การกระจายตัวและแหล่งกำเนิดของโลหะหนักในตะกอนธารน้ำ ในบริเวณสันปันน้ำถ้ำทะลุ อำเภอบันนังสตา จังหวัดยะลา ภาคใต้ ประเทศไทย

นางสาว นันท์นภัส ณัชชากุลทรัพย์

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DISTRIBUTION AND SOURCES OF HEAVY METALS IN STREAM SEDIMENTS IN TUM TALU WATERSHED BUNNUNG SATA YALA SOUTHERN THAILAND

Miss Nannapat Natchakunlasap

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นันท์นภัส ณัชชากุลทรัพย์ : การกระจายตัวและแหล่งกำเนิดของโลหะหนักในตะกอนธารน้ำ ในบริเวณสันปันน้ำถ้ำทะลุ อำเภอบันนังสตา จังหวัดยะลา ภาคใต้ ประเทศไทย (DISTRIBUTION AND SOURCES OF HEAVY METALS IN STREAM SEDIMENTS IN TUM TALU WATERSHED, BUNNUNG SATA, YALA, SOUTHERN THAILAND) อ. ที่ปรึกษา : รศ. ดร. ปัญญา จารุศิริ, อ.ที่ปรึกษาร่วม : รศ. ดร. รอน วอทกิ้นส์ 101 หน้า ISBN 974-17-6456-1

งานวิจัยนี้เป็นการศึกษาเพื่อหาลักษณะ การกระจายตัวและแหล่งกำเนิดของโลหะหนัก ในตะกอนธารน้ำ ในบริเวณสันปันน้ำถ้ำทะลุ เนื่องมาจากไม่นานมานี้พบการปนเปื้อนของโลหะหนักในแม่น้ำปัตตานี เหมืองร้างในสันปันน้ำถ้ำทะลุถูกสงสัยว่า น่าจะเป็นแหล่งที่มาของโลหะหนักปนเปื้อนในระบบน้ำผิวดินและน้ำใต้ดิน การออกภาคสนามและการสุ่มเก็บตัวอย่างตะกอนธารน้ำถูกนำมาเพื่อวิเคราะห์หารูปแบบการกระจายตัวและแหล่งกำเนิดของโลหะหนัก ตะกอนธารน้ำขนาดละเอียดซึ่งถูกรวบรวมมาจาก63ตำแหน่ง นำมาผ่านการย่อยบางส่วน และวิเคราะห์หาค่าโลหะหนัก ด้วยเครื่องวิเคราะห์ไอซีพีโออีเอส

กองของเสียจากเหมือง, หน้าเหมืองร้างและ การรั่วของที่ฝังกลบของเสีย ได้ระบายน้ำกรดเหมือง ซึ่งเป็นตัวชี้ชัดถึงแหล่งที่มาของสารปนเปื้อน รูปแบบการกระจายตัวของความเข้มข้นของโลหะหนัก ในตะกอนธารน้ำนั้นแสดงค่าสูงในบริเวณตอนล่างสายน้ำของเหมืองร้างและที่ฝังกลบของเสีย ตรงกันข้ามกับบริเวณตอนบนสายน้ำของเหมืองร้าง แสดงค่าต่ำกว่า ความเข้มข้นของโลหะ อาร์เซนิก, ตะกั่ว และทองแดง ค่อยลดลงทีละน้อยไปจากแหล่งกำเนิดในเหมืองร้างและที่ฝังกลบของเสียในบริเวณตอนล่างสายน้ำ แต่ความเข้มข้นของสังกะสี และแคดเมียม เพิ่มขึ้นทีละน้อย พบการปนเปื้อนของโลหะ อาร์เซนิก, แคดเมียม, ตะกั่ว, ทองแดง และสังกะสีในตะกอนธารน้ำตั้งแต่ตอนบนสายน้ำของเหมืองร้าง และพบการปนเปื้อนอย่างมาก ตอนล่างสายน้ำของเหมืองร้างและที่ฝังกลบของเสีย แต่ไม่พบการปนเปื้อนของโลหะโครเมี่ยม ในสันปันน้ำนี้

กิจกรรมของมนุษย์ในสันปันน้ำเช่น การกระจายของของเสียโลหะหนักจากเหมืองร้างและโดยเฉพาะอย่างยิ่ง การรั่วของที่ฝังกลบของเสียซึ่งบรรจุไปด้วยของเสียอันตราย เป็นแหล่งกำเนิดของโลหะหนักเป็นพิษ ปนเปื้อนในตะกอนธารน้ำในสันปันน้ำถ้ำทะลุ อย่างไรก็ตาม แหล่งแร่สกานร์และสินแร่ซึ่งปรากฏอยู่ในธรรมชาติเป็นแหล่งกำเนิดส่วนน้อยมากโดยธรรมชาติ

สาขาวิชา...การจัดการสิ่งแวดล้อม.....ลายมือชื่อนิสิต.....

ปีการศึกษา.....2547.....ลายมือชื่ออาจารย์ที่ปรึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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KEY WORD: DISTRIBUTION / SOURCES / HEAVY METALS / STREAM SEDIMENTS / THUM TALU

NANNAPAT NATCHAKUNLASAP : DISTRIBUTION AND SOURCES OF HEAVY METALS IN STREAM SEDIMENTS IN TUM TALU WATERSHED BUNNUNG SATA YALA SOUTHERN THAILAND. THESIS ADVISOR: ASSOC. PROF. PUNYA CHARUSIRI, Ph.D., ASSOC. PROF. RON WATKINS, 101 pp. ISBN 974-17-6456 -1

Recently metals contamination in the Pattani river has become an acute problem of Pattani city. The abandoned mines in the Tum Talu watershed are suspected to be sources of heavy metals pollution in surface and groundwater system. Field investigations and stream sediments sampling have been carried out to examine the distribution pattern and sources of toxic metals. Fine fractions of stream sediments collected from 63 locations underwent partial digestion, and were analyzed by ICP-OES for As, Cd, Pb, Cr, Cu and Zn concentrations. Mine waste dumps, mineralized outcrops and landfill leaks discharging typical acid mine drainage clearly indicate that they are sources of contaminant metals. Distribution patterns show markedly high levels of metals in the downstream areas of abandoned mines and landfills. Concentrations of As, Pb and Cu decrease slightly downstream areas, away from sources at abandoned mines and landfills, but Zn and Cd concentrations gradually increase. The As, Cd, Pb, Cu and Zn concentrations begin to be contaminated upstream areas of abandoned miens and seriously contaminated downstream areas of abandoned mines and landfills. Chromium concentration is not a contaminant in this watershed. Antropogenic activity in the watershed, waste emanating from abandoned mines and especially leakages from landfills which contain hazardous wastes, are major sources of toxic metals contaminating stream sediments in the Tum Talu watershed. However, mineralization of skarns and ores which are considered as being natural occurrences are very minor sources.

Field of study..Environmental Management....Student's signature…….

Academic year. ……..2004……..Advisor's signature…….……...

Co-advisor's signature……..……

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CHAPTER I

INTRODUCTION

1.1 History

Tum Talu Watershed (Figure 1.1), Bunnung Sata, Yala, southern Thailand, is a headwater of the Pattani River which rises in the Bunnung Sata district, passes through Yala province, and flows into the Gulf of Thailand at Pattani Bay. In the past, there have been several tin mines which operated in this watershed. In 1985, most of the mines ceased their activities as a result of the collapse of tin prices in the world market. Consequently, some tailings piles, mineralised outcrops, waste rock, and a sludge lagoon, which are all hazardous wastes, were left over without any environmental protection measures in place.

The polluted environments of the watershed have been investigated by researchers (see Varathorn, 1997 and Geater et al., 2000). The streams were found to contain lead levels that exceeded permissible values of river and drinking water quality standards of the World Health Organization (WHO) at 0.05 mg/l during 1986-1992 and 1996-1997 (Varathorn, 1997). The stream sediments contained lead levels that were more than 3,333 mg/kg of sediment (Varathorn, op. cit). School children (6-12 years) living in the area had blood lead levels exceeding 10 mg/dl (Geater et al., 2000).

These problems were of great concern to the Thai government. During 2000-2002, the area was the site of remediation projects by the Division of Based-Industry and Mines, the Department of Mineral Resources. Mine wastes, including tailings, low-grade ores and waste rocks, were dumped into double lined landfills. Even though care has been taken in the area, contamination still exists. Streams running out of the watershed still contained arsenic and lead contents above the standards for drinking water 0.01mg/l for arsenic and 0.05 mg/l for lead (Department of Mineral and Resources, 2000).

Nowadays, particular sources of heavy metals in the watershed still have not yet been identified. The abandoned mines seem to be obvious potential sources of metals

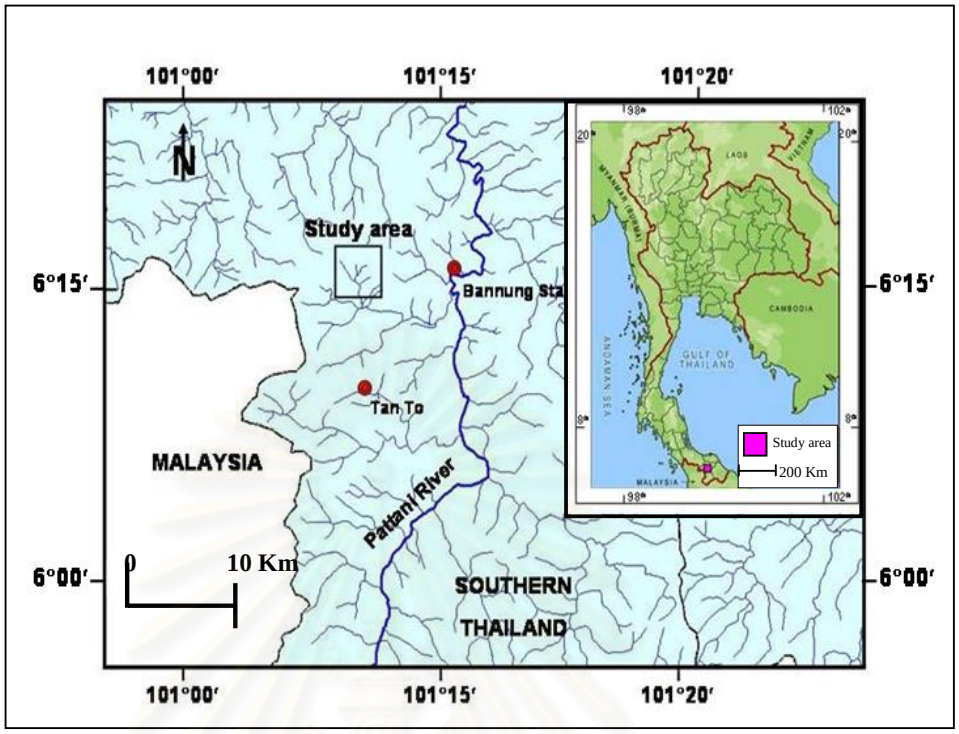

Figure 1.1 Index map showing location of the study area in the Tum Talu watershed, which is a head water of the Pattani river

pollution, however, ore deposits and rocks in the natural ecosystem may also pollute through natural exposures. To identify pollutant sources and to distinguish between natural and anthropogenic sources of metals in the watershed is, therefore, quite taxing.

1.2 Objectives

The aims of the study are to evaluate the metals distribution pattern of the Tum Talu watershed and to identify possible source areas.

1.3 Scope

Metals concentrations in the stream sediments were determined by partial metal geochemistry using modification of the standard method of EPA 3025 A; microwave assisted acid digestion of sediments. The metal distribution patterns are illustrated by elemental maps. The source locations of metals were pointed out by field evidence and abnormally high concentration values. To distinguish between anthropogenic and natural sources, statistics were applied using univariate and bivariate methods.

1.4 Expected results

For the remedial investigation (RI) of abandoned mines, the site characterization study is necessary to identify sources, to determine the extent of metals contamination, and to investigate hazardous areas. In providing this information, the results of the study will be invaluable to decision makers in designing practicable site remedial plans, and to environmental scientists/managers and technologists in the prevention of pollution from future operations.

CHAPTER II

BACKGROUND

2.1 Study area

2.1.1 Location

Tum Talu watershed, Bannang Sata district, Yala province, southern Thailand (Figure 2.1) is situated between latitudes 6° 17′ 14′′and 6° 14′ 24′′N and longitudes 101° 8′ 2′′and 101° 12′ 14′′E. It appears on the topographic map scale 1:50,000 series, L7017 map sheet 5221IV (Amphoe Yaha) and 5221III (Amphoe Than To) at approximate horizontal grid references of 6935500N to 6932500N and vertical grid references of 7361500E to 7428750E. It covers a total area of approximately 21 km^2. The area is located in a humid region having two marked seasons: the dry season from January to June, and the rainy season from June to December.

2.1.2 Geography and Geology

Based on landscape analyses using aerial photographs and field investigations, the study area can be divided into 3 geographic terrains, namely high mountain terrain, hill terrain and plain (Figure 2.2). The high mountain terrain has elevations of 250 to 920 meters above mean sea level (amsl). The elevated ridge has a NW-SE trend and covers 75% of the study area. The maximum altitude of the area is about 914 m amsl. The intermountain plain has elevations of 50 to 80 amsl and occupies 5% of the study area. The hill terrain occupies the remaining 20%. Streams can be divided into 2 types, permanent streams (flow all year round) and intermittent streams (seasonal flow). On the basis of topographic map analysis, drainage patterns can be divided into 2 types parallel pattern and dendritic pattern. The latter is more common and the former is found only in areas of high elevation.

The area is underlain by three main rock types (Figure 2.3) which are carbonate

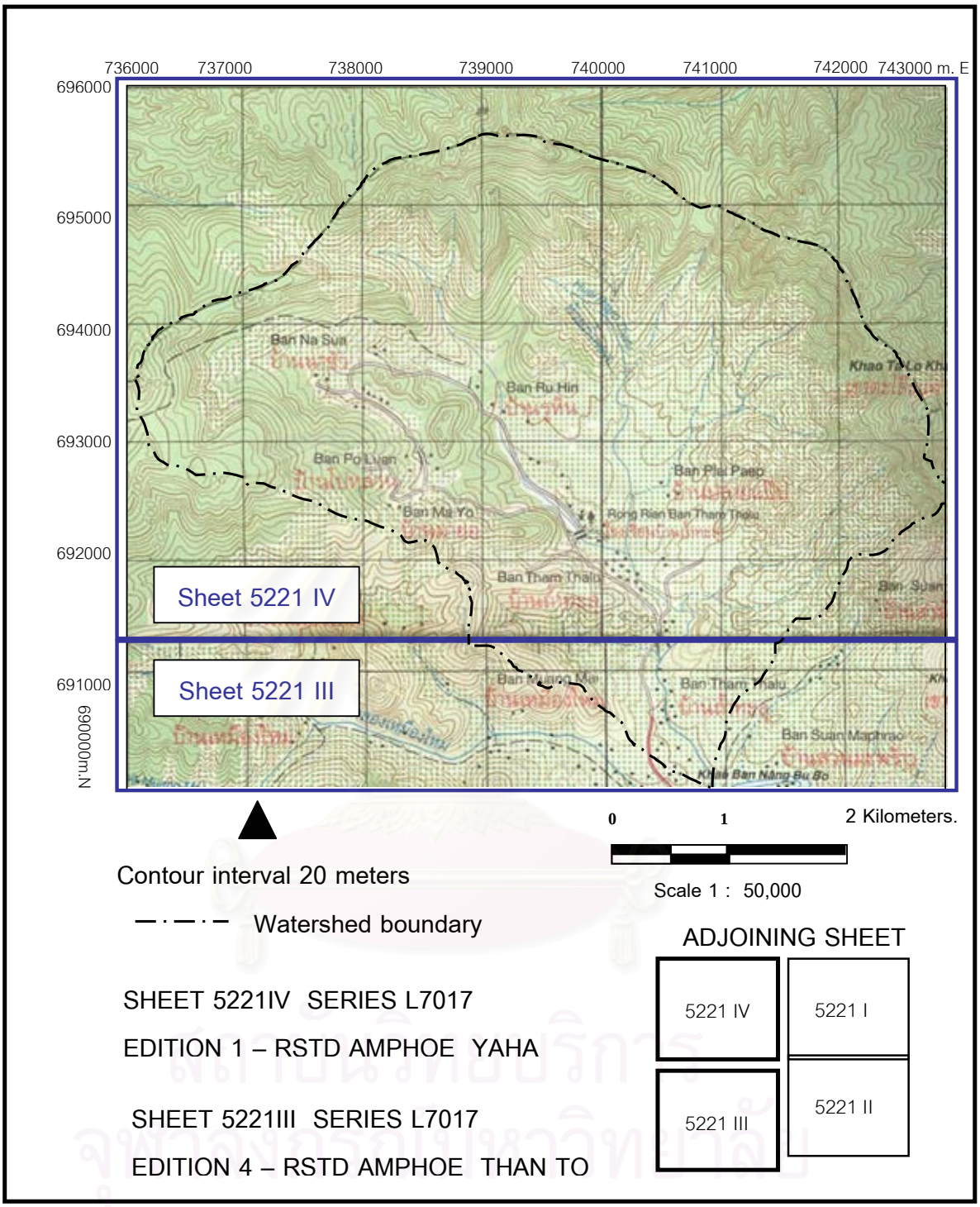

Figure 2.1 The topographic map showing the location of Tum Talu watershed, Yala province

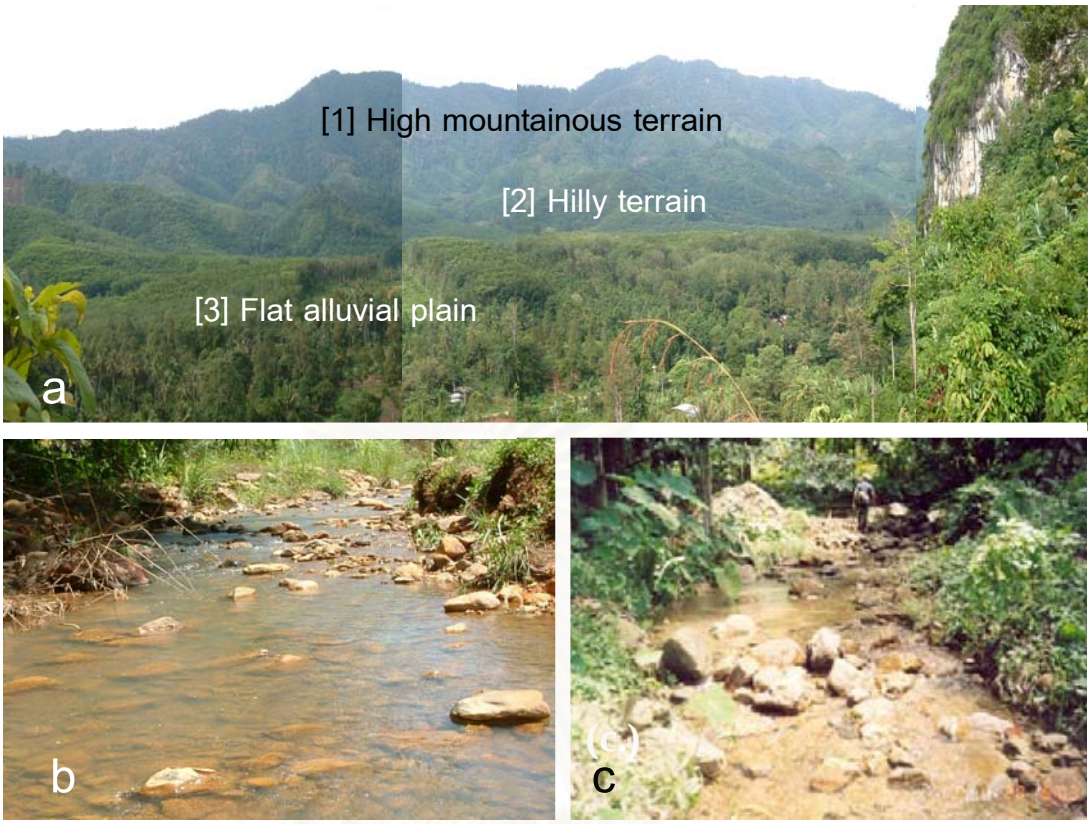

Figure 2.2 (a) General physiographic features of the study area with 3 kinds of topography including [1] high mountainous terrain, [2] hilly terrain, and [3] flat alluvial plain, (b) Geomorphology of downstream channels with cobbles and pebbles and (c) nature of the upstream channel surrounded by dense vegetation.

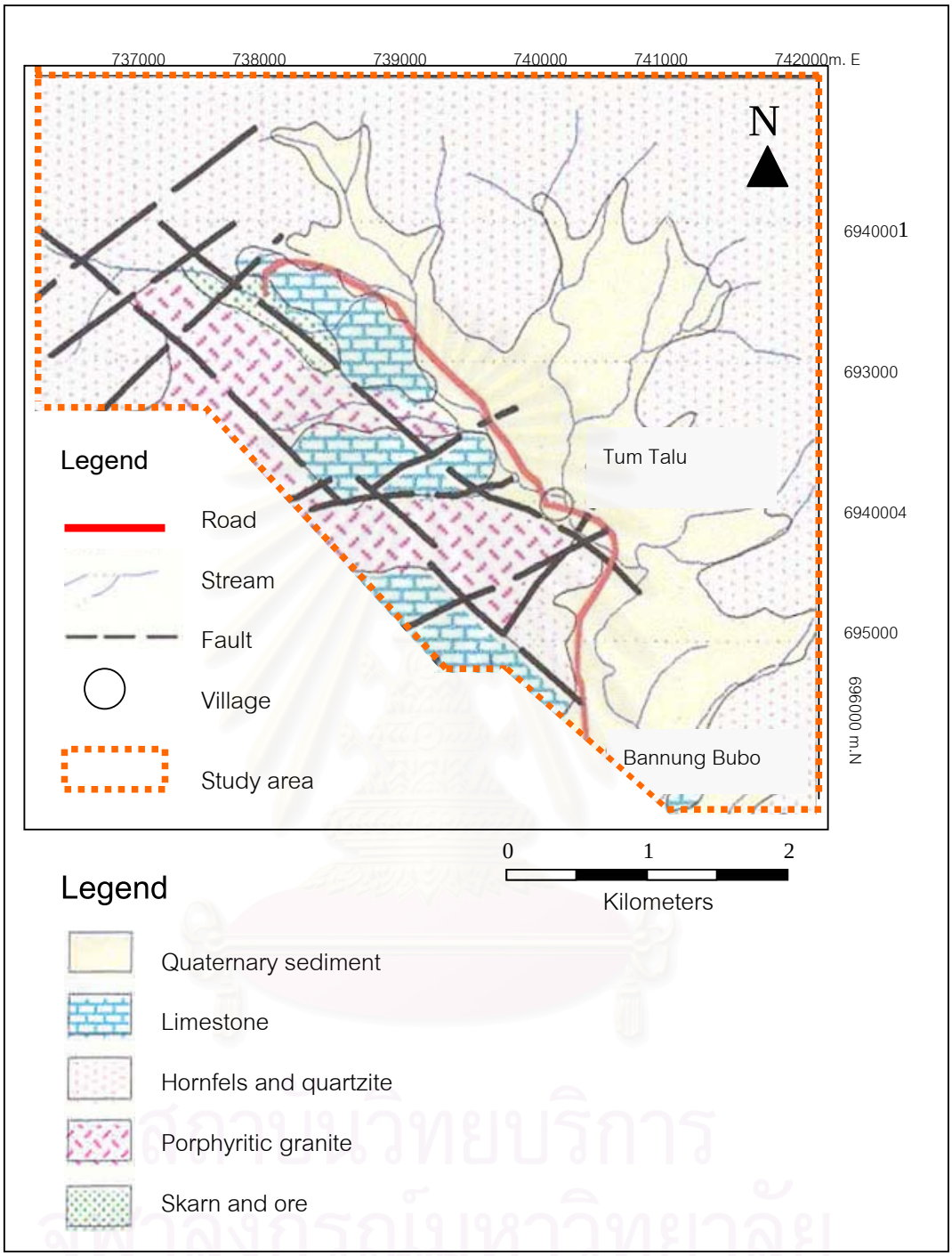

Figure 2.3 Geological map of the study area (Department of Mineral and Resources, 2001).

rocks, granitoids and metamorphic rocks. Of these rocks, metamorphic rocks are the most common and are found in about 50 percent of the mapped area. Carbonate rocks are exposed in the centre and in the west of the study area. Granitoids are found in the west and occupy about 20 percent of the total area, intruding into the clastic and carbonate host rocks, which later metamorphosed into quartzite, hornfels, marbles and skarn. Quartzite and hornfels occupy about 50 percent of the total area and are distributed in the north and northeast. Marble and skarn are found in the middle and to the west. Metal-sulfide veins cut through the skarn rocks and form cassiterite-skarn-sulfides type deposits. The zone of tin-sulfide deposition occurs along the contact between granite and limestone (Charusiri and Charusiri, 2000). Tin mineralisation occurs in the eastern part of the area and in the NW-SE trending fault zones (Department of Mineral and Resources, 2001). Tin concentrations are usually high in this type of ore body and mineral assemblages including galena (PbS), sphalerite (ZnS), pyrrhotite ($Fe_{1-x}S$), magnetite (Fe_3O_4), arsenophyrite (FeAsS), hematite (Fe_2O_3), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), argentite (AgS), calcite ($CaCO_3$) and minor amounts of garnet, have been reported by Department of Mineral and Resources (2000).

2.1.3 Abandoned tin-mines

The Tum Talu watershed contains 4 abandoned tin mines, namely Euro-Thai (Nasua), Tum Talu, Po Luan and Bu Lunt. Euro-Thai and Tum Talu were large scale mines with ore processing plants, while Po Luan and Bulunt were much smaller operations.

Euro-Thai (Figure 2.4 a.) is a 0.5 km^2 open-pit mine and is located upstream, in the northwest of the watershed. Tin was produced at about 1,600 tons annually (Mineral and Resources Department, 2000). The Tum Talu (Figure 2.4 b), Po Luan (Figure 2.4 c) and Bu Lunt (Figure 2.4 d) were water flush mines. After the collapse of tin prices on the world market in 1985, Tum Talu, Po Luan and Bu Lunt were closed but Euro-Thai become a mine for lead products until it was closed in 1992.

Recently, both the abandoned Tum Talu and Euro-Thai mines came under the auspices of the Prevention and Remediation of Toxic Metals Project 2000 – 2002, of

Figure 2.4 Abandoned quarries in the Tum Talu watershed area. (a) The Tum Talu mine, (b) general features of the Euro-Thai mine, (c) part of the exposed mine front of the Po Luan mine, (d) and the Bu Lunt mine.

Figure 2.5 The watershed area surrounding the Euro-Thai mine was under remediation. (a) and (b) Cut- and fill- slope bench nearby the abandoned mine was taken to be in dumped in the pit. (c) Landfills were built on stream banks.

the Department of Based-Industry and Mine, Ministry of Industry. At Euro-Thai mine, soil derived from a nearby mountain (Figure 2.5 a), was unsystematically dumped into the pit (Figure 2.5 b) and buried the weathered ore outcrops, which became exposed on the western side of the mine stream. Double lined landfills, which are lined by compact clays and PVC, and covered by clays and soil were built on the bank of the stream (Figure 2.5 c). They contain 50,000 m^3 tailings each. Some waste rocks and tailings were buried in the landfills, however, mineralized outcrops and waste rock are still exposed in places.

