบ microwave digestion และวิเคราะห์หาปริมาณโลหะหนักด้วยแรงเครื่อง Atomic Absorption Spectrophotometer นอกจากนี้ยังศึกษาผลกระทบของฤดูกาลที่มีต่อคุณภาพน้ำทางเคมีและกายภาพ

ผลการศึกษาแสดงให้เห็นว่าปริมาณของโลหะหนักแต่ละชนิดในตัวอย่างดินตะกอน น้ำ และสัตว์น้ำ เรียงตามลำดับดังนี้ Fe > Zn > Cu > Pb > Cd เมื่อเปรียบเทียบโลหะหนักที่สะสมอยู่ในดินตะกอน น้ำ และสัตว์น้ำมีความเข้มข้นเรียงตามลำดับดังนี้ ดินตะกอน > หอยเชอร์รี่ > ปลา > น้ำ ปริมาณของโลหะหนักในดินตะกอนมีค่ามากที่สุดที่จุดเก็บตัวอย่าง A ซึ่งเป็นบริเวณที่มีการเลี้ยงหมูกันมาก และน้อยที่สุดที่จุดเก็บตัวอย่าง B บริเวณหลังโรงงานรับซื้อของเก่าซึ่งมีแต่กิจกรรมการเกษตร โลหะหนักในสัตว์น้ำพบว่ามีปริมาณมากที่สุดที่จุดเก็บตัวอย่าง A และน้อยที่สุดที่จุดเก็บตัวอย่าง D โดยการใช้ประโยชน์ที่ดินบริเวณนี้จะเป็นฟาร์มเลี้ยงกุ้งเป็นส่วนใหญ่ ส่วนปริมาณโลหะหนักในน้ำที่จุดเก็บตัวอย่าง E ซึ่งเป็นบริเวณที่มีฟาร์มเลี้ยงกุ้งมากมีค่ามากที่สุดและจุดเก็บตัวอย่าง A มีค่าน้อยที่สุด สำหรับการศึกษาในแต่ละฤดูกาลพบว่าฤดูหนาวมีปริมาณโลหะหนักในน้ำมากที่สุด ตามด้วยฤดูฝน และฤดูร้อน ขณะที่ปริมาณโลหะหนักในดินตะกอนและหอยเชอร์รี่จะพบมากที่สุดในฤดูฝน ฤดูหนาว และฤดูร้อน ตามลำดับ การศึกษาคุณภาพน้ำทางเคมีและกายภาพ พบว่าในฤดูร้อนคุณภาพน้ำอยู่ในเกณฑ์ดีกว่าฤดูหนาวและฤดูฝน การสะสมของโลหะหนักในสัตว์น้ำมีความสัมพันธ์กับปริมาณของโลหะหนักในดินตะกอนและในน้ำขึ้นอยู่กับชนิดของโลหะหนัก แหล่งที่อยู่อาศัย พฤติกรรมการหาอาหาร และกลไกการปล่อยโลหะหนักของสัตว์น้ำ

อย่างไรก็ตามปริมาณความเข้มข้นของโลหะหนักในการศึกษานี้มีค่าไม่เกินระดับที่ยอมรับได้ของการบริโภคของมนุษย์ของหลายองค์กร

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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
ms/cm	Millisiemen per centimetre
kg	Kilogram
mg	Milligram
µg	Microgram
g	Gram
mL	Millilitre
L	Litre
cm	Centimetre
m^3	Cubic metre
ppt	Part per thousand
^oC	Degree Celsius
Cd	Cadmium
Fe	Iron
Cu	Copper
Pb	Lead
Zn	Zinc

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CHAPTER I
INTRODUCTION

1.1 Statement of the problem

Water pollution becomes a significant problem because water is an essential natural resource for human life. Furthermore, watert is an important resource in developing economics and society in terms of agriculture, industry and various facilities (Datchaneekul, 2005). Rivers not only supply water for human consumption but also receive wastewaters discharged from all human activities. In the past two decades there have been an increasing public awareness of the harzards that exist from the contamination of the environment by toxic substances. Aquatic ecosystem is one facet of the impact of toxic substances on the natural environment (Dix, 1981).

Trace elements occur in minute concentration in biological systems. They may exert beneficial of harmful effects on plant, animal, and human life depending upon the concentration (Forstner and Wittman, 1981). These elements are introduced into aquatic systems, rivers, lakes or oceans through atmospheric fallout, dumping wastes, accidental leaks, runoff of terrestrial systems (industrial and domestic effluents) and geological weathering (Al-Yousuf *et al.*, 2000). The distribution of dissolved trace metals differed depending on hydrologic conditions, partly because of the dilution of upstream inputs during flood periods (Chiffoleau *et al.*, 1999). Through the processes of precipitation, sedimentation and a variety of factors such as chemical reactivity, land use pattern and biological productivity, some of the heavy metals that are introduced in an aquatic system are deposited in the sediment aquatic plants and organisms (Zhang and Huang, 1993; Jain and Sharma, 2001).

Although some heavy metals such as manganese, iron, copper, and zinc are essential micronutrients, others such as mercury, cadmium, and lead are not required even in small amounts by any organism (Laws, 1945). Some heavy metals became a matter of concern because of their toxicity and tendency to accumulate in food chains. Fish, mollusc or another aquatic life located at the end of the aquatic food chain may

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accumulate metals and pass them to human beings through food causing chronic or acute diseases (Laws, 1945; Forstner and Wittman, 1981; Jorgensen and Pedersen, 1994). Recent researches have found that even low levels of lead, mercury, cadmium, aluminum and arsenic can cause a wide variety of health problems (Forstner and Wittman, 1981).

The study area of the Phi Lok canal system in Praek Nam Daeng sub-district, Amphawa district, Samut Songkhram province has intense activities in the industrial and agricultural sectors. As the city becomes more industrially developed, the degree of pollution in the canal seems to become worse (Begum *et al.*, 2005). Furthermore, most people about 90% usually use water in these canals for agricultural activities such as paddy fields, vegetable farms, fish raising pond, and shrimp farms (Pipoplabanan, 2002). Effluents from the agricultural activities containing fertilizers and pesticides reach the canal, enhancing the canal's metal burden (Papagiannis *et al.*, 2004; Albanis *et al.*, 1986; Kalfakakou and Kallistratos, 1987). The study area is in the Lower Mae Klong flood plain where all the canals are linked as the network together (Pipoplabanan, 2002). The Mae Klong river, 138 km long, starts from the confluence of the Kwai Noi and Kwai Yai rivers in Kanchanaburi province and flows through Ratchaburi and Samut Songkhram provinces into the gulf of Thailand (Schwartz *et al.*, 1995; Censi *et al.*, 2006; Thailand Environment Foundation, 1997). Therefore, a lot of subtances can accumulate and deposit in the lower area of river.

At present, water system in the study area was clearly divided in two parts, the freshwater part in the upper reach of the Phi Lok canal system and the saltwater part in the lower area of the Phi Lok canal system. Rama II highway and soil embankment were divisible line. There are watergates constructed by Royal Irrigation Department on every canal. Since then, the ecological systems of the canals had been changed and the activities of two parts were completely difference.

All of these causes have inevitably increased the levels of heavy metals in natural water. The water quality in the canals has becoming lower and this has an effect on the aquatic life. Thus, it is necessary to study the accumulation and distribution of heavy metals in aquatic ecosystem to make sure that the water quality and aquatic animas do not constitute a risk for human health.

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The aim of the study is to determine the accumulation of heavy metals (Cd, Cu, Fe, Pb and Zn) in water, sediment and aquatic animals in the Phi Lok canal system during the period of one year. Monitoring of physico-chemical parameters of the water quality and their contents of heavy metals were important to increase the ubderstanding of heavy metal accumulations in water and aquatic animals in the gulf of Thailand. Furthermore, the result may become of initial information to resource managers for managing of sustainable natural water resources in the future.

1.2 Objectives of the study

The aim of the study is to study the accumulation and distribution of five heavy metals (Cd, Cu, Fe, Pb and Zn) in water, sediment, *Pomacea canaliculata* and some fish species in the Phi Lok canal system, Amphawa district, Samut Songkhram province. To fulfill the aim of the study, the specific objectives are as follows:

1. To determine five heavy metal concentrations (Cd, Cu, Fe, Pb and Zn) in water, sediment, *P. canaliculata* and some fish species in five sampling sites of the Phi Lok canal system.
2. To compare the heavy metal concentrations in water with those in sediment, *P. canaliculata* and some fish species during the collection period from June 2004 to April 2005.
3. To investigate the effect of land use along the Phi Lok canal system on heavy metal accumulations in water, sediment, *P. canaliculata* and some fish species.
4. To determine the physico-chemical parameters of water quality of the Phi Lok canal system.

1.3 Scope of the study

1. The Phi Lok canal system started from the Wan Dao canal at Wat Wan Dao, Wan Dao sub-district, Pak Tho district, Ratchaburi province and continued to the Prudu canal and the Phi Lok canal of Prak Nam Daeng sub-district, Amphawa district, Samut Songkhram provice (see the detailed map of Figure 3.1 in Chapter 3). There are five sampling sites in the Phi Lok canal system. Three sampling sites in the freshwater

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part consist of one sampling site in the Wan Dao canal and two sampling sites in the Phi Lok canal. The other two sampling sites in the saltwater part were located in the Phi Lok canal in the mangrove forest.

2. Samples were collected every two months throughout the year (June, 2004, August 2004, October 2004, December 2004, February 2005 amd April, 2005), from five different sampling sites of the study area.

3. Heavy metals of Cd, Cu, Fe, Pb and Zn were studied.

4. Water quality parameters determined were water temperature, pH, Total Dissolved Solid (TDS), Biochemical Oxygen Demand (BOD), Dissolved Oxygen (DO), hardness, phosphate and nitrate.

5. At least one local species of fish were chosen in each sampling site of the study area depending upon the seasonal variation.

6. *P. canaliculata* represented the three sampling sites of freshwater part. Mollusc can not be collected in two sampling sites of saltwater part.

1.4 Limitation of the study

Some aquatic animal samples can not be collected in some months.

1.5 Operational definitions

1. **Accumulation**: The amount of heavy metals in water, sediment, *P. canaliculata* and tissues of some fish species in the Phi Lok canal system.

2. **Distribution**: The distribution is refered to where heavy metals are determined in five sampling sites and in sample collection period during June 2004 to April 2005 (every two months: June 2004, August 2004, October 2004, December 2004, Febuary 2005 and April 2005).

3. **Aquatic organisms**: Aquatic organisms in the study are *P. canaliculata* and some fish species in the Phi Lok canal system.

4. **Internal organs**: The organs of fish species for example liver, kidney and gill of fish.

5. **Muscle**: Meat or flesh of fish species.

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1.6 Conceptual framework

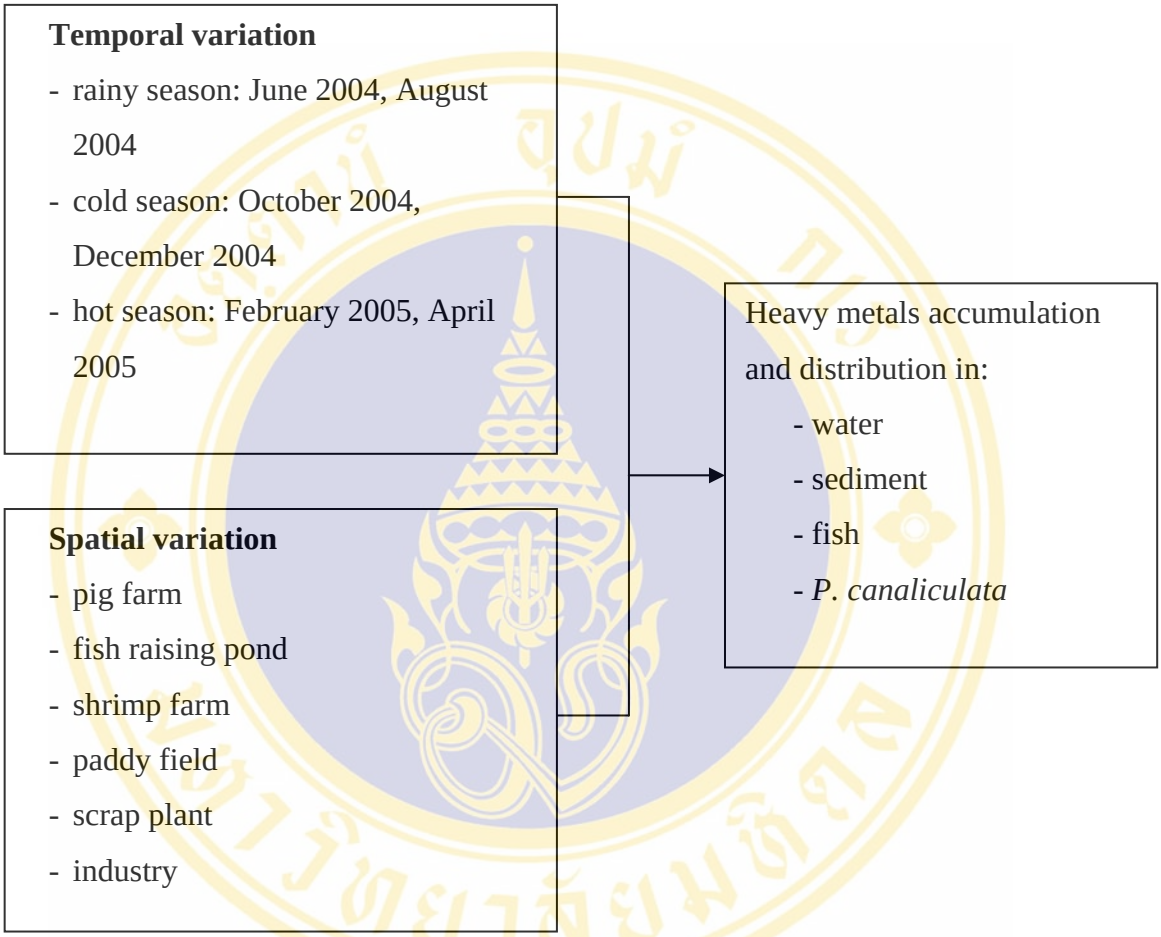

Figure 1-1 Conceptual framework of the study

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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 basin in the Chao Phraya delta. The Chao Phraya delta comprises of three major basins, Chao Phraya, Tha Chin and Mae Klong basins. The Mae Klong river supports fisheries, transportation and recreation and receives wastewater discharged. There are many environmental problems such as water pollution and ecological deterioration in these basins. Deterioration of river water quality has the greatest environmental impact (Simachaya *et al.*, 2002).

The Mae Klong river is classified in Class 3 of the Surface Water Quality Standards. Water quality monitoring results during the last decade (1984 to 1995) were to be fair and good. The Mae Klong river is less polluted. The major contributors to pollution were generated mainly from domestic and industrial activities. The first three major polluted contributors in the Mae Klong river regarding the respective parameters weare high fecal and total coliform bacteria, high total solids and high turbidity (Simachaya *et al.*, 2002).

2.1.1 Water quality situation of the Phi Lok canal system

The Phi Lok canal is the small canal in Phraek Nam Daeng sub-district. Pipoplabanan (2002) studied the way of life in changing riverine ecosystem in the Phi Lok canal and mentioned that water pollution had significantly impacted on the area. Wastes from shrimp farms and frozen shrimp factories were discharged into the canals. Until 1999, the water quality was very polluted and this affected to water use of the local people. Conflicts amongst the different water user groups had been occurred and it was a big civil court case at that time. Moreover, wastewaters from toxic soils leaked through the watergates. The wastewater from factories and agricultural farms has strongly impacted on the local fisheries and ecological system.

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2.2 Water pollution

2.2.1 Sources of water pollution

The Missouri Botanical Garden (2002) divided specific sources of water pollution in three groups.

1) Water pollution from farming

Farms often use large amounts of herbicides and pesticides, both of which are toxic pollutants. These substances are particularly dangerous to life in rivers, streams and lakes, where toxic substances can build up over a period of time. Farms also frequently use large amounts of chemical fertilizers that are washed into the waterways and damage the water supply and the life within it. Fertilizers can increase the amounts of nitrates and phosphates in the water, which can lead to the process of eutrophication. Furthermore, allowing livestock to graze near water source often results in organic waste products being washed into the waterways. This sudden introduction of organic material increases the amount of nitrogen in the water, and can also lead to eutrophication.

2) Water pollution from business

Clearing of land can lead to erosion of soil into the river. Water can become contaminated with toxic or radioactive materials from industry, mine sites and abandoned hazardous waste sites. Moreover, acid precipitation is caused when the burning of fossil fuels emits sulfur dioxide into the atmosphere. The sulfur dioxide reacts with the water in the atmosphere, creating rainfall which contains sulfuric acid. As acid precipitation falls into lakes, streams and ponds, it can lower the overall pH of the waterway, kill vital plant life, thereby affect the whole food chain. It can also leach heavy metals from the soil into the water, kill fish and other aquatic organisms. Because of this, air pollution is potentially one of the most threatenting forms of pollution to aquatic ecosystems.

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3) Water pollution from households

Sewages generated by houses or runoff from septic tanks into nearby waterways, introduce organic pollutants that can cause eutrophication. Including, fertilizers, herbicides and pesticides used for lawn care were leached and contaminate the waterways.

Improper disposal of hazardous chemicals were leached by the rain and run off into the drainage that introduce toxic materials into to the ecosystem, contaminating the water supplies in a way that can harm aquatic organisms. Besides, leaks of oil and antifriction from a car on a driveway can be washed off by the rain into nearby waterways. It makes water pollution.

In the study area, there are many agricultural activities such as pig farms, fish raising ponds, shrimp farms, vegetable farms and paddy fields. So wastewaters are discharged from these activities. In the hot season when the water in the canal was very low due to tidal period and closure of the watergates of the dam in the upstream area by the Royal Irrigation Department. Some agricultural activities such as fish farms, paddy fields, etc. suffered from lack of water for usage. Sometimes the floating plants such as water hyacinth, morning glory, etc. grew in the canal and obstructed water flow. This also affected to the water quality and aquatic organisms.

2.2.2 Effects of water pollution

The effects of water pollution include poisonous drinking water, poisionous food animals (due to these organisms having bioaccumulated toxins from the environment over their life spans), unbalanced river and lake ecosystems that can no longer support full biological diversity, deforestation from acid rain, and many other effects. These effects are, of course, specific to the various contaminants (Land Development Department, 1995).

The effects of water pollution may be considered under six categories as follows (Dix, 1981):

(1) physical effects, such as suspended particle solids that cause water turbidity, cooling water that raises water temperature, and oily surface films that restrict the reoxygenation of water;

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(2) oxidation effects caused by bacterial action or chemical oxidation of inorganic and organic substances, both of which significantly reduce the dissolved oxygen content of water;

(3) toxic chemical effects caused by a range of substances that cause immediate or cumulative physiological changs in plants, animals, and humans;

(4) chemical nutrient effects resulting from high concentrations of nitrates and phosphates;

(5) pathogenic effects caused by micro-organisms, where bacteria and viruses are present in sufficient numbers to cause a health hazard;

(6) radionuclide effects, caused by the accumulation of radioactive substances in food organisms, which produce human body changes.

The toxic chemical effects were very interesting, especially heavy metals. Because heavy metals and chemical substance were used as raw material in specified businesses. The by-products of the production processes were hazardous to the human health in many ways.

2.3 Heavy metal pollution

2.3.1 Sources and effects of heavy metal

2.3.1.1 Sources of heavy matals can be divided into five categories as follows (Alloway and Ayres, 1993):

1) Geochemical sources

In geological terms, heavy metals are included in the group of elements referred to as ‘trace elements’ which together constitute less than 1% of the rocks in the earth’s crust; the macroelements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, P and S) comprise 99% of the earth’s crust. The natural enrichment of metals in the soils may still give rise to harmful effects in living organisms.

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2) Agricultural materials

Agriculture constitutes one of the very important non-point sources of metal pollutants. The main sources are:

- impurities in fertilizers: Cd, Cr, Mo, Pb, U, V, Zn (e.g. Cd and U in phosphatic fertilizers);
- pesticides: Cu, As, Hg, Pb, Mn, Zn (e.g. Cu, Zn and Mn-based fungicides, Hg seed dressings, historical Pb-As orchard sprays);
- desiccants: As for cotton;
- wood preservatives: As, Cu;
- wastes from intensive pig and poulty productions: Cu, As;
- composts and manures: Cd, Cu, Ni, Pb, Zn, As;
- sewage sludge: especially Cd, Ni, Cu, Pb, Zn (also many other elements);
- corrosion of metal objects (e.g. galvanized metal roofs and wire fences: Zn, Cd).

3) Metallurgical industries

Many heavy metals are used in specialist alloys and steels: V, Mn, Pb, W, Mo, Cr, Co, Ni, Cu, Zn, Sn, Si, Ti, Te, Ir, Ge, Tl, Sb, In, Cd, Be, Bi, Li, As, Ag, Sb, Pr, Os, Nb, Gd. Hence both the manufacture and disposal, or recycling, of these alloys in scrap metal can lead to environmental pollution of wide range of metals.

4) Waste disposal

Many metals, especially Cd, Cu, Pb, Sn and Zn, are dispersed into the environment in leachates from landfills, which pollute soils and ground waters, and in fumes from incinerators.

5) Other sources

Other significant sources of heavy metal pollution in manufacture (sometimes in use) and disposal include:

- Batteries – Pb, Sb, Zn, Cd, Ni, Hg, Pm
- Pigments and paints – Pb, Cr, As, Sb, Se, Mo, Cd, Ba, Zn, Co, I, Ti
- Catalysts – Pt, Sm, Sb, Ru, Co, Rh, Re, Pd, Os, Ni, Mo, I
- Polymer stabilizers – Cd, Zn, Sn, Pb (from incineration of plastics)

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- Printing and graphics – Se (xerox process), Pb, Cd, Zn, Cr, Ba
- Medical uses: dental alloy – Ag, Sn, Hg, Cu, Zn
  drugs/medicinal preparations – As, Bi, Sb, Se, Ba, Ta, Li, Pt
- Additives in fuels and lubricants – Se, Te, Pb, Mo, Li

2.3.1.2 Toxicity of heavy metals

Heavy metals are dangerous because they tend to accumulate. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and ground water (Lenntech, 2005a). Figure 2-1 shows the pathway that follows the heavy metals from the first step of the pollution to the final.

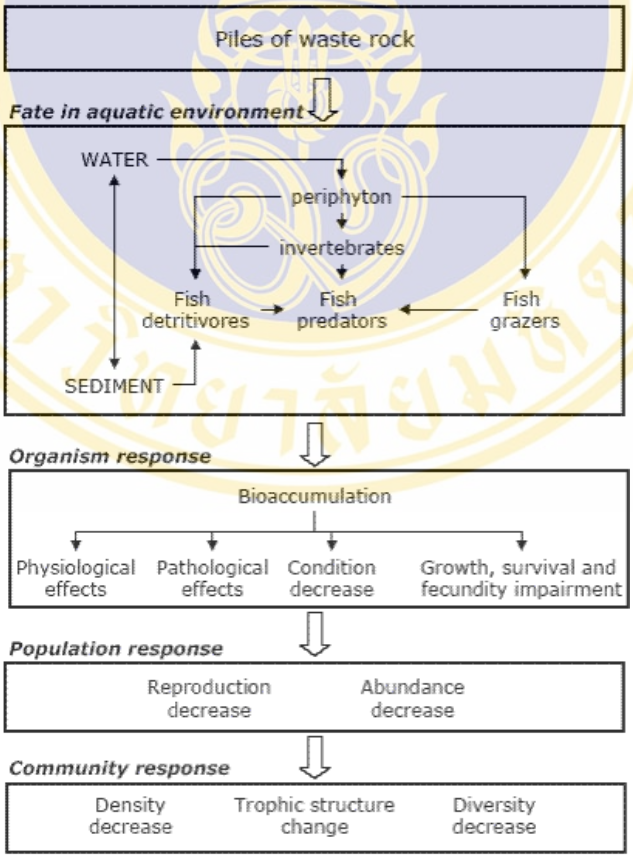

Figure 2-1 Fate of heavy metals and responses in different levels in ecosystem

Source: Lenntech (2005a)

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Heavy metal toxins contribute to a variety of adverse health effects. These exist over 20 different heavy metal toxins that have impacts on human health and each toxin will produce different behavioral physiological and cognitive changes in an exposed individual. The degree to which a system organ tissue or cell is affected by a heavy metal toxin depends on the toxin itself and the individual's degree of exposure to the toxin (Extremehealthusa, 2005).

The toxicity of heavy matals can be listed in order of decreasing toxicity as Hg>Cd>Cu>Zn>Ni>Pb>Cr>Al>Co, although this is only approximate as the vulnerability of species to individual metals varies. Toxicity also varies according to environmental conditions that control the chemical speciation of the metals (Gray, 1999).

Aquatic organisms may be adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system. Furthermore, the ability of aquatic organisms to adsorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1992 cited by WATERSHEDSS, 2006). With the exception of mercury, little metal bioaccumulation has been observed in aquatic organisms. Metals may enter the systems of aquatic organisms via three main pathways (Connell *et al*., 1984 cited by WATERSHEDSS, 2006):

1) Free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused into the blood stream.

2) Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream.

3) Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water.

Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacea can excrete essential metals, such as copper, zinc, and iron, that are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success. However, research has shown that bivalves are not able to successfully regulate metal uptake (Connell *et al*., 1984 cited by WATERSHEDSS, 2006).

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The most important disasters with heavy metals were recorded as follows (Lenntech, 2005c; ICETT, 1998):

1. Spanish nature reserve contaminated after environmental disaster: In 1998 to 2004, toxic chemicals in water from a burst dam belonging to a mine contaminated the Coto de Donana nature reserve in the southern Spain. About 5 million m^3 of mud containing sulphur, lead, copper, zinc and cadmium flowed down the Rio Guadimar. Experts estimated that Europe's largest bird sanctuary, as well as the Spain's agriculture and fisheries, will suffer permanent damage from the pollution.

2. Itai-itai disease was found in the cadmium (Cd) polluted Jinzu river basin in Toyama prefecture, and has been generally recognized since the 1950's by the effort of inhabitants. The strange disease that appeared in the downstream basin of the Jinzu river around 1912 was called by locals "itai-itai byo" ("itai" being what Japanese people say when infilicate with pain and "byo" literally meaning disease). In came by this name because of the way victims cried out "itai-itai" under the excruciating pain they endured. Women were mostly afflicted with pain across their entire body and more severe cases suffered broken bones when trying to move by their own.

2.3.2 Heavy metals in the study

2.3.2.1 Cadmium

1) Uses of cadmium

Cadmium is primary used in electroplating. A thin layer of cadmium is deposited by electrolysis on metal object made of steel, iron, and brass to prevent corrosion. It provides good electric conductivity, high ductile and good corrosion resistance to tropical atmosphere, saltwater, and alkali substances. Also, cadmium is used as the anode in nickel-cadmium batteries. The advantage of these batteries are rechargeable, have a long lifetime and low self-discharge rate, operate over a wide temperature range, and deliver a maximum currents with a low voltage drop. The disadvantage of these batteries is their low energy density and high cost. In addition, cadmium is used in pigment in coloring glass, elastics, textiles, paper, rubber, printing inks, ceramic glaze and fireworks.

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In the study area, cadmium may be discharged from the scrap plant at the sampling site B (Pipoplabanan, 2002).

2) Environmental effects of cadmium

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing.

Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are for instance zinc production, phosphate ore implication and bio industrial manure. Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Because of regulations only little cadmium now enters the water through disposal of wastewater from households or industries.

Another important source of cadmium emission is the production of artificial phosphate fertilizers. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions is dumped by production companies. Cadmium can be transported over great distances when it is absorbed by sludge. This cadmium-rich sludge can pollute surface waters as well as soils.

Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants. Cows may have large amounts of cadmium in their kidneys due to this. Earthworms and other essential soil organisms are extremely susceptive to cadmium poisoning. They can die at very low concentrations and this has consequences for the soil structure. When cadmium concentrations in soils are high they can influence soil processes of micro-organisms and threat the whole soil ecosystem.

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In aquatic ecosystems cadmium can accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Saltwater organisms are known to be more resistant to cadmium poisoning than freshwater organisms.

Animals eating or drinking cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage. The most serious cases of environmental pollution by cadmium occurred in Japan. This disease was known as Itai-Itai, characterized by severe back and joint pains, kidney lesions, protein and sugar in the urine and decalcification of the bones, leading sometimes to multiple functions (Bunsong, 2003).

2.3.2.2 Copper

1) Sources of exposure

Copper occurs naturally in elemental form and as a component of many different compounds. The most toxic form of copper is thought to be that in the divalent state cupric (Cu^{2+}). Because of its high electrical conductivity copper is used extensively in the manufacturing of electrical equipment and different metallic alloys. Copper is released into the environment primarily through mining sewage treatment plants solid waste disposal welding and electroplating processes electrical wiring materials plumbing supplies (pipes faucets braces and various forms of tubing) and agricultural processes. It is present in the air and water due to natural discharges like volcanic eruptions and wind blown dust. Drinking water sources become contaminated with copper primarily because of its use in many different types of plumbing supplies. It is a common component of fungicides and algaecides and agricultural use of copper for these purposes can result in its presence in soil ground water farm animals (grazing animals like cows and horses etc.) and many forms of produce. Copper is also present in ceramics jewelry monies (coins) and pyrotechnics. Though copper is an essential trace element required by the body for normal physiological processes increased exposure to copper containing substances can result in copper toxicity and a wide variety of complications (ATSDR, 2004).

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In the sampling site A of the study area, there were many pig farms that may discharge wastewater into the canals especially in the rainy season. It may be a source of copper in the canal.

2) Environmental effects of copper

The world's copper production is still rising. This basically means that more and more copper ends up in the environment. Rivers are depositing sludge on their banks that is contaminated with copper, due to the disposal of copper-containing wastewater. Copper enters the air, mainly through release during the combustion of fossil fuels. Copper in air will remain there for an eminent period of time, before it settles when it starts to rain. It will then end up mainly in soils. As a result soils may also contain large quantities of copper after copper from the air has settled. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. Because copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals.

When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions.

Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near copper-disposing factories. Due to the effects upon plants copper is a serious threat to the productions of farmlands. Copper can seriously influence the proceedings of certain farmlands, depending upon the acidity of the soil and the presence of organic matter. Despite of this, copper-containing manures are still applied (Lenntech, 2005c).

