การประเมินความเสี่ยงของสารหนูในดินที่ปนเปื้อนต่อน้ำบาดาลระดับตื้นในตำบลองค์พระ จังหวัดสุพรรณบุรี ประเทศไทย

นายวีรวุฒิ เทียนขาว

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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RISK ASSESSMENT OF ARSENIC FROM CONTAMINATED SOILS TO SHALLOW GROUNDWATER IN ONG PHRA SUBDISTRICT CHANGWAT SUPHAN BURI, THAILAND

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A Thesis Submitted in Partial Fulfillment of the Requirements
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สารหนู (*As*) เป็นมลพิษที่พบได้ทั่วโลกโดยมีการรับสารหนูเข้าสู่ร่างกายผ่านอาหารและน้ำดื่ม และงานวิจัยก่อนหน้าได้ทำการวิเคราะห์ปริมาณสารหนูรวมในดินจากตัวอย่างทั่วประเทศ พบว่ามีค่าเฉลี่ยอยู่ที่ 30 mg/kg และพบว่ามีบางพื้นที่มีค่าสูงกว่าค่าเฉลี่ยหลายเท่า โดยเฉพาะพื้นที่ ตำบลองค์พระ อำเภอด่านช้าง จังหวัดสุพรรณบุรี ซึ่งเป็นเหมืองเก่า อย่างไรก็ตาม ปริมาณสารหนูรวมในดินอาจยังไม่เพียงพอในการประเมินความเสี่ยงของการปนเปื้อนในพื้นที่ งานวิจัยนี้จึงนำวิธีประเมินความอ่อนไหว DRASTIC มาพิจารณาร่วมกับปัจจัยการเคลื่อนตัวและปัจจัยการปนเปื้อนซึ่งได้จากการสกัดแบบต่อเนื่องเพื่อใช้ในการสร้างแผนที่ความเสี่ยงของสารหนูจากดินที่ปนเปื้อนต่อแหล่งน้ำบาดาลระดับตื้น จากการนำดิน 39 ตัวอย่างมาวิเคราะห์พบว่า ได้ค่าสารหนูรวมระหว่าง 4.8 – 1,070.4 mg/kg โดยมีค่าเฉลี่ย 171.8 mg/kg ผลการสกัดแบบต่อเนื่องพบว่าสารหนูส่วนใหญ่อยู่ในลำดับปฏิกิริยาออกซิเดชั่นและลำดับที่คงตัว ซึ่งแสดงให้เห็นว่าสารหนูในดินของพื้นที่ศึกษามีศักยภาพในการกระจายตัวสู่สิ่งแวดล้อมต่ำ และการพิจารณาความอ่อนไหว DRASTIC จาก 7 ปัจจัยของพื้นที่ ได้ค่าคะแนนอยู่ในช่วง 59 – 147 แบ่งเป็นสามช่วงคะแนนคือ ค่าความอ่อนไหวต่ำ มีคะแนนน้อยกว่า 100 และ ค่าความอ่อนไหวปานกลางและสูงมีค่าคะแนน ระหว่าง 100 ถึง 130 และ คะแนนมากกว่า 130 ตามลำดับ โดยพื้นที่ที่มีค่าความอ่อนไหวสูงคิดเป็น 18.65 % ซึ่งเป็นพื้นที่ตามทางน้ำ และพื้นที่ที่มีค่าความอ่อนไหวปานกลาง 34.88 % และพื้นที่ที่มีค่าความอ่อนไหวต่ำเท่ากับ 46.47 % เป็นพื้นที่ราบและภูเขาตามลำดับ และบริเวณพื้นที่เหมืองเก่านั้นมีค่าความอ่อนไหวอยู่ในช่วงปานกลางและสูง เมื่อตรวจสอบปริมาณสารหนูในน้ำบาดาลระดับตื้นทั้งฤดูฝนและฤดูร้อน พบว่าบ่อหมายเลข 3 มีปริมาณสารหนูสูงเกินค่ามาตรฐานน้ำดื่มในฤดูร้อน จากนั้นได้นำปริมาณสารหนูในน้ำบาดาลระดับตื้นมาสร้างแผนที่การกระจายตัวของสารหนูเพื่อใช้ในการพิจารณาร่วมกับแผนที่ความเสี่ยงสองแผนที่ ที่สร้างจากค่าความอ่อนไหวด้วยวิธี DRASTIC กับค่าการเคลื่อนตัวและค่าการปนเปื้อน พบว่าแผนที่ความเสี่ยงที่สร้างจากค่าการปนเปื้อนใช้ในการอธิบายการปนเปื้อนของสารหนูในน้ำใต้ดินระดับตื้นได้ดีกว่าแผนที่ความเสี่ยงที่สร้างจากค่าการเคลื่อนตัว

ภาควิชา ธรณีวิทยา ลายมือชื่อนิสิต ....

สาขาวิชา โลกศาสตร์ ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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KEYWORDS: ARSENIC; CONTAMINATED SOIL; SEQUENTIAL EXTRACTION; DRASTIC

WEERAWUT TIANKAO: RISK ASSESSMENT OF ARSENIC FROM CONTAMINATED SOILS TO SHALLOW GROUNDWATER IN ONG PHRA SUBDISTRICT CHANGWAT SUPHAN BURI, THAILAND. ADVISOR: ASST. PROF. SRILERT CHOTPANTARAT, Ph.D., CO-ADVISOR: ARANYA FUANGSWASDI, Ph.D., 106 pp.

Arsenic (*As*) is a global pollutant and people are exposed to *As* through food and drinking water. In the previous research, total *As* concentration in agricultural soils in Thailand has an average concentration of 30 mg/kg. However, some areas were found many times of *As* concentration in soils higher than the mean *As* concentration, especially soil samples collected in Tambon Ong Phra , Amphoe Dan Chang, Changwat Suphan Buri. However, the total contents of *As* in soils do not provide enough information to indicate the potential risk into the groundwater environment. Therefore, in this study, the DRASTIC vulnerability integrated with the mobility factor (MF) and the contamination factor (CF), derived from the sequential extraction procedure, has been developed to construct the risk assessment map of *As* contaminated soils into the shallow groundwater system. The 39 soil samples were analyzed *As* in each fraction using the sequential extraction technique. The concentrations of total *As*, sum of *As* in each fraction, in soil ranged from 4.8 – 1,070.4 mg/kg, with an average value of 171.8 mg/kg. The results of sequential extraction revealed that most *As* were in the oxidable and residual fractions, leading to low potential of releasing into the surrounding environments. The Index of DRASTIC vulnerability, overlaid of 7 thematic layers, was in the range of 59 – 147 and was categorized into three zones according to the groundwater vulnerability classification as follows: low (index <100), moderate (index 100–130) and high (index > 130). Around 18.65 % of the area showed high vulnerability, found along the waterway, and around 34.83 % and 46.47 % of the area were in the zones of moderate and low vulnerability, found in the plain and mountainous areas, respectively. Interestingly, the DRASTIC index of the old tin mine was indicated as the zone of moderate and high vulnerability. Moreover, the investigation of *As* concentrations in groundwater was carried out in dry and wet seasons and found that *As* in well no. 3 was higher than the drinking water standard only in the dry season. The distribution maps of *As* in shallow groundwater were generated and further used to compare with the risk maps. Finally, two risk maps were created by integrating the DRASTIC map with MF and CF and found that the risk map generated from CF was able to explain *As* contaminated in shallow groundwater better than the other risk map derived from MF.

Department:	Geology	Student's Signature	....
Field of Study:	Earth Sciences	Advisor's Signature	....
Academic Year:	2014	Co-Advisor's Signature	....

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CHAPTER I

INTRODUCTION

1.1 Introduction

Arsenic (*As*) is one of the most toxic substances, which can be found in the environment. Exposure to sufficiently high concentrations of *As* in natural environment, such as in surface water, groundwater, sediment, and soil, has proved to be harmful to the human health and ecosystem. The main pathways of an exposure to the human beings include ingestion of drinking water and consumption of foods. A significant route for *As* exposure is consumption of groundwater that has been reported from different parts of the world (Bhattacharya et al., 1997; Bhattacharya et al., 2002b; Muhammad and Muhammad, 2011; Quazi et al., 2011; Smedley and Kinniburgh, 2002; Zhiyuan et al., 2014).

For the abandoned mine, the mining wastes consist of roaster piles, tailings ponds, waste rock piles and acid mine water. Percolation from the tailing ponds can leak and eventually contaminate into groundwater system and move down-gradient from the ponds. Moreover, the groundwater and acid mine water, leached from the roaster, tailings, waste piles discharged into a nearby stream, and finally adversely affect aquatic ecosystems. In particular, the main concentrations of concern are As, iron, copper, lead, manganese, nickel, and zinc with levels exceeding water quality criteria in the stream around mining areas.

Heavy metals naturally occur as a result of mineral deposition processes. Arsenic is usually an unusable by-product that may be introduced into the environment through the natural process of erosion of mineral deposits or through mining and milling of these deposits. Metals or mineral decomposition products may present in mine water, mine dump rock, mill tailings or nearby soils, or water bodies (Alshaebi et al., 2009).

Most tin ores are found in alluvial deposits and mining operations by dredging and gravel pumping, which use water for the mechanical separation of tin ore from the tin-bearing earth.. The tailings are therefore grouped into two main types, which are slime and sand, including gravel as a minor proportion. The coarser materials are found close to the discharge point with a continuous gradation to fine particle at the lower end of the slope. It is formed the fan shaped tailings(Tanpibal and Sahunalu, 1989).

Several authors (Grangeia et al., 2011; Raigb-Pichardoa et al., 1996) reported the characteristics of tin mine tailings. In sand tailings, the absence of organic matter and the predominance of coarse materials, mainly sand or inert quartz particles, lead to excessive drainage, and low water and nutrient retention capacities. The slime railings, consisting of high contents of silt and clay particles, are generally consolidated and compact upon drying. Infiltration is restricted and water-logged conditions often prevail. When dry, large cracks appear at the surface and the materials show a laminar structure. Organic matter content is fairly higher than in the sand tailings, providing a greater nutrient retention capacity.

Thailand is one of several countries in Southeast Asia, having problems of the tin residue. The waste piles, resulting from tin mining contain high arsenic (as arseno-pyrite). The case had been discovered for decades at Ronphibun Sub-district, Nakorn Si Thammarat, a province in the southern part of Thailand (Smedley and Kinniburgh, 2002; Williams et al., 1996).

Health problems were first recognised in the area in 1987. Around 1000 people have been diagnosed with *As*-related skin disorders, particularly in and close to Ron Phibun town (Choprapawon and Rodcline, 1997; Fordyce et al., 1995; Williams et al., 1996). The affected area lies within the South-East Asian Tin Belt. Arsenic concentrations are found at up to 5000 μg/L in shallow groundwaters from the Quaternary alluvial sediment that has been extensively dredged during tin-mining operations. Moreover the result of the measurement of As content in water and soils in other old Tin mine at Dan Chang, Suphan Buri found As contamination in the soils and tap water (Pansamut and Wattayakorn, 2010). Especially, the result form health risk assessment of As contamination project in 2010 at Tambon Ong Phra is a risk of cancer with As exposure.

Heavy metals contaminated in soil can be leached and finally result in contamination in groundwater. Risk assessment of As contaminated in soils, leached into groundwater can be determined from both of vulnerability of aquifer and potential release of As into the groundwater system. DRASTIC method is commonly used for assessing of aquifer vulnerability , developed by Aller (Aller et al., 1987). Furthermore, the aquifer vulnerability from DRASTIC then used to combine with the potential release of arsenic, which is indicated by the sequential extraction of metals in contaminated soils. Finally, integration of the vulnerability of the area and potential risks of the study area can be applied to determine the risk assessement of groundwater contamination in this area.

1.2 Objectives

1. To investigate the arsenic concentrations in soil in the study area.
2. To evaluate risk assessment of arsenic from soils to shallow groundwater.

1.3 Scopes

1. The study area is about 188 square kilometers and is located in Ong Phra subdistrict, Changwat Suphan Buri with an old mine and the part of Somdet Charoen subdistrict, Changwat Kanchanaburi.
2. The soil sampling has been limited to the top soil, 0 - 15 cm depth.

