การกระจายตัวของแคดเมียมในตะกอนท้องน้ำและตะกอนแขวนลอย บริเวณลุ่มน้ำแม่ตาว และลุ่มน้ำแม่กุ ในอำเภอแม่สอด จังหวัดตาก

นางสาวภาราดา มณีวงศ์

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CADMIUM DISTRIBUTION IN STREAM SEDIMENT AND SUSPENDED SOLIDS ALONG HUAI MAE TAO AND HAUI MAE KU, MAE SOT DISTRICT, TAK PROVINCE.

Miss Parada Maneewong

A Thesis Submitted in Partial Fulfillment of the Requirements
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ภาราดา มณีวงศ์ : การกระจายตัวของแคดเมียมในตะกอนท้องน้ำและตะกอนแขวนลอย บริเวณลุ่มน้ำแม่ตาว และลุ่มน้ำแม่กุ ในอำเภอแม่สอด จังหวัดตาก (CADMIUM DISTRIBUTION IN STREAM SEDIMENT AND SUSPENDED SOLIDS ALONG HUAI MAE TAO AND HAUI MAE KU, MAE SOT DISTRICT, TAK PROVINCE) อ. ที่ปรึกษา: ผศ.ดร. จักรพันธ์ สุทธิรัตน์, อ.ที่ปรึกษาร่วม: ดร.จันทรา ทองคำเภา, 87 หน้า. ISBN 974-14-2920-7

งานวิจัยนี้เป็นการศึกษาการกระจายตัวของโลหะแคดเมียมในตะกอนท้องน้ำและตะกอนแขวนลอยจากห้วยแม่ตาวและห้วยแม่กุ อ.แม่สอด จ.ตาก ซึ่งเป็นบริเวณที่ประสบปัญหาการปนเปื้อนของแคดเมียมในพื้นที่เกษตรกรรม และส่งผลต่อผลิตผลทางการเกษตร โดยเฉพาะข้าว ซึ่งส่งผลกระทบโดยตรงต่อสุขภาพของประชากรในพื้นที่ อ.แม่สอด ทั้งนี้สภาพเศรษฐกิจของท้องถิ่นยังได้รับผลกระทบจากสถานการณ์ดังกล่าว ทำให้รัฐบาลประกาศห้ามเกษตรกรปลูกข้าวในพื้นที่ และจำเป็นอย่างยิ่งที่ต้องจ่ายค่าชดเชยให้แก่เกษตรกร

ในการศึกษาครั้งนี้มุ่งเน้นศึกษาการกระจายตัวของแคดเมียมในตะกอนท้องน้ำและตะกอนแขวนลอยจากห้วยแม่ตาว ห้วยแม่กุ และห้วยหนองเขียว (พื้นที่ควบคุม) นอกจากนี้ตัวอย่างตะกอนท้องน้ำยังถูกวิเคราะห์สัดส่วนทางพันธะ(Fraction) ที่สำคัญของแคดเมียมในตะกอน เพื่อบ่งชี้ถึงศักยภาพของแคดเมียมที่จะมีผลกระทบต่อสิ่งแวดล้อมและมนุษย์ ตัวอย่างทั้งหมดที่แยกสัดส่วนทางพันธะและตัวอย่างที่ย่อยเพื่อหาค่าแคดเมียมรวมและสังกะสีรวมนำมาวิเคราะห์ด้วยเครื่องไอซีพี-โออีเอส ผลการศึกษาพบว่าห้วยแม่ตาวซึ่งรับน้ำโดยตรงจากดอยผาแดง มีปริมาณแคดเมียมมากกว่าห้วยอื่นทั้งในตัวอย่างตะกอนท้องน้ำและตะกอนแขวนลอย ขณะที่ห้วยหนองเขียวพบปริมาณโลหะแคดเมียมต่ำที่สุด เมื่อพิจารณาการศึกษาสัดส่วนทางพันธะของแคดเมียมในห้วยแม่ตาวพบว่า อยู่ในรูปแบบที่สามารถแตกตัวได้ง่าย (BCR1) และมีผลกระทบต่อสิ่งแวดล้อมสูง ส่วนในห้วยแม่กุพบว่าแคดเมียมส่วนใหญ่จะอยู่ในรูปของ (BCR2) และในรูปของแคดเมียมที่แตกตัวยากที่สุด (Final Residue) นั่นคือพันธะของแคดเมียมกับซิลิเกต และห้วยหนองเขียวพบว่า ส่วนมากอยู่ในรูปพันธะที่แตกตัวยาก หลักฐานดังกล่าวแสดงให้เห็นว่าห้วยแม่ตาวเป็นพื้นที่ที่มีความเสี่ยงต่อการปนเปื้อนของแคดเมียมในพืชและสิ่งมีชีวิตมากกว่าห้วยอื่นๆในพื้นที่ศึกษา

จากผลการศึกษาและลักษณะของภูมิประเทศ บ่งชี้ว่าห้วยแม่ตาวมีความสัมพันธ์โดยตรงกับพื้นที่แหล่งศักยภาพของแร่สังกะสี และเป็นพื้นที่ที่มีการสะสมตัวของแคดมียม และสังกะสีสูง โดยเฉพาะจากการพังทลายของหน้าดินตามธรรมชาติ รวมทั้งกิจกรรมการใช้ประโยชน์ทรัพยากรธรรมชาติของมนุษย์ ก็เป็นผลให้พื้นที่นี้มีความเสี่ยงสูงในการปนเปื้อนของแคดเมียมในผลิตผลทางการเกษตร นอกจากนี้กิจกรรมการทำเหมืองเป็นอีกสาเหตุหนึ่งในการเพิ่มปริมาณแคดเมียมและสังกะสีในพื้นที่ดังกล่าว ดังนั้นเพื่อการวางแผนป้องกันการปนเปื้อนและการบำบัดพื้นที่ปนเปื้อนในอนาคตให้ถูกต้องรัดกุม จำเป็นอย่างยิ่งที่จะต้องพิจารณาถึงสาเหตุการปนเปื้อนให้ครบถ้วน และนำไปสู่การจัดการด้านทรัพยากรแร่ และสิ่งแวดล้อมอย่างยั่งยืน

สาขาวิชา...การจัดการสิ่งแวดล้อม (สหสาขาวิชา).. ลายมือชื่อนิสิต.....ภาราดา มณีวงศ์.....

ปีการศึกษา.....2548..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4789495520: MAJOR ENVIRONMEMTAL MAMAGEMENT
KEY WORD: CADMIUM / CONTAMINATED SEDIMENT /
SEQUENTIAL EXTRACTION OF CADMIUM / BCR THREE-STEP

PARADA MANEEWONG: CADMIUM DISTRIBUTION IN STREAM SEDIMENT AND SUSPENDED SOLIDS ALONG HUAI MAE TAO AND HAUI MAE KU, MAE SOT DISTRICT, TAK PROVINCE. THESIS ADVISOR: ASSISTANT PROFESSOR CHAKKAPAN SUTTHIRAT, Ph.D., THESIS CO-AVISOR: CHANTRA TONGCUMPOU, Ph.D. 87.PP ISBN 974-14-2920-7

This research was focused on distribution of cadmium in stream sediment and suspended solids from Huai Mae Tao and Huai Mae Ku creeks in Mae Sot District, Tak Province. The surrounding areas have been found cadmium contamination in paddy field and rice grain, besides cadmium was also detected in blood of local villagers. Moreover, the local economic is also threaten because rice cultivation has been prohibited by the government policy; consequently, compensation of hundreds million baht per year has to be paid to the farmers.

Twenty eight stream sediment and eleven suspended solids samples with surrounding water samples were collected from Huai Mae Tao, Huai Mae Ku and Huai Nong Khieo (control site), before all samples were analyzed using ICP-OES for total cadmium and zinc concentrations. In addition, significant fractions of cadmium and zinc in stream sediment samples were determined using BCR Three-step; these fraction would give better idea to indicate potential cadmium impacting directly to the environment and human health. Analytical results show that soluble cadmium contents in all water samples are lower than the detection limit. Huai Mae Tao creek which is directly influenced by mining activities obtained the highest total cadmium and zinc concentrations in both stream sediment and suspended solids while Huai Nong Khieo creek yielded the lowest concentrations. Regarding sequential analyses, cadmiums in stream sediments from Huai Mae Tao contain mostly extractable forms (BRC1 and BRC2) which are very easily transferred into living organism; on the other hand, those from Huai Mae Ku are significantly characterized by BCR2 and final residual and those from Huai Nong Khieo are mainly in final residual form. It seems likely that sediments from Huai Mae Tao have more potential to effect the environment.

In conclusion, Huai Mae Tao creek, closely related to zinc deposit, consequently contains high levels of total cadmium and zinc by natural processes (e.g. erosion and weathering) that are actually risky to agriculture, besides human activities may activate cadmium accumulation in the area. Apart form mining activity, agricultural processes would be taken into consideration for further discussion and subsequently protection and remediation plans. Eventually, it would lead to sustainable management of mineral resource and environment.

Field of Study: Environmental Management Student's signature.....

Academic year 2005 Advisor's signature.....

Co-advisor's signature.....

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CONTENTS

PAGE

LIST OF TABLES

PAGE

LIST OF FIGURES

PAGE

PAGE

CHAPTER I
INTRODUCTION

1.1 General Statement

Zinc is an essential raw material used in many industries, especially construction, motor, toy industry, etc. In the current situation, consumption of zinc has been highly increased since the world economic status is rising up. Thailand has to import zinc mineral with high value for industries of the country. Table1.1 shows that approximate 1,500 million baths have been spent annually. In Thailand, the largest zinc deposit is located at Mae Sot District, Tak Province, which has been operated for longer than 20 years. Zinc mines in this area have been producing average 160,000 tons of zinc supplying to the industries since 1982 (Department of Primary Industry and Mines, 2006). Zinc deposits have been discovered along the eastern part where is occupied by high mountainous terrain. On the other hand, the western Mae Sot area is widely used for agriculture; these lowland areas are mostly categorized as river terraces and alluvial plains, in which several drainage systems are recognized.

Therefore, the main career of Mae Sot's population is agriculture. The cultivation in this area can be divided into 2 types following the geographic features. Firstly, highland is generally used for growing corn, beans, soybeans, garlic and some lettuces; moreover, this area is partly occupied by paddy field where has been cultivated for only one time a year during the rainy season. Secondly, lowland is mostly occupied by paddy fields which have produced very famous jasmine rice supplied to the market; besides, they were rewarded as top quality jasmine rice by the Ministry of Agriculture in years1997. Rice growing is normally started in May when is the beginning of rainy season. Water supply to the lowland paddy field has been irrigated from the natural streams in which some of them appear to be passing through zinc mine and zinc potential areas. Consequently, rice produced around the area has higher risk to heavy metal contamination.

Table 1.1 Statistics of zinc import, consumption and production in Thailand during years 1998-2003 (from Department of Primary Industries and Mines, 2004).

Import			Consumption				Production	
Year	Zinc Ore		Zinc Alloy		Zinc Metal		Zinc Ore	
	Quantity (Tones)	Value (Million Bath)	Quantity (Tones)	Value (Million Bath)	Quantity (Tones)	Value (Million Bath)	Quantity (Tones)	Value (Million Bath)
2003	151,623	1,636.90	29,118	1,416.1	62,754	2,424.8	148,297	964.9
2002	153,129	1,234.30	22,502	1,091.3	62,535	2,395.7	151,876	946.5
2001	210,345	2,106.9	20,655	1,051.1	51,990	2,341.0	159,093	1,392.5
2000	173,930	2,029.7	15,425	936.9	58,541	2,913.4	159,093	1,392.5
1999	143,269	1,495.1	12,261	660.9	51,249	2,267.6	185,752	1,475.0
1998	135,863	1,603.1	7,735	447.3	32,864	1,588.9	195,122	1,508.0

In the nature, about 3-5% of cadmium can substitute in crystal structure of zinc minerals (e.g. sphalerite, ZnS; hemimorphite, $Zn_4(Si_2O_7)(OH)_2 2H_2O$; smithsonite, $ZnCO_3$) which their forms are very stable. In addition, cadmium usually has low solubility under neutral condition. Hence, there is normally low risk of cadmium contamination in the usual environment.

Recently, Thailand has faced to cadmium contamination in agricultural system at Mae Sot District, in which it has caught attention of many organizations. The cadmium contamination state is quite critical. This is because cadmium is not only found in lowland soil surrounding the zinc mines but it is also detected in water and agriculture products (i.e. garlic, rice and soy bean). There is about 0.5-218 mg/kg cadmium in soil, which exceeds the standard by 72 times (EEC: The Economic Community about 3 mg/kg); 1.3-6.3 mg/kg cadmium in garlic; and 0.34-3.37 mg/kg

cadmium in soy beans, which exceeds the standard by 1.7-16.8 times (CCFAC: Codex Committee on Food Additives and Contaminants < 0.2mg/kg). Rice from Pha Dae and Mae Toa villages contains average cadmium concentration of 1.33 mg/kg. 80% or 944 tons of rice contain about 0.3-2 mg cadmium per one kg rice, which is moderate level of cadmium contamination and it is not safe for human health. 11% or 130 tons of rice containing 0.3-2 mg of cadmium per kg of rice have to be destroyed (Simmons et al., 2003). Therefore, the agriculture areas are encountering to the cadmium contamination, including Pha Dae and Mae Toa Mai Villages in Phra Tat Padaeng Sub-District, Mae Sot District, Tak Province. They have been subsequently prohibited for cultivation of rice by the Royal Thai Government since 2004. In addition, the Ministry of Natural Resources and Environment bought 130 tons of cadmium-contaminated rice from Mae Sot District, Tak Province and then destroyed them all. Consequently, the Royal Thai Government had to compensate about 100 million baht/year to the local agriculturists. In addition, the Mining Company, Padaeng Industry Plc. and Tak Mining Co. agreed to support 1.1 million baht for the compensation in 2004, even there is no conclusive evidence to indicate that their mining activities are main source of cadmium contamination.

Moreover, 20% of the population in Mae Sot have accumulated cadmium in their blood and urine exceeding the normal level (up to 6-10 µg/g creatinine for moderate high level and >10 µg/g creatinine for high level). The WHO standard of cadmium in blood and urine are 5µg/l and 2µg/l, respectively. In addition, these people may reveal indication of irreversible renal dysfunction and urinary calculus since they have consumed cadmium contaminated rice and water for long period of time (Department of Disease Control, 2004).

As mentioned above, the agriculture system in Mae Sot appears to have been oppressed by cadmium contamination. Therefore, identifications of the exact source of the contamination, nature of cadmium, and level of cadmium in soil are very crucial for protection and remediation plans in the future. These data will in turn reduce the present threat and further unexpected impact. This research was planed to investigate trace metals, particularly Cd and Zn, in stream sediment and suspended solids in Huai Mae Tao, Huai Mae Ku and Huai Nong Khieo; moreover, crucial

fractions, directly impacting the environment, will be determined from the stream sediment. Subsequently, all the data are used to indicate the significant cause of cadmium contamination.

1.2 Objectives

The main purpose of this study is to find out the main cause of cadmium contamination in Mae Sot area. Although, cadmium contents in paddy field and crop have been analyzed by some workers, cadmium distributions within stream sediment and suspended solids have not been taken into account. To clarify the specific source of cadmium contamination in this area, two main specific objectives of this study are therefore defined as below.

1. To investigate cadmium distributions of stream sediment and suspended solids along Huai Mae Tao and Huai Mae Ku.

2. To estimate crucial faction of cadmium in stream sediment that might impact the environment in the study area.

1.3 Hypothesis

Cadmium contamination in the study area would be involved partially by zinc mining activity.

1.4 Scope of Study

The study area is located in Mae Sot District which is adjacent to zinc mines and also part of a famous agriculture area, paddy field in particular. There are two main streams, running through the zinc potential areas, namely Huai Mae Toa and Huai Mae Ku. Huai Mae Toa initiates from Doi Phadaeng where zinc mineral deposits and mines situate, whereas Huai Mae Ku is in nearby catchment in which may have been partly influenced by the mining activity. This study is focused on

sediments in both creeks. There are two types of sediment samples, i.e. stream sediment and suspended solids. The suspended solids samples are assumed as representative of the most recent sediment supplied into the study area and the stream sediment are somehow older in periods of weathering and transportation, which however would came from the same sources. Chemical characteristics of both sample types should lead to point out the exact source of the cadmium contamination. Moreover, cadmium bioavailable fractions in the stream sediment were also studied to identify the significant cadmium form, potentially harming the human health. The analytical results were compared with samples from creek (Huai Nong Khieo) where there is no mining around. In addition, analyses of soil from surrounding paddy field provided by other workers are also taken into interpretation. Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was engaged for quantitative analyses.

1.5 Research Plan and Organization of Thesis

The environmental problem of cadmium contamination in agriculture area in Mae Sot District have appeared to be the great concern of many organizations for a few years; however, the main sources of the contamination are still not exactly defined. This is because of natural complexity. This research is focused on the distribution of cadmium in stream sediment and suspended solids along Huai Mae Tao and Huai Mae Ku in Mae Sot District, Tak Province. That would be part of information to indicate real source of the problem. Generally, regional drainage patterns have originated in the eastern mountainous area and it is running westwards to lowland and flood plain before assembling into Mae Mieo River. Huai Mae Tao and Huai Mae Ku creeks have similar water irrigation that have originated from Doi Phadaeng hill, the most significant zinc deposit of the country, and adjacency before flowing westwards to the main water supply for cultivation. Therefore, contamination of cadmium in paddy field can be probably caused by geologic setting, mining activity, or cultivation. All of the facts would be taken into account without bias; subsequently, results from many studies including this research are analyzed together.

This research was planed to start from literature reviews which involve current situation, nature of cadmium and zinc, general information of Mae Sot District including geology, geography, etc. All of the information gives a rough idea to design the research procedure. Field investigation is very necessary work that has to be carried out before the other steps, because it should lead to understanding real situation and feature of the area. Consequently, sample locations were designed on the basis of those information. Three types of samples were collected for this study. They are stream sediment, suspended solids and water. The next important step of this research is chemical analyses that actually have many digestion procedures for analyses depending on specific purpose. EPA standard methods were selected to digest all sample types for total concentration of elements under this environmental interest. In addition, fraction concentrations in stream sediment were analyzed after digestion following the BCR three steps suggested by Tessier et al. (1979). Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was engaged for all quantitative analyses. Finally, all results are analyzed and discussed to reach objectives of the research. The research plan is described in Figure 1.1.

According to those steps of study and their results, this thesis report is arranged into 5 chapters. The first chapter, was already reported, reveals background, motivation and objective of this study; besides, rough idea of methodology is also briefed in this chapter. However, detailed information of background and methodology are described in chapters 2 and 3, respectively. Subsequently, results of each study step are reported in the chapter 4. Then all earned data from this study are integrated with other information to discuss in particular aspects as presented in chapter 4. Finally, conclusions and recommendation are carried out and stated in chapter 5.

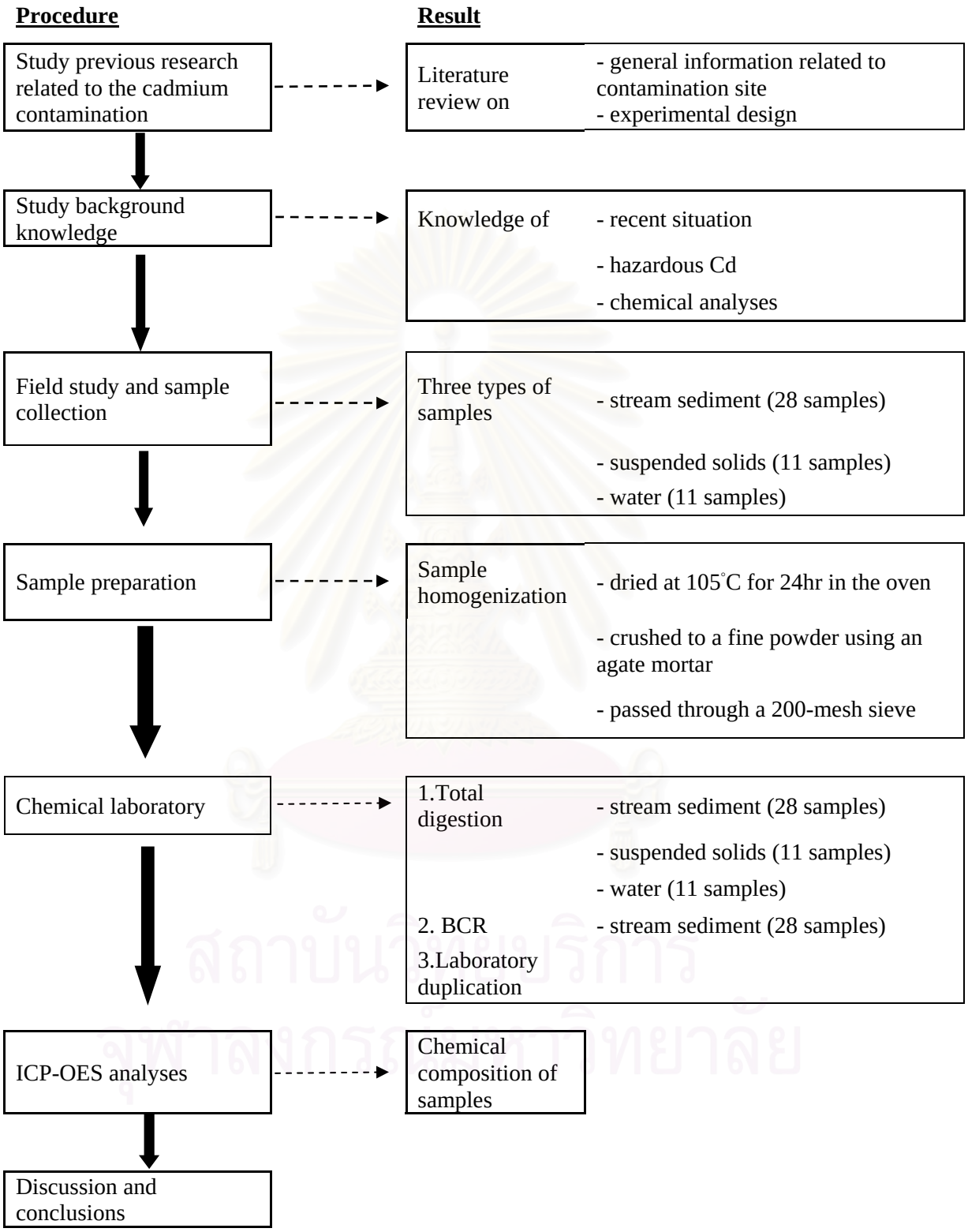

Figure 1.1 Schematic diagram showing the procedure and expected results of each step.