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2.3.2.3 Iron

1) Uses of iron

Iron and its alloy are used mainly in the construction, transportation, machine-manufacturing, and energy industries (e.g., magnets). As for other basic manufacturing industries, it consumes large quantities of resources and inturn produces atmospheric, water-borne and solid wastes (Merian, 1991).

About 98% of iron ore are used for making steel, one of the greatest inventions and most useful materials ever created. Iron alloy with small amounts of chromium improve durability and prevent rust; nickel increases durability and resistance to heat and acid; manganese increases strength and resistance to wear; and vanadium increases strength and springiness. These alloys are used to make construction, automobile, and other form of transportation such as trucks, trains and train trucks. In addition, powder iron is used in metallurgy products, magnets, autoparts and catalyst. Iron blue is used in paint, printing inks, plastic, cosmetics, artist colors, laundry blue, paper, dying and fertilize. Black iron oxide is used in pigment, metallurgy, medicine, magnetic inks and in ferrets for eletronic industry (Bunsong, 2003).

2) Environmental effects of iron

Iron is a metal of low toxicity. Only iron concentrations exceeding 10 to 200 mg/L of nutrient solution have been found to be toxic to plants, and amounts in excess of 200 mg/day are considered toxic for man (Bowen, 1979).

Almost no information is available on the toxic effects of iron on the mucroorganisms commonly found in river and lakes (Merian, 1991).

Iron (III)-O-arsenite, pentahydrate may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment (Lenntech, 2005c).

2.3.2.4 Lead

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but

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tarnishes upon exposure to air. Lead pipes bearing the insignia of Roman emperors, used as drains from the baths, are still in service. Alloys include pewter and solder. Tetraethyl lead ($PbEt_4$) is still used in some grades of petrol (gasoline) but is being phased out on environmental grounds. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements (Lenntech, 2005b).

1) Production and use

Lead (Pb) is widely distributed in the rocks and soils of the earth's crust, although the mean concentration is only 12 – 20 ppm. Lead is mined primarily from deposits of the mineral galena, or lead sulfide (PbS). Since metallic lead can be separated from PbS by heating to low temperatures easily achieved by burning wood or charcoal, it was not difficult for early civilization to extract lead. From written and archeological evidence, it is known that Pb was used by the Egyptians as long ago as 1500 BC. The Romans used lead extensively to line their aquaducts and water mains, and both the Greeks and Romans used Pb to line cooking vessels, since bronze pots tend to give food a bitter taste. At least one author has suggested that endemic lead poisoning caused by the consumption of contaminated food and drink contributed significantly to the fall of the Roman empire. The use of lead or lead salts to sweeten wine was common in Europe after the ninth century, and associated outbreaks of lead poisoning were not infrequent. In colonial America lead poisoning was also problem, mainly due to the use of lead condensing tubes for distilling rum and to the use of earthenware with a high Pb content.

2) Environmental effects of lead

Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead-cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, oxides) will originate. These lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This lead-cycle caused by human

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production is much more extended than the natural lead-cycle. It has caused lead pollution to be a worldwide issue.

Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes and solid waste combustion, also contribute. Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only convert to other forms.

Lead accumulates in the bodies of water organisms and soil organisms. These will experience health effects from lead poisoning. Health effects on shell fish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. That is why we now begin to wonder whether lead pollution can influence global balances.

Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.

There is a large variability of lead concentration in individual foods depending on various factors including the geographic location in which the food was grown. However, in foods of animal origin: muscle meat, unprocessed milk, and eggs have a relatively low lead content, whereas organ meat, partecularly kidney and to a lesser extent liver, is substantially higher in lead concentration (Merian, 1991).

3) Lead in the freshwater environment

Beside the normal changes in freshwater due to metals, lead has it own characteristics. The chemical properties of lead make it a useful material, so it is used widely in pipes, battery cases, paints, ect. and tetraethyl lead is used as a petrol additive. A total of 4 million tons of lead are mined worldwide in one year. It becomes extracted from the galena ore (PbS). The latter has been the most important source of organic lead to the environment and has been widely dispersed, with contamination increasing sharply from the 1950's, even in remote areas, with the growth in the number of automobiles (Lenntech, 2005b). The use of lead in ammunition has created some serious environmental problems. Organolead compounds have been used extensively for control of caterpillars on fruit crops.

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2.3.2.5 Zinc

1) Health effects of zinc

Zinc is a very common substance that occurs naturally. Many foodstuffs contain certain concentrations of zinc. Drinking water also contains certain amounts of zinc, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the zinc amounts in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers (Lenntech, 2005c).

Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.

In the work place environment zinc contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity (Bertin and Bourg, 1995).

2) Effects of zinc on the environment

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing. Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters.

Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to

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biomagnify up the food chain. According to Henkin *et al.* (1979) the average zinc content of most sea fish between 3 and 8 ppm, with certain kinds of fish and molluscs containing up to about 25 ppm and maximum values of up to 50 ppm in individual animals. Crustaceans contain 7 to about 50 ppm of zinc with maximum values reaching a little over 100 ppm. Freshwater organisms exhibit similar zinc concentrations.

Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater.

Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microrganisms and earthworms. The breakdown of organic matter may seriously slow down because of this.

2.4 Heavy metal distribution and accumulation in aquatic ecosystem

Ultimately soil and sediment serve as sinks for toxic metals, while water and air are primarily transport media (Adair *et al.*, 2002). Metal transport in water is largely dependent on solubility. Parameters such as pH, alkalinity, salinity and dissolved organic metter greatly influence metal solubility in natural waters (Stumm and Morgan, 1992; Ownby *et al.*, 2001). Particle flocculation in slow flowing water bodies such as lakes or estuaries cause increased metal deposition into sediment.

Heavy metals may affect organisms directly by accumulating in the body or indirectly to the next trophic level of the food chain (Altindag and Yigit, 2005). Aquatic organism take up trace metals from both water and food. The bioaccumulation of trace metals depends on the physiological accumulation pattern of the species concerned for a particular metal. If organisms with accumulation pattern with increasing dependence on storage accumulation follow sequentially along a food chain, the effect will mimic biomagnification of trace metals along food chains (Triquet *et al.*, 1993; Wang, 2002).

The factors that affect the uptake (bioavailability) of trace metals from solution and food, either of which may involve or be affected by metals in sediments, are crucial in determining the kinetics of uptake, and potentially of subsequent

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accumulation. In solution many of these factors are external physico-chemical factors such as salinity and the presence of chelating agents (Rainbow, 1995). Factors affecting uptake from food include the nature of metal binding in the food and the digestive (assimilatory) powers of the animal (Wang, 2002). The bioavailability of metals in ingested sediments is also affected by factors such as the organic and inorganic constituents of the sediment, affecting relative binding affinities for the metals (Luoma and Fisher, 1997; Bryan and Langston, 1992).

2.5 Study area of Samut Songkhram province

Samut Songkhram, a coastal province at the mouth of the Mae Klong river, is 63 kilometers southwest of Bangkok. It occupies an area of 416.7 square kilometers and is administratively divided into three districts (Amphoes): Muang Samut Songkhram (locally called Mae Klong), Amphawa, and Bang Khonthi. The districts are further subdivided into 38 communes (tambon) and 284 villages (Sawadee.com, 2000; Wikipedia, 2005). Neighboring provinces are (from the south clockwise) Phetchaburi, Ratchaburi and Samut Sakhon provinces.

The province is the smallest of all Thai provinces area. The area is a low basin with many canals. With several canals (khlong) the water of the river is spread through the province for irrigation. At the coast, there are many salt pans for producing sea salt. The main activities in the coastline of Samut Songkhram province, include aquaculture, salt pan, and fishery, particularly razor clam harvesting. Fish, shellfish and jellyfish are important fishery products from the area (Piumsomboon, 2005). Agriculture and food industries account for only a small proportion of land use. Samut Songkhram is the province of fertile land, of plants and food grains, the production source of vegetables and fruits, as well as a vast variety of seafood products (Tourism Authority of Thailand, 2005).

2.6 Biology and ecology of aquatic organisms in the study

In the study area, there are many fish species such as *T. trichopterus, C. striatus, N. kapirat* and *P. schwanenfeldii* etc. in the freshwater part. While *V. siheli,*

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O. marmorata and *A. truncatus* were found in the saltwater part. Some fish species such as *O. mossambicus* was found both in the freshwater and saltwater parts. These fishes are local fish species. However, only four fish species (*T. trichopterus, C. jullieni, O. mossambicus* and *V. siheli*) were mostly found at the sampling site and were chooen to be determined in the study.

Apple snail was the alian species that was mostly found in the agricultural area in Thailand. In Phraek Nam Daeng sub-district, it was also found especially in paddy fields. Pokethitiyook (2005) classified the apple snail species found in the study area as *Pomacea canaliculata* (Lamarck, 1819) (Family: Ampullariidae). It was chosen for analysis of heavy metals in three sampling sites of the freshwater part.

2.6.1 Biology and ecology of *Trichogaster trichopterus* (Pallas, 1770)

2.6.1.1 Taxonomic hierarchy

Kingdom Animalia -- Animal
Phylum Chordata -- chordates
Subphylum Vertebrata -- vertebrates
Superclass Osteichthyes -- bony fishes,
Class Actinopterygii -- poisson, ray-finned fishes, spiny rayed fishes
Subclass Neopterygii
Infraclass Teleostei
Superorder Acanthopterygii
Order Perciformes -- perch-like fishes
Suborder Anabantoidei -- labyrinthfishes
Family Osphronemidae Bleeker, 1859 -- giant gouramis
Subfamily Luciocephalinae Bleeker, 1860
Genus Trichogaster Bloch and Schneider, 1801
Species *Trichogaster trichopterus* (Pallas, 1770) -- three-spot gourami

Source: Rainboth (1996)

Common name: Three-spot gourami

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2.6.1.2 Description

Color in light brown; shoulders with irregular dark marks, yellowish on opercles and thorax; median fins and pectorals brown, ventrals yellowish. Mouth very small, very oblique, upper jaw vertical and somewhat protractile, lower jaw prominent. Scales of moderate size, irregularly arranged. Lateral line curved, irregular. Caudal fin slightly emarginate or truncate. With 8 to 9 dorsal-fin branched rays; 33 to 38 branched anal-fin rays; black spot in middle of side and at caudal-fin base. Body with numerous narrow irregular oblique bars (Rainboth, 1996).

It is identified by the arrangement of spots - one at the base of the tail, another in mid-flank, and the third being the eye. The fins are attractively patterned with lines and speckles, particularly the tail fin. The mouth is small, and it feeds on plankton, tiny insects and the larvae of crustaceans (Lekagul and Mcneely, 2005).

Figure 2-2 Characteristics of *Trichogaster trichopterus*

Source: Vidthayanon *et al.* (1997)

2.6.1.3 Biology

The three-spot Gourami is a handsome fish much loved by aquarists. In its native habitat, it survives in a variety of waters including slow forest stream, freshwater swamps and lakes.

Found in marshes, swamps and canals. Inhabits shallow sluggish or standing-water with a lot of aquatic vegetation. Occurs in seasonally flooded forests throughout the middle and lower Mekong. Undertakes lateral migrations from the Mekong mainstream, or other permanent water bodies, to flooded areas during the flood season and returns to the permanent water bodies at the onset of the dry season. Feeds on zooplankton, crustaceans and insect larvae. Processed into salted, dried fish in Java.

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Also marketed fresh and commonly seen in the aquarium fish trade. Aquarium keeping: minimum aquarium size 100 cm (Rainboth, 1996).

2.6.1.4 *Trichogaster trichopterus* in Thailand.

The species is widely distributed in Southeast Asia including Thailand, Indochina, Peninsular Malaysia, Singapore, Borneo and the Philippines.

In Thailand it is found in the Mekong, Chao Phraya, Maeklong, Salween, Peninsular and Southeast river systems. In Chiang Khong and Nong Khai provinces, it is uncommon in the Mekong river, but common in small streams and canals. At Mukdahan district, it migrates from the Mekong river into its tributaries (Vidthayanon *et al.*, 1997).

2.6.2 Biology and ecology of *Cirrhinus jullieni* Sauvage, 1878

2.6.2.1 Taxonomic hierarchy

Kingdom	Animalia -- Animal
Phylum	Chordata
Class	Actinopterygii (ray-finned fishes)
Order	Cypriniformes (carps)
Family	Cyprinidae (Minnows or carps)
Genus	Cirrhinus
Species	*Cirrhinus jullieni*

Source: Adapted from Roberts (1997)

Common name: Mud carp

Figure 2-3 Characteristics of *Cirrhinus jullieni*

Source: Roberts (1997)

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2.6.2.2 Description

Predorsal profile relatively steep; rostral barbels well developed, length more than one-half eye diameter; maxillary barbels absent. Somewhat similar to the much larger species *C. molitorella*, from where it differs markedly in coloration. Also, it is deeper bodied, especially anteriorly, and has a larger, more falcate anal fin, the distal end of which extends posteriorly to below posteriormost scales on caudal fin; 13 to 14 branched dorsal-fin rays; 65 to 68 gill rakers on lower arm of first arch; faint dark blotch on body above pectoral fin; smooth upper lip, lower lip weakly papillate. Body without reticulate pattern; pectoral, pelvic, anal and lower caudal lobe usually bright red.

2.6.2.3 Biology

Cirrhinus jullieni can live in benthopelagic, potamodromous, freshwater and brackish. Inhabits midwater to bottom depths of rivers, occurring in the main stem and on the floodplains, including freshwater areas that undergo tidal fluctuation. Feeds on algae, detritus and occasionally benthic invertebrates. Often marketed fresh and used to make prahoc (Roberts, 1997).

2.6.3 Biology and ecology of *Oreochromis mossambicus* (Peters, 1852)

2.6.3.1 Taxonomic hierarchy

Kingdom Animalia -- Animal
Phylum Chordata
Class Actinopterygii (ray-finned fishes)
Order Perciformes (perch-likes)
Family Cichlidae (cichlids)
Subfamily Pseudocrenilabrinae
Genus Oreochromis
Species *Oreochromis mossambicus*

Source: Adapted from Trewavas (1982)

Common names: Mozambique tilapia, Java tilapia

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Figure 2-4 Characteristics of *Oreochromis mossambicus*

Source: Fish watcher record (2006)

2.6.3.2 Description

Jaws mature males enlarged, resulting in a concave upper profile. Female and non-breeding male silvery with 2 to 5 mid-lateral blotches and some of a more dorsal series. Breeding male black with white lower parts of head and red margins to dorsal and caudal fins. Scales on cheek usually in 3 rows. Caudal fin not densely scaled.

2.6.3.3 Biology

This species were distributed in Africa: Lower Zambezi, Lower Shiré and coastal plains from Zambezi delta to Algoa bay. Occurs southwards to the Brak river in the eastern Cape and in the Transvaal in the Limpopo system. Widely introduced for aquaculture, but escaped and established itself in the wild in many countries, often outcompeting local species. Most common in blind estuaries and coastal lakes. Also found in warm weedy pools of sluggish streams, canals, and ponds. Mainly diurnal. May form schools. Omnivorous, feeds on almost anything from algae to insects. Can be reared under hyper-saline conditions. Juveniles are carnivorous, adults tend to be herbivorous. Exhibits considerable plasticity in its feeding habits as well as in its reproductive biology (Trewavas, 1982).

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2.6.4 Biology and ecology of *Valamugil siheli* (Forskal, 1775)

2.6.4.1 Taxonomic hierarchy

Kingdom	Animalia -- Animal
Phylum	Chordata
Class	Actinopterygii (ray-finned fishes)
Order	Perciformes (perch-likes)
Family	Mugilidae (Mullets)
Genus	Valamugil
Species	*Valamugil siheli*

Source: Adapted from Myers (1991)

Common name: Bluespot gray mullet

Figure 2-5 Characteristics of *Valamugil siheli*

Source: Myers (1991)

2.6.4.2 Description

Bluish brown or green dorsally; flanks and abdomen silvery; dusky spots on upper row of scales, giving indistinct longitudinal stripes. Dorsal and upper lobe of caudal fin with dark-blue tip. Anal, pelvic, and pectoral fins yellow. Pectorals also with dark blue spot dorsally at origin. Pectoral-fin axil scale very long (Myers, 1991).

2.6.4.3 Biology

Inhabits coastal waters but enters estuaries and rivers where it feeds on microalgae, filamentous algae, forams, diatoms, and detritus associated with sand and mud. Forms schools. Also caught using stakenets, barrier nets, and pouch nets during

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spawning; also taken as bycatch. Marketed fresh and perhaps salted, boiled (Thailand), canned or frozen (Australia); roe salted (Myers, 1991).

2.6.5 Biology and ecology of *Pomacea canaliculata* (Lamarck, 1819)

A freshwater snail with a voracious appetite for water plants including lotus, water chestnut, taro, and rice. Introduced widely from its native South America by the aquarium trade and as a source of human food, it is a major crop pest in south east Asia (primarily in rice) and Hawaii (taro), and poses a serious threat to many wetlands around the world through potential habitat modification and competition with native species.

2.6.5.1 Taxonomic hierarchy

Kingdom	Animalia -- Animal
Phylum	Mollusca
Class	Gastropoda -- Snails
Subclass	Prosobranchia
Order	Caenogastropoda -- Mesogastropoda
Superfamily	Ampullarioidae
Family	Ampullariidae -- Apple snail
Genus	*Pomacea*
Species	*Pomacea canaliculata* (Lamarck, 1819)

Source: Adapted from Ghesquiere (2005)

(a) *Pomacea canaliculata* (b) Eggs of *P. canaliculata*

Figure 2-6 Characteristics of *Pomacea canaliculata*

Source: Ghesquiere (2005)

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Taxonomic name: *Pomacea canaliculata* (Lamarck, 1819)

Synonym: *Ampullaria canaliculata* Lamarck, 1819

Common names: Apple snail (English), Channeled apple snail (English), Gelbe Apfelschnecke (German), Golden apple snail (English), Golden kuhol (English-Philippines), Miracle snail (English-Philippines)

2.6.5.2 Description

Large (up to 10 cm), more or less globular freshwater snails. Aquarium trade snails are often smaller. Shell color generally brownish or greenish, often with spiral banding patterns around the whorls. Some aquarium bred animals are bright golden yellow. Body color can vary from dark, almost black to pale cream. Their presence is often first noted by observation of their bright pink egg masses laid on solid surfaces up to about 50 cm above the water surface.

2.6.5.3 Habitat description

P. canaliculata is widely distributed in lakes, ponds and swamps throughout its native range of the Amazon inferior basin and the Plata basin. This amphibious animal remains submerged during the day, hidden in vegetation near the surface. It is more active during the night, and leaves the water in search for fresh vegetation. The activity rate of this snail varies highly with the water temperature. At 18° C they hardly move around, this in contrast with higher temperatures e.g. 25° C. Nevertheless, *P. canaliculata* is more resistant to lower temperatures than most other snails from the genus *Pomacea* (Ghesquiere, 2005).

Longevity is up to 4 years. Reproductive maturity is reached in 3 months to 2 years, depending on ambient temperature regime.

Sexes are separate. Females lay clusters of bright pink eggs attached to solid surfaces (rocks, walls, logs, emergent vegetation, trash) up to usually about 50 cm above the water surface. Eggs generally hatch within 7 to 15 days, but may take longer, probably depending on ambient temperature regime. Reproductive output can be enormous. Clutch size is up to 1000, but averages probably 200 to 300. Clutches are laid every few weeks.

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2.6.5.4 General impacts

P. canalicualata was originally introduced from South America to South-east Asia around 1980, as a local food resource and as a potential gourmet export item. The markets never developed; the snails escaped or were released, and *P. canaliculata* became a serious pest of rice throughout many countries of South-east Asia. In the Philippines, it is considered the number one rice pest and has caused huge economic losses. It was introduced to Hawaii in 1989, probably from the Philippines, and for the same reasons as for its initial introduction to South-east Asia. Again, the snails rapidly escaped or were released and quickly became major taro pests. *P. canaliculata* can spread rapidly from agricultural areas into wetlands and other natural freshwater systems where it may have a serious impact. These potential impacts could involve destruction of native aquatic vegetation leading to serious habitat modification, as well as competitive interactions with the native aquatic fauna, including native snails. Already, introduced *P. canaliculata* has been implicated in the decline of native species of Pila apple snails in South-east Asia. Also, native species of Pila in the Philippines are reported to have declined as a result of extensive pesticide applications against introduced *P. canaliculata*. Climatic modeling has shown that it has the potential to spread to many as yet uninfested parts of the world, for instance the huge rice-growing areas of India. It has already been introduced to the USA and threatens the major rice-crops of Texas and California. Australia in particular is extremely concerned about its potential introduction to natural wetlands (e.g., Kakadu) as well as to rice-growing areas (Robert, 2005).

2.7 Relevant researches

Pipoplabanan (2002) studied the way of life in changing riverine ecosystem: a case study of the Phi Lok canal in the Lower of Mae Klong flood plain. The purpose of the study is to investigate the changes in a community's way of life in the Lower Mae Klong flood plain and it is reverine ecosystem as it is affected by water pollution. The result showed that at least as far back as 1927 the community of the Phi Lok canal depended on self-sufficient economy of paddy rice farming, coconut orchards and the harvesting of natural crops. Most villages cooporated in these activities. From 1976 to

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1979, crucial changes to the ecological system occurred as a result of severe droughts, the construction of a reservoir at Sri Nakarin dam and the invasion of sea water into the lower part of the Mae Klong river. To resolve these problems, a watergate and soil embankment were constructed. This resulted in the separation of the Phi Lok canal community into two distinct areas: the freshwater part in the upper reaches of the flood plain and the saltwater part in the lower area. Since then, agricultural production has dramatically changed by irrigation, production know-how and modern knowledge and technology. In the freshwater part, most villagers cultured gourami while the rest produced paddy rice twice a year along with an assortment of vegetables. In the saltwater part, villagers adjusted their way of life by establishing natural shrimp farms. The change in agricultural production has decreased the value of work-sharing among groups of villagers.

All types of wastewaters were released into the canal. For the attempts to solve the problems, the villagers had made the following recommendations: a) the construction of the new watergate that covers the canal width, b) to schedule the opening and closing periods of the watergate, c) to occasionally dredge the canal sediments, d) to treat the wastewater and e) to generate the condition that imitates the natural flooding regimes over the Lower Mae Klong flood plain in order to wash away the pollutants accumulated.

The study of Chaiyabutr (1998) was on some heavy metals in water, sediment and various tissues of some fish species in the Mae Klong river. It was found that the concentrations of zinc, lead, copper, cadmium and manganese in water and the concentrations of lead, copper and manganese in sediments reached their peaks in the cold season but decreased in the hot and rainy seasons. The concentration of cadmium in sediment reached its peak in the rainy season, but decreased in the cold and hot seasons. The concentration of zinc in sediment reached its peak in the hot season, but decreased in the rainy and cold seasons. The concentrations of zinc, lead, cadmium and manganese in herbivorous and carnivorous fish tissue, and copper in herbivorous fish tissue were high in the hot season but were low in the rainy and cold seasons. The concentration of copper in carnivorous fish tissue was high in the cold season, and was low in the rainy and hot seasons. The average concentrations of five heavy metals in water in the descending order are as follows: zinc, lead, copper, manganese and

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cadmium. In sediment, the average concentrations of five heavy metals in the descending order are as follows: manganese, zinc, lead, copper and cadmium. In fish tissue, the average concentrations of five heavy metals in the descending order are as follows: zinc, copper, lead, manganese and cadmium. In fish organs, it was found that copper, lead and manganese were high in digestive tract and zinc and cadmium in kidney.

Bunsong (2003) studied the distribution and accumulation of some heavy metals in water, sediment and aqutic organisms in the Phasicharoen canal, Thailand. It was found that concentrations of dissolved iron, manganese and zinc in surface water showed the most variation and were highest at Khratumbaen district. Concentrations of chromium, copper, iron, lead, manganese and nickel in sediment were high at Nongkham district. Plankton and water hyacinth from Nongkham and Khratumbaen districts contained very high concentrations of chromium, copper, nickel and zinc, while concentrations of iron and lead were considerably high at Phasicharoen district. In addition, the accumulations of heavy metals in target tissues of fish and mollusc were found at high concentrations at these areas as well. When comparing the heavy metal contents among the aquatic organisms, it was found that plankton had the highest levels of chromium, iron, lead, manganese, nickel and zinc. These heavy metals were higher in the roots of water hyacinth than in the leaves. Fish livers and kidneys accumulated at high levels of iron, zinc, and copper while manganese and zinc were detected in the gills at high concentrations. Molluscs accumulated at high levels of iron, zinc and copper in the foot, while manganese was at high level in the gills. Iron, zinc, manganese and copper accumulated at high levels in both the foot and the gill, whereas the mantle had lowest concentrations of these heavy metals. These results showed that bioaccumulation of heavy metals occurs in the organisms at the lower levels of the food chain and no biomagnification was detected at the upper levels, except for copper in molluscs and fish.

The study of Demirak *et al.* (2005) was on heavy metals in water, sediment and tissuse of *Leuciscus cephalus* from a stream in the southwestern of Turkey. Heavy metal concentrations of cadmium, chromium, copper, lead and zinc were measured in water, bottom sediment and tissues (muscle and gills) of *L. cephalus* from the Dipsiz stream in the Yatagan basin. Concentrations of cadmium, lead, zinc and chromium in

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the gills were higher than those in the muscle; however, copper concentrations were higher in the muscle than in gills. Heavy metal concentrations in *L. cephalus* muscle were below the legal limits for human consumption, although chromium, lead and zinc concentrations in the gills were above the limits in the fish collected from the Dipsiz stream. On the other hand, no correlation was found between metal concentrations in water and sediment or between metal concentrations in water and muscle and gills of *L. cephalus*. A positive correlation was found between copper and zinc concentrations in the sediment and in fish tissues, whereas there was no relationship between other metal concentrations in the sediment and water, and muscle and gills of *L. cephalus*. As with water, lead and cadmium concentrations in particular were higher in sediment than those in the background levels.

Chale (2002) studied the trace metal concentrations (copper, lead, iron, manganese, zinc and cadmium) in water, sediments, various fin fish species and a bivalve (*Mutela spekei*) from Lake Tanganyika. The centrapomid, *Lates stappersii* and the clupeids *Limnothrissa miodon* and *Stolothrissa tanganicae* are the most important commercial species in the lake followed by *L. marie*. Lead and cadmium concentrations are of concern to human health. The mean concentrations of the two metals in the commercial fish species are as follows: *L. stappersii* (5.03 μg Pb/g, 0.28 μg Cd/g); *L. marie* (4.96 μg Pb/g, 0.25 μg Cd/g); *L. miodon* (4.64 μg Pb, 0.38 μg Cd); and *S. tanganicae* (4.96 μg Pb/g, 0.39 μg Cd/g). Lead and iron concentrations in the bivalve species were exceptionally high, being 11.08 and 6.54 mg/g, respectively.

The study of Altindag and Yigit (2005) was to assess heavy metal concentrations in the food web of Lake Beysehir, Turkey. The results showed heavy metal accumulations in descending order are as follows: Cd > Pb > Cr > Hg in water, Pb > Cd > Cr > Hg in sediment, Pb > Cd > Cr > Hg in plankton, and Cd > Pb > Cr > Hg in the muscles and gills of chub, carp, tench, except for the muscle of pike perch are as follows: Pb > Cd > Cr > Hg (Pb in the food web in descending order as follows: water > plankton > sediment > fish tissues, except for chromium. According to international criteria and Turkish regulations, heavy metal concentrations especially cadmium and lead in Lake Beysehir were markedly above the permissible levels for drinking water.

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Canli and Atli (2003) studied the relationships between heavy metal concentrations (cadmium, chromium, copper, iron, lead and zinc) and the size of six Mediterranean fish species. The results showed that heavy metal concentrations in the muscle, gill and liver of six fish species (*Sparus auratus, Atherina hepsetus, Mugil cephalus, Trigla cuculus, Sardina pilchardus and Scomberesox saurus*) from the northeast Mediterranean sea were measured and the relationships between fish size (length and weight) and metal concentrations in the tissues were investigated by linear regression analysis. Metal concentrations (as μg/g dry weight) were highest in the liver, except for iron in the gill of *S. saurus* and lowest in the muscle of all fish species. Highest concentrations of cadmium (4.50 mg/kg), chromium (17.10 mg/kg) and lead (41.20 mg/kg) were measured in the liver tissues of *T. cuculus, S. pilchardus* and *A. hepsetus*, respectively. The liver tissues of *M. cephalus* showed strikingly high copper concentrations (202.80 mg/kg). The gill of *S. saurus* was the only tissue that showed highest iron concentration (885.50 mg/kg). Results of linear regression analysis showed that, except in a few cases, significant relationships between metal concentrations and fish size were negative.

Begum *et al.* (2005) studied the selected elemental composition of the muscle tissues of three fish species from the freshwater of Dhanmondi lake in Bangladesh. The heavy metal concentrations of three fish species, *Tilapia nilotica*, *Cirrhina mrigala* and *Clarius batrachus*, were determined using atomic absorption spectrometry and the following results (in μg/g dry weight) were obtained: calcium 4999, sodium 3183, magnesium 2193, iron 131, zinc 60.1, manganese 17.5, copper 5.07, lead 2.08 and nickel 1.91. Since the commission regulation setting the maximum lead level for the muscles of fish, released from the European Communities (EC), followed by the European Union (EU), is 0.2 mg/kg wet weight, corresponding to 0.96 μg/g dry weight, considerable attention should be paid to the lead content in freshwater fish species in Bangladesh. Furthermore, continuous monitoring of heavy metal concentrations in edible freshwater fish will be needed in Bangladesh.

Al-Yousuf *et al.* (2000) studied trace metal concentrations in liver, skin and muscle of fish species, *Lethrinus lentjan* in relation to body length and sex. Monitoring the concentration of the major heavy metals at different sites along the western coast of the United Arab Emirates (UAE) on the Arabian gulf was studied.

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The concentrations of zinc, copper and manganese were found to follow the order: liver > skin > muscle while the cadmium level follows the sequence: liver > muscle > skin. The influence of fish sex and body length on the metal accumulation of those metals in the tested fish organs was critically investigated. The average metal concentrations in liver, skin and muscle of female fish were found to be higher than those found in the male fish.