2.2 Theoretical background

Mineralized outcrops, tailings and waste rocks are hazardous wastes that can generate environmental problems, such as acid mine drainage, and metals contamination of ground water, surface water and sediments. Acid mine drainage (AMD) (see US EPA, 2000) or acid rock drainage (ARD) are generated from mine wastes, waste materials, overburdens, tailings, or mine structures, such as pits or underground workings. AMD is generated when metal sulfide minerals are oxidized. For example, pyrite (Fe_2S) undergoes chemical oxidation, which is described in equation (2.1) in the following reactions:

$$FeS_{2(s)} + 14O_{2(g)} + 4H_2O_{(l)} \text{ ---> } 4Fe^{2+}_{(aq)} + 8SO_4^{2-}{}_{(aq)} + 8H^+_{(aq)} \quad (2.1)$$

Iron II ions (Fe^{2+}) and acidic hydrogen ions are released into the streams that runoff the mine drainage tunnels or tailings piles. Iron II ions are oxidized to form iron III ions as shown in equation (2.2) in the following reaction:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \text{ ---> } 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \quad (2.2)$$

The iron III ions (Fe^{3+}) now hydrolyze in water to form iron III hydroxides. This process releases even more hydrogen ions into the aquatic environment which continues to reduce the pH. The iron III hydroxide formed in this reaction is called "yellow boy", a yellowish-orange precipitate that turns the acidic runoff in the streams to

an orange or red color and covers the stream beds with slimy coatings. Aquatic life that dwells on the bottom channel of the stream is soon killed off. Equation (2.3) describes this reaction.

$$4Fe^{3+}_{(aq)} + 12\ H_2O_{(l)} \quad ---> \quad 4Fe(OH)_{3(s)} + 12H^{+}_{(aq)} \qquad (2.3)$$

The net result of equations 1-3, is that the pyrite is oxidized releasing acidic hydrogen ions into the water and coating the stream bed with "yellow boy". The sum of equations 1-3 is equation (4) which is shown in the following reaction

$$4FeS_{2(s)} + 15O_{2(g)} + 14H_2O_{(l)} \quad ---> \quad 4Fe(OH)_{3(s)} + 8SO_4^{2-}{}_{(aq)} + 16H^{+}_{(aq)} \qquad (2.4)$$

Sulfides of copper, zinc, cadmium, lead and arsenic undergo similar geochemical reactions resulting in the contribution of toxic metals into mine water and sediments. The contaminated sediments will be a long-term source of metals through potential re-dissolution in the water. This can lead to chronic contamination of surface water and becomes a risk to human health, aquatic and non-aquatic life through contamination of the food chain (Tom, R.G. and James, 2004).

2.2.1 Origin and sources of metals

Metals contamination of stream sediments can originate from both natural sources and human activity. For example, dissolved metal pollutants from industrial waste water discharged into surface water partition to sediments in the stream (US EPA, 2000). In addition, fine-grained waste materials and eroded materials from mineralized outcrops, pits, tailings piles, overburden piles, ore stock piles and access roads, can become sediments in the natural streams.

Natural sources of metals in the environment depend largely on rock type, the processes by which they are formed, and those which affect them after lithification. Potentially toxic metals are found in trace amounts in rock-forming minerals, mainly concentrated in ever decreasing volumes/mass of residual magma. Most metals tend to concentrate in host residual (hydrothermal) fluids during the later stages of magma

differentiation. They may be injected or infiltrated into enclosing rocks and precipitated as ore minerals as temperatures drop and chemical reactions take place between hydrothermal fluids and rocks. These ores include Hg as cinnabar (HgS), As as arsenopyrite (FeAsS), Pb as galena (PbS), Zn as sphlerite (ZnS), Cu as chalcopyrite ($CuFeS_2$) and Fe as pyrite (FeS_2). Still others may be hosted in ore minerals. Good examples are Cd which substitutes in part for Zn in sphalerite (Zn[Cd]S), and As which can accompany Fe in the mineral pyrite ($Fe[As]S_2$).

2.2.2 Metals in surficial environment

The surficial environment is the environment of weathering, erosion, and sedimentation at the surface of the Earth. It is characterized by low temperatures, nearly constant low pressures, abundant free oxygen, water, CO_2 and the mobility/immobility of elements in environmental media (Rose et al., 1979). The chemical elements are mobilized by physical, chemical and biological vectors. Elements move in solution as cations, anions and ionic complexes. They may incorporate into solid inorganic phases (e.g., sediments, suspended sediments, particulates from natural or anthropogenic emissions) or are absorbed/adsorbed by them. The same is true for solid, perhaps vital, organic phases (e.g., soft and hard parts of organisms, particulate organic carbon). In these modes the elements are transported to depositional environments on land or in water bodies by geologic agents, such as water, wind and glacial ice following surface drainage, aquifer flowpath, wind driven water and atmospheric currents. Mobilized heavy metals in an element assemblage can be carried in speciated forms to an environment in concentrations significantly higher than natural levels (Siegel, 2002).

The physical transport of solid matter by moving water leads to a geochemical fractionation based on size and specific gravity as gradient lessens, hydraulic energy drops, and sedimentation take place. The fractionation may be evident in the sand size fraction of water-borne sediments where heavy minerals drop out of the transport mode as a function of their specific gravity. Sulfide ore minerals, such as sphalerite (ZnS), Chalcopyrite ($CuFeS_2$), and associated non-ore minerals, such as pyrite (FeS_2) decompose readily and rapidly under aqueous oxidizing conditions (Siegel, 2002). They

release heavy metals to environments along with acid-producing hydrogen ions that can initiate the occurrence of acid mine drainage. Heavy metals released during oxidation mainly sorb to fine-size solids with charged substrates, such as amorphous and crystalline iron and manganese oxyhydroxides, clay minerals (e.g. smectite/montmorillonite) and particulate organic matters. Concentration and mobilization of potentially toxic metals, is abetted as fine-size sediment contacts mobilized metals during physical transport. For example, As is adsorbed onto Fe oxide phases and Pb sorbs to Mn oxide phases, whereas other potentially toxic metals such as Cd, Co, Cu, Mo, Ni, V and Zn sorb to smectites. Particulate organic carbon phases in the fine-size sediment fraction can carry high concentrations of Hg, Cu, Ni, V and Zn (Siegel, 2002).

Factors, such as pH, redox potential and temperature by themselves, but mainly in combination with and often abetted by bacterial processes, affect the solubility, mobilization and precipitation/deposition of potentially toxic metals. These and several other factors in complex reactions determine the chemical forms (metal species) that are introduced to an environment. They also influence changes of metals species that may take place once equilibrium is established during interaction with an environment (Drever, 1997). Other important parameters that affect heavy metals mobility in an environment include soil/ sediment textural heterogeneity (e.g. grain size), soil/sediment matrix composition (e.g. mineralogy, organic matter content), and fluid or particle interaction with interstitial or overlying water and organism activity (Siegel, 2002).

2.2.3 Metals in stream sediments

Metals in stream sediments can be in the form of primary ore minerals, eroded secondary ore minerals, precipitates from stream water, and exchangeable elements absorbed on Fe- or Mn- oxides, organic matters and clays. Primary sphalerite is still the main pool of Zn and Cd in stream sediment. The dominant form of primary sphalerite is in the sand fraction. In contrast, Pb is related to carbonates; for example, Pb is bound to carbonates, such as calcite, and/or precipitated as a pure form as cerrussite ($PbCO_3$). The absolute concentration of Pb in the silt fraction is much higher than that in the sand

fraction (Song et al., 1999). Cerrussite tends to be concentrated in the silt fraction and is even a minor component of the clay-size fraction. Cerussite alone cannot account for all the Pb in this size range. However, Pb adsorbed to clay minerals, organic matters and/or amorphous Fe and Mn oxides, is proportionally more important for the <63μm fraction. As, Cd, Cu, Fe, Mn, Pb and Zn is adsorped on clay particles nearly as silt but twice that adsorped to sand at the station near mining area and decreasing downstream by distance (Tutep, 1994). Pb is likely to be mobilised in the wider environment principally by the processes that effect the transport and deposition of suspended and fine sediment. Although, cerrussite is the main lead mineral in stream sediments near the mine site, a combination of weathering, in-stream processes and hydrodynamic dispersal may change this pattern further down stream (Hillier et al., 2001). Lead is potentially affected by absorption into iron and manganese oxyhydrosides, and Cd is potentially affected by adsorption on calcite. Adsorption is pH dependent. Lead adsorbs most effectively at the lowest pH, followed by Cd. Arsenic mobility is controlled by 2 processes: adsorption and desorption reactions and solid-phase precipitation and dissolution reactions (Drever, 1997). Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface, is an example of desorption. Solid-phase precipitation is the formation as solid phase from components present in aqueous solution. Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, the presence of competing anions, and solid-phase structural changes at the atomic level. High concentrations of arsenic are often associated with iron oxides and sulfide minerals (Drever, 1997).

2.2.4 Pathway and human health effects

There are three principle pathways through which potentially toxic metals released from natural sources can access living things. The first is through the atmosphere, directly or indirectly through atmospheric deposition to soils and water. A second is through drinking water, water used for cooking, and irrigation waters for food crops. The third, fed from the atmosphere-water-soil complex, is through the food web.

The health effects of lead include impaired mental and physical development, decreased heme biosynthesis, elevated hearing threshold and decreased serum levels of vitamin D. The neurotoxicity of lead is of particular concern, because evidence from prospective longitudinal studies has shown that neurobehavioral effects, such as impaired academic performance and deficits in motor skills, may persist even after Pb levels have returned to normal. Long term exposure to inorganic arsenic can cause darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles and torso. Long-term exposure to low levels of cadmium in air, food or water leads to a build up of cadmium in the kidneys and possible kidney disease called " Itai-Itai". The Itai-Itai disease is caused by chronic cadmium poisoning (Friberg et al., 1976).

Copper and zinc are essential nutrients. However, excess of these elements can be toxic to the body and cause a variety of health problems. Excess copper can cause "Idiopathic Copper Taxicosis" and "Wilson's Disease" which is a genetic defect. Also, it can have very negative effects on woman reproduction system and hormones. Copper can be stored in many tissues and organs such as liver and brain. Excess copper can even be deposited in the eyes causing a coppering to form in the cornea. This happens in extreme cases or Wilson's Disease. Pregnant woman can also transfer excess copper to her fetus while it is developing in the womb. The baby will be born with excess copper and may be prone toward bowel problems and allergies, asthma and skin problems (Biamonte, 2002). Eating large amounts of zinc can cause stomach cramps, nausea, and vomiting. Taken over an extended period of time in high amounts, zinc can cause anemia, damage the pancreas, and lower levels of high density lipoprotein cholesterol. Breathing dust or fumes containing large amounts of zinc can cause a short-term disease called "metal fume fever". This disease is an immune response affecting the lungs and body temperature (ANL, 2001)

CHAPTER III

METHODOLOGY

3.1 Sample Planning

There are many kinds of maps that require preparation in this step. Topographic map scale 1: 50,000 (series L7017, map sheet 5221IV, Amphoe Yaha and map sheet 5221III, Amphoe Than To) were prepared for location, accessibility and drainage analysis. Geologic map scale 1:50,000 and geological data were prepared to identify the geology of the study area. Aerial photographs at 1:15,000 scale were interpreted for stream characteristics, landuse, mines, possible sample locations and for evidence of the built environment. All materials were analyzed to determine sample collection design, preservation, transportation and time schedule.

3.2 Sample Collection

Stream sediment samples were collected from the annual stream flood at an average density of 3 samples per 1 km^2, following the method described by Rose et al. (1979). The selected samples were taken up and downstream from the mine sites at intervals of 500 m. Sample site locations are shown in Figure 3.1. 500-g samples from each location were collected from the surface of the stream bottom to a depth of 10 cm at a point near the thalweg (Hillier et al., 2001). The fine-grained parts of modern stream sediments (<0.15 mm) were processed in the field by wet sieving through nylon mesh using stream water and then stored in plastic bags. Analytical duplicate samples were inserted into each analytical block of 4 km^2. Information on the sampling site, such as position, average width, average depth, pH of water and circumstance around the site, were recorded on water proof paper.

3.3 Sample Preservation and Transportation

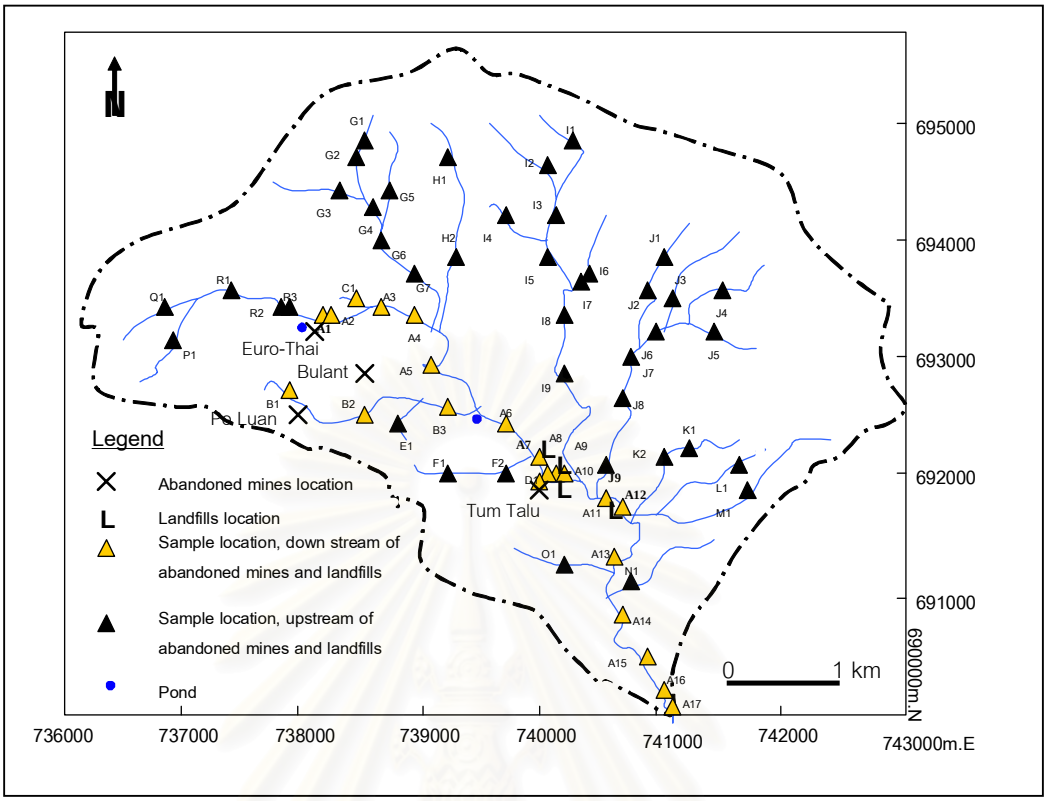

Figure 3.1 Map of the study area in the Tum Talu watershed, Yala province, showing location of stream sediment samples.

The samples were air-dried at room temperature (33-35 °C) at the campsite. The dried samples were placed in clean plastic bags and packed in plastic boxes.

3.4 Sample Preparation

Samples were air-dried at 40°C in an oven for 6 hours. The dried samples were disaggregated using a porcelain pestle and mortar and sieved to <177μm, using nylon cloth. The grain size fraction chosen for stream sediment analysis follows the recommendations of UNESCO and IGCP (Darnley et al., 1995) for environmental and resource management in geochemical investigations. Contact with metals was avoided throughout these operations to prevent metal contamination.

3.5 Sample analysis

3.5.1 Metal analysis

Partial extraction was obtained by acid digestion, modifying the standard method of EPA method 3051 A: microwave assisted acid digestion of sediments. In the first step approximately 0.5 g of each representative dried samples were weighed into microwave vessels, then 9 mL concentrated nitric acid and 3 mL concentrated hydrochloric acid were added and mixed thoroughly with the samples. The vessels were placed in and heated by the microwave digester for 10 minutes at 200 °C. The resultants were filtered through a Whatman GC filter and were diluted with deionized water to 100 mL. These solutions were stored in plastic bottles for further chemical analysis.

To evaluate the precision of test, Japanese certified reference materials, provided by the Geological Survey of Japan, including JSJ-Jsd1, Jsd2 and Jsd3, were submitted to the same procedure and analyzed as unknown samples.

Metallic elements (Pb, Cd, Cr, Cu, Zn, As) were determined in extracts from partial extraction by inductively coupled plasma optical emission spectrometry (ICP-OES). The calibration of the equipment was achieved using standard solutions with

concentrations adapted to the work curves.

3.5.2 Carbon and Sulfur analysis

Carbon and sulfur contents were determined by a Carbon and Sulfur (C+S) determinator (model Eltra CS-2000) at Curtin University, Perth, WA. Approximately, 0.2g of sample was weighed into a porcelain crucible and 0.7g of iron and 2.0g of tungsten were added and mixed thoroughly with the samples. Then the sample crucible was taken into the C&S determinator for analysis. To calibrate the instrument, Canadian certified reference materials (STSD-2) and sulfur ore 0.328% were analyzed in duplicate.

3.6 Data analysis

Metal concentrations were statistically analyzed for the production of geochemical maps. Statistical descriptive values: mean, median, mode standard deviation, variance, skew ness, kurtosis, range, maximum, minimum, percentiles and the statistic frequency value: cumulative percent were calculated by statistical software SPSS version 9.0.

Histograms and plots of cumulative frequency distribution on probability papers (or log probability paper) were calculated and drawn by the computer program to aid in the interpretation of Polymetallic assay and Geochemical information (PERES version 2.0). The calculation procedure follows Sinclair's (1976) methodology.

3.7 Mapping

A variety of maps, single elemental maps which show concentrations of metals, carbon and sulfur contents and anomaly maps which show locations of anomalies were made by hand draft using Microsoft Power Point 2000 software.

Figure 3.2 (a.) The main stream at location 740988E 0692067N in the study area, (b.) Wet sieving using stream water in the field, (c.) Dried samples before being dry sieved, (d.) Filtration after adding mixed acid, (e.) Microwave model digester and (f.) Eltra CS 4000 Carbon and sulfur determinator.

Table 3.1 Procedure for partitioning a single population into two normally distributed populations (Sinclair, 1976).

Step	Description
(i)	Convert the data to logarithms if necessary.
(ii)	Classify by concentration into 10-20 groups, with at least 5 samples in most of the groups.
(iii)	Compute cumulative percentages, starting at high concentrations, ending with 100% at low concentration.
(iv)	Plot the cumulative percentages against the lower class limit on probability paper and draw a smooth curve through the points.
(v)	If the data plot is a S-shaped curve, select the inflection point of the curve. This point defines the approximate proportions of the two populations. If the shape is more complicated, see Sinclair (1976).
(vi)	For class 1, compute PA = P1 /*f*A where P1 is the observed cumulative percentage for class 1, and *f*A is the proportion of samples falling in population A.
(vii)	Plot a new point at PA and the lower limit of class 1. Continue step (vi) until the inflection point is reached or until newly calculated points markedly diverge from a straight line.
(viii)	Draw a line to fit the points plotted in step (vii). This line defines the anomalous population.
(ix)	Compute analogous points starting at low concentrations, using *f*B (proportion of samples in population B, as determined by the inflection point), and cumulative percentages computed as 100-P. Draw a line for background population.
(x)	Check the calculated populations by combining them in the proper proportions, using Pm = *f*APA + *f*BPB, where Pm is the cumulative percentage in the mixture. Plot the values of Pm and compare with the original points. Repeat using a slightly different inflection point if necessary.

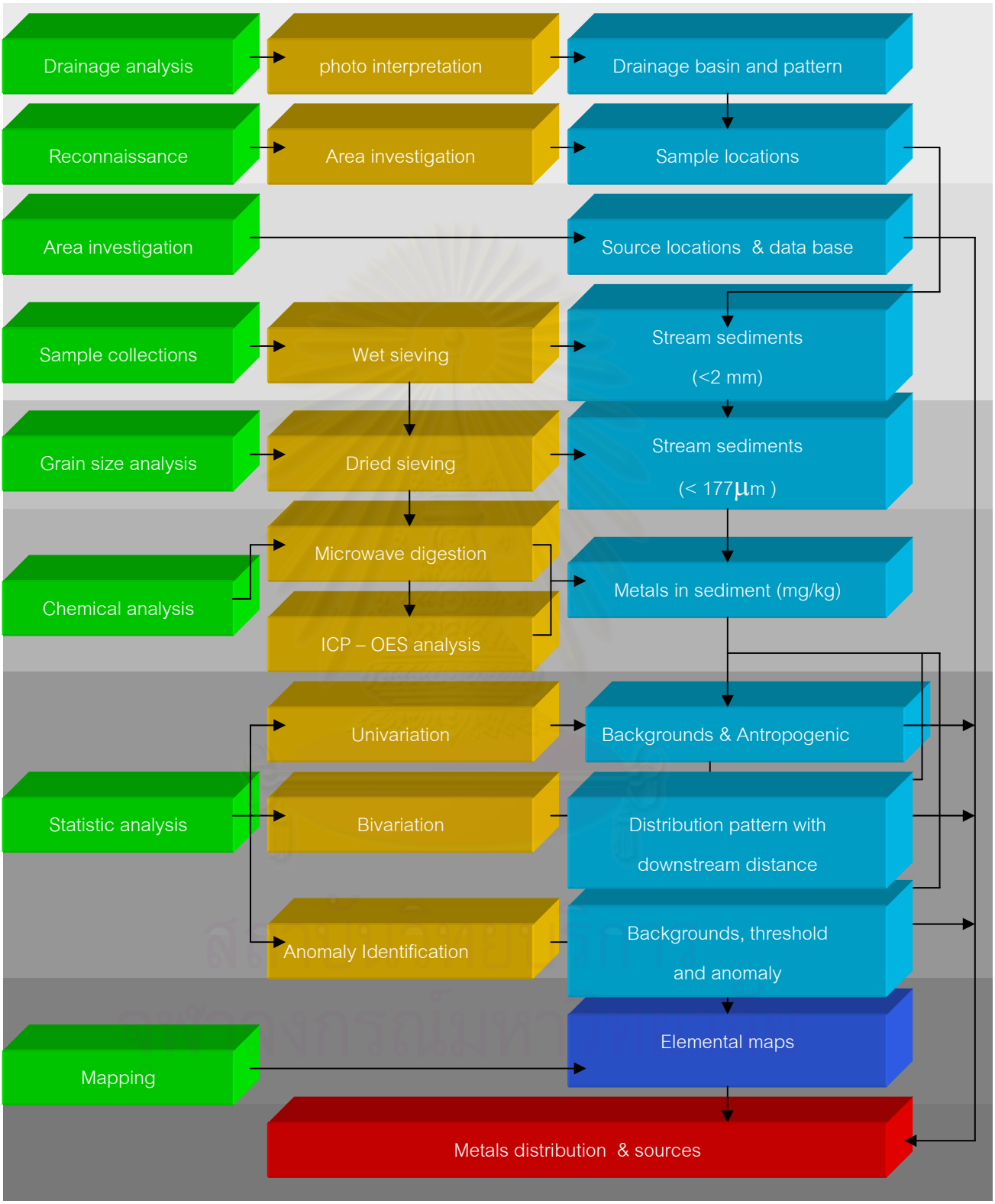

Figure 3.3 The flow chart showing methodology applied in this study.

CHAPTER IV

RESULTS

4.1 Sources

Based upon the current field investigation, it is likely that the sources of metals in the watershed study area can be divided into 2 types:- man-made (anthropogenic) and natural. The anthropogenic sources are mine structures, such as mineralized outcrops, pits, mine access roads and landfill leakages. The natural sources are background rocks outcropping in the study area, including hornfels, granite, limestone, skarn and ores, and quaternary sediments

4.1.1 Anthropogenic sources

The major mining fronts are at Euro-Thai, Tum Talu, Bu Lunt and Po Luan. The Euro-Thai outcrops (Figure 4.1a), located at 738103E 693425N are exposed on the western bank of the stream. The size of the Euro-Thai mine site is approximately 7 x 90 x 8 m^3. It is composed of weathered ores and some waste rocks. The Tum Ta Lu outcrop (Figure 4.2 a, b, c) is located at 739917E 691969N and crops out on the main road of the watershed. Its size is approximately 800 x 400 x 140 m^3. It comprises the products of weathered ores, such as arsenopyrite, Pb-As sulphide, iron ores and wastes of granitic rocks.

The mine pit (Figure 4.2 c) is at Euro-Thai and is located at 737946E 693352N. Its size is approximately 70 x 100 x 60 m^3. Water of the pit is acid with the pH ranging from 2 to 3. It is clearly observed that the mine access road to Euro-Thai was constructed using dumped waste rocks (Figure 4.1 e)

Areas of landfill are located at 739850E 692126N, 740218E 692195N, 740212E 691954N. Some of them seem to be leaking (Figure 4.3 a). The leaks appear at grid references 740075E 691977N and 740116E 691989N. Reddish and acidic (pH 4-5) leachate (Figure 4.3 b) flowed directly into the stream (Figure 4.3 c). At least 500 meters

Figure 4.1 Anthropogenic sources of metals at the Euro-Thai abandoned mine. (a.) A waste pile dumped at the bank of the stream. (Long-axis of photograph is about 1.5 m.) (b) Reddish drainage from the waste pile. (c) The artificial pit (about 70 x 100 x 60 m^3) with strongly contaminated greenish-colored water. (d) Dumped waste rocks for road access to mine site. (e) Strongly weathered disposed wastes near the mine site.

Figure 4.2 Views showing anthropogenic sources of discarded rocks and wastes of low-grade ores at the Tum Talu abandoned mine. Weathered surface of mineralized outcrops with little vegetation covers (a) and (b). (c) Unreclaimed mine site. Orange-red colored acid mine drainage from exposed waste rocks (d) and (e). (f) Acid drainage from the mine

Figure 4.3 Leakage water from the western landfill wall (a). Orange-red leachates from the landfill (pebbles are about 5-15 cm) (b). The leachates flow directly into a natural stream (c). The orange – red leachate downstream (d). Leachate from waste rock built up landfill walls (e). Leachates near landfills and Tum Talu mine at 740754E 691356N (f).

downstream of the leachate inflow, the sediments become orange-red in color (Figure 4.3 d). In addition, at grid reference 7401102E 691985N, the landfill wall constructed from waste rocks also produced reddish leachate (Figure 4.3 e).

4.1.2 Natural sources

Based on the results of the short-period field investigation, it is quite possible that the natural sources of the watershed are porphyritic biotite-granites (Figure 4.4 a), hornfels (meta shale) (Figure 4.4 b), ores, skarns, limestones (marbles) and Quaternary sediments.

4.2 Partial digestion

The partial metals in sediments collected at 63 sites during 15 May to 8 June 2003 are summarized in Table 4.1. Precision and percentage of coefficient of variation (CV) or relative standard deviation (RSD) are shown in Table 4.2. The percentage RSD of all elements is less than 10%. The range of concentrations of the elements is between 2 – 140 ppb for the instrumental blank and 4.3 – 540 ppb for the method blank (microwave assisted digestion). Calculation details of the accuracy, the precision, and the blank concentrations are illustrated in the appendix.