1.4 Limitation

1. Soil samples in some areas were not collected because of the road construction and disturbance preparing for the next crop.
2. Some groundwater samples cannot be collected because some wells are damaged and abandoned as useless.

CHAPTER II

THEORETICAL AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Chemical properties of Arsenic

Arsenic (*As*) is a chemical element with atomic number 33. *As* occurs as a metallic element (As^{o}) and metallic compound arsenate (As^{5+}), arsenite (As^{3+}), or arsine (As^{3-}) as shown in Figure 2.1. The chemical character of *As* depends on oxidation state or chemical form through chemical or biological reactions, which are common in the environment.

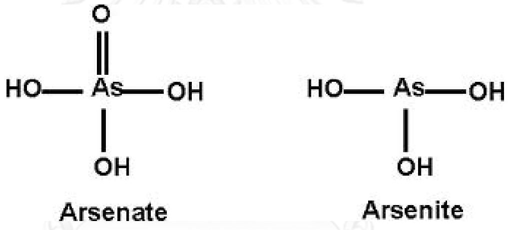


Figure 2.1 Chemical structure of arsenate and arsenite

As in groundwater most often occurs from geogenic sources, arsenite or arsenate. Anthropogenic *As* may have any form including organic arsine species such as trimethylarsine (see Figure 2.2).

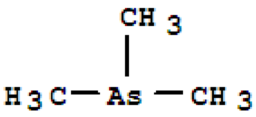


Figure 2.2 Chemical structure trimethylarsine

2.1.2 Mobility and Absorption of *As*

The mobility of *As* controlled by redox conditions, pH, biological activity, and adsorption/desorption reactions. *As* in groundwater often occurs from geogenic sources, arsenite or arsenate. Anthropogenic *As* may have any form including organic arsine species.

Dissociation of proton (H^+) from Arsenate and Arsenite in aqueous solution , dissociation constant, pK_a of arsenate and arsenite (Tallman and Shaikh, 1980) are as follows:

Arsenate , H_3AsO_4 pK_1=2.19, pK_2= 6.64, pK_3= 11.5

Arsenite , H_3AsO_3 pK_1=9.20, pK_2= 14.22, pK_3= 19.22

Therefore speciation of arsenate and arsenite in solution or water varies with pH as illustrated in Figure 2.3.

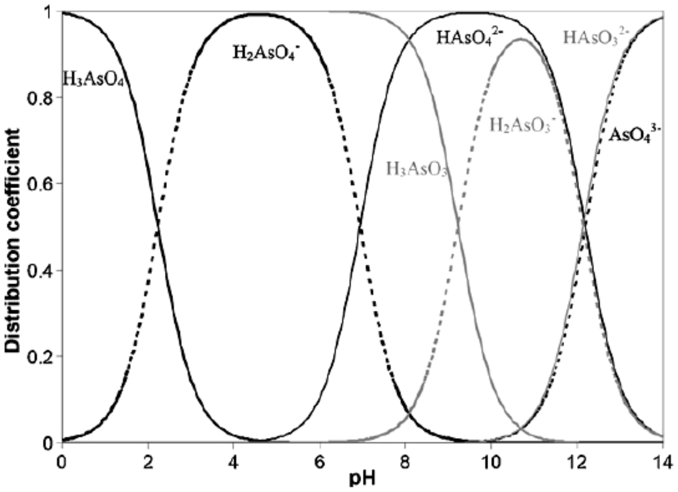


Figure 2.3 Speciation of arsenite and arsenate with pH (Sadiq et al., 2002)

The most common adsorption reactions are based on ion exchange between charged adsorption sites and charged soluble ions. However, another mechanism is also responsible for adsorption, London Van der Waals bonding. Consequently, some degree of immobilization can occur with soluble species that are not ionized. *As* immobilization through ionic adsorption can be controlled within normal oxidizing Eh/pH conditions. *As* in oxidizing redox conditions are adsorb on surface of metal oxide and in reducing redox conditions arsenite form is dominant and not adsorb on metal oxide surface (Welch et al., 1988).

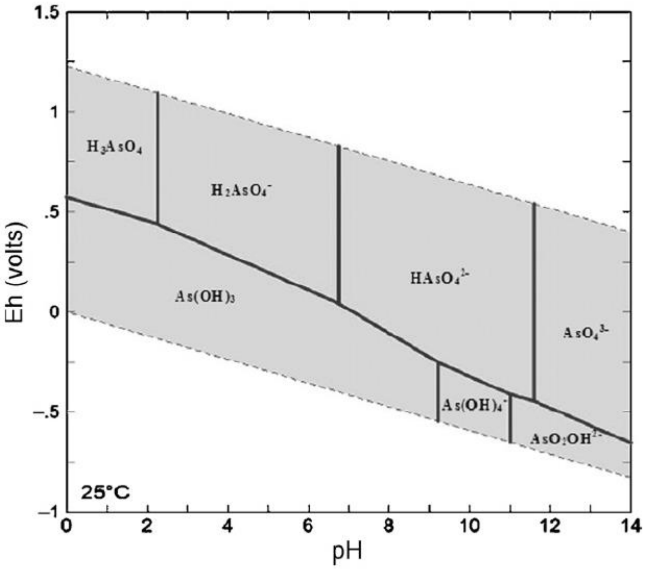


Figure 2.4 Arsenic forms with Eh–pH condition

2.1.3 Groundwater and groundwater flow

Groundwater is the water found underground in the cracks and spaces in soil, sand and rock. It is stored in and moves slowly through geologic formations of soil, sand and rocks, so-called aquifers. Aquifer can be divided into two regions are the vadose zone, also termed the unsaturated zone , where there are still pockets of air that contain some water, but can be filled with more water as well as the saturated zone, where all available spaces are filled with water.

Aquifer can be classified in two types: confined and unconfined aquifers. Confined or artesian aquifer, in which the groundwater is bounded between layers of impermeable substances (semipervious strata) like clay or dense rock. When tapped by a well, water in confined aquifers is forced up, sometimes above the land surface. Unconfined aquifers, an aquifer in which the water table is at or near atmosphere pressure and is the upper boundary of the aquifer. Since this aquifer is not under pressure, the water level in a well is the same as the water table outside the well.

2.1.4 Groundwater vulnerability assessment

Morris and Foster, 2000 (Morris and Foster, 2000) defined groundwater pollution risk as the probability that groundwater in the aquifer will become contaminated to an unacceptable level by activities on the immediately overlying land surface. They described groundwater risk assessment as the process, used to predict the possibility of groundwater contamination from pollutants. The concept of groundwater vulnerability can be defined as the possibility of percolation and diffusion of contaminants from the ground surface into the groundwater system. Vulnerability is usually considered as an intrinsic property of a groundwater system that depends on its sensitivity to human and natural impacts. Integrated vulnerability combines intrinsic vulnerability with the risk of the groundwater being exposed to the loading of pollutants from certain sources.

The term of groundwater vulnerability to contamination was introduced by French hydrogeologist J. Margat in 1968. Several approaches for developing aquifer vulnerability assessment maps were adopted such as DRASTIC (Aller et al., 1987), GOD (Foster, 1987), AVI (Van Stempvoort et al., 1993), and SINTACS (Civita, 1994) and so forth. Sample of groundwater vulnerability method (Civita, 1993) were shown in Table 2.1.

Table 2.1 Methods their parameters of the groundwater vulnerability

METHOD		BASIC PARAMETERS													
REFFERENCE	TYPE	PRECIPITATION RATE & CHEMICAL COMPOSITON	TOPOGRAPHIC SURFACE SLOPE VARIABILITY	STREAMFLOW NETWORK DENSITY	CHARACTERISTIC OF SOIL				PHYSICAL &CHEMICALPROPERTIES	AQUIFER CONNECTIONS TOSURFACE WATER	CHAR ACTERISTICS OF THE UNSATURATED ZONE	DEPTH TO WATER	WATER LEVEL CHANGES	HYDROGEOLOGICAL FEATURES	AQUIFER HYDRAULICCONDUCTIVITY
					THICKNESS TEXTURE&MINERALOGY	EFFECTIVE MOISTURE	NE T RECHARCE	PERMEABILITY							
Albinet & Margat (1970) B.R.G.M. (1976)	HCS								•		•	•		•	•
Varana (1968) Olmer & Rezac (1974)	HCS										•			•	
Fenge (1976)	RS				•					•	•	•	•	•	•

METHOD		BASIC PARAMETERS													
REFFERENCE	TYPE	PRECIPITATION RATE & CHEMICAL COMPOSITON	TOPOGRAPHIC SURFACE SLOPE VARIABILITY	STREAMFLOW NETWORK DENSITY	CHARACTERISTIC OF SOIL				PHYSICAL &CHEMICALPROPERTIES	AQUIFER CONNECTIONS TOSURFACE WATER	CHAR ACTERISTICS OF THE UNSATURATED ZONE	DEPTH TO WATER	WATER LEVEL CHANGES	HYDROGEOLOGICAL FEATURES	AQUIFER HYDRAULICCONDUCTIVITY
					THICKNESS TEXTURE&MINERALOGY	EFFECTIVE MOISTURE	NE T RECHARCE	PERMEABILITY							
Josopait & Schwerdfeger (1979)	HCS									•	•	•		•	•
Zampetti (1983) Fried (1987)	AR										•	•			
Villumsea et al. (1983)	RS				•						•	•	•	•	•
Haertle (1983)	MS										•	•			
Vrana (1984b)	HCS	•			•						•			•	
Subirana Asturias & Casas Ponsati (1984)	HCS								•		•	•		•	•
Engelen (1985)	MS								•		•	•		•	
Zaporozec (1985)	RS				•	•	•	•			•	•		•	
Breeusvsma et al. (1986)	HCS				•	•	•	•	•	•	•	•			•
Sotornikova & Vrba (1987)	RS						•					•	•	•	
Ostry et al. (1987)	HCS				•			•				•		•	
Ministry Flemish Comm (1986)	MS				•			•				•		•	
Carter et al. (1987) Palmer (1988)	MS				•		•	•						•	
Marcolongo & Pretto (1987) Method 1	RS				•				•	•	•				
Marcolongo & Pretto (1987) Method 2	AR					•				•	•	•			
GOD - Foster (1987)	RS										•	•		•	
Schmidt (1987)	RS				•				•		•	•			
Trojan & Perry (1988)	PCSM	•	•				•			•	•	•		•	
Civita in Benacchio et al. (1988)	HCS								•		•	•		•	•

METHOD		BASIC PARAMETERS													
REFFERENCE	TYPE	PRECIPITATION RATE & CHEMICAL COMPOSITON	TOPOGRAPHIC SURFACE SLOPE VARIABILITY	STREAMFLOW NETWORK DENSITY	CHARACTERISTIC OF SOIL				PHYSICAL &CHEMICALPROPERTIES	AQUIFER CONNECTIONS TOSURFACE WATER	CHAR ACTERISTICS OF THE UNSATURATED ZONE	DEPTH TO WATER	WATER LEVEL CHANGES	HYDROGEOLOGICAL FEATURES	AQUIFER HYDRAULICCONDUCTIVITY
					THICKNESS TEXTURE&MINERALOGY	EFFECTIVE MOISTURE	NE T RECHARCE	PERMEABILITY							
DRASTIC – Aller et al. (1987)	PCSM		•		•					•	•	•		•	•
SINTACS – Civita (1990a)	PCSM		•	•	•				•	•	•	•		•	•

Where

AR - Analogical Relations
HCS - Hydrogeological Complex and Setting
MS - Matrix System
PCSM - Point Count System Model
RS - Rating System

DRASTIC is a well known method, developed for the US Environmental Protection Agency (EPA) by Aller (Aller et al., 1987), It has been used in several regions.