Lau *et al.* (1998) studied accumulation of heavy metals in freshwater molluscs. Three freshwater mollusc species were collected at the point source of the heavy metal pollutants and analysed for the heavy metal contents in their tissues and shells. Two of the mollusc species (*Brotia costula* and *Melanoides tuberculata*) are purely freshwater species while *Clithon* sp. nr *retropictus* is able to survive in fresh and brackish water environments. *B. costula* and *Clithon* sp. are the edible species which are sold in the market. Accumulations of arsenic, copper, iron, selenium and zinc in all the three mollusc species were determined and the level of arsenic in the tissues of *B. costula* and the *Clithon* sp. was much higher than the permissible level for human consumption. The mollusc species also demonstrated different preferences for the uptake of different metals. Variations in the heavy metal contents in the shell and tissues of the same species were also observed.

Kruawal *et al.* (2005) studied the chemical water quality in Thailand and its impacts on the drinking water production in Thailand. Thirty-six different samples from surface waters from the Chao Praya and Mae Klong rivers, tap waters, bottled drinking waters, groundwaters and commercial ice cubes around the Bangkok area were collected. The extensive survey showed that for all water samples investigated there was only a minor pollution which could be traced back to the analyses performed including amongst others total organic carbon, inorganics and heavy metals, pesticides, organochlorine compounds, volatile organic compounds, surfactants, pharmaceuticals and disinfection by-products. The concentration of disinfection by-products was higher in tap water produced from the Chao Praya river than from the Mae Klong river. Disinfection by-products were also found in bottled drinking water. Commercial ice cubes contained anionic surfactants and their metabolites at elevated concentrations. The data of this study constitute the first set of homogenous data for

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the chemical water quality and also aid development of new water quality criteria in Thailand.

Censi *et al.* (2006) studied heavy metals in coastal water systems. A case study from the northwestern gulf of Thailand. The result showed that a geochemical survey of the northwestern part of the Gulf of Thailand (Inner gulf) was carried out in order to define the concentrations and distribution patterns of selected heavy metals (vanadium, chromium, cobolt, nickel, copper, zinc, and uranium) in the coastal system and estuarine area of the Mae Klong river. The results indicated the presence of two different sources of heavy metals in the studied environment and allowed the authors to identify a lithogenic component that significantly influenced the composition of coastal waters and suspended particulate matter (SPM). Comparison of the normalized heavy metal concentrations both in the studied samples and in those reported for the Sn-W ores present in the surrounding areas suggested an important anthropogenic contribution to the chemistry of the seafloor sediments. Vanadium and nickel enrichment factors (EF) calculated for coastal waters indicated that contamination by hydrocarbons discharged took place in the investigated area.

Usero *et al.* (2003) compared metal concentrations in water and sediment with those in the muscle and livers of three fish species (grey mullet; *Liza aurata*, eel; *Anguilla anguilla* and common sole; *Solea vulgaris*) caught in four seawater reservoirs (two in the Odiel estuary and two in the Bay of Cadiz). The concentrations of a large number of metals in the water, sediment and fish were higher in the Odiel reservoirs than in those in the Cadiz. The authors found high metal-enrichment factors in the liver as compared to muscle (over 100 for iron and copper and around 5 for zinc, nickel, cadmium and lead). The three fish species showed differences in metal contents. For example, eels accumulated more metals in muscle and grey mullet in the liver. The metal levels found in muscle in the three species were reservoirs, and zinc levels in liver were over the maximum in eels from one of the Odiel marshes. Significant correlations ($p < 0.05$) were obtained for the levels of numerous metals in water, sediment and fish.

Sekhar *et al.* (2003) measured the concentration of selected heavy metals, i.e., zinc, copper, cadmium, lead, chromium, nickel and cobolt in sediment samples and three edible fish (*Channa striata*, *Catla catla* and *Oreochromis mossambicus*) in

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Kolleru lake, the largest freshwater lake in the districts of East and West Godavari of Andhra Pradesh, India. The investigation aimed at revealing differences in the accumulation pattern of heavy metals in fish inhabiting sediments characterized by varying metals bioavailability. The metal concentrations were found to be greater than the background concentrations of sediments indicating the anthropogenic origin of metals. Good recovery values were obtained for metal contents in sediments and fish. Large fractions of zinc, cadmium and copper were associated with mobile fraction of sediments and showed greater bioaccumulation in fish whereas nickel and cobolt were least mobilisable. The results clearly indicated that the fish of Kolleru lake are contaminated with metals and not advisable for human consumption.

Karadede *et al.* (2004) studied distribution of some heavy metals (cobolt, copper, iron, manganese, molydinum, nickel and zinc) in three different organs of mullet, *Liza abu*, and catfish, *Silurus triostegus*, from Ataturk Dam Lake located on Eupharates (Turkey). Copper and molybdenum concentrations were below limits of detection in all fish organs, whereas nickel was also below limits in organs of mullet. The metal accumulation in the liver and gill of *L. abu* and *S. triostegus* was found to be rather high in comparison with the muscle. In general, the concentrations are similar to those determined in the Tigris river. The metals (cobolt, copper, iron, manganese, molybdenum, nickel and zinc) were found in fish muscle at mean concentrations under the permissible limits proposed by FAO.

Papagiannis *et al.* (2004) evaluated the level of contamination of two essential heavy metals (copper and zinc) appearing at high concentrations in four fish species, *Cyprinus carpio*, *Silurus aristotelis*, *Rutilus ylikiensis*, and *Carassius gibelio*, in Lake Pamvotis. The Lake Pamvotis (NW Greece) is a typical Mediterranean ecosystem of great importance in regard to biodiversity and to aesthetic value. Metal concentrations were measured by atomic absorption spectrophotometry in three different tissues (muscle, liver, and gonads) in order to assess the fish contamination. A two-factor analysis of variance, based on the procedure of general linear models, was employed in which fish species (four levels) and fish tissue (three levels) were examined for potential influence on copper and zinc concentrations. Differences between level means per factor were treated using Tukey's multiple comparisons of means. The study showed that *C. carpio* and *R. ylikiensis* presented the highest metal

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content. Tissues analysis revealed that liver and gonads accumulated the highest levels of copper and zinc. Metal concentrations in the edible part of the examined fish (muscle) were in the safety-permissible levels for human consumption.

Turkmen *et al.* (2005) determined concentrations of cadmium, iron, lead, zinc, copper, manganese, nickel, chromium, cobalt and aluminum in three commercially valuable fish species, *Saurida undosquamis*, *Sparus aurata*, *Mullus barbatus*, from Iskenderum bay in August 2003. The concentration of metals was measured by atomic absorption spectrophotometry (AAS). Heavy metal concentrations in examined fish species ranged as follows: copper 0.01 to 4.16; iron 0.82 to 27.35; lead 0.09 to 6.95; zinc 0.60 to 11.57; copper 0.04 to 5.43; manganese 0.05 to 4.64; nickel 0.11 to 12.88; chromium 0.07 to 6.46; cobolt 0.03 to 5.61; aluminium 0.02 to 5.41 mg kg^{-1} dry weight. The concentration of metals was significantly affected by the sampling site and fish species. Heavy metals in the edible parts of the investigated fish were in the permissible safety levels for human users.

Usero *et al.* (2005) determined concentration of heavy metals in the two most abundant species of bivalve molluscs along the Atlantic coast of southern Spain (*Donax trunculus* and *Chanelea gallina*) and in the sediments where they live. The results showed that the area near the mouth of the Huelva estuary were found the highest metal concentratrions in sediments and in the two bivalve species. This is not surprising, considering that the Huelva estuary is the mouth of the Tinto and Odiel rivers, which have one of the highest levels of metal pollution of all the rivers of Europe. The two species of bivalves have different amounts of metals in their tissues. The concentrations of chromium, copper, lead, zinc, arsenic and mercury in *D. trunculus* were significantly higher ($p<0.05$) than in *C. gallina*; however, *C.gallina* contained more nickel and cadmium. In both species, the most abundant elements were copper and zinc, while mercury showed the lowest values. There is a significant correlation ($p<0.05$) for concentrations of copper, lead, zinc and mercury in *D.trunculus* and *C. gallina* relative to their concentrations in surface sediments.

Tuzen (2003) determined the concentrations of heavy metals (lead, cadmium, iron, copper, manganese and zinc) in fish samples using graphite furnace atomic absorption spectrophotometry after dry ashing and wet ashing methods. Different matrix modifiers were used for the stabilization of the analyte. Good accuracy was

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assured by the analysis of biological reference materials. Recoveries were quantitative for all elements studied (≥95%). The relative standard deviations were less than 7% for all elements.

Karadede and Unlu (2000) measured the concentration of heavy metals (cadmium, cobolt, copper, iron, mercury, manganese, molybdenum, nickel, lead and zinc) in water, sediment and fish species (*Acanthobroma marmid*, *Chalcalburnus mossulensis*, *Chondrostoma regium*, *Carasobarbus luteus*, *Capoetta trutta* and *Cyprinus carpio*) from the Ataturk Dam Lake, Turkey. Among the heavy metals studied cadmium, cobolt, mercury, molybdenum and lead were not detected in water, sediments and fish samples, while nickel was found at undetectable levels in fish samples. Levels of copper, iron, manganese and zinc varied depending on different tissues. The results of this study indicated that a general absence of serious pollution in the dam lake is due to heavy metals, where as the concentrations of elements found could mainly be attributed to geological sources.

Sirichotiwong (2006) studied five heavy metals (cadmium, copper, iron, lead and zinc) in water, sediment and Snakeskin Gaurani fish (*Trichogaster pectoralis* Regan) collected from the fish raising pond at Phraek Nam Daeng sub-district, Amphawa district, Samut Songkhram province**.** The heavy metal concentrations in the descending order are as follows: Pb > Cu > Zn > Fe > Cd in water; Fe > Zn > Cu > Pb > Cd in sediment; Fe > Zn > Cu > Pb > Cd in muscle and Fe > Zn > Cu > Pb > Cd in internal organ. The result revealed no significant differences in any heavy metals in water and sediment. The amount of heavy metals accumulated was higher in internal organs than in muscle in all six months, except lead in September and October. From this study, it was found that iron, copper and zinc levels were unacceptable for human consumption according to FAO/WHO (1989) but acceptable for the ANZFA standard.

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CHAPTER III
MATERIALS AND METHODS

3.1 Study area

3.1.1 Location and Land Use

The Phi Lok canal system consisted of three parts which were the Wan Dao canal (a canal part from Wat Wan Dao to the junction with the Pradu canal), the Pradu canal (the portion between the Wan Dao canal and the Phi Lok canal) and the Phi Lok canal. However, the Phi Lok canal is the most important part where four out of five sampling stations were located. The Phi Lok canal system was situated in Phraek Nam Daeng sub-district, Amphawa district, Samut Songkhram province. Phraek Nam Daeng sub-district has 34 canals connecting as the network covering the area.

The Phi Lok canal is a small waterway that branches out from the Pradu canal, a tributary of the Mae Klong river that is one of the main and important rivers in the central part of Thailand. The Phi Lok canal is about 4.5 km long. It runs from west to east to the Gulf of Thailand. There are five branches, i.e., the Rang Kwai canal, the Tamon canal, the Khwang canal, the Takeed canal and the Jed canal. The Phi Lok canal flows into the Yi San canal and the Gulf of Thailand at Bang Tabun district, Phetchaburi province. The canal receives water mainly from the Wat Pradu canal and also water and wastewater from interconnected canals such as the Rang Kwai and Tamon canals.

At present, the water system of the the Phi Lok canal system was clearly divided in two parts, i.e., the freshwater part in upper reaches of the Phi Lok canal and the saltwater part in the lower area of the Phi Lok canal. Rama II highway and soil embankment were divisible line. In the major canals, there are watergates constructed by the Royal Irrigation Department to prevent the salt intrusion into the freshwater part.

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The major activities of the study area (see Figure 3-1) are described as follows. The pig farms are operated all year round and wastewater is normally produced everyday. This activity is the major source of wastewater discharged into Pak Tho district, Ratchaburi province and the canal system (Phangsombut, 2005). The pig farms are the major activity in sampling site A.

Normally, rice has grown 2 to 3 batches per year depending on the water availability of precipitation and irrigation. Most paddy fields are planted around May and harvested around September or November. The freshwater is pumped from the canal to the fields after the rice has grown around 20 days. Around one month before the harvesting period the farmer drains the water off from the fields into the canal. The paddy fields were the major land use characteristic of sampling sites A and B in the study area

For the fish raising ponds, the period for fish raising is around eight months. It starts around April and ends around November to December. The canal water is pumped up from the canal to fill up the pond before the raising period starts. Also the canal water is occasionally pumped into the pond to maintain the water level. After the harvesting is completed, the fish farmer pumps the water and sediment out from the pond into the canal to expose and dry the pond for one month before the new raising period starts (Sirichotiwong, 2006). The fish raising pond was the major land use characteristic of sampling sites B and C in the study area

The shrimp farms are operated all year round. The shrimp farmers pumped the brackish water from the canal around the high tide period depending on the number of shrimp larvae in the ponds the farmer needs. The shrimps were harvested every month during the low tide period. The farmers pumped the water through the net next to the out let and shrimps were collected. The pond water and sediment are pumped out from the farms into the canal around February to May to expose and dry the pond. The shrimp farm was the major land use characteristic of sampling sites D and E.

And the last land use type, the industry and village highly concentrated in Pak Tho district, Ratchaburi province. In 2004, total population of Pak Tho district was

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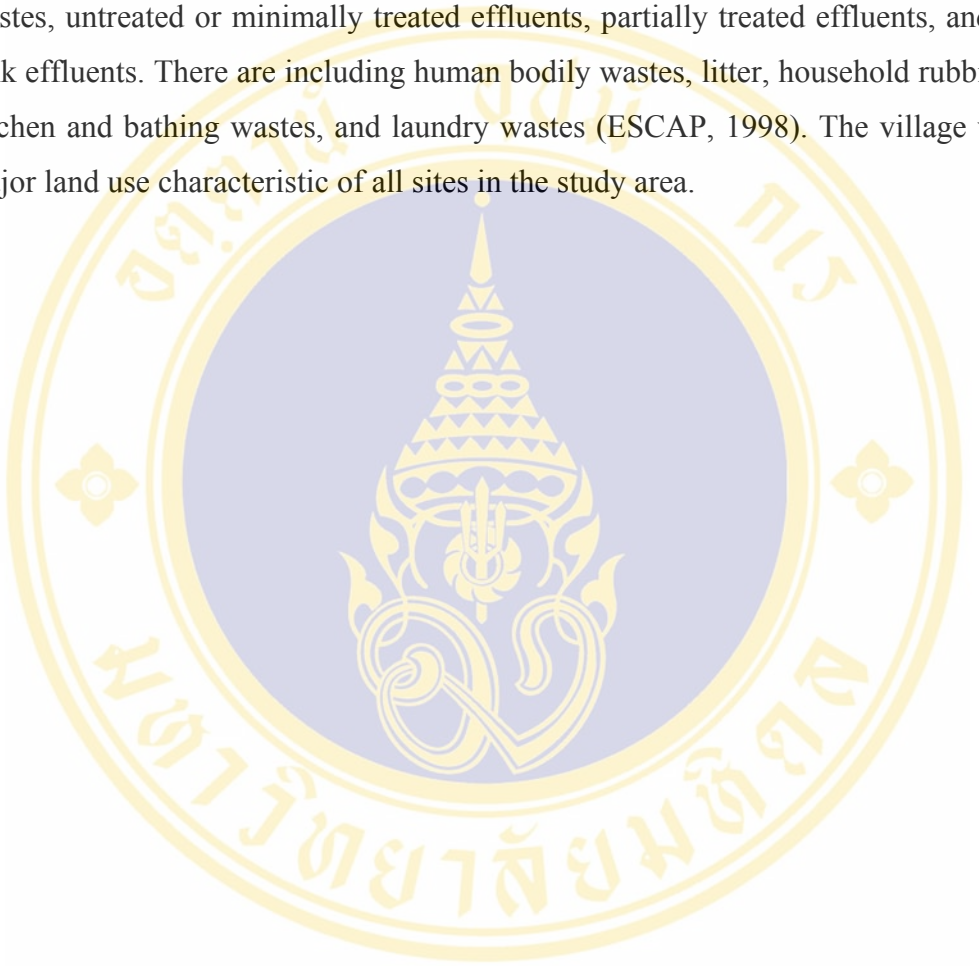
60,185 inhabitants (Ratchaburi, 2005). The industry and villages were the major land use characteristic of all sites in the study area especially site A.

And the last one, the communities were located in all sites. The waste waters from the villages are discharged into waterways and water bodies including untreated wastes, untreated or minimally treated effluents, partially treated effluents, and septic tank effluents. There are including human bodily wastes, litter, household rubbish, and kitchen and bathing wastes, and laundry wastes (ESCAP, 1998). The village was the major land use characteristic of all sites in the study area.



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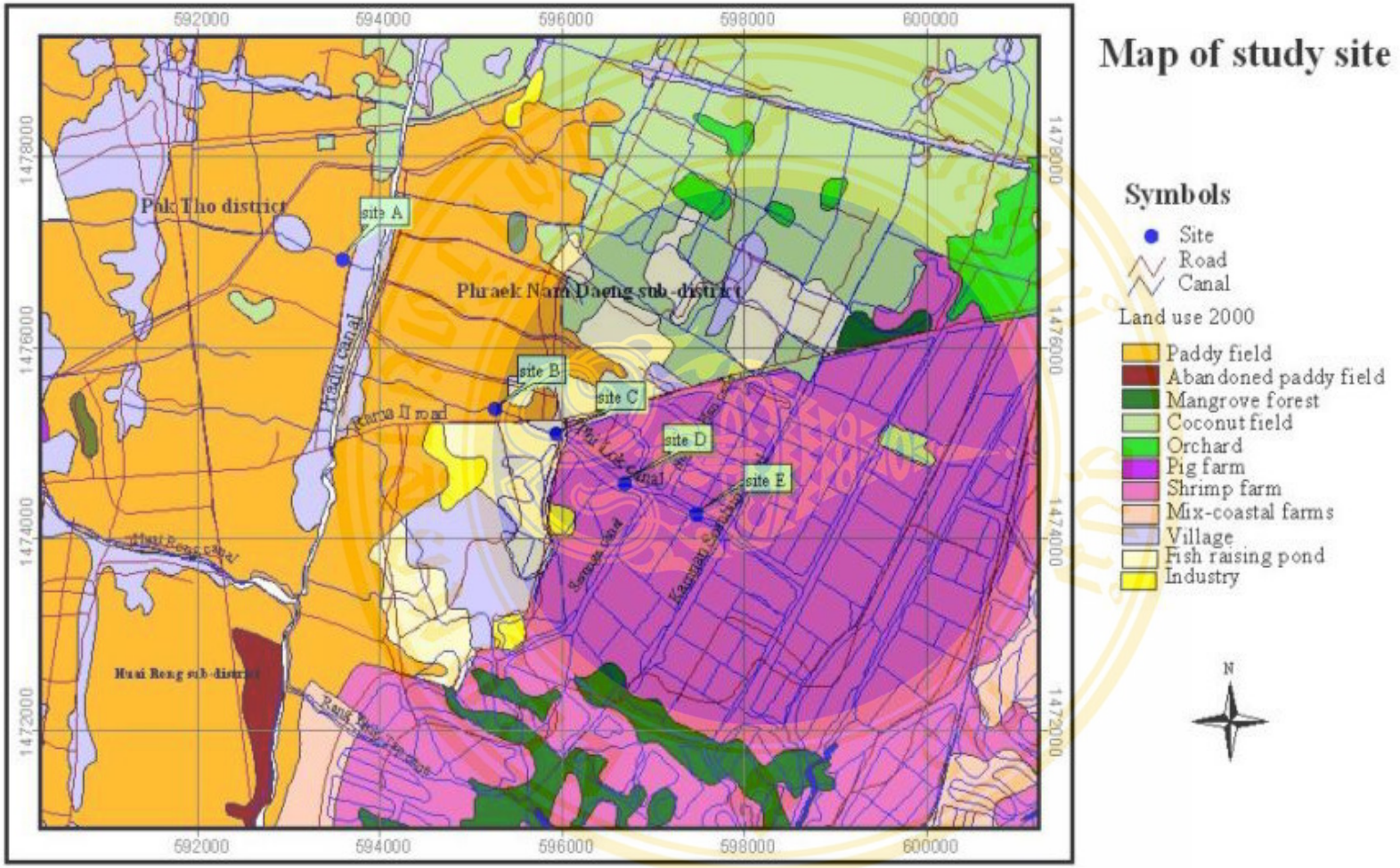

Figure 3-1 Map of five sampling sites in the Phi Lok canal system

Source: Land Development Department, 2000

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3.1.2 Sampling sites

Five sampling sites of the Phi Lok canal system are shown in Figure 3.1. The activities of each sampling site are described as follows.

Sampling sites A, B and C were in the freshwater part whereas sampling sites D and E were in the saltwater part.

Sampling site A was the only site that was not situated in Phraek Nam Daeng sub-district but situated in Wan Dao sub-district, Pak-Tho district, Ratchaburi province. The major activities of this site were paddy fields and pig farms. In addition, sampling site A also received wastewater from the upstream area of Pak-Tho district, Ratchaburi province where many pig farms were located. The environment of this sampling site are shown in Figure 3-2.

Figure 3-2 Sampling site A at the Phi Lok canal system

Sampling site B was located behind the scrap plant (Figure 3-3). The plant occasionally burnt the used battery. Moreover, wastewaters from soaking and washing used paper were discharged from the plant once or twice per month (Pipoplabanan, 2002). It was the major source of some heavy metals contaminated in the Phi Lok canal water. The major activities of this site were paddy fields and fish raising ponds.

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(a) Characteristics of the Phi Lok canal at sampling site B (b) The scrap plant

Figure 3-3 Sampling site B at the Phi Lok canal

Sampling site C was located around 10 m upstream in front of the watergate at the Phi Lok canal. The watergate normally blocked the seawater to flow to the freshwater part but allows only the freshwater to flow out to the seawater part when the freshwater is over the blockage panal (Figure 3-4). However, most of the time the water can not flow easily so the stagnant condition occurred and caused the bloom of aquatic plants in front of the watergate. Most villagers in this sampling site raise gourami and orchards.

(a) Characteristics of the Phi Lok canal (b) Watergate near sampling site C

Figure 3-4 Sampling site C at the Phi Lok canal

Sampling site D was located about 100 m before the Samnga junction. It is the first sampling site of the seawater part and about 800 m from the watergate. This sampling site was in the mangrove area (Figure 3-5). Major land use activity was extensive shrimp farm.

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(a) Water level in December (b) Water level in June

Figure 3-5 Water regimes of the saltwater part of the Phi Lok canal at sampling site D

The last sampling site in the Phi Lok canal system is sampling site E. It is located after the Samnga and Saphan Hun junctions and before the Phi Lok canal running into the Kamnan Sombun canal. The major land use activity of extensive shrimp farms was found in sampling site E. Figure 3-6 shows the environment of this sampling site.

(a) Water level in December (b) Water level in June

Figure 3-6 Water regimes of the saltwater part of the Phi Lok canal at sampling site E

3.2 Sampling duration

Samples were collected from each site every two months from June 2004 to April 2005. The first sample collection was taken in June 2004: the second, third,

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fourth, fifth, and sixth collections were done in August 2004, October 2004, December 2004, February 2005 and April 2005, respectively.

3.3 Analysis of physico-chemical parameters of water sample

3.3.1 Sample collection and Preservation

Five sampling sites along the canal system were chosen for collecting water samples for physico-chemical parameters. Samples were taken from three sampling points along the cross section of each sampling site: middle-width of the canal, one-third of the width of the canal and two-thirds of the width of the canal.

At each sampling site, the width and depth were measured. Then, six water parameters, i.e., pH, conductivity, salinity, water temperature, dissolved oxygen and transparency were measured in-situ.

Water samples were collected at one-third of the depth of the canal by using the grab water sampler and stored in polyethylene bottles and BOD glass bottles, and then kept in an ice box prior to analysis in the laboratory for six parameters: dissloved oxygen, biochemical oxygen demand, nitrate, phosphate, hardness and total dissolved solid.

3.3.2 Sample analysis

The equipments and methods in analysis of water samples are described in Standard Method for Examination of Water and Wastewater (APHA *et al.*, 1995) and presented in Table 3-1.

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Table 3-1 Analytical method of physico-chemical parameters of water sample

Parameters determined by using analytical equipments in the field	
Parameters	Analytical equipments
pH	pH meter
Conductivity (ms/cm)	Conductivity meter
Salinity (ppt)	Conductivity meter
Water temperature (°C)	DO meter
Dissolved oxygen (mg/L)	DO meter
Transparency (cm)	Secchi disc
Parameters analysed in the laboratory	
Parameters	Analytical methods
Dissolved oxygen (mg/L)	Azide modification of iodometric method
Biochemical oxygen demand (mg/L)	Azide modification of iodometric method
Total dissolved solid (mg/L)	Gravimetric method
Nitrate (mg/L)	Bruzine method
Hardness (mg/L)	EDTA titrimetric method
Phosphate (mg/L)	Ascorbic acid method

3.4 Heavy metal analysis

3.4.1 Samples collection and preservation

The collected samples are water, sediment and aquatic animals. Samples of mollusc (*P. canaliculata*) were collected only in the freshwater part (sampling sites A, B and C). For fish samples, various species were collected depending on avalibility.

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1) Water

At each sampling site, water samples of 1000 mL were collected from the surface water at about 30 cm deep by using the grab water sampler and stored in polyethylene bottles. The water samples were taken at three sampling points as follows: one-third of the width, in the middle of the width and two-thirds of the width of the canal. The water samples were preserved with 0.5 mL of concentrated HNO_3 (Diagomanolin *et al.*, 2004), and then kept in an ice box and transferred to the refrigerator at 4°C until to analysis in the laboratory.

2) Sediment

About 0.5 kg of sediment samples were collected using the bottom grab sampler at the top 20 cm. of the bottom sediment. The samples were placed in plastic bags, which were then tightly closed. They were kept in ice box, prior to analysis in the laboratory. After their arrival, they were suddenly air-dried (Usero *et al.*, 2005).

3) Fish

Samples of some fish were collected at least one species at each sampling site depending upon the seasonal variation. The samples were collected by local fisherman with a net (Figure 3-7) and placed in plastic bags, which were then tightly closed. They were immediately stored in ice box prior to dissection and analysis in the laboratory.

Figure 3-7 Samples of some fish collected by local fisherman with a net

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4) Mollusc

P. canaliculata was collected at sampling sites of the freshwater part by hand-picking by local people. Because it was commonly found only in the freshwater part but not in the saltwater part. Depending on size, 5 to 10 mollusc specimens were placed in labelled plastic bags which were then tightly closed. They were immediately stored in ice box, prior to dissection and analysis in the laboratory.

3.4.2 Sample preparation

1) Sediment

The sediment samples were dried at ambient air condition for a week and then oven-dried at 80°C until a constant weight. The samples were crushed and homogenized in a baked clay mortage, and sieved through a 2 mm sieve. The fraction < 2 mm was chosen for chemical analysis (Sekhar *et al.*, 2003). The powdered samples were preserved in clean and dry plastic bags and kept in the silica gel cabinets until analysis.

2) Fish

Fish samples were thawed at room temperature and the total body length was recorded (Henry *et al*., 2004). The whole fish samples were cut into small pieces with a stainless steel knife and washed with tap water followed by distilled water. They were dried at 80°C in an oven until a constant weight. Then they were homogenized in a baked clay mortage. The fine sample was stored in plastic bags and kept in the silica gel cabinets until analysis.

3) Mollusc

The mollusc specimens were thawed at room temperature and the size was recorded. Tissues of the mollusc were removed from the shell and cut into small pieces using the stainless steel knife. The samples were dried at 80°C in an oven until a 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 cabinets for further analysis (Lau *et al.*, 1998).

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3.4.3 Sample digestion

Sample digestion was performed using a Milestone Laboratory Systems model MLS-1200 MEGA. Samples were digested with concentrated nitric acid in a closed system of microwave digestion system. The advantages of microwave digestion against the classical methods are the shorter time, less consumption of acid and keeping volatile compounds in the solutions (Turkmen *et al.*, 2005; Krushevska *et al.*, 1993).

1) Water

10 mL of the water samples were placed into the digestion vessels and 6 mL of concentrated nitric acid were then added. The digestion were performed in a microwave digester to prepare the samples for analysis using the microwave digestion programme.

2) Sediment

The homogenized sediment samples were weighed to approximately 0.5 g on an analytical balance and transferred into the digestion vessels. The sediment samples were digested with 10 mL of concentrated nitric acid. The digestion was carried out in a microwave digester using the microwave digestion programme.

3) Fish and mollusc

Approximately 0.5 g of samples were weighed and transferred into the digestion vessels. The samples were digested with 8 mL of concentrated nitric acid. The digestion was carried out in a microwave digester using the microwave digestion programme.

After completion of the microwave digestion programme, samples were allowed to cool to room temperature. Then, 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% of concentrated nitric acid. The samples were stored in 60 mL polyethylene bottles and kept in refrigerator until analysis.

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3.4.4 Preparation of reagents and standard solutions

All reagents are of analytical reagent grade. Distilled water were used throughout the study. High purify argon was used as inert gas (Karadede *et al.*, 2004). 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. Baker/E Merck standards and instrumental calibrated standard solutions were prepared from commercial materials

3.4.5 Atomic absorption detection

All the digested samples were analyzed in triplicates for the metals; Cd, Cu, Fe, Pb and Zn by using atomic absorption spectrophotometer. The absorption lines for metals are 213.9 nm of zinc, 324.7 nm of copper, 228.8 nm of cadmium, 248.3 and 392.0 nm of iron and 217.0 and 283.3 nm of lead.

Metal concentrations: Cu, Fe and Zn in the filtered digested samples were determined by flame atomic absorption spectrometer (FAAS), performed using a Varian atomic absorption spectrophotometer model spectraAA-55 (Varian spectrAA 220FS flame atomic absorption spectrophotometer)(Figure 3-8).

Figure 3-8 Varian spectrAA 220FS flame atomic absorption spectrophotometer

While Pb and Cd were determined by graphite furnance atomic absorption spectrometer(GFAAS), performed using a Varian spectrAA 220Z grabhite furnace atomic absorption spectrophotometer (Figure 3-9).

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Figure 3-9 Varian spectrAA 220Z graphite furnace atomic absorption spectrophotometer

3.5 Data conversion

Heavy metal contents from analysis by atomic absorption spectrophotometer in mg/L (or µg/L) were converted into mg/kg (or µg/kg) by using the following formula.

$$\text{Dried sample in mg/kg} = (A-B) \times (V/W)$$

Where: A= concentration of heavy metal in the digested sample in mg/L
B= concentration of heavy metal in the digested blank in mg/L
V= total digested volume at the end of the digestion process in mL
W= weight of sediment and plant materials samples in g.