4.3 Geochemical statistics

Descriptive statistics of the As, Pb, Cd, Cu, Zn, Cr, C and S concentrations of stream sediments from Tum Talu watershed are summarized in Table 4.3 Average concentration is 1,293.50 mg/kg for As, 7.64 mg/kg for Cd, 29.96 mg/kg for Cr, 189.62 mg/kg for Cu, 2,255.25 mg/kg for Pb, 564.89 mg/kg for Zn, 1.44 wt% for C and 0.17 wt% for S. Concentration range are 7.25 – 6,161.53 mg/kg for As, 0.22 – 28.84 mg/kg for Cd, 2.11 – 88.51mg/kg for Cr, 9.18 – 630.80 mg/kg for Cu, 3.45 – 19,540.88 mg/kg for Pb, 12.70 – 2,841.42 mg/kg for Zn, 0.12 – 5.10 wt% for C, and 0.01 – 1.81 wt% for S.

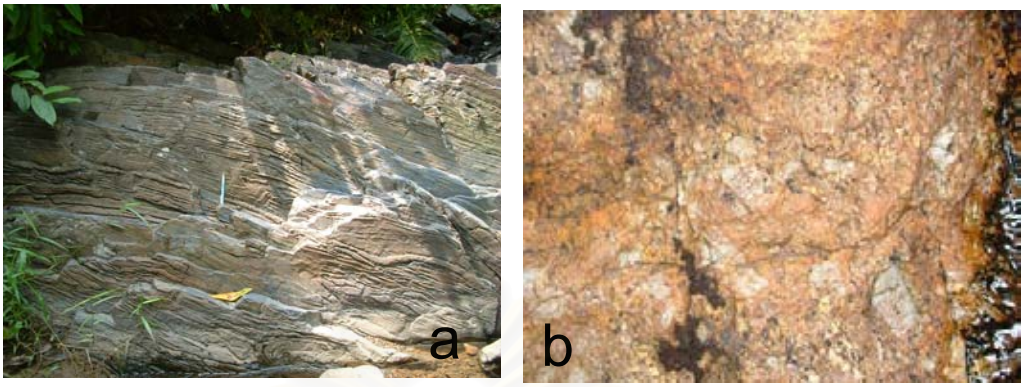

Figure 4.4 Natural exposures of hornfels (meta-shale) (a) and coarse-grained porphyritic granite (b).

Table 4.1

Results of partial extraction applied to the stream sediments samples from Tum Talu watershed area, Yala.

Sites	Distance (m.)	pH	C [wt%]	S [wt%]	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg))
A1	2313	5.8	0.28	0.63	1,940	14	30	359	2,575	1,616
A2	2325	5.8	0.25	0.73	1,580	8	ND	187	1,759	848
A3	2838	6.7	0.12	0.09	970	6	22	160	654	580
A4	3145	6.5	0.24	0.23	1,454	11	ND	298	1,083	1,575
A5	3950	7.2	0.74	0.07	860	14	11	202	766	1,508
A6	4800	7.1	0.53	0.09	2,893	13	32	255	989	996
A7	5225	6.7	0.79	0.02	3,667	16	29	337	2,279	1,367
A8	5375	5.2	0.87	0.33	3,402	21	46	319	6,728	1,915
A9	5538	5.2	0.50	0.99	6,162	13	32	190	14,470	698
A10	5550	6.7	0.40	0.12	2,164	12	49	411	7,742	1,290
A11	6013	7.0	0.37	0.12	3,442	16	19	553	11,515	1,479
A12	6213	7.2	0.51	1.81	3,692	22	ND	562	11,475	1,710
A13	7088	7.1	1.32	0.03	60	3	14	ND	107	156
A14	7275	ND	1.14	0.60	4,067	29	89	631	9,835	2,841
A15	7738	7.0	1.36	0.37	3,304	20	ND	494	6,705	1,632

Table 4.1 (continued)

Sites	Distance (m.)	pH	C [wt%]	S [wt%]	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
A16	8188	6.7	1.27	0.20	2,850	20	33	400	5,725	2,338
A17	8295	ND	1.81	0.22	3,846	26	48	537	7,789	2,556
B1	273	6.5	1.29	0.04	2,486	ND	38	100	1,807	86
B2	1235	6.8	0.69	0.55	2,860	4	ND	110	460	123
B3	2135	7.0	1.60	0.01	1,197	2	19	120	248	69
C1	0	6.9	0.44	0.23	2,812	22	55	349	2,730	1,282
D1	5950	4.0	0.14	0.27	1,899	8	31	470	19,541	576
E1	0	6.2	3.94	0.03	705	1	18	48	135	44
F1	725	6.7	4.88	0.04	76	ND	35	107	67	166
G1	0	7.2	0	0	447	8	40	127	581	560
H1	403	6.1	2.27	0.03	78	ND	17	62	42	49
H2	925	6.8	0.62	0.04	826	4	30	136	977	184
I1	270	7.2	2.82	0.05	7	1	21	ND	24	41
I2	425	6.1	1.16	0.02	ND	ND	ND	ND	10	13
I3	0	7.2	0.60	0.03	37	ND	32	103	3	90
I4	838	7.2	0.57	0.01	38	0	25	90	47	89
I5	1,025	7.0	0.26	0.04	11	ND	9	ND	25	35

Table 4.1 (continued)

Sites	Distance (m.)	pH	C [wt%]	S [wt%]	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
I6	0	7.2	0.92	0.03	62	2	ND	63	46	85
I7	1,545	7.1	0.58	0.02	54	2	15	77	30	73
J1	353	7.0	2.43	0.05	44	4	30	83	75	143
J2	1,288	6.9	1.97	0.02	112	2	31	92	22	107
K1	0	7.0	3.87	0.03	12	2	ND	38	32	37
K2	400	6.7	2.69	0.04	53	1	15	9	104	57
K3	1,058	7.0	2.15	0.05	42	1	21	65	575	51
K4	1,410	7.2	2.85	0.06	218	2	29	49	56	147
K5	0	7.0	0.76	0.01	135	1	17	52	84	54
K6	0	7.0	1.69	0.07	39	2	40	52	42	194
K7	0	7.2	2.69	0.05	114	1	25	ND	34	87
K8	0	6.8	0.48	0.04	99	ND	12	72	57	63
K9	2,000	6.5	1.83	0.03	57	2	20	82	30	64
L1	2,500	7.0	3.19	0.05	41	2	ND	53	43	78
L2	0	6.9	0.83	0.01	82	2	41	ND	28	62
L3	0	6.8	2.71	0.05	ND	1	30	ND	21	25
L4	0	7.0	2.93	0.06	18	ND	16	32	17	37

Table 4.1 (continued)

Sites	Distance (m.)	pH	C [wt%]	S [wt%]	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
L5	538	7.1	0.31	0.02	13	ND	35	96	8	54
L6	1,263	7.3	1.08	0.02	52	2	37	65	36	155
L7	1460	7.4	0.67	0.50	4,210	23	51	559	9,461	2,279
L8	0	7.0	0.00	0.00	119	1	13	ND	788	175
L9	1,905	6.7	2.02	0.03	78	3	42	77	254	120
M1	0	7.1	0.00	0.00	83	1	38	39	42	102
M2	0	7.2	0.31	0.03	76	2	19	54	406	58
N1	0	7.0	1.39	0.03	64	1	38	62	29	75
O1	0	6.9	0.00	0.00	75	3	27	ND	31	62
P1	0	6.7	1.36	0.02	672	2	28	81	685	72
Q1	0	6.5	2.05	0.03	58	ND	55	53	34	46
R1	1,488	7.0	5.10	0.07	1,967	7	43	178	1,132	382
R2	1,938	6.2	2.35	0.08	2,093	4	36	180	3,075	238
R3	1,980	6.5	0	0	3,175	2	2	181	5,390	454

Table 4.2 Precision and percentage of coefficient of variation (CV) or relative standard deviation (RSD) of partial digestion test.

Sample No.	Measurements	As	Cd	Cr	Cu	Pb	Zn
5-1-1timeB	1	30.23	0.08	0.27	1.10	59.65	3.50
5-1-1timeB	2	30.74	0.08	0.30	1.24	57.63	3.55
5-1-1timeB	3	31.60	0.08	0.31	1.24	60.12	3.63
	Mean	30.86	0.08	0.29	1.19	59.13	3.56
	STDVS	0.57	0.00	0.02	0.07	1.08	0.05
	RSD	0.02	0.04	0.06	0.05	0.02	0.01
	%RSD	1.84	3.93	5.60	5.49	1.83	1.44

STDVS = Standard deviation

Frequency tables and histograms of As, Pb, Cd, Cu, Zn and Cr concentrations are shown in Tables 4.4 - 4.9 and Figures 4.5 – 4.10, respectively. As displayed in the histograms, distribution of As, Cd, Cr, Cu, Pb and Zn concentrations are not a normal distribution.

Cumulative percent scale on probability paper plotted against log concentration of As, Cd, Cr, Cu, Pb and Zn are shown in Figure 4.11. The As, Cd, Cr, Cu, Pb and Zn concentration shows a non-linear log relationship. In addition, they clearly show multiple S-shaped curves. In contrast, Cr concentrations show quite simply, two S-shape curves. It may be summarized that the As, Cd, Cu, Pb a1nd Zn concentrations have a poly-modal distribution while Cr concentration has a uni-modal distribution.

There are five inflection points, which divide the whole As, Cd, Cu, Pb and Zn concentrations into 6 groups of population and two inflection points, which divide the whole Cr concentration into 3 groups of population. These are shown in Figures 4.12 – 4.14. The range of As concentration is 1,967 – 6,162 mg/kg for the population of group *1*, 672 – 1,967 mg/kg for the population of group *2*, 218 – 672 mg/kg for the population of group *3*, 18 – 218 mg/kg for the population of group *4*, 12 – 18 mg/kg for the population of group *5* and 0 –12 mg/kg for the population of group *6*. The range of Cd concentration is 20.38 – 28.84 mg/kg for the population of group *1*, 11.91 – 20.38 mg/kg for the population of group *2*, 4.50 – 11.91 mg/kg for the population of group *3*, 1.96 – 4.50 mg/kg for the population of group *4*, 1.07 – 1.96 mg/kg for the population of group *5* and 0 – 1.07 mg/kg for the population of group *6*. Cu concentration varies from 359 – 631 mg/kg for the population of group *1*, 319 – 349 mg/kg for the population of group *2*, 178 – 319 mg/kg for the population of group *3*, 90 – 298 mg/kg for the population of group *4*, 48 – 90 mg/kg for the population of group *5* and 0 – 48 mg/kg for the population of group *6*. Pb concentration is 5,725 – 19,541 mg/kg for population of group1, 685 – 5,725 mg/kg for population of group 2, 248 – 685 mg/kg for population of group 3, 67 – 248 mg/kg for the population of group *4*, 22 – 67 mg/kg for the population of group *5* and 0 – 22 mg/kg for the population *6*. The range of Zn concentration is 1,575 – 2,842 mg/kg for the population of group *1*, 382 – 1,367 mg/kg for the population of group *2*, 238 – 382 mg/kg for the population of group 3, 90 – 328 mg/kg for the population of group *4*, 44 – 90 mg/kg for the population of group *5* and 0 – 44 mg/kg for

Table 4.3 The descriptive statistics of metals, carbon and sulfur concentrations in the stream sediments of the Tum Talu watershed

		Arsenic (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)	Carbon (wt%)	Sulfur (wt%)
N	Valid	61	53	54	54	63	63	57	57
	Missing	2	10	9	9	0	0	6	6
Mean		1,209	7.40	30.12	188	2,247	542	1.46	0.17
Median		135	3.00	29.81	105	248	123	1.14	0.05
Mode		7.25	1.13	2.11	9.18	3.45	12.7	0.31	0.03
Std. Deviation		1,517	8.00	14.61	171	4,094	748	1.20	0.30
Variance		2,302,756	64.05	213.40	29,327	16,760,283	559,836	1.44	0.09
Skewness		1.15	1.18	1.17	1.21	2.33	1.53	1.22	3.58
Std. Error of Skewness		0.31	0.33	0.32	0.32	0.30	0.30	0.32	0.32
Kurtosis		0.47	0.11	3.53	0.23	5.46	1.26	1.13	15.70
Std. Error of Kurtosis		0.60	0.64	0.64	0.64	0.59	0.59	0.62	0.62
Range		6,154	28.62	86.40	622	19,537	2,829	4.98	1.80
Minimum		7	0.22	2.11	9	3	13	0.12	0.01
Maximum		6,162	28.84	88.51	631	19,541	2,841	5.10	1.81
Percentiles	10	37	1.09	13.52	49	23	42	0.28	0.02
	20	52	1.45	17.32	54	31	57	0.46	0.03
	30	63	1.68	20.38	69	42	70	0.59	0.03
	40	81	2.18	26.54	83	63	87	0.77	0.04
	50	135	3.00	29.81	105	248	123	1.14	0.05
	60	882	5.21	32.14	160	666	179	1.36	0.06
	70	1,951	10.21	36.81	196	1,122	573	1.91	0.09
	80	2,856	14.79	39.89	349	3,538	1,306	2.53	0.23
	90	3,622	21.78	48.30	515	8,792	1,679	2.98	0.56
	100	6,154	28.84	88.51	631	19,541	2,841	5.10	1.81

Table 4.4 Classification of log concentration for arsenic, As.

Log mg/kg	Number of samples	Cumulative number	Cumulative Percent
0.80-1.00	1	61	100.0
1.00-1.20	3	58	95.1
1.20-1.40	1	47	77.0
1.40-1.60	3	41	67.2
1.60-1.80	10	38	62.3
1.80-2.00	9	33	54.1
2.00-2.20	4	32	52.5
2.20-2.40	1	32	52.5
2.40-2.60	0	28	45.9
2.60-2.80	1	19	31.1
2.80-3.00	5	9	14.8
3.00-3.20	3	6	9.8
3.20-3.40	6	5	8.2
3.40-3.60	11	2	3.3
3.60-3.80	3	1	1.6

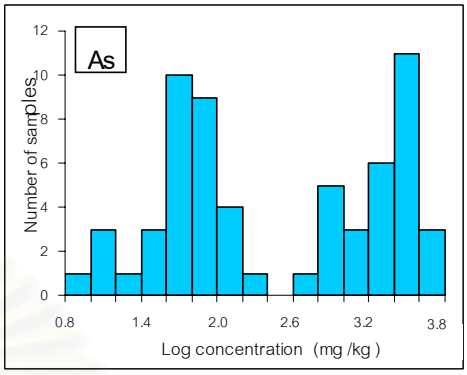

Figure 4.5 Histogram plotted from data of table 4.4

Table 4.5 Classification of log concentration for cadmium, Cd.

Log mg/kg	Number of samples	Cumulative number	Cumulative Percent
(-0.65)-(-0.53)	1	53	100.0
(-0.53)-(-0.41)	0	52	98.1
(-0.41)-(-0.29)	0	52	98.1
(-0.29)-(-0.17)	1	52	98.1
(-0.17)-(0.05)	1	51	96.2
(-0.05)-(0.07)	5	50	94.3
0.07-0.19	4	45	84.9
0.19-0.31	9	41	77.4
0.31-0.43	5	32	60.4
0.43-0.55	3	27	50.9
0.55-0.67	3	24	45.3
0.67-0.79	0	21	39.6
0.79-0.91	5	21	39.6
0.91-1.03	1	16	30.2
1.03-1.15	4	15	28.3
1.15-1.27	3	11	20.8
1.27-1.39	6	8	15.1
1.39-1.51	2	2	38.0

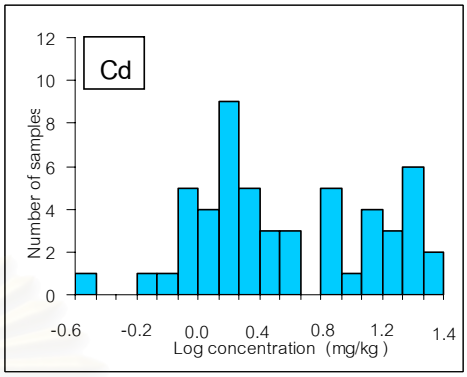

Figure 4.6 Histogram plotted from data of table 4.5

Table 4.6 Classification of log concentration for chromium, Cr.

Log mg/kg	Number of samples	Cumulative number	Cumulative Percent
0.30-0.40	1	54	100.0
0.40-0.50	0	53	98.1
0.50-0.60	0	53	98.1
0.60-0.70	0	53	98.1
0.70-0.80	0	53	98.1
0.80-0.90	0	53	98.1
0.90-1.00	1	53	98.1
1.00-1.10	2	52	96.3
1.10-1.20	4	50	92.6
1.20-1.30	8	46	85.2
1.30-1.40	5	38	70.4
1.40-1.50	11	33	61.1
1.50-1.60	12	22	40.7
1.60-1.70	6	10	18.5
1.70-1.80	3	4	7.4
1.80-1.90	0	1	1.9
1.90-2.00	1	1	1.9

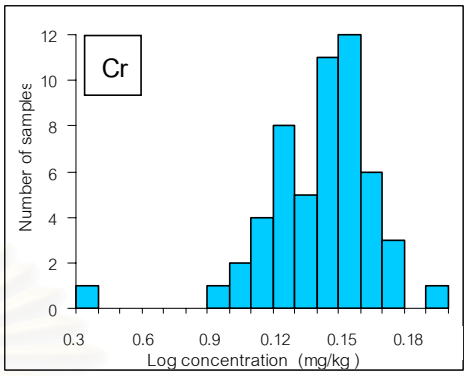

Figure 4.7 Histogram plotted from data of table 4.6

Table 4.7 Classification of log concentration for copper, Cu.

Log mg/kg	Number of samples	Cumulative number	Cumulative Percent
0.90-1.02	1	54	100.0
1.02-1.14	0	53	98.1
1.14-1.26	0	53	98.1
1.26-1.38	0	53	98.1
1.38-1.50	1	53	98.1
1.50-1.62	2	52	96.3
1.62-1.74	7	50	92.6
1.74-1.86	6	43	79.6
1.86-1.98	8	37	68.5
1.98-2.10	6	29	53.7
2.10-2.22	2	23	42.6
2.22-2.34	6	21	38.9
2.34-2.46	1	15	27.8
2.46-2.58	5	14	25.9
2.58-2.70	4	9	16.7
2.70-2.82	5	5	9.3

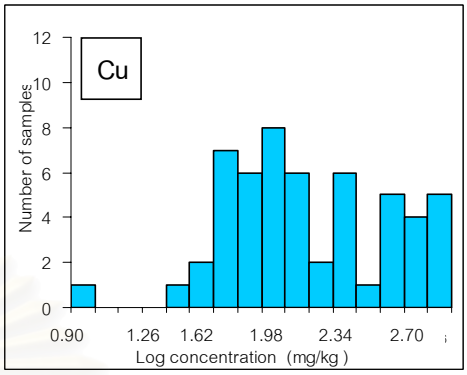

Figure 4.8 Histogram plotted from data of table 4.7

Table 4.8 Classification of log concentration for lead, Pb.

Log mg/kg	Number of samples	Cumulative number	Cumulative Percent
0.5-0.75	1	63	100.0
0.75-1.00	2	62	98.4
1.00-1.25	1	60	95.2
1.25-1.50	9	59	93.7
1.50-1.75	12	50	79.4
1.75-2.00	3	38	60.3
2.00-2.25	3	35	55.6
2.25-2.50	2	32	50.8
2.50-2.75	2	30	47.6
2.75-3.00	8	28	44.4
3.00-3.25	3	20	31.7
3.25-3.50	5	17	27.0
3.50-3.75	1	12	19.0
3.75-4.00	7	11	17.5
4.00-4.25	3	4	6.3
4.25-4.50	1	1	1.6

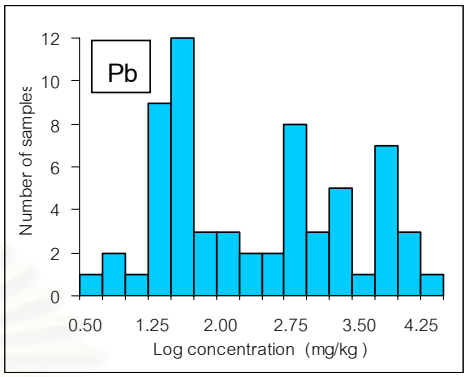

Figure 4.9 Histogram plotted from data of table 4.8

Table 4.9 Classification of log concentration for zinc, Zn.

Log mg/kg	Number of samples	Cumulative number	Cumulative Percent
1.00-1.15	1	63	100.0
1.15-1.30	0	62	98.4
1.30-1.45	1	62	98.4
1.45-1.60	3	61	96.8
1.60-1.75	7	58	92.1
1.75-1.90	11	51	81.0
1.90-2.05	7	40	63.5
2.05-2.20	6	33	52.4
2.20-2.35	4	27	42.9
2.35-2.50	1	23	36.5
2.50-2.65	1	22	34.9
2.65-2.80	4	21	33.3
2.80-2.95	2	17	27.0
2.95-3.10	1	15	23.8
3.10-3.25	9	14	22.2
3.25-3.40	3	5	7.9
3.40-3.55	2	2	3.2

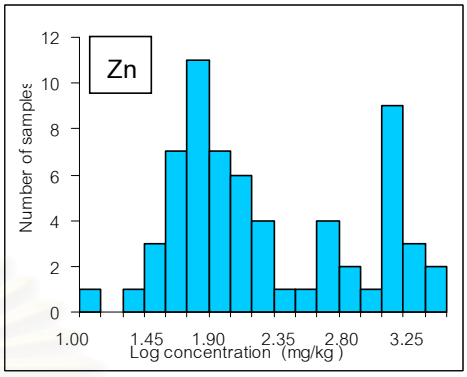

Figure 4.10 Histogram plotted from data of table 4.9

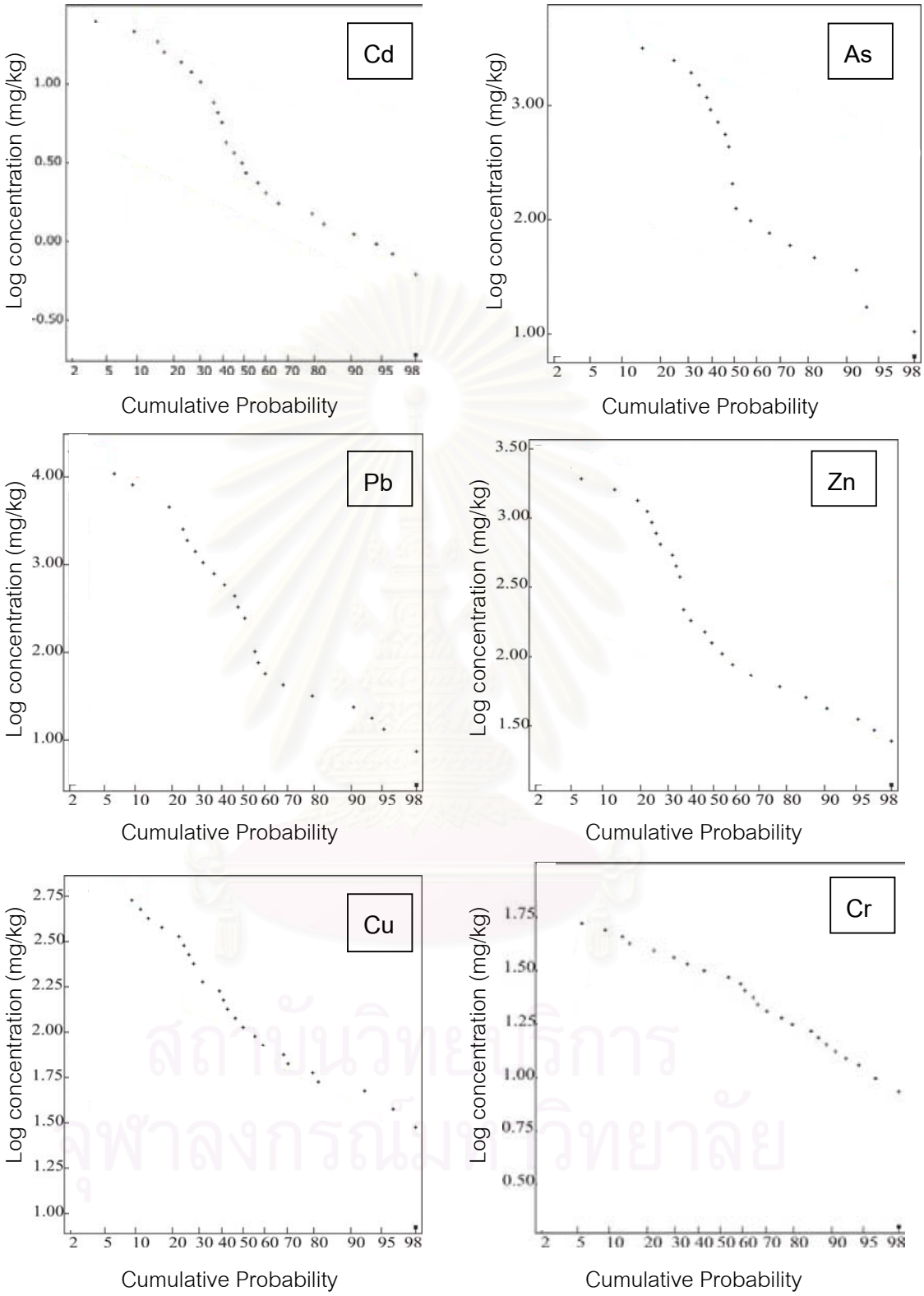

Figure 4.11 Cumulative percentage plotted on probability paper against log concentration of As, Cd, Cr, Cu, Pb and Zn. Graphs are non-linear and show multiple S-shape curves.

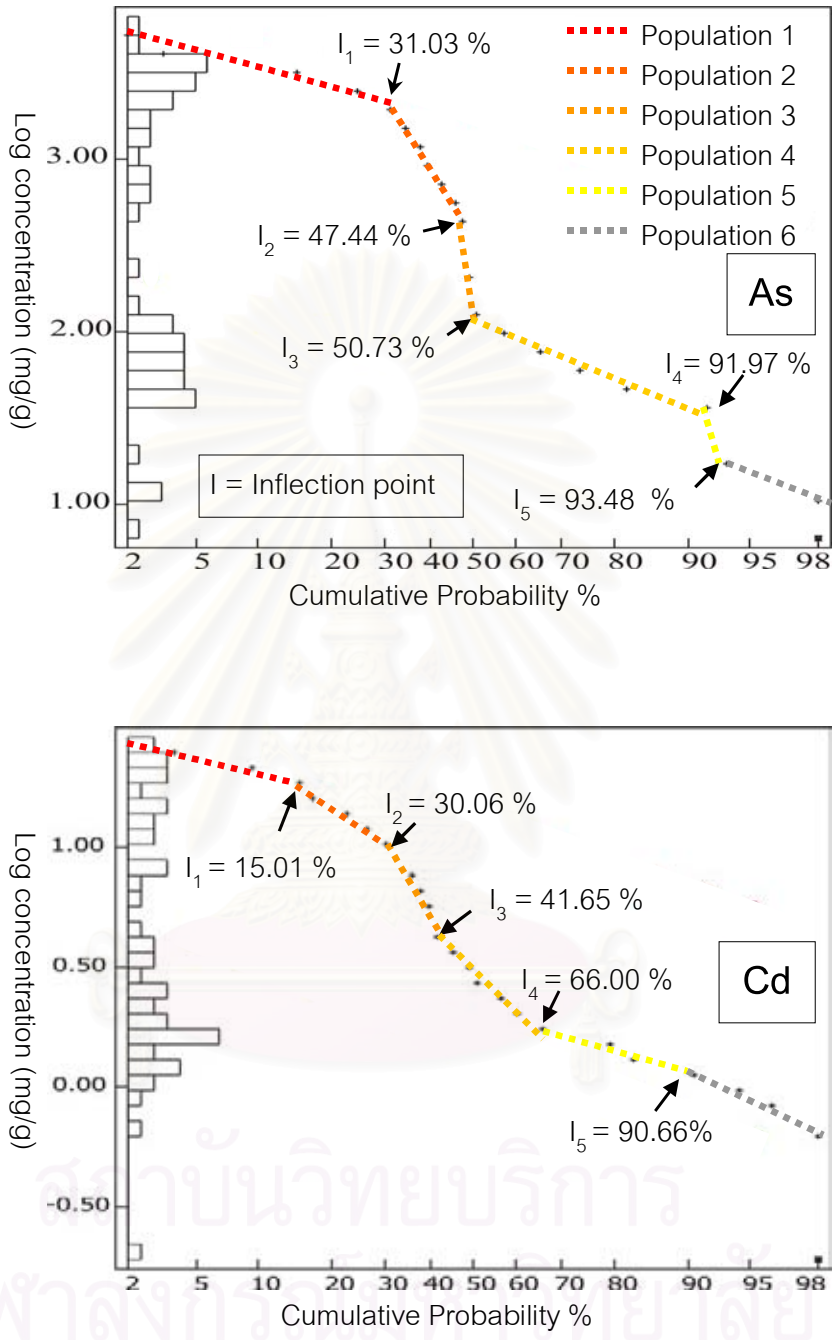

Figure 4.12 Cumulative percentage scale on probability paper plotted against log concentration of the As and Cd. Graphs show multiple S-shape curves. Inflection points divide data into sub-populations.