2.1.4.1 DRASTIC model

The DRASTIC model was developed by the U.S. Environmental Protection Agency (EPA) to evaluate groundwater pollution potential for the entire United States proposed by Aller and others (Aller et al., 1987). DRASTIC methodology is based on weighting and rating method that assesses vulnerability by means of seven parameters including Depth to Groundwater table (D), Net Recharge (R), Aquifer Media (A), Soil Media (S), Topography (T), Impact of Vadose Zone Media (I) and Hydraulic Conductivity of the Aquifer (C).

Each of the hydrogeologic parameters is assigned a rating from 1 to 10 based on a range of values. The ratings are then multiplied by a relative weight ranging from 1 to 5 (Table 2.2). The most significant factors have a weight of 5 and the least significant have a weight of 1.

Table 2.2 Assigned weight for DRASTIC parameters (Aller et al., 1987)

Hydrogeologic parameters	Weighting Factor of DRASTIC
D-Depth to Groundwater table	5
R-Net Recharge	4
A-Aquifer Media	3
S-Soil Media	2
T-Topography	1
I-Impact of Vadose Zone Media	5
C-Aquifer Hydraulic Conductivity	3

The equation for determining the DRASTIC index (Aller et al., 1987) is:

$$\text{DRASTIC Index} = D_rD_w + R_rR_w + A_rA_w + S_rS_w + T_rT_w + I_rI_w + C_rC_w$$

Where

D, R, A, S, T, I, C : Hydrogeologic parameters of DRASTIC
r : rating score of parameter
w : weighting score of parameter

The hydrogeologic factors are described as:

1. Depth to Water (D): The depth to water is the distance from the ground surface to the water table. It determines the depth of the material through which a contaminant must travel before reaching the aquifer. Thus, the shallower the water depth, the more vulnerable the aquifer is to pollution.

2. Net Recharge (R): The primary source of recharge is precipitation, which infiltrates through the ground surface and percolates to the water table. Net recharge is the total quantity of water per unit area, which reaches the

water table. The more the recharge, the greater the chance for contaminants to reach the water table.

3. Aquifer Media (A): Aquifer media refers to the consolidated or unconsolidated rock that serves as an aquifer. The larger the grain size and the more fractures or openings within the aquifer, the higher the permeability and vulnerability of the aquifer. In unconsolidated aquifers, the rating is based on the sorting and amount of fine material within the aquifer. In consolidated aquifers, the rating is based on the amount of porosity, fractures and bedding planes.

4. Soil Media (S): Soil media is the upper weathered zone of the ground surface. Soil has a significant impact on the amount of recharge that can infiltrate into the ground. In general, the less the clay shrinks and swells and the smaller the grain size of the soil, the less likely contaminants will reach the water table.

5. Topography (T): Topography refers to the slope of the land surface. Topography helps control the possibility that a pollutant will run off or remain long enough to infiltrate through the ground surface. Where slopes are low, there is little runoff, and the potential for pollution is greater. On the other hand, if slopes are steep, runoff capacity is high and the potential for pollution to groundwater is lower.

6. Impact of the Vadose Zone Media (I): The vadose zone is the unsaturated zone above the water table. The texture of the vadose zone determines the time of travel of the contaminant through it. In surficial aquifers, the ratings for the vadose zone are generally the same as the aquifer media. Sometimes a lower rating is assigned if the aquifer media is overlain by a less permeable layer.

7. Hydraulic Conductivity of the Aquifer (C): Hydraulic conductivity refers to the rate at which water flows horizontally through an aquifer. The higher the conductivity, the more vulnerable the aquifer.

2.1.4.2 Groundwater Vulnerability Assessment

Risk of groundwater contamination can be estimated by Vulnerability of the area and potential pollution load at each location. Foster and Hirata (Foster and Hirata, 1988) estimate the risk of groundwater contamination from the interaction between aquifer vulnerability and the surface pollution load. The risk of the aquifer can be calculated by the arithmetic product of the indexes of the aquifer vulnerability times the pollution load as shown in the following equation (Gonzalez et al., 1997) :

$$R = L \times V$$

Where: R = Risk value

L = The potential pollution load

V = Groundwater vulnerability

Risk value can be classified in 4 levels as: low, medium, high and very high value and use further to identify area at risk.

The contamination factor is used to indicate the degree of environmental contamination (Abrahim and Parker, 2008) and evaluate anthropogenic influences of heavy metals in sediments (Esin, 2010).

The contamination factor is calculated as the ratio between the sediment metal content at a given station and average shale values of the metal (Krauskopf, 1985). The contamination factor is measured by the following equation: (Hakanson, 1980)

$$C_f = C_M / C_N$$

Where: C_M = concentration of each metal in the soil

C_N = baseline or background value of the specific metal

2.2 Literature reviews

Arsenic (*As*) is a global environmental pollutant. Exposure is via the environment and drug use. *As* contamination in drinking water is the main source of exposure and occurs in many countries, such as India, Bangladesh, China, Taiwan, Thailand, Chile, Argentina and Romania. Concentrations of arsenic in affected areas are several times higher than the maximum contamination level at 10 µg/L. Long-term ingestion of inorganic *As* other than organic *As* causes multisystem adverse health effects because organic forms are less toxic and rapidly excreted from body via urine. The clinical manifestations of chronic arsenic exposure are skin lesions, cardiovascular disease, neurological effects, chronic lung disease, cerebrovascular disease, reproductive disease, adverse renal affects, developmental abnormalities, hematological disorders, diabetes mellitus and cancers of skin, lung, liver, kidney and bladder (Bhattacharya et al., 2002a; Singh et al., 2007).

As in groundwater is mainly from natural geological sources. Especially in the form of arsenite (III) and arsenate (V), *As* concentration found in groundwater from acidic volcanic rocks media or volcanic sedimentary aquifer is found in *As* concentrations exceed the standard at 50 µg/L (Smedley and Kinniburgh, 2002). *As* caused by human activities are compounds with a variety of organic and inorganic compounds (Mandal and Suzuki, 2002).

Shiomi (Shiomi, 1994) reported toxicology of *As*, the high-toxic group is inorganic form such as trivalent arsenite, *As*(III) and pentavalent arsenate, *As*(V) and the less-toxic is organic form, trimethylate as arsenobetain (AB), in addition, the determination of total *As* in a contamination area is not enough to assess the level of contamination (Koch I. et al., 2000)

The mean concentration of *As* from earth' crust is 2 – 3 mg/kg (Tanaka, 1988) and found in over 200 ores, with the main form of arsenopyrite (FeAsS), realgar (As_4S_4) and orpiment (As_2S_3) .and inorganic form exposure to soil, where it depends on an amount in parent rock, human activities, climate, form of compound and redox conditions in soil (Yan-Chu, 1994).

The species of *As* in water depends on the pH and redox potential existing in that system, pentavalent arsenate, *As*(V) in oxidized conditions and trivalent arsenite, *As*(III) in reducing conditions (Pokroviski et al., 1996), mobility and adsorption in media of sediment, clay and soil depend on form of *As* compound, and precipitate form are sulfides and arsenides.

Mining and refining, chemical for agriculture, coal electric power plants and wood product factory used chromate copper arsenate as a main source of *As* contamination (Nriagu and Pacyna, 1988).

Ganesh Chandra Saha and Ashraf Ali M. (Saha and Ashraf Ali M, 2007) found the paddy field with height contamination irrigated water (79 - 436 µg/L) cause to height contamination soil at depth 0 – 75 mm.

Zarcinas (Zarcinas et al., 2004) found height contamination of heavy metals in soil and crop in Thailand. Analyzed arsenic (*As*) cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) in soil associated to amounts of Al and Fe.

In Ron Phibun district, Nakhon Si Thammarat province, Thailand, *As* concentration were found in soil from arsenopyrite and pyrite with weathering granite rock and Tin mine (Williams, 1997). Oshikawa (Oshikawa et al., 2007) found *As* contamination in urine of people in southern of Thailand although they did not use contaminated water for drinking and cooking.

Pansamut and Wattayakorn (Pansamut and Wattayakorn, 2010) analyzed *As* in water around the old Tin mine in Tambon Ong Phra of Dan Chang district, Suphan Buri Province, during October 2008 - January and March 2009 and found that concentration of *As* was in range 32 µg/L - 748 µg/L and over than 80 samples in old mine has high over limit of WHO at 50 µg/L.

Orathai Sukreeyapongse et al. (Orathai et al., 2009) analyzed *As* in agriculture soil 634 samples, concentration in range 0.005 - 64 mg/kg with an average of 30 mg/kg. Samples at Amphoe Ron Phibun, Nakhon Si Thammarat has contaminated in soil 2.53 - 151 mg/kg, in water 0.007 µg/L - 0.036 mg/L and crop 0.009 - 7.70 mg/kg. Tambon Ong Phra, Dan Chang district, Suphan Buri has *As*-contaminaed in soil 8.96 - 92.35 mg/kg and crop 0.009 - 1.235 mg/kg. Moreover, they found that *As* in crop was associated with *As* concentration in soil.

Environmental Resource and Training Centre (ERTC) reported of concentration of *As* in soil and water in Dan Chang district, Changwat Suphan Buri, Thailand during February and April 2009. The result is shown in Table 2.3.

Table 2.3 *As* concentrations in soil surface water and tab water in Tambon Ong Phra and Tambon Wang-kun at February and April 2009

Area	Soil (mg/kg)	Surface water (µg/L)	Tap water (µg/L)
Tambon Ong Phra	22.46 – 380.10 mean = 115.42	6.03 – 644.60 mean = 196.28	0.34 - 754.40 mean = 299.70
Tambon Wang-kun	5.27 – 340.70 mean = 78.16	38.30 – 141.70 mean = 90.72	5.57 – 141.70 mean = 73.35

The Health risk assessment of *As* contamination project on 2010 in this area was done by Probabilistic risk assessment (PRA), indicating that 2 Sub districts (Ong Phra and Wang-Kun) are in risk to cause cancer due to arsenic exposure.

Vulnerability assessment of groundwater contamination has been recognized for its ability to delineate areas which may be susceptibly contaminated, as a result of anthropogenic activities at/or near the earth’s surface. The aquifer vulnerability uses these following factors: depth to water (D), net recharge (R), aquifer media (A),soil media (S), topography (T), impact of vadose zone (I), and hydraulic conductivity (C), so-called DRASTIC. This empirical model has been proposed by the U.S. Environmental Protection Agency (Aller et al., 1987)

Rashid et al. (Rashid et al., 2009) used DRASTIC for Yamuna-Krishni sub-watershed, the part of Ganga plain in India. Aquifer vulnerability are in the range of 140 – 180 and were defined into 4 range as Low (140-150), moderate (150-160), high (160-170) and very high (170-180). There are 7 %, 40 % and 53 % of the area in low, moderate as well as high and very high vulnerability. Ckakraborty et al. (Surajit et al., 2007) used the modified DRASTIC for Malda, India. The alluvial sediment aquifer has be polluted by pesticide. The parameters in Modified DRASTIC method has been adjusted the rating score to suit the area. For examples, modified rating score with depth, recharge, slope and impact of vadose zone was carried out.

Nannoni et al. (Nriagu and Pacyna, 1988) analyzed heavy metal (i.e., As, Cd, Cu, Pb, Sb and Zn) in soil of mine to indicate contamination potential of heavy metal with the sequential extraction.

According to the studies of Rauret et al. (Rauret et al., 1999) and Pueyo et al. (Pueyo et al., 2001), the sequential extraction procedures have 5 steps as shown in Table 2.4

Table 2.4 extract agent and ratio of sample for soil sequential extraction

No.	Soil extracted	Extract Agent	soil (g): volume (mL)
A	Soluble	Ultrapure water	1:2
B	Extractable	0.11 M CH_3COOH	1:40
C	Reducible	0.5 M NH_2OH, HCl pH 1.5	1:40
D	Oxidable	8.8 M H_2O_2 +1 M CH_3COONH_4	1:50
E	Residual	HNO_3 + HCl+ HF+$HClO_4$	1:30

Mobility and potential bioavailability of As, Cd, Cu, Pb, Sb and Zn are in soils as well as the main solid phases that ruled their distribution and behavior in soil. The mobility of heavy elements in soils was assessed by using a “Mobility Factor (MF)” index calculated on the basis of the following equation:

$$MF = \frac{\left(F_{sol} + F_{ext}\right)}{\left(F_{sol} + F_{ext} + F_{red} + F_{oxi} + F_{res}\right)} \times 100$$

The descending order of mobility in contaminated soils was as follows: Cd >>Zn >> Pb >> Sb > As > Cu. The mobility of heavy elements was considerably higher in contaminated soils with respect to uncontaminated ones.