3.6 Statistical analysis

Statistical analysis of data will be carried out with the SPSS statistical program. (SPSS for Window 11.0 (Vanitbancha, 2005)). One-way Analysis of Variance (ANOVA) and correlation will be used in the study. Statistic explanation such as mean value, minimum value and maximum value were used to explain results as well.

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CHAPTER IV
RESULTS

The study of accumulation and distribution of some heavy metals in water, sediment, *Pomacea canaliculata* and some fish species in the Phi Lok canal system, Samut Songkhram province were took place during June 2004 to April 2005. The results of the study were presented as follows.

4.1 Physico-chemical parameters of water

The water samples in the Phi Lok canal system were collected from June 2004 to April 2005. The physico-chemical parameters of biochemical oxygen demand (BOD_5), dissolved oxygen (DO), nitrate (NO_3^-), phosphate (PO_4^{3-}), pH, total dissolved solid (TDS), temperature, conductivity, salinity and hardness were investigated.

Temperature and pH were determined as showed in Figure 4-1 and overall average values varied in rather narrow range. The temperature values varied from 24.18 to 31.18°C in the freshwater part (sampling sites A to C) and the average value was 28.16°C. The highest value was found at sampling site B in April and the lowest value was found at sampling site A in December. In the saltwater part (sampling sites D and E), the temperature values varied from 23.62 to 30.71°C and the average value was 28.38°C. The highest value was found at sampling site E in April and the lowest value was found at sampling site E in December. The average temperature value in the freshwater and saltwater parts seemed to be nearly equal values during the collection period.

The pH values varied from 7.27 to 7.90 in the freshwater part and the average value was 7.51. The highest value was found at sampling site C in June and the lowest value was found at sampling site A in October. In case of the saltwater part, pH values varied from 7.49 to 7.91 and the average value was 7.72. The highest value was found at sampling site D in December and the lowest value was found at sampling site E in April.

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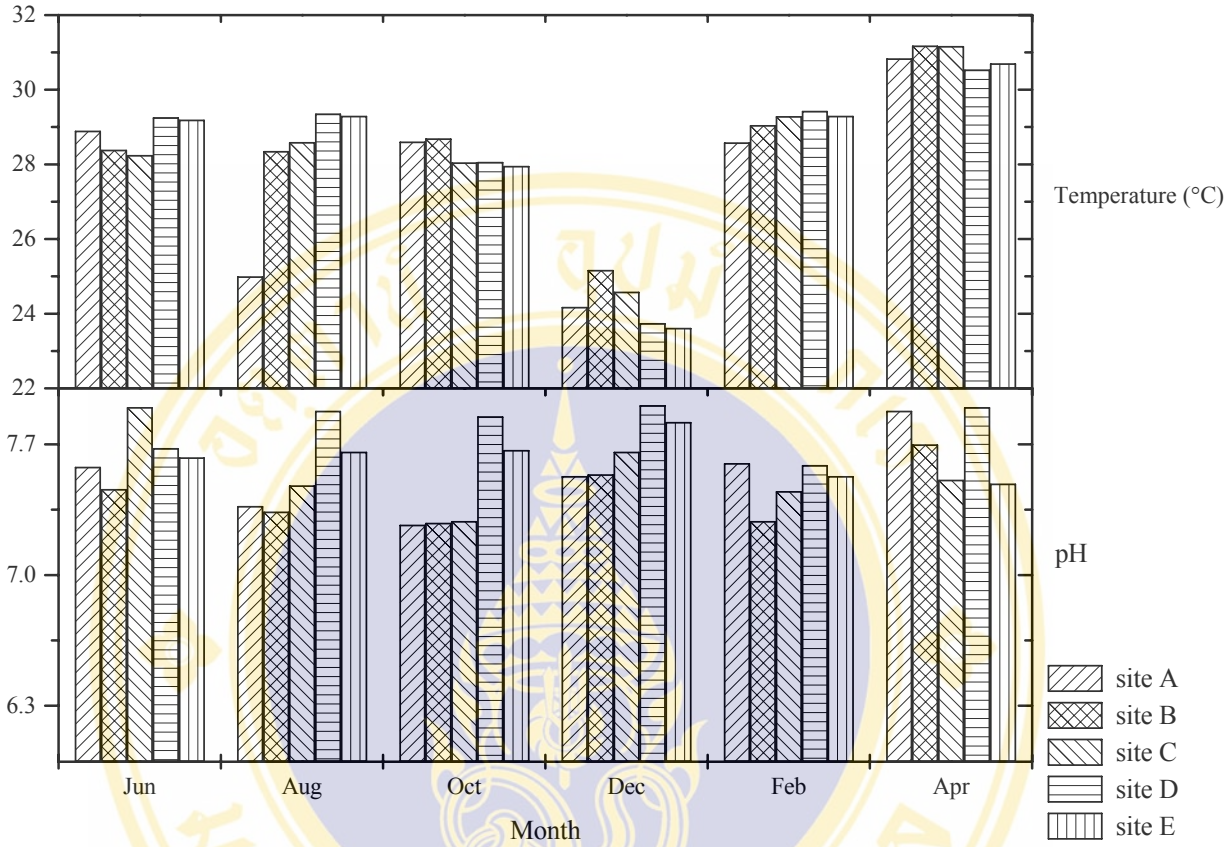

Figure 4-1 Average values of temperature and pH during the collection period

Phosphate and nitrate (NO_3^-) were determined as showed in Figure 4-2. Phosphate values varied from not detected to 0.06 mg/L in the freshwater part and the average value was 0.03 mg/L. In the saltwater part, phosphate values varied from not detected to 0.04 mg/L and the average value was 0.02. Phosphate in the freshwater part were higher than in the saltwater part. Phosphate values were higher at sampling site B than other sasmpling sites in June and this month seemed to be higher average values than other months. For sampling site A, phosphate values were higher than other sampling sites in August and December. In October, phosphate values were not different when comparing among five sampling sites, whereas sampling site A phosphate values were very high in February. The lowest values appeared in April.

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Nitrate (NO_3^-) values varied from 0.08 to 8.47 mg/L in the freshwater part. The average value was 2.74 mg/L. The highest values were found at sampling site A in December and the lowest values were found at sampling site A in April. In the saltwater part, nitrate varied from 0.07 to 5.73 mg/L and the average value was 2.44 mg/L. The highest values of the saltwater part were found at sampling site D in December, whereas the lowest values were found at samplig site E in April. Also in April, the lowest values appeared in every sampling site.

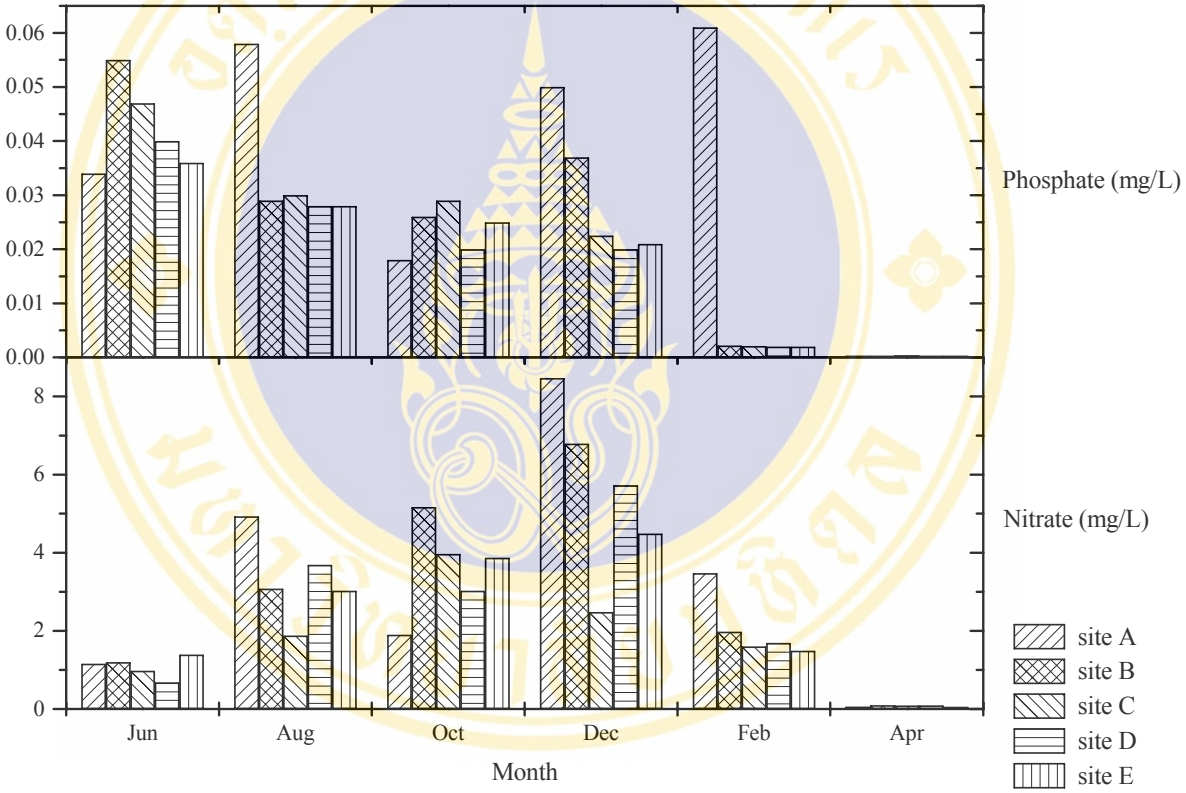

Figure 4-2 Average values of phosphate and nitrate during the collection period

Because of the agricultural activities such as paddy field, vegetable farm and fish farm containing fertilizers and pesticides, were found in the freshwater part more than those in the saltwater part. Thus, the values of phosphate and nitrate in the freshwater part were higher.

Dissolved oxygen (DO), and biochemical oxygen demand (BOD_5) were determined as showed in Figure 4-3.

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Dissolved oxygen (DO) varied from 0.14 to 9.20 mg/L in the freshwater part and the average value was 2.69 mg/L. The highest values were found at sampling site C in December and the lowest values were found at sampling site B in December. In case of the saltwater part, DO values varied from 2.25 to 6.13 mg/L and the average value was 3.87 mg/L. The highest values of the saltwater part were found at sampling site E in August, whereas the lowest values were found at sampling site D in February.

Biochemical oxygen demand (BOD_5) varied from 0.48 to 8.07mg/L in the freshwater part and the average value was 4.38mg/L. The highest values were found at sampling site A in August and the lowest values were found at sampling site A in April. In the saltwater part, BOD varied from 1.20 to 8.57 mg/L and the average value was 3.87 mg/L. The highest values of the saltwater part were found at sampling site E in August, whereas the lowest values were found at sampling site E in February.

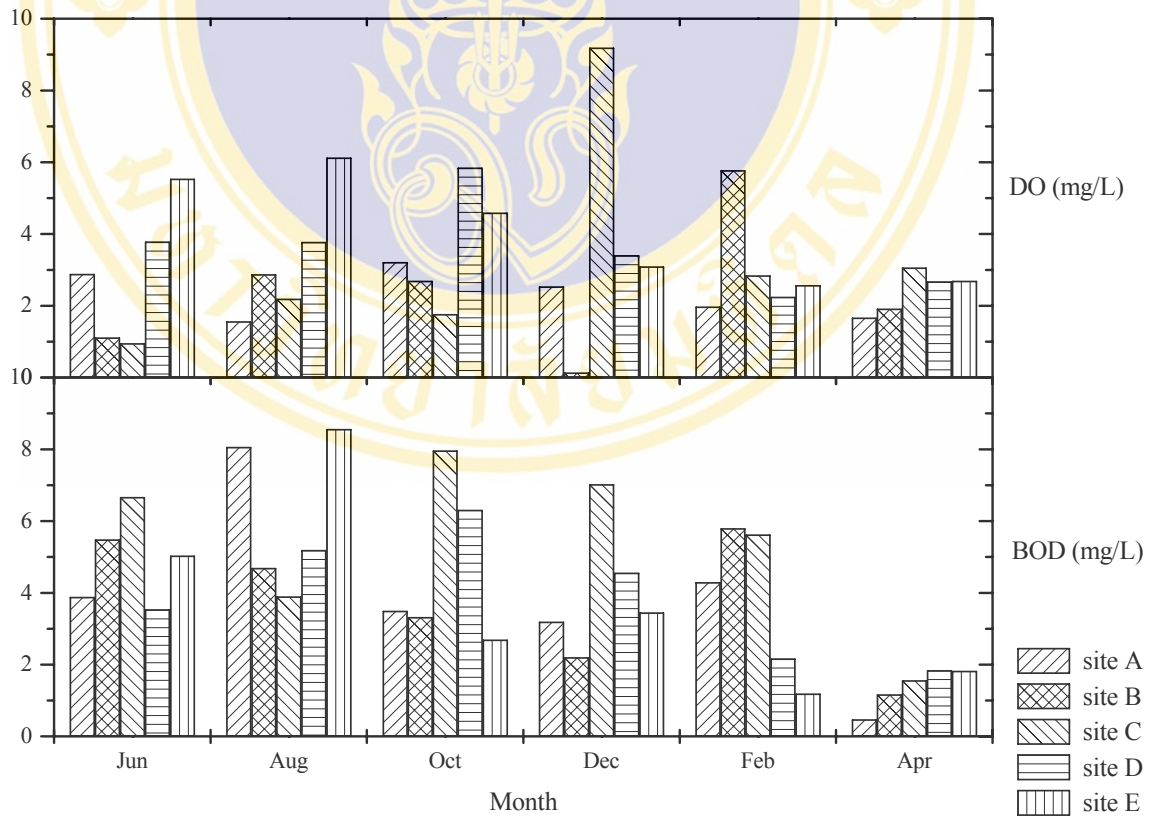

Figure 4-3 Average values of DO and BOD during the collection period

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Total dissolved solid (TDS), hardness, conductivity, and salinity were determined as showed in Figure 4-4. The results of these parameters can clearly devided into two periods, June to October and December to April.

From June to October in the rainy and cold seasons, when water level was rather high from the precipitation. The salinity was diluted by freshwater. Thus, salinity values and also TDS, hardness and conductivity values were very low, especially in the freshwater part.

Total dissolved solid (TDS) varied from 388.00 and 6732.67 mg/L and the average value was 1745.19 mg/L. The highest values were found at sampling site C in February and the lowest values were found at sampling site A in February. In the saltwater part, TDS varied from 2127.00 to 38142.00 mg/L and the average value was 15405.81 mg/L. The highest values of the saltwater part were found at sampling site E in April, whereas the lowest values were found at sampling site D in October.

Hardness varied from 119.00 and 5383.33 mg/L and the average value was 1267.58 mg/L. The highest values were found at sampling site B in April and the lowest values were found at sampling site B in October. In the saltwater part, hardness varied from 470.33 to 4566.67 mg/L and the average value was 2719.06 mg/L. The highest values of the saltwater part were found at sampling site D in February, whereas the lowest values were found at sampling site D in October.

Conductivity varied from 0.50 to 32.77 ms/cm and the average value was 7.12 ms/cm. The highest values were found at sampling site C in February and the lowest values were found at sampling site A in October. In the saltwater part, hardness varied from 2.18 to 35.04 ms/cm and the average value was 18.30 ms/cm. The highest values of the saltwater part were found at sampling site D in February, whereas the lowest values were found at sampling site D in August.

The last parameter of water quality in the study, salinity varied from 0.20 and 20.50 ppt and the average value was 4.08 ppt. The highest value was found at sampling site C in February and the lowest value was found at sampling site A in August. In the saltwater part, hardness varied from 1.17 to 21.95 ppt and the average value was 11.09 ppt. The highest value of the saltwater part was found at sampling site D in February, whereas the lowest value was found at sampling site D in August.

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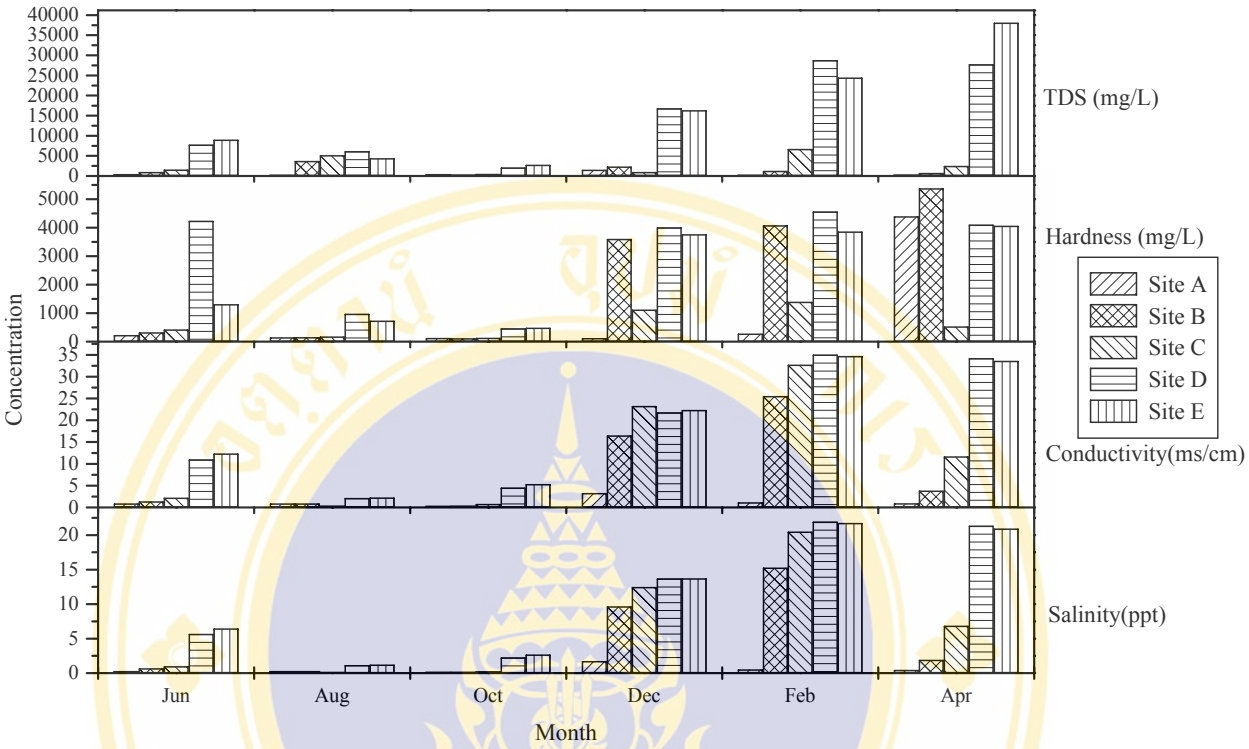

Figure 4-4 Average values of TDS, hardness, conductivity and salinity during the collection period

4.2 Heavy metals in water, sediment and aquatic animals

4.2.1 Heavy metal concentrations in water samples

Heavy metal concentrations in the Phi Lok canal system water were measured at the five sampling sites during June 2004 to May 2005. The detectable heavy metals in water samples are listed in Table 2 of Appendix. The concentrations were reported as microgram per litre (μg/L) of water samples.

4.2.1.1 Cadmium (Cd) concentrations in water

Distribution of Cd in water collected from five sampling sites is shown in Figure 4-5.

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Sampling site A, the mean Cd concentrations exhibited the lowest concentration at 0.001 μg/L in April and the highest concentration at 0.108 μg/L in December.

Sampling site B, the mean Cd concentrations exhibited the lowest concentration at 0.021 μg/L in August and the highest concentration at 0.180 μg/L in December, while the concentration in April was undetectable.

Sampling site C, the mean Cd concentrations exhibited the lowest concentration at 0.017 μg/L in June and the highest concentration at 0.074 μg/L in October and December, while the concentration in April was undetectable.

Sampling site D, the mean Cd concentrations exhibited the lowest concentration at 0.006 μg/L in August and the highest concentration at 0.127 μg/L in December, while the concentration in June and April were undetectable.

Sampling site E, the mean Cd concentrations exhibited the lowest concentration at 0.007 μg/L in April and the highest concentration at 0.089 μg/L in December.

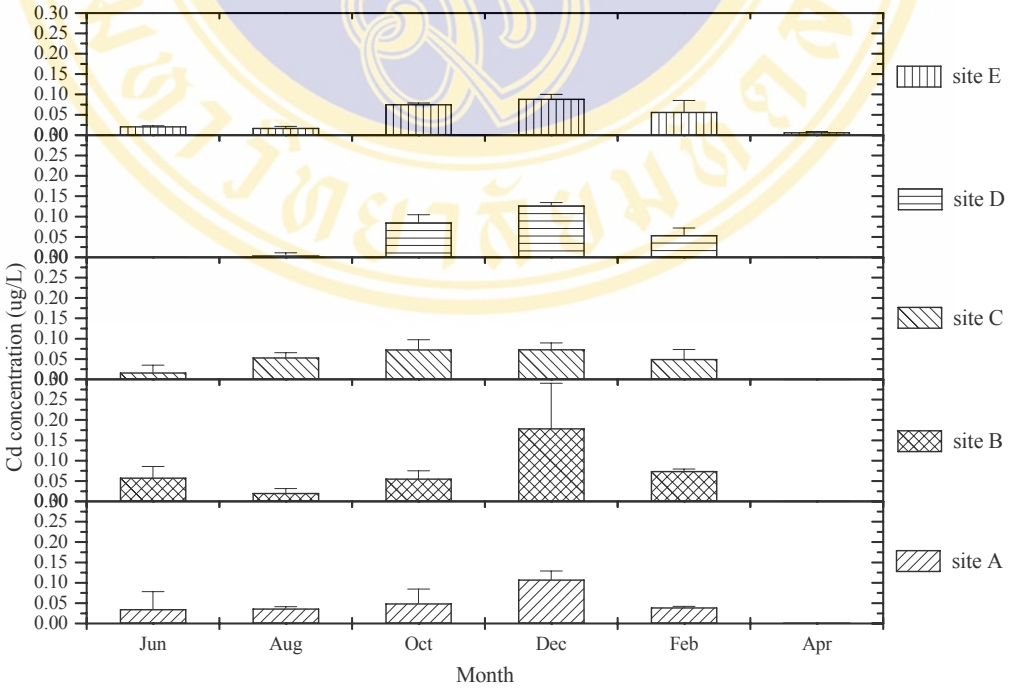

Figure 4-5 Distribution of Cd in water collected from five sampling sites

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4.2.1.2 Copper (Cu) concentrations in water

Distribution of Cu in water collected from five sampling sites is shown in Figure 4-6.

Sampling site A, the mean Cu concentrations exhibited the lowest concentration at 23.33 μg/L in February and the highest concentration at 69.00 μg/L in December, while the concentration in August was undetectable.

Sampling site B, the mean Cu concentrations exhibited the lowest concentration at 1.00 μg/L in June and the highest concentration at 80.66 μg/L in December.

Sampling site C, the mean Cu concentrations exhibited the lowest concentration at 2.00 μg/L in February and the highest concentration at 71.67 μg/L in October.

Sampling site D, the mean Cu concentrations exhibited the lowest concentration at 1.00 μg/L in August and the highest concentration at 71.67 μg/L in October.

Sampling site E, the mean Cu concentrations exhibited the lowest concentration at 1.33 μg/L in February and April and the highest concentration at 71.67 μg/L in October.

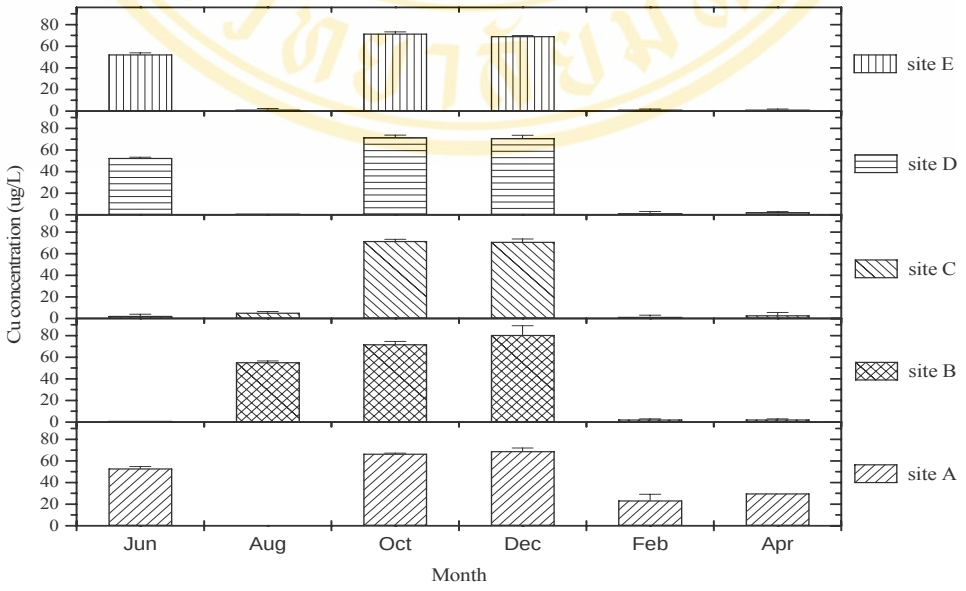

Figure 4-6 Distribution of Cu in water collected from five sampling sites

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4.2.1.3 Iron (Fe) concentrations in water

Distribution of Fe in water collected from five sampling sites is shown in Figure 4-7.

Sampling site A, the mean Fe concentrations exhibited the lowest concentration at 44.00 μg/L in April and the highest concentration at 123.33 μg/L in February.

Sampling site B, the mean Fe concentrations exhibited the lowest concentration at 30.00 μg/L in February and the highest concentration at 90.33 μg/L in August.

Sampling site C, the mean Fe concentrations exhibited the lowest concentration at 34.67 μg/L in April and the highest concentration at 120.33 μg/L in August.

Sampling site D, the mean Fe concentrations exhibited the lowest concentration at 45.67 μg/L in February and the highest concentration at 131.67 μg/L in August.

Sampling site E, the mean Fe concentrations exhibited the lowest concentration at 47.33 μg/L in February and the highest concentration at 403.33 μg/L in October.

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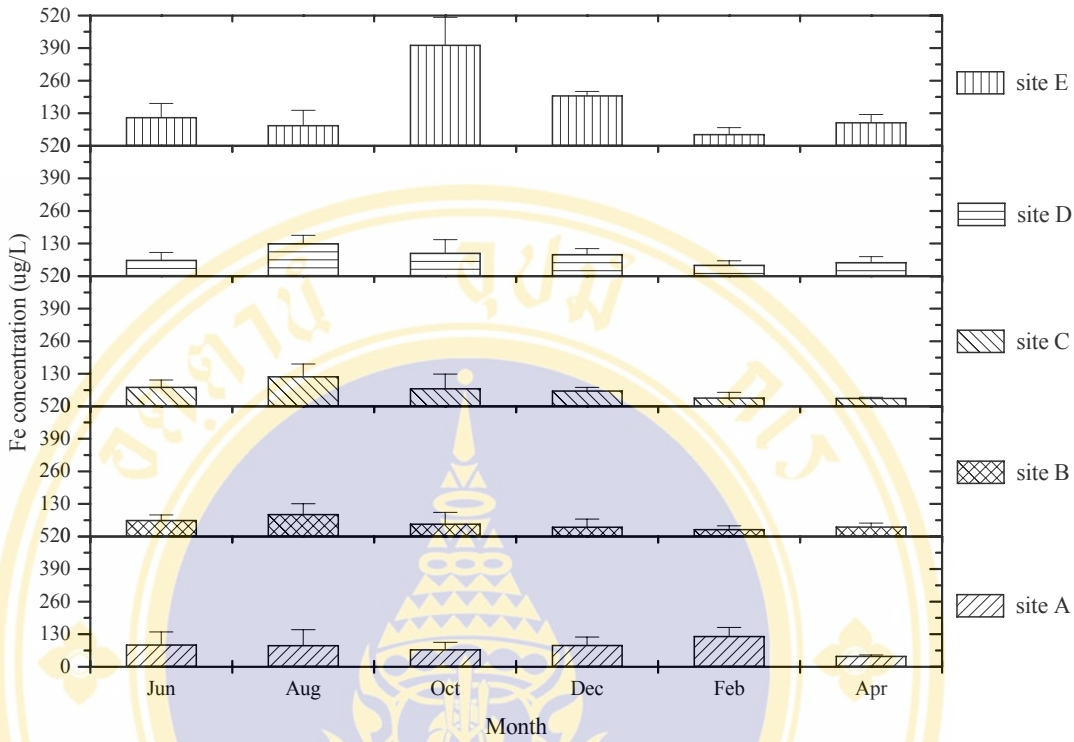

Figure 4-7 Distribution of Fe in water collected from five sampling sites

4.2.1.4 Lead (Pb) concentrations in water

Distribution of Pb in water collected from five sampling sites is shown in Figure 4-8.

Sampling site A, the mean Pb concentrations exhibited the lowest concentration at 0.21 μg/L in June and the highest concentration at 2.26 μg/L in December.

Sampling site B, the mean Pb concentrations exhibited the lowest concentration at 0.02 μg/L in April and the highest concentration at 2.68 μg/L in December, while the concentration in June was undetectable.

Sampling site C, the mean Pb concentrations exhibited the lowest concentration at 0.17 μg/L in June and the highest concentration at 2.37 μg/L in December.

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Sampling site D, the mean Pb concentrations exhibited the lowest concentration at 0.10 μg/L in April and the highest concentration at 2.43 μg/L in December.

Sampling site E, the mean Pb concentrations exhibited the lowest concentration at 0.21 μg/L in April and the highest concentration at 2.56 μg/L in December.