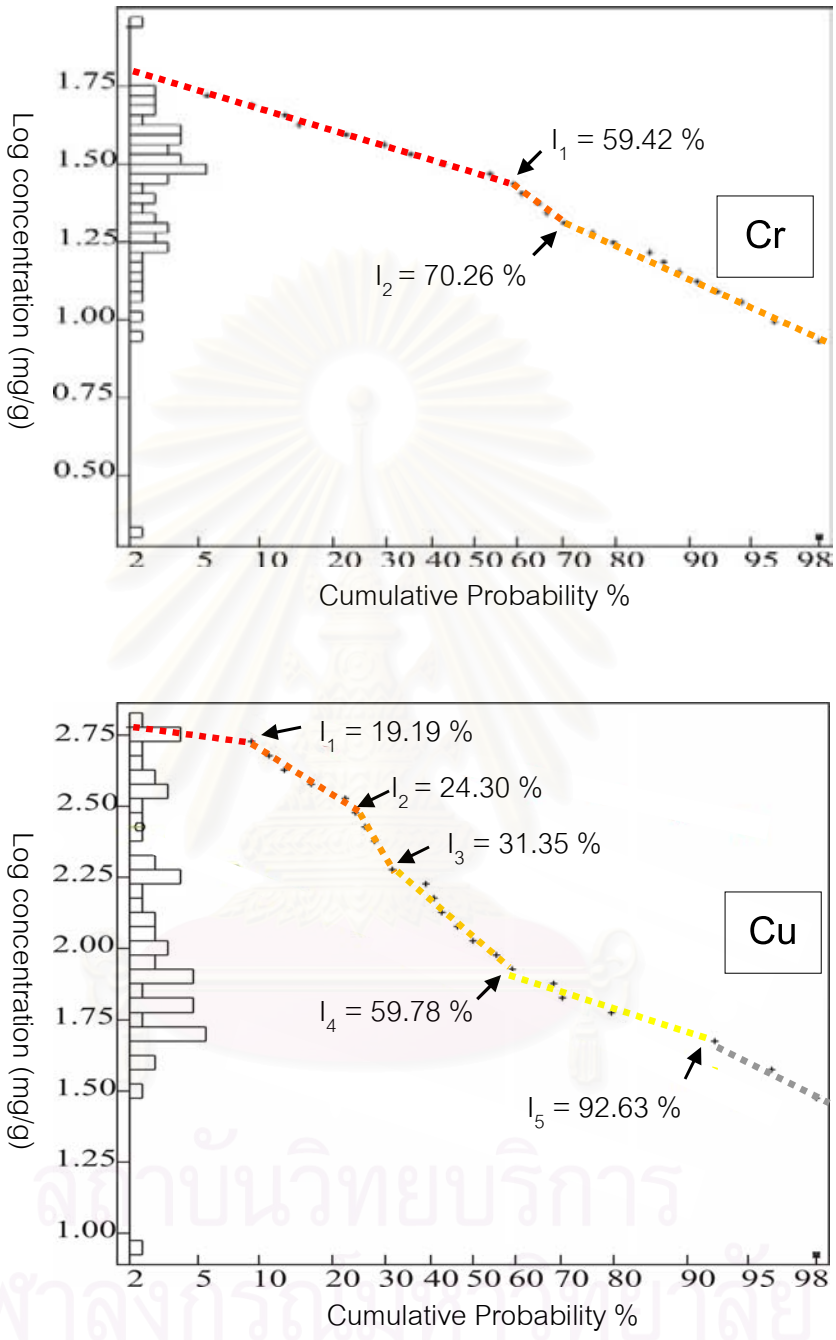

Figure 4.13 Cumulative percentage scale on probability paper plotted against log concentration of Cr and Cu. Graphs show multiple S-shape curves. Inflection points divide data into sub-populations.

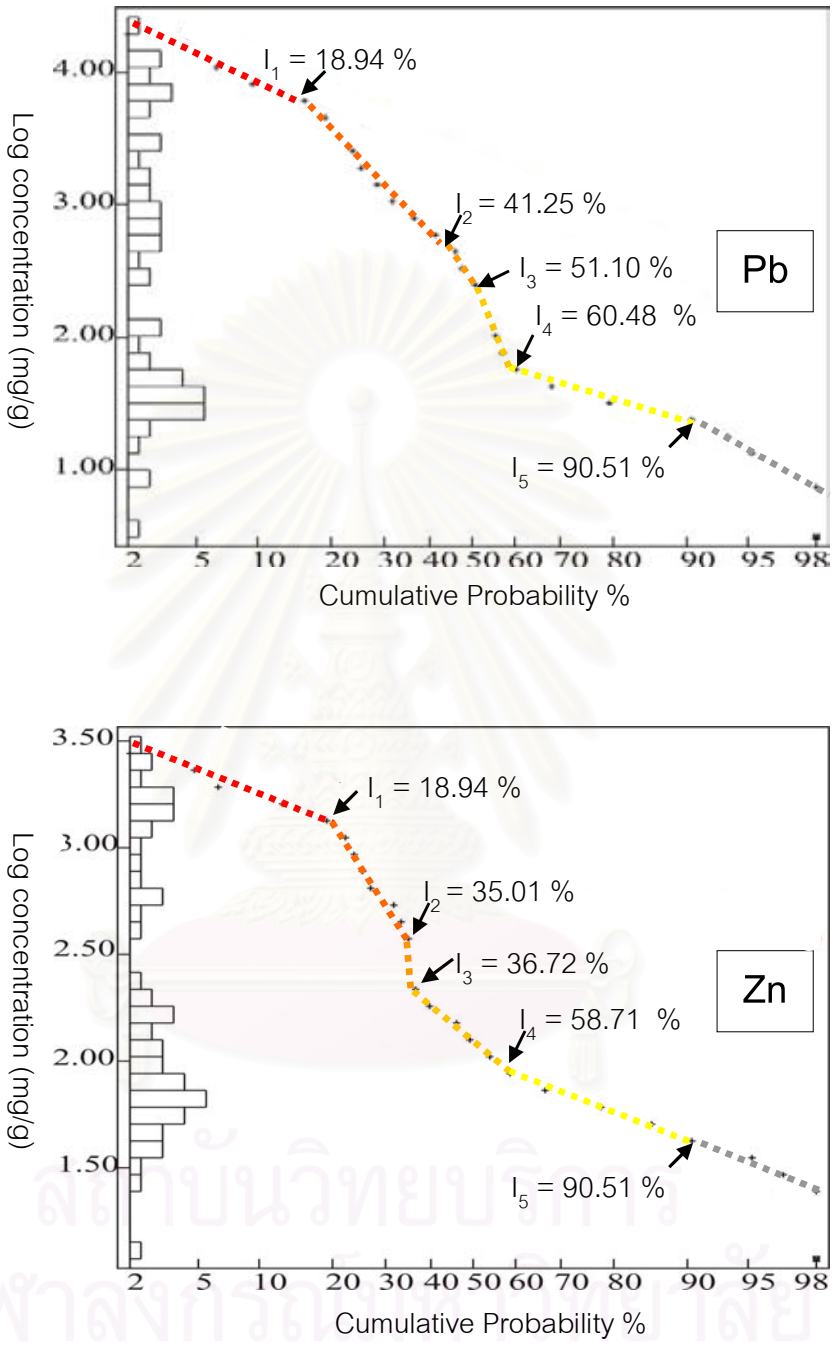

Figure 4.14 Cumulative percentage scale on probability paper plotted against log concentration of Pb and Zn. Graphs show multiple S-shape curves. Inflection points divide data into sub-populations.

the population of group *6*.

4.4 Distribution pattern

Elemental maps of the As, Cd, Cu, Pb, Zn and Cr concentrations are shown in Figures 4.15 – 4.17. Differently colored shaded proportional circles represent ranges of the As, Cd, Cu, Pb, Cr and Zn concentrations. The concentrations ranges of population group *1*, group *2*, group *3*, group *4*, group *5*, group *6* and group *7* are represented by red, dark orange, pale orange, dark yellow, pale yellow and grey circles, respectively. Divisioning elemental concentrations are shown in Table 4.10. Wholly elemental concentrations were divided into 7 classes for the As, Cd, Cu, Pb and Zn concentrations and 3 classes for Cr concentrations. A red tone of circles represent the elemental concentrations downstream of abandoned mines and landfills while the green tone of circles represent the elemental concentrations upstream of abandoned mines and landfills.

4.4.1 Arsenic

The first and highest range of As concentration (1,967 – 6,162 mg/kg) was mainly distributed in the middle and in the south of the study area. This concentration range begins a kilometer upstream of landfills and tends to continue downstream of these landfills. Remains were distributed in the west, at the Po Luan mines, upstream of Euro – Thai for around a kilometer and downstream of Euro-Thai's access road of waste rocks and Euro-Thai's mine waste storage area. The second high range of concentration (672 – 1,967 mg/kg) was mainly distributed in the west. This concentration range started at the Euro - Thai mine and then continued downstream for approximately 3 kilometers. Remains were at downstream of the Tum Talu mine and upstream of abandoned mines and landfills in the west. The third high range of concentration (218 - 672 mg/kg) had a narrow distribution. It exited only in upstream of abandoned mines and landfills in the west and the north. The low range of concentration (12 –218 mg/kg) distributes in the north, in the northeast, in the east and in the west. The low range of (0 – 12 mg/kg) was

distributed in the north, in the northeast and in the east and tends to be limited to upstream of abandoned mines and landfills in mountainous terrain.

4.4.2 Cadmium

The first high range of Cd concentration (20.38 – 28.84 mg/kg) was mainly distributed in the middle and in the south of the study area. This concentration started at landfills and continued 700 meters downstream of landfills and the Tum Talu mine. Remains were in the northwest of the study area. It appeared downstream of Euro-Thai's mine road of waste rock and Euro-Thai's mine waste storage area. The second high range of Cd concentration (11.91 – 20.38 mg/kg) were observed in the middle of the study area. This concentration appeared around landfills, starting 500 meters upstream of landfills and continuing 500 meters downstream of landfills and the Tum Talu mine. The third high range of concentration (4.50 – 11.91 mg/kg) were found in the northwest of the study area. This concentration began 1.3 kilometers upstream of the Euro-Thai mine and continued 3 kilometers downstream of the mine. The forth rank of concentration (1.96 – 4.50 mg/kg) was mainly distributed in the west of the study area. This concentration started at Po Luan mine and continued downstream for approximately 1.5 kilometers. Remains were distributed in the east. The lowest range of concentration (0 – 1.96 mg/kg) was chiefly distributed in the north, the northeast and in the east of the study area. This concentration tended to be upstream of abandoned mines and landfills.

4.4.3 Chromium

The lowest range of Cr concentration (28.1 – 88.6 mg/kg) contained the highest population of concentrations in the study area. The concentration range of 0 – 67 mg/kg was mainly distributed in the mountainous, hilly and plain terrain underlain by hornfels and channel sediments in the north, the northwest and the west of the study area. Some was distributed in hilly terrain of granite in the east. The concentration range of 67- 654 mg/kg was distributed in hilly terrain occupied by hornfels in the north of the study area.

Concentrations of 654 – 5,390 mg/kg were widely distributed, particularly in hilly terrain dominated by granite, skarn, limestone and channel sediments in the east of the study area. Some were distributed in relatively flat terrain covered with channel sediments in the west. The highest concentration range of 5,390 –19,541 mg/kg was chiefly distributed in the plain terrain covered with channel sediments in the middle and in the south of the study area

4.4.4 Copper

The highest range of Cu concentration (359 – 631 mg/kg) was mainly distributed in the middle part of the study area. This range started at the Tum Talu mine and landfills and continued downstream. Remains were distributed in the west at the Euro – Thai mine and in the east. The second high range of concentration (319 – 359 mg/kg) was distributed in the center at landfills and approximately 200 meters upstream of landfills. In addition, it was also in the west downstream of Euro-Thai's mine road by waste rock and Euro-Thai's mine waste storage area. The third high range of concentration (178 – 319 mg/kg) was distributed in the west of the study area. It occurred approximately 500 meters upstream of the Euro – Thai mine. The forth range of concentration (90 – 298 mg/kg) was rather widespread. This range was distributed downstream of both the Euro - Thai and Po Luan mines. It tended to continuously spread along 2.5 kilometers downstream of Euro – Thai and approximately 2 kilometers downstream of the Po Luan mine. Remains were in the west, the east and the northeast of the study area. They tended to appear at headwaters in mountainous terrain. The low range of concentration (0 – 90 mg/kg) was distributed in the north, northeast and the east of the study area. This range tended to be upstream of abandoned mines and landfills.

4.4.5 Lead

The highest concentration range (5,725 – 19,541 mg/kg) was distributed in the middle and southern parts of the study area. This range started at the Tum Talu mine and landfills and tended to continue downstream of these. The second concentration

range (685 – 5,725 mg/kg) was distributed in the western and middle parts of the area. This range began approximately one kilometer upstream of the Euro-Thai mine and continued downstream to landfill areas. Remains were distributed in mines in the west, such as the Po Luan mine and in upstream abandoned mines and landfills in the east. The third ranked concentration range (248 – 685 mg/kg) was chiefly distributed in the west. This range appeared downstream of Euro-Thai's mine road and its mine waste storage area. It also occurred at the Euro-Thai and Po Luan mines. Remains were in the east upstream of abandoned mines and landfills. The forth ranked concentration range was distributed both in the west and north of the study area. It usually occurred at the headwaters in the mountains. The low range of concentration (0 – 67 mg/kg) was commonly distributed in the north, the northwest and in the west. It tended to be upstream of abandoned mines and landfills.

4.5.6 Zinc

The highest range of concentration (1,575 – 2,842 mg/kg) was mainly distributed in the center and in the south of the study area. This range started at landfills and tended to continue downstream. Remains were in the west near the west pile of the Euro-Thai mine and also appeared about a kilometer downstream of the mine. It was also found that Zinc remains continued downstream for approximately a kilometer along the limestone basement. The second high range of concentration (382 – 1,367 mg/kg) was widely observed in the west and in the middle of the study area. This range appeared 2 kilometers upstream of the Euro-Thai mine, at the Euro – Thai mine, downstream of Euro-Thai's mine access road of waste rocks and at Euro-Thai's mine waste storage area. Zinc continued downstream for about 500 meters. It started again around 500 meters upstream of landfills, at landfills and downstream of the Tum Talu mine. The third ranked concentration range (238 –382 mg/kg) was found in the west, around 500 meters upstream of the Euro –Thai mine on skarn basement. The low range of concentration (44 – 382 mg/kg) was widely distributed in the north, in the northeast, in the east, and in the west, upstream of abandoned mines and landfills. In addition, it appeared at the Po Luan mine and continued downstream. The lowest range of

Table 4.10 Class interval of As, Pb, Cd, Cu, Zn, Cr, C and S concentrations in the Tum Talu watershed

	Population	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb(mg/kg)	Zn (mg/kg)
Class 1	Population 1	1,967 - 6,162	20.38 - 28.84	28.1 - 88.6	359 - 631	5,725 - 19,5411	1,575 - 2,842
Class 2	Population 2	672 - 1,967	11.91 - 20.38	21.8 - 28.1	319 - 359	685 - 5,725	382 - 1,575
Class 3	Population 3	218 - 672	4.50 - 11.91	0 - 21.3	178 - 319	248 - 685	238 - 382
Class 4	Population 4	18 - 218	1.96 - 4.50	-	90 - 298	67 - 248	90 - 238
Class 5	Population 5	12 - 18	1.07 - 1.96	-	48 - 90	22 - 67	44 - 90
Class 6	Population 6	0 - 12	0 - 1.07	-	0 - 48	0 - 22	0 - 44

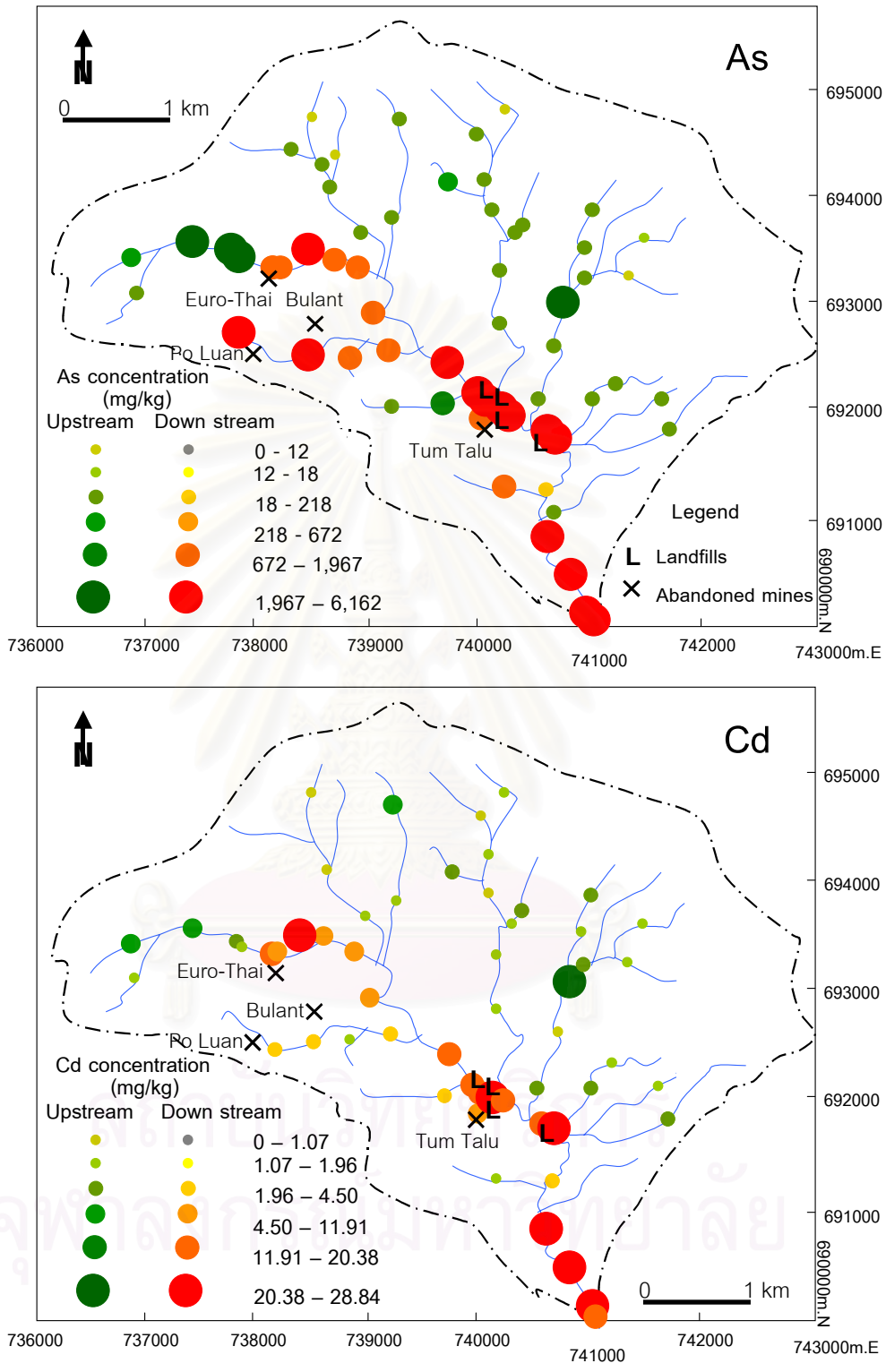

Figure 4.15 Geochemical maps of the Tum Talu watershed area showing the relief of As and Cd concentrations upstream and downstream of abandoned mines and landfills.

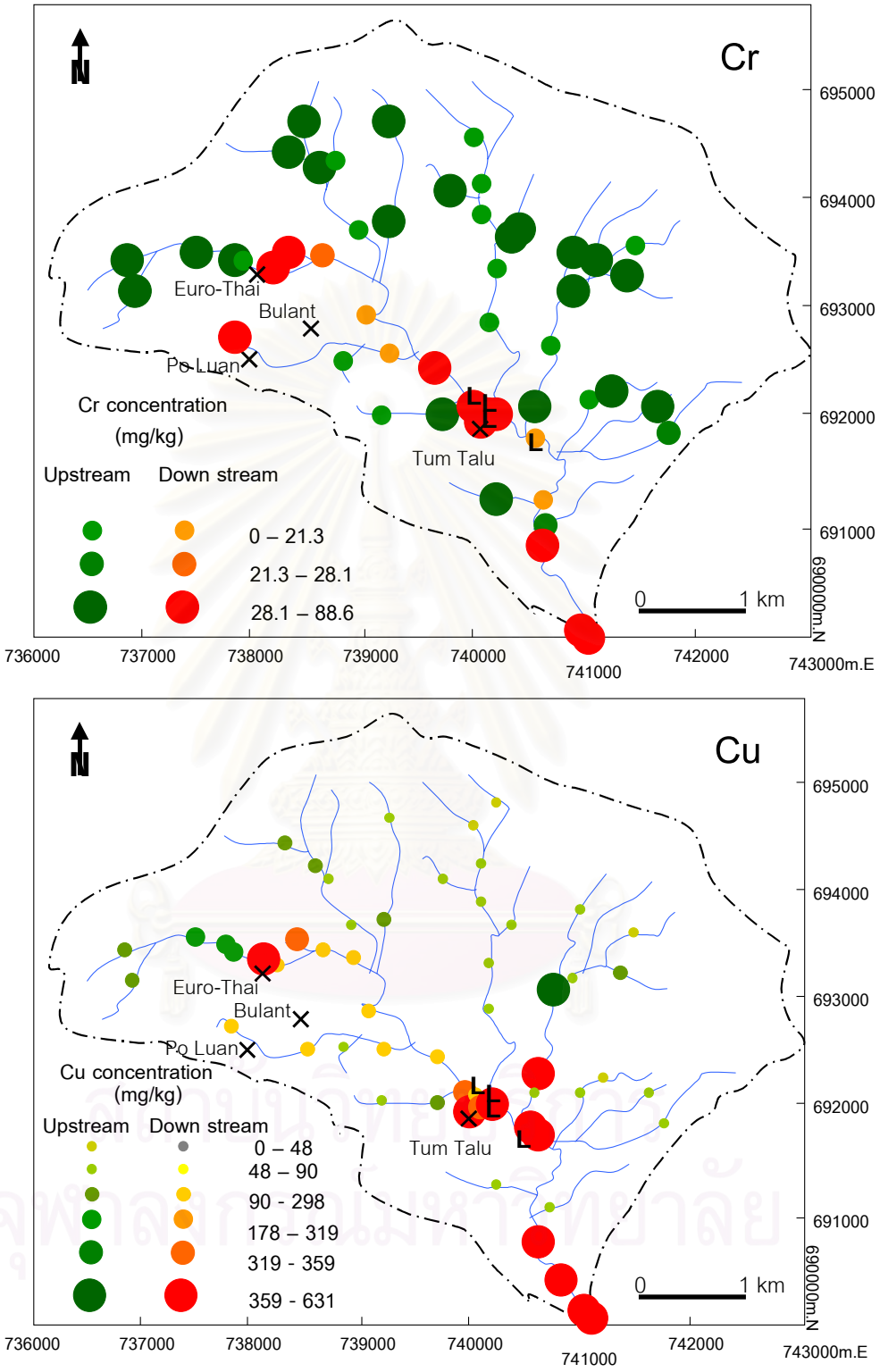

Figure 4.16 Geochemical maps of the Tum Talu watershed area showing the relief of Cr and Cu concentrations upstream and downstream of abandoned mines and landfills.

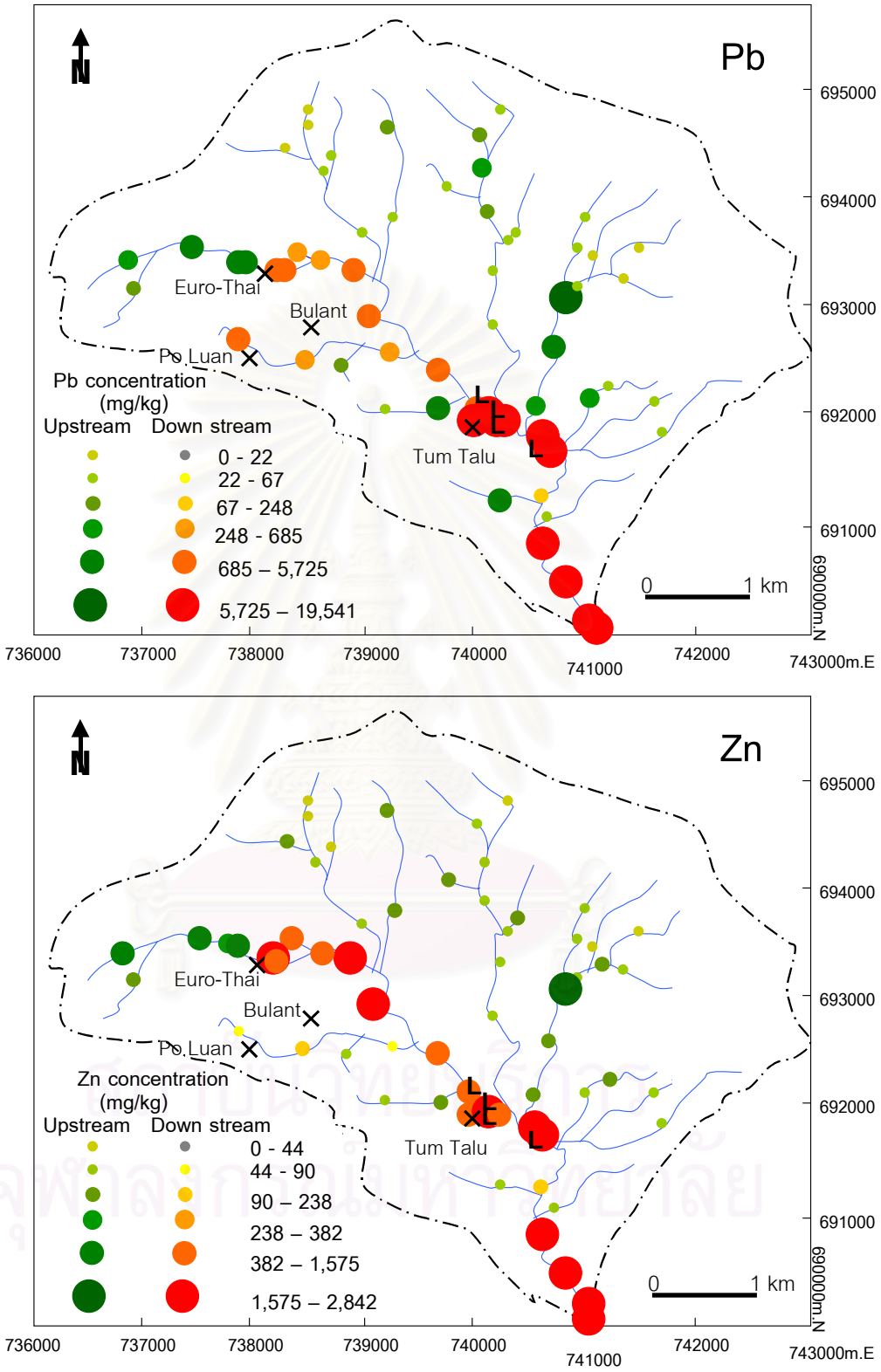

Figure 4.17 Geochemical maps of the Tum Talu watershed area showing the relief of Pb and Zn concentrations upstream and downstream of abandoned mines and landfills.