CHAPTER II
THEORETICAL BACKGROUND

2.1 Study Area

The study area is located in Mae Sot District which contains zinc potential area and zinc mines surrounded by agriculture area. Apart from zinc deposit, there are other mineral resources in Mea Sot District that are also economical high. Mineral resources of Mae Sot District are summarized in Figure 2.1. The study area is situated between latitudes 16° 37' and 16° 39'N and longitudes 98° 37' and 98° 40'E, it is approximately 11 km southeast of Mae Sot and about 500 km north of Bangkok. It appears on the topographic map scale 1: 50,000 series L 7017 sheet 4742III (Amphoe Mae Sot) at 1838000N to 1843000N and series L 7017 sheet 4742III (Amphoe Mae Sot) 457500E to 464000E as shown in Figure 2.2. The land use in this area and adjacency are for agriculture, because the main career of Mae Sot's population is farmers (Figure 2.3). The agriculture product, especially rice, was guaranteed the quality from Ministry of Agriculture. The area is occupied by mountainous terrain on the east and alluvial plain on the west. Climate is similar to the other parts of the country which is characterized by tropical savanna. Three seasons are recorded, including dry season from February to May, rainy season from middle of May to October and winter season from October to middle of February.

Based on landscape analyses using aerial photographs and field investigations, the study area can be divided into two distinctive features (Figures 2.4 and 2.5), they are high mountain terrain and alluvial plain. The high mountain terrain is on the eastern part of area where zinc deposits and mines are located; the highest elevation is about 690 meters above mean sea level at Pra That Padaeng. The western part of area is alluvial plain influenced by several creeks which are mostly running westwards to the floodplain of the Mae Meoi River. The drainage pattern identically present in the study area is dendritic pattern. The dendritic pattern is characterized by the orders of stream distributing as similar to veins of leaf. In addition, there are many canals and

spillways constructed for agriculture in the study area. However, agriculture areas are usually impacted by flood in the rainy season.

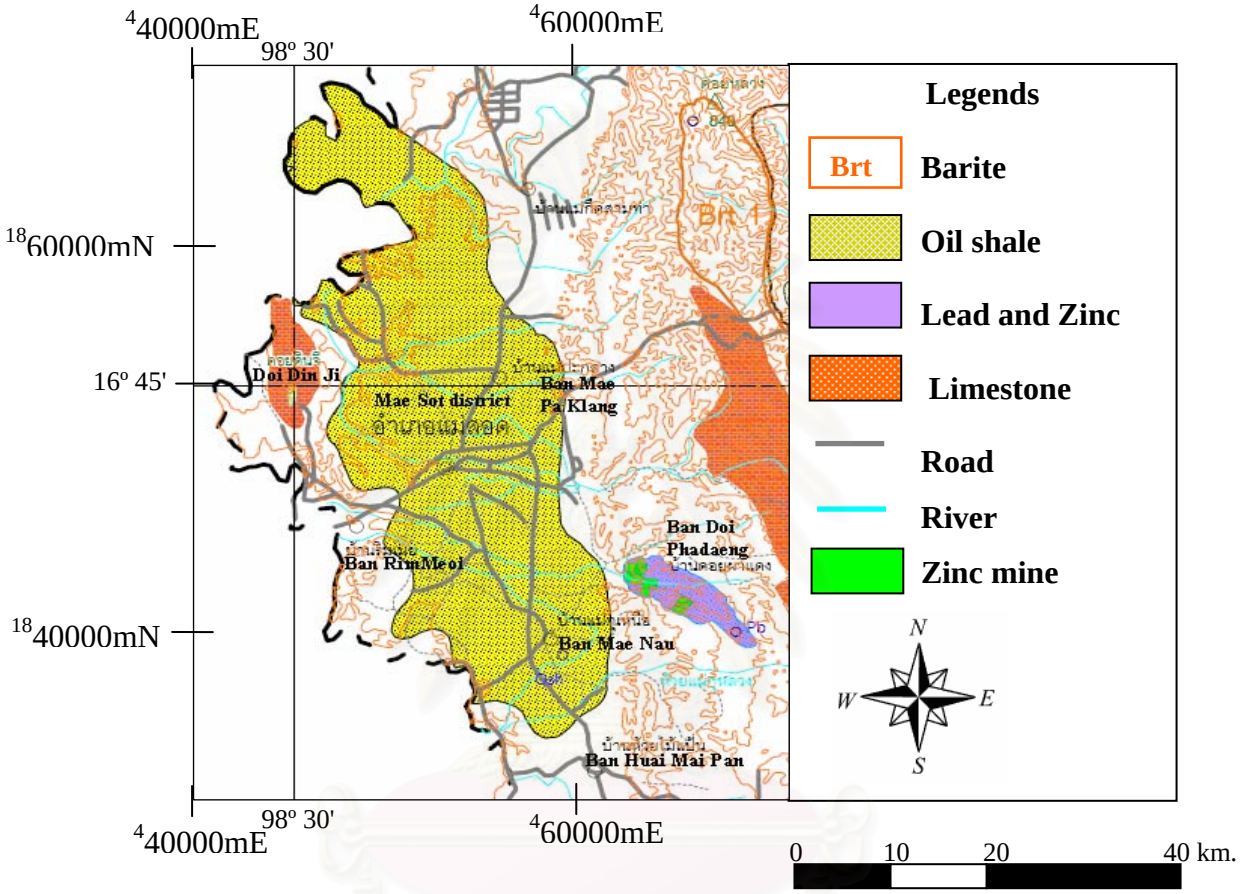

Figure 2.1 Map of mineral resources around Mae Sot District, (Department of Mineral Resources, 2001).

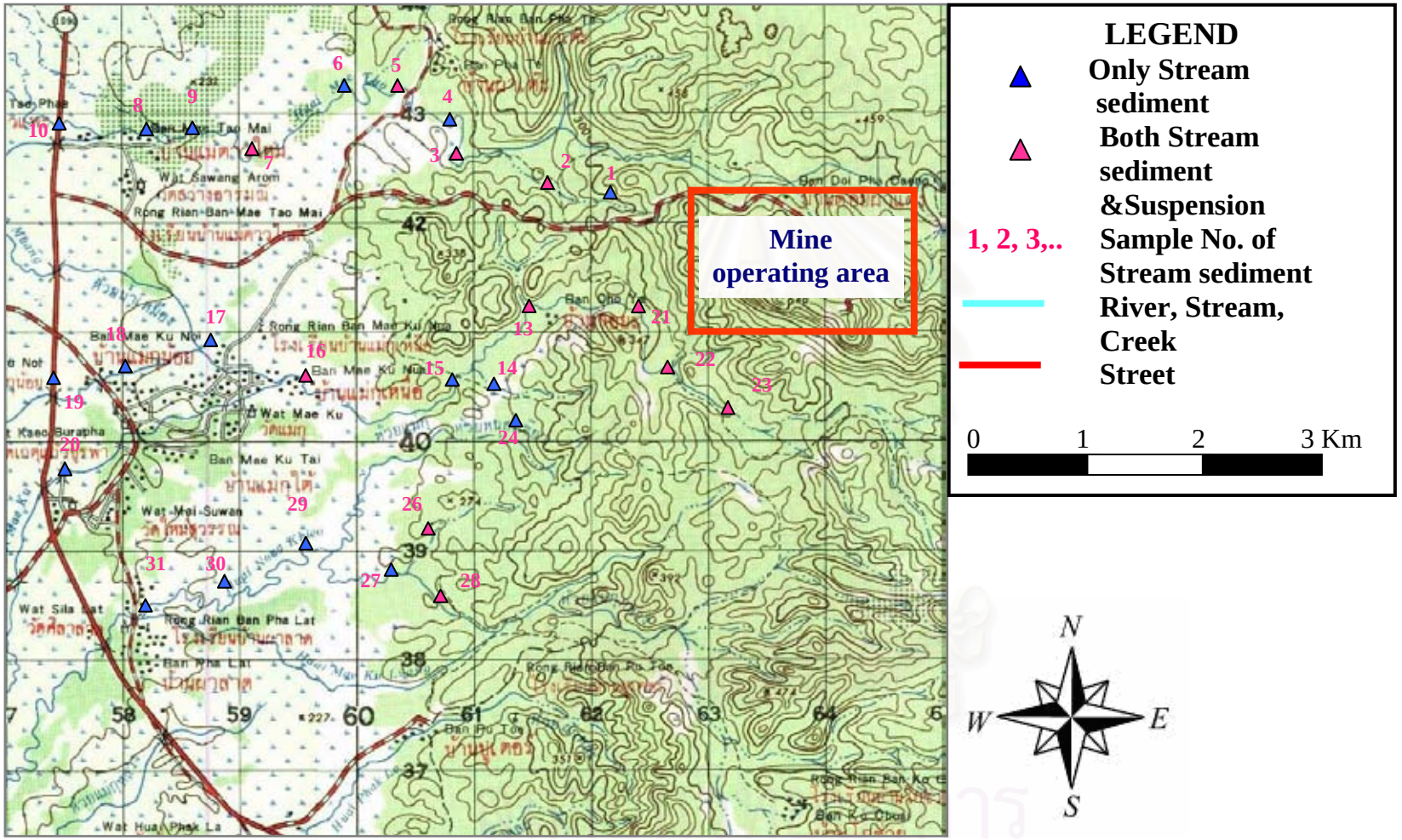

Figure 2.2 Topographic map (scale 1: 50,000 by Royal Thai Survey Department, 1984) revealing the locations of sample collection under this study and zinc mining area.

Figure 2.3 Landuse in Mea Sot District is predominately occupied by agriculture area, especially paddy field.

Figure 2.4 General landform in the east of study area is mainly mountainous terrain.

Figure 2.5 Some streams in the western lowland of Mae Sot District.

2.2 Geology and Mining

Padaeng Zinc Deposit is associated with the Huai Hin Fon Formation of Upper Triassic-Jurassic age (Figure 2.6). The Huai Hin Fon Formation includes limestone and fossiliferous limestone interbedded with calcareous shale, sandstone and lime-conglomerate. This rock unit lays approximately NNW trending with SSW dipping. The eastern part of the rock unit disconformably contacts with massive limestone, unfossiliferous grey dolomitic limestone, shale and sandstone of the Doi Phawar Formation of Permain age. The western part of the unit underlies the Mae Sot Formation of Tertiary age. The major structure is a NW-SE trending fault. The Padaeng deposit consists mainly of secondary zinc minerals namely smithesonite ($ZnCO_3$) hemimorphite ($Zn_4Si_2O_7$ $(OH)_2$* H_2O) with small amount of hydrozincite ($2ZnCO_3$*$Zn(OH)_2$) and loseyite $(Mn, Zn)_7(OH)_{10}(CO_3)_2$) (Naraballobh et al., 1992).

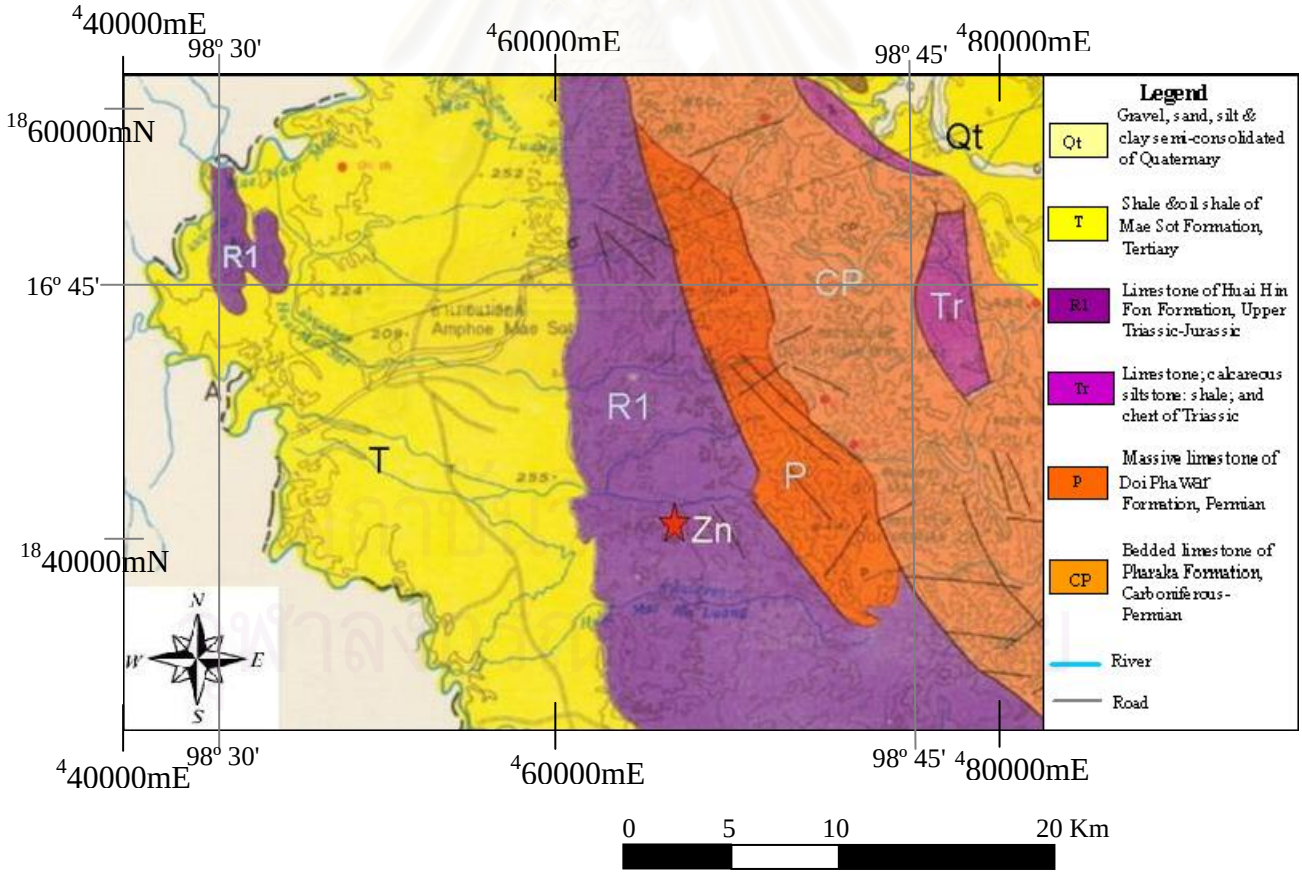

Figure 2.6 Regional geology of the study area showing rock units and structure as well as zinc deposit (Zn) (Department of Mineral Resources, 1976).

The open cut mining has been operated for ore recovery in Padeang deposit. High grade ores are directly transported to the smelting plant, while low grade ores are concentrated using chemical floatation. Waste rocks and overburdens have been dumped in several places within the conceded mining area. Rock fragments, sediments and soils in the mine area, when impacted by rain and transported by runoff in form of sheet flow, are controllably running into cannels before flowing to a number of settling ponds. All sediments are left to settle in the ponds before water is pumped to use in the mining activities and some of them may be drained into the Huai Mae Toa creek (Figure 2.7).

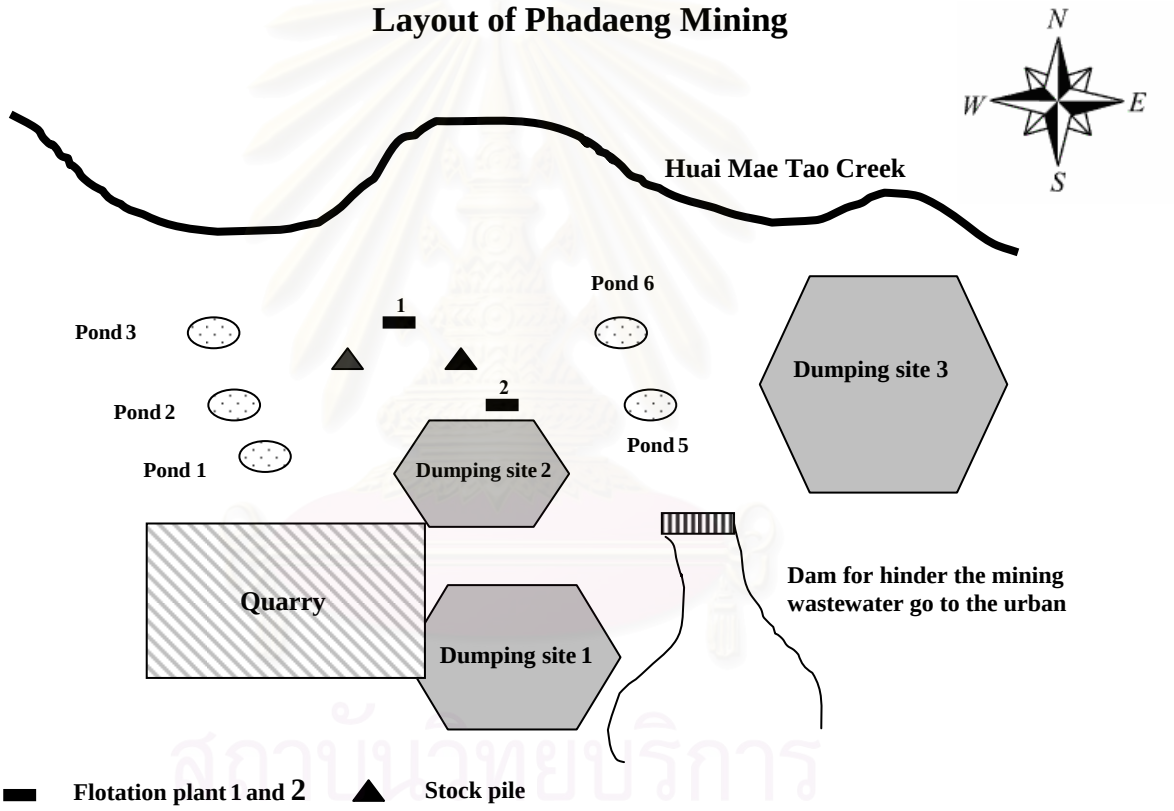

Figure 2.7 Layout of Phadaeng zinc mining showing a number of settling ponds to protect flooded sediment transporting directly into Huai Mae Tao Creek.

2.3 Cadmium (Cd) and Environmental Impacts

There are many cases of environmental impact from the mining activity, demonstrating that the miners did not take the environmental issue into consideration. This problem not only has an effect on ecology but also impacts human health by various exposure pathways. Heavy metals from an open-cast mine of the ore mining and processing enterprises may be scattered by the prevailing winds throughout the environment within a radius of 8-12 km, and transferred via irrigation waters to agriculture arable land for several kilometers away (Kalandadze, 2003). In Thailand, the contamination of cadmium and zinc in paddy soils and elevated levels of cadmium in rice grain along downstream fields of zinc occurrences are related to suspended solids that are transported to the field via irrigation supply (Simmons et al., 2005).

Cadmium can be discovered as an impurity element in zinc, lead and cupper minerals including carbonate and sulfide mineral groups (see Table 2.1). In the nature, cadmium is a soft bluish-white metal which is easily cut with a knife and similar in many respects to zinc. Cadmium most often occurs in small quantities associated with zinc copper and lead ores, such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and galena (PbS). Greenockite (CdS) is the only mineral of any consequence bearing cadmium. Therefore, cadmiums are mainly obtained as a by-product in treatment processes of zinc, copper, and lead ores. Among sedimentary rock types, carbonaceous shales, formed under the reducing conditions, usually contain high cadmium contents. The major uses of cadmium are component in rechargeable nickel-cadmium batteries, pigments, stabilizers in plastics, and protective plating for metals.

Table 2.1 General concentrations of cadmium presented as impurity in some minerals and a cadmium mineral called *greenockite* (Mineral Data Publishing, 2001-2005).

Mineral	Concentration of Cd
Greenockite (CdS)	77.8%
Sphalerite (ZnS)	0.0001-2%
Smithsonite ($ZnCO_3$)	0.1-2.35%;
Chalcopyrite ($CuFeS_2$)	< 0.4-110 ppm
Galena (PbS)	< 10-3000 ppm;

Normally, 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 by weathering of rock and some cadmium is released into air through forest fires and volcanoes. Moreover, metal industry, mining of zinc and lead ores, and manufacturing of phosphorus fertilizers have been the dominant sources of industrial cadmium emissions to the environment. The application of fertilizers contaminating cadmium has also led to the deposition of significant amounts of cadmium on agricultural land (Oliver et al., 1994).

Cadmium is strongly adsorbed to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, because cadmium uptaking to foodchain will be increased. Acidified soil enhances effectively cadmium uptake of plant. This is a potential danger to animals and humans that are dependent upon the plants for survival. Forms of cadmium in soil can be roughly grouped into 3 categories. Firstly, cadmium species in solution phase will be readily available to be absorbed by a living organization. While cadmium compounds in the second form, adsorbed phase, are considered to be potentially bioavailable, when environmental condition is encouraging. The third form, fixed/retained phase, includes mineral phase such as carbonate, sulfide, and oxide, organic bound phase and crystalline phase. It is likely to be unavailable to plants and animals. However, long process of development through time on the physical and chemical properties of mineral phase may possibly evolve its properties to the second and ultimately the first forms.

Cadmium can accumulate in animal and human bodies, especially when they eat multiple plants. This can result in them suffering from high blood-pressure, liver disease, and nerve or brain damage. In addition, it can induce the irreversible renal dysfunction (Nogawa and Kido, 1993). The long-term consumption of cadmium contamination in food has resulted in chronic and acute human Cd disease as manifested by the Itai-Itai disease, a form of osteomalacia and proximal tubular renal dysfunction, respectively. In addition, human health problems are exacerbated by the fact that the Fe, Zn and Ca contents in rice grain are insufficient for human need (Pedersen and Eggum, 1983; Shimada et al., 1977; Tohyama et al., 1982; Nogawa et al., 1983; Kido et al., 1988).

Humans today are exposed to cadmium, close to the level that affects kidney function. In order to take effective measures to decrease cadmium levels in the environment and food stuffs, knowledge of the sources and levels of cadmium in the agricultural environment is necessary. The FAO/WHO Joint Expert Committee on Food Additives and Contaminants (JECFA) has established a provisional tolerable weekly intake of cadmium (PTWI); the PTWI is set at 7 μg/kg body weight.

2.4 Zinc (Zn) and Environmental Impacts

Zinc is a lustrous bluish-white metal. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. It is used principally for galvanizing iron, more than 50% of metallic zinc goes into galvanizing steel, but is also important in the preparation of certain alloys (Table 2.2). It is used for negative plates in some electric batteries and for roofing and gutters in building construction. Zinc is a very common substance that occurs naturally. Many foodstuffs contain naturally certain little concentrations of zinc.