CHAPTER III

MATERIALS AND METHODS

3.1 STUDY AREA

3.1.1 Location and climate

Dan Chang is the northwestern district of Suphan Buri Province (Figure 3.1). The terrain of Dan Chang is high mountain ranges in the west and undulating to rolling terrain and slope down to the east. Annual rainfall in Dan Chang disctrictis 915.34 mm.

Ong Phra sub-district is one of 7 sub-districts in Dan Chang with population of about 7,000 people who are mainly in agricultural sector. The old tin mine in Tambon Ong Phra is approximately 80 km west of Dan Chang District, and south-west of the old mine is tambon Sombut-Jarern, Nong Prue, Kanchanaburi. The old mine areas are clustered in 13 pits as shown in Figure 3.5. (Latitudes 14 49’22”- 14 50’32” N and longitudes 99 21’12” - 99 22'22” E)

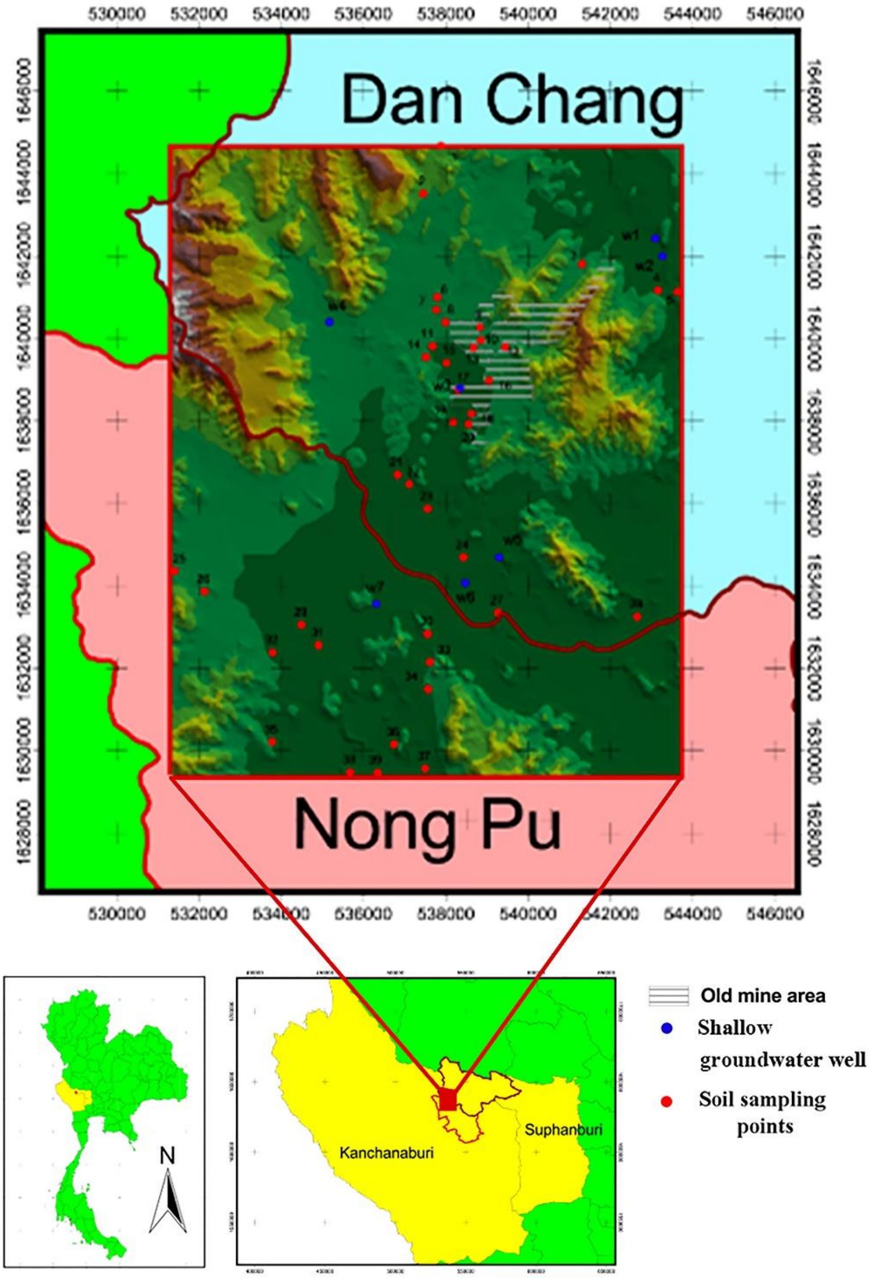


Figure 3.1 Location of study area in Ong Phra Subdistrict, Dan Chang District, Supan Buri Province

3.1.2 Geology and hydrogeology

Geology and hydrogeology of study area were classified by secondary data (such as rock types, well log of groundwater exploration), obtained from the Department of Mineral Resources (DMR) and the Department of Groundwater

Resources (DGR). Three cross-section lines were shown in Figures 3.2-3.5. Line A-A' passes from NW to SE that shows separation of terrain upstream as the site of old mine and downstream as granite range and the terrain covering with clay and laterite.