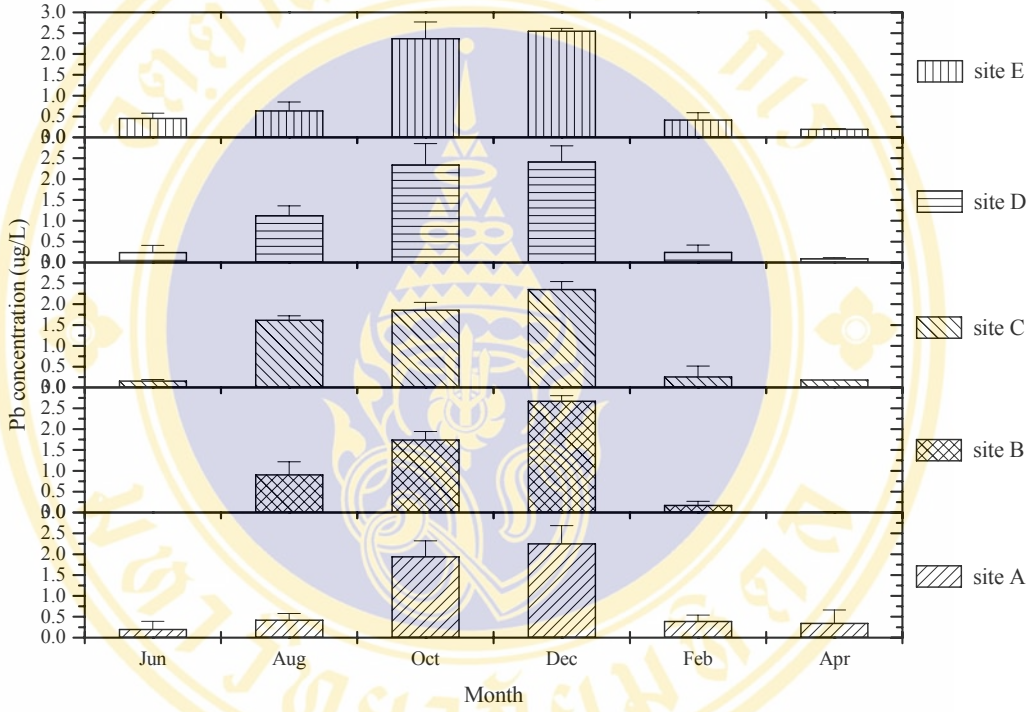

Figure 4-8 Distribution of Pb in water collected from five sampling sites

4.2.1.5 Zinc (Zn) concentrations in water

Distribution of Zn in water collected from five sampling sites is shown in Figure 4-9.

Sampling site A, the mean Zn concentrations exhibited the lowest concentration at 11.33 μg/L in August and the highest concentration at 141.00 μg/L in October.

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Sampling site B, the mean Zn concentrations exhibited the lowest concentration at 17.57 μg/L in June and the highest concentration at 153.67 μg/L in December.

Sampling site C, the mean Zn concentrations exhibited the lowest concentration at 26.33 μg/L in February and the highest concentration at 144.33 μg/L in October.

Sampling site D, the mean Zn concentrations exhibited the lowest concentration at 26.67 μg/L in February and the highest concentration at 180.33 μg/L in October.

Sampling site E, the mean Zn concentrations exhibited the lowest concentration at 24.00 μg/L in February and the highest concentration at 125.33 μg/L in October.

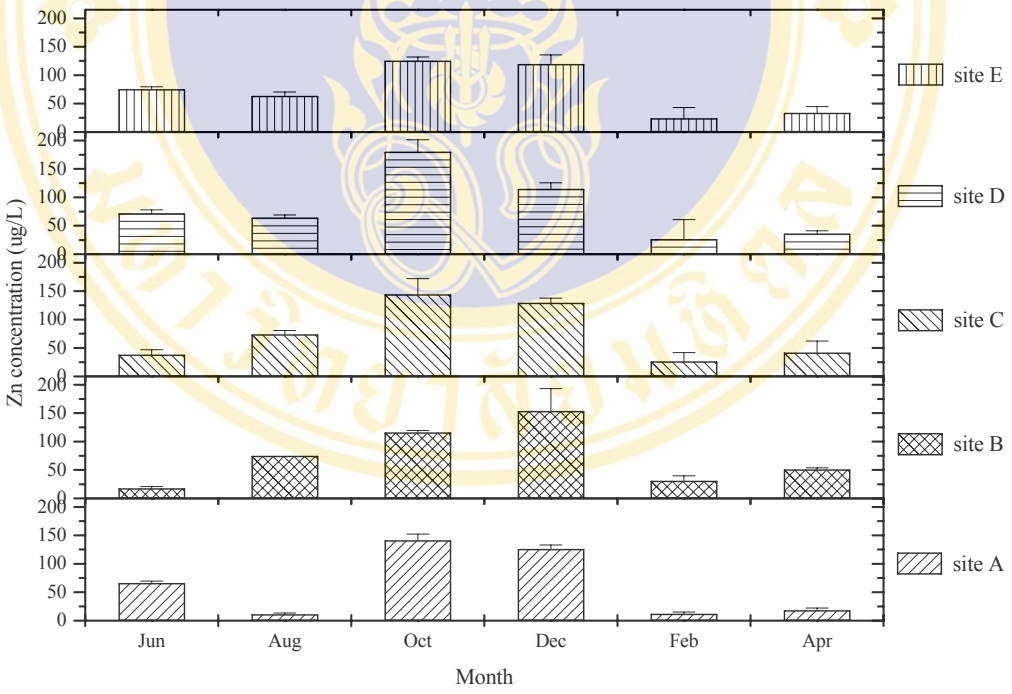

Figure 4-9 Distribution of Zn in water collected from five sampling sites

4.2.2 Heavy metal concentrations in sediment

Heavy metal concentrations in sediment samples from the five sampling sites of the Phi Lok canal system during June 2004 to May 2005 are reported in Table 3 of

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Appendix. The concentrations were reported as milligram per kilogram dry weight (mg/kg dry wt) of sediment samples.

4.2.2.1 Cadmium (Cd) concentrations in sediment

Distribution of Cd in sediment collected from five sampling sites is shown in Figure 4-10.

Sampling site A, the mean concentrations of Cd in sediment varied from the lowest concentration at 0.001 mg/kg in February to the highest concentration at 0.005 mg/kg in August.

Sampling site B, the mean concentrations of Cd in sediment varied from the lowest concentration at 0.002 mg/kg in February to the highest concentration at 0.009 mg/kg in June.

Sampling site C, the mean concentrations of Cd in sediment varied from the lowest concentration at 0.001 mg/kg in February to the highest concentration at 0.007 mg/kg in August.

Sampling site D, the mean concentrations of Cd in sediment varied from the lowest concentration at 0.004 mg/kg in June to the highest concentration at 0.005 mg/kg in August.

Sampling site E, the mean concentrations of Cd in sediment varied from the lowest concentration at 0.003 mg/kg in June to the highest concentration at 0.006 mg/kg in October.

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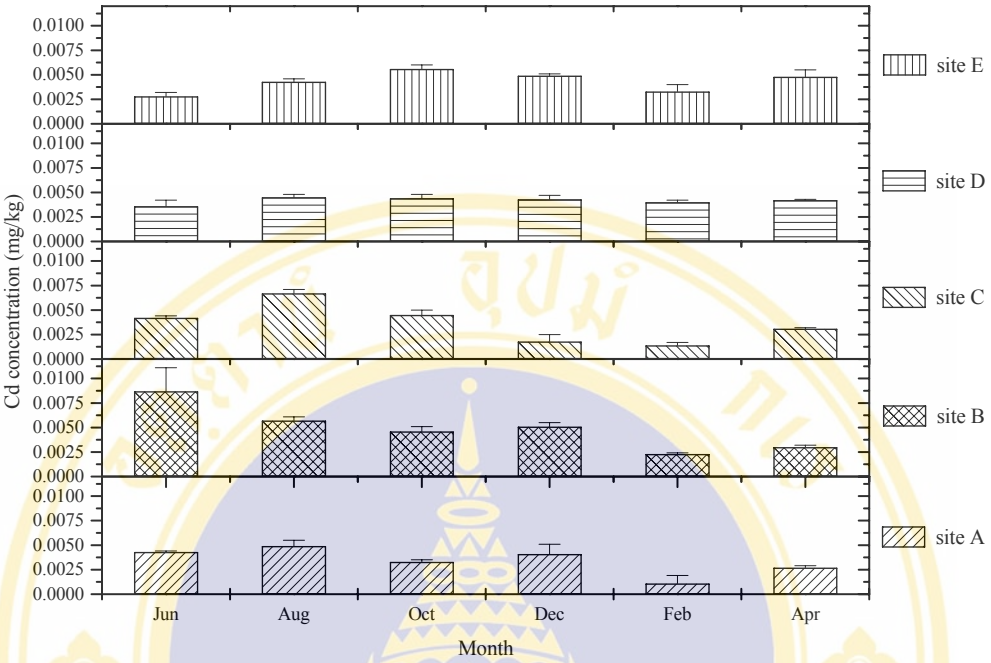

Figure 4-10 Distribution of Cd in sediment collected from five sampling sites

4.2.2.2 Copper (Cu) concentrations of in sediment

Distribution of Cu in sediment collected from five sampling sites is shown in Figure 4-11.

Sampling site A, the mean concentrations of Cu in sediment varied from the lowest concentration at 11.87 mg/kg in April to the highest concentration at 39.30 mg/kg in June, whereas the concentration in August was undetectable.

Sampling site B, the mean concentrations of Cu in sediment varied from the lowest concentration at 0.40 mg/kg in August to the highest concentration at 20.07 mg/kg in June.

Sampling site C, the mean concentrations of Cu in sediment varied from the lowest concentration at 7.67 mg/kg in April to the highest concentration at 17.37 mg/kg in August.

Sampling site D, the mean concentrations of Cu in sediment varied from the lowest concentration at 8.17 mg/kg in April to the highest concentration at 15.30 mg/kg in June, whereas the concentration in August was undetectable.

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Sampling site E, the mean concentrations of Cu in sediment varied from the lowest concentration at 8.07 mg/kg in April to the highest concentration at 15.60 mg/kg in June.

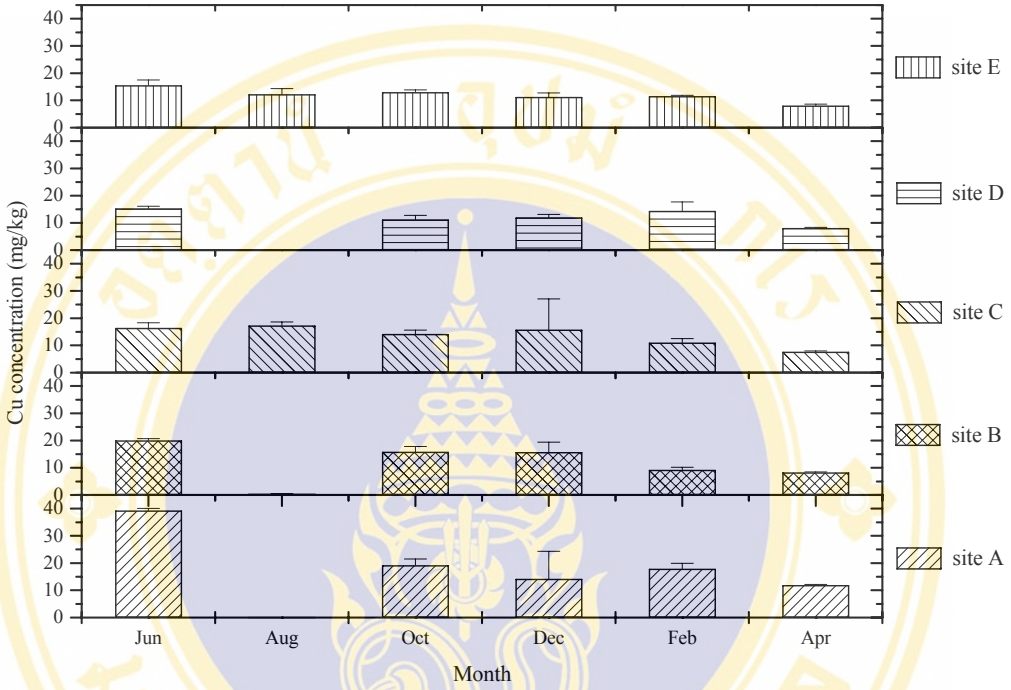

Figure 4-11 Distribution of Cu in sediment collected from five sampling sites

4.2.2.3 Iron (Fe) concentrations in sediment

Distribution of Fe in sediment collected from five sampling sites was shown in Figure 4-12.

Sampling site A, the mean concentrations of Fe in sediment varied from the lowest concentration at 17032.83 mg/kg in August to the highest concentration at 22377.40 mg/kg in June.

Sampling site B, the mean concentrations of Fe in sediment varied from the lowest concentration at 11581.60 mg/kg in December to the highest concentration at 20797.47 mg/kg in April.

Sampling site C, the mean concentrations of Fe in sediment varied from the lowest concentration at 16616.20 mg/kg in December to the highest concentration at 23387.03 mg/kg in August.

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Sampling site D, the mean concentrations of Fe in sediment varied from the lowest concentration at 18238.60 mg/kg in October to the highest concentration at 21509.87 mg/kg in June.

Sampling site E, the mean concentrations of Fe in sediment varied from the lowest concentration at 18333.57 mg/kg in December to the highest concentration at 22742.40 mg/kg in August.

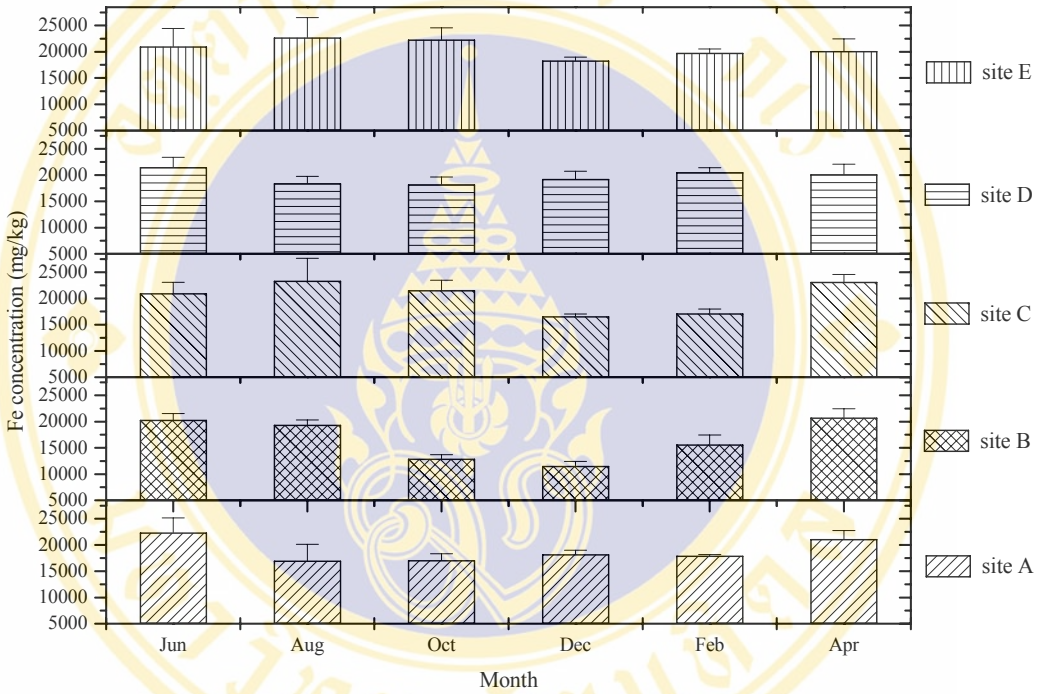

Figure 4-12 Distribution of Fe in sediment collected from five sampling sites

4.2.2.4 Lead (Pb) concentrations in sediment

Distribution of Pb in sediment collected from five sampling sites is shown in Figure 4-13.

Sampling site A, the mean concentrations of Pb in sediment varied from the lowest concentration at 14.33 mg/kg in June to the highest concentration at 32.67 mg/kg in February.

Sampling site B, the mean concentrations of Pb in sediment varied from the lowest concentration at 10.00 mg/kg in August to the highest concentration at 34.33 mg/kg in February.

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Sampling site C, the mean concentrations of Pb in sediment varied from the lowest concentration at 9.67 mg/kg in August to the highest concentration at 68.00 mg/kg in October.

Sampling site D, the mean concentrations of Pb in sediment varied from the lowest concentration at 6.00 mg/kg in August to the highest concentration at 66.33 mg/kg in December.

Sampling site E, the mean concentrations of Pb in sediment varied from the lowest concentration at 9.67 mg/kg in August to the highest concentration at 46.67 mg/kg in October.

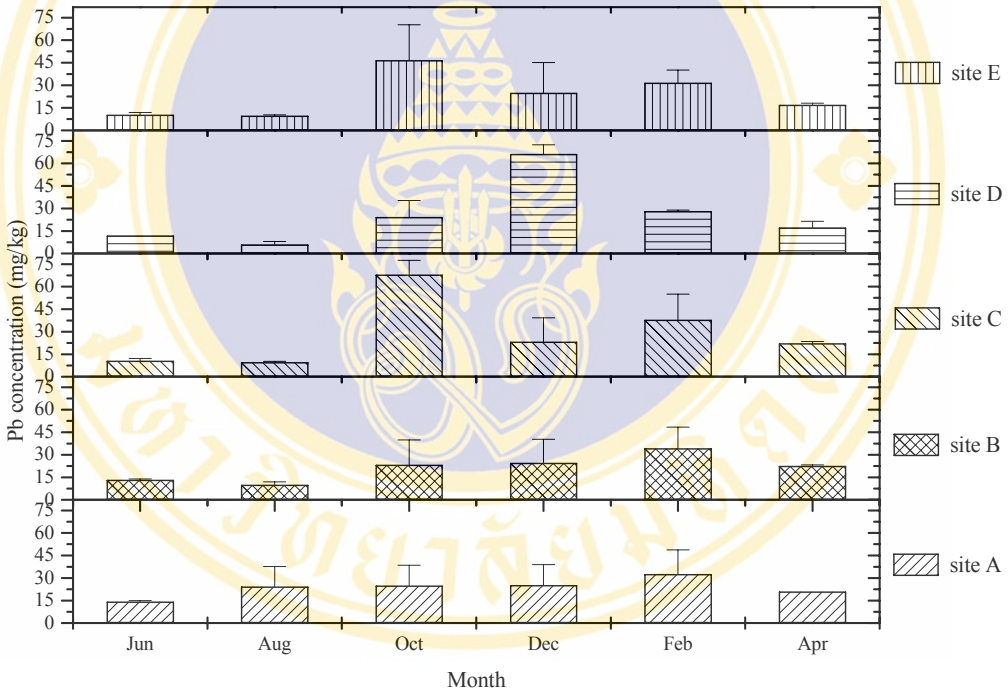

Figure 4-13 Distribution of Pb in sediment collected from five sampling sites

4.2.2.5 Zinc (Zn) concentrations of in sediment

Distribution of Zn in sediment collected from five sampling sites is shown in Figure 4-14.

Sampling site A, the mean concentrations of Zn in sediment varied from the lowest concentration at 54.67 mg/kg in October to the highest concentration at 91.57 mg/kg in June.

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Sampling site B, the mean concentrations of Zn in sediment varied from the lowest concentration at 52.93 mg/kg in April to the highest concentration at 82.53 mg/kg in August.

Sampling site C, the mean concentrations of Zn in sediment varied from the lowest concentration at 52.13 mg/kg in April to the highest concentration at 76.37 mg/kg in August.

Sampling site D, the mean concentrations of Zn in sediment varied from the lowest concentration at 49.03 mg/kg in October to the highest concentration at 63.37 mg/kg in June.

Sampling site E, the mean concentrations of Zn in sediment varied from the lowest concentration at 51.10 mg/kg in February to the highest concentration at 60.90 mg/kg in June.

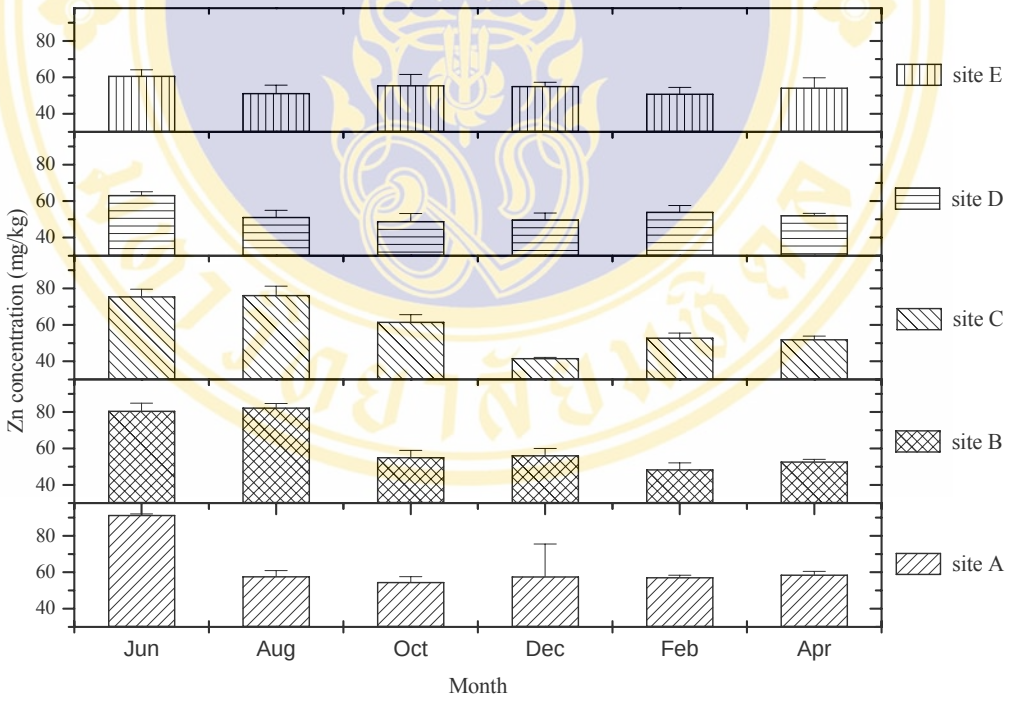

Figure 4-14 Distribution of Zn in sediment collected from five sampling sites

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4.2.3 Heavy metal concentrations in some fish species

4.2.3.1 Availability of fish samples during the collection period

The availability of fish species and the average length of each species in the study are shown in Tables 4-1 and 4-2. Several fish species were found in the Phi Lok canal system. *Tichogaster trichopterus* and *Cirrhinus jullieni* were the two fish species that were found in freshwater environment. They were only collected at sampling sites A, B and C that were at the upper reaches of the Phi Lok canal. *Valamugil siheli* was more tolerant towards saltwater. They could be found at the brackish water (sampling sites D and E), downstream of the Phi Lok canal. While *Oreochromis mossambicus* was found in both freshwater and saltwater. They can also be reared under hyper-saline conditions (Trewavas, 1982) so they could be collected at sampling sites C, D and E. Nevertheless, four fish species could not be collected in every two months between June 2004 and April 2005. However for some collection periods such as sampling sites A and B in February and sampling site C in December, more than one fish species were collected. Sometimes no fish species were found because the water level was very high so the local fisherman could not catch them by the net. Nevertheless, at least one fish species was collected for heavy metal determination. Also some samples of fish species especially the small fish species were not enough for heavy metal determination. They would not be discussed in the study.

Table 4-1 Availability of fish species during collection period

Sampling site	Months					
	Jun	Aug	Oct	Dec	Feb	Apr
A	-	TT	TT	CJ	TT NK*	CJ
B	-	-	TT	TT	TT PS*	TT
C	-	TT	-	TT CJ OM	TT	TT
D	VS	VS	OM AT*	VS	-	VS
E	VS	VS	OMA*	OM	-	VS

Remark: (*), samples were not determined for heavy metals; (-), no sample was collected; TT, *Tichogaster trichopterus*; CJ, *Cirrhinus jullieni*; NK, *Notopterus kapirat*; PS, *Puntius schwanenfeldii*; OM, *Oreochromis mossambicus*; AT, *Arius truncatus*; VS, *Valamugil siheli*; OXM, *Oxyeleotris marmorata*

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Table 4-2 The average length of fish species

Fish species	Number	Average length (cm)
T. trichopterus	33	7.88
C. jullieni	9	9.72
O. mossambicus	9	10.88
V. siheli	21	12.57

4.2.3.2 Heavy metal concentrations in some fish species

Heavy metal concentrations in some fish species from the five sampling sites of the Phi Lok canal system during June 2004 to May 2005 are reported in Table 4-3. Although many researchers have presented the metal contents in various tissues, such as liver, kidneys, gill, gonads and muscles of fish (Papagiannis *et al.*, 2004; Karadede and Unlu, 2000; Denton and Burdon-Jones, 1986; Chale, 2002; Chaiyabutr, 1998; Al-Yousuf *et al.*, 2000), in this study the whole body were evaluated for the metal concentration in *T. trichopterus*, *C. jullieni*, *O. mossambicus* excepted in *V. siheli* were detemined both in muscle and internal orga separately. The concentrations of Fe, Cu, Zn, Cd and Pb were expressed in milligram per kilogram dry weight (mg/kg dry wt.) of samples. Cd and Pb concentrations were low in all of fish species, whereas Fe concentration was higher in every sampling site.

In sampling site A, the Fe and Pb concentrations in *T. trichopterus* were higher than Fe concentrations in *C. jullieni*. In contrast, Cu and Zn concentrations in *C. jullieni* were higher than those in *T. trichopterus.* Cd concentration was not detected in *T. trichopterus*.

In sampling site B, *T. trichopterus* was only found in the sampling site. The whole body of *T. trichopterus* was determined for heavy metal concentrations. The heavy metal concentrations can be presented in descending order as follows; Fe > Zn > Cu > Pb > Cd.

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Table 4-3 Heavy metal concentrations (mg/kg dry weight) in fish species at each sampling site

Sampling site and fish species	N	Cd mg/kg dry wt.	Cu mg/kg dry wt.	Fe mg/kg dry wt.	Pb mg/kg dry wt.	Zn mg/kg dry wt.
Sampling site A						
T. trichopterus[*,**]	9	nd	1.94 ± 1.15	885.51 ± 365.85	1.01 ± 0.23	45.15 ± 19.19
C. jullieni[*,**]	6	0.002 ± 0.001	3.65 ± 1.25	62.68 ± 16.23	0.22 ± 0.02	83.55 ± 15.40
Sampling site B						
T. trichopterus[*,**]	12	0.002 ± 0.000	2.47 ± 1.53	487.38 ± 315.81	0.47 ± 0.38	65.10 ± 14.39
Sampling site C						
T. trichopterus[*,**]	12	0.002 ± 0.001	3.58 ± 0.96	1205.42±1266.49	1.05 ± 0.89	57.65 ± 22.14
C. jullieni[*,**]	3	0.003 ± 0.000	6.93 ± 0.58	1269.83±104.77	1.47 ± 0.10	55.67 ± 2.46
O. mossambicus[*,**]	3	0.015 ± 0.001	7.20 ± 1.15	85.57 ± 3.67	0.41 ± 0.06	53.08 ±10.24
Sampling site D						
O. mossambicus[*,**]	3	0.004 ± 0.000	4.20 ± 0.50	2750.77±101.25	2.39 ± 0.02	25.97 ± 1.53
V. siheli						
- Muscle	12	0.003 ± 0.001	3.95 ± 2.00	144.86 ±153.40	0.53 ± 0.09	22.12 ± 13.39
- Internal organ	9	0.007 ± 0.002	6.99 ± 3.72	413.58 ±358.11	0.48 ± 0.16	57.56 ± 34.92
Sampling site E						
O. mossambicus[*,**]	3	0.014 ± 0.002	13.30 ± 2.29	287.37 ±42.46	0.47 ± 0.08	35.73 ± 7.91
V. siheli						
- Muscle	9	0.002 ± 0.000	2.37 ± 0.32	50.28 ±15.40	nd	13.4 ± 4.84
- Internal organ	9	0.010 ± 0.002	5.50 ± 4.48	1224.30 ±486.51	1.45 ±1.46	54.90 ± 34.04

Remarks: * mean ± SD; ** heavy metal determined in the whole body; nd, not detected

In sampling site C, three fish species (*T. trichopterus*, *C. jullieni* and *O. mossambicus*) were found. Fe concentrations were highest in *C. jullieni* followed by *T. trichopterus* and *O. mossambicus*. Cu concentrations were highest in *O. mossambicus* followed by *C. jullieni* and *T. trichopterus*. Zn concentrations in all three fish species were found nearly equal. Pb concentration was lowest in *O. mossambicus* and Cd concentration was very low.

In sampling site D, *O. mossambicus* was also found because it can be reared under hyper-saline conditions (Trewavas, 1982). The heavy metal concentrations can

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be presented in descending order as follows; Fe > Zn > Cu > Pb > Cd. Furthermore, *V. siheli* was also found. This species was only one species that can be dissected into muscles and internal organ separately. The heavy metal concentrations of internal organ were higher than those of the muscles in most metals except Pb. The heavy metal concentrations in the muscles of *V. siheli* can be presented in descending order as follows; Fe > Zn > Cu > Pb > Cd.

In sampling site E, two fish species similar to those found in sampling site D were also found. The heavy metal concentrations of *O. mossambicus* can be presented in descending order as follows; Fe > Zn > Cu > Pb > Cd. All heavy metal concentrations in the internal organ of *V. siheli* were higher than those in the muscles. The heavy metal concentrations in the muscles of *V. siheli* can be presented in descending order as follows; Fe > Zn > Cu > Cd. Pb concentration was not detected in the muscles of *V. siheli*.

Figure 4-15 shows the heavy metal distribution in *T. trichopterus* during the collection period. In sampling site C, Fe concentrations were highest in August. The lowest Fe concentrations were found at sampling site C in February. Cu concentrations of *T. trichopterus* collected at sampling sites B and C in December were similar. The lowest concentrations of Cu were found in October. Zn concentrations were found highest in February at sampling site C and the lowest were found in August at sampling site A. Cd concentrations were very low in every sampling site and was not detected at sampling site A in August and February. Pb concentrations of *T. trichopterus* at sampling site C in August were highest, whereas Pb concentrations at sampling site B in February were lowest.