Zinc is the 23rd most abundant element in the Earth's crust. The dominant ore is zinc blende, also known as sphalerite. Other important zinc ores are wurzite, smithsonite and hemimorphite. The main zinc mining areas of the world are Canada, Russia, Australia, USA and Peru'. World production exceeds 7 million tones a year and commercially exploitable reserves exceed 100 million tones. More than 30% of the world's need for zinc is met by recycling.

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. Some soils are heavily contaminated with zinc, and these are found in areas where zinc has been mined or refined, or sewage sludge from industrial areas has been used as fertilizer.

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. 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.

Table 2.2 Varieties of zinc and their applications for industry.

Type of Zinc	**Applications**
Primary metal (Zn)	Die casting in automobile industry
Zinc oxide	White pigment in watercolors or paints, and activator in rubber industry
Pigment zinc	In plastics, cosmetics, photocopier paper, wallpaper, printing inks etc.

The cadmium concentration and Cd:Zn ratio of the cadmium source is key factors fro environmental impact. The lower cadmium concentration and lower Cd: Zn ratio likely increase bioavailable; consequently, Cd will accumulate in crops. Zinc and cadmium are affected similarly by soil proportion in many ways, and cadmium inhibits zinc uptaking by root and transport to shoots. For some crops, cadmium inhibits zinc transportation to grain or other storage tissue. For example, lettuce tries to take up zinc in a high Cd:Zn environment, but the plant accumulates more cadmium and became zinc deficient because zinc activity is so low in the calcareous soil. Actual Zn deficiency has been repeatedly observed to cause higher Cd accumulation in plants (Oliver et al., 1994). The bioavailable Cd in each plant is uneven. The rice grain accumulates cadmium higher than zinc and iron comparative to those in rice stem and leaf, thus resulting in high Cd:Zn and Cd:Fe ratios in the rice grain, which significantly increases the risk to human health (Chaney et al., 1996; Simmons et al., 2003). Therefore, land with Cd + Zn contamination is not suitable for paddy-rice or tobacco production (Chaney and Ryan, 1994).

2.5 Metal Fractions and BCR Extraction

In the environmental field, determination of total metal concentrations in sediment dosage does not give sufficient information about the mobility of metals. Metals may be bound to particulate matter by several mechanisms such as particle surfaces absorption, ion exchange, co-precipitation and complexation with organic substances. Not all of heavy metals in soil are available for plant uptaking, only the dissolved metals content in soil solution is moveable enough for plant to absorb. Therefore, heavy metals speciation in form of water soluble fraction and free weak acid soluble fraction out of total heavy metal content in soil as illustrated in Figure 2.7 are the maximum amount of heavy metals possibly uptaken by plant. However, actual bioavailability of heavy metals by each species of plant must be determined from the plant itself. Although cadmium soil always generates cadmium crops as previous research has shown, it may be not true since the cadmium form is not bioavailability. Chemical extraction is played an important role to define metal fractions, which can be related to chemical species, as well as to potentially mobile, bioavailable, or ecotoxic phase of sample. The mobile fraction is defined as the sum of amount dissolved in the liquid phase and an amount which can be transferred into the liquid phase. It has generally accepted that ecological effects of metals are related to such mobile fractions rather than the total concentration.

There are many methods for determining the different forms of metals. The BCR three-step sequential extraction procedure is one of them, which was proposed by the Standards, Measurements and Test Programme (SM&T-formerly Community Bureau of Reference, BCR) of the European Union. It was applied for the determination of trace metals (e.g. Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) binging various forms in sediment. It is strongly recommended to quantify the fractions of metal characterized by the highest mobility and availability applied for sample which the total concentration is high enough. This procedure provides a measurement of extractable metals from a reagent such as acetic acid (0.11 mol/l), hydroxlyammonium chloride (0.1 mol/l) and hydrogen peroxide (8.8 mol/l), plus ammonium acetate (1 mol/l), which are exchangeable, reducible and oxidizable metals, respectively. There are many researchers have studied about this procedure

and results indicated that this procedure gave excellent recoveries for all six elements (e.g. Cu, Cr, Cd, Zn, Ni and Pb) (Coetaee et al., 1995). The concentration of metal extracted by the various reagents above gave a good reproducibility on species bonded to carbonates, to Fe/Mn-oxides, and the residual fraction (Accomasso et al, 1993). Characters of each fraction are simplified and shown in Figure 2.8 which some descriptions of these fractions are given below.

BCR I Exchangeable: This fraction shows the amount of each element that would be released into the environment if the conditions become more acidic. There are water-soluble, easily exchangeable (non-specifically adsorbed) and bond to carbonate which is susceptible to change of pH and sorption–desorption processes. Besides, the plants have an excellent uptake this fraction so the heavy metal is undoubtedly inserted into food chain. It is the most dangerous for the environment.

BCR II Reducible: This fraction theoretically represents the contents of each metal bond to iron and manganese oxides. These oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (Panda et al., 1995). However, the levels extracted in this stage would be influenced by the efficiency and selectivity of reagents used in the previous stages. Therefore, the results may be too high if the carbonates have not been completely dissolved or too low if parts of the iron and manganese hydroxides have already been extracted.

BCR III Oxidiziable: Trace metals may bond to various forms of organic matter. The complexation and peptrization properties of natural organic matter are well recognized, as the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals. The situation obtaining an oxidizing condition may occur during dredging.

Final residual: The final fraction should be calculated as the difference between the aqua-regia extractable metal contents and the sum of the metal contents released by the sequential extractions. Trace metals in the first three fractions are considered relatively more mobile and bioavailable than those in the residual fractions (Tack and

Verloo, 1995; Ma and Rao, 1997). In this fraction, metals with the strongest association to crystalline structures of the minerals and which are therefore the most difficult to separate from the sediments when they are extracted (Kersten and Forstner, 1991).

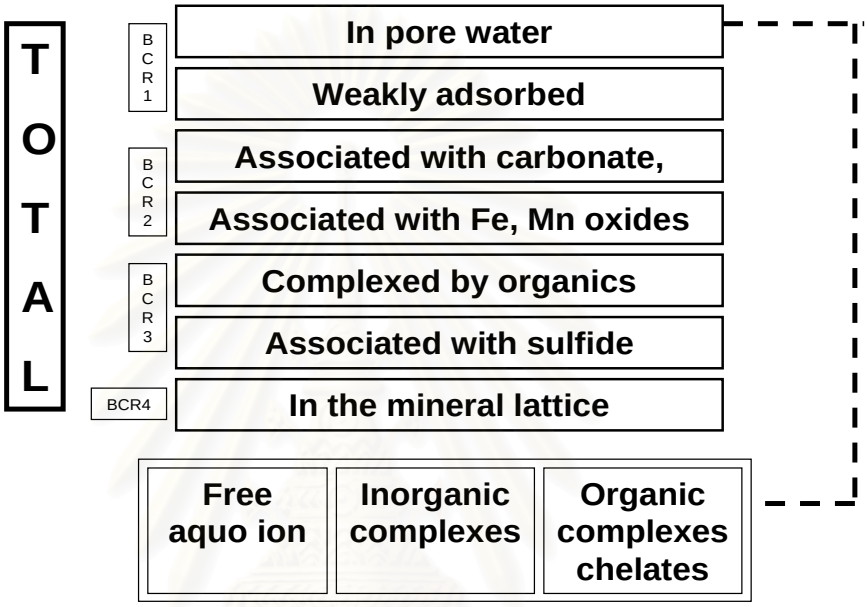

Figure 2.8 Chemical fractions of metals in sediments and their characters (NRC-EHWM, 2004).

CHAPTER III
METHODOLOGY

3.1 Introduction

This research is emphasized on cadmium distribution in sediments along streams in the study area. The samples collected for this research include stream sediment, suspended solids and water. Chemical analyses of all samples were carried out in form of total concentrations which were digested following the EPA standard method. In addition, fractional concentrations of stream sediment were collected using BCR three-step method. Analytical methods were mostly calibrated by Natural Matrix Certified Reference Material (standard soil), Catalog No. CRM025-050 (Lot No. JG025) and standard sediment (LGC6137). Moreover, field investigation, sample collection and sample preparation and chemical analysis are described below.

3.2 Field Investigation

This research is ongoing from the aspect of cadmium contamination in this area, which many organizations have studied on it. Then, there are also many publications giving general and local information such as geologic setting, landuse, and cadmium-zinc situation. Moreover, topographic map scale 1:50,000 (series L7017 sheet 4742III, Amphoe Mae Sot) was prepared for landform feature, accessibility and drainage analysis. Aerial photos, scale 1:15,000, were interpreted for drainage pattern and appropriate sample locations. Methodology and time schedule were then designed for the whole thesis research.

From data mentioned above, they show that the study area is located in Mae Moie River Basin, in which it consists of 7 subcatchments (Figure 3.1). The study area is located only in the area of Mae Toa and Mae Ku subcatchments. All drainage systems in this area present most likely dendritic pattern that is compatibly running from east mountainous area to west low land before merging into Mae Moie River.

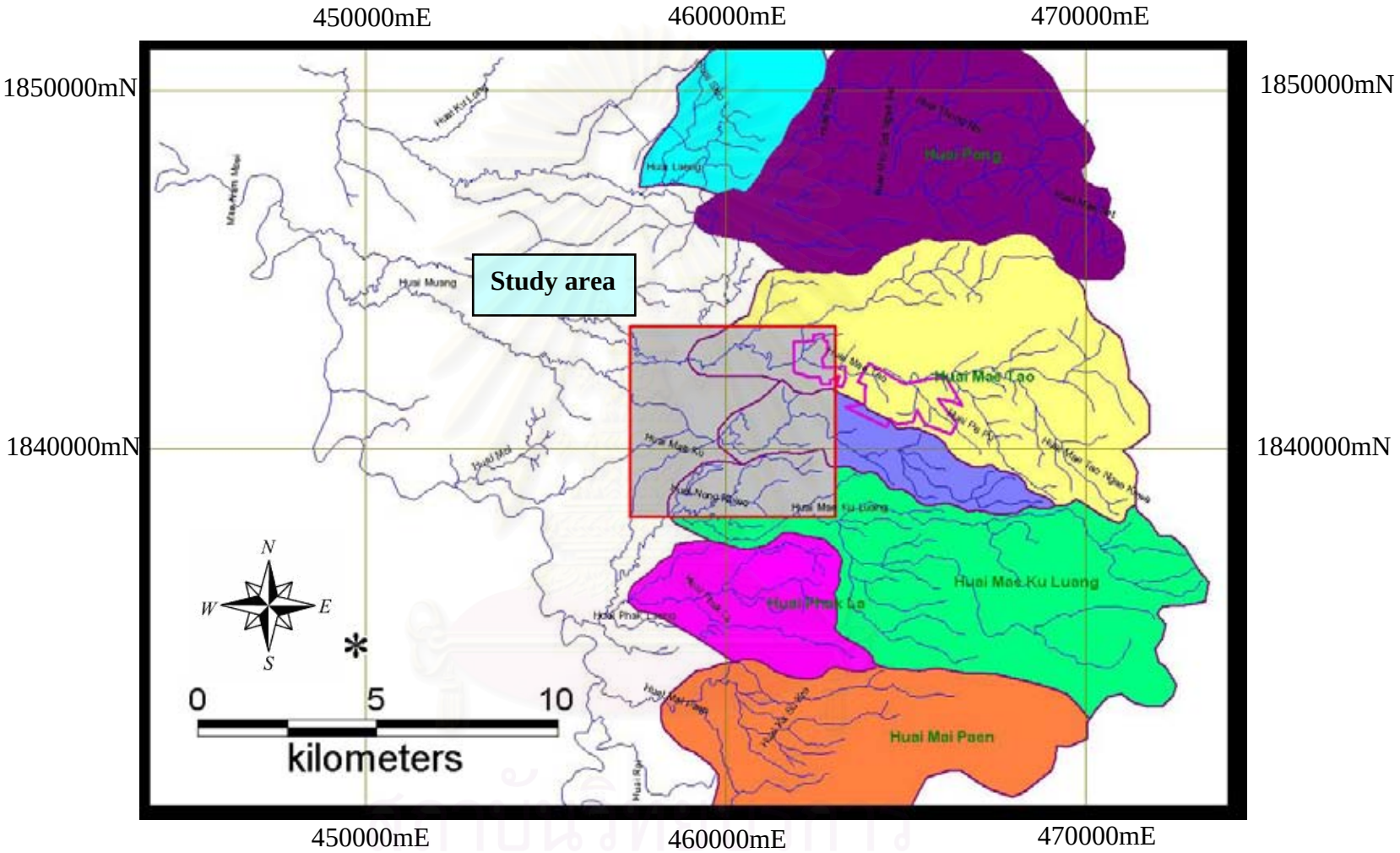

Figure 3.1 Map showing the Mae Mieo Basin consisting of 7 subcatchments while the study area is situated between Huai Mae Tao, Huai Mae Ku and Huai Mae Ku Luang.

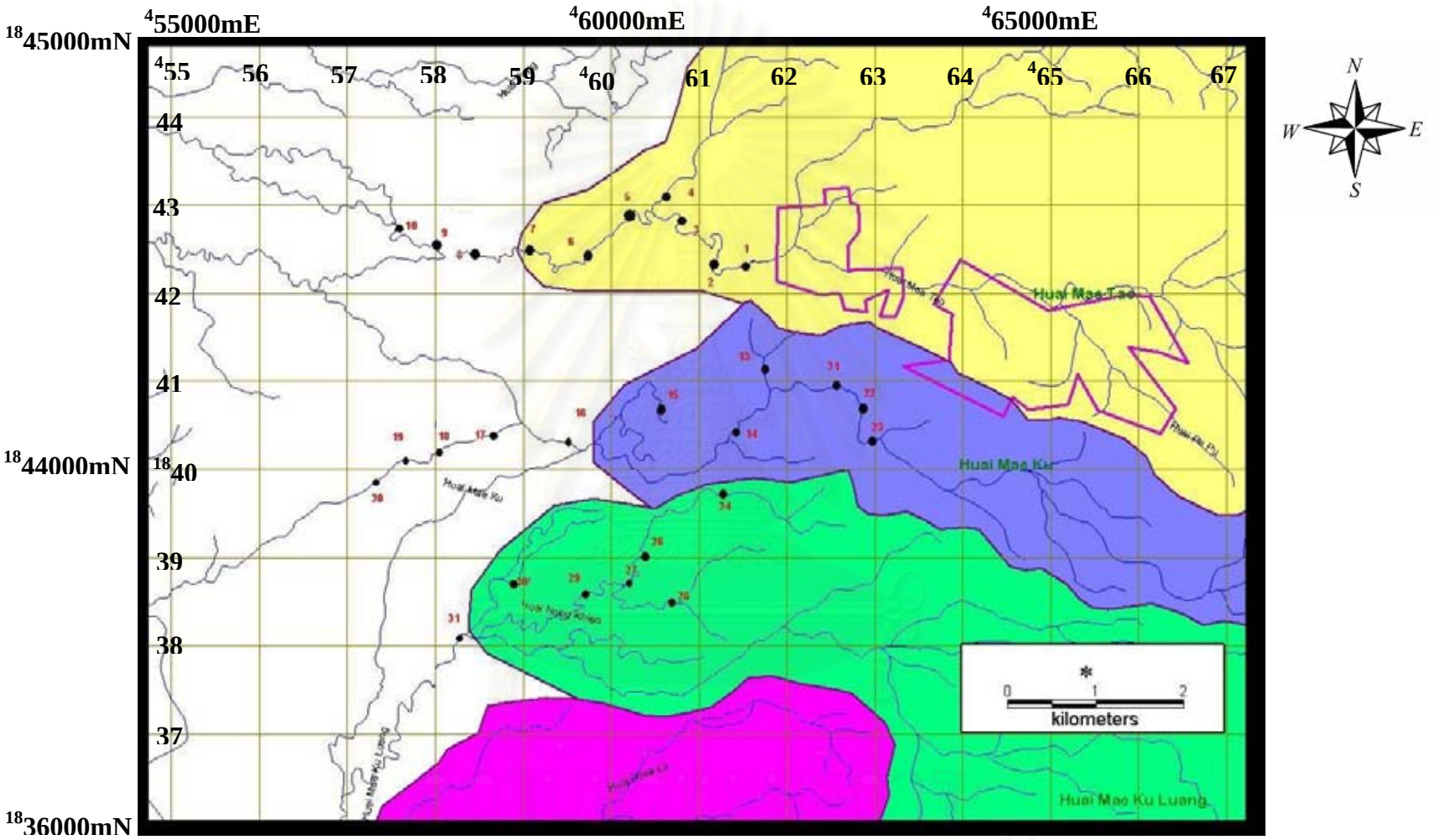

Figure 3.2 Map showing the locations of stream sediment samples

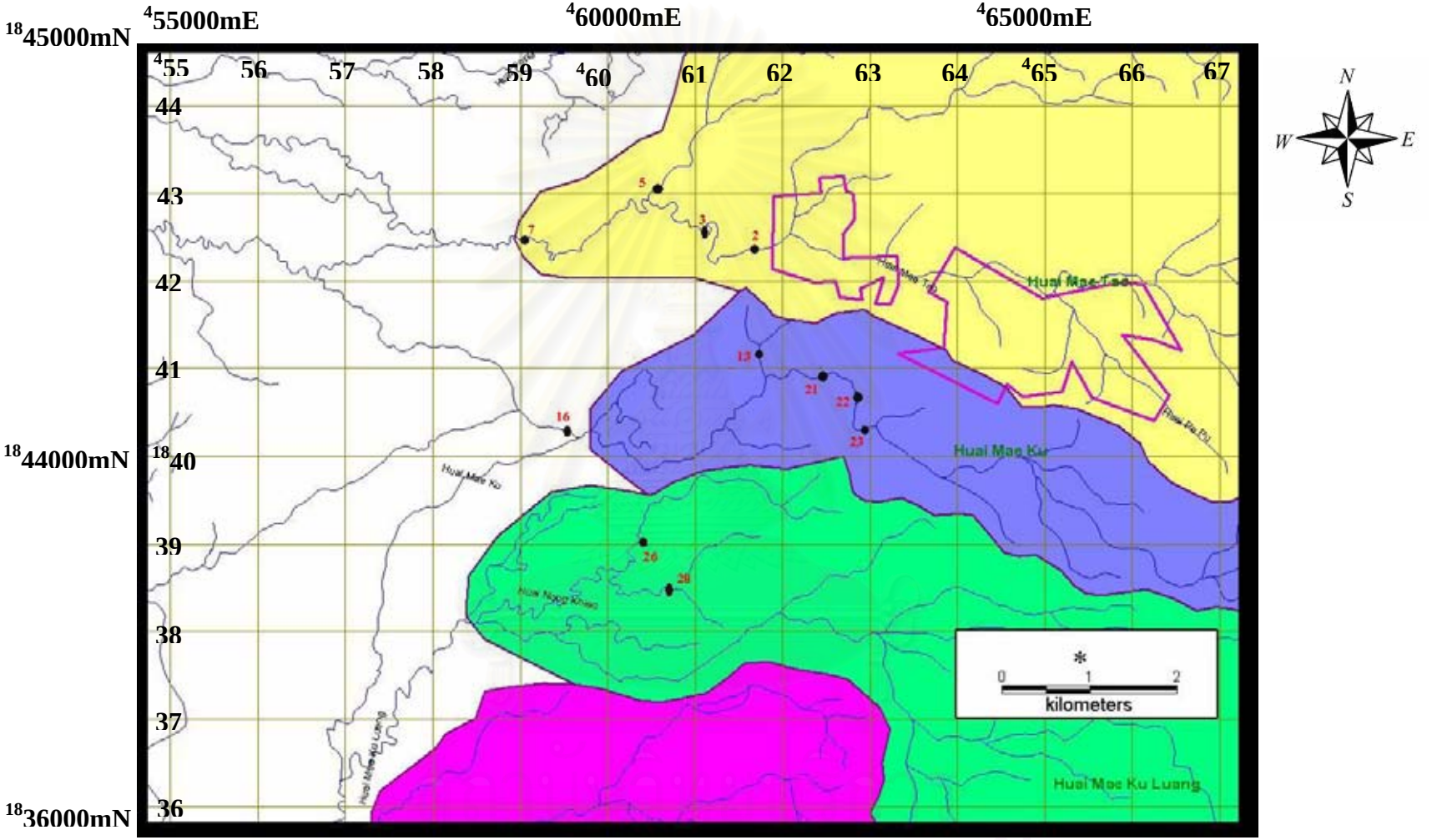

Figure 3.3 Map showing locations of suspended solids samples

Mae Toa subcatchment directly receives runoff from Doi Phadaeng (zinc deposit). All amounts of sediments are eroded from country rocks and soil cover of the hilly area including place of zinc mines. Subsequentlt, it discharges to hill slope, foothill and alluvial plain before the runoff moves westwards to supply the Mae Moie River. It should be noted that alluvial plain in this area is ordinarily used for growing rice and situating many villages; besides, abnormal levels of cadmium in rice grain, paddy soil and blood of villagers have been reposted from some particular area in the Mae Toa subcatchment.

Mae Ku subcatchment is situated along south boundary of zinc mine. In this area, a creek that has high risk to cadmium contamination is Huai Mae Ku because of it has originated along south hilly area of Doi Phadaeng. On the other hand, Huai Nong Khieo situates in the Mae Ku Luang subcatchment, in which its tributaries do not relate to Doi Phadaeng. Consequently, it was designed as very suitable control creek for the study.

Field investigation was taken place at the end of May, rainy season. Sample locations were planed on the basis of geographical feature, drainage pattern and mining location (Figure 3.2 and 3.3). Geographic references (UTM grid) of all samples were checked using Goble Positioning System (GPS) during the survey. Apart from sample collection, feature and general information of all sample sites in the study area are also observed. For example, cultivation in this area is prohibited by the Royal Thai Government, therefore it seems no agricultural activities in the area (Figure 3.4a), whereas cattle still appears in this area (Figure 3.4b).

a)

b)

Figure 3.4 Some geographical features in the study area; a) the agriculture was inactive because of the governmental prohibition; b) cattle (e.g. buffaloes) still existed in cultivation area.

3.3 Sample Collection

Three sample groups (i.e. stream sediment, suspended solid, and water) were collected for the investigation. All samples were taken along Huai Mae Toa creek, Huai Mae Ku creek and Huai Nong Khieo creek (for control samples). pH values were measured before collecting all of the sediment samples (Figures 3.5a and b).

Stream sediment: Sample spacing was set at about 1 km; however, it depends on topography, particularly stream bending and junction. Samples from the top layer (0-5 cm) of sediment set in stream were collected in polyethylene containers; then, all waters were drained out as much as possible after mixed water-sediment was sampled. This was suggested by Peter et al. (2001).