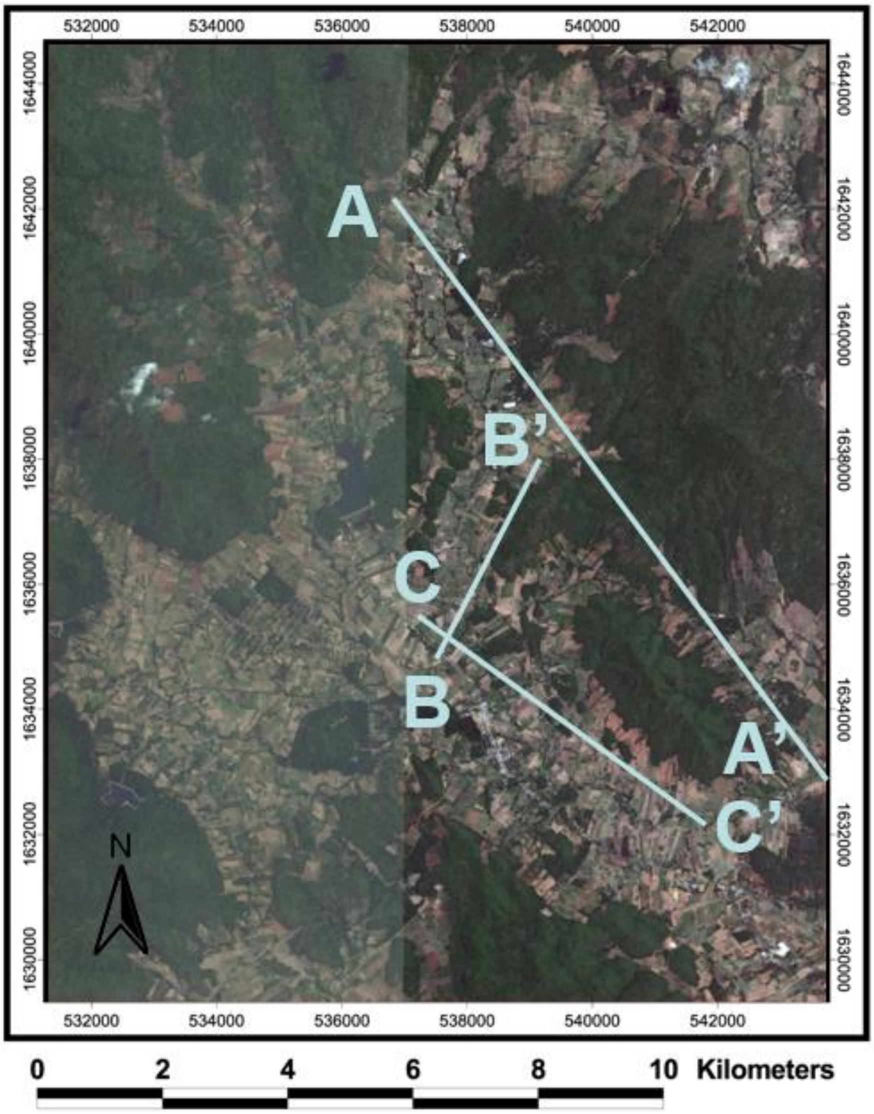


Figure 3.2 The lines of cross sections of study area

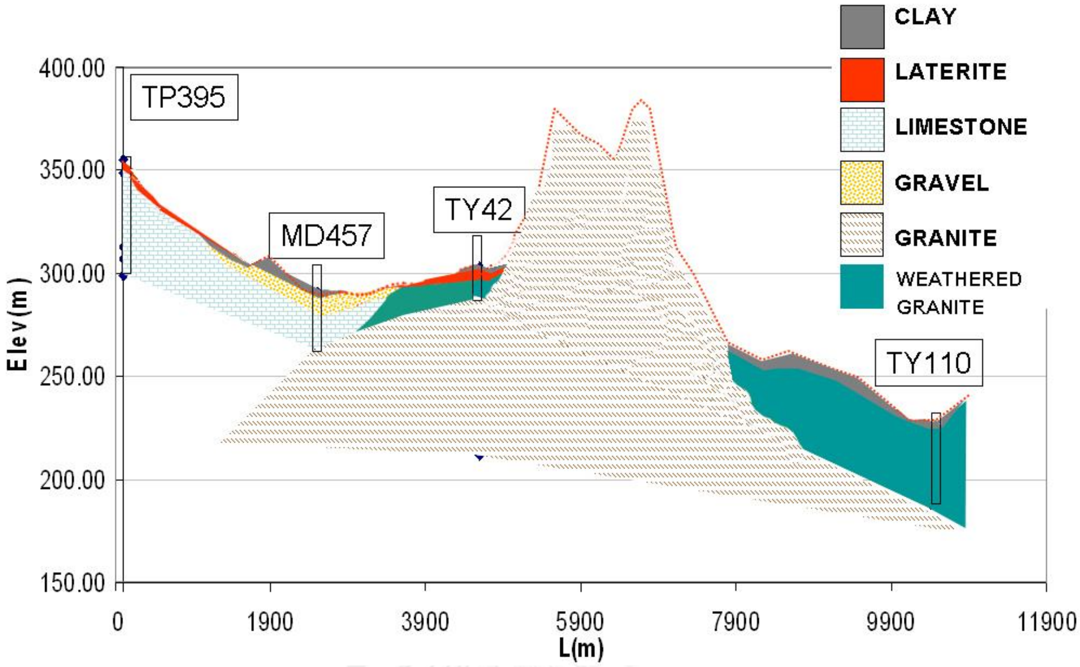


Figure 3.3 The cross section, Line A-A', of study area

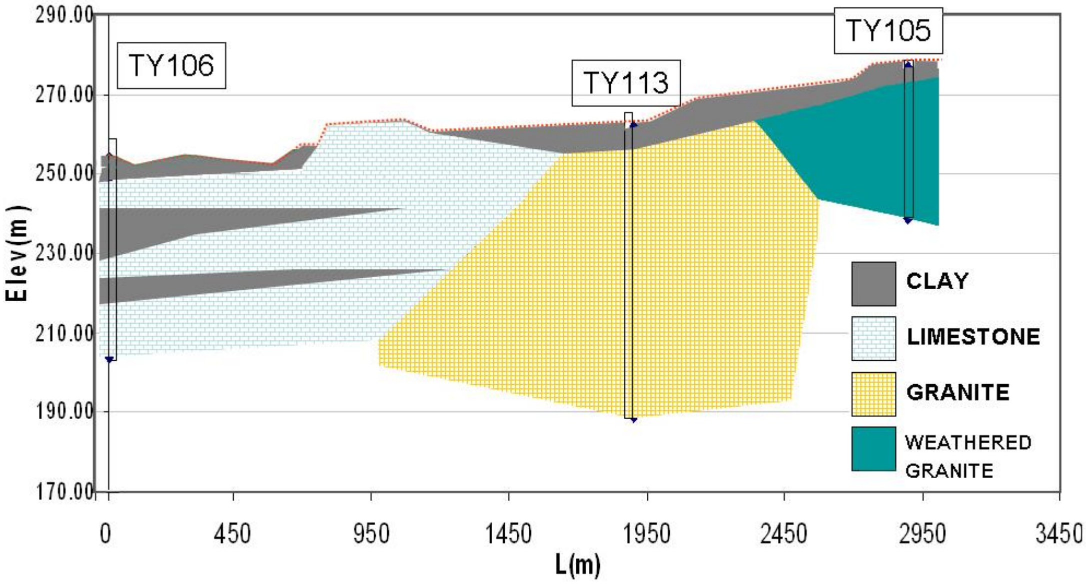


Figure 3.4 The cross section, Line B-B', of study area

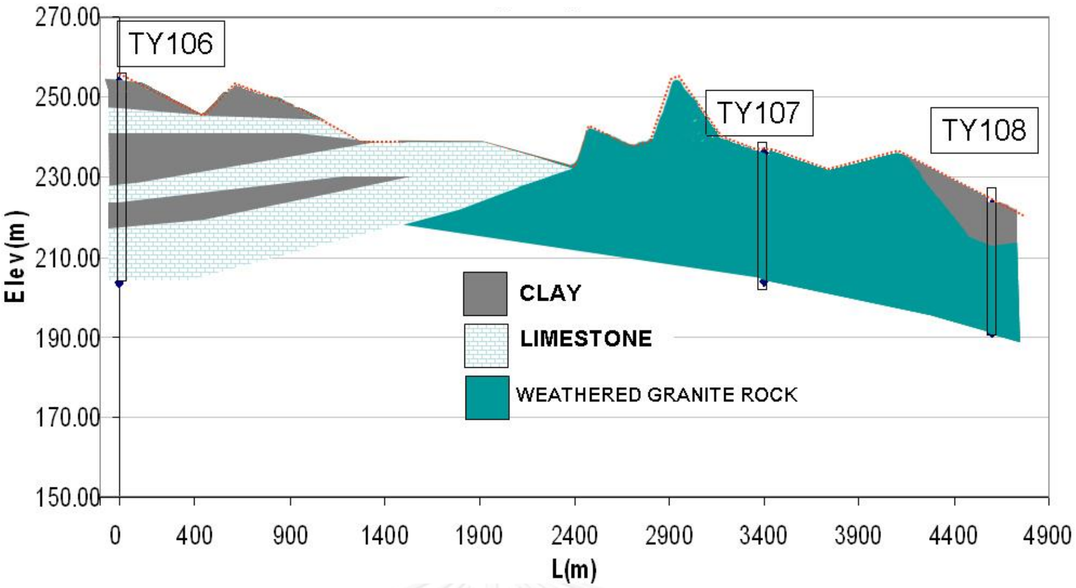


Figure 3.5 The cross section, Line C-C', of study area

The line B-B' in the north to south direction, shown plain area of Ban Kok Chang, is covered by clay sediment, which laid on granite and limestone layers. The line C-C' in the NW to SE direction in downstream of plain area is covered by terrain sediment and limestone.

Geology

Geology of the study area, mostly comprises of terrain and colluvium deposit of Quaternary age and Ordovician limestone shown in Figure 3.6

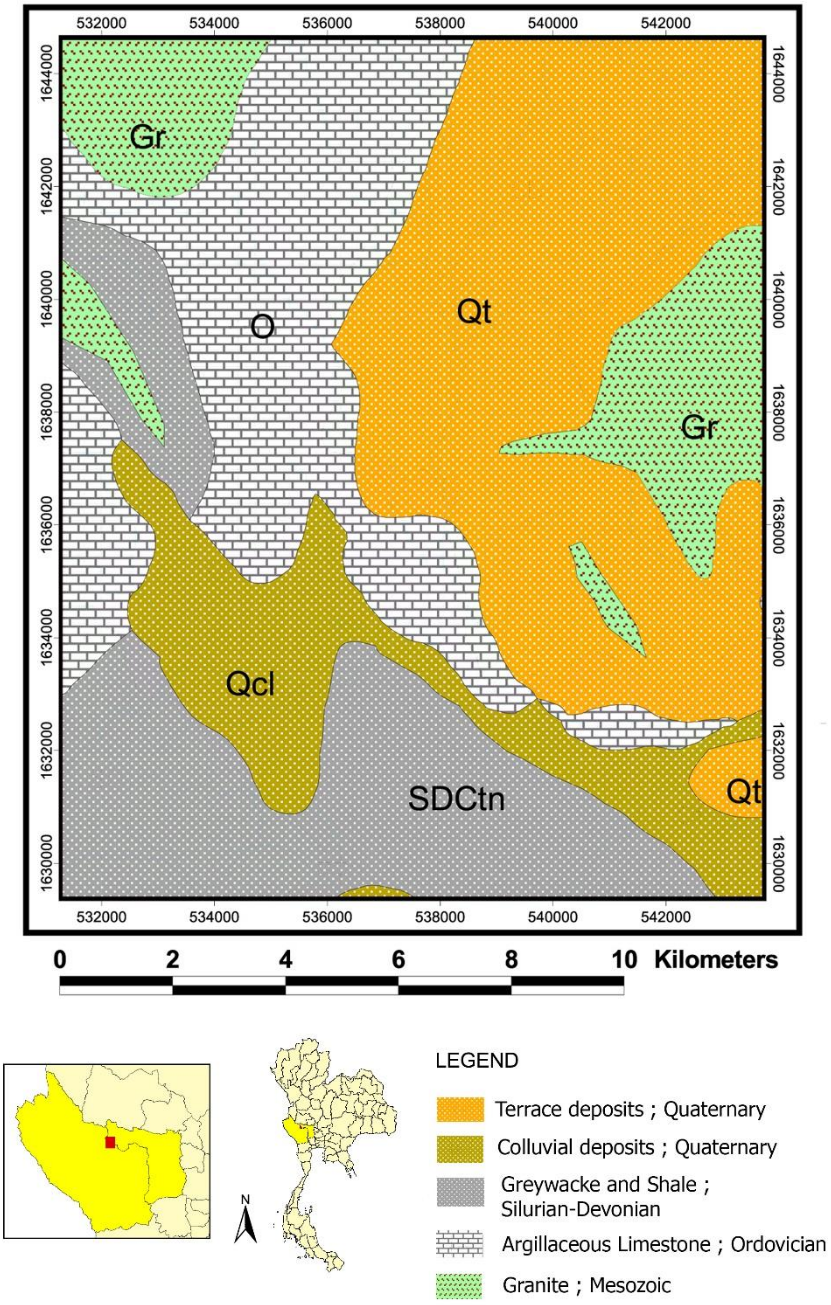


Figure 3.6 Geological map of the study area

(Data derived from the Department of Mineral Resources, Thailand)

Hydrogeology

Hydrogeologic units in the study area consist of two main types of aquifer, which are unconsolidated and consolidated media. The geological map (**Figure 3.7**) showed that unconsolidated aquifers, Colluvium (Qcl) and terrain deposit (Qt) Units and the consolidated aquifers, granite, Ordovician limestone (Ols), and Silurian-Devonian Metamorphic (SDmm) and Permo-Carboniferus metasedimentary (PCms) units. Groundwater samples were collected in shallow well located in the terrain deposit aquifer (Qt).

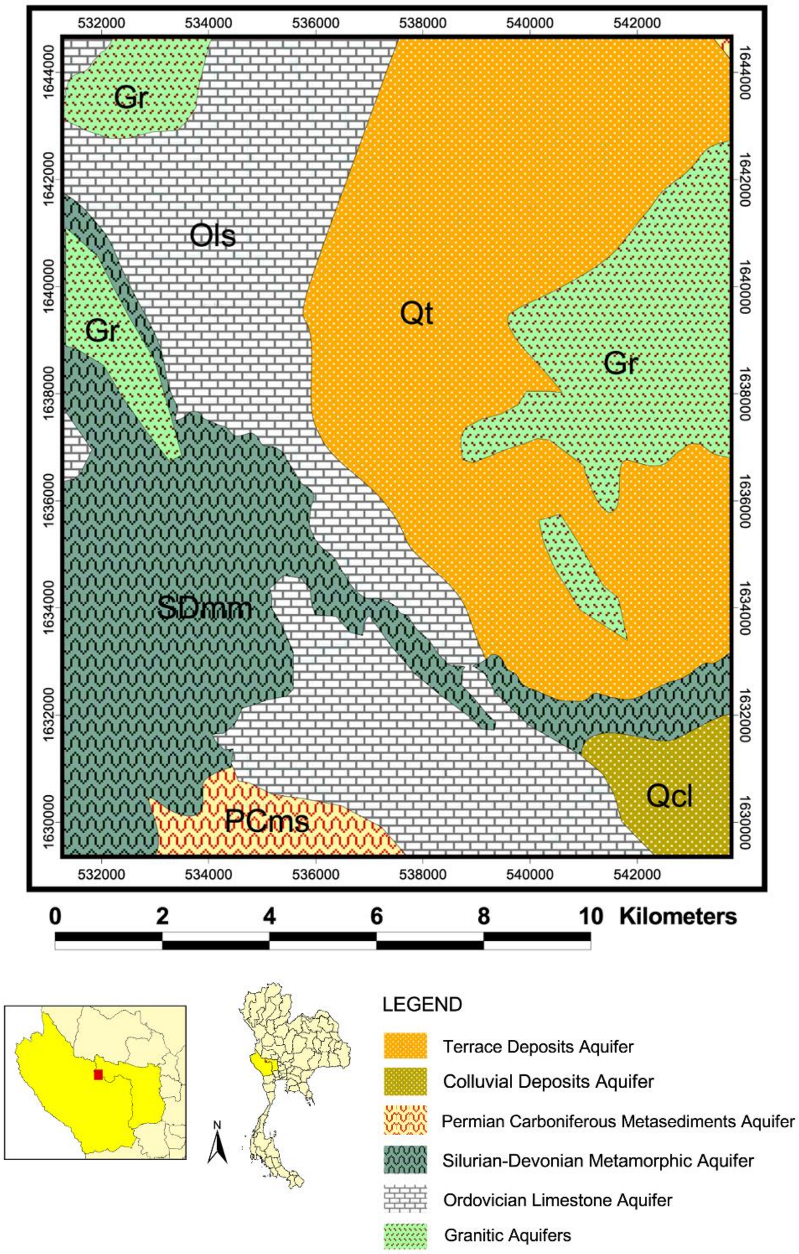


Figure 3.7 Hydrogeological map of the study area

(Data derived from Departement of Groundwater Resources, Thailand)

Land use

The area of Suphan Buri is about 535,800.8 hectares and is divided into agriculture 60.08 %, forestry 10.45 % and urbanization 29.46 % (Panarat et al., 2013). The northern part of the study area are Phu Toei National Park and most area are agriculture, the area of old mine has been turning into agricultural areas such as corn, sugar cane and cassava. Land use classification of the study area can be divided into four types as following: forest, agriculture, wet land and urban as shown in Figure 3.8.