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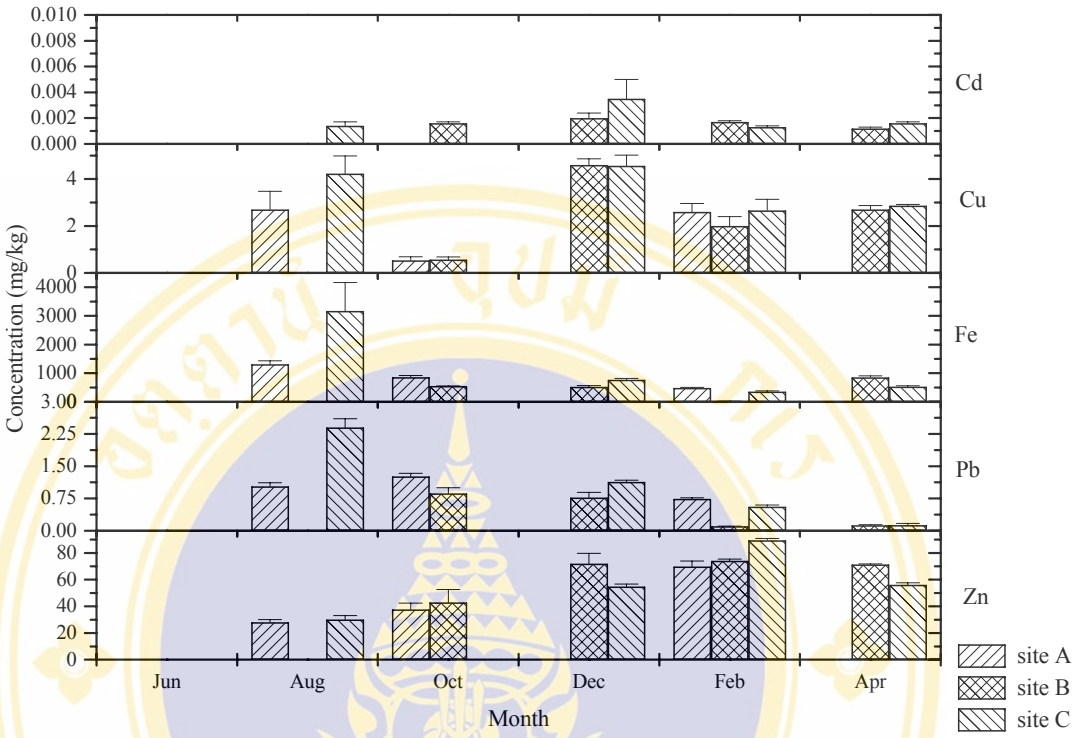

Figure 4-15 Monthly variation of the heavy metal concentrations in *T. trichopterus*

Figure 4-16 shows the monthly variation of heavy metal concentrations in *C. jullieni*. Fe, Cu, Cd and Pb concentrations were higher at sampling site C than those at sampling site A in December, whereas Zn concentration was higher at sampling site A. In April, *C. jullieni* samples were only found at sampling site A. However, Pb concentration was not detected.

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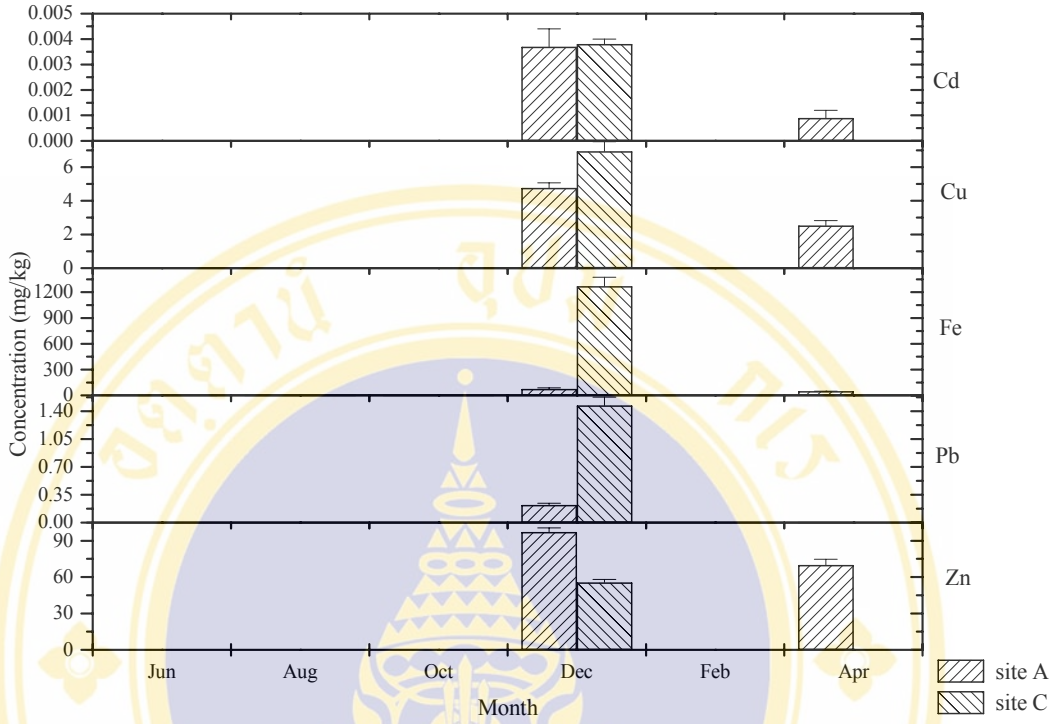

Figure 4-16 Monthly variation of the heavy metal concentrations in *C. jullieni*

In case of *O. mossambicus*, monthly variation of the heavy metal concentrations are shown in Figure 4-17. Fe showed the highest concentrations at sampling site D in October, whereas Cu concentration was highest at sampling site E in December followed by sampling site C in December and sampling site D in October. Zn concentration at sampling site C was higher than that at sampling site E in December. Cd concentrations of *O. mossambicus* were high at both sampling sites A and E in December. Pb concentrations were low at both sampling sites C and E in December, whereas Pb concentrations at sampling site D in October were very high.

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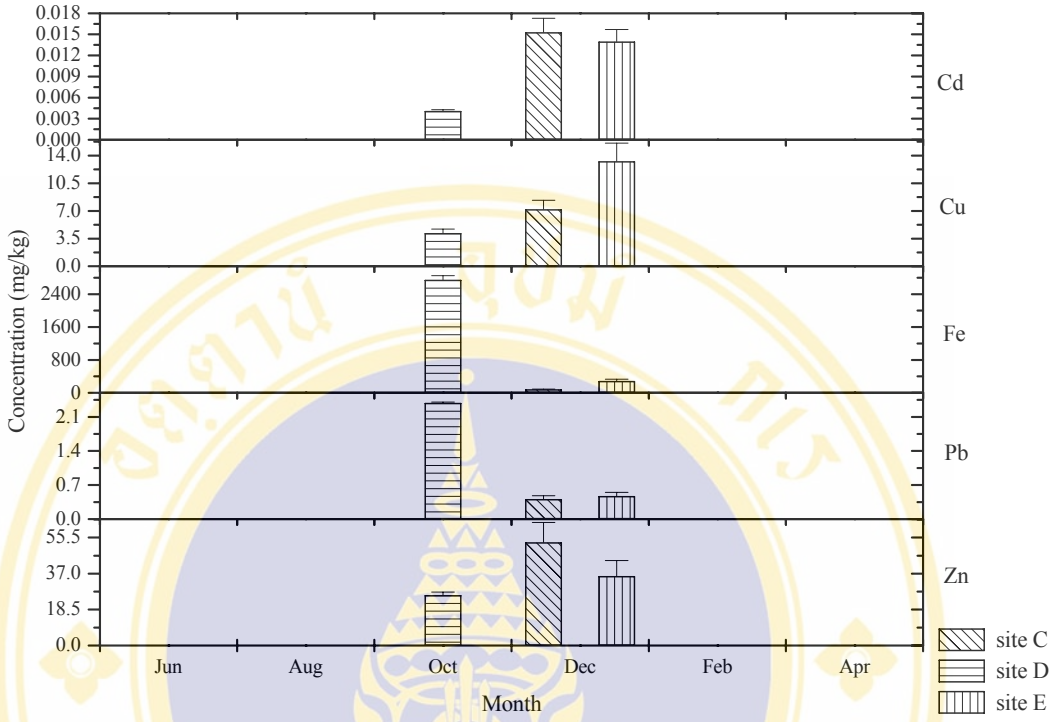

Figure 4-17 Monthly variation of the heavy metal concentrations in *O. mossambicus*

In most collection periods except in December, fish samples of *V. siheli* were dissected into the muscle and the internal organ. All heavy metal concentrations were much higher in the internal organ than in the muscle. *V. siheli* samples in December could not dissect into the muscle and the internal organ because of the low number of the samples. The heavy metal concentrations in December can be presented in descending order as follows; Fe > Zn > Cu > Pb > Cd.

The heavy metal concentrations in the muscle of *V. siheli* are shown in Figure 4-18. The Fe concentrations were very high in August at sampling site D. Cu concentration was not detected in June and August at both sampling sites D and E. Zn concentrations collected from sampling sites D and E were highest in April followed by those in June and August. Cd concentration was not detected in June and August, whereas in April the concentrations were higher in sampling site E than in sampling site D. Pb concentrations of the muscle were not detected in all samples except the sample in December which the whole body was analysed.

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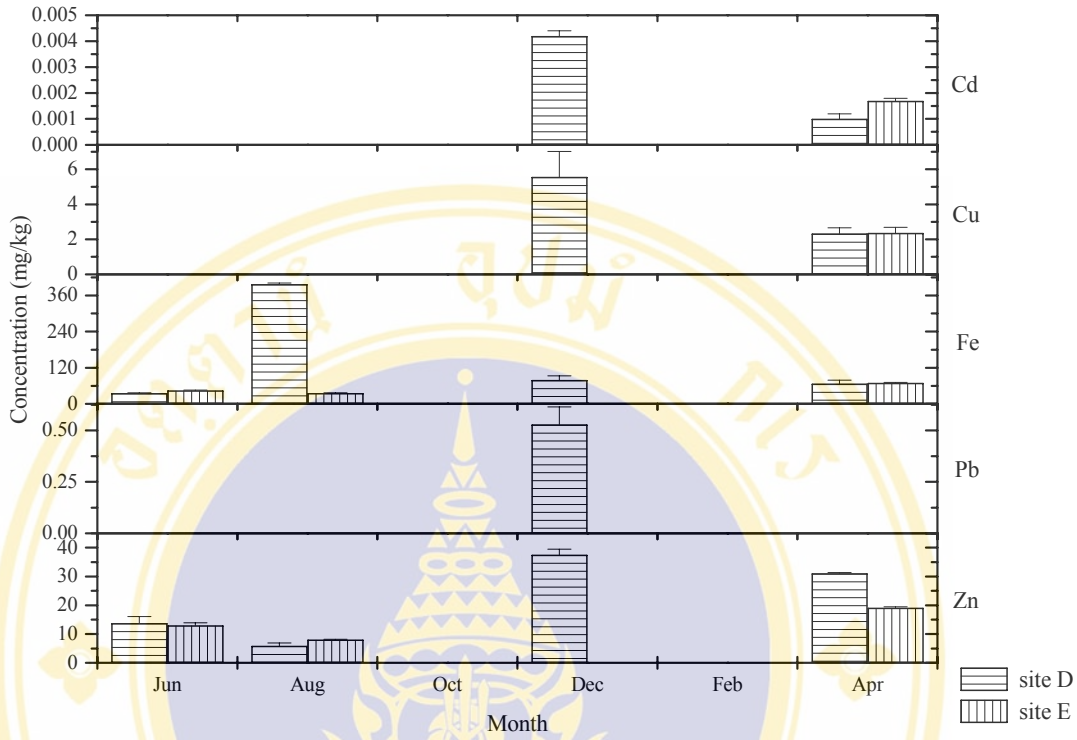

Figure 4-18 Monthly variation of the heavy metal concentrations in muscle of *V. siheli*

The heavy metal concentrations in the internal organ of *V. siheli* are shown in Figure 4-19. Fe concentrations were higher in sampling site E than in sampling site D in June, August and April. Cu and Zn concentrations were higher in sampling site D than in sampling site E in June and August, whereas Cu and Zn concentrations in April at sampling site E were higher. Cd concentration was very low in all sampling sites. Except in April, Cd concentration was not detected in the muscle of *V. siheli*. Pb concentrations were highest at sampling site E in August. They were not detected at sampling site D in June and April.

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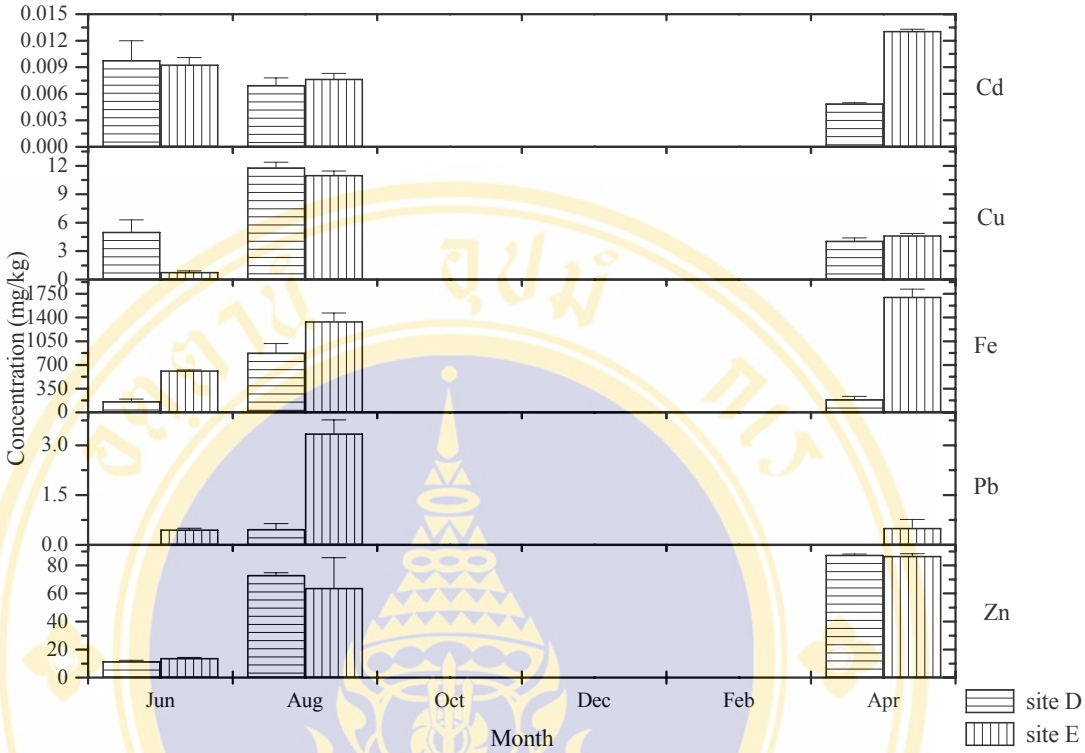

Figure 4-19 Monthly variation of the heavy metal concentrations in the internal organ of *V. siheli*

4.2.4 Heavy metal concentrations in *P. canaliculata*

4.2.4.1 Availability of *P. canaliculata* samples in the Phi Lok canal system

P. canaliculata samples in this study were found only in some collection periods as shown in Table 4-4. *P. canaliculata* was only found in the freshwater part of sampling sites A, B and C which were at the upper reaches of the Phi Lok canal system. Mollusc samples were sampled every two months between June 2004 to April 2005. However, mollusc samples could not be collected in December 2004 at sampling site A, whereas they were not found in Febuary and April 2005 at sampling site B. This may be due to the use of mollusc pesticides by farmers in paddy fields.

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Table 4-4 Availability of *P. canaliculata*

Sampling site	Month					
	Jun	Aug	Oct	Dec	Feb	Apr
A	X	X	X	-	X	X
B	X	X	X	X	-	-
C	X	X	X	X	X	X

Remarks: X, mollusc sample was collected; -, no sample was collected

4.2.4.2 Heavy metal concentrations in *P. Canaliculata*

Heavy metal concentrations in *P. canaliculata* from the five sampling sites of the Phi Lok canal system during June 2004 to May 2005 are presented in Table 4-5. The concentrations were reported as milligram per kilogram dry weight (mg/kg dry weight) of samples. The results in Table 4-5 show that the average values and standard deviation of heavy metal concentrations in the whole body of *P. canaliculata*.

Table 4-5 Heavy metal concentrations (mg/kg dry weight) in *P. canaliculata*

Sampling site	N	Cd mg/kg dry wt.	Cu mg/kg dry wt.	Fe mg/kg dry wt.	Pb mg/kg dry wt.	Zn mg/kg dry wt.
Sampling site A	15	0.007 ± 0.002	49.12 ±39.19	1455.03 ± 864.24	1.35 ± 1.23	130.07 ± 69.86
Sampling site B	12	0.005 ± 0.001	61.86 ±25.16	1321.13 ± 940.94	1.46 ± 0.79	78.81 ± 82.73
Sampling site C	18	0.008 ± 0.011	22.80 ±18.57	900.87 ± 381.61	0.64 ± 0.55	91.29 ± 55.54

Cd concentrations were highest in sampling site C (0.008 ± 0.011 mg/kg dry weight) and the lowest concentrations were found in sampling site B (0.005 ± 0.001 mg/kg dry weight). Cu concentrations were higher in sampling site B (61.86 ± 25.16 mg/kg dry weight) than in other sampling sites. The highest Fe concentrations were found in sampling site A followed by sampling sites B and C. Pb concentrations were very low in sampling site C (0.64 ± 0.55 mg/kg dry weight), whereas Pb concentrations at sampling sites A and B were similar (1.35 ± 1.23 and 1.46 ± 0.79 mg/kg dry weight, respectively). Zn concentrations were highest in sampling site A (130.07 ± 69.86 mg/kg dry weight) and the lowest concentrations were found in sampling site B (78.81 ± 82.73 mg/kg dry weight).

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When comparing the heavy metal concentrations in *P. canaliculata* among three sampling sites during June to April 2005, the results can be presented in Figure 4-20. The highest concentration of Cd was found at sampling site C in August and the lowest concentration was found at sampling site C in October. The highest Cu concentration was found at sampling site A in June and the lowest concentration was found at sampling site C in October. The highest Fe concentration was found at sampling site B in June and the lowest concentration was found at sampling site B in December. The highest Pb concentration was found at sampling site A in August and the lowest concentration was found at sampling site C in June and April. The highest Zn concentration was found at sampling site A in October and the lowest concentration was found at sampling site C in June.

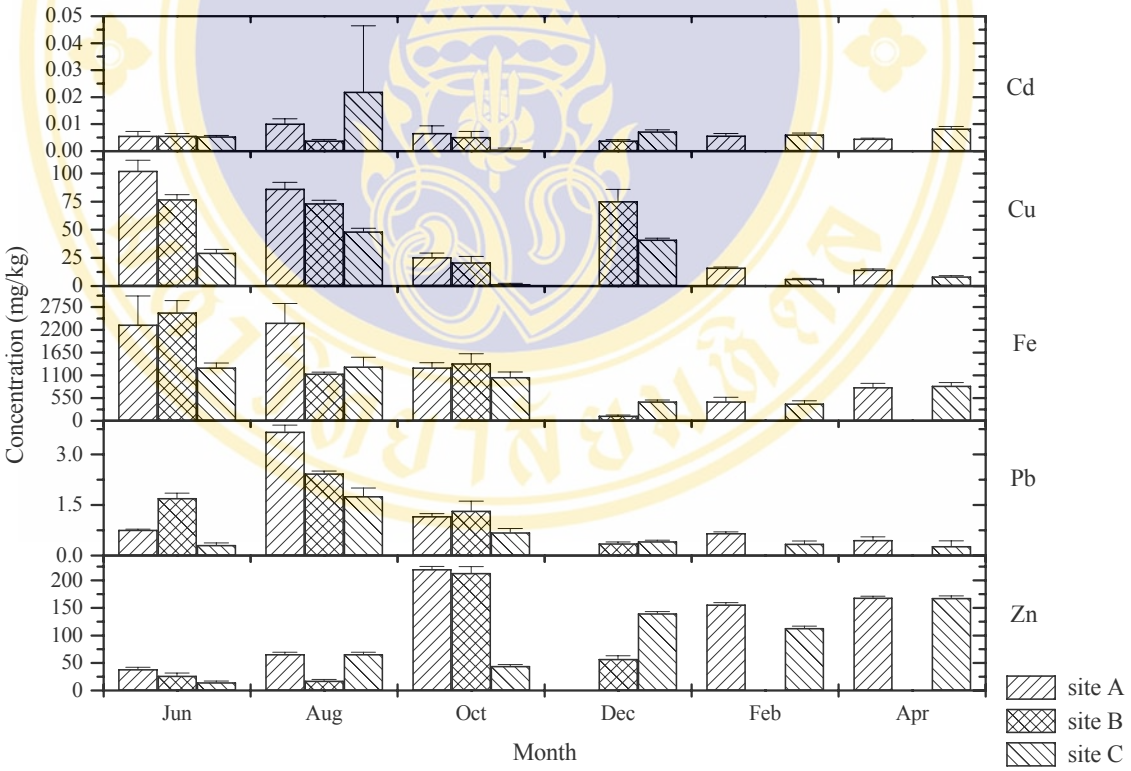

Figure 4-20 Monthly variation of heavy metal concentrations in *P. canaliculata*

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CHAPTER V
DISCUSSIONS

5.1 Water quality of the Phi Lok canal system

Water quality regulations in Thailand divided inland waters in to five classes. Class 1, extra clean fresh surface water resources used for conservation not necessary pass through water treatment process require only ordinary process for path ogenic destruction and for ecosystem conservation where basic organisms can breed naturally. Class 2, very clean fresh surface water resources used for consumption which require ordinary water treatment process before use, aquatic organism of conservation, fisheries and recreation. Class 3, medium clean fresh surface water resources used for consumption, but passing through an ordinary treatment process before using and for agriculture. Class 4, fairly clean fresh surface water resources used for consumption, but requires special water treatment process before using and for industry. Class 5, the source which are not classification in classes 1 to 4 and used for navigation (Pollution Control Department, 2000). The Mae Klong river was classified into class 3. Water quality monitoring results during the last decade (1984 to 1995) were to be fair and good water quality (Simachaya *et al.*, 2002).

The pH values in the freshwater part of the Phi Lok canal system were lower than the maximum values of the surface water quality standards of Thailand (class 3) (Table 5-1). In addition, the pH values in the Phi Lok canal system in 2004 varied in the small range when compared to the pH values in the other canals (the Saphan Han, Kamnan Sombun, Samnga and Rang Thap Tap canals) (Roachanakanan, 2005). However, the maximum pH value of the present study was close to that of the Mae Klong river reported by Kruawal *et al.* (2005).

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Table 5-1 Physico-chemical parameters of water quality in the freshwater part by the present study, previous studies and the surface water quality standards

Physico-chemical parameters of water quality				
Parameter	pH	DO mg/L	BOD mg/L	NO_3- mg/L
This study, 2004 (min-max)	7.27-7.90	0.14-9.20	0.48-8.07	0.08-8.47
Surface Water Quality Standards of Thailand (class 3)[1]	5.00-9.00	4.00	2.00	5.00
Phi Lok canal, 2003[2]	6.41-7.94	0.00-3.93	2.34-6.63	0.09-5.94
Saphan Han canal, 2003[2]	6.56-8.68	0.07-10.97	3.65-7.52	0.06-6.10
Kamnan Sombun canal, 2003[2]	6.56-9.08	2.03-9.17	1.87-7.15	0.07-5.43
Samnga canal, 2003[2]	6.51-7.58	0.27-4.33	2.24-7.02	0.11-3.26
Rang Thap Tap canal, 2003[2]	6.64-8.12	0.64-4.25	2.27-15.91	0.09-4.07
Mae Klong river (mean values, 2003)[3]	7.98	6.08	1.00	-
Lower Chao Praya river[4]	-	1.20	1.80	0.45
Lower Tha Chin river[4]	-	0.90	3.70	1.30

Remarks: [1] Pollution Control Department (2000); [2] Roachanakanan (2005); [3] Kruawal *et al.* (2005); [4] Water Quality Management Bureau (2004)

The maximum values of DO, BOD and NO_3- exceeded the permissible limits of the surface water quality standards of Thailand (class 3) (Table 5-1). Furthermore, the minimum value of DO in the Phi Lok canal system was lower than the Kamnan Sombun, Samnga and Rang Thap Tap canals except the Saphan Han canal reported by Roachanakanan (2005), and also lower than the mean value of the Mae Klong river reported by Kruawal *et al.* (2005) and the lower Chao Praya river reported by Water Quality Management Bureau (2004). The maximum value of BOD of the present study was higher than that of the Saphan Han, Kamnan Sombun, Samnga canals except the Rang Thap Tap canal (Roachanakanan, 2005). In case of NO_3-, the maximum value of the present study was higher than that of every canal determined in 2003 (Roachanakanan 2005) and the lower Chao Praya river and the lower Tha Chin river (Water Quality Management Bureau 2004). The water quality of the Phi Lok

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canal system in the freshwater part can be considered to be worse than other water sources and be classified into class 4 (fairly clean fresh surface water resources used for consumption, but requires special water treatment process before using and for industry) of the surface water quality standards.

Table 5-2 Physico-chemical parameters of water quality in the saltwater part by the present study, previous studies and the coastal water quality standards

Physico-chemical parameters of water quality				
Parameter	pH	DO mg/L	BOD mg/L	NO_3- mg/L
This study, 2004 (min-max)	7.49-7.91	2.25-6.13	1.20-8.57	0.07-5.73
Coastal water quality standards of Thailand (class 4)[1]	7.00-8.50	4	-	-
Phi Lok canal, 2003[2]	6.51-8.02	0.59-10.02	1.87-6.74	0.09-6.46
Saphan Han canal, 2003[2]	6.78-8.90	1.12-8.30	1.13-5.72	0.06-4.98
Kamnan Sombun canal, 2003[2]	6.71-8.57	1.73-6.20	1.40-6.97	0.07-5.87
Samnga canal, 2003[2]	6.48-7.57	1.49-11.35	0.67-3.93	0.12-6.07
Rang Thap Tap canal, 2003[2]	6.83-7.78	2.23-5.45	1.68-14.91	0.13-3.83

Remarks: [1] Water Quality Management Bureau (2004); [2] Roachanakanan (2005)

The results in Table 5-2 shows that the maximum value of pH in the saltwater part of the present study did not exceed the coastal water quality standards (class 4) currently effective in Thailand (Water Quality Management Bureau, 2004). However, the maximum value of pH of this study was lower than that in the Phi Lok, Saphan Han and Kamnan Sombun canals determined in 2003, whereas the maximum values of pH in the Samnga and Rang Thap Tap canals were lower than that in this study. On the other hand, the mimimum value of DO was lower than that of the standards. When comparing with the mimimum values of DO in the Saphan Han, Kamnan Sombun, Rang Thap Tap and Samnga canals were lower than that in this study. The maximum value of BOD in this study were higher than that in the Saphan Han, Kamnan Sombun and Samnga canals except the Rang Thap Tap canal (Roachanakanan, 2005).

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5.2 Heavy metal concentrations in water

All five heavy metal concentrations in water collected from the Phi Lok canal system did not exceed Thailand's surface water quality standards for class 3 and Thailand's coastal water quality standards for class 4 (Pollution Control Department, 2000) (Table 5-3). However, Cd concentrations in this study were higher than those in the Bang Pakong river (Pollution Control Department, 1995) and the River Fez in Morocco (Koulal *et al.*, 2004). While Cd concentrations in the Lower Chao Praya basin reported by Kumnermanee (1997) were higher than those in this study. Cu concentrations in water of the Phi Lok canal system were higher than those in the Mae Klong river (Kruawal *et al.*, 2005), the Bang Pakong river (Pollution Control Department, 1995) and River Sebou in Morocco (Koulal *et al*., 2004), whereas Cu concentrations of River Fez in Morocco were higher than those in this study. Pb concentrations in the Phi Lok canal system were lower than those in the Mae Klong river (Kruawal *et al.*, 2005), the Lower Chao Praya basin (Kumnermanee, 1997), the Bang Pakong river and the Chanthaburi river (Pollution Control Department, 1995) and River Fez in Morocco (Koulal *et al.*, 2004). Zn concentrations in water of the Phi Lok canal system were higher than those in other water sources except in River Fez in Morocco (Kruawal *et al.*, 2005; Pollution Control Department, 1995; Kumnermanee, 1997; Koulal *et al.*, 2004).

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Table 5-3 Comparison of the heavy metals in water (µg/L) from the Phi Lok canal system, other literature and the standards of Thailand

Location	Cd µg/L	Cu µg/L	Fe µg/L	Pb µg/L	Zn µg/L
This study: Phi Lok canal system	0.05 ±0.05[b]	0.05 ±0.05[b]	88.38 ±76.18[b]	1.07 ±0.96[b]	73.61 ±50.03[b]
Surface water quality standards (class 3)[1]	5.00	5.00	-[a]	50.00	1000.00
Coastal water quality standards (class 4)[1]	0.50	0.50	-[a]	50.00	100.00
Mae Klong river, Thailand[2]	<0.10	<0.10	600.00	2.00	<20.00
Lower Chao Praya basin[5]	1.19	1.19	-	6.77	15.40
Bang Pakong river, Thailand[3]	0.03-0.12[c]	0.03-0.12[c]	-	1.67-2.82[c]	2.00-6.25[c]
Prasae river, Rayong province, Thailand[3]	-	-	-	-	1.98
Chanthaburi river, Thailand[3]	-	-	-	0.12	1.98
River Fez, Morocco[4]	0.01 ±0.02[b]	0.01 ±0.02[b]	-	1.14	130.00 ±0.40[b]
River Sebou, Morocco[4]	0.07 ±0.01[b]	0.07 ±0.01[b]	-	1.50 ±0.01[b]	14.69 ±0.02[b]
				0.50 ±0.01[b]	

Remarks: [a] Iron was not specified in the standards; [b] mean SD; [c] min-max; [1] Pollution Control Department (2000); [2] Kruawal *et al.* (2005); [3] Pollution Control Department (1995); [4] Koulal *et al.* (2004); [5] Kumnermanee (1997)

5.3 Heavy metal concentrations in sediment

The Cd concentrations in the Phi Lok canal system were lower than those in lake Beysehir (Altindag and Yigit, 2005), River Danube (Woitke *et al.*, 2003), Mai Po Marshes Nature Reserve in Hong Kong (Liang and Wong, 2003) and Axios River in Greece (Karageorgis *et al.*, 2003) (Table 5-4). However, Cd concentrations of the present study were close to those of the Dipsiz stream in Turkey reported by Demirak *et al.* (2005). Cu concentrations in this study were lower than those in Buyuk Menderes river in Turkey (Akcay *et al.*, 2003), River Danube (Woitke *et al.*, 2003), Mai Po Marshes Nature Reserve in Hong Kong (Liang and Wong, 2003), Ell Ren river in Taiwan (Chen and Lin, 2001) and Axios river in Greece (Karageorgis *et al.*, 2003). But Cu concentrations in this study were higher than those in Dipsiz stream in Turkey

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(Demirak *et al.*, 2005). Fe concentrations were always found in high concentrations in many places including in the Phi Lok canal system. Nevertheless, Fe concentrations in the Phi Lok canal system were lower than those in River Danube (Woitke *et al.*, 2003). In contrast, Fe concentrations in this study were higher than those in Sunderban mangrove system in India (Guhathakurta and Kaviraj, 2000). Pb and Zn concentrations in the present study were lower than those reported in other literature except in Dipsiz stream in Turkey (Demirak *et al.*, 2005; Altindag and Yigit, 2005; Akcayh *et al.*, 2003; Woitke *et al.*, 2003; Liang and Wong, 2003; Chen and Lin, 2001; Karageorgis *et al.*, 2003).