Suspended solids and water: Two liters of water had to be collected at tributaries, junctions and stream bends. Because sediment supply and stream velocity are changed; besides, sediments are deposited differently along these points. Consequently, samples were collected at the center of stream (Figure 3.5) to represent suspended solids and water supplying throughout the area.

a)

b)

Figure 3.5 Stream sediments and suspended solids were collected at the center of stream along tributary (a) and junction (b).

3.4 Sample Preparation

Stream sediment: Samples were taken to laboratory immediately after they were collected. Afterwards, the samples were dried at 105 ◦C in an electric oven; then the dried samples were crushed to fine powders using an agate mortar before passing through a 200-mesh sieve (see Figure 3.6). They subsequently were homogenized and stored in polyethylene bags until their analyses. Precautions had to be taken to avoid contamination during sampling, drying, grinding, sieving, and storage. The particles less than 200 mesh (< 74 μm) in the soil samples, which are representative of true sediment, were used for analysis as suggested by Tessier et al. (1979).

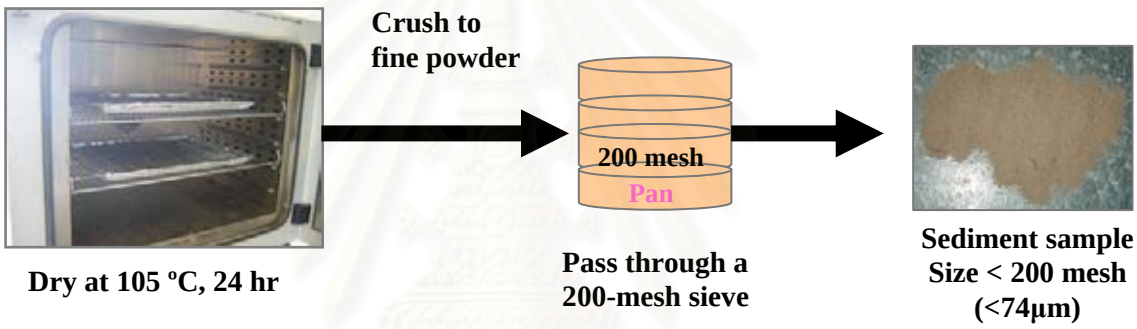

Figure 3.6 Sample preparation procedures for stream sediment.

Suspended solids and water: Two liters of water have to be filtered using a pre-weighed filter paper (GFC WATTMAN) combined with a vacuumed pump. The 125 ml of filtered water were collected in polyethylene bottle, fixed with concentrated nitric acid before stored within low temperature below 4 ^{o}C to minimize microbiological decomposition of solids. The residue retained on the filter was collected in a Petri dish and dried in an oven at 60^{o}C for 24 hrs (Figure 3.7).

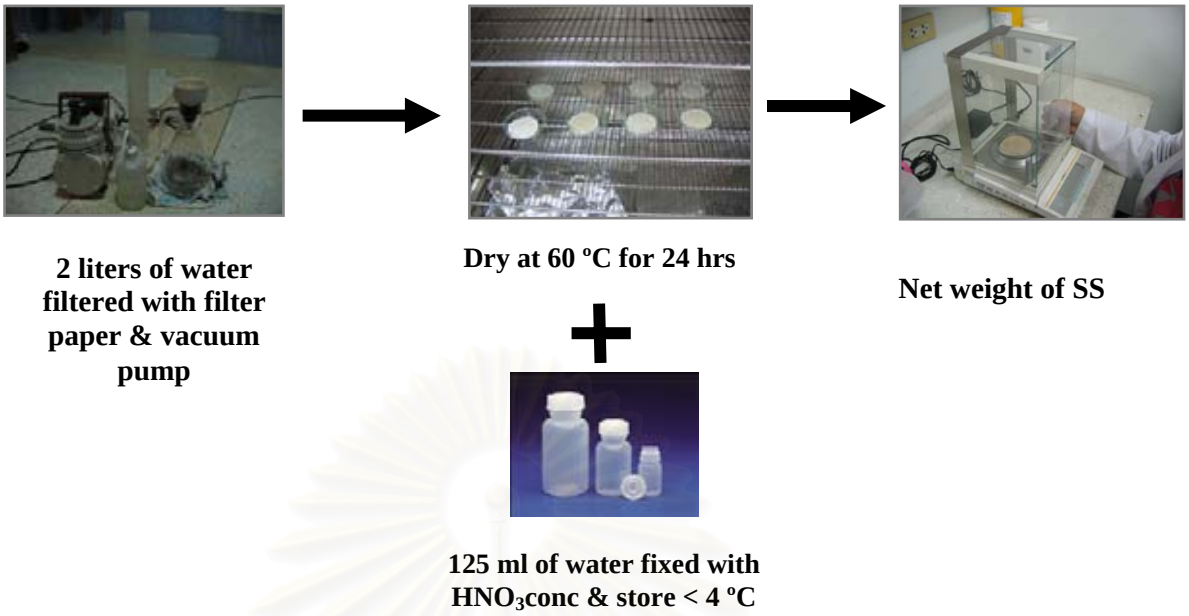

Figure 3.7 Sample preparation procedures for suspended solids and water.

3.5 Chemical Laboratory

3.5.1 Total Digestion

Microwave-assisted acid solubilization has been proved to be the most suitable method for the digestion of complex matrices such as sediments and soil. This method shortens the digestion time, reduces the risk of external contamination and uses smaller quantities of acid (Wang et al., 2004). However, there are different procedures required for appropriate sample types. Details of standard digestion techniques used for the samples under this study are stated below.

Stream sediment (EPA method 3051): After 0.5 g of soil was placed in a digestion vessel, 5 ml of 65% HNO_3 were added and the vessel was closed with a Teflon cover. Then, the sample was heated at 170±5ºC for approximately 5.5 minutes and remained at 170-180ºC for another 10 minutes to accelerate the leaching process by microwave digestion system. After cooling, the solution was filtered by membrane

filter of 0.45 μm pore diameter. Finally, the filtered solution was further diluted in 50 ml volumetric flask. The sample is now ready to be analyzed by ICP.

Suspended solids (EPA method 3050B): After the suspended solids was mixed 10 ml of 1:1 HNO_3, the sample was covered with a watch glass. Then, the sample was heated to 95±5 ºC and refluxed for 10 to 15 minutes without boiling. When the sample was allowed to cool, 5 ml of concentration HNO_3 was added and covered and refluxed for 30 minutes. If brown flumes were generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 ml of HNO_3conc.) over and over until no brown flame was given off by the sample indicating the complete reaction with HNO_3. The solution was evaporated to approximately 5 ml without boiling or heating at 95±5 ºC for 2 hrs. After the sample had been cooled, 2 ml of water and 30 ml of 30% H_2O_2 were added into the sample. In addition, 1 ml of 30% H_2O_2 was continuously added with warming until the generated sample appearance was unchanged. The sample had to be heated until the volume had been reduced to about 5 ml. Finally, the sample was diluted to 100 ml with D.I. water after cooling. Particulates in the digested should be removed by filter (Wattman No.41). The sample was ready for ICP analysis.

Water (EPA method 3015A): The sample solution had to be mixed thoroughly to achieve homogeneity. For each digestion procedure, 45 ml of water sample was sucked using pipette and put into a digestion vessel. After 50 ml of 65% HNO_3 was added; the vessel had to be closed with Teflon cover. Then, the sample was heated at 170±5 ºC for approximately 10 minutes and remained at 170±5 ºC for another 10 minutes to accelerate the leaching process by microwave digestion system. After cooling, the solution was filtered by membrane filter of 0.45 μm pore diameter. The filtered solution was further diluted in 100 ml volumetric flask. Then the sample was ready for ICP analysis.

3.5.2 BCR Three-Step Digestion

Stream sediment samples were prepared for fractional analyses. The reason is to identify cadmium and zinc in fractions that may harm the human health and

environment. Actually, the fractional analyses should be applied to suspended solids samples, but their amounts after filtration are very little. BCR three-step digestion was selected for this study. Reagents used and the BCR procedure are described below.

Acetic acid, 0.11 mol/l: After 25 ml of glacial acetic acid was added to about 0.5 l of distilled water in a 1 l volumetric flask, it had to be made up to 1 l with distilled water. Then, 250 ml of this solution was taken and diluted to 1 l with distilled water to obtain an acetic acid solution of 0.11 mol/l.

Hydroxylamine hydrochloride, 0.5 mol/l (Freshly): 34.75 g of hydroxylamine hydrochloride was dissolved in 400 ml distilled water. This solution had to be transferred to a 1 l volumetric flask and added, by means of a volumetric pipette, 25 ml of 2 mol/l HNO_3.

Hydrogen Peroxide, 8.8 mol/l: used the hydrogen peroxide as supplied by the manufacturer.

Ammonium acetate, 1.0 mol/l: 77.08 g of ammonium acetate had to be dissolved in 800 ml distilled water. Then, this solution was adjusted the pH to 2.0±0.1 with concentration HNO_3 and made up to 1 l with distilled water.

BCR procedure: **was described into three steps that are summarized in Figure 3.8 and detailed below.**

Step 1: After 40 ml of acetic acid (0.11 mol/l) was added to 1 g soil in a 50 ml centrifuge screw cap tube, the sample had to be extracted by shacking for 16 hrs at room temperature. Finally, the residue was washed by adding 20 ml distilled water in centrifuge screw cap tube, shacking for 10 minutes.

Step 2: 40 ml of freshly prepared hydroxylamine hydrochloride (0.5 mol/l) was added to the residue from step 1 and then shaking for 16 hrs at room temperature. The residue had to be washed by adding 20 ml distilled water in centrifuge screw cap tube, shacking for 10 minutes.

Step 3: 10 ml of hydrogen peroxide (8.8 mol/l) had to be added to residue carefully, in small aliquots to avoid losses due to violent reaction; then, the sample was shacked and transferred to 30 ml beaker. The sample was continuously digested at 80±2 °C by hot plate and then the volume was reduced to less than 3 ml. A further aliquot of 10 ml of hydrogen peroxide (8.8 mol/L) had to be added and heated the beaker aliquot to 85±2 °C and digest until the volume of liquid to about 1ml. Finally, 50 ml of ammonium acetate (1.0 mol/l) was added to the cool moist residue and shacked for 16hrs at room temperature.

Step 4: The residue was analyzed using Aqua Regia Procedure. After residue was mixed with 10 ml mixture of 1:3 concentration of nitric acid (3.3 ml) to concentration of hydrochloric acid (6.7 ml.), the sample was heated to 95±5°C without boiling. Then, the volume was reduced to less than 3 ml and it was allowed to cool. Finally, the sample was diluted to 50 ml with D.I. water. Particulates in the digested should be removed by filter (Wattman No.41). Then, the solution sample was ready for ICP analysis.

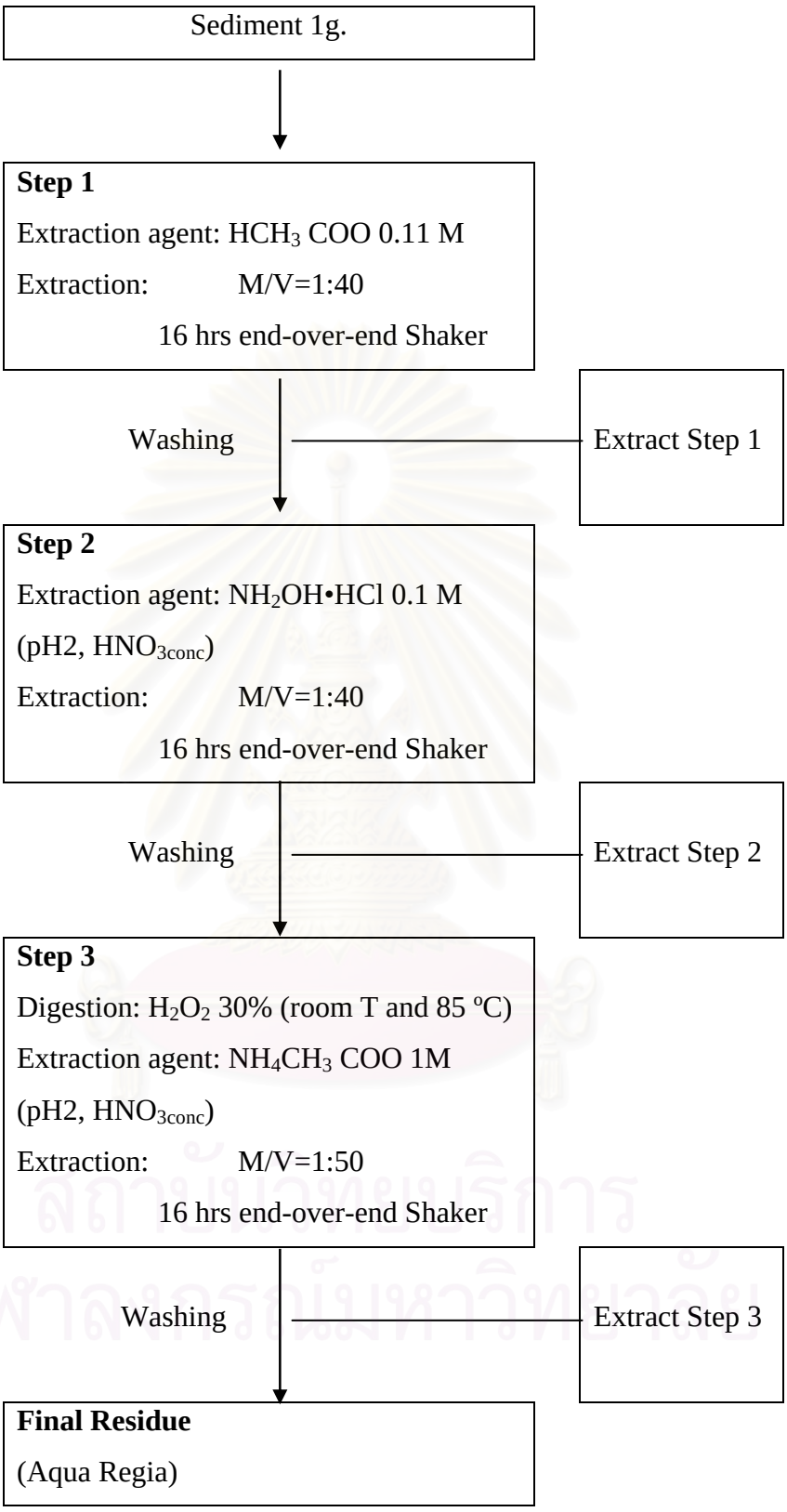

Figure 3.8 BCR sequential extraction scheme.

CAHPTER IV
RESULTS AND DISCUSSIONS

4.1 Total Cadmium and Zinc in Suspended Solids

Four, five, and two suspended solids samples were collected from Huai Mae Tao creek, Huai Mae Ku creek, and Huai Nong Khieo creek, respectively. Then, these samples were prepared for total cadmium and zinc analyses using microwave digestion based on EPA method 3050B. Subsequently, all solution samples were analyzed by ICP-OES. Tables 4.1 to 4.3 show the analytical results of each creek which sample numbers in the tables are arranged in order to present sample locations from upstream mountain to downstream alluvial plain. In addition, sample numbers 1 and 2 from Huai Mae Tao creek are located very close to the zinc mine. Averages of cadmium concentration were calculated as 18.27 mg/kg, 7.75 mg/kg, and 6.32 mg/kg for samples from Huai Mae Tao, Huai Mae Ku, and Huai Nong Khieo, correspondingly. Huai Mae Tao also yields the highest average zinc concentration of 7,767.14 mg/kg while Huai Mae Ku contains an average of 7,722.99 mg/kg and Huai Nong Khieo obtains 6,232.97 mg/kg. As a result, it can observe that the concentrations of both zinc and cadmium in Huai Mae Tao yield the highest averages. However, all three creeks have unusually high zinc-contained suspended solids which may be in turn indicate zinc potential area. Although, cadmium presented in most suspended solids samples are likely higher than the normal that should be due to the nature background of zinc prospect area, average cadmium concentration from Huai Mae Tao is somehow higher than 2 and 3 times of those averages in Huai Mae Ku and Huai Nong Khieo, respectively. In addition, the tendency of cadmium and zinc distribution slightly decreases from eastern mountainous area to western lowland as shown in Figures 4.1 and 4.2.

Table 4.1 Total concentrations of Zn and Cd in suspended solids from Huai Mae Tao creek, analyzed using ICP-OES.

Huai Mae Tao				
Sample no.	**X UTM**	**Y UTM**	**SS_Zn (mg/kg)**	**SS_Cd (mg/kg)**
2	461740	1842420	10628.17	43.01
3	460960	1842550	11419.96	10.04
5	460450	1843220	5403.85	11.42
7	459110	1842570	3616.59	8.58
Mean			**7767.14**	**18.27**

Table 4.2 Total concentrations of Zn and Cd in suspended solids from Huai Mae Ku creek, analyzed using ICP-OES.

Huai Mae Ku				
Sample no.	**X UTM**	**Y UTM**	**SS_Zn (mg/kg)**	**SS_Cd (mg/kg)**
23	463000	1840300	14434.06	14.13
22	462910	1840700	5369.18	5.36
21	462500	1841000	5635.56	6.56
12	461490	1841120	3794.33	5.04
16	459640	1840480	9381.81	7.64
Mean			**7722.99**	**7.75**

Table 4.3 Total concentrations of Zn and Cd in suspended solids from Huai Nong Khieo creek, analyzed using ICP-OES.

Huai Nong Khieo				
Sample no.	**X UTM**	**Y UTM**	**SS_Zn (mg/kg)**	**SS_Cd (mg/kg)**
28	460800	1838400	6430.22	6.32
26	460500	1839000	6035.72	6.32
Mean			**6232.97**	**6.32**

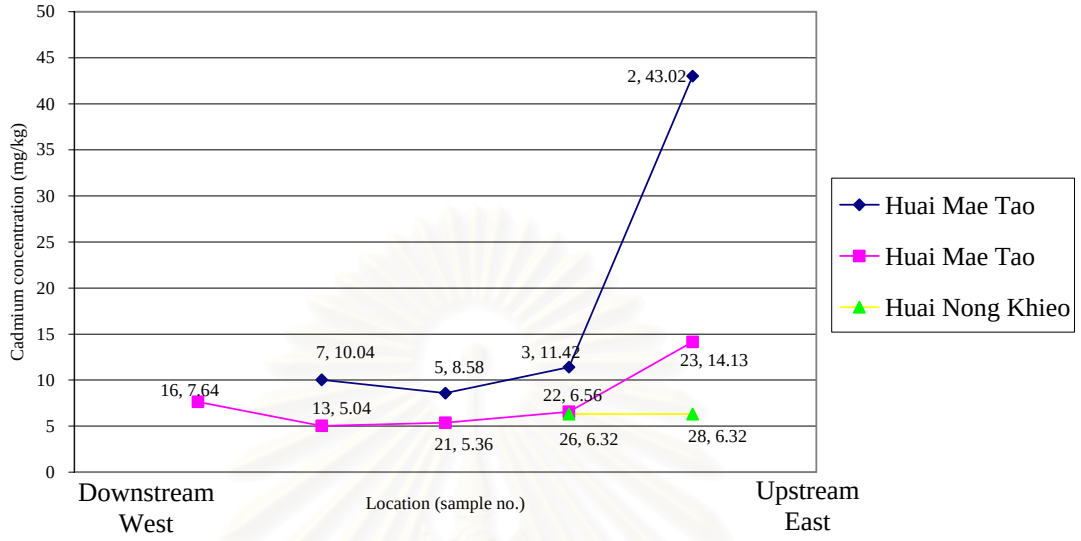

Figure 4.1 Distribution of total cadmium concentrations in suspended solids in the study area, plotted relatively along east mountainous area to west lowland.

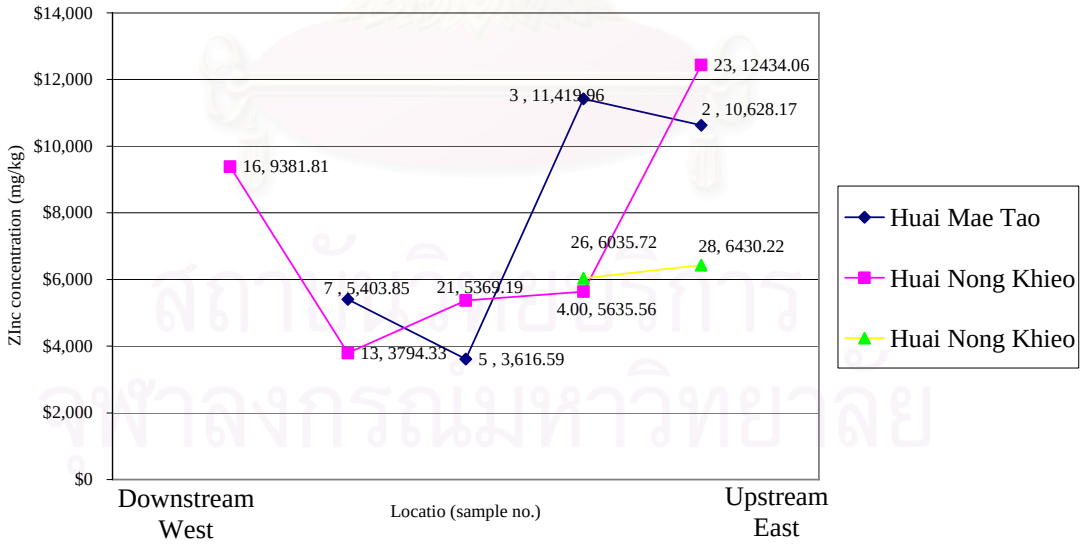

Figure 4.2 Distribution of total zinc concentration in suspended solids in the study area, plotted relatively along east mountainous area to west lowland.

4. 2 Total Cadmium and Zinc in Stream Sediment

Total concentrations of cadmium and zinc in stream sediment are the main aim for this research. The samples were digested using microwave digestion technique, EPA method 3051. Stream sediment samples were collected from Haui Mae Tao, Huai Mae Ku, and Huai Nong Khieo with numbers of ten, eleven, and seven samples, respectively. Analytical means from duplicate results of representative analyses of are shown in Tables 4.4 to 4.6, and all analyses are summarized in Appendix B, tables B-2 to B-7. Stream sediments from Huai Mae Tao yield average zinc content of 1,231.47±10.76 mg/kg and average cadmium content of 37.11±0.33 mg/kg. Samples collected from Huai Mae Ku contain averages of 316.55±3.66 mg/kg and 7.99±0.01 mg/kg for total zinc and total cadmium. The control samples from Huai Nong Khieo show averages of 63.08±0.84 mg/kg and 5.67±0.10 mg/kg for total zinc and total cadmium. In addition, it is obviously observed that Huai Mae Tao appears to have the highest concentrations of zinc and cadmium as showed in Figures 4.3 and 4.4. Normally, the concentrations of heavy metals are likely decreasing towards west lowland and alluvial; however, analyses are mostly fluctuated.