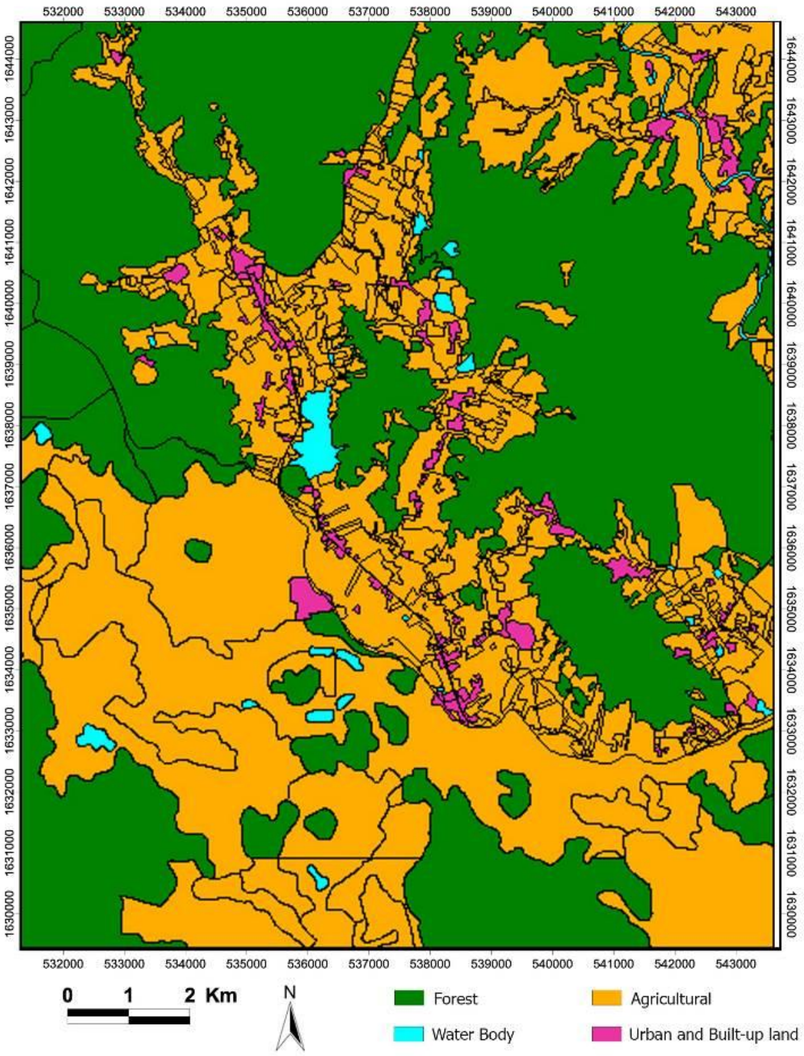


Figure 3.8 Land-use map of the study area

(Data derived from the Department of Land Development, Thailand)

Old mine area

The old tin mine in Ong Phra consisted of 13 sites as shown in Figure 3.9. They had been operated since 1983 and the last mining activities was expired in 2004. The old tin mine had been abandoned for 10 to 24 years. The details of this mine were presented in Table 3.1

Table 3.1 Mining license and operation date information of old mine in Ong Phra*

No	Mining License No	Operation year	Expiry year	Duration (y)	Abandoned (y)
1	22126/13709	1984	1991	7	24
2	22165/13909	1986	1999	13	16
3	22184/13519	1983	2004	21	11
4	22185/13852	1986	1993	7	22
5	22186/13716	1984	1992	8	23
6	22189/13853	1986	1993	7	22
7	24628/13916	1986	2001	15	14
8	24631/13914	1986	2002	16	13
9	24632/13915	1986	2004	18	11
10	24633/13913	1986	2004	18	11
12	24635/13911	1986	2001	15	14
13	24636/13912	1986	2003	17	12

***** Data: Department of Primary Industries and Mines – DPIM

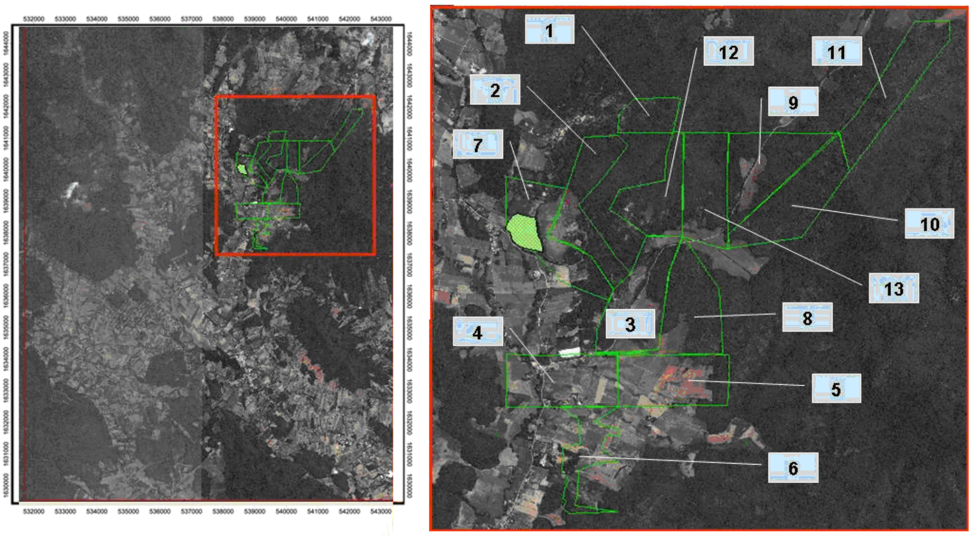


Figure 3.9 The site of old mine in Ong Phra

(Data derived from the Department of Mineral Resources, Thailand)

3.2 Methodology

In this study, 39 soil samples representing the study area were randomly collected from different sites and 21 groundwater samples, including ring wells, shallow wells and tubedeep wells. Basic cations and anoins in groundwater samples were then analyzed as described in the Section 3.2.3. Moreover, *As* in soil and groundwater were analyzed by using a Graphite Furnace Atomic Absorption (GFAAS). Spatial distribution maps for *As* distribution were constructed using inverse distance weighted method in Arc View GIS software. The details of analysis method for groundwater and soil were presented in the following sections.

3.2.1 Soil Sampling

The Study area is in the Ong Phra and is bounded by a 12.3 x 15.3 km. With the reference of the WGS84 datum, the area was located in zone 47 in the north hemisphere at an easting of 531352-543693 and a northing of 1629410-1644604. The soil sampling was conducted in June 2014, and 39 selected sampling points were located in upstream, downstream and old mining sites as shown in Figure 3.10 .Soil samples were taken at the 15 cm depth and were stored them in polypropylene bags and transported back to laboratory. Soil samples were dried overnight at 50 °C, crushed into fine particle and then sieved through a 10-mesh sieve in order to eliminate stones and other materials extraneous to soil, then stored in polyethylene bags at room temperature prior to analysis.

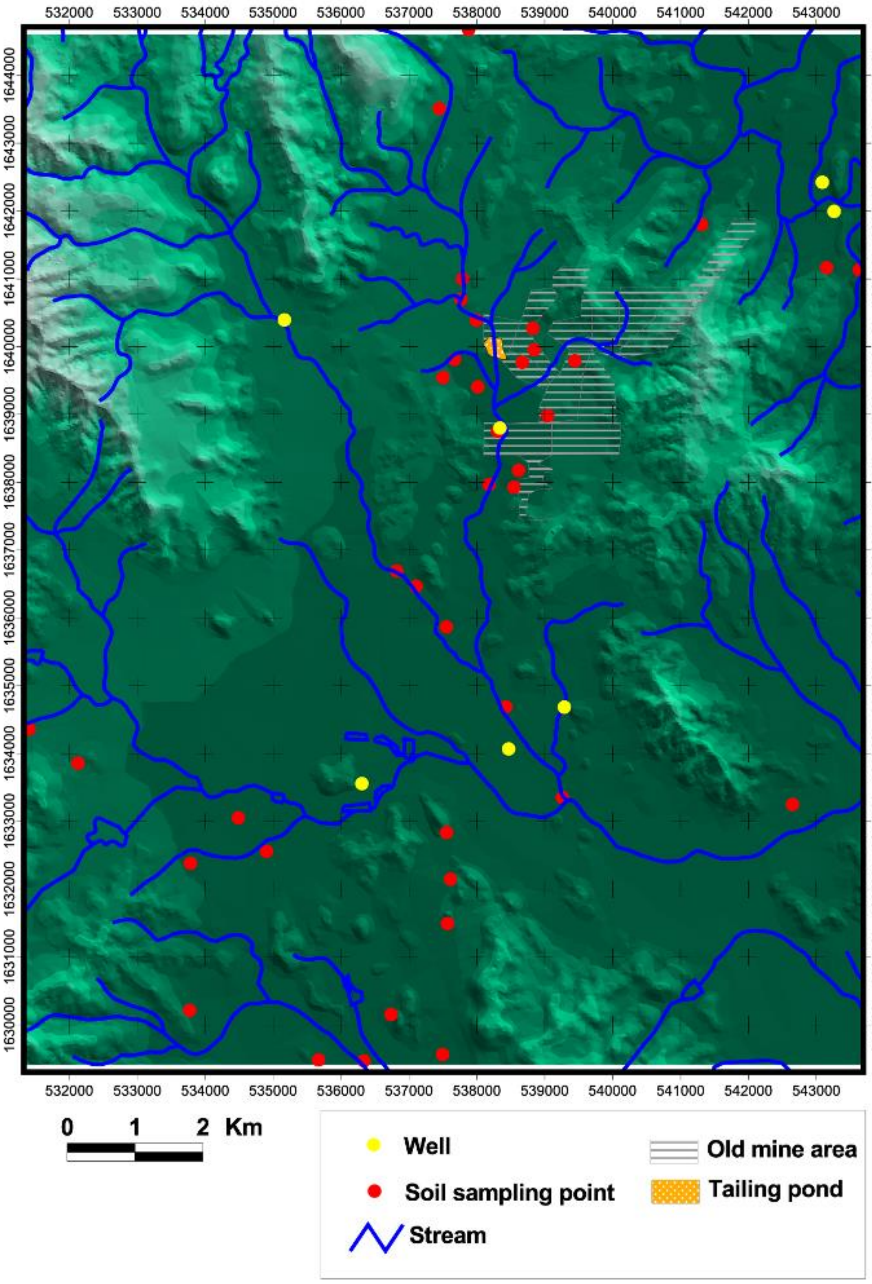


Figure 3.10 Locations of soil sampling points and groundwater wells

3.2.2 Groundwater Sampling

The sampling of groundwater were focused on wells currently in use, and they were found only private 7 ring wells and 14 public tube wells as described the details in Tables 3.2 and 3.3, respectively. In this area, some wells cannot be collected since they were abandoned and dried after the Sub district Administrative Organization have operated the tap water from the storage reservior.

Table 3.2 Locations of groundwater wells - ringwells

No	Position		Name of area	note
	E	N		
1	543060	1642365	Rural Roads 4031, Wung Yaw	Use
2	543234	1641935	Rural Roads 4031, Wung Kwai	Use
3	538312	1638741	Ban Kok Chang	Use
4	535135	1640337	Ban Sai Thong	Use
5	539260	1634623	Khaoyai temple	Use
6	538438	1634009	Ban Muang Thao	Use
7	536277	1633497	Tum Wang Hin temple	Use
8	533333	1635399	Ban Baramee	damaged
9	534435	1634963	Soi Pan Plang	Hand pump
10	541727	1642732	Huay Jorakae temple	dried

Table 3.3 Locations of groundwater wells – tubewells

no	Position		Name of area	Note
	E	N		
1	542740	1642997	Lawa Wung Kwai School	Use
2	536739	1642088	Numtok Saitong Tanple	Use
3	535212	1640502	Ban-Tungmakok School	Use
4	535559	1639268	Ong Phra office	Use
5	538540	1637378	Wat Kok Chang school	Use
6	536673	1633873	Pracha Mongkol School	Use

no	Position		Name of area	Note
	E	N		
7	538441	1633431	Pamai-Uthit School	Use
8	539981	1633444	Bankaow-Yai 01	Use
9	541026	1632769	Bankaow-Yai 02	Use
10	542571	1632983	Ban-Paiseetong	Use
11	542685	1634261	Ban-Paiseetong school	Use
12	541574	1631189	Som Det Charoen Temple	Use
13	541972	1630669	Ban-Nongpukwan	Use
14	535577	1629399	Kaow-hin-tung School	Use

Procedures for groundwater sampling The depth to groundwater table was measured by electrical groundwater-level and ground water sample was then pumped through a flow-through cell, containing multi-measuring probes to measure ground water parameters such as pH, electrical conductivity (EC), dissolved oxygen (DO) and oxidation-reduction potential (ORP). The initial 5-10 min of pumped water was discarded, and then groundwater samples were collected in rinsed polyethylene bottles. After that the collected groundwater samples were divided into 2 bottles. The first bottle were added with nitric acid; HNO_3 of concentrated, 5 mL for metal content analysis. The other was collected to analyze other parameters (anions and cation). All of samples were immediately stored in cooled container and kept at below 4 ^{o}C until analysis.