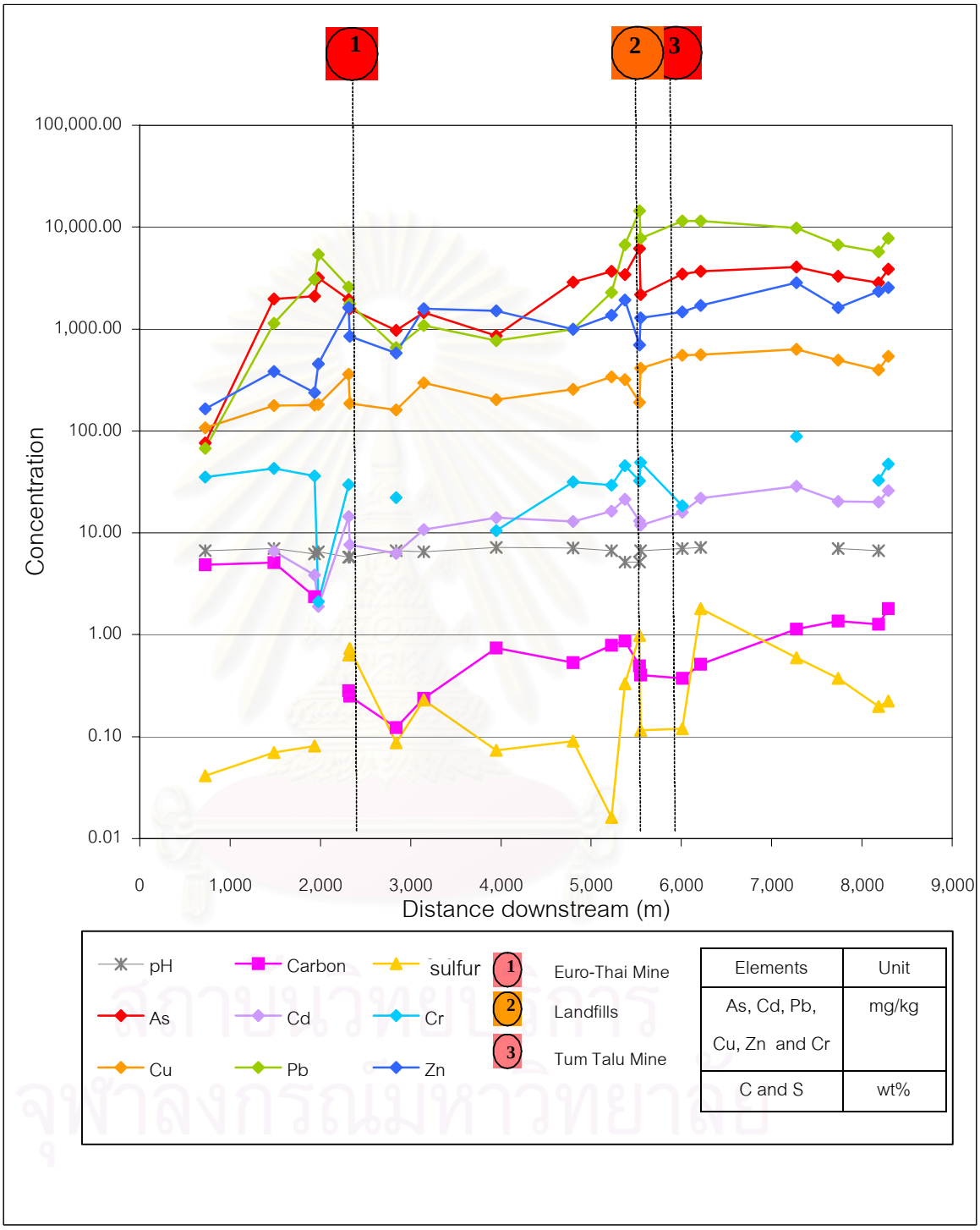

Figure 4.18 Distribution pattern along distance downstream shows As, Cd, Pb, Cu, Zn, Cr, C and S concentrations of samples that were influenced by abandoned mines and landfills.

concentration (0 – 44 mg/kg) was chiefly distributed in the north and the northeast, upstream of abandoned mines and landfills in mountainous terrain.

4.5 Geochemical anomalies

In the study, subdivision of anomaly follows the works of Hawkes and Web (1962). Range concentrations of probable anomaly, possible anomaly and non-anomaly are summarized in Table 4.11. Concentration range of probable anomaly was 4,098 – 6,162 mg/kg for As, 24.69 – 28.84 mg/kg for Cd, 54.89 – 88.51 mg/kg for Cr, 560.51 – 630.80 mg/kg for Cu, 11,507 – 19,540.88 mg/kg for Pb, and 2,326.25 – 2,841.42 mg/kg for Zn. Concentration range of possible anomaly was 3,621.97 – 4997.09 mg/kg for As, 21.78 – 24.69 mg/kg for Cd, 48.3 – 54.89 mg/kg for Cr, 515.31 – 560.51 mg/kg for Cu, 8,792.04 – 11,496.68 mg/kg for Pb and 1,678.70 – 2,326.25 mg/kg for Zn. Concentration range of non-anomaly was 0 - 3,621.97 mg/kg for As, 0 - 21.78 mg/kg for Cd, 0 - 48.3 mg/kg for Cr, 0 - 515.31 mg/kg for Cu, 0 - 8,792.04 mg/kg for Pb and 0 - 1,678.70 mg/kg for Zn. Owing to the small amount of non-anomalous population (background population), the threshold of 2.5% of the total amount of anomalous non-anomalous population is not shown in the map in Figure 4.19 – 4.21.

Elemental anomaly maps of As, Cd, Cu, Pb, Zn and Cr are shown in Figure 4.19 – 4.21 Differently shaded proportional circles represent ranges of As, Cd, Cu, Pb, Cr, Zn, C and S concentrations. Probable, possible and non-anomaly are represented by red, green and grey circles, respectively.

4.5.1 Arsenic

Probable anomalies of As are at 2 sites. Both occur in the plain terrain which is covered with channel sediments, in the middle and in the west of the investigated area. Possible anomalies appear in the middle and the south of the study area.

4.5.2 Cadmium

Table 4.11 Range concentrations of probably anomaly, possible anomaly and non-anomaly of the Tum Talu watershed.

	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Probably anomaly	4,098 - 6,162	24.6 - 28.9	54.8 - 88.6	560 - 631	11,507 - 19,541	2,326 - 2,842
Possible anomaly	3,621 - 4,998	21.7 - 24.7	48.3 - 54.9	515 - 561	8,792 - 11,497	1,678 - 2,327
Non anomaly	0 - 3,621	0 - 24.7	0 - 48.3	0 - 515	0 - 8,792	0 - 1,678

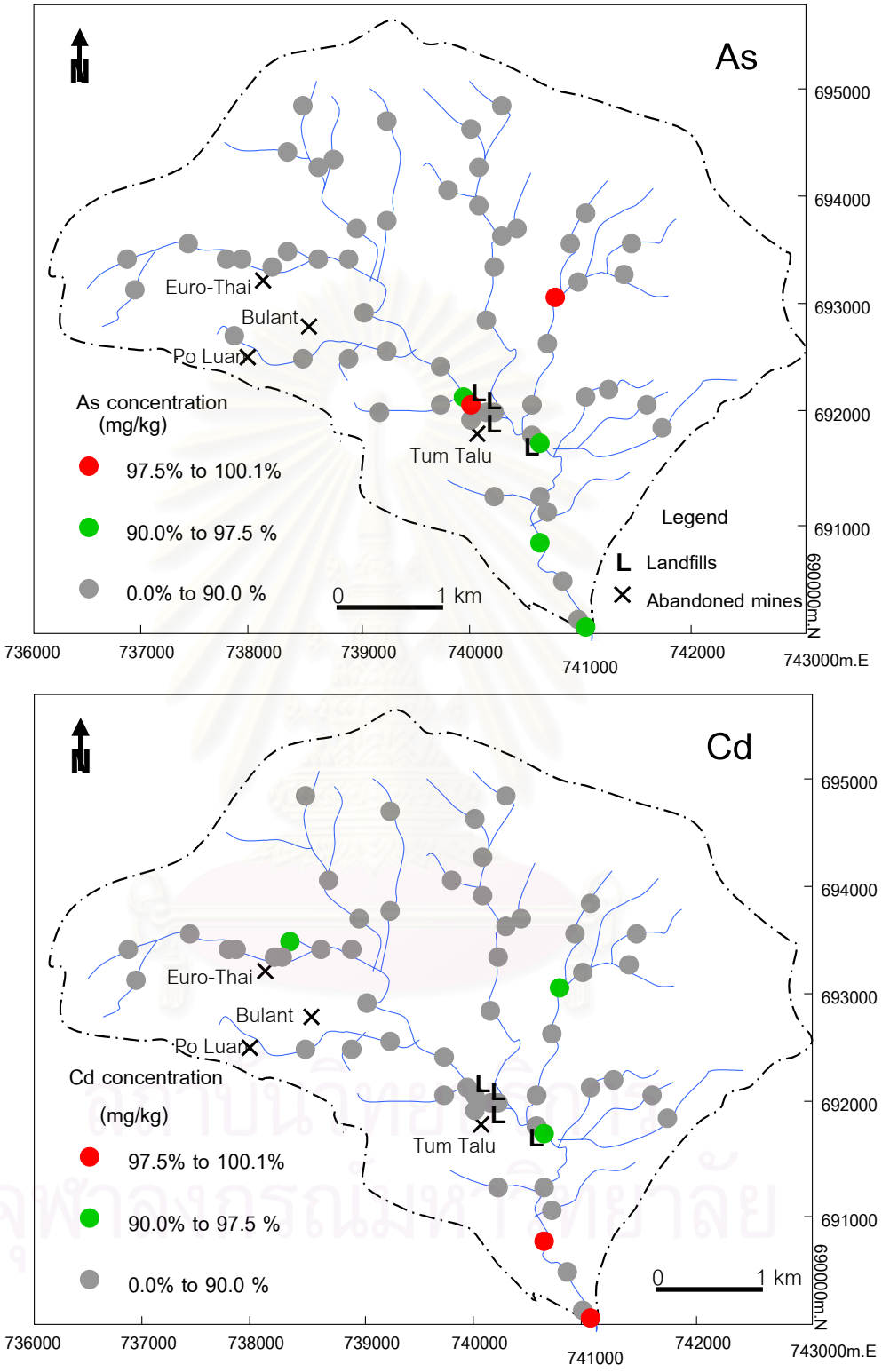

Figure 4.19 Geochemical maps of the Tum Talu watershed catchment area showing where As and Cd concentrations are probable anomalies (red tone), possible anomalies (green tone) and others (grey tone).

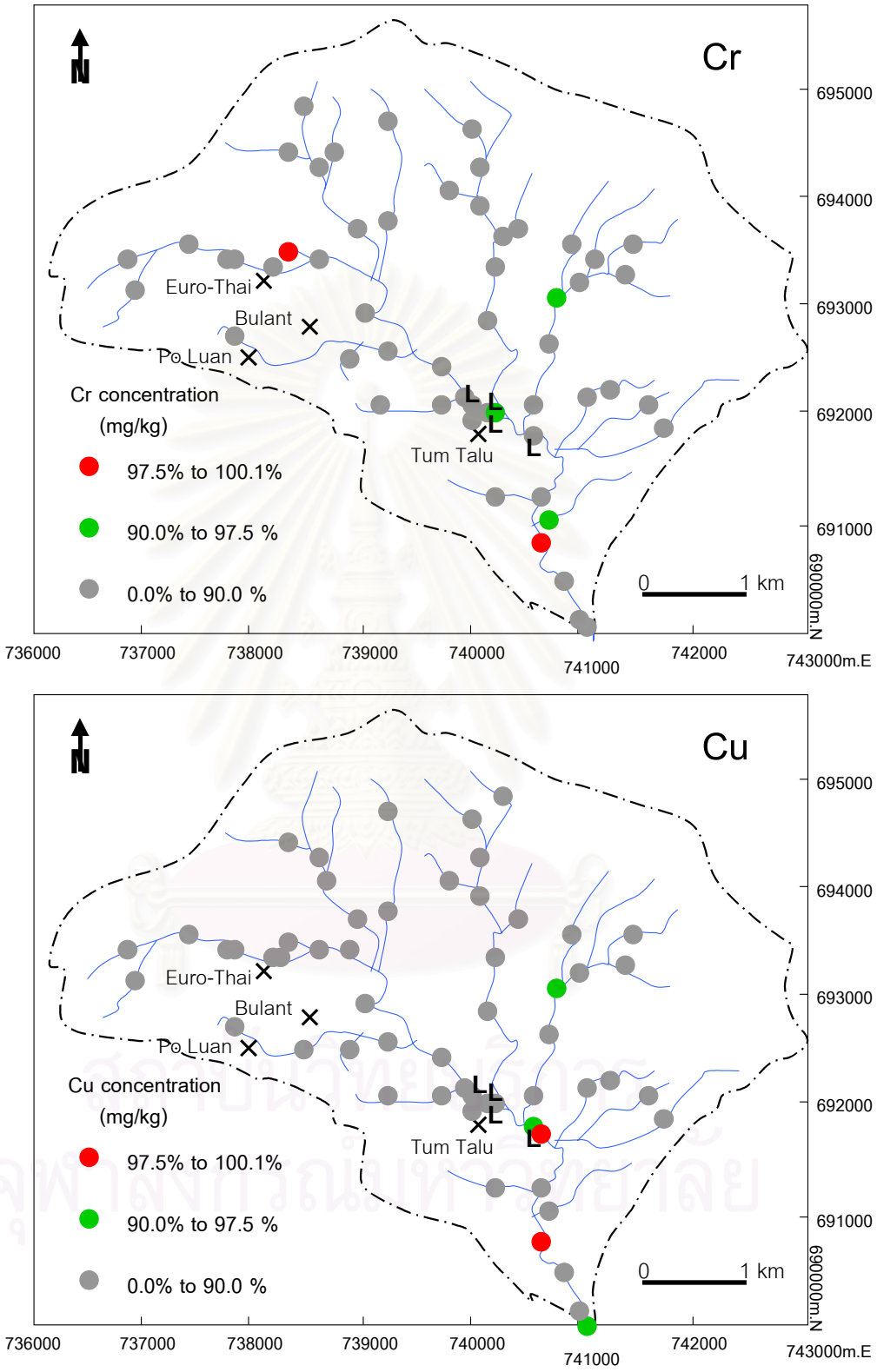

Figure 4.20 Geochemical maps of the Tum Talu watershed catchment area showing where Cr and Cu concentrations are probable anomalies (red tone), possible anomalies (green tone) and others (grey tone).

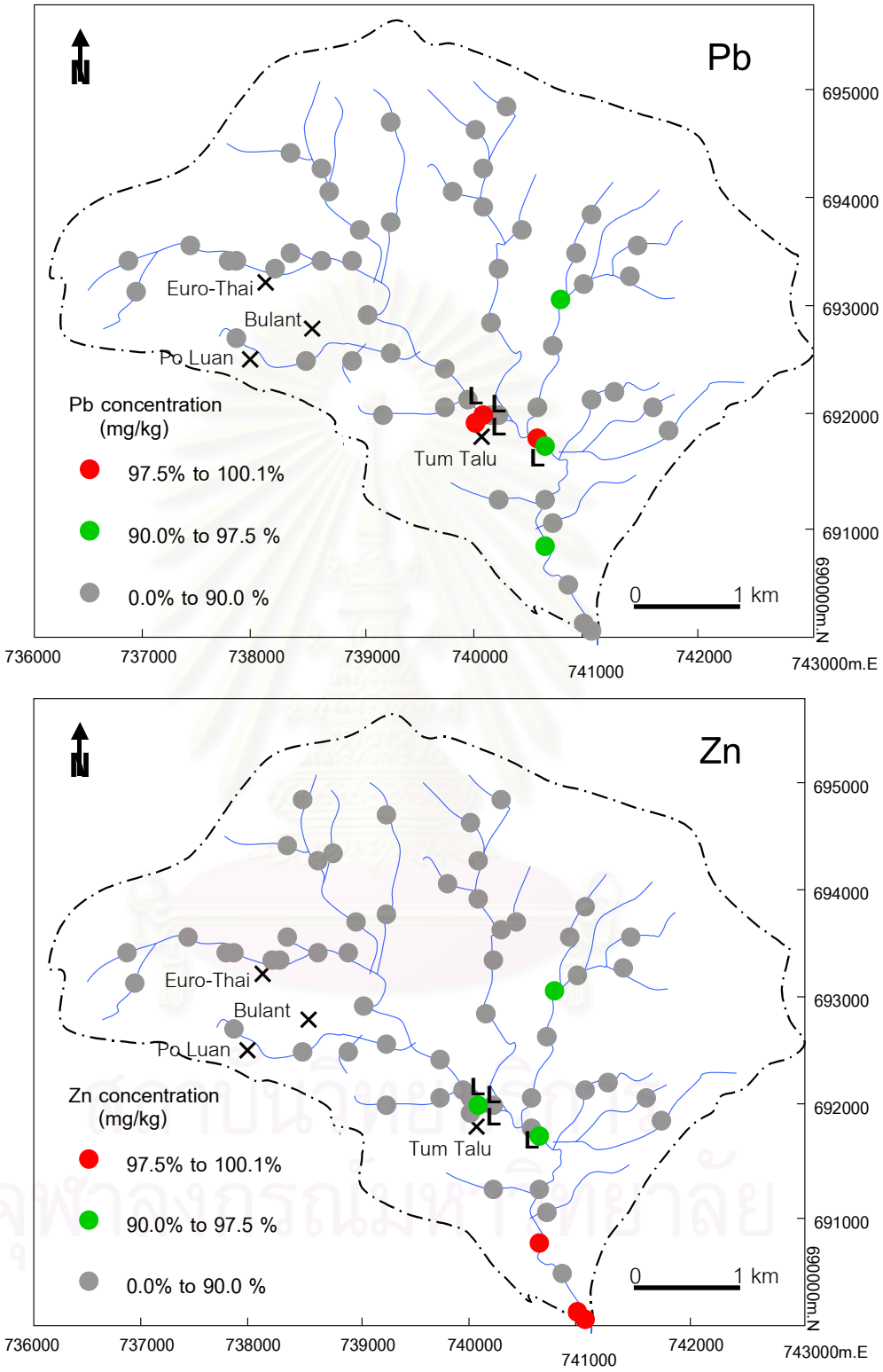

Figure 4.21 Geochemical maps of the Tum Talu watershed catchment area showing where Pb and Zn concentrations are probable anomalies (red tone), possible anomalies (green tone) and others (grey tone).

Probable anomalies of cadmium are at 2 locations. Both appear in the plain terrain covered with channel sediments in the south. Possible anomalies are at 3 locations, two of which appear in the plain terrain which is covered with channel sediments distributed in the west and in the middle of the study area. The other appears in hilly terrain underlain by recrystallized limestone (marble) in the east.

4.5.3 Chromium

Probable anomalies are at 2 points. One appears in the hilly terrain occupied by recrystallized limestone (marble) in the east and the other in the plain terrain covered with channel sediments in the middle part of the study area. Possible anomalies mainly appear in the plain terrain of channel sediments in the middle, except one which appears in the east.

4.5.4 Copper

Probable anomalies of Cu occur at 2 points, both appearing in the plain terrain occupied by channel sediments. Possible anomalies also appear in the plain terrain, and they are widely distributed. Two of them appear in the northern and southern parts of the surveyed area, and the others appear in the west of the study area.

4.5.5 Lead

Probable anomalies of Pb are 3 point locations, all present in the plain terrain covered with channel sediments, in the middle of the study area. Possible anomalies are at 2 sites which appear in the south of probable anomalies and one that appears in the east.

4.5.6 Zinc

Probable anomalies of Zn are at 3 points, all of them situated in the plain terrain occupied by channel sediments in the south of the study area. Possible anomalies mainly appear in the plain terrain of channel sediments in the north of probable anomalies, except one point that appears in the east of the study area.

CHAPTER V

DISCUSSION

5.1 Geochemical distribution and sources.

Naturally, distribution patterns of elements reflect simply the distribution of lithologic units (Rose et al, 1979). This is also true in the Tum Talu watershed where, the distribution pattern of elements is related to lithologic units. As shown in table 5.1, the concentration of metals in skarn and ores, which concentrated potentially toxic metals are the highest. Granite is the second. Its average concentration is little higher than hornfels. Due to influence by man-made activities, this assertion is particular true for distribution of elements upstream of abandoned mines and landfills.

As earlier mentioned in Chapter 4, the geochemical results imply that there is more than one geochemical effect on stream sediments downstream of pollution sources. It is likely that for the Tum Talu watershed, there are more than one source of high anomalies. Generally, natural sources of stream sediments are base rocks distributed within the watershed area. Moreover, sediments derived from mine wastes in abandoned mines and landfill leakage can accumulate in the streams as well. So it is quite possible that these anthropogenic sites are additional sources of metals in the watershed. As show in Figure 5.1, pie diagram which displays various geochemical effects on ranges As concentration. The arsenic concentration between 1,967 and 6,163 mg/kg; is grouped in the anomalous concentration group *1*, the largest proportion of the effects which is downstream Tum Talu mines and landfills; and the group accounts for 32 %. The downstream landfills, downstream Euro-Thai and upstream skarn and ores rank second, making up 17 % of each. The Third is the downstream Po Luan mine, which is responsible for 11 %. The other effect is upstream hornfels, which contributes 6 % of the total geochemical effects in this level of concentration. The arsenic concentration ranges from 672 – 1,967 mg/kg is illustrated in Figure 5.2, and it is defined as the anomalous concentration group *2*, the largest proportion of the effects caused by downstream Euro-Thai mine. It alone a ccounts for 50%, whereas upstream

Table 5.1 Statistics of As, Cd, Pb, Cu, Cr, Zn concentrations as well as carbon and sulfur contents of stream sediments in the Tum Talu watershed. The table shows metals concentration in downstream of the natural sources which classified by geology.

		C [wt%]		S [wt%]		As (mg/kg)	
Lithology	*N*	Range	Mean + SD	Range	Mean + SD	Range	Mean + SD
Skarn	3	2.35 - 5.10	3.73 + 1.94	0.07 - 0.08	0.08 + 0.01	1967 - 3175	2412 + 664
Granite	5	0.62 - 4.88	2.93 + 1.88	0.03 - 0.04	0.04 + 0	76 – 826	426 + 347
Hornfel	32	0.26 - 3.87	1.66 + 1.04	0.01 - 0.07	0.03 + 0.02	7 – 672	86 + 119

		Cd (mg/kg)		Pb (mg/kg)		Cu (mg/kg)	
Lithology	*N*	Range	Mean + SD	Range	Mean + SD	Range	Mean + SD
Skarn	3	1.9 - 6.6	4.1 + 2.4	1132 - 5390	3199 + 2132	178 - 181	180 + 2
Granite	5	1.1 - 7.8	4.2 + 3.4	42 - 977	361 + 408	48 - 136	96 + 39
Hornfel	32	0.2 - 4.5	1.7 + 0.9	3 - 788	116 + 202	9 - 103	64 + 22

		Zn (mg/kg)		Cr (mg/kg)	
Lithology	*N*	Range	Mean + SD	Range	Mean + SD
Skarn	3	238 - 454	358 + 110	2 - 40	27 - 22
Granite	5	44 - 560	201 + 211	17 - 43	28 - 10
Hornfel	32	13 - 194	80 + 44	9 - 55	27 - 11

N = Number of samples

SD = Standard deviation

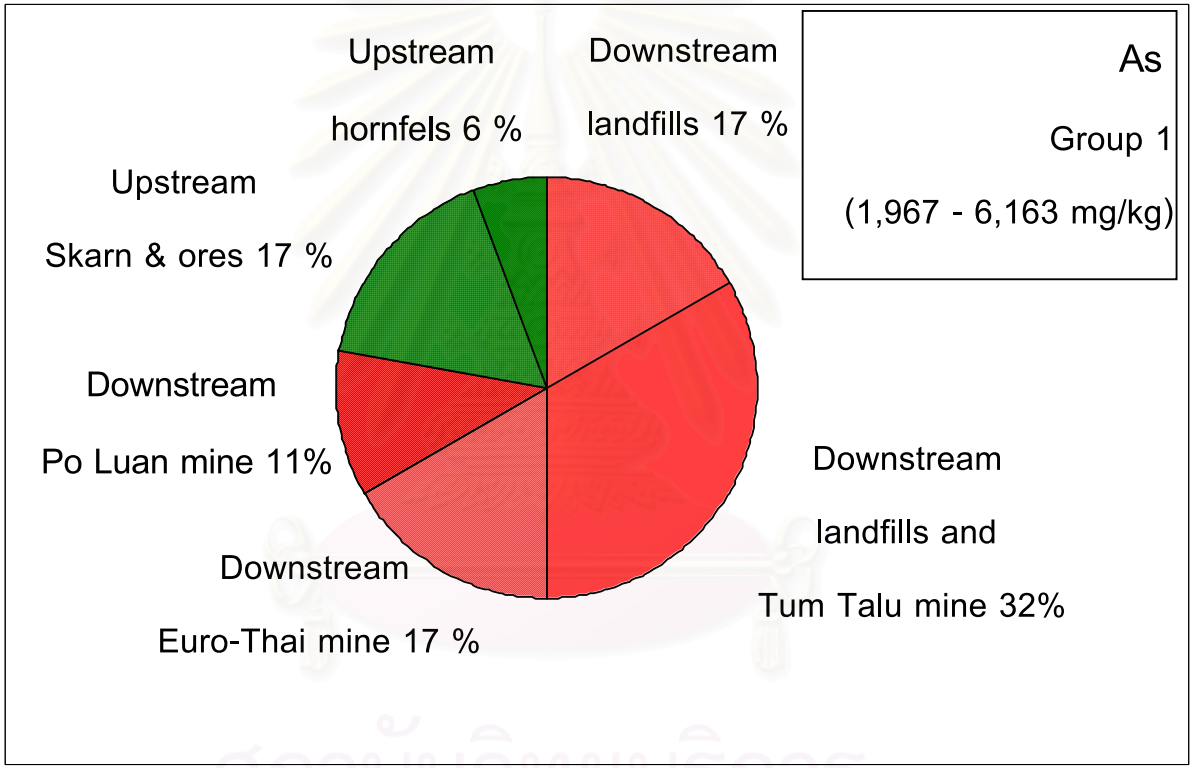

Figure 5.1 Pile diagram showing different types of arsenic concentration ranging 1,967 - 6,136 mg/kg, for the Tum Talu watershed area.