Table 4.4 Representative analyses of total Zn and Cd in stream sediments from Huai Mae Tao.

Huai Mae Tao				
Sample No.	**X UTM**	**Y UTM**	**Total Zn (mg/kg)**	**Total Cd (mg/kg)**
1	462200	1842210	1487.30±32.62	24.53±1.65
5	460450	1843220	976.10±30.82	35.17±1.54
6	460000	1843200	720.59±14.31	22.85±0.68
7	459110	1842570	2300.00±59.23	66.19±1.52
8	458170	1842190	1524.80±39.95	39.73±1.43
Average			**1231.47±10.76**	**37.11±0.33**

Table 4.5 Representative analyses of total Zn and Cd in stream sediments from Huai Mae Ku.

Huai Mae Ku				
Sample No.	**X UTM**	**Y UTM**	**Total Zn (mg/kg)**	**Total Cd (mg/kg)**
22	462910	1840700	217.85±27.67	7.69±0.28
13	461490	1841120	106.73±11.52	4.93±1.02
16	459640	1840480	579.90±30.05	13.03±00.09
17	458500	1840230	399.85±39.07	9.63±0.75
18	458060	1840550	40.77±1.76	5.50±0.25
20	457680	1839720	456.17±12.66	9.61±0.39
Average			**316.55±3.66**	**7.99±0.01**

Table 4.6 Representative analyses of total Zn and Cd in stream sediment from Huai Nong Khieo.

Huai Nong Khieo				
Sample No.	**X UTM**	**Y UTM**	**Total Zn (mg/kg)**	**Total Cd (mg/kg)**
24	461360	1840000	28.388±2.03	3.759±0.44
27	460200	1838700	17.869±3.86	2.735±0.11
29	459800	1839000	77.152±3.54	6.083±0.17
31	458230	1838430	99.771±3.63	7.914±0.03
Average			**63.08±0.84**	**5.67±0.10**

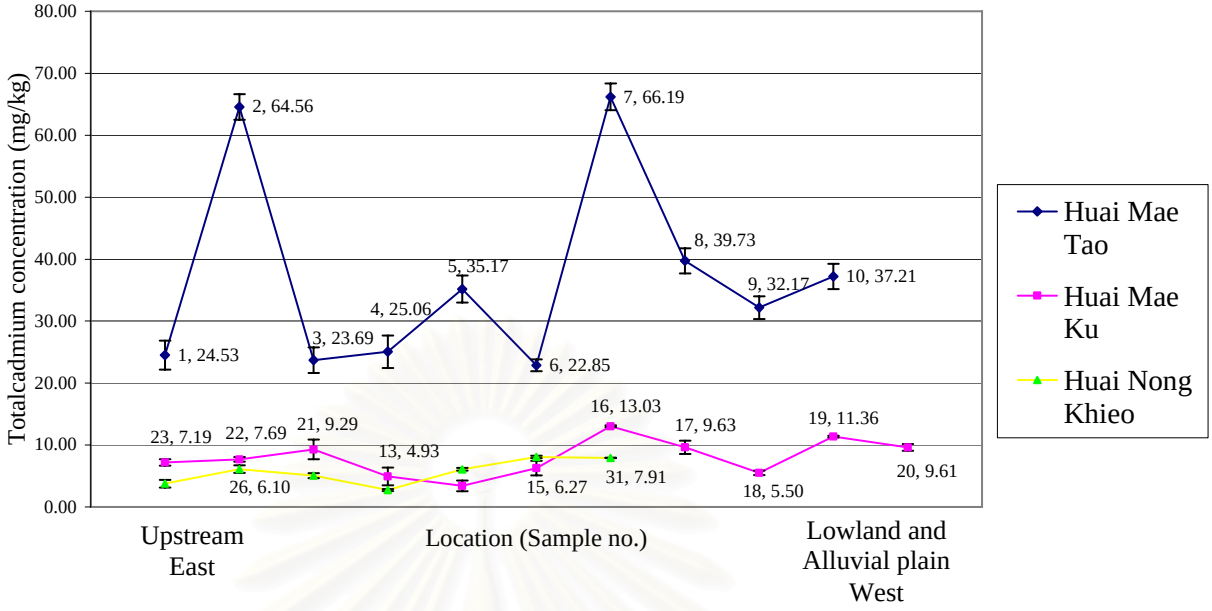

Figure 4.3 Distribution of total cadmium in stream sediments from different creeks, plotted comparatively from east to west localities.

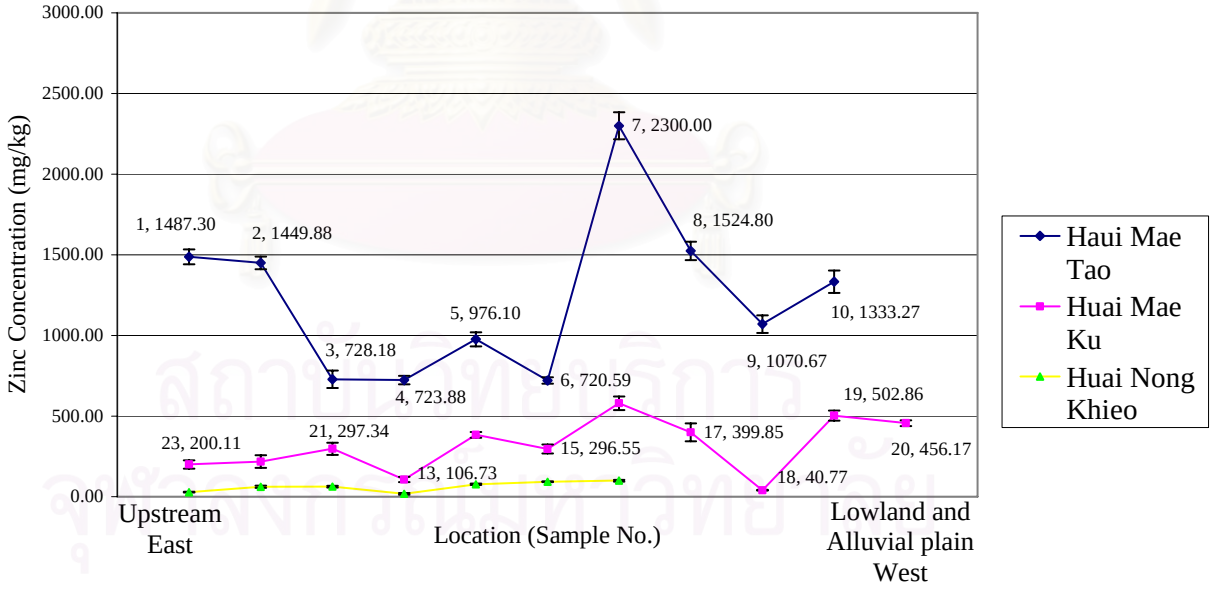

Figure 4.4 Distribution of total zinc in stream sediments from different creeks, plotted comparatively from east to west localities.

4.3 Fractional Cadmium and Zinc in Stream Sediment

Sequential extraction of cadmium and zinc in stream sediment is prepared using BCR three-step method as reposted before. They were analyzed in order to identify the most significant form of cadmium and zinc in those stream sediments. Average of duplicate analyses of representative results obtained from this procedure is summarized in Tables 4.7 to 4.9 for zinc analyses and Tables 4.10-4.12 for cadmium. In conclusion, the crucial forms of zinc in stream sediments from both Huai Mae Tao and Huai Mae Ku are BCR1 (av. 436.79±0.70 and 142.62±1.59 mg/kg) and BCR2 (av. 438.58±0.48 and 188.72±0.72 mg/kg), while those from Huai Nong Khieo are mostly characterized by BCR2 (av. 30.28±0.44 mg/kg) with accessories of BCR3 (av. 13.23±0.15 mg/kg) and final residual (av. 14.46±0.14 mg/kg). Regarding cadmium, analyses from Huai Mae Tao likely indicate that BCR1 (av. 9.63±0.70 mg/kg) and BCR2 (av. 8.69±0.11 mg/kg) are the most significant, whereas those from Huai Mae Ku BCR1 (av. 2.68±0.10 mg/kg), BCR2 (av. 4.5±0.06 mg/kg) and final residual (av. 3.29±0.01 mg/kg) are quite similar. Stream sediments (control sample) from Huai Nong Khieo clearly contain cadmium in dominant form of final residual (av. 2.48±0.01 mg/kg).

Table 4.7 Sequential extraction analyses of zinc in stream sediments from Huai Mae Tao.

Huai Mae Tao						
Sample No.	**X UTM**	**Y UTM**	**BCR1 Zn (mg/kg)**	**BCR2 Zn (mg/kg)**	**BCR3 Zn (mg/kg)**	**Final Zn (mg/kg)**
1	462200	1842210	152.31±0.01	246.75±0.41	31.69±0.06	371.99±0.17
2	461740	1842420	650.57±0.00	572.09±0.11	48.70±0.20	76.45±0.13
4	460880	1842980	227.03±0.01	270.19±0.43	23.02±0.02	42.39±0.04
7	459110	1842570	939.56±0.09	851.12±1.42	79.67±0.10	62.12±0.03
9	458300	1842840	361.85±0.01	414.57±0.58	28.83±0.49	44.81±0.06
10	457600	1842760	467.48±0.01	489.09±0.28	43.42±0.08	46.40±0.22
Average			**436.79±0.02**	**438.58±0.48**	**38.52±0.15**	**80.556±0.11**

Table 4.8 Sequential extraction analyses of zinc in stream sediments from Huai Mae Ku.

Huai Mae Ku						
Sample No.	**X UTM**	**Y UTM**	**BCR1 Zn (mg/kg)**	**BCR2 Zn (mg/kg)**	**BCR3 Zn (mg/kg)**	**Final Zn (mg/kg)**
23	463000	1840300	80.71±1.17	89.22±0.11	2.22±0.03	27.50±0.02
13	461490	1841120	74.96±2.89	39.57±1.41	nd	14.04±0.05
16	459640	1840480	215.97±2.32	363.70±0.35	9.69±0.20	42.84±0.15
18	458060	1840550	nd	43.91±1.30	nd	18.26±0.07
19	457560	1840200	198.96±1.83	310.02±0.19	32.09±0.07	66.47±0.31
Average			**142.62±1.59**	**188.1.0±0.72**	**25.31±0.33**	**30.05±0.11**

nd = not detected

Table 4.9 Sequential extraction analyses of zinc in stream sediments from Huai Nong Khieo.

Huai Nong Khieo						
Sample No.	**X UTM**	**Y UTM**	**BCR1 Zn (mg/kg)**	**BCR2 Zn (mg/kg)**	**BCR3 Zn (mg/kg)**	**Final Zn(mg/kg)**
26	460500	1839000	0.11±0	33.84±0.49	0.83±0.17	18.75±0.12
28	460800	1838400	nd	26.42±0.52	0.99±0.07	14.78±0.16
27	460200	1838700	nd	8.95±0.67	nd	11.73±0.12
29	459800	1839000	0.37±0.04	44.75±0.17	9.77±0.17	14.41±0.01
30	458980	1838560	1.63±0.07	53.54±0.08	2.27±0.18	15.82±0.06
Average			**0.852±0.06**	**30.28±0.44**	**13.23±0.15**	**14.46±0.14**

nd = not detected

Table 4.10 Sequential extraction analyses of cadmium in stream sediments from Huai Mae Tao.

Huai Mae Tao						
Sample No.	**X UTM**	**Y UTM**	**BCR1_Cd (mg/kg)**	**BCR2_Cd (mg/kg)**	**BCR3_Cd (mg/kg)**	**Final Cd (mg/kg)**
1	462200	1842210	8.55±0.09	9.20±0.02	0.59±0.02	6.81±0.01
2	461740	1842420	35.94±0.92	37.42±0.08	1.03±0.01	2.79±0.02
3	460960	1842550	6.57±0.06	12.29±0.12	0.82±0.01	3.51±0.02
5	460450	1843220	16.43±1.35	20.76±0.39	0.96±0.01	2.53±0.01
7	459110	1842570	28.80±0.07	19.76±0.08	1.38±0.01	2.71±0.00
Average			**9.63±0.70**	**8.69±0.11**	**0.22±0.12**	**1.28±0.01**

Table 4.11 Sequential extraction analyses of cadmium in stream sediments from Huai Mae Ku.

Huai Mae Ku						
Sample No.	**X UTM**	**Y UTM**	**BCR1_Cd (mg/kg)**	**BCR2_Cd (mg/kg)**	**BCR3_Cd (mg/kg)**	**Final Cd (mg/kg)**
21	462500	1841000	2.76±0.09	3.97±0.04	0.22±0.01	3.13±0.01
14	461100	1840420	0.49±0.03	1.29±0.02	0.19±0.00	2.34±0.02
15	460890	1840590	1.52±0.04	4.69±0.01	0.15±0.00	3.12±0.02
16	459640	1840480	3.90±0.15	10.98±0.11	0.29±0.00	3.47±0.01
17	458500	1840230	4.45±0.11	6.37±0.31	0.30±0.00	3.10±0.00
18	458060	1840550	0.20±0.01	0.95±0.01	0.28±0.01	4.32±0.00
19	457560	1840200	5.64±0.22	6.55±0.19	0.42±0.01	4.53±0.00
Average			**2.68±0.10**	**4.50±0.06**	**0.26±0.01**	**3.29±0.01**

Table 4.12 Sequential extraction analyses of cadmium in stream sediment from Huai Nong Khieo.

Huai Nong Khieo						
Sample No.	**X UTM**	**Y UTM**	**BCR1_Cd (mg/kg)**	**BCR2_Cd (mg/kg)**	**BCR3_Cd (mg/kg)**	**Final Cd (mg/kg)**
24	461360	1840000	0.17±0.02	0.77±0.01	0.38±0	2.06±0
28	460800	1838400	nd	1.03±0.04	0.20±0	2.52±0.01
27	460200	1838700	0.32±0.01	0.45±0.02	nd	2.17±0.01
31	458230	1838430	0.11±0	1.89±0.02	nd	2.37±0
Average			**0.20±0.01**	**1.38±0.03**	**0.32±0.00**	**2.48±0.01**

nd = not detected

4.4 Discussions

In this study, twenty-eight stream sediment samples, eleven suspended solids and eleven water samples were collected from different creeks for chemical analysis as reported above. Cadmium and zinc show potential or significant environmental impact to the ecosystem and human health. Therefore, cadmium and zinc have been brought into attention for evaluation and discussion on some aspects.

4.4.1 Suspended Solids and Water

The determination of cadmium and zinc concentrations in water shows very low cadmium and zinc values (lower than the detection limit of ICP) in comparison with the standard of surface water suggested by Pollution Control Department (Zn ≤ 1.0 mg/l and Cd ≤ 0.05[1] or 0.005[2] mg/l). That means cadmium and zinc in this case are not soluble form. Besides, the pH values of water are mostly neutral to slightly high, varying in a narrow range of about 7-8.5. This condition actually enhances insoluble form of heavy metals including cadmium and zinc. Then, heavy metals cannot mobile and distribute away from source.

[1] when water hardness not more than 100 mg/l as $CaCO_3$

[2] when water hardness more than 100 mg/l as $CaCO_3$

The suspended solids from Huai Mae Tao creek yielded the highest average (18.26 mg/kg) of total cadmium concentrations (Table 4.13). Total cadmium concentrations in control suspended solids taken from Huai Nong Khieo creek reveal an average of about 6.32 mg/kg that is more or less close to average (7.75 mg/kg) of those from Huai Mae Ku creek. Regarding total zinc concentrations, averages of Huai Mae Tao and Huai Mae Ku are likely identical which are 7,767.14 and 7,722.99 mg/kg, respectively, whereas the average taken from Huai Nong Khieo (6,232.97 mg/kg) is moderately lower. Although, suspended solids is representative of recent sediment that can be traced back to characteristic of its hosts these analytical results are different from those obtained from stream sediments. This may be effected by less amounts of suspended solids that can be collected from the field (see Appendix B, Table B-1), this limitation would restrict interpretation of analytical result in term of absolute value. However, correlation of these analyses would give an idea of nature and distribution of the metals. As reported above, zinc concentrations from all creeks are not cearly different as shown in the stream sediment that will be reported in the next section. In addition, average ratios of Cd:Zn in suspended solids from Huai Mae Tao, Huai Mae Ku and Huai Nong Khieo are calculated as 0.0023, 0.001 and 0.001, respectively. Cadmium distribution in suspended solids indicates clearly that Huai Mae Tao creek may be supplied by higher cadmium-bearing sediment. On the other hand, the other streams contain about equal cadmium concentrations in suspended solids. Then nature and environmental condition of catchment would be dissimilar between Huai Mae Tao and the rest.

Table 4.13 Summary of total Zn and Cd concentrations in suspended solids taken from different creeks, showing maximum, minimum and average values.

Huai Mae Tao					
Sample No.	**X UTM**	**Y UTM**	**Total Cd (mg/kg)**	**Total Zn (mg/kg)**	**pH**
5(min)	460450	1843220	10.04	3,616.59	8.34
2(max)	461740	1842420	43.01	10,628.17	8.08
Average ± SD			**18.26±16.54**	**7,767.14±3844.51**	**8.23±0.17**
Huai Mae Ku					
Sample No.	**X UTM**	**Y UTM**	**Total Cd (mg/kg)**	**Total Zn (mg/kg)**	**pH**
21(min)	462500	1841000	5.36	5,369.19	8.11
23(max)	463000	1840300	14.13	12,434.33	8.16
Average± SD			**7.74±3.72**	**7,723.00±4275.58**	**8.17±0.24**
Huai Nong Khieo					
Sample No.	**X UTM**	**Y UTM**	**Total Cd (mg/kg)**	**Total Zn (mg/kg)**	**pH**
26(min)	460500	1839000	6.315	6,035.72	8.12
28(max)	460800	1838400	6.319	6,430.22	8.39
Average± SD			**6.32±0.003**	**6,232.97±278.96**	**8.26±0.29**

4.4.2 Total Zinc and Cadmium in Stream Sediment

For evaluation of the cadmium distribution in stream sediment from Mae Sot District, total concentration was firstly determined. Twenty-eight of stream sediment samples were collected from three streams in the study area; they are from Huai Mae Tao, Huai Mae Ku and Huai Nong Khieo as shown in Figure 3.2. Total concentrations of cadmium and zinc were determined and some results showing maximum-minimum ranges and average of each creek are shown in Table 4.14; all analyses are also arranged in Appendix B, Table B-2 to B-7. Total zinc concentrations in stream sediments from Huai Mae Tao (av. 1,231.47±10.76 mg/kg) and Huai Mae Ku (av. 316.55±3.66 mg/kg) are higher than total cadmium concentration in stream sediment (control samples) from Huai Nong Khieo (63.08±0.84 mg/kg). However, total cadmium concentrations significantly reveal that cadmium distribution along Huai Mae Tao (av. 37.11±0.33 mg/kg) is much higher than those in Huai Mae Ku (7.99±0.01 mg/kg) and Huai Nong Khieo (5.67±0.10 mg/kg). In addition, the baseline value of the soil in contaminated area of Mae Sot District is about 3 mg/kg (NRC-EHWM, 2004) which is not higher than the standard of heavy metal in soil of

Thailand (37mg/kg) (PCD, 2004). Hence, cadmium distributions in the studied stream sediment are conclusively higher than the soil, this is due to natural occurrences of zinc mineral in the area. However, total cadmium distribution in Huai Mae Tao is approximately higher than four times of those in Huai Mae Ku and Huai Nong Khieo which is comparable to the ratio present in suspended solids as discussed in the last section. However, average ratios of Cd: Zn of stream sediment from Huai Mae Tao, Huai Mae Ku and Huai Nong Khieo are calculated as 0.03, 0.025 and 0.09, respectively. That is unlikely to state that Cd distribution in Huai Mae Tao, in which appears to have been influenced partly by mining activity, is higher than those in the other streams.

Relation between total Zn and Cd concentrations in all creeks can be present graphically in Figure 4.5, which reveals quite good relation. It was expected that cadmium concentration directly vary with zinc concentration. Nevertheless, the high baseline content of stream sediment and the unusual cadmium-sediment appear not only in the zinc mining effluence area but also reveal in the west of study area. Therefore, the transformation of surface covering to ore potential area is a dramatic factor for cadmium releasing to the environment; these processes are weathering, erosion and anthropogenic activity. The most predominant anthropogenic activities in this area are implicated to living styles of local people such as deforestation, cultivation or mechanic excavation and also mining activities. Runoff and rainfall are also main factors to wash and transport these sediments. In conclusion, anthropogenic activity and rainfall rate are the most significant factor for cadmium distribution in this area.

Table 4.14 Summary of total Zn and Cd concentrations in stream sediment taken from different creeks, showing maximum, minimum and average values.