3.2.3 Analysis of groundwater sample and soil

3.2.3.1 Groundwater parameters

The chemical analysis was carried out for Na^+, K^+, Mg^{2+} and Ca^{2+} and analyzed by Graphite Furnace Atomic Absorption (GFAAS) ; whereas the Cl^- and

NO_3^- were analyzed by ISE and CO_3^{2-}, HCO_3^- were analyzed by volumetric titration methods, while SO_4^{2-} was analyzed by spectrophotometer method.

The concentration of eight major ions were plotted using the Piper diagram to classify water types as shown in Figure 3.7 (Rustem et al., 2012)

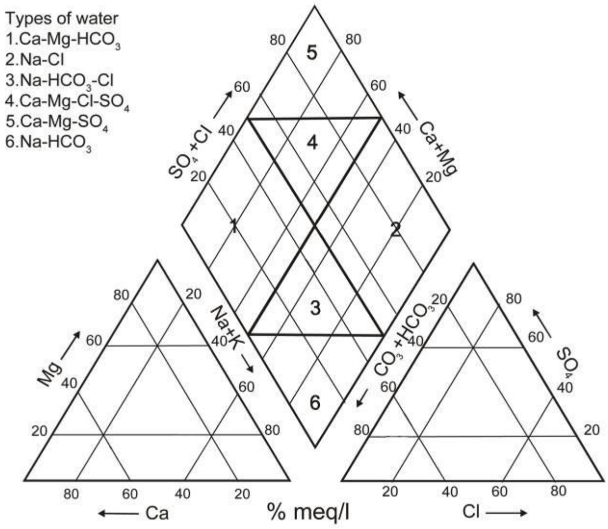


Figure 3.11 Type of water with Piper diagram (adapted from Rustem et al, 2012)

3.2.3.2 Sequential Extraction Method

The sequential extraction procedure used in this study was followed the study of Nannoni et al. (Nannoni et al., 2011). Five steps of the sequential extraction procedure were carried out in order to define the partitioning of *As* in the water soluble, extractable, reducible, oxidable and residual fractions. The procedure is based on the BCR protocol, proposed by the Community Bureau of Reference (Rauret et al., 1999) and the water-soluble and residual fractions were also considered.

The sequential extraction procedure was performed using 1 g of soil sample in a 50 mL polypropylene centrifuge tube. After reaction with the extraction reagent of each step, the mixture was centrifuged in order to separate the supernatant and the residue. The supernatant was used for analytical determinations and the residue was washed with deionized water and dried prior to the next extraction step.

Step 1 : Add 2 ml of DI water to 1 g of sediment in a 100 ml centrifuge tube, shaking (30±10 rpm) for 1 h at 22±5 °C (overnight), and then separate the extract from the solid residue by centrifugation at 3000 g for 20 min, decant the supernatant liquid into a polyethylene container and store at 4 °C until the samples are analyzed, then wash the residue by adding 20 ml of DI water shaking for 15 min and centrifuging for 20 min at 3000 g, decant the supernatant and discard.

Step 2: Add 40 ml of acetic acid, 0.11 mol l^{-1} to residue from step 1, shaking (30±10 rpm) for 16 h at 22±5 °C (overnight), and then separate the extract from the solid residue by centrifugation at 3000 g for 20 min, decant the supernatant liquid into a polyethylene container and store at 4 °C until the sample are analyzed, after that, wash the residue by adding 20 ml of DI water shaking for 15 min and centrifuging for 20 min at 3000 g, decant the supernatant and discard.

Step 3: Add 40 ml of freshly prepared hydroxyl ammonium chloride, 0.5 mol l^{-1} to the residue from step 2, shaking for 16 h at 22±5 °C (overnight), separate the extract from the solid residue by centrifugation and decantation and store at 4 °C until the samples are analyzed, and then, wash the residue by adding 20 ml of DI water shaking for 15 min and centrifuging for 20 min at 3000 g, decant the supernatant and discard.

Step 4: Add 10 ml of hydrogen peroxide, 8.8 mol l^{-1} to the residue from step 3, digest at room temperature for 1 h with occasional manual shaking, continue the digestion for 1 h at 85±2 °C in a water bath, then reduce the volume to less than 3 ml by heating of the uncovered tube. Add a further aliquot of 10 ml of hydrogen peroxide, heat the covered tube again for 1 h at 85±2 °C, remove the cover and reduce the volume of liquid to about 1 ml (do not take to complete dryness). Add 50 ml of ammonium acetate, 1.0 mol l^{-1} (adjust the pH to 2.0±0.1 with concentrated nitric acid) to the cool residue, shake for 16 h at 22±5 °C (overnight), separate the extract from the solid residue by centrifugation at 3000 g for 20 min, and decant the supernatant liquid into a polyethylene container and store at 4 °C until the samples are analyzed. After that, wash the residue by adding 20 ml of DI water shaking for 15 min and centrifuging for 20 min at 3000 g, decant the supernatant and discard.

Step 5: the last residue was digested with a mixture of nitric acid/hydrochloric acid. Add concentrated nitric acid 3.5 ml and concentrated hydrochloric acid 10.5 ml, acid solubilization in a graphite digestion system, store at 4 °C until the samples are analyzed.

3.2.3.3 Arsenic analysis

For total recoverable *As*, water sample was acidified at the time of collection with nitric acid. The measurements were conducted at the Instrumentation Center of Silpakorn University. An ICP-OES was used to determine the concentrations in mg/l of the solutions of each of the five steps of the sequential extraction method at detection limit 0.005 ppm.

For *As* in groundwater sample was preserved with acid and analyzed by graphite furnace atomic absorption spectrometer (GFAAS), standards linearity assay, a blank and 3 calibration standards (25, 50 and 100 ppb).

3.2.4 DRASTIC map

The vulnerability map is based on the DRASTIC index (Di) which is computed as the weighted sum overlay of the seven layers using the following equation:

$$\text{DRASTIC Index } (D_i) = D_rD_w + R_rR_w + A_rA_w + S_rS_w + T_rT_w + I_rI_w + C_rC_w$$

The source of data for seven parameters was shown in Table 3.4. Field study for groundwater table level and secondary data were obtained from different resources and format as shown in Table 3.4. The layer of DRASTIC model used weighting score as original scoring of Aller (Aller et al., 1987), except weighting of net recharge were applied the method of Piscopo (Piscopo, 2001). Weighting of each parameter were show in Table 3.5.

Table 3.4 Data used for creation of hydro-geological parameters for DRASTIC model

no.	Data type	Sources	Format	Output layer
1	Water table level	Primary data : Field study	Table	Depth of water (D)
2	Average annual rainfall	Secondary data : Meteorological Dept., Thailand	Table	Recharge (R)
3	Hydrogeology map	Secondary data : Dept. of Groundwater Resources, Thailand	Map	Aquifer (A)
4	Soil map	Secondary data: Land Development Dept., Thailand	Map	Soil (S)
5	Topographical map	Secondary data: The Royal Thai Survey Dept.	Map	Topography (T)
6	Geological profile	Secondary data: Dept. of Mineral Resources, Thailand	Map	Impact of vadose zone (I)
7	Hydraulic conductivity	Secondary data : Dept. of Groundwater Resources, Thailand	Map, Table	Hydraulic conductivity (C)

Table 3.5 Weighting score of DRASTIC parameters (Aller et al., 1987)

No.	Factors	Relative weights
1	Depth to water	5
2	Net Recharge	2
3	Aquifer media	3
4	Soil media	2
5	Topography	1
6	Impact of the vadose zone	5
7	Hydraulic Conductivity	3

After preparing of parameters above, the rate and weigh of such parameter were interpolated by IDW (Inverse Distance Weighted) method, which estimates cell values by averaging the values of nearby sample data points. Theme table of shape file (.shp) was the z value used in spatial interpolation. It was operated with the nearest neighbor using the default power of 2.

CHAPTER IV

RESULTS

4.1 ANALYTICAL RESULTS

Physiographically, the Dan Chang subdistrict is more or less flat and can be divided into high-hill of Phu Toei National Park and flat plain area. The area bordering the north is a hilly terrain, whereas the north-east and south-west area are separated by mountain and ridge. Groundwater in the area occurs in the shallow terrain deposit aquifer and in the deeper aquifer. The flow of groundwater is from north to south in each sub watershed. The topography and groundwater flow indicated the flow pass through old mine from north to the east terrain (Figure 4.1).

4.1.1 Groundwater parameters and Piper Diagram

The level of shallow wells are decreases in dry event but some well as number 5 and 6 were higher (Table 4.1) but over all of flow direction do not different in Figure 4.1 . Chemical parameters of groundwater wet and dry event as show in table 4.2. The groundwater pH ranged from 5.2–5.9 with a mean pH of 5.5 and 5.6 for wet and dry events, respectively, indicating a mildly acidic water. A mean electrical conductivity value of 633 and 638 µs/cm for wet and dry events, respectively.

The concentration of eight major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}) are represented on the Piper diagram by grouping the (Na^+ with K^+) and the (CO^{3-} with HCO^{3-}). Results of cations and anions are given in Tables 4.3 and 4.4, respectively. *As* such, the number of parameters are thus reduced for plotting into six parameters. On the Piper diagram, the relative concentration of the cations and anions are plotted in the lower triangles, and the resulting two points are extended into the central field to represent the total ion concentration. The Piper trilinear diagram is very useful in classifying the hydrochemical facies of the water samples according to their dominant ions. The water type in the area is mainly $Ca\text{-}HCO_3$ water (Figure 4.2), typical of shallow, fresh ground waters

Table 4.1 Groundwater level in wet and dry events

No	Position		Name of area	Ground surface level (m)	Depth water level (m)	
	E	N			Wet event	Dry event
1	543060	1642365	Rural Roads 4031, Wung Yaw	246	3.28	4.32
2	543234	1641935	Rural Roads 4031, Wung Kwai	244	4.83	5.40
3	538312	1638741	Ban Kok Chang	275	2.03	2.75
4	535135	1640337	Ban Sai Thong	322	3.83	3.95
5	539260	1634623	Khao Yai temple	243	6.40	5.25
6	538438	1634009	Ban Muang Thao	232	3.44	3.07
7	536277	1633497	Tum Wang Hin temple	261	15.36	16.52