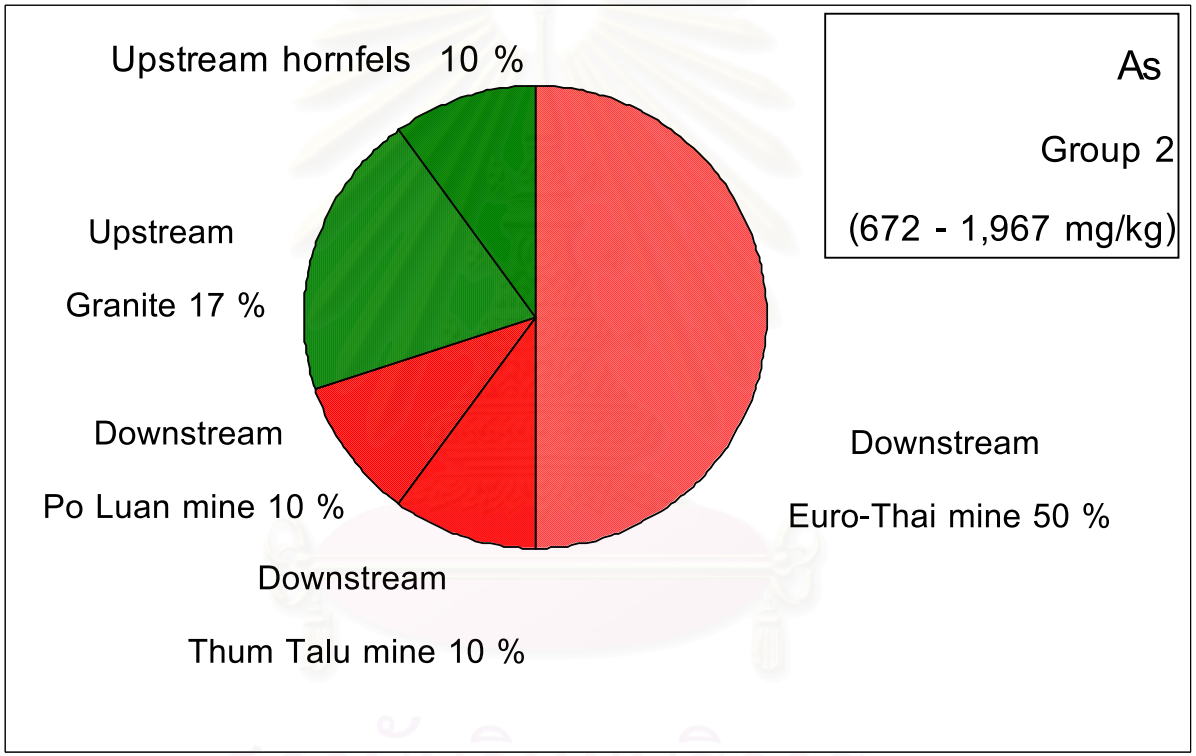

Figure 5.2 Pile diagram showing different types of arsenic concentration ranging 672 – 1,967 mg/kg, for the Tum Talu watershed area.

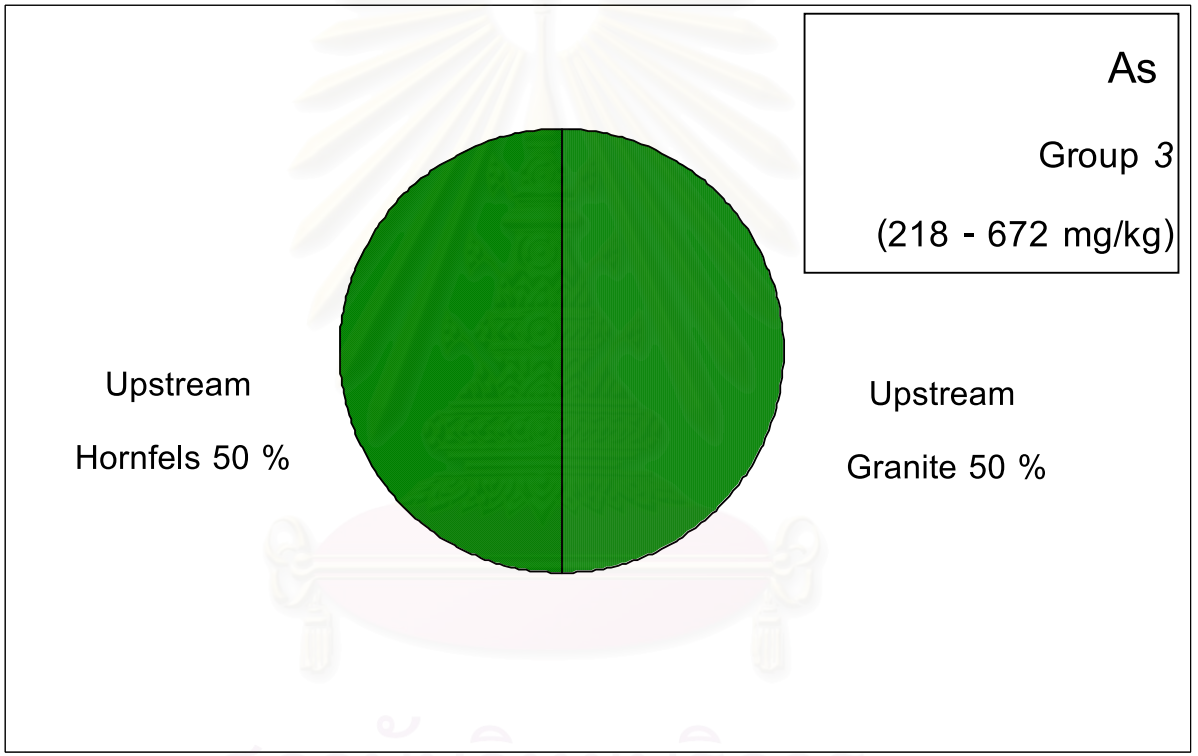

Figure 5.3 Pile diagram showing different types of arsenic concentration ranging 218 – 672 mg/kg, for the Tum Talu watershed area.

granite ranks second constituting 17 %. Third is the downstream Tum Talu mine, downstream Po Luan and upstream hornfels, which are individually responsible for 10 %. The result for anomalous concentration group 2 does not seem much different from group *1.* It can be concluded that not only the abandoned mines and landfills which are anthropogenic sources, giving anomalous concentration of arsenic, but also natural sources do. Above all, this conclusion implies that human activities become the majority cause of abnormally high elemental (heavy metals) concentrations for stream sediment in the Tum Talu watershed.

As shown in the earlier maps, high concentrations of all metals are quite related sources, especially arsenic and lead. Their high concentrations present near the landfills and the Tum Talu mine, whereas anomalies of Cu, Cd and Zn are present a few kilometers from sources. This phenomenon may be due to speciation and mobility of individual elements under similar physiochemical conditions. The geochemical mobility of each element is shown in Table 5.2. Arsenic, Cd, Zn and Cu are moderately mobile under oxidizing conditions with pH < 4. Arsenic and Zn are moderately mobile and Pb, Cd and Cu are slightly mobile under the oxidizing condition with pH 5-8. Mellor (2001) has reported from his study on a lead and zinc in the Wallsen Burn, and urban catchment in Tyneside, UK, that the potential mobility of zinc is considerably greater than that of the lead in stream sediments. Metals with relatively high mobility will be moved farther away distance downstream of sources. This can be explained within the case of the Tum Talu watershed area, why Zn anomaly moves away from sources while Pb shows anomaly only at sources. Moreover, this truth is clearly supported by Pb speciation. Lead in stream sediments frequently is in forms of lead sulfide such as galena (Pb_2S) or lead carbonates, as cerrusite ($PbCO_3$) (Song et al., 1999) whose their specific gravities are 7.4 - 7.6 and 6.58, respectively. The high specific gravity of Pb governs Pb ores to move proximally from sources. Both speciation and mobility are adequate support for the observation that lead should have anomalous concentration at sources. Unlike Zn and Pb metals, As which is moderately mobile is not present far away from sources, but it still appears nearby sources. This may be due to geochemical speciation of arsenic. High concentration of As may come from arsenic-bearing sulfide minerals, such as arsenopyrite [As_2S]. The mineralogical data from the study of

Table 5.2 Potentially toxic metals' mobilities in supergene (e.g., soil) environments with different pH and oxidizing-reducing conditions (Siegel, 2002).

Relative mobility	Oxidizing (pH 5-8)	Oxidizing (pH < 4)	Reducing
Very mobile	Mo, (Se)		
Moderately mobile	**Zn**, V, **As** (Hg, Sb)	**Zn**, **Cd**, Hg, **Cu**, Co, Ni, V, **As**, Mn	Mn
Slightly mobile	Mn, **Pb**, **Cu**, Ni, Co, (**Cd**)		Fe
Immobile	Fe, Sc, Ti, Sn, (**Cr**)	Fe, Sc, Ti, Sn, **As**, Mo, Se	Fe, Ti, Sn, Cu, **Pb**, **Zn**, **Cd**, Hg, Ni, Co, **As**, Sb, V, Se, Mo, **Cr**

Song et al. (1999) of chemical and mineralogical forms of lead, zinc and cadmium in particle size fractions of some waste, sediments and soil in Korea suggest that arsenopyrite is frequently found both in mine waste dumps and stream sediments derived from the wastes. However, for the Tum Talu watershed there is not enough data to support this conclusion. Additionally, anomaly of concentration of As may be related to Fe^{+3} hydroxide or the so-called "yellow boy" (Tom and James, 2004). As can precipitate with the "yellow boy" and coat on stream beds. Acid mine drainage (AMD) from oxidation of pyrite often contains large concentrations of both iron and arsenic. Downstream from its source, iron from AMD precipitates via hydrolysis contributing new suspended sediments as ocherous precipitates of $Fe(OH)_3$. These sediments are enriched with arsenic. The study of iron minerals from "yellowboy" in the sediments of streams receiving AMD by Bigham et al. (1990) show that "yellowboy" from these sediments contained > 2000 (mg/kg) of arsenic. These high levels of arsenic were found in sediments collected from both Europe and North America. This enrichment of sediments with arsenic can be caused by coprecipitation of arsenic with iron or by arsenic adsorption on $Fe(OH)_3$ sediments but the exact forms of arsenic in these sediments are largely unknown (Nriagu, 1994). Additionally, cadmium is slightly mobile under an oxidizing condition with pH 5-8, therefore its mobility should be similar to that of Pb, but actually it is not. This may be due to it speciation. Result of direct observations on the stream sediments Song et al. (1999) indicates that the primary sphalerite is still the main pool of the Zn and Cd. Consequently, mobility of Cd should be related to Zn because Cd is a solid solution substituting in part for Zn in sphalerite (Zn[Cd]S) (Siegel, 2000).

5.2 Extention of contaminated sediments

As visualized in the previous section, some locations in the Tum Talu watershed have significantly high metal concentrations. This is particularly true downstream of the abandoned mines and landfills, where markedly abnormally high concentrations of As, Cd, Pb, Cu and Zn were found in sediments. Although, this phenomenon suggests that downstream sediments were impoverished by metal contamination, the stream

sediments quality standards need to be applied to samples for a clear indication level of the

contamination levels in the watershed.

The standards of metals levels suggested by the Dutch Ministry of Housing, Spatial Planning and Environment target and intervention values for soil/sediment remediation (Table 5.3) were applied for this study. This standard has been long established and the intervention values are based on extensive studies of both human and eco-toxicological effects of soil contaminants. In addition, they assist in the assessment of contaminated soils/sediments and sites that pose potential concern, as well as providing a means for screening out those soils/sediments that do not warrant additional attention (Macklin et al., 2003).

The Dutch intervention values for soil/sediment remediation are considered to be numeric manifestations of the concentrations above which there can be said to be a case of serious contamination. These values indicate the concentration levels of metals above which the functionality of soil for human, plant, and/or animal life may be seriously compromised or impaired. Concentrations that do not exceed intervention values can therefore, be considered to be uncontaminated (Macklin et al., 2003). The Dutch target values indicate the level at which there is a sustainable soil quality and gives an indication of the benchmark for environmental quality in the long term on the assumption of negligible risk to the ecosystem (Macklin op.cit.)

In this study, As, Cd, Cr, Cu, Pb and Zn concentrations in stream sediments are plotted in the form of proportional circles on a series of drainage network maps (Figures 5.22 and 5.23); the larger circles show higher metal concentrations. Black circles denote where metal concentrations exceed intervention values (As 55 mg/kg; Cd 12 mg/kg; Cr 380 mg/kg; Cu 190 mg/kg; Pb 530 mg/kg; and Zn 360 mg/kg), grey circles denote where metal concentrations exceed target values (As 29 mg/kg; Cd 0.8 mg/kg; Cr 100 mg/kg; Cu 36 mg/kg; Pb 85 mg/kg; and Zn 140 mg/kg) and open circles show where metal values do not exceed target values.

Arsenic concentrations in all samples upstream of the abandoned Euro – Thai mine are above the intervention value (55 mg/kg), suggesting that stream sediments

Table 5.3 Target values and soil remediation intervention values for selected metals in soils from the Dutch Ministry of Housing, Spatial Planning and Environment (VROM, 2001). Values have been expressed as concentrations in a standard soil (10% organic matter, 25% clay).

Elements	Target value (mg/kg)	Intervention value (mg/kg)
As	29	55
Cd	0.8	12
Cr	100	380
Cu	36	190
Pb	85	530
Zn	140	720

begin to be seriously contaminated by arsenic upstream of the abandoned mine. And downstream of the Euro – Thai mine, the arsenic concentration slightly decreases downstream of the Euro-Thai mine. Arsenic values increase to above fifty times intervention values (2,750 mg/kg) at a few kilometers upstream of Euro-Thai landfills and markedly a peak at landfills. They also tend to dramatically increase downstream of the Tum Talu mine and landfills. This suggests that sediments downstream of Tum Talu are very seriously contaminated with arsenic.

Cadmium concentrations are above the target value (0.8 mg/kg) at all sample sites. These levels are above the intervention value at 12 mg/kg about 1.5 kilometers downstream of the Euro-Thai mine and then gradually increase. It suggests that Cd begins to seriously contaminate sediments at this location. The cadmium concentration is above two times the intervention value approximately 3 kilometers downstream of the Tum Talu mines and landfills. It can be concluded that stream sediments begin to be seriously contaminated approximately 3 kilometers downstream of the Tum Talu mines.

In general, chromium concentration is below target (100 mg/kg) and intervention values (380 mg/kg) at all sample sites. This indicates that stream sediments aren't contaminated by chromium.

Like cadmium concentration levels, copper concentrations are invariably above the target value (36 mg/kg) at all sample sites. Concentrations exceed the intervention value (190 mg/kg) at the Euro-Thai mine and then gradually increase downstream of the mine. At the landfill site concentration rises to above two times at the intervention value and steadily increases downstream. It can be summarized that stream sediments begin to be seriously contaminated at Euro-Thai and are further contaminated downstream of the landfill.

Pb concentrations are above the intervention value (530 mg/kg) upstream of the Euro-Thai mine and these tend to decrease at the downstream area from the mine. They increase sharply again around landfill sites and at the Tum Talu mine. At these locations, Pb concentrations are above 20 times the intervention value. Therefore, stream sediments are considered to be extremely contaminated upstream of the Euro-Thai mine and are seriously contaminated by the Tum Talu mine and landfills.

In the Euro-Thai mine downstream area, the zinc concentrations begin above the target value at all sample sites and tends to decline slightly until the landfill sites. Concentration increase gradually for almost all samples and are more than two times the intervention value approximately 2 kilometers downstream of the landfills and the Tum Talu mine. Therefore, on the basis of zinc concentration levels, the stream begins to be seriously contaminated at this site.

Notice that metals contamination begins to be serious downstream of abandoned mines and almost all metals seriously contaminate sediments in the vicinity of landfills. These results also agree with the previous section elucidates that abandoned mines and landfills may be sources of this serious contamination of sediments.

The potential risk of metals contamination to human health and ecosystem seems to be greatest in the vicinity of abandoned mines and landfills because of serious metals contamination, but for Cr there is a negligible risk. Although, there are low risk above background, the risk particularly for As and Pb should be concerned because the contamination also extends to upstream of mines.

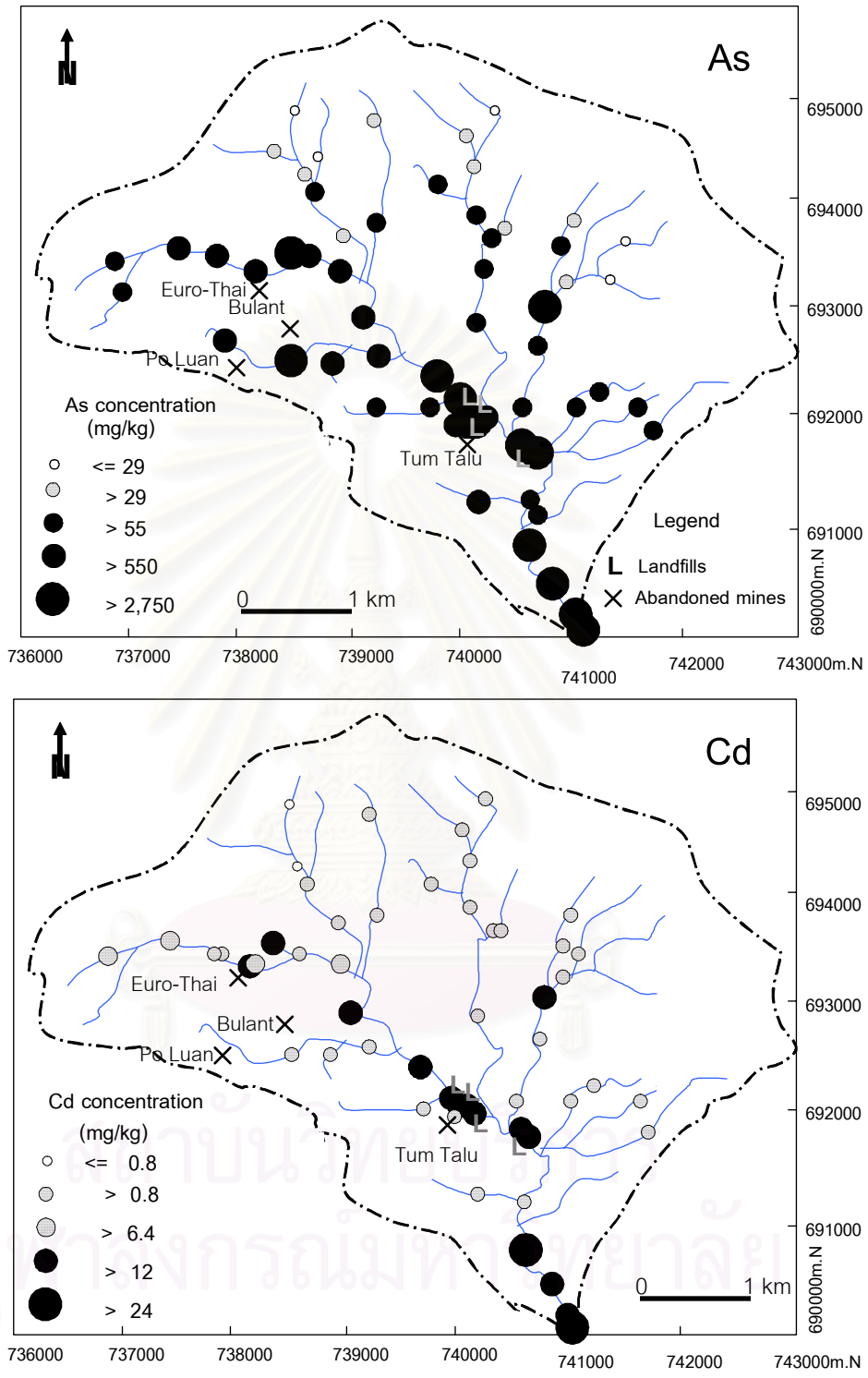

Figure 5.4 Stream sediment concentrations of As and Cd in Tum Talu catchment. Shaded proportional circles show where concentrations fall either below (white) or above (grey) Dutch target values, or where they exceed (black) Dutch intervention values for soil remediation.

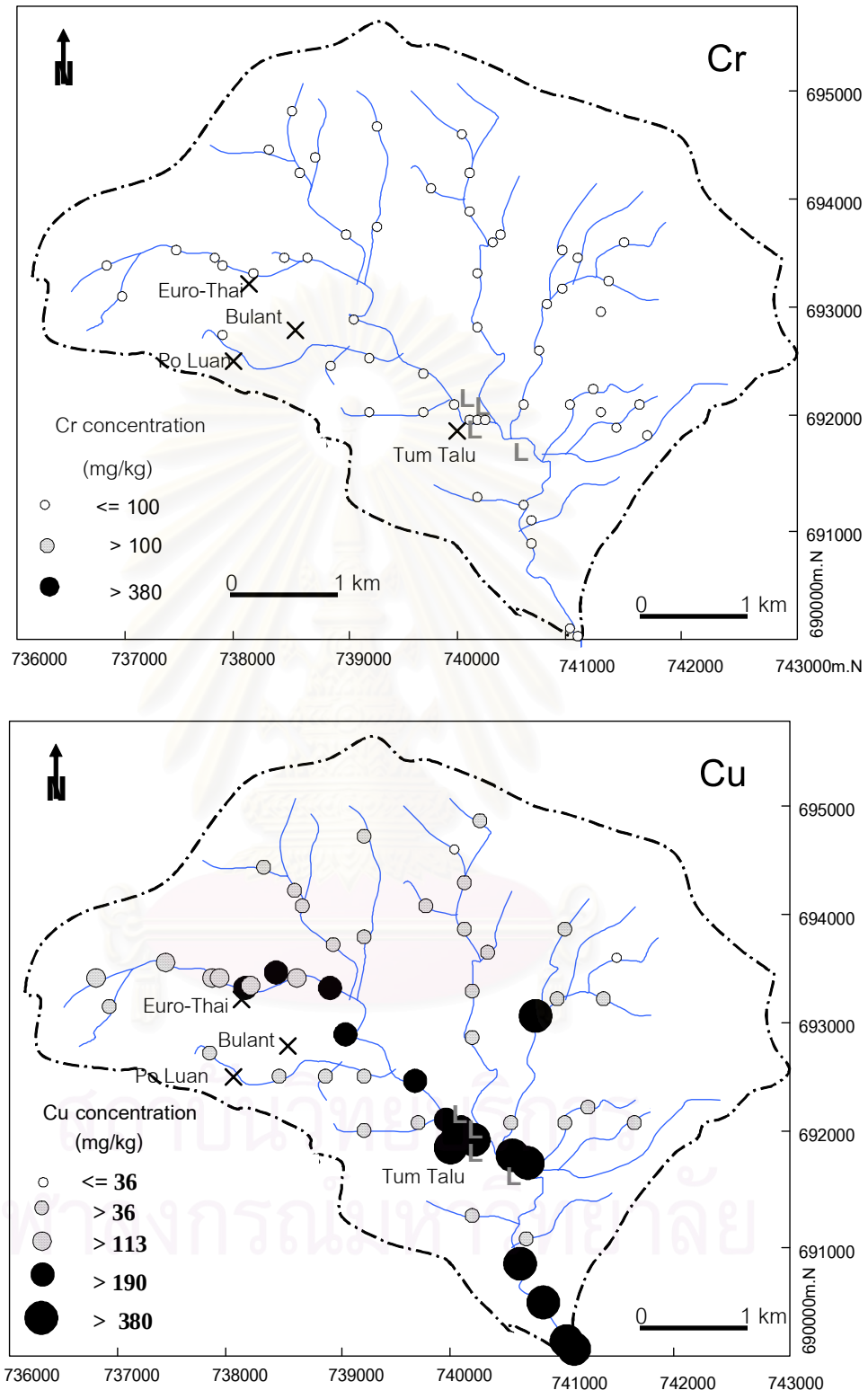

Figure 5.5 Stream sediment concentrations of Cr and Cu in Tum Talu catchment. Shaded proportional circles show where concentrations fall either below (white) or above (grey) Dutch target values, or where they exceed (black) Dutch intervention values for soil remediation.

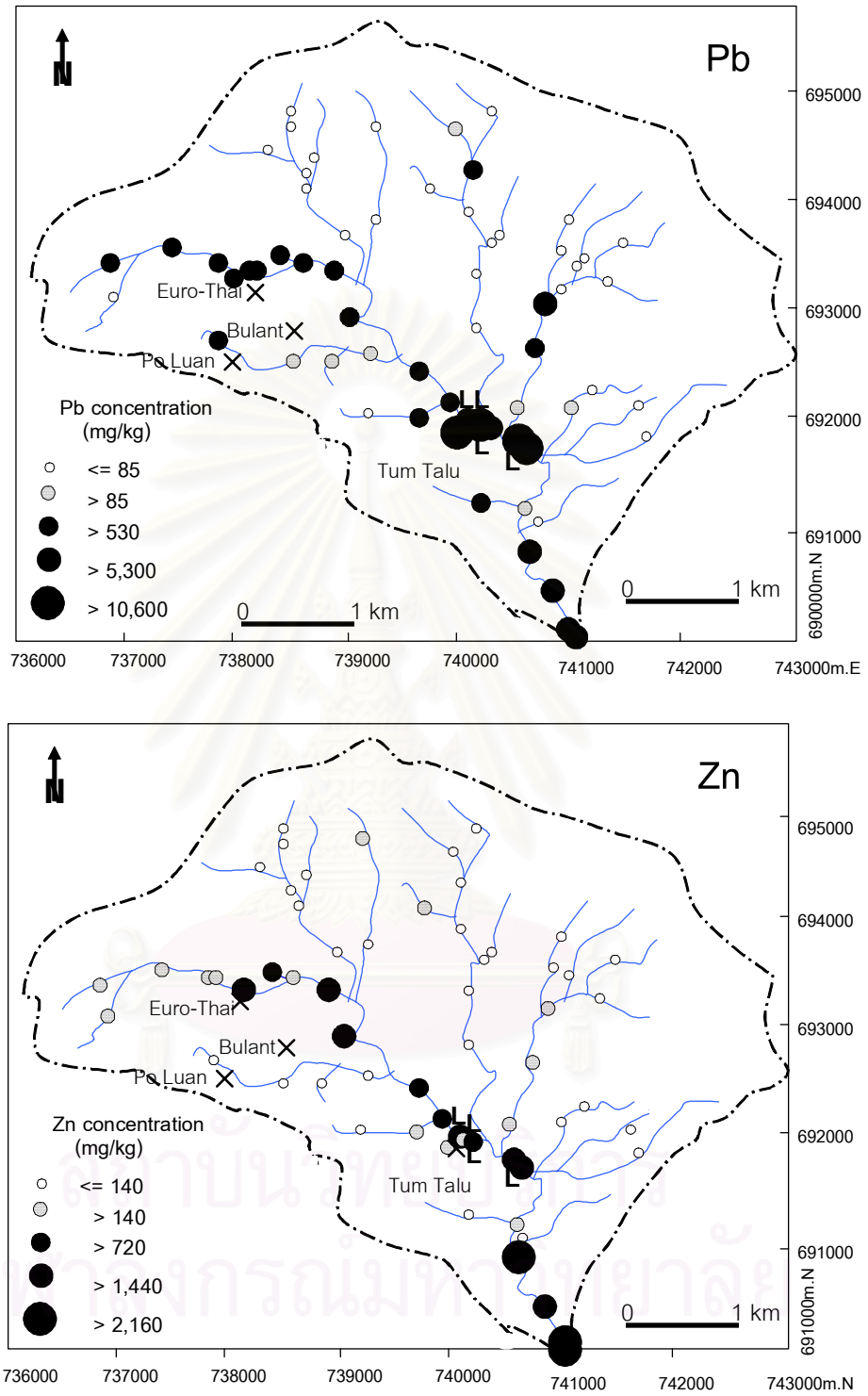

Figure 5.6 Stream sediment concentrations of Pb and Zn in Tum Talu catchment. Shaded proportional circles show where concentrations fall either below (white) or above (grey) Dutch target values, or where they exceed (black) Dutch intervention values for soil remediation.