Huai Mae Tao					
Sample No.	**X UTM**	**Y UTM**	**Total Cd (mg/kg)**	**Total Zn (mg/kg)**	**pH**
6(min)	460000	1843200	22.85±0.68	720.59±14.31	8.13
7(max)	459110	1842570	66.19±1.52	2300.00±59.23	8.08
Average			**37.11±0.33**	**1,231.47±10.76**	**8.16±0.17**

Huai Mae Ku					
Sample No.	**X UTM**	**Y UTM**	**Total Cd (mg/kg)**	**Total Zn (mg/kg)**	**pH**
14(min)	461100	1840420	3.40±0.62	383.94±12.43	7.66
16(max)	459640	1840480	13.03±0.09	579.90±30.05	7.96
Average			**7.99±0.01**	**316.55±3.66**	**7.98±0.24**
Huai Nong Khieo					
Sample No.	**X UTM**	**Y UTM**	**Total Cd (mg/kg)**	**Total Zn (mg/kg)**	**pH**
27(min)	460200	1838700	2.74±0.11	17.87±3.86	8.07
30(max)	458980	1838560	8.06±0.14	93.34±1.23	7.50
Average			**5.67±0.10**	**63.08±0.84**	**7.89±0.29**

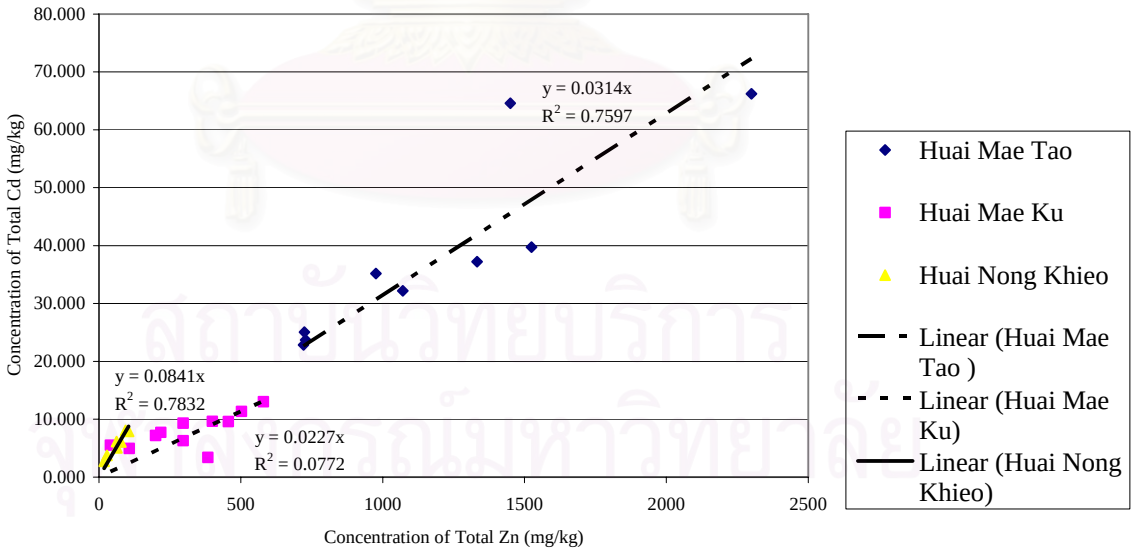

Figure 4.5 Graphically correlation between total cadmium and total zinc in stream sediment samples taken from Huai Mae Tao, Huai Mae Ku and Huai Nong Khieo creeks.

4.4.3 Fractional Zinc and Cadmium in Stream Sediment

Because only some parts of the total amount of heavy metals in sediments may be considered as bioavailable, mobile and potentially toxic in the environment, the partitioning of cadmium was investigated in stream sediment using BCR Three-Step Sequential Extraction Procedure, obtained from the Standards, Measurements and Test Programme (SM&T formerly Community Bureau of Reference, BCR). Quality of the analytical data was check with standard materials, CRM LGC6137 and CRM025-505. Concentrations of cadmium and zinc in the stream sediment from three creeks analyzed within four fractions are summarized in Figures 4.6 to 4.11. The Y-axis indicates the percentage of extracted solutions compatible to the three fractions and the residual phase of the BCR.

The extractable fractions of cadmium in 0.11M acetic acid (fraction 1) and 0.5M hydroxlylamine hydrochloride (fraction 2) predominately present in stream sediment of Huai Mae Tao, they contain about 36.21% and 51.38% each phase of total value (Figure 4.6). Stream sediment from Huai Mae Ku principally reveals high BCR fraction 2 for 30-40% (Figure 4.7). On the other hand, final residue of cadmium is the majority in stream sediment from Huai Nong Khieo (60.91%) (Figure 4.8). The results obtained from the BCR three-step have been summarized in distribution graphs for zinc. Zinc was revealed as mobile major compound with percentages of extraction in the first and the second steps of approximately 45-50% for each fraction, especially in Huai Mae Tao and Huai Mae Ku (Figures 4.9 and 4.10). In the other hand, the dominant fraction of zinc in Huai Nong Khieo (Figure 4.11) presents in the second step (approximately 50%) and final residue (approximately 30.91%) which bond to various carbonate and Fe, Mn oxide, respectively.

High proportion of metals (e.g. Cd: Zn in this case) and general low levels of extractable metals in stream sediment from Huai Nong Khieo indicate that sediment is crucially in stable from and relatively unpolluted. Because of most stream sediment in Huai Nong Khieo came from the country rock which have less zinc potential, besides surface soil in this area has only been disturbed by cultivation; therefore, these sediments were hardly generated and transformed. They can be used as control

samples. Cadmium and zinc in stream sediment from Huai Nong Khieo likely have stronger bond than those from other creeks. Hence, cadmium and zinc in stream sediments from Huai Mae Ku and Huai Nong Khieo would be easily taken up by living organisms. Cadmium has been concerned as hazardous implication to the environment. Moreover, the high content of cadmium in Huai Mae Tao and Huai Me Ku in the first and second steps which is an extractable fraction suggested by Tessier et al., 1979 and Peter et al., 2001 may point to association of human activities (Tuzen, 2003).

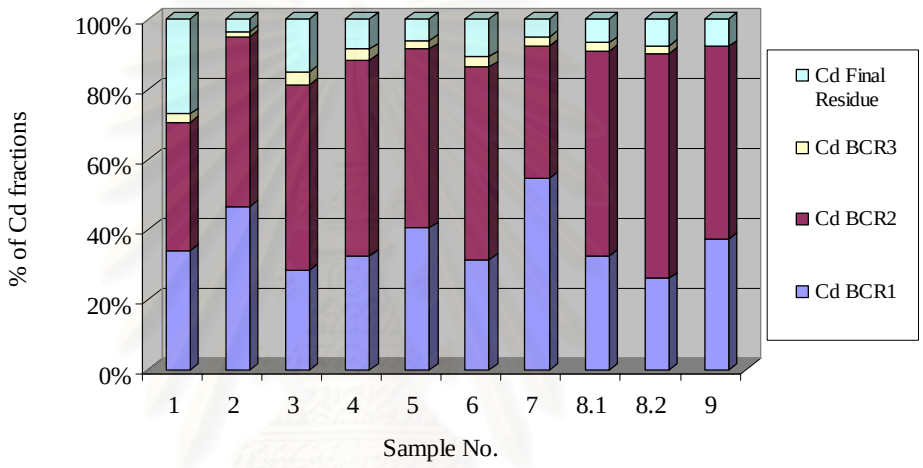

Figure 4.6 Fractional percentage of cadmium in stream sediments from Huai Mae Tao.

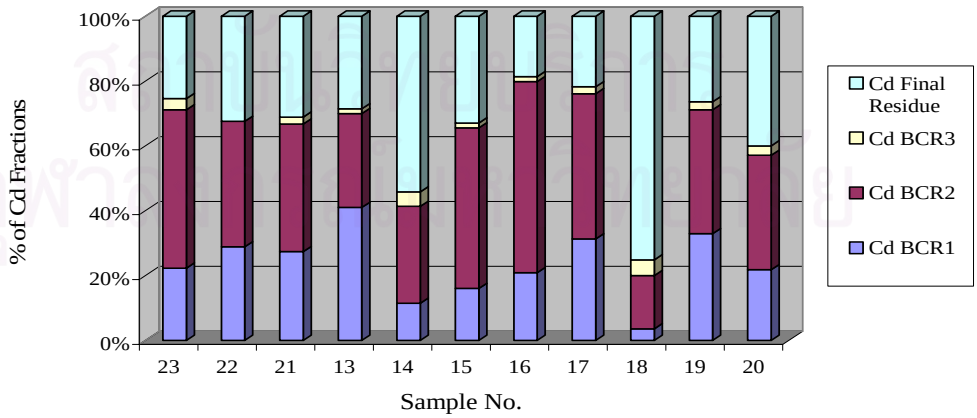

Figure 4.7 Fractional percentage of cadmium in stream sediments from Huai Mae Ku.

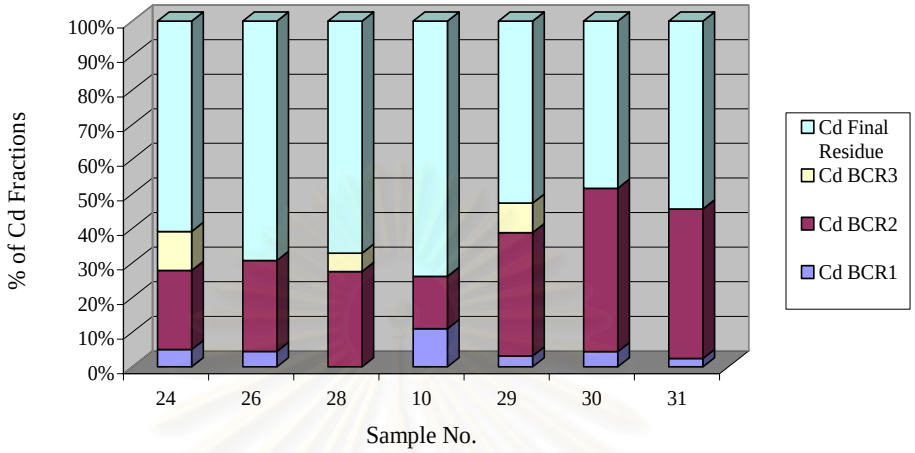

Figure 4.8 Fractional percentage of cadmium in stream sediments from Huai Nong Khieo.

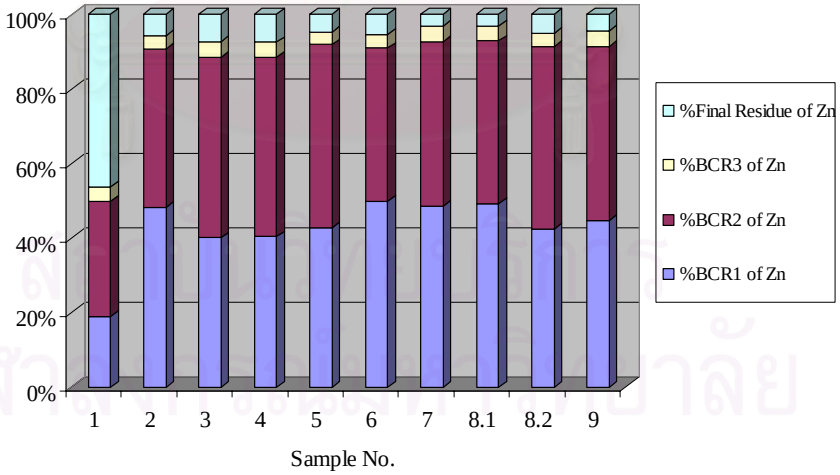

Figure 4.9 Fractional percentage of zinc in stream sediments from Huai Mae Tao.

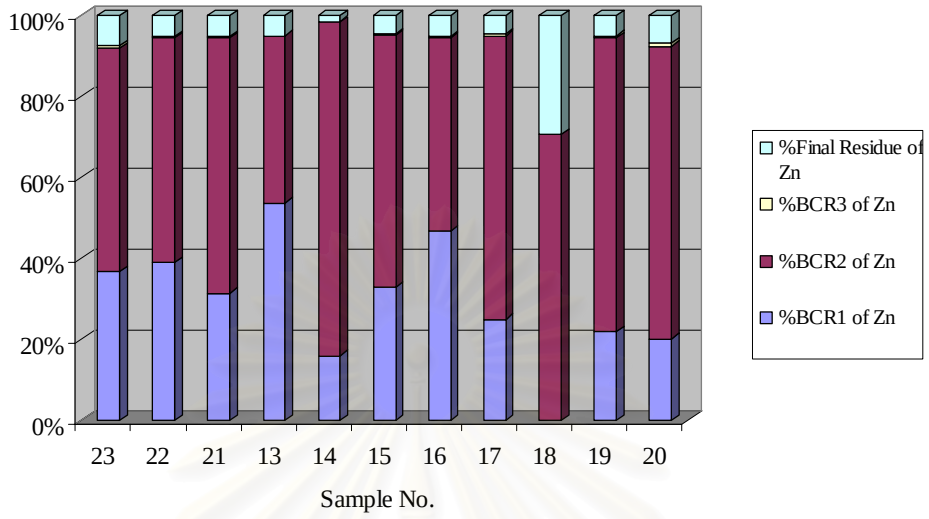

Figure 4.10 Fractional percentage of zinc in stream sediments from Huai Mae Ku.

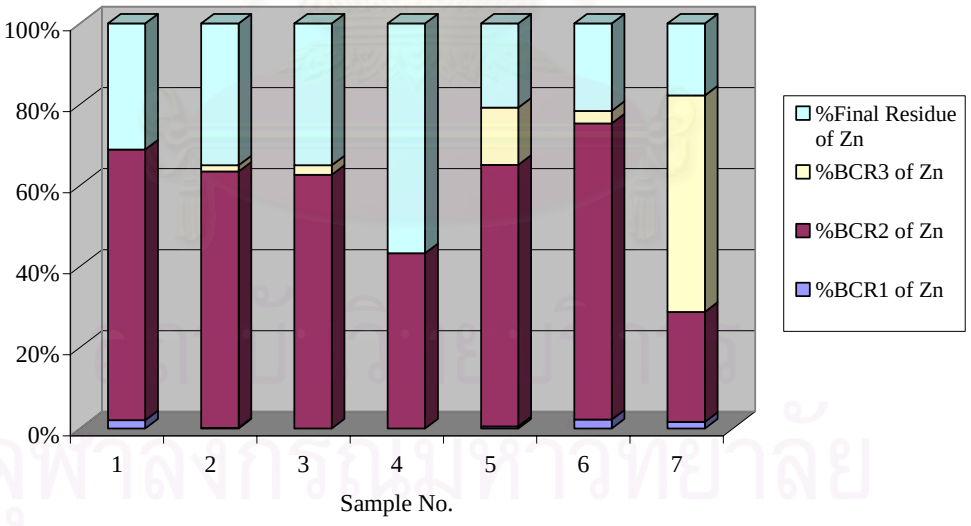

Figure 4.11 Fractional percentage of zinc in stream sediments from Huai Nong Khieo.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Huai Mae Tao shows obviously high concentrations of heavy metals (Zn and Cd). Huai Mae Tao has been typically discharged runoff with sediment from Doi Phadaeng where a few zinc mines have been operated. The concentration of cadmium from tailing pond and sedimentation pond of Phadaeng Mine contain approximately 195-1,260 mg/kg reported by DPIM (2004). The highest cadmium analyzes under this research shows 66.19 mg/kg in stream sediment from Huai Mae Tao, whereas sediment from Huai Nong Khieo in which located at another site of Doi Phadaeng reveals only 8.06 mg/kg of cadmium content. Therefore, comparison of these data indicates that cadmium-sediment may be partly involved by zinc mining, besides; cultivation in this area has also increased cadmium indirectly in soil and sediment.

Furthermore, in this case, the water samples were also analyzed to quantify cadmium and zinc concentration but the results showed the cadmium and zinc concentration were lower than the detection limit of ICP. Hence, it implied that cadmium and zinc in this case are not soluble form.

The recent sediments or suspended solids also reveal high cadmium concentration. Doubtfully, the cadmium content in suspended solids is lower than cadmium content in stream sediments. The difference of these values may be ascribed to the stage of evolution or the level of alteration of the sediment. The duration is a significant factor (Figure 5.1). Perhaps, the effect from cadmium contamination would take Phadaeng mine to design more consideration in environmental aspect.

The crucial fraction of cadmium is revealed as BCR2, bonding with manganese and iron oxides, in Huai Mae Tao. Stream sediment from Huai Mae Ku shows dominant cadmium formed as BCR2 and final residual, whereas sediment from Huai Nong Khieo present the most abundant cadmium in final residual which formed

in mineral lattice. As a result, it would be implied that bioavailability of cadmium in Huai Mae Tao is higher than those in Huai Mae Ku and Huai Nong Khieo, respectively.

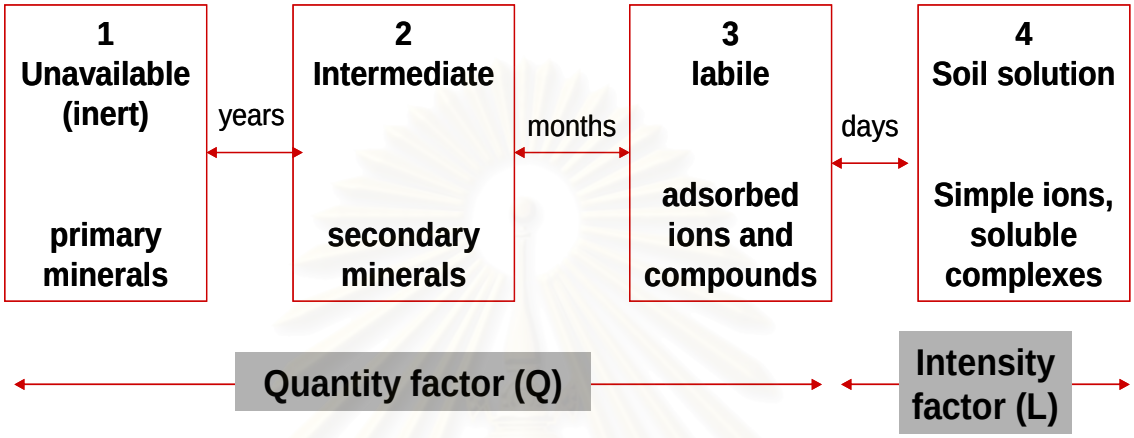

Figure 5.1 Development of soil from sediment **(**NRC-EHWM, 2004; modified from Thornton, 1995).

Huai Mae Tao is directly related to zinc deposits. Human activities, as mentioned above, were important cause of cadmium contamination. The sediment from sedimentation pond and tailing pond of zinc mining may be accidentally become the major source of cadmium in the area. However, cultivation and natural weathering of soil and rock should also be taken into account because of the high nature background of the zinc prospect area.

Because of this research was focused on sediment which amount of sediment depends on season or intensity of runoff. Therefore, the sediment samples should be collected in dry season for completion of research. However, the accessibility to sample location in rainy season should be taken into consideration. Since high amount of precipitation (rain) in Mae Sot area may be an obstruction. Furthermore, it should collect in every year to observe variation of heavy metal in the study area. In addition, a number of samples are very significant about analytical results.

5.2 Recommendations

Because of this research was focused on sediment which amount of sediment depends on season or intensity of runoff. Therefore, the sediment samples should be collected in dry season for completion of research. However, the accessibility to sample location in rainy season should be taken into consideration. Since high amount of precipitation (rain) in Mae Sot area may be an obstruction. Furthermore, it should be collected in every year to observe variation of heavy metals in the study area. In addition, amount of samples are very important for statistically sound. Cadmium and zinc concentrations in surrounding paddy soil and other agricultural lands would be taken into account for further discussion. That would in turn lead to more understanding on source and accumulation of cadmium in the area. However, cultivation procedure is a crucial aspect that might accidentally increase cadmium level in the soil such as using contaminated fertilizer. Finally, sediments from all settling ponds in zinc mines should be analyzed annually for evaluation of environmental impact; consequently, protection plan will be designed to reduce the threat.

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APPENDICES

Appendix-A

Detailed Procedure for Samples Analysis

A-1 Sampling and Preservation

(a.) Composite sample **:**

(1) Stream sediment samples are prepared by thoroughly mixing several grab samples, which are collected at difference locations.

(2) Water and suspended solid are collected in plastic bottom.

(b.) Sample preservation techniques:

Sample	Container type/Volume	Preservation	Holding Time
Water	Plastic /1L	$HNO_3$to pH<2	6 months
Stream sediments	Plastic/ 1-0.5 kg of sample	-	6 months
Suspended solid	On GFC Filtered paper in Petri-dish	-	Analyzed as soon as possible

A-2 Analytical techniques:

(a) Physical properties studies:

Sample	Parameters	Instruments	Location
Water	pH , Temperature	pH Meter	On site
	Total Solid: Total dissolved solid	Suction Flask 500 mL and Buchner funnel	On site

(b) Chemical properties studies:

Microwave Digestion technique & Inductively Coupled Plasma (ICP)

Sample	Parameters	Instruments/techniques	EPA Method
Water	Heavy Metals	(1) Microwave Digestion technique	Method 3015A
		(2) Inductively Coupled Plasma (ICP)	Method 200.7
Suspended solid	Heavy Metals	(1)Microwave Digestion technique	Method 3051
		(2) Inductively Coupled Plasma (ICP)	Method 200.7
sediments	Heavy Metals	(1) Microwave Digestion technique	Method 3051
		(2) Inductively Coupled Plasma (ICP)	Method 200.7
	Sequential Extraction	(1) Inductively Coupled Plasma (ICP)	BCR three-step

Apparatus and Materials

1. Microwave Digestion system: Milestone Ethos SEL
2. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES): Varian vista MPX Axial
3. pH meter
4. Analytical balance 4 digits
5. Drying Oven
6. Shaker
7. Filter paper – 0.45 μm pore diameter membrane filter or equivalent
8. Glasswares and Others

Note: All laboratory glassware and plasticware were first cleaned with deionised water then with nitric acid 10% (for at least 12 hr.) and rinse again with double deionised water.

Reagents

Total acid digestion

(1) Deionized Water

(2) Nitric acid (concentrated), 65 % HNO_3

(3) Nitric acid, 1 % (v/v) HNO_3

(4) Hydrochloric acid (concentrated), 37 % HCl

(5) Hydrogen peroxide (30%), H_2O_2

BCR three-step

(1) Deionized Water

(2) Glacial acetic acid

(3) Hydroxylamine Hydrochloride

(4) Nitric acid, 2M

(5) Hydrogen Peroxide, 8.8M.

(6) Ammonium acetate, 1.0mol/L

Certified reference material

Natural matrix certified reference material, catalog No. CRM 025-050, Lot No: JG 025 and LGC6137 were used for validating the method in this paper

Procedure

a. Net weight of suspended solid

$$SS_{weight} = A-(B \times C)$$

where

A = weight of filtered paper plus residual (g)

B = weight of filter paper (g)

C = A number of filtered paper (g)

b. Total acid digestion procedure

- **Stock standard solution:** ICP-Multi-Element standard solution at 1000 ppm.
- **Working standard solution:** Prepared ICP-Multi-Element standard solution of 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.4, 0.6, 0.8, 1.0, 5 and 10 ppm. (Adjusted volume with 1 % (v/v) HNO_3)

c. Calculation method

The result in μg/kg (ppm) should be calculated as follows:

Result = (A X B / C) X 1000

where

A = Result from analysis in μg/L

B = Volume of the digested samples in liter (L)

C = Weight of the digested sample in gram (g)

A-3 Accuracy & Precision

% Recovery = (Result *100)/True Value

Total digestion			
CRM (mg/Kg) CRM 025-050		**Analyse result (mg/Kg)**	**% Recovery**
Cd	**369**	365.13	98.95
		342.12	92.71
Zn	**51.8**	49.65	95.85
		48.60	93.82
Sequential extraction			
CRM (mg/Kg) LGC6137		**Analyze result (mg/Kg)**	**% Recovery**
Cd	**231**	228.69	98.70
		241.24	104.43
Zn	**0.5**	0.60	120.00
		0.49	97.40

Appendix-B

Analytical Results

Table B-1 Results of total cadmium and zinc concentration analyses in suspended solid and weight of suspended solid.