Table 5-4 Comparison of the heavy metals in sediment (mg/kg dry weight) from the Phi Lok canal system and other literature

Location	Heavy metal concentration				
	Cd mg/kg dry weight	Cu mg/kg dry weight	Fe mg/kg dry weight	Pb mg/kg dry weight	Zn mg/kg dry weight
Lake Beysehir, Turkey[1]	12.10-14.25[a]	NA	NA	31.10-33.45[a]	NA
Dipsiz stream, Turkey[2]	nd-0.014	Nd-0.033[a]	NA	nd-1.388[a]	0.015-0.107[a]
Buyuk Menderes river, Turkey[3]	NA	140 ±3[b]	NA	128 ±15[b]	160±15[b]
Sunderban mangrove system, India[4]	NA	NA	715.0-10068.8[a]	NA	40.8-3448.3[a]
River Danube[5]	<1.1-25.9[a]	31.3-662.9[a]	17600-56700[a]	14.7-107.6[a]	83-622[a]
	1.2±0.6[b]	65.7±12.3[b]	29700 ±1900[b]	46.3±6.8[b]	187±25[b]
Mai Po Marshes Nature Reserve, Hong Kong[6]	nd-3.46[a]	18.8-86.6[a]	NA	17.1-90.7[a]	55.6-328.0[a]
	1.05±0.823[b]	42.8±16.7[b]	NA	52.6±12.2[b]	149±53.6[b]
Ell Ren river, Taiwan[7]	NA	191 ±7[b]	NA	143±11[b]	401±25[b]
Axios river, Greece[8]	1-11[a]	14-93[a]	NA	11-140[a]	42-271[a]
This study: Phi Lok canal system[9]	nd-0.011[a]	0.30-40.10[a]	10593.6-27035.0[a]	4.00-77.00[a]	37.30-91.90[a]
	0.004 ±0.002[b]	13.84±6.95[b]	19338.81 ± 3196.53[b]	24.59±17.12[b]	58.80 ±11.85[b]

Remarks: [a] min-max; [b] mean SD; nd, not determined; NA, not analysed; [1] Altindag and Yigit (2005); [2] Demirak *et al.* (2005); [3] Akcay *et al.* (2003); [4] Guhathakurta and Kaviraj (2000); [5] Woitke *et al.* (2003); [6] Liang and Wong (2003); [7] Chen and Lin (2001); [8] Karageorgis *et al.* (2003); [9] the present study

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At present, the sediment standards, criterial or benchmark for heavy metal contents were not available in Thailand. Table 5-5 shows the permissible limits of heavy metal concentrations in sediments from Sweden (Bunsong, 2003) and Hong Kong (Liang and Wong, 2003). In both standards of the Swedish Environmental Protection Agency Standard and Hong Kong Environmental Protection Department, three levels of permissible limits are set as follows: low or uncontaminated level, moderately contaminated level and seriously contaminated level. The average and maximum values of Cd and Zn concentrations of the present study did not exceed the permissible limits of the low level of the Swedish and Hong Kong standards. The average values of Cu and Pb concentrations did not exceed the the permissible limits of the low level of both standards. However, the maximum values of Cu and Pb concentrations in some sampling site exceeded the permissible limits of the low level but did not exceed those of the moderately level. Therefore, at present the sediments of the Phi Lok canal system can be used for agricultural activities.

Table 5-5 The legistrations of heavy metal concentrations (mg/kg dry weight) in sediments of various organizations

Standards	Cd mg/kg dry weight	Cu mg/kg dry weight	Pb mg/kg dry weight	Zn mg/kg dry weight
The Swedish	0.2-0.7[a]	10.0-25.0[a]	5.0-30.0[a]	70.0-175.0[a]
Environmental Protection	0.7-2.0[b]	25.0-50.0[b]	30.0-50.0[b]	175.0-300.0[b]
Agency Standard (1991)[1]	2.0-5.0[c]	50.0-150.0[c]	50.0-400.0[c]	300.0-1000.0[c]
Hong Kong Environmental	0.0-0.9[a]	0-54[a]	0-64[a]	0-140[a]
Protection Department[2]	1.0-1.4[b]	55-64[b]	65-74[b]	150-190[b]
	>1.5[c]	>64[c]	>75[c]	>200[c]

Remarks: [a] low level or uncontaminated level; [b] moderately contaminated level; [c] seriously contaminated level; [1] Bunsong (2003); [2] Liang and Wong (2003)

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5.4 Heavy metal concentrations in some fish species

The Cd concentrations in four fish species in this study were lower than those in other fish species of the Northeast Mediterranean sea (Turkmen *et al.*, 2005; Begum *et al.*, 2005). Lake Beysehir in Turkey (Altindag and Yigit, 2005) and the Sunderban mangrove system in India (Guhathakurta and Kaviraj, 2000) (Table 5-6). On the other hand, the Cu concentrations in fish species collected from the Phi Lok canal system were higher than those in fish species collected from the Northeast Mediterranean sea (Turkmen *et al*,. 2005). However, the Cu concentrations in the muscle of mullet (*V. siheli*) in this study were lower than those in the Northeast Mediterranean sea reported by Canli and Atli (2003). Fe concentrations in the muscle of fish species collected from the Phi Lok canal system were higher than those in other fish species collected from Mediterranean sea especially in *O. mossambicus* (the same family to *Tilapia nilotica*). Fe concentrations in the whole body of Tilapia collected from the Phi Lok canal were igher than those in Tilapia collected from Dhanmondi lake in Bangladesh (Begum *et al.*, 2005). Pb concentrations in fish species collected from Mediterranean sea (Turkmen *et al.*, 2005; Canli and Atli, 2003) and from Dhanmondi lake in Bangladesh (Begum *et al.*, 2005) were higher than those in this study. While Pb concentrations in fish species collected from Lake Beysehir in Turkey (Altindag and Yigit, 2005) were close to those collected from the Phi Lok canal system. Zn concentrations in fish species in this study were higher than those collected from the Sunderban mangrove system in India reported by Guhathakurta and Kaviraj (2000). The results showed that heavy metal concentrations in fish species varied widely depending on where the animals were caught (Turkmen *et al*., 2005).

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Table 5-6 Comparison of the heavy metals (mg/kg dry weight) in some fish species from the Phi Lok canal system and other literature

Location	Heavy metal concentration				
	Cd mg/kg dry weight	Cu mg/kg dry weight	Fe mg/kg dry weight	Pb mg/kg dry weight	Zn mg/kg dry weight
Phi Lok canal system[1]					
*T. trichopterus***	0.001-0.005[a]	0.40-5.00[a]	14.20-4312.10[a]	0.10-2.63[a]	26.10-91.10[a]
	0.002±0.000[b]	2.73±1.34[b]	857.07±846.23[b]	0.83 ±0.65[b]	56.95±19.90[b]
*C. jullieni***	nd-0.05[a]	2.20-7.60[a]	50.10-1347.20[a]	0.196-1.592[a]	53.17-101.19[a]
	0.003±0.001[b]	4.74±1.94[b]	465.07±605.98[b]	0.83±0.69[b]	74.26±18.55[b]
*O. mossambicus***	0.004-0.018[a]	3.70-15.80[a]	83.30-2822.20[a]	0.37-2.40[a]	24.33-64.88[a]
	0.110±0.005[b]	8.23±4.22[b]	1041.23± 1286.29[b]	1.09 ±0.97[b]	38.26±13.56[b]
V. siheli					
- Muscle	0.001-0.004[a]	2.00-7.20[a]	34.70-401.80[a]	0.47-0.63[a]	5.00-38.78[a]
	0.002±0.001[b]	3.42±1.78[b]	104.32±123.84[b]	0.53±0.09[b]	18.39±11.29[b]
- Internal organ	0.005-0.013[a]	0.70-12.20[a]	132.60-1784.70[a]	0.31-3.72[a]	11.40-88.70[a]
	0.009±0.003[b]	6.23±40.70[b]	818.94±587.98[b]	1.20±1.32[b]	56.23±33.48[b]
Fish raising pond					
T. pectoralis[2]					
- Muscle**	0.001±0.001[b]	19.77±1.93[b]	56.68±20.96[b]	1.08±0.21[b]	58.58±7.61[b]
- Internal organ**	0.005±0.002[b]	30.01±4.03[b]	2425.09±75.91[b]	1.28±0.34[b]	67.00±9.35[b]
NE Mediterranean sea, Turkey[3]					
M. barbatus	0.831	2.201	9.682	1.808	4.078
S. aurata	1.341	1.239	13.166	2.314	4.873
Dhanmondi lake, Bandladesh[4]					
Tilapia nilotica	NA	5.57±0.25[b]	110.00±5.00[b]	2.10±0.20[b]	56.30±1.30[b]
NE Mediterranean sea, Turkey[5]					
Mugil cephalus					
- Muscle	0.66±0.08[b]	4.41±1.67[b]	38.71±18.28[b]	5.32±2.33[b]	37.39±6.88[b]
- Liver	1.64±0.91[b]	202.80 ±265.80[b]	370.43±252.70[b]	12.59±5.80[b]	110.03 ±34.58[b]
- Gill	4.85±1.41[b]	13.48±7.34[b]	275.67±71.28[b]	8.95±3.07[b]	71.21±14.24[b]

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Table 5-6 Comparison of the heavy metals (mg/kg dry weight) in some fish species from the Phi Lok canal system and other literature (continue)

Location	Heavy metal concentration				
	Cd mg/kg dry weight	Cu mg/kg dry weight	Fe mg/kg dry weight	Pb mg/kg dry weight	Zn mg/kg dry weight
Lake Beysehir, Turkey[6]					
L. cephalus					
- Muscle	0.570-0.585[a]	NA	NA	0.255-0.440[a]	NA
- Gill	0.540-0.640[a]	NA	NA	0.110-0.605[a]	NA
C. carpio					
- Muscle	0.500-0.585[a]	NA	NA	0.255-0.350[a]	NA
- Gill	0.575-0.740[a]	NA	NA	0.170-0.670[a]	NA
L. lucioperca					
- Muscle	0.620-0.665[a]	NA	NA	0.675-0.680[a]	NA
- Gill	0.590-0.635[a]	NA	NA	0.300-0.460[a]	NA
T. tinca					
- Muscle	0.565-0.630[a]	NA	NA	0.170-0.660[a]	NA
- Gill	0.530-0.595[a]	NA	NA	0.175-0.300[a]	NA
Sunderban mangrove system, India[7]					
Liza parsia	0.11-0.15[a]	NA	185.00-215.00[a]	NA	1.40-272.20[a]

Remarks: [a] min-max; [b] mean ±SD; nd, not determined; NA, not analysed; ** heavy metal determined in the whole body; [1] the present study; [2] Sirichotiwong (2006); [3] Turkmen *et al.* (2005); [4] Begum *et al.* (2005); [5] Canli and Atli (2003); [6] Altindag and Yigit (2005); [7] Guhathakurta and Kaviraj (2000)

Table 5-7 shows the standards of heavy metal concentrations in animals and food from various international organizations. In general, it can be suggested that most heavy metal concentrations in four fish species collected from the Phi Lok canal system did not exceed the standards and guidelines. The maximum values of Pb concentrations in *T. trichopterus* at sampling site A and the average values of Pb concentrations in the internal organ of *V. siheli* at sampling site E did not exceed the tolorance level in fish (FAO/WHO, 1989) and Turkish Guidelines (Turkisk Environmental Guidelines, 1988). Most heavy metal concentrations in four fish

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species were within the permissible limits of various international organizations for human consumption, therefore it is safe to consume the four fish species.

Table 5-7 The legislations of heavy metal concentrations (mg/kg/day) in animals and food of various international organizations

Standard and guideline	Cd mg/kg	Cu mg/kg	Fe mg/kg	Pb mg/kg	Zn mg/kg
Tolorance Level in Fish[1]	0.1	-	-	0.5	50
Turkish Guidelines[2]	0.1	20	-	1	50
The Recommended Dietary Allowance (RDA)[3]	-	7-13	8-18	-	8-13
The Australian Accepted Limits[4]	-	10	-	-	150
The Hungarian Food Standards[4]	-	60	-	-	80
The Canadian Food Standards[4]	-	100	-	-	100
European Communities (2000)[5*]	1.0	30	-	1.5	100
Codex Alimentarius Food Quality Control[6]	2.0	50	-	2.0	-

Remarks: * the European Union legislations for bivalve molluscs; [1] FAO/WHO (1989); [2] Demirak *et al.* (2005) ; [3] Bunsong (2003); [4] Papagiannis *et al.* (2004); [5] Usero *et al.* (2005); [6] Food and Agriculture Organization of the United Nations (2006)

5.5 Heavy metal concentrations in *P. canaliculata*

The comparison of heavy metals in *P. canaliculata* from the Phi Lok canal system and other literature values is shown in Table 5-8. Cd, Cu and Pb concentrations in *P. canaliculata* in this study were lower than those collected from mollusc species from Fanube harbours in Vienna (Gundacker, 2000). Zn concentrations of this study were close to those of Danube harbours were close. The concentrations of Cu and Zn in *P. canaliculata* from the Phi Lok canal system were lower than those in mollusc species collected from the downstream of Sg Sarawak Kanan in Malaysia (Lau *et al.*, 1998).

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Table 5-8 Comparison of the heavy metals in mollusc species from the Phi Lok canal system and other literature

Location	Heavy metal concentration				
	Cd mg/kg dry weight	Cu mg/kg dry weight	Fe mg/kg dry weight	Pb mg/kg dry weight	Zn mg/kg dry weight
Phi Lok canal system[1]					
P. canaliculata					
	nd-0.05[a]	2.00-113.20[a]	110.20-2954.20[a]	0.18-3.90[a]	12.90-223.80[a]
	0.007±0.007[b]	41.98±32.49[b]	1197.66 ±760.29[b]	1.10±0.95[b]	100.89±70.12[b]
Danube harbours, Vienna[2]					
Radix ovata					
Downstream of Sg Sarawak Kanan, Malaysia[3]	1.00±0.30[b]	185.00±12.00[b]	NA	1.41±0.80[b]	1.00±8.00[b]
Brotia costula					
M. tuberculata	nd	83.330±2.357[b]	NA	nd	173.330±8.450[b]
	nd	115.000±2.357[b]	NA	nd	126.670±6.236[b]

Remarks: [a] min-max; [b] mean ±sd; NA, not analysed; [1] the present study; [2] Gundacder (2000); [3] Lau *et al.* (1998)

5.6 Heavy metal concentrations in the Phi Lok canal system

The heavy metals in the four media can be presented in the descending order as follows: sediment > mollusc > fish > water. The heavy metal concentrations were highest in sediment because sediment serve as sinks for toxic metals, while water is primarily transport media (Adair *et al*., 2002). However, the water chemistry of the system controls the rate of adsorption and desorbtion of metals to and from sediment (WATERSHEDSS, 2006).

In case of mollusc and fish species, several studies suggested that fish and crustacea can excrete essential metals that are present in excess. Some can also excrete non-esential metals, although this is met with less success. On the other hand, aquatic plants and bivalves are not able to successfully regulate metal uptake (Connell *et al*.,

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1984 cited by WATERSHEDSS, 2006). Thus, the heavy metal concentrations in mollusc were higher than those in fish.

5.7 Correlation between water, sediment, *P. canaliculata* and some fish species

Correlation coefficients between the heavy metal concentrations in water, sediment and aquatic animals at each sampling site are presented in Table 5-9. Statistical analysis of data was carried out with the SPSS for Window 11.0 statistical program (Vanitbancha, 2005). Partial correlations were also used in the study. When correlation coefficients between animals and sediment were analyzed, water variable were controlled. In the other hand, sediment variable were controlled when animals and water were analyzed.

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Table 5-9 Correlation coefficients between the heavy metal concentrations in water, sediment and aquatic animals at each sampling site with the significant level at 0.05

Sampling site	Aquatic animal species	Water					Sediment				
		Cd	Cu	Fe	Pb	Zn	Cd	Cu	Fe	Pb	Zn
A	*T. trichopterus*	-	-0.94	-	0.74	-	-	-	-	-	-
	C. jullieni	0.98	0.99	-	-	0.98	-	-	-	-	-
	P. canaliculata	-	-	-	-	0.66	-	0.96	-	-	-0.81
B	*T. trichopterus*	-	-	-	0.89	-	-	-	-	-	-
	P. canaliculata	-	-	-	-0.96	-	-	-	0.68	-	-0.75
C	*T. trichopterus*	-	0.63	0.84	0.61	-0.76	-	0.60	-	-	-0.79
	O. mossambicus	-	-	-	-	-	-	-	-	-	-
	C. jullieni	-	-	-	-	-	-	-	-	-	-
	P. canaliculata	-	-	-	0.50	-	-	0.49	0.54	-	-0.85
D	*O. mossambicus*	-	-	-	-	-	-	-	-	-	-
	V. siheli	-0.64	-	0.66		-0.93	-	-	-	-	-0.86
E	*O. mossambicus*	-	-	-	-	-	-	-	-	-	-
	V. siheli	-0.81	-0.96	-	-	-0.83	-	0.76	-	-	-

Remark: - = non computable

5.7.1 Correlation between water, sediment and *T. trichopterus*

Cu concentrations between *T. trichopterus* and water were negative for sampling site A, whereas those between *T. trichopterus*, water and sediment were positive for sampling site C. The correlations between Pb concentrations of *T. trichopterus* and water were positive for sampling sites A, B and C. Although, there was no correlation between Fe concentrations in water, sediment and those in *T. trichopterus* in each sampling site separately (Table 5-9), but there was either positive or negative correlations between Fe concentrations in water, sediment and those in *T. trichopterus* as presented in Table 5-10. The relationship may be explained by feeding habits of *T. trichopterus*. This species inhabits in shallow sluggish or standing-water with a lot of aquatic vegetation. During the flooding period, they undertake lateral migration from the permanent water bodies or mainstream and return to their old habitat at the onset of the dry season (Rainboth, 1996). Thus, heavy metal concentrations in water have higher effect on *T. trichopterus* than those in sediment.

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However, sediment has indirect effect on the three-spot gourami feeding on zooplankton and crustaceans that live in/ on/ near the bottom of the canal.

5.7.2 Correlation between water, sediment and *C. jullieni*

Table 5-9 shows the positive correlations of Cd, Cu and Zn concentrations between water and *C. jullieni* for sampling site A. There was no correlation between sediment and *C. jullieni* for each sampling site separately, but the negative correlations were found between Cd and Fe concentrations in sediment and those in *C. jullieni* as shown in Table 5-10. Because this species inhabited in midwater to bottom depth of river and lived with algae, detritus and occasionally benthic invertebrates (Roberts, 1997). Thus, water and sediment have an effect on heavy metal concentrations accumulated in this species.

5.7.3 Correlation between water, sediment and *O. mossambicus*

Table 5-9 shows that there was no correlation between heavy metal concentrations in water, sediment and those in *O. mossambicus*. However, the Zn concentrations in water were shown negative correlation to *O. mossambicus* concentrations (Table 5-10). It can not be discussed on the relationship between the species and water and sediment based on the present data.

5.7.4 Correlation between water, sediment and *V. siheli*

V. siheli commonly inhabits in saltwater. Table 5-9 shows that the correlations between Cd and Zn concentrations in water and those in *V. siheli* were negative for sampling site D, whereas the correlations between Fe concentrations in water and those in *V. siheli* were positive for sampling site D. Furthermore, the correlations between Cu concentrations in sediment and those in *V. siheli* were positive at sampling site E. The correlations between Cd, Cu and Zn concentrations in water and those in *V. siheli* were negative (Table 5-10). *V. siheli* inhabits in coastal waters but enters estuaries and rivers where it feeds on microalgae, filamentous algae, forams, diatoms, and detritus associated with sand and mud. Thus, heavy metals in both water and sediment have an effect on heavy metals accumulated in *V. siheli*.

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5.7.5 Correlation between water, sediment and *P. canaliculata*

The correlations between Zn concentrations in water and those in *P. canaliculata* were positive for sampling site A and Pb concentrations for sampling site C (Table 5-9). However, the correlations between Pb concentrations in water and those in *P. canaliculata* were negative for sampling site B. The correlations between heavy metal concentrations in water, sediment and *P. canaliculata* are presented in Table 5-10. The correlations between Cu concentrations in sediment and those in *P. canaliculata* were positive, whereas the correlations between Zn concentration in sediment and those in mollusc were negative. The heavy metal concentrations in water and sediment may have less effect on heavy metal concentrations in mollusc than in fish. *P. canaliculata* as the amphibious animal remains submerged during the day, hides in vegetation near the surface and appetites for variety of water plants. Heavy metals may transfer from water plants that they feed. Water and sediment seem to be indirectly affected to the species. The correlations between heavy metal concentrations of *P. canaliculata* and the shoot of *Ipomoea aquatica*, the common aquatic plant in the Phi Lok canal system (Lertprasert, 2006), were analyzed. The results showed that the correlation coefficients between Cu, Fe and Pb concentrations in *P. canaliculata* and those in the shoot of *I. aquatica* were positive (Table 5-11). While there was no correlation between Cd and Zn concentrations in *P. canaliculata* and those in the shoot of *I. aquatica*. Thus, Cu, Fe and Pb exhibited biomagnification from aquatic plants to mollusc.

Results from the field and laboratory experiments showed that accumulation of heavy metal in aquatic animals is mainly dependent upon water concentrations of heavy metal and exposure period (Canli and Atli, 2003). Although some other environment factors such as ecological needs and physico-chemical parameters of water play significant roles in heavy metal accumulation (Kalay *et al.*, 1999; Kalay and Canli, 2000; Bryan and Langston, 1992). Feeding habits of the aquatic animals were also found to affect heavy metal accumulation in different species (Amundsen *et al.*, 1997; Mormede and Davies, 2001; Romeao *et al.*, 1999; Desimone *et al.*, 2003). Futhermore, heavy metal concentrations in muscles of fish varied widely depending in where the animals were caught (Turkmen *et al.*, 2005).

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Table 5-10 Correlation coefficients between the heavy metal concentrations in water, sediment and aquatic animals with the significant level at 0.05

Aquatic animal species	Water					Sediment				
	Cd	Cu	Fe	Pb	Zn	Cd	Cu	Fe	Pb	Zn
T. trichopterus	-	-	0.50	0.52	-	-	-	0.39	-	-0.48
C. jullieni	0.97	0.86	-	-	-	-0.81	-	-0.77	-	-
O. mossambicus	-	-	-	-	-0.73	-	-	-	-	-
V. siheli	-0.51	-0.50	-	-	-0.87	-	-	-	-	-0.76
P. canaliculata	-	-	-	-	-	-	0.43	-	-	-0.68

Remark: - = non computable

Table 5-11 Correlation coefficients between the heavy metal concentrations in *P. canaliculata* and the shoot of *Ipomoea aquatica* with the significant level at 0.05

	Shoot of *Ipomoea aquatica*[1]				
	Cd	Cu	Fe	Pb	Zn
P. canaliculata	-	0.37	0.57	0.39	-

Remark: - = non computable; [1] Lertprasert (2006)

5.8 Transfer factor

Transfer factor (TF) indicates whether heavy metal bio-magnification takes place through the trophic chain. A transfer factor greater than 1 indicates bioaccumulation (Kalfakakour and Akrida-Demertzi, 2000). TF is given as the quotient of:

$$TF = \frac{\text{Concentration of pollutant in fish}}{\text{Concentration of pollutant in ecosystem}}$$

A study on the transfer factor of heavy metal concentrations through the torophic chain of the river proved the existence of bioaccumulation in fish (Amiard *et*

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al., 1980). Kalfakakour and Akrida-Demertzi (2000) studied the transfer factor of heavy metals in fish from lake ecosystems, which include water, aquatic plants and sediment. They also reported that Ca, Mg, Fe, Cu, Zn and Pb exhibited bioaccumulation from water to fish. Rashed (2001) studied the transfer factor of heavy metals from the Nasser lake water, aquatic plants and sediment to fish (*T. nilotica*). The results showed that the transfer of Co, Cr, Cu, Fe, Mn, Ni, Sr and Zn in fish from water were greater than 1, and this means that the fish undergo bioaccumulation of these elements from the lake water. The order of transfer factor is as follows: Zn > Fe > Mn > Sr > Co > Ni > Cu > Cr. By comparing transfer factor of the study elements from water, aquatic plant and sediment, the transfer factor of water is greater than the others.

In this study, the transfer factors of Cd, Cu, Fe, Pb and Zn in some fish species and *P. canaliculata* were determined (Table 5-12). The results showed that the transfer factors of five heavy metals in all fish species from water were greater than 1. However, the transfer factors of Cd and Zn in *V. siheli*, the transfer factor of Zn in *C. jullieni* and the transfer factor of Cd in *O. mossambicus* from sediment were greater than 1. The transfer factors of five heavy metals in *P. canaliculata* from water were greater than 1. The transfer factors of Cd and Cu in *P. canaliculata* from sediment were greater than 1, whereas the transfer factors of Cd and Cu in *P. canaliculata* from sediment were less than 1.

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Table 5-12 The transfer factor of heavy metals in some fish species and *P. canaliculata* from the Phi Lok canal ecosystem

Transfer factor	Cd	Cu	Fe	Pb	Zn
P. canaliculata/water	134.62	1166.11	17612.65	1100.00	1420.99
P. canaliculata/ sediment	1.75	2.87	0.06	0.04	1.63
T. trichopterus/ water	38.46	75.83	12603.97	830.00	802.11
T. trichopterus/ sediment	0.50	0.19	0.05	0.03	0.92
C. jullieni/ water	57.69	131.67	6839.26	850.00	1045.92
C. jullieni/ sediment	0.75	0.32	0.02	0.03	1.20
O. mossambicus/ water	2466.67	249.39	8749.83	1090.00	490.51
O. mossambicus/ sediment	27.75	0.68	0.05	0.04	0.71
V. siheli/ water	177.78	206.67	6775.38	1070.00	853.72
V. siheli/ sediment	2.00	0.56	0.04	0.04	1.23

5.9 Effected of land use on accumulation and distribution of heavy metals in water and sediment in the Phi Lok canal system

5.9.1 Water

The heavy metal concentrations in five sampling sites can be presented in the descending order as follows: Fe>Zn>Cu>Pb>Cd

When comparing the annual means of heavy metal concentrations in water among five sampling sites of the Phi Lok canal system, it can be presented in descending order as follows;

Cd: Sampling sites B>A, C, D, E

Cu: Sampling sites A>B, D, E>C

Fe: Sampling sites E>A, D, C>B

Pb: Sampling sites B, C, D, E>A

Zn: Sampling sites D>C, B, E>A

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When comparing the heavy metal concentrations in water among five sampling sites in seasonal variation, it can be presented in descending order as follows;

Cd: cold>rainy, hot

Cu: cold>rainy>hot

Fe: cold, rainy>hot

Pb: cold>rainy>hot

Zn: cold>rainy>hot

5.9.2 Sediment

The heavy metal concentrations in five sampling sites can be presented in the descending order as follows: Fe>Zn>Pb>Cu>Cd

When comparing the annual means of heavy metal concentrations in sediment among five sampling sites of the Phi Lok canal system, it can be presented in descending order as follows;Cd: Sampling sites B>E, D>C, A

Cu: Sampling sites A>B, C, D, E

Fe: Sampling sites E, C>D, A>B

Pb: Sampling sites C>D>A, E>B

Zn: Sampling sites A, B>C>E>D

When comparing the heavy metal concentrations in sediment among five sampling sites in seasonal variation, it can be presented in descending order as follows;

Cd: rainy, cold>hot

Cu: rainy, cold>hot

Fe: rainy, hot>cold

Pb: cold, hot>rainy

Zn: rainy>cold, hot

5.9.3 Sources of heavy metals from land use in the study

As mentioned earlier, the neighboring canals which received wastewaters from the agriculture, aquaculture and industry flow into the Phi Lok canal system. The heavy metal discharges from aquaculture are the main source of heavy metal contamination in the canal system. The Phi Lok canal system may be sources as well

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as sinks for heavy metal contaminants, the persistent materials. If metals are accumulated in above-ground tissues, they may pass on the contaminants to higher trophic level consumers. This result can be explained by the different the activities located at different study sites. Heavy metals and other materials such as nutrients from different land use activities of the present study and literature are showed in Table 5-13.

Table 5-13 Heavy metals and other materials from literature and the present study in relation with the land use activities of the sampling sites

Sampling site	Source	Heavy metals and other materials (from literature)	Results of the present study
A	pig farm, paddy field	Cu, Cd, Pb, Zn PO_4^{3-}, NO_{3-}	Cu in water and sediment; PO_4^{3-}, NO_{3-}
B	fish raising pond, paddy field, scrap plant	Cd, Cu, Pb, Zn PO_4^{3-}, NO_{3-}	Cd, Pb in water, Cd in sediment; PO_4^{3-}, NO_{3-}
C	fish raising pond, orchards, village	Cd, Cu, Pb, Zn organic matters,	Pb in sediment, BOD
D	shrimp farm, mangrove area	Pb, Zn	Zn in water, Pb in sediment
E	shrimp farm, mangrove area	Pb, Zn	Fe in water and sediment; BOD in the hot season

At sampling site A, the main activities are paddy fields and pig farms. Animal manures contain heavy metals as well as nutrients and trace elements. Besides feed stuffs and feed additives, potential sources of heavy metals in animal manure are

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disinfectants, bedding materials, corrosion and wear and tear of stable equipment or storage containers as well as building materials, and paints. It was found that on farm level feed concentrates contribute to most of the inputs of Cu and Zn. Dach and Starmans (2005) found that the estimate heavy metals input by animal manure and mineral fertilizer were Cd, Cu, Pb and Zn. Therefore, the extremely high concentrations of Cu and Zn found in sediment may be from the manures, feed additives from pig farms

At sampling site C, the major activity is fish raising pond. During the three months of June to August, the canal water was pumped into the pond and stopped pumping in September until the end of the rearing period of November (Sirichotiwong, 2006). Therefore from November the fish raising pond was in stagnant condition and the wastewater was discharged from the fish raising pond into the Phi Lok canal system. Sirichotiwong (2006) found that Fe concentrations were much higher in sediment than those of other heavy metals, although, Cd concentrations in water and sediment are lowest in the fish raising pond. So the heavy metal accumulated in the environment at this site may be from drainage water (including uneaten feed, fertilizer, sediment) to the Phi Lok canal system.