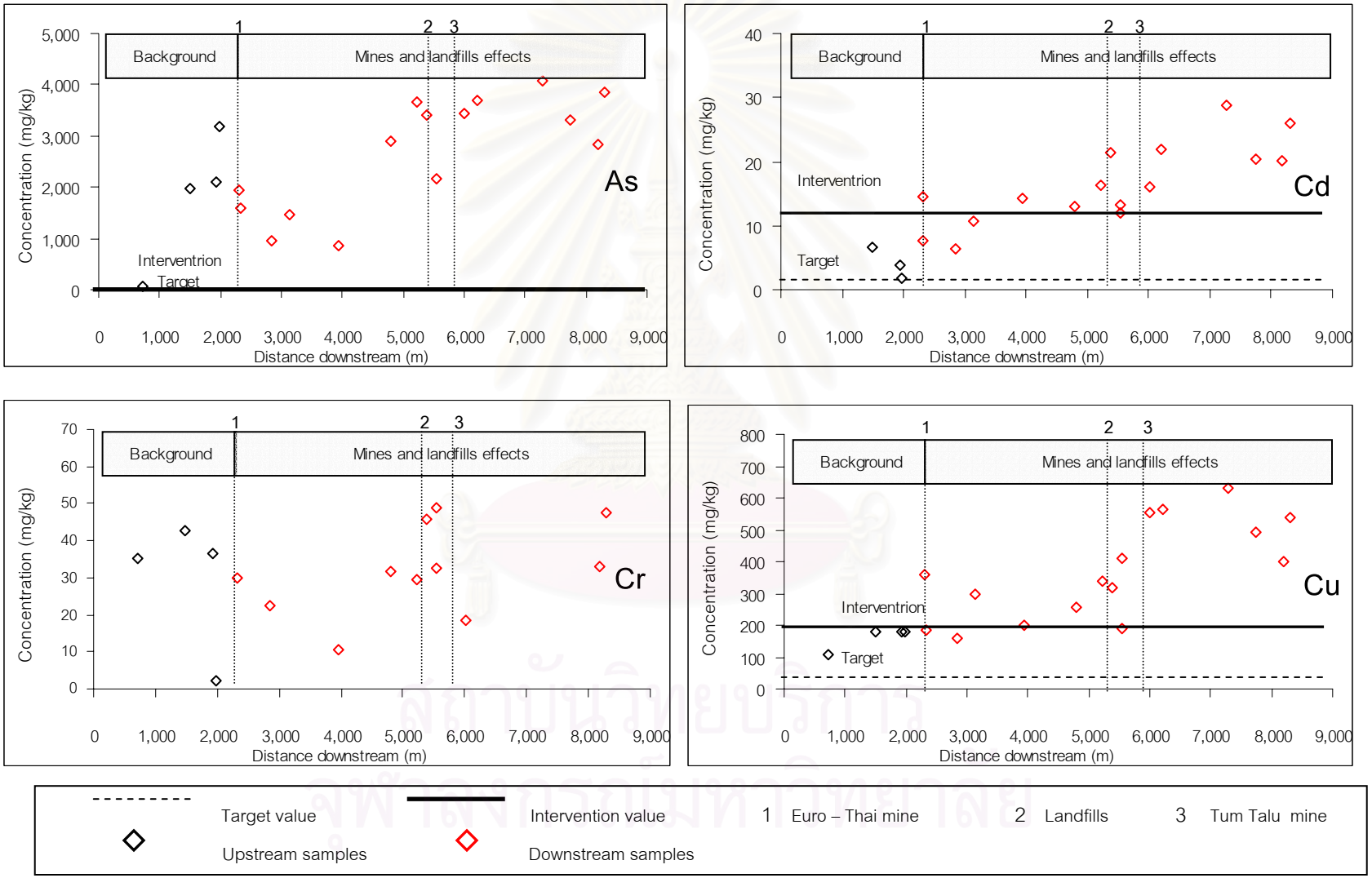

Figure 5.7 Downstream changes in stream sediments of metal concentration (As, Cd, Cr and Cu) in the Tum Talu watershed.

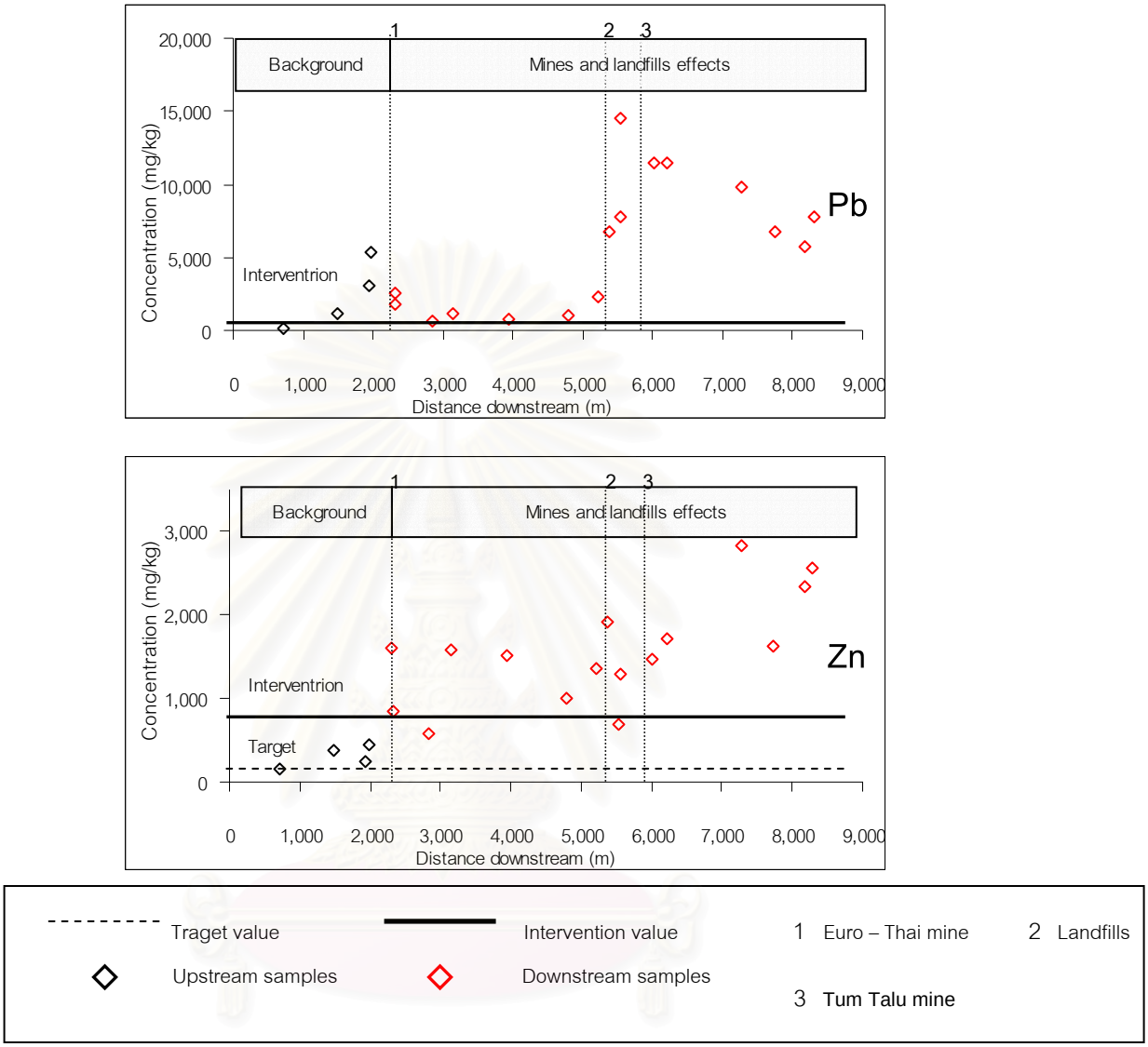

Figure 5.8 Downstream changes in stream sediments of metal concentration (Pb and Zn) in the Tum Talu watershed.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

Mine waste dumps, mineralized outcrops and landfill leaks discharging typical acid mine drainage clearly indicate that they are major sources of metals contaminants in the abandoned mine area.

Distribution patterns show high levels of metals and sulfur and low levels of carbon in the downstream areas of abandoned mines and landfills. In contrast, metals and sulfur show low concentrations while carbon has high levels upstream of abandoned mines and landfills.

Concentrations of As, Pb and Cu decrease slightly downstream, away from sources at abandoned mines and landfills, but Zn and Cd concentrations gradually increase. The distance between recognized sources and maxima of concentrations in stream sediments strongly suggests that metals are being released in solution and are subsequently being immobilized in the stream sediments.

Comparing metals concentrations with the Dutch standard value, As, Pb, Cu and Zn begin to contaminate upstream of abandoned mine areas and seriously contaminate sediments downstream of abandoned mines and landfill areas. These suggesting that the greatest concerned should be spend in downstream of abandoned mines and landfills areas.

Antropogenic activity in the watershed, such as man-made dam and metal waste emanating from abandoned mines and especially landfill leakage which contain hazardous wastes, are major sources of toxic metals contaminating stream sediments in the Tum Talu watershed. However, mineralization of skarns and ores which are considered as being naturally occurrences are very minority sources by natural exposure.

6.2 Recommendations

The remediation project in 2000-2002 helps to decrease erosion of hazardous waste materials entering into the stream directly. However, the sources of metals such as pit, waste rocks and gung which didn't remove from the study area are still exist underground. They could be the potential sources of metals contamination in groundwater.

The mineralized outcrops that contains huge amount of hazardous waste materials should be covered by some kind of plants to protect erosion of these materials in to the stream quickly.

The landfill leakages suggesting that the landfills should be repaired and moved to another place. Enormous amounts of hazardous waste should be stabilized firstly and then placed into the genuine secure landfills. And those secure landfills should correctly make of proper materials and located far away from the bank of the stream.

Awareness and careless of metal contamination in the study area should be pronounce for dwelling and villagers. For example, children don't play in the stream. Don't catch and eat fishes or aquatic animals from the stream. Don't drink water and consume water from the stream especially, downstream of Tum Talu and the landfills.

The study of sedimentary composition in quantitative and qualitative analyses, as sequential leaching and selective leaching will help to understand more about sedimentary characteristics and the nature of metal speciation. It will also be helpful in predicting transportation of contaminated sediments downstream

REFERENCES

ANL. Human Health Effect Sheet: Zinc [Online]. 2001. Available from: www.ead.anl.gov/pub/doc/zinc.pdf

Apodaca, L.E.; Driver, N.E.; and Bails, J.B. Occurence, transport, and fate of trace elements, Blue River Basin, Summit Country, Colorado: An integrated approach. Environmental Geology 39, 8 (June 2000): 901-913.

Biamonte, M. Copper and Health Problems [Online]. 2002. Available from: http://www.copper.org/copperhome/Env-health/environmentandhealth-health.html.

Bigham, J.M., Schwertmann, U., Carlson, L., and Murad, E. A poorly crystallixed oxyhydrosulfate of iron formed by bacterial oxidation of Fe (II) in acid mine water. Geochimisty Cosmochim Acta 54 (1990): 2743-2758.

Boni, M.; Costabile, S.; Vivo, D.B.; and Gasparrini, M. Potential environmental hazard in the mining district of southern Iglesiente SW sardinia, Italy. Journal of Geochemical Exploration 67 (1999): 417-430.

Carlo, E.H.D., and Anthony, S.S. Spatial and temporal variability of trace element concentrations in an urban subtropical watershed, Honoluu, Hawaii. Appiled Geochemistry 17 (2002): 475-792.

Charusiri, B. and Charusiri P. Geology and Sn-Mineraliztion at Pinyo mine, Yala, Southern Thailand. Proceedings of the Conferences on the Development Geology for Thailand into the Year. (2000): 169-188.

Clark, M.W.; Smith, J.V.; and Walsh, S.R. The distribution of heavy metals in and abandoned mining area: a case study of Strauss Pit, the Drake mining area, Australia: implications for the environmental management of mine sites. Environmental Geology 10, 6 (2001): 655-663.

Darnley, A.G.; Bjorklund, A.; Bolviken, B.; Gustavsson, N.; Koval, P.V.; Plant, J.A.; Steefetl, A.; Tauchid, M. and Xie Xuejing. A Global Geochemical Data B ase for Environmental and ResourcesManagement. Paris: UNESCO Publishing. 1995.

Department of Mineral and Resources. Sn-Pb-Zn Ore in Bunnung Sta, Yaha, Tanto, Yala. Bangkok. DMR. 2001. (Unpublish Manuscipt).

Department of Mineral and resources. Geochemistry and mineral exploration. Economic Geology (Thailand) 3 (March 2000): 1-8.

Department of Mineral and Resources Department. Prevention and remediation of toxic metals in the abandoned mines in Tum Talu, Bunnung Sta Yala. Bangkok. DMR. 2000. (Mimoeographed).

Department of Mineral and resources, Department, Case study of a Typical Complex Tin Processing Technique with Particular Reference to Physical Properties. Bangkok: Seatrad center technical publication, 2001. (Mimoeographed)

Dinelli, E.; Lucchini, F.; Fabbri, M.; and Cortecci, G. Metal distribution and environmental problems related to sulfide oxidation in the Libiola copper mine area, Ligurian Apennines, Italy. Journal of Geochemical Exploration. 74 (2001):141-152.

Drever, J.I. The Geochemistry of Natural Water: Surface and Groundwater environment. 3 rd ed. The United States of America: Prentice-Hall, 1997.

Evans, A.M. Introduction to Mineral Exploration. The Great Britain. Blackwell Science. 1995.

Faculty of Science and Technology , Prince of Songkla University. Remediation Plan of lead contamination in Puttani river. 1-3 vol. Bangkok: Pollution Prevention Division, 2002. (Unpublish Manucript).

Friberg, L., Piscator, M., Nordberg, F. G.and Kjellstrom, T. Cadmium in the Environment. 2nd ed. The United States of America. CRC press.1976.

Geater, A., Duerawee, M., Chompikul, J., Cairatanaanokorn, S., Pongsuwan, N. and Chongsuivatwon, V. Blood lead levels among schoolchildren living in Pattani River Basin: Two contamination scenario [Online] 2000. Available from: http://www.clib.psu.ac.th/acad_43/gala1.htm

Hawkes and Web. Geochemistry in Mineral Exploration. The Great Britian. Blackwell Science, 1962.

Hillier, S.; Suzuki, K.; and Cotter, H. J. Quantitative determination of cerussite (lead carbonate) by X-ray powder diffraction and inferences for lead speciation and transport in stream sediments from a former lead mining area in Scotland. Applied Geochemistry 16 (2001): 597-608.

Hudson-Edwards, K.A.; Mackin, M.G.; Curtis, C.D.; and Vaughan D.J. Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne basin, northest England: implications for metal-contaminated river systems. Environmental Science Technology 30 (1996): 72-80.

Hutchinson, T.C. and Meema K.M. Lead, mercury, cadmium and arsenic in the environment. The Great Britain. John Wiley and sons. 1978.

Jung, D.M.; Thornton, I.; and Chon, H.T. Arsenic, Sb and Bi contamination of soils, plants, waters and sediments in the vincity of the Dalsung Cu-W mine in Korea. The Science of the Total Environment 195 (2002): 81-89.

Macklin, G. M., Paul A., Dan, B., Tom, J. C., Basarab, D., Andy, J.H. and Sorin, Z. The Long term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailing dam failures in Maramures County, upper Tisa Basin, Romania. Applied Geochemistry. 18 (2003): 241-257.

Marini, L.; Ottonello, G.; Canepa, M.; Cipolli, F.; and Vetuschi, Z.M. Detection of Hg pollution by stream sediment geochemistry in the Bisago valley Genoa, Italy. Environmental Geology 40, 1/2 (2000): 234-242.

Mellor, A. Lead and zinc in the Wallsen Burn, and urban catchment in Tynesid, UK. The science of the Total Environment 269 (2001): 49-63.

Naseem, S.; Sheikh, A.S.; Qadeeruddin, M.; and Shirin, K. Geochemical stream sediment survey in Winder Valley Balochistan, Pakistan. Journal of Geochemical Exploration. 76. (2002):1-12.

Nriagu, J.O. Arsenic in the environment: cycling and characterization. 26-27 vol. The United states of America: John Wiley and sons, 1994.

Odum, H.T. Heavy Metals in the Environment: Using Wetland for their Removal. New York. Lewis publishers, 2000.

Ridgway, J.; Breward, N.; Langston, W.J.; Lister, R; Rees, J.G.; and Rowlatt, S.M. Distinguishing between natural and anthropogenic sources of metals entering the Irish Sea. Applied Geochemistry 18 (2003): 283-309.

Rose, W.A., Hawkes, H.E., and Webb, J.S. Geochemistry in Mineral exploration. 2nd. Ed. London: Academic Press, 1979.

Siegel, R.F. Environmental Geochemistry of Potentially Toxic Metals. Germany: Springer Verlag. 2002.

Sinclair, A.J. Probability Graphs. Association Exploration Geochemists. 4 vol. 1976.

Song,Y.; Wilson; M.J., Moon; H.S.; Bacon, J.R.; and Bain, D.C. Chemical and Mineralogical forms of lead, zinc and cadmium in particle size fractions of some wastes, sediments and soils in Korea. Applied Geochemistry. 14. (1999):621-633.

Swennen, R.; Van der Sluys, J. Zn, Pb, Cu and As distribution patterns in over blank and medium-order stream sediment samples: their use in exploration and environmental geochemistry. Journal of Geochemical Exploration. 65 (1998):27-45.

Swan, A.R.H. and Sandilands, M. Introduction to Geological Data Analysis. London. Black well science. 1995.

Teixeira, E.C.; Sanchez, J.C.D.; Migliavacca, D.; Binotto, R.B.; and Fachel, J.M.G. Environmental assessment: study of metals in fluvial sediments in sites impacted by coal processing and steel industry activities. Fuel 79(2000): 1539-1546.

Tom, R.G. and James. The science of Acid Mine Drainage and Passive Treatment [Online]. 2004. Available from: http://www.dep.state.pa.us/dep/deputate/mines/bamr/amd/sciences_of_amd.html

Tutep., D. Contamination of metals in stream sediments of the Pattani river in Changwat Yala [On-line].1994. Available from: http://www.envi.psu.ac.th/foem/e thesis027.pdf

Thornton, I. Applied Environmental Geochemistry. New York. Academic Press. 1993.

U.S. EPA. The Remedial Investigation: Site Characterization and Treat ability Study [Online]. 1989. Available from: http://www.epa.gov/superfund/resources/remedy/pdf/93-55301fs2.pdf

U.S. EPA. Abandon mine site characterization and clean up handbook (EPA910-B-00-001). [Online]. 2000. Available from: http://www.epa.gov/superfund/resources/remedy/pdf/amscch.pdf.

U.S. EPA. Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils. [Online]. 2000. Available from: http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3051a.pdf

Varathorn, P. Heavy metals in Pattani River Basin [Online]. 1997. Available from: http://www.anamai.moph.go.th/factsheet/health1-1_en.htm

VROM. Intervention and traget values-soil quality standards [Online]. 2001. Available from: http://www.minvrom.nl/minvrom/docs/bodem/annexS&I2000.pdf

APPENDICES

APPENDIX I : Table I 1 Description of stream sediments samples in Tum Talu Watershed.

Anal Chem. no.	Field no.	East	North	Day	Rock type	Elevation (m.)	Wide (m.)	Level (m.)	pH	Color	Type of samples	Degree of samples	Stream section no.	Sample order	Basin Order	Distance down stream (m.)	Note
A1	2-1-1t	737946	0693352	18-05-03	O	303	1.0	10	5.8	OR	I	G	1	5		2313	Weathered ore on west side
A2	2-1-1Wo	737946	0693352	18-05-03	O	303	1.0	10	5.8	OR	I	G	1	6		2325	From weathed ore , mine waste
A3*	14-1-1	738484	0693587	01-06-03	L	325	1.5	10-20	6.7	Y	I	G	1	7		2838	* Get effect of soil dump in
A4*	10-4-1	738789	0693436	28-05-03	L	209	1	10-20	6.5	Y	I	G	1	8		3145	DMR. Remediation project.
A5*	10-3-1	739124	0692925	28-05-03	L	184	2.5	10-30	6.5	Y	I	G	1	9		3950	(Covered mine waste). Lime St.
A6	5-7-1	739692	0692461	21-05-03	A	178	2.5	10-40	7.1	B	I	G	1	10		4800	Lime surrounded
A7	5-5-1	739850	0692126	21-05-03	L	151	2.5	10-70	6.7	RB	I	G	1	11		5225	Lime & hydrotermal surrounds
A8	5-3-1	740070	0691969	21-05-03	A	148	3	10-50	5.6	R	I	G	1	12		5375	Landfill leachate, point 1
A9	5-1-1	740116	0691981	21-05-03	A	148	2.5	10-50	5.2	R	I	G	1	13		5538	Landfill leachate, point 2,
A10	5-2-1	740136	0691981	21-05-03	A	148	2.5	20-30	6.7	YR	I	G	1	14		555	Downstream of leachate.
A11	3-7-1	740261	0691847	19-05-03	A	149	-	20	7	OR	I	G	1	15		6013	D.St. of Tum Talu mines
A12	3-4-1	740988	0692067	19-05-03	A	155	-	30-50	7.2	RB	I	G	1	16		6213	D. St. of Tum Talu mines.
A13	3-2-1	740547	0691112	19-05-03	A	156	-	30-50	7.1	B	I	P	1	17		7088	Clean and clear water
A14	15-2-1	740516	06900695	03-06-03	A	223	3	10-40	-	B	I	G	1	18		7275	Wide, bed load depth >5cm.
A15	15-1-1	740800	0690354	03-06-03	A	223	4	10-40	7.0	B	I	G	1	19		7738	Wide, bed load depth >5cm.
A16	1-1-1	740852	0689925	17-05-03	A	119	4	10-40	6.7	B	I	G	1	20		7188	Hand collection.

Anal Chem. no.	Field no.	East	North	Day	Rock type	Elevation (m.)	Wide (m.)	Level (m.)	pH	Color	Type of samples	Degree of samples	Stream section no.	Sample order	Basin Order	Distance down stream (m.)	Note
A17	17-3-1			05-06-03	A	-	-	-	-	B	M	G	1	21		8295	-
B1	9-1-1	737782	0692872	26-05-03	G	444	1	5-10	6.7	YR	C	G	4	1		273	Po Luan, Small mine
B2	9-2-1	738369	0692535	26-05-03	G	350	2	10-20	6.8	B	C	G	4	2		1235	D. St. Po Luan & Bulunt mine
B3	10-1-1	739240	0692550	28-05-03	G	200	2.5	10-15	7.0	B	C	G	4	1		2135	Granite surround.
C1	14-2-1	738083	0693701	01-06-03	L	348	1	5	7.0	B	C	G	1	1		-	D.St. of Nasua tailling storage.
D1	5-4-1	739917	0691969	21-05-03	O	153	0.05	5-10	4.0	Y	C	G	6	1		5370	Tum Talu mine, AMD.
E1	9-3-1	738555	0692595	26-05-03	G	385	1	10-20	6.4	B	C	G	4	3		-	Granite surround, q.dry stream.
F1	18-2-1	739230	0692003	06-06-03	G	119	0.6	10-20	6.1	B	C	G	5	1		403	Granite surround
F2	5-6-1	739624	0692057	21-05-03	G	159	1.5	10-20	6.8	B	C	P	5	2		925	Granite surround, q.dry stream.
G1	12-4-1	738551	0694893	30-05-03	H	-	1	10-20	7.2	B	C	G	2	1		270	Quite (q.) dry stream, hornfel
G2	18-1-1	738500	0694700	06-06-03	H	-	1	5-10	6.1	DB	C	G	2	2		425	-
G3	12-5-1	738307	0694483	30-05-03	H	458	1.5	10-25	7.2	B	C	G	2	1		-	Duplicate, good sample.
G4	12-3-1	738586	0694417	30-05-03	H	365	2.0	10-20	7.2	B	C	G	2	3		838	-
G5	12-2-1	738763	0694489	30-05-03	H	366	1.2	10-15	7.1	B	C	G	2	1		1025	-
G6	12-1-1	738571	0694113	30-05-03	A	368	1.5	10-15	7.3	B	C	G	2	4		-	50 m. D.St. of Dam.
G7	14-4-1	738938	0693770	01-06-03	A	224	1	20-30	6.7	B	C	G	2	5		1545	-
H1	11-1-1	-	-	29-05-03	H	-	4	5-10	7.0	B	C	G	3	1		353	Up stream of village tap water
H2	11-2-1	739193	0693756	29-05-03	H	210	2	5-15	6.9	B	C	G	3	2		1288	-
I1	7-3-1	740015	0694621	23-05-03	C	240	1	10	7.0	B	C	G	7	1		5575	In the Forest, very clean, clear

Anal Chem. no.	Field no.	East	North	Day	Rock type	Elevation (m.)	Wide (m.)	Level (m.)	pH	Color	Type of samples	Degree of samples	Stream section no.	Sample order	Basin Order	Distance down stream (m.)	Note
I2	7-4-1	740046	0694469	23-05-03	C	353	-	-	-	B	C	G	7	1		400	-
I3	7-2-1	740108	0694214	23-05-03	H	240	2	10-50	7.0	B	C	G	7	2		1058	Village tap water
I4	16-1-1	739843	0694080	04-06-03	H	161	0.06	5-10	7.2	B	C	G	7	1		1410	-
I5	7-1-1	740072	0693894	23-05-03	C	240	1	10	7.0	B	C	G	7	3		-	-
I6	6-4-1	740389	0693715	22-05-03	H	218	1	10	7.0	B	C	G	7	1		-	Near orange garden.
I7	6-3-1	740217	0693583	22-05-03	H	-	4	1-10	7.2	B	C	G	7	2		-	Waterfall of hornfel
I8	6-2-1	740097	0693284	22-05-03	A	215	1.5	10-20	6.8	B	C	G	7	4		-	-
I9	6-1-1	740127	0692864	22-05-03	A	160	1	10-20	6.5	B	C	G	7	5		2000	Burned garden.
J1	8-2-1	740974	0693844	25-05-03	A	264	1.5	10-20	7	B	C	G	8	1		250	-
J2	8-1-1	740926	0693575	25-05-03	A	353	4	20-40	6.9	LB	C	G	8	2		-	-
J3	8-4-1	741099	0693609	25-05-03	A	232	1	10-20	6.8	LB	C	G	8	1		-	-
J4	8-5-1	741452	0693515	25-05-03	A	315	2	10-40	7.0	B	C	P	8	1		-	-
J5	8-6-1	741446	0693171	25-05-03	A	288	0.08	10	7.1	B	C	P	8	1		538	-
J6	8-3-1	740955	0693107	25-05-03	A	228	2	10-20	7.3	RB	C	G	8	1		1263	Red in stream
J7	4-3-1	740779	0693075	20-05-03	A	220	1.5	10-40	7.4	B	C	v	8	3		1460	D.St. of Dam.
J8	4-2-1	740630	0692672	20-05-03	A	180	5	10-70	7.1	LB	C	G	8	4		1605	-
J9	4-1-1	740545	0692036	20-05-03	A	178	1	10-40	6.7	B	C	G	8	5		1905	-
K1	3-6-1	741120	0692117	19-05-03	A	189	-	10	7.1	DB	C	v	9	1		-	-

Anal Chem. No.	Field No.	East	North	Day	Rock Type	Elevation (m.)	Wide (m.)	Level (m.)	pH	Color	Type of samples	Degree of samples	Stream section No.	Stream section No.	Basin Order	Distance down stream (m.)	Note
K2	3-5-1	740988	0692067	19-05-03	A	155	-	5-10	7.1	RB	C	v	9	2		-	Red in stream.
L1	17-1-1	741665	0692039	05-06-03	H	194	2.5	5-40	7.0	B	C	G	10	1		-	-
M1	17-2-1	741713	0691828	05-06-03	H	245	1.0	10-20	6.9	B	C	G	10	1		-	-
N1	15-3-1	740537	0691002	03-06-03	A	149	6.5	5	6.5	B	C	v	12	1		-	Burned garden.
N2	15-4-1	740155	0691189	03-06-03	A	161	0.7	5-10	6.7	B	C	G	11	1		-	Quite dry stream
O1	13-1-1	736905	0693299	31-05-03	G	547	2.5	10-40	7.4	B	C	G	1	1		688	Granite, quartz vein, tap water
O2	13-2-1	736800	0693500	31-05-03	G	420	0.8	5-10	7.2	B	C	v	1	1		-	Narrow stream
Q3	13-3-1	737426	0693594	31-05-03	G	368	1	10-15	7.0	B	C	G	1	2		1488	Narrow stream
Q4	2-4-1	737527	0693535	18-05-03	O	318	1	10	6.2	B	C	G	1	3		1938	Hand collection
Q5	2-3-1	737690	0693470	18-05-03	O	317	1	10	6.5	B	C	G	1	4		1980	Hand collection.