SS		X UTM	Y UTM	pH	SS_Zn (mg/kg)	SS_Cd (mg/kg)	Weight (g/2l)
7	2	459110	1842570	8.37	5403.85	10.04	1.930
5	3	460450	1843220	8.34	3616.59	8.58	1.399
3	4	460960	1842550	8.12	11419.96	11.42	0.912
2	5	461740	1842420	8.08	10628.17	43.01	0.241
average				**8.2275**	**8554.90**	**21.00**	
16	1	461490	1841120	8.26	9381.81	7.64	0.747
13	2	459640	1840480	8.37	3794.33	5.04	3.641
21	3	462500	1841000	8.11	5369.19	5.36	1.696
22	4	462910	1840700	8.16	5635.56	6.56	1.705
23	5	463000	1840300	7.96	12434.06	14.13	0.345
average				**8.172**	**7322.99**	**7.75**	
28	4	460500	1839000	8.12	6035.72	6.32	1.674
26	5	460800	1838400	8.39	6430.22	6.32	1.056
average				**8.255**	**6232.97**	**6.32**	

Table B-2 Results of total zinc concentration analyses in stream sediment from Huai Mae Tao

Sample No.	X UTM	Y UTM	pH	Total Zn1 (mg/kg)	Total Zn2 (mg/kg)	Mean	SD
1	462200	1842210	8.31	1464.23	1510.37	1487.30	32.62
2	461740	1842420	8.37	1469.51	1430.25	1449.88	27.76
3	460960	1842550	8.34	701.25	755.11	728.18	38.08
4	460880	1842980	8.14	710.91	736.86	723.88	18.35
5	460450	1843220	8.12	954.31	997.90	976.10	30.82
6	460000	1843200	8.13	730.71	710.47	720.59	14.31
7	459110	1842570	8.08	2258.12	2341.88	2300.00	59.23
8	458170	1842190	8.3	1553.05	1496.55	1524.80	39.95
9	458300	1842840	8.03	1098.15	1043.20	1070.67	38.86
10	457600	1842760	7.79	1298.32	1368.21	1333.27	49.42
Average			**8.161**	**1223.86**	**1239.08**	**1231.47**	**10.76**

Table B-3 Results of total zinc concentration analyses in stream sediment from Huai Mae Ku.

Sample No.	X UTM	Y UTM	pH	Total Zn1 (mg/kg)	Total Zn2 (mg/kg)	Mean	SD
23	463000	1840300	8.26	187.21	213.01	200.11	18.24
22	462910	1840700	8.37	198.28	237.41	217.85	27.67
21	462500	1841000	8.11	278.63	316.05	297.34	26.46
13	461490	1841120	8.16	98.58	114.88	106.73	11.52
14	461100	1840420	7.66	375.15	392.73	383.94	12.43
15	460890	1840590	8.11	310.2	282.90	296.55	19.31
16	459640	1840480	7.96	601.14	558.65	579.89	30.05
17	458500	1840230	7.88	427.48	372.22	399.85	39.07
18	458060	1840550	7.65	42.01	39.53	40.77	1.76
19	457560	1840200	7.65	487.69	518.04	502.86	21.46
20	457680	1839720	8.03	447.22	465.12	456.17	12.66
Average			**7.99**	**313.96**	**319.14**	**316.55**	**3.66**

Table B-4 Results of total zinc concentration analyses in stream sediment from Huai Nong Khieo.

Sample No.	X UTM	Y UTM	pH	Total Zn1 (mg/kg)	Total Zn2 (mg/kg)	Mean	SD
24	461360	1840000	7.8	26.95	29.83	28.39	2.03
26	460500	1839000	8.12	58.87	65.63	62.25	4.78
28	460800	1838400	8.39	65.22	60.30	62.76	3.48
27	460200	1838700	8.07	15.14	20.60	17.87	3.86
29	459800	1839000	7.6	74.65	79.65	77.15	3.54
30	458980	1838560	7.5	94.21	92.47	93.34	1.23
31	458230	1838430	7.81	102.34	97.20	99.77	3.63
Average			**7.90**	**62.48**	**63.67**	**63.08**	**0.84**

Table B-5 Results of total cadmium concentration analyses in stream sediment from Huai Mae Tao.

Sample No.	X UTM	Y UTM	pH	Total Cd1 (mg/kg)	Total Cd2 (mg/kg)	Mean	SD
1	462200	1842210	8.31	23.36	25.69	24.53	1.65
2	461740	1842420	8.37	63.52	65.60	64.56	1.47
3	460960	1842550	8.34	22.66	24.72	23.69	1.46
4	460880	1842980	8.14	26.38	23.74	25.06	1.87
5	460450	1843220	8.12	36.26	34.08	35.17	1.54
6	460000	1843200	8.13	23.33	22.37	22.85	0.68
7	459110	1842570	8.08	65.12	67.26	66.19	1.52
8	458170	1842190	8.3	40.74	38.71	39.73	1.43
9	458300	1842840	8.03	31.25	33.09	32.17	1.30
10	457600	1842760	7.79	36.19	38.22	37.21	1.44
Average			**8.161**	**36.881**	**37.348**	**37.115**	**0.33**

Table B-6 Results of total cadmium concentration analyses in stream sediment from Huai Mae Ku

Sample No.	X UTM	Y UTM	pH	Total Cd1 (mg/kg)	Total Cd2 (mg/kg)	Mean	SD
23	463000	1840300	8.26	6.94	7.45	7.19	0.36
22	462910	1840700	8.37	7.89	7.50	7.69	0.28
21	462500	1841000	8.11	10.08	8.50	9.29	1.12
13	461490	1841120	8.16	4.21	5.65	4.93	1.02
14	461100	1840420	7.66	2.96	3.83	3.40	0.62
15	460890	1840590	8.11	6.85	5.69	6.27	0.82
16	459640	1840480	7.96	12.97	13.10	13.03	0.09
17	458500	1840230	7.88	9.1	10.16	9.63	0.75
18	458060	1840550	7.65	5.68	5.32	5.50	0.25
19	457560	1840200	7.65	11.28	11.43	11.36	0.11
20	457680	1839720	8.03	9.88	9.33	9.61	0.39
Average			**7.99**	**7.99**	**8.00**	**7.99**	**0.01**

Table B-7 Results of total cadmium concentration analyses in stream sediment from Huai Nong Khieo.

Sample No.	X UTM	Y UTM	pH	Total Cd1 (mg/kg)	Total Cd2 (mg/kg)	Mean	SD
24	461360	1840000	7.8	4.07	3.45	3.76	0.44
26	460500	1839000	8.12	6.4	5.80	6.10	0.42
28	460800	1838400	8.39	4.87	5.27	5.07	0.28
27	460200	1838700	8.07	2.81	2.66	2.74	0.11
29	459800	1839000	7.6	6.2	5.97	6.08	0.17
30	458980	1838560	7.5	7.96	8.16	8.06	0.14
31	458230	1838430	7.81	7.89	7.94	7.91	0.03
Average			**7.90**	**5.74**	**5.61**	**5.67**	**0.10**

Table B-8 Cadmium and zinc analyzed for sequential extraction.

Sample No.	Cd BCR1	mean	SD BCR1	Zn BCR1	mean	SD BCR1
1_1	9.24	8.55	0.99	152.32	152.32	0.01
1_2	7.85			152.31		
2_1	35.29	35.94	0.92	650.57	650.57	0.00
2_2	36.59			650.57		
3_1	6.61	6.57	0.06	222.38	222.38	0.00
3_2	6.53			222.38		
4_1	8.85	8.87	0.03	227.04	227.03	0.01
4_2	8.89			227.03		
5_1	17.38	16.43	1.35	384.67	384.67	0.00
5_2	15.47			384.67		
6_1	8.70	8.32	0.54	309.47	309.46	0.01
6_2	7.94			309.45		
7_1	28.30	28.80	0.70	939.62	939.56	0.09
7_2	29.30			939.50		
8_1	14.83	16.03	1.69	652.58	652.54	0.06
8_2	17.22			652.50		
9_1	11.36	11.65	0.40	361.86	361.85	0.01
9_2	11.93			361.85		
10_1	14.59	14.79	0.29	467.48	467.48	0.01

Sample No.	Cd BCR1	mean	SD BCR1	Zn BCR1	mean	SD BCR1
10_2	14.99			467.47		
23_1	2.42	2.34	0.11	81.54	80.71	1.17
23_2	2.26			79.88		
22_1	2.43	2.61	0.26	139.66	138.95	1.00
22_2	2.79			138.25		
21_1	2.83	2.76	0.09	157.03	155.51	2.15
21_2	2.70			153.99		
13_1	3.16	3.11	0.07	77.00	74.96	2.89
13_2	3.06			72.91		
14_1	0.51	0.49	0.03	87.09	86.97	0.17
14_2	0.48			86.85		
15_1	1.55	1.52	0.04	152.63	151.48	1.62
15_2	1.49			150.34		
16_1	3.79	3.90	0.15	217.61	215.97	2.32
16_2	4.00			214.33		
17_1	4.52	4.45	0.11	176.95	176.10	1.20
17_2	4.37			175.26		
18_1	0.21	0.21	0.01	nd	nd	nd
18_2	0.20			nd		
19_1	5.48	5.64	0.22	200.25	198.96	1.83
19_2	5.79			197.66		
20_1	2.39	2.41	0.03	147.65	146.55	1.56
20_2	2.44			145.45		
24_1	0.18	0.17	0.02	0.55	0.55	0.00
24_2	0.16			0.55		
26_1	0.20	0.20	0.01	0.11	0.11	0.00
26_2	0.20			0.11		
28_1	nd	-	-	nd	-	-
28_2	nd			nd		
27_1	0.33	0.32	0.01	nd	-	-
27_2	0.32			nd		
29_1	0.14	0.13	0.01	0.40	0.37	0.04
29_2	0.13			0.34		
30_1	0.25	0.27	0.02	1.66	1.63	0.07
30_2	0.28			1.60		
31_1	0.10	0.11	0.00	650.84	650.57	0.19
31_2	0.11			650.58		

Sample No.	Cd BCR2	mean	SD BCR2	Zn BCR2	mean	SD BCR2
1_1	9.21	9.20	0.02	247.03	246.75	0.41
1_2	9.19			246.46		
2_1	37.48	37.42	0.08	572.17	572.09	0.11
2_2	37.37			572.02		
3_1	12.37	12.29	0.12	268.97	268.76	0.29
3_2	12.21			268.56		
4_1	15.42	15.35	0.09	269.88	270.19	0.43
4_2	15.29			270.49		
5_1	21.04	20.76	0.39	440.11	440.00	0.15
5_2	20.49			439.89		
6_1	14.71	14.70	0.02	255.46	254.83	0.90
6_2	14.69			254.19		
7_1	19.71	19.76	0.08	850.12	851.12	1.42
7_2	19.82			852.13		
8_1	28.87	28.75	0.17	578.50	578.35	0.20
8_2	28.63			578.21		
9_1	28.86	28.83	0.05	414.15	414.57	0.58
9_2	28.79			414.98		
10_1	21.93	21.89	0.06	488.89	489.09	0.28
10_2	21.85			489.29		
23_1	5.18	5.13	0.07	89.30	89.22	0.11
23_2	5.08			89.14		
22_1	3.51	3.50	0.01	91.61	91.41	0.28
22_2	3.50			91.21		
21_1	3.96	3.97	0.01	128.18	128.21	0.04
21_2	3.98			128.24		
13_1	2.21	2.20	0.01	40.56	39.57	1.41
13_2	2.19			38.57		
14_1	1.31	1.29	0.02	354.57	353.36	1.72
14_2	1.28			352.15		
15_1	4.68	4.69	0.01	219.31	219.23	0.11
15_2	4.70			219.15		
16_1	11.06	10.98	0.11	363.95	363.70	0.35
16_2	10.90			363.46		
17_1	6.15	6.37	0.31	225.00	224.01	1.40
17_2	6.59			223.01		
18_1	0.95	0.95	0.01	44.83	43.91	1.30

Sample No.	Cd BCR2	mean	SD BCR2	Zn BCR2	mean	SD BCR2
18_2	0.94			42.99		
19_1	6.59	6.55	0.07	309.89	310.02	0.19
19_2	6.50			310.15		
20_1	3.91	3.91	0.00	214.09	213.34	1.06
20_2	3.91			212.59		
24_1	0.77	0.77	0.00	34.53	33.84	0.98
24_2	0.78			33.15		
26_1	1.12	1.17	0.06	18.24	17.89	0.49
26_2	1.21			17.54		
28_1	1.06	1.03	0.04	26.05	26.42	0.52
28_2	1.01			26.78		
27_1	0.43	0.45	0.02	8.48	8.95	0.67
27_2	0.46			9.42		
29_1	1.54	1.52	0.03	44.63	44.75	0.17
29_2	1.50			44.88		
30_1	2.86	2.84	0.03	53.59	53.54	0.08
30_2	2.81			53.49		
31_1	1.90	1.89	0.02	26.69	26.57	0.18
31_2	1.87			26.45		
Sample No.	**Cd BCR3**	**mean**	**SD BCR3**	**Zn BCR3**	**mean**	**SD BCR3**
1_1	0.60	0.59	0.02	31.73	31.69	0.06
1_2	0.57			31.65		
2_1	1.03	1.03	0.01	48.84	48.70	0.20
2_2	1.03			48.56		
3_1	nd	0.82	0.01	23.06	22.97	0.13
3_2	0.81			22.88		
4_1	0.85	0.86	0.01	46.03	23.02	0.02
4_2	0.85			23.00		
5_1	0.97	0.96	0.01	31.47	31.30	0.24
5_2	0.96			31.13		
6_1	0.77	0.77	0.01	23.59	23.47	0.16
6_2	0.78			23.36		
7_1	1.39	1.38	0.96	79.74	79.67	0.10
7_2	1.37			79.60		
8_1	1.17	1.16	0.01	52.16	52.14	0.03
8_2	1.16			52.12		

Sample No.	Cd BCR3	mean	SD BCR3	Zn BCR3	mean	SD BCR3
9_1	0.98	1.04	0.09	29.18	28.83	0.49
9_2	1.10			28.48		
10_1	1.03	1.07	0.05	43.48	43.42	0.08
10_2	1.10			43.37		
23_1	0.37	0.36	0.01	2.24	2.22	0.03
23_2	0.35			2.20		
22_1	nd	-	-	2.81	2.68	0.18
22_2	nd			2.55		
21_1	0.23	0.22	0.01	60.83	60.64	0.26
21_2	0.21			60.46		
13_1	0.11	0.11	0.01	nd	-	-
13_2	0.12			nd		
14_1	0.19	0.19	0.00	12.40	12.31	0.13
14_2	0.19			12.22		
15_1	0.14	0.15	0.00	34.75	34.55	0.29
15_2	0.15			34.35		
16_1	0.29	0.29	0.00	9.83	9.69	0.20
16_2	0.29			9.55		
17_1	0.30	0.30	0.00	40.47	39.31	1.64
17_2	0.30			38.15		
18_1	0.28	0.28	0.01	nd	-	-
18_2	0.27			nd		
19_1	0.42	0.42	0.01	32.13	32.09	0.07
19_2	0.41			32.04		
20_1	0.32	0.32	0.01	34.49	34.35	0.20
20_2	0.31			34.21		
24_1	0.38	0.38	0.00	nd	-	-
24_2	0.38			nd		
26_1	nd	-	-	0.95	0.83	0.17
26_2	nd			0.71		
28_1	0.20	0.20	0.00	1.05	1.00	0.07
28_2	0.20			0.95		
27_1	nd	-	-	nd	-	-
27_2	nd			nd		
29_1	0.36	0.36	0.00	9.89	9.77	0.17
29_2	0.37			9.65		
30_1	nd	-	-	2.40	2.28	0.18

Sample No.	Cd BCR3	mean	SD BCR3	Zn BCR3	mean	SD BCR3
30_2	nd			2.15		
31_1	nd	-	-	52.40	52.30	0.14
31_2	nd			52.20		
Sample No.	**Cd BCR4**	**mean**	**SD BCR4**	**Zn BCR4**	**mean**	**SD BCR4**
1_1	6.83	6.81	0.01	372.12	371.99	0.17
1_2	6.80			371.87		
2_1	2.82	2.79	0.02	76.54	76.45	0.13
2_2	2.75			76.35		
3_1	3.52	3.51	0.01	41.64	41.48	0.22
3_2	3.50			41.32		
4_1	2.36	2.35	0.01	42.42	42.39	0.04
4_2	2.33			42.36		
5_1	2.56	2.53	0.02	42.40	42.32	0.11
5_2	2.49			42.25		
6_1	2.88	2.88	0.00	33.51	33.46	0.07
6_2	2.88			33.41		
7_1	2.72	2.71	0.00	62.14	62.12	0.03
7_2	2.71			62.10		
8_1	3.35	3.33	0.01	44.16	44.14	0.03
8_2	3.31			44.12		
9_1	3.49	3.44	0.03	44.85	44.81	0.06
9_2	3.40			44.77		
10_1	3.13	3.13	0.00	46.56	46.40	0.22
10_2	3.12			46.24		
23_1	2.68	2.67	0.01	27.52	27.50	0.02
23_2	2.66			27.49		
22_1	2.95	2.93	0.01	4.59	4.54	0.07
22_2	2.92			4.50		
21_1	3.15	3.13	0.01	8.82	8.81	0.01
21_2	3.12			8.80		
13_1	2.17	2.17	0.00	14.07	14.04	0.05
13_2	2.16			14.00		
14_1	2.37	2.34	0.02	nd	-	-
14_2	2.31			nd		
15_1	3.14	3.12	0.02	16.04	15.96	0.11
15_2	3.10			15.88		

Sample No.	Cd BCR4	mean	SD BCR4	Zn BCR4	mean	SD BCR4
16_1	3.48	3.47	0.01	42.95	42.84	0.15
16_2	3.46			42.74		
17_1	3.10	3.10	0.00	37.28	37.26	0.03
17_2	3.09			37.24		
18_1	4.32	4.32	0.00	18.31	18.26	0.07
18_2	4.32			18.21		
19_1	4.53	4.53	0.00	66.69	66.47	0.31
19_2	4.52			66.25		
20_1	4.44	4.43	0.00	64.98	64.80	0.26
20_2	4.42			64.61		
24_1	2.06	2.06	0.00	8.40	8.33	0.10
24_2	2.06			8.25		
26_1	3.08	3.07	0.00	18.83	18.75	0.12
26_2	3.06			18.66		
28_1	2.53	2.52	0.01	14.89	14.78	0.16
28_2	2.51			14.67		
27_1	2.18	2.17	0.01	11.81	11.73	0.12
27_2	2.16			11.65		
29_1	2.26	2.25	0.01	14.41	14.41	0.01
29_2	2.23			14.40		
30_1	2.93	2.90	0.02	15.86	15.82	0.06
30_2	2.87			15.78		
31_1	2.38	2.37	0.00	17.66	17.39	0.38
31_2	2.37			17.12		

nd= not detected

Table B-9 Results of zinc analysis in stream sediment of Huai Mae Tao.

Sample No.	X UTM	Y UTM	pH	Total Zn (mg/kg)	BCR1 (mg/kg)	BCR2 (mg/kg)	BCR3 (mg/kg)	Final (mg/kg)	Sum Zn (mg/kg)
1	462200	1842210	8.31	1487.30	178.82	394.05	22.69	402.49	998.05
2	461740	1842420	8.37	1449.88	650.57	572.09	48.70	76.45	1347.81
3	460960	1842550	8.34	728.18	222.38	268.76	22.97	41.48	555.59
4	460880	1842980	8.14	723.88	227.03	270.19	23.02	42.39	562.63
5	460450	1843220	8.12	976.10	384.67	440.00	31.30	42.32	898.29
6	460000	1843200	8.13	720.59	309.46	254.83	23.47	33.46	621.22
7	459110	1842570	8.08	2300.00	939.56	851.12	79.67	62.12	1932.47
8	458170	1842190	8.3	1524.80	652.54	578.35	52.14	44.14	1327.18
9	458300	1842840	8.03	1070.67	361.85	414.57	28.83	44.81	850.06
10	457600	1842760	7.79	1333.27	467.48	489.09	43.42	46.40	1046.39
Average			**8.16**	**1231.47**	**439.44**	**453.31**	**37.62**	**83.61**	**1013.97**

Table B-10 Results of zinc analysis in stream sediment of Huai Mae Ku.

Sample No.	X UTM	Y UTM	pH	Total Zn (mg/kg)	BCR1 (mg/kg)	BCR2 (mg/kg)	BCR3 (mg/kg)	Final (mg/kg)	Sum Zn (mg/kg)
23	463000	1840300	8.26	200.11	80.71	89.22	2.22	27.50	199.65
22	462910	1840700	8.37	217.85	138.95	91.41	2.68	4.54	237.58
21	462500	1841000	8.11	297.34	155.51	128.21	60.64	8.81	353.17
13	461490	1841120	8.16	106.73	74.96	39.57	-	14.04	128.56
14	461100	1840420	7.66	383.94	86.97	353.36	12.31	-	452.63
15	460890	1840590	8.11	296.55	151.48	219.23	34.55	15.96	421.22
16	459640	1840480	7.96	579.90	215.97	363.70	9.69	42.84	632.21
17	458500	1840230	7.88	399.85	176.10	224.01	39.31	37.26	476.68
18	458060	1840550	7.65	40.77	-	43.91	-	18.26	62.16
19	457560	1840200	7.65	502.86	198.96	310.02	32.09	66.47	607.53
20	457680	1839720	8.03	456.17	146.55	213.34	34.35	64.80	459.03
Average			**7.99**	**316.55**	**142.62**	**188.72**	**25.31**	**30.05**	**366.40**

Table B-11 Results of zinc analysis in stream sediment of Huai Nong Khieo.

Sample No.	X UTM	Y UTM	pH	Total Zn (mg/kg)	BCR1 (mg/kg)	BCR2 (mg/kg)	BCR3 (mg/kg)	Final (mg/kg)	Sum Zn (mg/kg)
24	461360	1840000	7.8	28.39	0.55	17.89	-	8.33	26.77
26	460500	1839000	8.12	62.25	0.11	33.84	0.83	18.75	53.53
28	460800	1838400	8.39	62.76	-	26.42	1.00	14.78	42.19
27	460200	1838700	8.07	17.87	-	8.95	-	11.73	20.68
29	459800	1839000	7.6	77.15	0.37	44.75	9.77	14.41	69.30
30	458980	1838560	7.5	93.34	1.63	53.54	2.28	15.82	73.27
31	458230	1838430	7.81	99.77	1.60	26.57	52.30	17.39	97.86
Average			**7.9**	**63.08**	**0.85**	**30.28**	**13.23**	**14.46**	**54.80**

Table B-12 Results of cadmium analysis in stream sediment of Huai Mae Tao.