Shrimp farm was the main land use activity at sampling sites D and E. Management of water quality was achieved by a combination of flushing the pond with clean seawater and of phytoplankton bloom by assessment of pond color. Water exchanges were frequent, especially during the latter half production. Accumulated sediment was known to be undesirable and was removed between production cycles. The organic component of the accumulated sediment is the mixture of pond soil organic content and detrital material. This detrital materials comprise sedimented organic materials from plankton, shrimp faeces and uneaten feed. Problems associated with the pond bottom and accumulated sediment occur when excessive organic materials build up causing release of ammonia, organic matter and acidic soils and hydrogen sulphide. The organic material released from the sediment tends to stimulate very heavy phytoplankton blooms. Not only problems from nutrients but also heavy metals accumulated in sediment and discharge water. Guhathakurta and Kaviraj (2000) found that the metal concentrations in pond water ranged as Cd, Fe, Pb and Zn were 0.04 to 0.10, 14.30 to 170.00, 0.03 to 0.16 and <0.01 to 9.66 µg/L, respectively

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and Zn concentrations in the surface layer of sediment ranged from 40.80 to 3448.30 mg/kg while that of Fe ranged from 7155.00 to 10068.80 mg/kg. Also the present study found that Fe, Pb and Zn contents in both water and sediment were higher than those found in the previous studies.

However, the results of the present study suggested that the Phi Lok canal system was relatively less contaminated with the growing concern on heavy metal contamination from upstream activities.

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CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

The accumulation and distribution of five heavy metals (Cd, Cu, Fe, Pb and Zn) in water, sediment, *P. canaliculata* and some fish species in the Phi Lok canal system varied widely depending on where and when the samples taken. The results from the study can be concluded as follows.

6.1.1 Heavy metal concentrations in water

The average heavy metal concentrations in water can be presented in descending order as follows; Fe>Zn>Cu>Pb>Cd

When comparing annual mean of heavy metal concentrations in water among five sampling sites of the Phi Lok canal system, it can be presented in the descending order as follows;

Cd: Sampling sites B>A, C, D, E

Cu: Sampling sites A>B, D, E>C

Fe: Sampling sites E>A, D, C>B

Pb: Sampling sites B, C, D, E>A

Zn: Sampling sites D>C, B, E>A

When comparing heavy metal concentrations in water among five sampling sites in seasonal variation, it can be presented in the descending order as follows;

Cd: cold>rainy, hot

Cu: cold>rainy>hot

Fe: cold, rainy>hot

Pb: cold>rainy>hot

Zn: cold>rainy>hot

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6.1.2 Heavy metal concentrations in sediment

The average heavy metal concentrations in sediment can be presented in the descending order as follows; Fe>Zn>Pb>Cu>Cd

When comparing annual mean of heavy metal concentrations in sediment amongst five sampling sites of the Phi Lok canal system, it can be presented in the descending order as follows;

Cd: Sampling sites B>E, D>C, A

Cu: Sampling sites A>B, C, D, E

Fe: Sampling sites E, C>D, A>B

Pb: Sampling sites C>D>A, E>B

Zn: Sampling sites A, B>C>E>D

When comparing heavy metal concentrations in sediment among five sampling sites in seasonal variation, it can be presented in the descending order as follows;

Cd: rainy, cold>hot

Cu: rainy, cold>hot

Fe: rainy, hot>cold

Pb: cold, hot>rainy

Zn: rainy>cold, hot

6.1.3 Heavy metal concentrations in aquatic animals

Most of heavy metal concentrations in aquatic animals correlated to those in sediment more than in water. Almost all the correlation coefficients between the heavy metals in aquatic animals and sediment were negative.

6.1.3.1 Heavy metal concentrations in *P. canaliculata*

The average heavy metal concentrations in *P. canaliculata* can be presented in the descending order as follows; Fe>Zn>Cu>Pb>Cd

When comparing annual mean of heavy metal concentrations in *P. canaliculata* amongst three sampling sites in the freshwater part of the Phi Lok canal system, it can be presented in the descending order as follows;

Cd: Sampling sites C>A>B

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Cu: Sampling sites B>A>C

Fe: Sampling sites A>B>C

Pb: Sampling sites B>A>C

Zn: Sampling sites A>C>B

When comparing heavy metal concentrations of *P. canaliculata* among three sampling sites in seasonal variation, it can be presented in the descending order as follows;

Cd: rainy>hot>cold, but not signigicantly

Cu: rainy>cold>hot

Fe: rainy>cold, hot

Pb: rainy>cold>hot

Zn: hot, cold>rainy

6.1.3.2 Heavy metal concentrations in fish species

The average heavy metal concentrations in four fish species can be presented in the descending order as follows; Fe>Zn>Cu>Pb>Cd

When comparing heavy metal concentrations of fish species in seasonal variation, it was found that different fish species had a different pattern of heavy metal accumulation. *T. trichopterus* accumulated higher Fe, Cu and Pb concentrations in the rainy season than those in the cold and hot seasons, whereas *V. siheli* accumulated higher Fe, Zn and Cd concentrations in the hot season than those in the rainy and cold seasons. Furthermore, the heavy metal accumulations in fish species also depend on their behavior and their feeding habits.

6.1.3.3 Acceptable levels of heavy metals in aquatic animals to human consumption

Most of heavy metal concentrations in fish and mollusc were in acceptable levels for food. Although, almost all of aquatic animals were still suitable for human consumption. However a potential dangerous may occur in the future depending on the agricultural and industrial development in this region.

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6.1.4 Heavy metals in the Phi Lok canal system

The heavy metal concentrations among the media can be presented in the descending order as follows: sediment > mollusc > fish > water.

6.1.5 Water quality in the Phi Lok canal system

Table 6-1 shows water quality situation of five sampling sites in the Phi Lok canal system from June 2004 to April 2005. When the physico-chemical parameters and heavy metal concentrations in the Phi Lok canal system were determined. The results showed that in the freshwater part, water quality in the Phi Lok canal system can be classified into class 4 in the surface water quality standards (Pollution Control Department, 2000). Water quality in class 4 is suggested to use for consumption and industry. However the present activities in the study area were based on agriculture while the water quality studied was suitable for industrial use. Therefore it can be suggested to improve the water quality especially DO and BOD. In the saltwater part, water quality in the Phi Lok canal system can be classified into class 4 in the coastal water quality standards (Pollution Control Department, 2000). Water quality in class 4 is suggested to use for mix-coastal farms. Thus, it is suitable for the activities on the sampling sites.

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Table 6-1 Water quality situation at five sampling sites in the Phi Lok canal system from June 2004 to April 2005

Sampling site	Land use	Water quality situation
A	pig farm, paddy field	Class 4 in Thailand's surface water quality standards (Pollution Control Department, 2000)
B	fish raising pond, paddy field, scrap plant	Class 4 in Thailand's surface water quality standards (Pollution Control Department, 2000)
C	fish raising pond, orchards	Class 4 in Thailand's surface water quality standards (Pollution Control Department, 2000)
D	shrimp farm, mangrove area	Class 4 in Thailand's coastal water quality standards (Pollution Control Department, 2000)
E	shrimp farm, mangrove area	Class 4 in Thailand's coastal water quality standards (Pollution Control Department, 2000)

6.2 Recommendations

6.2.1 Recommendations for further study

1. Owing to the limitation of fish samples, the heavy metal concentrations accumulated in both sex and different size of fish can not be carried out. Further studies should be conducted on the heavy metal concentrations in sex and size of fish and mollusc species from the Phi Lok canal system.

2. Results of the present study can be used as a part of information for Heavy metal flow analysis in the canal system and the Mae Klong river. More information on heavy metal concentrations in water and sediments from various agricultural and industrial activities should be studied. The material flow analysis is very useful tool for water management and should be applied to be used in the Phi Lok canal system.

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6.2.2 Recommendations for application

1. Although heavy metal accumulations in aquatic animals were lower than maximum permissible levels for human consumption. To prevent heavy metal poison, consumer should avoid eating them in the high accumulated season, especially in the cold season.

2. In the freshwater part of the Phi Lok canal system, some physico-chemical parameters of the water canal especially BOD and DO have to be treated before the water will be used for agricultural activities. Also the wastewater discharged into the canal system have to be treated.

3. Although heavy metal concentrations in sediments of the Phi Lok canal system were high but they are still within the standards and guidelines of international organizations. The proper method in managing the sediment is to pump up both sediment and water and to dry before further treatment of the dried sediment to remove the heavy metal contents. The conventional practice of dredging of the sediment and piling up along the canal banks should not be applied because heavy metal contents will retransport into the canal water.

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APPENDIX

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APPENDIX A

Table 1 Average of physical and chemical parameters of the Phi Lok canal in 2004

Site	Month	physical and chemical parameters									
		BOD	DO	Nitrate	Phosphate	TDS	Hardness	ph	Salinity	Conductivity	Temperature
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		ppt	ms/cm	(°C)
A	Jun	3.89	2.89	1.16	0.0340	595	231.33	7.58	0.40	0.92	28.90
	Aug	8.07	1.57	4.93	0.0580	400	153.33	7.37	0.40	0.92	25.00
	Oct	3.50	3.22	1.90	0.0180	596	132.67	7.27	0.24	0.50	28.61
	Dec	3.20	2.54	8.47	0.0500	1570	124.67	7.53	1.74	3.31	24.18
	Feb	4.30	1.98	3.48	0.0610	388	280.00	7.60	0.55	1.16	28.59
	Apr	0.48	1.67	0.08	0.0004	472	4400.00	7.88	0.47	0.97	30.84
B	Jun	5.49	1.12	1.20	0.0550	1000	328.00	7.46	0.70	1.41	28.39
	Aug	4.70	2.88	3.08	0.0290	3767	159.67	7.34	0.40	0.92	28.36
	Oct	3.33	2.70	5.17	0.0260	432	119.00	7.28	0.26	0.58	28.70
	Dec	2.21	0.14	6.79	0.0370	2376	3607.33	7.54	9.67	16.54	25.17
	Feb	5.80	5.78	1.98	0.0022	1267	4086.67	7.29	15.30	25.54	29.05
	Apr	1.17	1.92	0.10	0.0004	767	5383.33	7.70	1.94	3.88	31.18
C	Jun	6.67	0.96	0.98	0.0470	1609	429.67	7.90	1.00	2.26	28.25
	Aug	3.90	2.20	1.88	0.0300	5200	182.67	7.48	0.20	0.59	28.60
	Oct	7.97	1.77	3.97	0.0290	713	138.17	7.29	0.37	0.81	28.05
	Dec	7.03	9.20	2.48	0.0225	987	1126.67	7.66	12.49	23.27	24.59
	Feb	5.63	2.85	1.60	0.0021	6733	1400.00	7.45	20.50	32.77	29.29
	Apr	1.57	3.07	0.09	0.0005	2543	533.33	7.51	6.88	11.73	31.17

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Table 1 Average of physical and chemical parameters of Phi Lok canal in 2004 (Continue)

		physical and chemical parameters									
Site	Month	BOD	DO	Nitrate	Phosphate	TDS	Hardness	ph	Salinity	Conductivity	Temperature
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		ppt	ms/cm	(°C)
D	Jun	3.54	3.79	0.68	0.0400	7800	4242.00	7.68	5.69	11.02	29.26
	Aug	5.20	3.78	3.69	0.0280	6200	980.00	7.88	1.17	2.18	29.36
	Oct	6.32	5.85	3.03	0.0200	2127	470.33	7.85	2.27	4.56	28.07
	Dec	4.56	3.41	5.73	0.0200	16828	4010.67	7.91	13.73	21.80	23.75
	Feb	2.17	2.25	1.69	0.0020	28841	4566.67	7.59	21.95	35.04	29.43
	Apr	1.85	2.68	0.09	0.0004	27801	4108.33	7.90	21.37	34.24	30.54
E	Jun	5.04	5.54	1.39	0.0360	9067	1320.67	7.63	6.47	12.38	29.20
	Aug	8.57	6.13	3.03	0.0280	4433	738.00	7.66	1.23	2.28	29.30
	Oct	2.70	4.60	3.87	0.0250	2794	488.33	7.67	2.70	5.36	27.96
	Dec	3.46	3.10	4.49	0.0210	16373	3770.33	7.82	13.74	22.37	23.62
	Feb	1.20	2.58	1.49	0.0020	24465	3866.67	7.53	21.75	34.74	29.30
	Apr	1.83	2.70	0.07	0.0004	38142	4066.67	7.49	20.95	33.65	30.71

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Table 2 Heavy metal concentrations in water samples (μg/L) from the five sampling sites of the Phi Lok canal system

Sampling site	n	Fe μg/L	Cu μg/L	Zn μg/L	Cd μg/L	Pb μg/L
Site A						
Min-max	18	20.00-152.00	20.00-72.00	9.00-154.00	0.001-0.125	0.040-2.510
Mean ±STD		84.0 ± 40.0	39.0 ± 30.0	62.0 ± 50.0	0.045 ± 0.04	0.936 ± 0.89
Site B						
Min-max	18	3.00-131.00	1.00-87.00	15.00-177.0	nd-0.295	0.020-2.810
Mean ±STD		50.0 ± 30.0	36.0 ± 30.0	74.0 ± 50.0	0.065 ± 0.07	1.111 ± 1.04
Site C						
Min-max	18	18.00-155.00	1.00-74.00	16.00-176.0	nd-0.101	0.090-2.550
Mean ±STD		68.0 ± 40.0	26.0 ± 30.0	74.0 ± 50.0	0.045 ± 0.03	1.085 ± 0.93
Site D						
Min-max	18	34.00-167.00	1.00-74.00	6.00-193.00	nd-0.132	0.080-2.840
Mean ±STD		80.0 ± 30.0	33.0 ± 30.0	82.0 ± 50.0	0.046 ± 0.05	1.088 ± 1.03
Site E						
Min-max	18	19.00-470.00	1.00-73.00	12.00-133.0	0.006-0.970	0.200-2.620
Mean ±STD		158.0 ± 130.0	33.0 ± 30.0	74.0 ± 40.0	0.045 ± 0.03	1.117 ± 1.00

Table 3 Heavy metal concentrations in sediment samples (mg/kg) from the five sampling sites of the Phi Lok canal system

Sampling site	n	Fe mg/kg	Cu mg/kg	Zn mg/kg	Cd mg/kg	Pb mg/kg
Site A						
Min-max	18	14743.90-24190.70	5.00-40.10	37.30-91.90	0.002-.006	10.00-49.00
Mean ±STD		18978.74 ± 2647.27	20.50 ±10.86	62.99 ±14.69	0.003 ±0.001	23.78 ±11.23
Site B						
Min-max	18	10593.60-22498.70	0.30-20.80	44.50-84.50	0.002-0.113	7.00-48.00
Mean ±STD		16792.64 ± 3879.77	11.62 ± 6.79	62.71 ±14.27	0.005 ±0.002	21.39 ±12.30
Site C						
Min-max	18	16222.50-26364.10	7.40-28.70	41.40-80.90	0.001-0.007	7.00-77.00
Mean ±STD		20480.93 ± 3324.45	13.76 ± 5.32	60.14 ±13.30	0.004 ±0.002	28.67 ±22.29
Site D						
Min-max	18	16619.10-22857.10	8.00-17.90	44.50-64.50	0.003-0.005	4.00-72.00
Mean ±STD		19698.38 ± 1739.89	12.23 ± 2.99	53.36 ± 5.58	0.004 ±0.000	25.72 ±20.68
Site E						
Min-max	18	17307.00-27035.00	7.70-16.90	47.20-64.30	0.003-0.006	4.00-65.00
Mean ±STD		20743.37 ± 2597.07	11.95 ± 2.58	54.79 ± 4.91	0.004 ±0.001	23.39 ±17.34

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APPENDIX B

Table 4 Multiple comparisons of Cd concentrations in water, sediment and aquatic animals between seasonal variation

Multiple Comparisons

Dependent Variable		(I) SEASON	(J) SEASON	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
CD_WATER	Dunnett T3	rainy	cold	-.065067*	.0100011	.000	-.089902	-.040231
			hot	-.001467	.0070561	.995	-.018825	.015892
		cold	rainy	.065067*	.0100011	.000	.040231	.089902
			hot	.063600*	.0105899	.000	.037443	.089757
		hot	rainy	.001467	.0070561	.995	-.015892	.018825
			cold	-.063600*	.0105899	.000	-.089757	-.037443
CD_SED	Dunnett T3	rainy	cold	.000730	.0003808	.170	-.000210	.001670
			hot	.001997*	.0003897	.000	.001036	.002957
		cold	rainy	-.000730	.0003808	.170	-.001670	.000210
			hot	.001267*	.0002978	.000	.000535	.001998
		hot	rainy	-.001997*	.0003897	.000	-.002957	-.001036
			cold	-.001267*	.0002978	.000	-.001998	-.000535
CD_SNAIL	Dunnett T3	rainy	cold	.004081	.0025931	.335	-.002652	.010814
			hot	.002594	.0025297	.671	-.004029	.009218
		cold	rainy	-.004081	.0025931	.335	-.010814	.002652
			hot	-.001487	.0008433	.244	-.003654	.000681
		hot	rainy	-.002594	.0025297	.671	-.009218	.004029
			cold	.001487	.0008433	.244	-.000681	.003654
CD_FISH1	Dunnett T3	rainy	cold	-.000978	.0004242	.120	-.002184	.000229
			hot	-.000042	.0001654	.990	-.000826	.000743
		cold	rainy	.000978	.0004242	.120	-.000229	.002184
			hot	.000936	.0004008	.123	-.000236	.002109
		hot	rainy	.000042	.0001654	.990	-.000743	.000826
			cold	-.000936	.0004008	.123	-.002109	.000236
CD_FISH6	Dunnett T3	rainy	cold	.004196*	.0004792	.000	.002883	.005509
			hot	-.001904	.0020372	.736	-.008573	.004764
		cold	rainy	-.004196*	.0004792	.000	-.005509	-.002883
			hot	-.006100	.0019873	.071	-.012837	.000637
		hot	rainy	.001904	.0020372	.736	-.004764	.008573
			cold	.006100	.0019873	.071	-.000637	.012837

*. The mean difference is significant at the .05 level.

Remark: SED, sediment; Snail, *Pomacea canaliculata*; FISH1, *Tichogaster trichopterus* (Pallas, 1770); FISH6, *Valamugil siheli* (Forskal, 1775)

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Table 5 Multiple comparisons of Cu concentrations in water, sediment and aquatic animals between seasonal variation

Multiple Comparisons

Dependent Variable		(I) SEASON	(J) SEASON	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
FE_WATER	Dunnett T3	rainy	cold	-24.56667	22.10295	.610	-79.73422	30.60089
			hot	37.53333*	9.901612	.001	13.17882	61.88785
		cold	rainy	24.56667	22.10295	.610	-30.60089	79.73422
			hot	62.10000*	21.58379	.020	8.01807	116.18193
		hot	rainy	-37.53333*	9.901612	.001	-61.88785	-13.17882
			cold	-62.10000*	21.58379	.020	-116.18193	-8.01807
FE_SNAIL	Dunnett T3	rainy	cold	976.29222*	211.8301	.000	442.62611	1509.95833
			hot	1206.68056*	175.3808	.000	754.38203	1658.97908
		cold	rainy	-976.29222*	211.8301	.000	-1509.95833	-442.62611
			hot	230.38833	147.4583	.341	-153.02201	613.79868
		hot	rainy	-1206.68056*	175.3808	.000	-1658.97908	-754.38203
			cold	-230.38833	147.4583	.341	-613.79868	153.02201
FE_SED	Dunnett T3	rainy	cold	3102.58333*	823.4725	.001	1078.97526	5126.19141
			hot	1077.79333	696.7847	.333	-635.25190	2790.83857
		cold	rainy	-3102.58333*	823.4725	.001	-5126.19141	-1078.97526
			hot	-2024.79000*	764.6442	.031	-3908.49056	-141.08944
		hot	rainy	-1077.79333	696.7847	.333	-2790.83857	635.25190
			cold	2024.79000*	764.6442	.031	141.08944	3908.49056
FE_FISH1	Dunnett T3	rainy	cold	1565.59167	491.0515	.061	-93.37265	3224.55598
			hot	1790.53000*	494.4419	.037	136.85409	3444.20591
		cold	rainy	-1565.59167	491.0515	.061	-3224.55598	93.37265
			hot	224.93833*	85.23922	.043	5.79545	444.08122
		hot	rainy	-1790.53000*	494.4419	.037	-3444.20591	-136.85409
			cold	-224.93833*	85.23922	.043	-444.08122	-5.79545
FE_FISH6	Dunnett T3	rainy	cold	802.29167*	146.4000	.001	395.10619	1209.47714
			hot	-137.64167	370.3616	.974	-1273.18183	997.89850
		cold	rainy	-802.29167*	146.4000	.001	-1209.47714	-395.10619
			hot	-939.93333	340.3833	.101	-2096.49926	216.63259
		hot	rainy	137.64167	370.3616	.974	-997.89850	1273.18183
			cold	939.93333	340.3833	.101	-216.63259	2096.49926

*. The mean difference is significant at the .05 level.

Remark: Snail, *Pomacea canaliculata*; SED, sediment; FISH1, *Tichogaster trichopterus* (Pallas, 1770); FISH6, *Valamugil siheli* (Forskal, 1775)

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Table 6 Multiple comparisons of Fe concentrations in water, sediment and aquatic animals between seasonal variation

Multiple Comparisons

Dependent Variable		(I) SEASON	(J) SEASON	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
FE_WATER	Dunnett T3	rainy	cold	-24.56667	22.10295	.610	-79.73422	30.60089
			hot	37.53333*	9.901612	.001	13.17882	61.88785
		cold	rainy	24.56667	22.10295	.610	-30.60089	79.73422
			hot	62.10000*	21.58379	.020	8.01807	116.18193
		hot	rainy	-37.53333*	9.901612	.001	-61.88785	-13.17882
			cold	-62.10000*	21.58379	.020	-116.18193	-8.01807
FE_SNAIL	Dunnett T3	rainy	cold	976.29222*	211.8301	.000	442.62611	1509.95833
			hot	1206.68056*	175.3808	.000	754.38203	1658.97908
		cold	rainy	-976.29222*	211.8301	.000	-1509.95833	-442.62611
			hot	230.38833	147.4583	.341	-153.02201	613.79868
		hot	rainy	-1206.68056*	175.3808	.000	-1658.97908	-754.38203
			cold	-230.38833	147.4583	.341	-613.79868	153.02201
FE_SED	Dunnett T3	rainy	cold	3102.58333*	823.4725	.001	1078.97526	5126.19141
			hot	1077.79333	696.7847	.333	-635.25190	2790.83857
		cold	rainy	-3102.58333*	823.4725	.001	-5126.19141	-1078.97526
			hot	-2024.79000*	764.6442	.031	-3908.49056	-141.08944
		hot	rainy	-1077.79333	696.7847	.333	-2790.83857	635.25190
			cold	2024.79000*	764.6442	.031	141.08944	3908.49056
FE_FISH1	Dunnett T3	rainy	cold	1565.59167	491.0515	.061	-93.37265	3224.55598
			hot	1790.53000*	494.4419	.037	136.85409	3444.20591
		cold	rainy	-1565.59167	491.0515	.061	-3224.55598	93.37265
			hot	224.93833*	85.23922	.043	5.79545	444.08122
		hot	rainy	-1790.53000*	494.4419	.037	-3444.20591	-136.85409
			cold	-224.93833*	85.23922	.043	-444.08122	-5.79545
FE_FISH6	Dunnett T3	rainy	cold	802.29167*	146.4000	.001	395.10619	1209.47714
			hot	-137.64167	370.3616	.974	-1273.18183	997.89850
		cold	rainy	-802.29167*	146.4000	.001	-1209.47714	-395.10619
			hot	-939.93333	340.3833	.101	-2096.49926	216.63259
		hot	rainy	137.64167	370.3616	.974	-997.89850	1273.18183
			cold	939.93333	340.3833	.101	-216.63259	2096.49926

*. The mean difference is significant at the .05 level.

Remark: Snail, *Pomacea canaliculata*; SED, sediment; FISH1, *Tichogaster trichopterus* (Pallas, 1770); FISH6, *Valamugil siheli* (Forskal, 1775)

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Table 7 Multiple comparisons of Pb concentrations in water, sediment and aquatic animals between seasonal variation

Multiple Comparisons

Dependent Variable		(I) SEASON	(J) SEASON	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
PB_WATER	Dunnett T3	rainy	cold	-1.608407*	.1188652	.000	-1.901755	-1.315060
			hot	.409659*	.1004106	.001	.157287	.662031
		cold	rainy	1.608407*	.1188652	.000	1.315060	1.901755
			hot	2.018067*	.0784795	.000	1.822943	2.213190
		hot	rainy	-.409659*	.1004106	.001	-.662031	-.157287
			cold	-2.018067*	.0784795	.000	-2.213190	-1.822943
PB_SED	Dunnett T3	rainy	cold	-23.166667*	4.111348	.000	-33.479473	-12.853860
			hot	-14.500000*	2.194673	.000	-19.929937	-9.070063
		cold	rainy	23.166667*	4.111348	.000	12.853860	33.479473
			hot	8.666667	4.399878	.155	-2.259675	19.593008
		hot	rainy	14.500000*	2.194673	.000	9.070063	19.929937
			cold	-8.666667	4.399878	.155	-19.593008	2.259675
PB_SNAIL	Dunnett T3	rainy	cold	.980467*	.2888220	.008	.237830	1.723104
			hot	1.338683*	.2723772	.000	.626199	2.051168
		cold	rainy	-.980467*	.2888220	.008	-1.723104	-.237830
			hot	.358217*	.1200592	.022	.046247	.670187
		hot	rainy	-1.338683*	.2723772	.000	-2.051168	-.626199
			cold	-.358217*	.1200592	.022	-.670187	-.046247
PB_FISH1	Dunnett T3	rainy	cold	.708083	.3175857	.179	-.339219	1.755386
			hot	1.384833*	.3190220	.016	.339234	2.430432
		cold	rainy	-.708083	.3175857	.179	-1.755386	.339219
			hot	.676750*	.0961452	.000	.431505	.921995
		hot	rainy	-1.384833*	.3190220	.016	-2.430432	-.339234
			cold	-.676750*	.0961452	.000	-.921995	-.431505
PB_FISH6	Dunnett T3	rainy	cold	.905278	.4897369	.254	-.536911	2.347466
			hot	.922611	.5089822	.260	-.539015	2.384237
		cold	rainy	-.905278	.4897369	.254	-2.347466	.536911
			hot	.017333	.1552532	.999	-.789120	.823786
		hot	rainy	-.922611	.5089822	.260	-2.384237	.539015
			cold	-.017333	.1552532	.999	-.823786	.789120

*. The mean difference is significant at the .05 level.

Remark: SED, sediment; Snail, *Pomacea canaliculata*; FISH1, *Tichogaster trichopterus* (Pallas, 1770); FISH6, *Valamugil siheli* (Forskal, 1775)

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Table 8 Multiple comparisons of Zn concentrations in water, sediment and aquatic animals between seasonal variation

Multiple Comparisons

Dependent Variable		(I) SEASON	(J) SEASON	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
ZN_WATER	Dunnett T3	rainy	cold	-79.36667*	6.305277	.000	-94.85275	-63.88059
			hot	25.63333*	5.345980	.000	12.46338	38.80329
		cold	rainy	79.36667*	6.305277	.000	63.88059	94.85275
			hot	105.00000*	5.506917	.000	91.42317	118.57683
		hot	rainy	-25.63333*	5.345980	.000	-38.80329	-12.46338
			cold	-105.00000*	5.506917	.000	-118.57683	-91.42317
ZN_SED	Dunnett T3	rainy	cold	15.44000*	2.886970	.000	8.29254	22.58746
			hot	15.70333*	2.614606	.000	9.14252	22.26415
		cold	rainy	-15.44000*	2.886970	.000	-22.58746	-8.29254
			hot	.26333	1.550123	.998	-3.58603	4.11269
		hot	rainy	-15.70333*	2.614606	.000	-22.26415	-9.14252
			cold	-.26333	1.550123	.998	-4.11269	3.58603
ZN_SNAIL	Dunnett T3	rainy	cold	-96.75978*	20.56870	.001	-151.31763	-42.20193
			hot	-113.16944*	8.570115	.000	-135.21270	-91.12619
		cold	rainy	96.75978*	20.56870	.001	42.20193	151.31763
			hot	-16.40967	21.06747	.821	-71.81961	39.00028
		hot	rainy	113.16944*	8.570115	.000	91.12619	135.21270
			cold	16.40967	21.06747	.821	-39.00028	71.81961
ZN_FISH1	Dunnett T3	rainy	cold	-22.79583*	4.408767	.001	-34.87716	-10.71451
			hot	-43.14333*	3.062192	.000	-51.20659	-35.08008
		cold	rainy	22.79583*	4.408767	.001	10.71451	34.87716
			hot	-20.34750*	5.167196	.002	-33.75225	-6.94275
		hot	rainy	43.14333*	3.062192	.000	35.08008	51.20659
			cold	20.34750*	5.167196	.002	6.94275	33.75225
ZN_FISH6	Dunnett T3	rainy	cold	13.35833	8.013884	.309	-8.82239	35.53906
			hot	-61.44167*	8.452546	.000	-84.26710	-38.61624
		cold	rainy	-13.35833	8.013884	.309	-35.53906	8.82239
			hot	-74.80000*	3.117909	.000	-84.63478	-64.96522
		hot	rainy	61.44167*	8.452546	.000	38.61624	84.26710
			cold	74.80000*	3.117909	.000	64.96522	84.63478

*. The mean difference is significant at the .05 level.

Remark: SED, sediment; Snail, *Pomacea canaliculata*; FISH1, *Tichogaster trichopterus* (Pallas, 1770); FISH6, *Valamugil siheli* (Forskal, 1775)

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