Note : 1 Rock Type : A=Alluvial sediments, L=Limestone, O = Ores and Skarn, G=Granite and H=Hornfels and quartzite.

2 Color : YR= Yellowish Red, B= Brown, RB=Reddish Brown, DB=Dark Brown and LB=Light Brown.

3 Degree of samples: G=Good and P=Poor, V=Very Poor.

APPENDIX II : Table I 1 The instrumental blank of ICP-OES and method blank of microwave-assisted digestion.

Instrumental blank

Blank	As (ppb)	Cd (ppb)	Cr (ppb)	Cu (ppb)	Pb (ppb)	Zn (ppb)
Deionized water	2.488	1.979	30.71	130.93	46.73	ND
Deionized water	ND	ND	ND	ND	131.02	ND
Deionized water	ND	ND	ND	ND	61.752	ND
Average	2.488	1.979	30.71	130.93	79.834	ND

Method blank: (Microwave assisted digestion)

Blank	As (ppb)	Cd (ppb)	Cr (ppb)	Cu (ppb)	Pb (ppb)	Zn (ppb)
Blank 1	537.6	7.6	74.4	130.9	37.9	303.4
Blank 2	71.6	6.9	29.7	137.7	68.0	280.0
Blank 3	34.6	4.3	23.8	62.0	54.9	277.2
Blank 4	51.5	4.7	ND	144.5	88.8	268.3
Blank 5	51.6	7.2	76.7	151.1	27.5	336.0
Blank 6	35.6	5.3	20.9	183.1	87.0	232.7

APPENDIX III :

Table I 1 The frequency statistic of elements in stream sediment

As	(mg/kg)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	7.3	1.0	1.6	1.6	1.6
	10.6	1.0	1.6	1.6	3.3
	11.8	1.0	1.6	1.6	4.9
	12.7	1.0	1.6	1.6	6.6
	18.1	1.0	1.6	1.6	8.2
	36.9	1.0	1.6	1.6	9.8
	37.9	1.0	1.6	1.6	11.5
	38.7	1.0	1.6	1.6	13.1
	41.1	1.0	1.6	1.6	14.8
	42.5	1.0	1.6	1.6	16.4
	44.3	1.0	1.6	1.6	18.0
	52.1	1.0	1.6	1.6	19.7
	52.9	1.0	1.6	1.6	21.3
	54.2	1.0	1.6	1.6	23.0
	57.4	1.0	1.6	1.6	24.6
	58.5	1.0	1.6	1.6	26.2
	60.0	1.0	1.6	1.6	27.9
	61.8	1.0	1.6	1.6	29.5
	64.0	1.0	1.6	1.6	31.1
	75.1	1.0	1.6	1.6	32.8
	75.9	1.0	1.6	1.6	34.4
	76.4	1.0	1.6	1.6	36.1
	77.9	1.0	1.6	1.6	37.7
	78.1	1.0	1.6	1.6	39.3
	82.4	1.0	1.6	1.6	41.0
	83.4	1.0	1.6	1.6	42.6
	98.5	1.0	1.6	1.6	44.3
	111.7	1.0	1.6	1.6	45.9
	113.8	1.0	1.6	1.6	47.5
	119.1	1.0	1.6	1.6	49.2
	135.3	1.0	1.6	1.6	50.8
	217.7	1.0	1.6	1.6	52.5
	446.6	1.0	1.6	1.6	54.1
	672.2	1.0	1.6	1.6	55.7
	704.6	1.0	1.6	1.6	57.4
	826.3	1.0	1.6	1.6	59.0
	860.4	1.0	1.6	1.6	60.7
	970.2	1.0	1.6	1.6	62.3
	1196.6	1.0	1.6	1.6	63.9
	1454.1	1.0	1.6	1.6	65.6
	1580.0	1.0	1.6	1.6	67.2
	1899.0	1.0	1.6	1.6	68.9
	1939.7	1.0	1.6	1.6	70.5
	1967.3	1.0	1.6	1.6	72.1
	2093.4	1.0	1.6	1.6	73.8
	2164.2	1.0	1.6	1.6	75.4
	2485.8	1.0	1.6	1.6	77.0
	2812.0	1.0	1.6	1.6	78.7
	2850.1	1.0	1.6	1.6	80.3
	2860.4	1.0	1.6	1.6	82.0
	2892.9	1.0	1.6	1.6	83.6
	3175.1	1.0	1.6	1.6	85.2
	3303.6	1.0	1.6	1.6	86.9
	3401.6	1.0	1.6	1.6	88.5
	3442.4	1.0	1.6	1.6	90.2
	3666.9	1.0	1.6	1.6	91.8
	3692.4	1.0	1.6	1.6	93.4
	3845.8	1.0	1.6	1.6	95.1
	4067.1	1.0	1.6	1.6	96.7
	4210.0	1.0	1.6	1.6	98.4
	6161.5	1.0	1.6	1.6	100.0
	Total	61.0	96.8	100.0	
Missing	System	2.0	3.2		
Total		63.0	100.0		

Cd	(mg/kg)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	0.2	1.0	1.6	1.9	1.9
	0.7	1.0	1.6	1.9	3.8
	0.9	1.0	1.6	1.9	5.7
	1.1	1.0	1.6	1.9	7.5
	1.1	1.0	1.6	1.9	9.4
	1.1	2.0	3.2	3.8	13.2
	1.2	1.0	1.6	1.9	15.1
	1.2	1.0	1.6	1.9	17.0
	1.4	1.0	1.6	1.9	18.9
	1.5	1.0	1.6	1.9	20.8
	1.5	1.0	1.6	1.9	22.6
	1.6	1.0	1.6	1.9	24.5
	1.6	1.0	1.6	1.9	26.4
	1.7	2.0	3.2	3.8	30.2
	1.7	1.0	1.6	1.9	32.1
	1.7	1.0	1.6	1.9	34.0
	1.9	1.0	1.6	1.9	35.8
	1.9	1.0	1.6	1.9	37.7
	2.0	1.0	1.6	1.9	39.6
	2.3	1.0	1.6	1.9	41.5
	2.3	1.0	1.6	1.9	43.4
	2.4	1.0	1.6	1.9	45.3
	2.5	1.0	1.6	1.9	47.2
	2.5	1.0	1.6	1.9	49.1
	3.0	1.0	1.6	1.9	50.9
	3.2	1.0	1.6	1.9	52.8
	3.6	1.0	1.6	1.9	54.7
	3.7	1.0	1.6	1.9	56.6
	3.9	1.0	1.6	1.9	58.5
	4.5	1.0	1.6	1.9	60.4
	6.3	1.0	1.6	1.9	62.3
	6.6	1.0	1.6	1.9	64.2
	7.7	1.0	1.6	1.9	66.0
	7.8	1.0	1.6	1.9	67.9
	7.9	1.0	1.6	1.9	69.8
	10.8	1.0	1.6	1.9	71.7
	11.9	1.0	1.6	1.9	73.6
	12.9	1.0	1.6	1.9	75.5
	13.1	1.0	1.6	1.9	77.4
	14.1	1.0	1.6	1.9	79.2
	14.5	1.0	1.6	1.9	81.1
	16.0	1.0	1.6	1.9	83.0
	16.4	1.0	1.6	1.9	84.9
	20.2	1.0	1.6	1.9	86.8
	20.4	1.0	1.6	1.9	88.7
	21.5	1.0	1.6	1.9	90.6
	22.0	1.0	1.6	1.9	92.5
	22.0	1.0	1.6	1.9	94.3
	23.0	1.0	1.6	1.9	96.2
	26.0	1.0	1.6	1.9	98.1
	28.8	1.0	1.6	1.9	100.0
	Total	53.0	84.1	100.0	
Missing	System	10.0	15.9		
Total		63.0	100.0		

Cr	(m/kg)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	2.1	1.0	1.6	1.9	1.9
	8.9	1.0	1.6	1.9	3.7
	10.5	1.0	1.6	1.9	5.6
	12.2	1.0	1.6	1.9	7.4
	13.0	1.0	1.6	1.9	9.3
	14.0	1.0	1.6	1.9	11.1
	14.6	1.0	1.6	1.9	13.0
	15.3	1.0	1.6	1.9	14.8
	16.5	1.0	1.6	1.9	16.7
	16.7	1.0	1.6	1.9	18.5
	17.3	1.0	1.6	1.9	20.4
	17.8	1.0	1.6	1.9	22.2
	18.6	1.0	1.6	1.9	24.1
	19.2	1.0	1.6	1.9	25.9
	19.3	1.0	1.6	1.9	27.8
	20.2	1.0	1.6	1.9	29.6
	20.6	1.0	1.6	1.9	31.5
	21.3	1.0	1.6	1.9	33.3
	22.3	1.0	1.6	1.9	35.2
	24.8	1.0	1.6	1.9	37.0
	25.0	1.0	1.6	1.9	38.9
	26.5	1.0	1.6	1.9	40.7
	28.1	1.0	1.6	1.9	42.6
	28.8	1.0	1.6	1.9	44.4
	29.3	1.0	1.6	1.9	46.3
	29.6	1.0	1.6	1.9	48.1
	29.7	1.0	1.6	1.9	50.0
	29.9	1.0	1.6	1.9	51.9
	30.2	1.0	1.6	1.9	53.7
	30.7	1.0	1.6	1.9	55.6
	30.9	1.0	1.6	1.9	57.4
	31.8	1.0	1.6	1.9	59.3
	32.1	1.0	1.6	1.9	61.1
	32.5	1.0	1.6	1.9	63.0
	32.9	1.0	1.6	1.9	64.8
	34.9	1.0	1.6	1.9	66.7
	35.1	1.0	1.6	1.9	68.5
	36.3	1.0	1.6	1.9	70.4
	37.3	1.0	1.6	1.9	72.2
	37.7	1.0	1.6	1.9	74.1
	37.9	1.0	1.6	1.9	75.9
	38.0	1.0	1.6	1.9	77.8
	39.5	1.0	1.6	1.9	79.6
	39.9	1.0	1.6	1.9	81.5
	40.7	1.0	1.6	1.9	83.3
	41.5	1.0	1.6	1.9	85.2
	42.9	1.0	1.6	1.9	87.0
	45.6	1.0	1.6	1.9	88.9
	47.6	1.0	1.6	1.9	90.7
	49.0	1.0	1.6	1.9	92.6
	51.0	1.0	1.6	1.9	94.4
	54.8	1.0	1.6	1.9	96.3
	55.0	1.0	1.6	1.9	98.1
	88.5	1.0	1.6	1.9	100.0
	Total	54.0	85.7	100.0	
Missing	System	9.0	14.3		
Total		63.0	100.0		

Cu	(mg/kg)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	9.2	1.0	1.6	1.9	1.9
	31.7	1.0	1.6	1.9	3.7
	38.0	1.0	1.6	1.9	5.6
	38.9	1.0	1.6	1.9	7.4
	48.3	1.0	1.6	1.9	9.3
	49.0	1.0	1.6	1.9	11.1
	51.9	1.0	1.6	1.9	13.0
	52.0	1.0	1.6	1.9	14.8
	53.0	1.0	1.6	1.9	16.7
	53.1	1.0	1.6	1.9	18.5
	54.0	1.0	1.6	1.9	20.4
	62.2	1.0	1.6	1.9	22.2
	62.4	1.0	1.6	1.9	24.1
	63.4	1.0	1.6	1.9	25.9
	64.6	1.0	1.6	1.9	27.8
	65.4	1.0	1.6	1.9	29.6
	71.7	1.0	1.6	1.9	31.5
	76.6	1.0	1.6	1.9	33.3
	76.7	1.0	1.6	1.9	35.2
	81.3	1.0	1.6	1.9	37.0
	81.7	1.0	1.6	1.9	38.9
	82.7	1.0	1.6	1.9	40.7
	89.6	1.0	1.6	1.9	42.6
	92.0	1.0	1.6	1.9	44.4
	95.8	1.0	1.6	1.9	46.3
	99.9	1.0	1.6	1.9	48.1
	102.7	1.0	1.6	1.9	50.0
	107.1	1.0	1.6	1.9	51.9
	109.9	1.0	1.6	1.9	53.7
	120.5	1.0	1.6	1.9	55.6
	126.8	1.0	1.6	1.9	57.4
	136.5	1.0	1.6	1.9	59.3
	160.4	1.0	1.6	1.9	61.1
	177.9	1.0	1.6	1.9	63.0
	179.9	1.0	1.6	1.9	64.8
	181.4	1.0	1.6	1.9	66.7
	186.8	1.0	1.6	1.9	68.5
	190.2	1.0	1.6	1.9	70.4
	202.0	1.0	1.6	1.9	72.2
	254.7	1.0	1.6	1.9	74.1
	297.8	1.0	1.6	1.9	75.9
	318.6	1.0	1.6	1.9	77.8
	337.1	1.0	1.6	1.9	79.6
	349.0	1.0	1.6	1.9	81.5
	358.9	1.0	1.6	1.9	83.3
	399.6	1.0	1.6	1.9	85.2
	410.7	1.0	1.6	1.9	87.0
	470.0	1.0	1.6	1.9	88.9
	494.1	1.0	1.6	1.9	90.7
	536.6	1.0	1.6	1.9	92.6
	552.5	1.0	1.6	1.9	94.4
	559.0	1.0	1.6	1.9	96.3
	561.9	1.0	1.6	1.9	98.1
	630.8	1.0	1.6	1.9	100.0
	Total	54.0	85.7	100.0	
Missing	System	9.0	14.3		
Total		63.0	100.0		

Pb	(mg/kg)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	3.5	1.0	1.6	1.6	1.6
	8.0	1.0	1.6	1.6	3.2
	9.9	1.0	1.6	1.6	4.8
	17.5	1.0	1.6	1.6	6.3
	21.0	1.0	1.6	1.6	7.9
	22.4	1.0	1.6	1.6	9.5
	24.4	1.0	1.6	1.6	11.1
	25.4	1.0	1.6	1.6	12.7
	28.4	1.0	1.6	1.6	14.3
	29.1	1.0	1.6	1.6	15.9
	29.7	1.0	1.6	1.6	17.5
	30.3	1.0	1.6	1.6	19.0
	30.8	1.0	1.6	1.6	20.6
	32.1	1.0	1.6	1.6	22.2
	34.3	1.0	1.6	1.6	23.8
	34.4	1.0	1.6	1.6	25.4
	35.8	1.0	1.6	1.6	27.0
	41.6	1.0	1.6	1.6	28.6
	41.8	1.0	1.6	1.6	30.2
	42.2	1.0	1.6	1.6	31.7
	43.3	1.0	1.6	1.6	33.3
	45.5	1.0	1.6	1.6	34.9
	47.2	1.0	1.6	1.6	36.5
	55.6	1.0	1.6	1.6	38.1
	56.8	1.0	1.6	1.6	39.7
	67.5	1.0	1.6	1.6	41.3
	75.2	1.0	1.6	1.6	42.9
	83.6	1.0	1.6	1.6	44.4
	103.8	1.0	1.6	1.6	46.0
	107.0	1.0	1.6	1.6	47.6
	135.5	1.0	1.6	1.6	49.2
	247.5	1.0	1.6	1.6	50.8
	253.8	1.0	1.6	1.6	52.4
	405.8	1.0	1.6	1.6	54.0
	460.3	1.0	1.6	1.6	55.6
	574.9	1.0	1.6	1.6	57.1
	581.0	1.0	1.6	1.6	58.7
	653.8	1.0	1.6	1.6	60.3
	685.1	1.0	1.6	1.6	61.9
	766.1	1.0	1.6	1.6	63.5
	787.6	1.0	1.6	1.6	65.1
	976.9	1.0	1.6	1.6	66.7
	989.5	1.0	1.6	1.6	68.3
	1083.3	1.0	1.6	1.6	69.8
	1131.8	1.0	1.6	1.6	71.4
	1759.5	1.0	1.6	1.6	73.0
	1807.2	1.0	1.6	1.6	74.6
	2278.9	1.0	1.6	1.6	76.2
	2575.4	1.0	1.6	1.6	77.8
	2730.0	1.0	1.6	1.6	79.4
	3075.3	1.0	1.6	1.6	81.0
	5389.7	1.0	1.6	1.6	82.5
	5724.6	1.0	1.6	1.6	84.1
	6705.5	1.0	1.6	1.6	85.7
	6728.3	1.0	1.6	1.6	87.3
	7742.4	1.0	1.6	1.6	88.9
	7788.6	1.0	1.6	1.6	90.5
	9461.0	1.0	1.6	1.6	92.1
	9834.6	1.0	1.6	1.6	93.7
	11475.4	1.0	1.6	1.6	95.2
	11514.5	1.0	1.6	1.6	96.8
	14469.9	1.0	1.6	1.6	98.4
	19540.9	1.0	1.6	1.6	100.0
	Total	63.0	100.0	100.0	

Zn	(mg/kg)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	12.7	1.0	1.6	1.6	1.6
	25.3	1.0	1.6	1.6	3.2
	34.7	1.0	1.6	1.6	4.8
	36.6	1.0	1.6	1.6	6.3
	37.0	1.0	1.6	1.6	7.9
	41.3	1.0	1.6	1.6	9.5
	44.0	1.0	1.6	1.6	11.1
	45.9	1.0	1.6	1.6	12.7
	49.0	1.0	1.6	1.6	14.3
	51.4	1.0	1.6	1.6	15.9
	54.1	1.0	1.6	1.6	17.5
	54.4	1.0	1.6	1.6	19.0
	57.1	1.0	1.6	1.6	20.6
	57.9	1.0	1.6	1.6	22.2
	62.0	1.0	1.6	1.6	23.8
	62.1	1.0	1.6	1.6	25.4
	62.7	1.0	1.6	1.6	27.0
	64.1	1.0	1.6	1.6	28.6
	69.1	1.0	1.6	1.6	30.2
	71.7	1.0	1.6	1.6	31.7
	72.7	1.0	1.6	1.6	33.3
	75.4	1.0	1.6	1.6	34.9
	78.4	1.0	1.6	1.6	36.5
	84.9	1.0	1.6	1.6	38.1
	86.0	1.0	1.6	1.6	39.7
	87.1	1.0	1.6	1.6	41.3
	89.1	1.0	1.6	1.6	42.9
	90.3	1.0	1.6	1.6	44.4
	101.8	1.0	1.6	1.6	46.0
	106.8	1.0	1.6	1.6	47.6
	120.4	1.0	1.6	1.6	49.2
	122.5	1.0	1.6	1.6	50.8
	142.9	1.0	1.6	1.6	52.4
	147.1	1.0	1.6	1.6	54.0
	154.7	1.0	1.6	1.6	55.6
	156.0	1.0	1.6	1.6	57.1
	165.6	1.0	1.6	1.6	58.7
	175.2	1.0	1.6	1.6	60.3
	184.4	1.0	1.6	1.6	61.9
	193.8	1.0	1.6	1.6	63.5
	238.4	1.0	1.6	1.6	65.1
	382.5	1.0	1.6	1.6	66.7
	454.0	1.0	1.6	1.6	68.3
	560.2	1.0	1.6	1.6	69.8
	576.3	1.0	1.6	1.6	71.4
	579.9	1.0	1.6	1.6	73.0
	697.6	1.0	1.6	1.6	74.6
	848.4	1.0	1.6	1.6	76.2
	995.5	1.0	1.6	1.6	77.8
	1282.0	1.0	1.6	1.6	79.4
	1290.3	1.0	1.6	1.6	81.0
	1367.4	1.0	1.6	1.6	82.5
	1479.1	1.0	1.6	1.6	84.1
	1507.7	1.0	1.6	1.6	85.7
	1575.4	1.0	1.6	1.6	87.3
	1616.0	1.0	1.6	1.6	88.9
	1631.7	1.0	1.6	1.6	90.5
	1710.0	1.0	1.6	1.6	92.1
	1914.5	1.0	1.6	1.6	93.7
	2279.0	1.0	1.6	1.6	95.2
	2338.1	1.0	1.6	1.6	96.8
	2556.0	1.0	1.6	1.6	98.4
	2841.4	1.0	1.6	1.6	100.0
	Total	63.0	100.0	100.0	

C	(wt%)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	0.1	1.0	1.6	1.8	1.8
	0.1	1.0	1.6	1.8	3.5
	0.2	1.0	1.6	1.8	5.3
	0.3	1.0	1.6	1.8	7.0
	0.3	1.0	1.6	1.8	8.8
	0.3	1.0	1.6	1.8	10.5
	0.3	2.0	3.2	3.5	14.0
	0.4	1.0	1.6	1.8	15.8
	0.4	1.0	1.6	1.8	17.5
	0.4	1.0	1.6	1.8	19.3
	0.5	1.0	1.6	1.8	21.1
	0.5	1.0	1.6	1.8	22.8
	0.5	1.0	1.6	1.8	24.6
	0.5	1.0	1.6	1.8	26.3
	0.6	1.0	1.6	1.8	28.1
	0.6	1.0	1.6	1.8	29.8
	0.6	1.0	1.6	1.8	31.6
	0.6	1.0	1.6	1.8	33.3
	0.7	1.0	1.6	1.8	35.1
	0.7	1.0	1.6	1.8	36.8
	0.7	1.0	1.6	1.8	38.6
	0.8	1.0	1.6	1.8	40.4
	0.8	1.0	1.6	1.8	42.1
	0.8	1.0	1.6	1.8	43.9
	0.9	1.0	1.6	1.8	45.6
	0.9	1.0	1.6	1.8	47.4
	1.1	1.0	1.6	1.8	49.1
	1.1	1.0	1.6	1.8	50.9
	1.2	1.0	1.6	1.8	52.6
	1.3	1.0	1.6	1.8	54.4
	1.3	1.0	1.6	1.8	56.1
	1.3	1.0	1.6	1.8	57.9
	1.4	2.0	3.2	3.5	61.4
	1.4	1.0	1.6	1.8	63.2
	1.6	1.0	1.6	1.8	64.9
	1.7	1.0	1.6	1.8	66.7
	1.8	1.0	1.6	1.8	68.4
	1.8	1.0	1.6	1.8	70.2
	2.0	1.0	1.6	1.8	71.9
	2.1	1.0	1.6	1.8	73.7
	2.2	1.0	1.6	1.8	75.4
	2.3	1.0	1.6	1.8	77.2
	2.4	1.0	1.6	1.8	78.9
	2.4	1.0	1.6	1.8	80.7
	2.7	2.0	3.2	3.5	84.2
	2.7	1.0	1.6	1.8	86.0
	2.8	1.0	1.6	1.8	87.7
	2.9	1.0	1.6	1.8	89.5
	2.9	1.0	1.6	1.8	91.2
	3.2	1.0	1.6	1.8	93.0
	3.9	1.0	1.6	1.8	94.7
	3.9	1.0	1.6	1.8	96.5
	4.9	1.0	1.6	1.8	98.2
	5.1	1.0	1.6	1.8	100.0
	Total	57.0	90.5	100.0	
Missing	System	6.0	9.5		
Total		63.0	100.0		

S	(wt%)	Frequency	Percent	Valid Percent	Cumulative Percent
Valid	0.0	4.0	6.3	7.0	7.0
	0.0	7.0	11.1	12.3	19.3
	0.0	10.0	15.9	17.5	36.8
	0.0	6.0	9.5	10.5	47.4
	0.1	6.0	9.5	10.5	57.9
	0.1	2.0	3.2	3.5	61.4
	0.1	3.0	4.8	5.3	66.7
	0.1	1.0	1.6	1.8	68.4
	0.1	2.0	3.2	3.5	71.9
	0.1	2.0	3.2	3.5	75.4
	0.2	1.0	1.6	1.8	77.2
	0.2	1.0	1.6	1.8	78.9
	0.2	2.0	3.2	3.5	82.5
	0.3	1.0	1.6	1.8	84.2
	0.3	1.0	1.6	1.8	86.0
	0.4	1.0	1.6	1.8	87.7
	0.5	1.0	1.6	1.8	89.5
	0.6	1.0	1.6	1.8	91.2
	0.6	1.0	1.6	1.8	93.0
	0.6	1.0	1.6	1.8	94.7
	0.7	1.0	1.6	1.8	96.5
	1.0	1.0	1.6	1.8	98.2
	1.8	1.0	1.6	1.8	100.0
	Total	57.0	90.5	100.0	
Missing	System	6.0	9.5		
Total		63.0	100.0		

BIOGRAPHY

Miss Nannapat Natchakunlasap was born on June 9, 1980 in Bangkok, Central Thailand. She finished the high school study in 1998 from Suwannaramwittayakom high school, then entered Chulalongkorn University. She received a Bachelor of Science degree in Geology from the Department of Geology, Faculty of Science, Chulalongkorn Univeristy in 2001. Then she pursued the Master's degree international program in environmental management, Chulalongkorn University