Sample No.	X UTM	Y UTM	pH	Total Cd (mg/kg)	BCR1 (mg/kg)	BCR2 (mg/kg)	BCR3 (mg/kg)	Final (mg/kg)	Sum (mg/kg)
1	462200	1842210	8.31	24.53	8.55	9.20	0.59	6.81	25.15
2	461740	1842420	8.37	64.56	35.94	37.42	1.03	2.79	77.18
3	460960	1842550	8.34	23.69	6.57	12.29	0.82	3.51	23.19
4	460880	1842980	8.14	25.06	8.87	15.35	0.86	2.35	27.42
5	460450	1843220	8.12	35.17	16.43	20.76	0.96	2.53	40.68
6	460000	1843200	8.13	22.85	8.32	14.70	0.77	2.88	26.67
7	459110	1842570	8.08	66.19	28.80	19.76	1.38	2.71	52.65
8	458170	1842190	8.3	39.73	16.03	28.75	1.16	3.33	49.26
9	458300	1842840	8.03	32.17	11.65	28.83	1.04	3.44	44.95
10	457600	1842760	7.79	37.21	14.79	21.89	1.07	3.13	40.87
Average			**8.16**	**37.12**	**15.59**	**20.90**	**0.97**	**3.35**	**40.80**

Table B-13 Results of cadmium analysis in stream sediment of Huai Mae Ku.

Sample No.	X UTM	Y UTM	pH	Total Cd (mg/kg)	BCR1 (mg/kg)	BCR2 (mg/kg)	BCR3 (mg/kg)	Final (mg/kg)	Sum (mg/kg)
23	463000	1840300	8.26	7.19	2.34	5.13	0.36	2.67	10.50
22	462910	1840700	8.37	7.69	2.61	3.50	-	2.93	9.05
21	462500	1841000	8.11	9.29	2.76	3.97	0.22	3.13	10.08
13	461490	1841120	8.16	4.93	3.11	2.20	0.11	2.17	7.59
14	461100	1840420	7.66	3.40	0.49	1.29	0.19	2.34	4.32
15	460890	1840590	8.11	6.27	1.52	4.69	0.15	3.12	9.48
16	459640	1840480	7.96	13.03	3.90	10.98	0.29	3.47	18.64
17	458500	1840230	7.88	9.63	4.45	6.37	0.30	3.10	14.21
18	458060	1840550	7.65	5.50	0.21	0.95	0.28	4.32	5.75
19	457560	1840200	7.65	11.36	5.64	6.55	0.42	4.53	17.13
20	457680	1839720	8.03	9.61	2.41	3.91	0.32	4.43	11.07
Average			**7.99**	**7.99**	**2.68**	**4.50**	**0.26**	**3.29**	**10.71**

Table B-14 Results of cadmium analysis in stream sediment of Huai Nong Khieo.

Sample No.	X UTM	Y UTM	pH	Total Cd (mg/kg)	BCR1 (mg/kg)	BCR2 (mg/kg)	BCR3 (mg/kg)	Final (mg/kg)	Sum (mg/kg)
24	461360	1840000	7.8	3.76	0.17	0.77	0.38	2.06	3.39
26	460500	1839000	8.12	6.10	0.20	1.17	-	3.07	4.43
28	460800	1838400	8.39	5.07	-	1.03	0.20	2.52	3.75
27	460200	1838700	8.07	2.74	0.32	0.45	-	2.17	2.94
29	459800	1839000	7.6	6.08	0.13	1.52	0.36	2.25	4.27
30	458980	1838560	7.5	8.06	0.27	2.84	-	2.90	6.00
31	458230	1838430	7.81	7.91	0.11	1.89	-	2.37	4.36
Average			**7.9**	**20.16**	**6.81**	**12.45**	**0.40**	**2.38**	**20.98**

Table B-15 Percentages of zinc fractions in the study area.

Sample No.	%BCR1 Zn	%BCR2 Zn	%BCR3 Zn	%Final Zn	Sample No.	%BCR1 Zn	%BCR2 Zn	%BCR3 Zn	%Final Zn	Sample No.	%BCR1 Zn	%BCR2 Zn	%BCR3 Zn	%Final Zn
1	18.73	30.34	3.90	45.73	**23**	40.42	44.69	1.11	13.78	**24**	2.06	66.83	-	31.11
2	47.16	41.47	3.53	5.54	**22**	58.48	38.47	1.13	1.91	**26**	0.20	62.21	1.53	34.46
3	39.13	47.29	4.04	7.30	**21**	44.03	36.30	17.17	2.49	**28**	-	62.61	2.36	35.03
4	39.45	46.95	4.00	7.37	**13**	58.31	30.78	-	10.92	**27**	-	43.27	-	56.73
5	41.83	47.85	3.40	4.60	**14**	19.21	78.07	2.72	-	**29**	0.52	63.36	13.83	20.40
6	48.67	40.08	3.69	5.26	**15**	35.96	52.05	8.20	3.79	**30**	2.18	71.68	3.05	21.18
7	47.48	43.01	4.03	3.14	**16**	34.16	57.53	1.53	6.78	**31**	1.61	26.67	52.50	17.46
8	48.01	42.55	3.84	3.25	**17**	36.94	46.99	8.25	7.82					
9	41.59	47.64	3.31	5.15	**18**	-	70.63	-	29.37					
10	43.64	45.66	4.05	4.33	**19**	32.75	51.03	5.28	10.94					
					20	31.93	46.48	7.48	14.12					
Average	**41.57**	**43.28**	**3.78**	**9.17**	**Average**	**39.22**	**50.27**	**5.87**	**10.19**	**Average**	**1.31**	**56.66**	**14.65**	**30.91**

Table B-16 Percentages of cadmium fractions in the study area.

Sample No.	% Cd BCR1	% Cd BCR2	% Cd BCR3	% Cd Final Residue	Sample No.	% Cd BCR1	% Cd BCR2	% Cd BCR3	% Cd Final Residue	Sample No.	% Cd BCR1	% Cd BCR2	% Cd BCR3	% Cd Final Residue
1	33.982	36.591	2.327	27.100	**23**	22.287	48.872	3.417	25.423	**24**	5.0142	22.859	11.296	60.831
2	46.567	48.486	1.338	3.609	**22**	28.844	38.718	-	32.438	**26**	4.4829	26.281	-	69.236
3	28.326	52.999	3.536	15.138	**21**	27.381	39.347	2.178	31.093	**28**	-	27.563	5.310	67.127
4	32.330	55.987	3.124	8.558	**13**	40.996	28.967	1.491	28.546	**27**	11.046	15.157	-	73.797
5	40.384	51.043	2.365	6.208	**14**	11.425	29.939	4.454	54.181	**29**	3.1452	35.631	8.538	52.686
6	31.202	55.105	2.888	10.804	**15**	16.037	49.492	1.535	32.935	**30**	4.4164	47.234	-	48.349
7	54.702	37.535	2.615	5.148	**16**	20.906	58.903	1.575	18.615	**31**	2.4301	43.235	-	54.335
8	32.534	58.355	2.355	6.756	**17**	31.285	44.819	2.117	21.779					
9	25.906	64.123	2.314	7.658	**18**	3.5614	16.445	4.849	75.144					
10	36.184	53.557	2.611	7.648	**19**	32.907	38.218	2.437	26.437					
					20	21.787	35.318	2.878	40.017					
Average	**36.212**	**51.378**	**2.547**	**9.863**	**Average**	**23.401**	**39.004**	**2.693**	**35.146**	**Average**	**5.09**	**31.14**	**8.38**	**60.91**

Appendix-C

Correlation plot of zinc

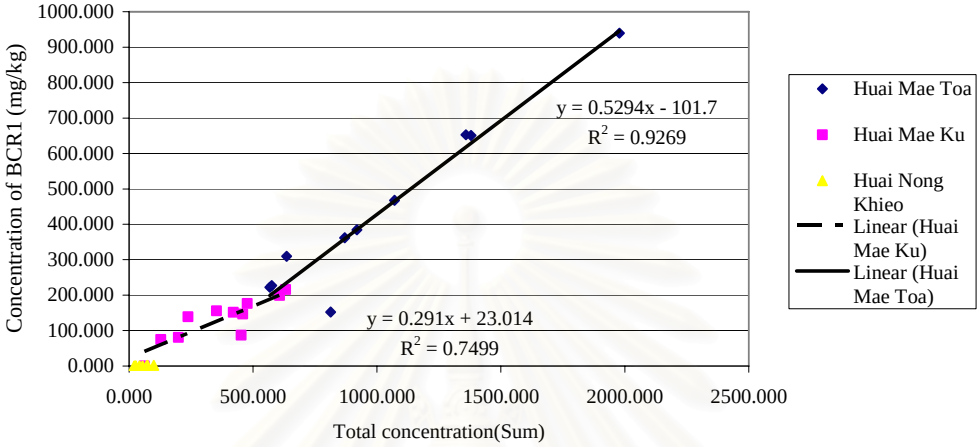

Figure C-1 Plots between BCR 1 of Zn and total Zn in each creek.

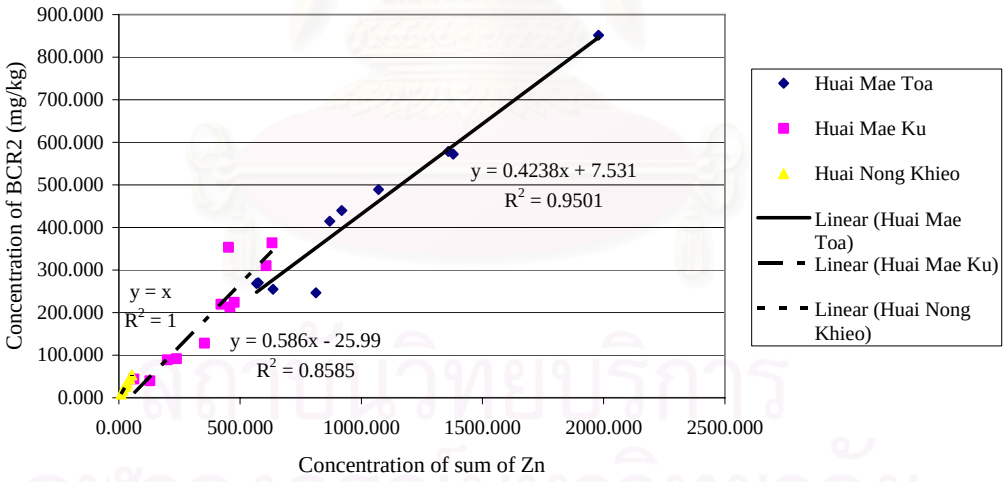

Figure C-2 Plots between BCR 2 of Zn and total Zn in each creek.

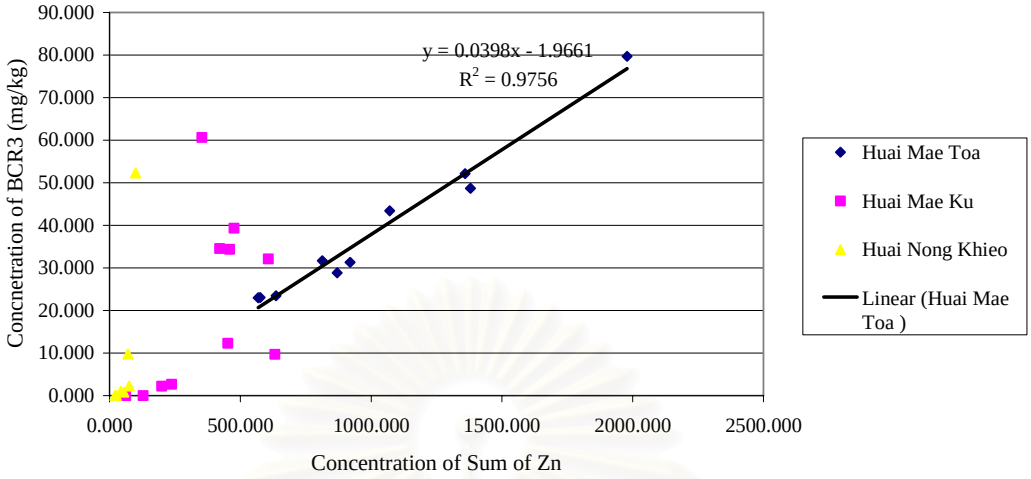

Figure C-3 Plots between BCR 3 of Zn and total Zn in each creek.

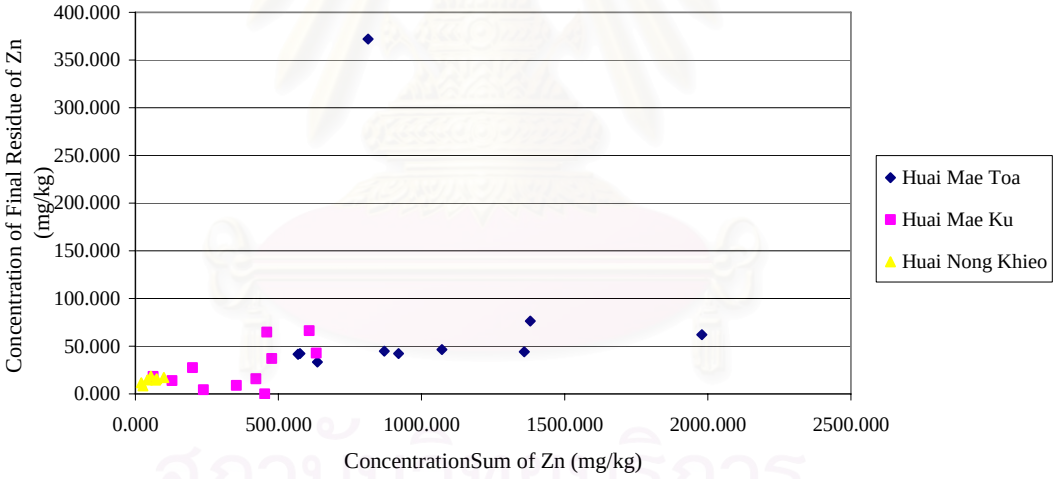

Figure C-4 Plots between BCR 4 of Zn and total Zn in each creek.

Appendix-D

Correlation plot ofcadmium

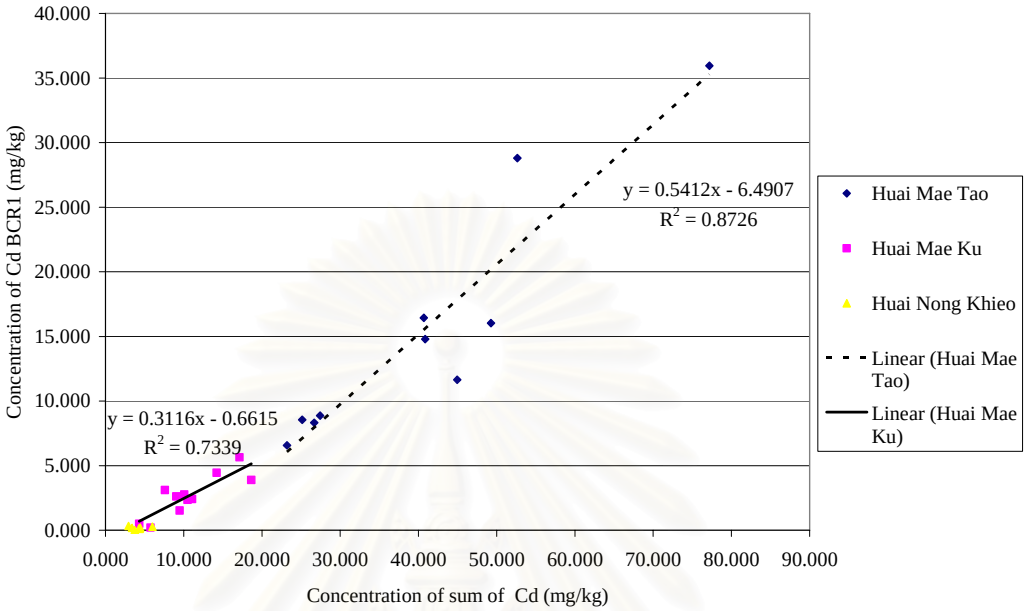

Figure D-1 Plots between BCR 1 of Cd and total Cd in each creek.

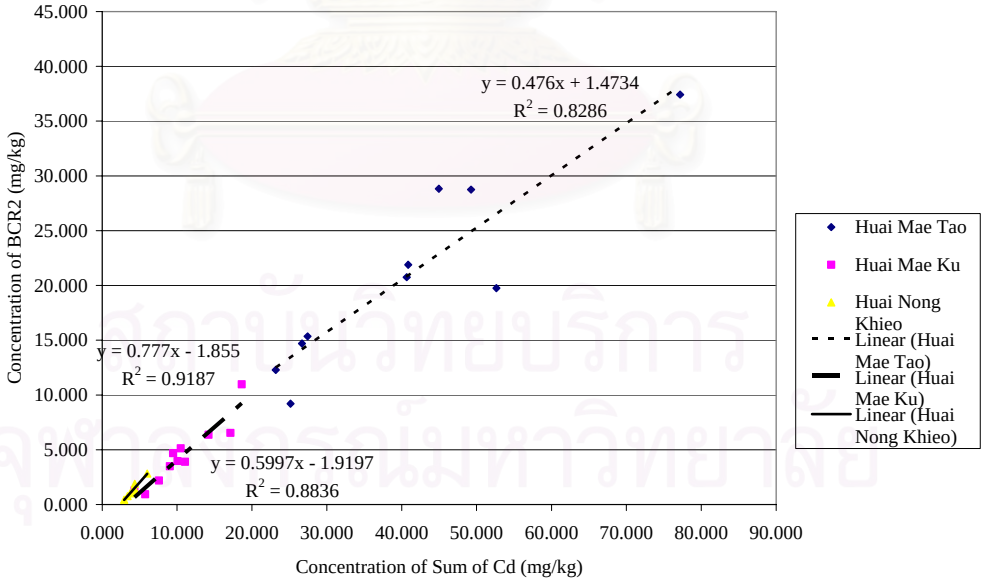

Figure D-2 Plots between BCR 2 of Cd and total Cd in each creek.

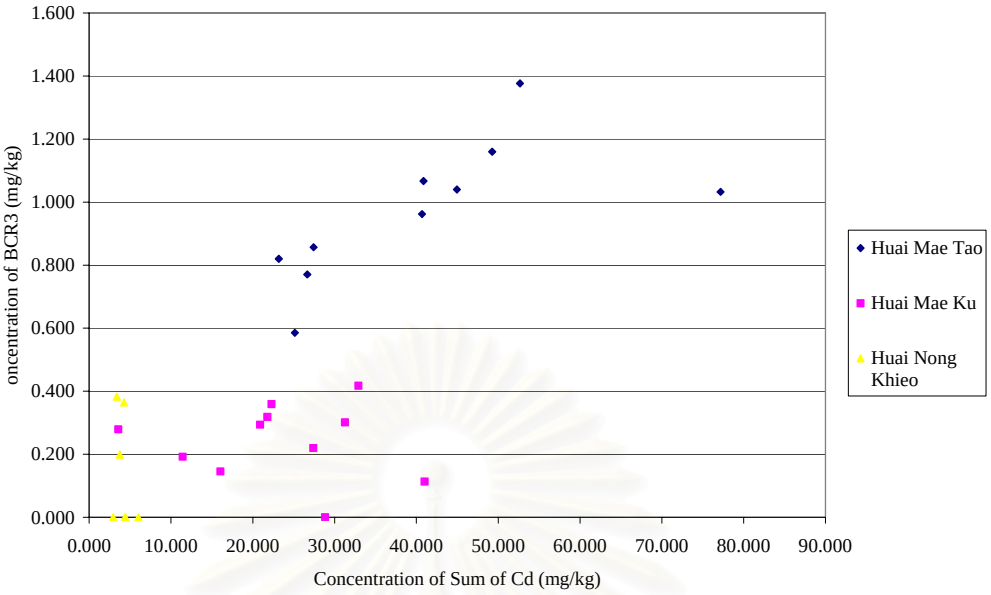

Figure D-3 Plots between BCR 3 of Cd and total Cd in each creek.

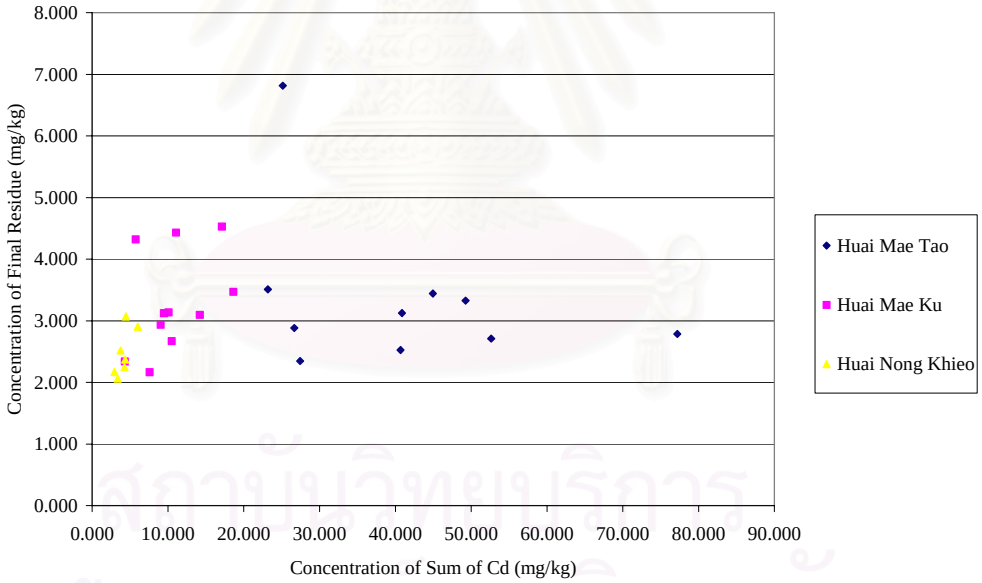

Figure D-4 Plots between BCR 4 of Cd and total Cd in each creek.

BIOGRAPHY

Miss Parada Maneewong was born on March 22, 1982 in Chonburi, Eastern of Thailand. She finished the high school study in 2000 from Rayongwittayakom School, and then entered Chulalongkorn University. She received a Bachelor of Science degree in Geology from the Department of Geology, Faculty of Science, Chulalongkorn University in 2004. Then she pursued the Master's degree international program in environmental management, Chulalongkorn University.