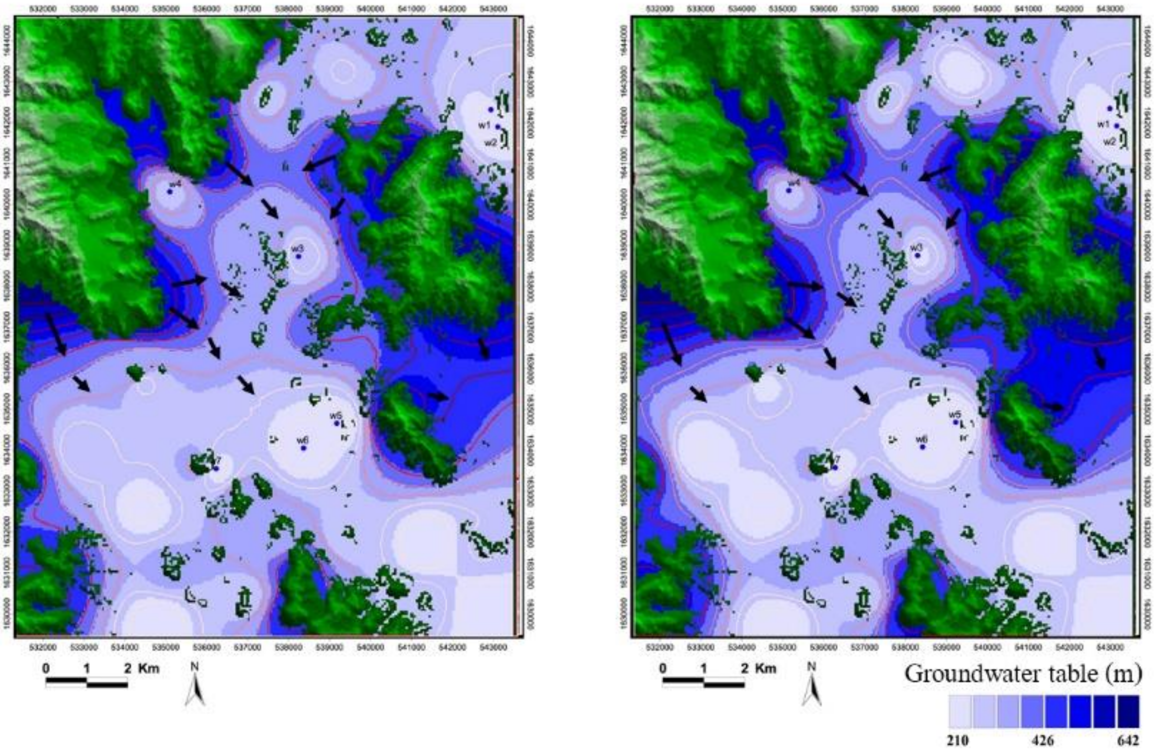


Figure 4.1 Groundwater Contour map (wet and dry event)

Table 4.2 Chemical parameters of groundwater wet and dry events

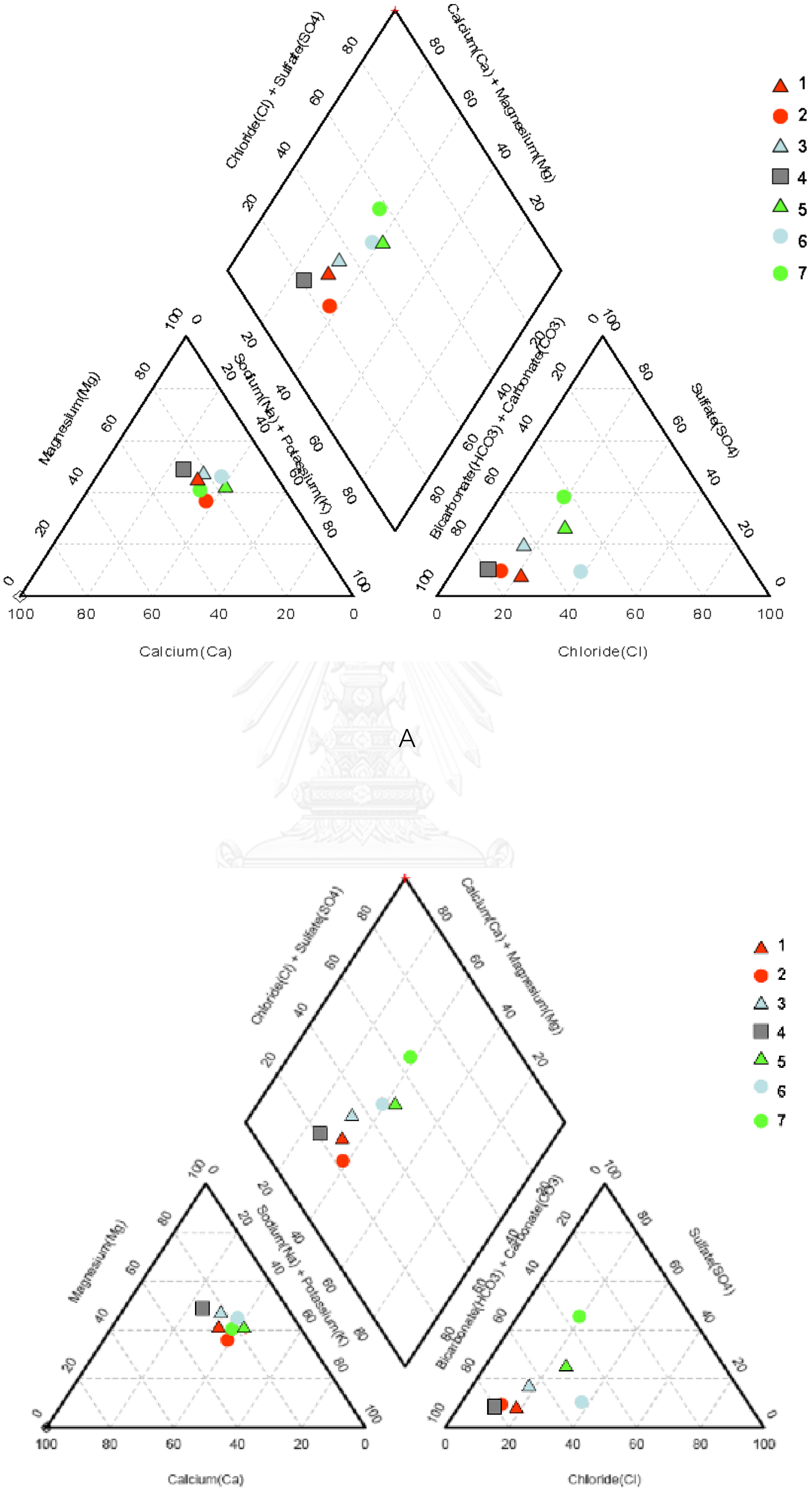
Well	position		pH		EC		ORP		DO		TDS	
	X	Y			μS/cm		mV		mg/L		mg/L	
			wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
1	543060	1642365	5.5	5.2	491	474	273.2	390.5	4.5	2.8	314	303
2	543234	1641935	5.3	5.5	725	655	336.7	293.1	4.4	2.2	464	419
3	538312	1638741	5.3	5.5	575	623	300.8	312.6	4.7	3.5	368	399
4	535135	1640337	5.7	5.9	492	490	253.7	281.6	4.6	5.8	315	313
5	539260	1634623	5.4	5.5	1032	971	315	327.7	4.3	2.1	660	621
6	538438	1634009	5.5	5.9	553	540	376.3	338.3	4.8	3.6	354	345
7	536277	1633497	5.7	5.9	564	711	335.5	344.7	4.4	3.1	361	455

Table 4.3 Cation contents in groundwater samples

Well	Cation mg/L									
	Ca^{2+}		Mg^{2+}		Na^{+}		K^{+}		total	
	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
1	19.69	19.00	19.03	21.24	29.00	27.98	0.48	0.45	68.17	68.67
2	19.87	17.94	17.15	15.35	33.23	29.79	0.48	0.43	70.36	63.51
3	19.31	20.93	25.07	27.10	32.14	34.69	0.48	0.52	76.79	83.24
4	19.88	19.74	22.33	21.86	21.07	20.86	0.49	0.48	63.36	62.94
5	20.28	19.08	33.19	32.05	53.04	49.86	0.25	0.23	106.54	101.22
6	19.44	18.94	27.05	28.31	54.21	52.62	0.48	0.46	100.92	100.33
7	18.60	30.15	21.22	29.46	37.02	46.63	0.42	0.52	77.02	106.76

Table 4.4 Anion contents in groundwater samples

Well	Anion mg/L							
	Cl^-		SO_4^{2-}		$HCO_3^- + CO_3^{2-}$		total	
	wet	dry	wet	dry	wet	dry	wet	dry
1	27.40	32.64	17.12	15.40	189.00	182.37	233.52	230.41
2	19.21	19.33	19.02	18.15	195.05	176.08	233.28	213.56
3	31.60	32.26	41.09	51.25	201.03	217.93	273.72	301.44
4	16.73	15.59	18.03	20.05	198.20	196.74	232.96	232.38
5	85.00	86.07	31.21	30.12	211.28	198.53	327.49	314.72
6	41.60	42.23	54.01	57.89	140.20	136.44	235.81	236.56
7	25.14	31.63	78.32	84.30	79.15	120.12	182.61	236.05



A

B

Figure 4.2 Piper diagram; A) Wet event B) Dry event

4.1.2 *As* in Groundwater

Concentrations of *As* in shallow groundwater in wet and dry events are shown in Table 4.5 and comparison of each point are shown in Figure 4.3.

Table 4.5 *As* concentration of 7 shallow wells in wet and dry seasons

Well	Name of area	*As* - µg/L[#]	
		September 2014	February 2015
1	Rural Roads 4031, Wung-yaw	nd	nd
2	Rural Roads 4031, Wung-kwai	nd	nd
3	Ban Kokchang	6	14
4	Ban Si-Thong	nd	nd
5	Khaoyai temple	nd	nd
6	Ban Muang-Thao	nd	1
7	Tum-wang-hin temple	nd	nd

[#] nd – not detected, below the limit of detection, LDL 1 µg/L

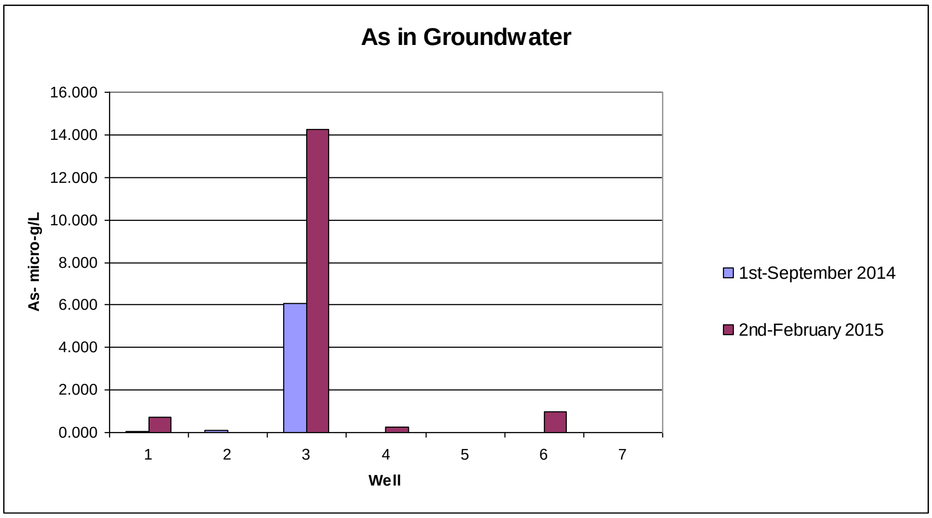


Figure 4.3 *As* concentration of 7 shallow wells in wet and dry seasons

The results of *As* and chemical parameters of 14 deep-tubewells are presented in Table 4.6, concentrations of arsenic are in range 0 – 43 μg/L.

Table 4.6 Chemical parameters and *As* concentrations of 14 tube wells in dry season (May 2015)

no	position		Name	pH	EC μg/cm	ORP mV	DO mg/l	TDS mg/l	*As*$^{\#}$ μg/L
	x	y							
1	542740	1642997	Lawa Wung Kwai School	6.67	1022	446.4	2.1	654	2
2	536739	1642088	Numtok Saitong Tanple	6.48	574	305.5	3.8	367	nd
3	535212	1640502	Ban Tung Makok School	7.03	530	349.8	3.7	339	nd
4	535559	1639268	Ong Phra office	7.22	197	286.4	3	126	nd
5	538540	1637378	Wat Kok Chang school	7.11	634	395.1	2.5	406	nd
6	536673	1633873	Pracha Mongkol School	6.43	761	292.1	3.8	487	nd
7	538441	1633431	Pamai Uthit School	7.09	656	398.1	2.7	420	nd
8	539981	1633444	Ban Kaow Yai 01	7.2	735	359	3	470	nd
9	541026	1632769	Ban Kaow Yai 02	7.33	798	335.1	2.7	511	nd
10	542571	1632983	Ban Paiseetong	7.88	467	425.5	3.4	299	43
11	542685	1634261	Ban Paiseetong School	7.98	587	388.2	3.2	376	27

no	position		Name	pH	EC	ORP	DO	TDS	*As*[#]
	x	y			µg/cm	mV	mg/l	mg/l	µg/L
12	541574	1631189	Som Det Charoen Temple	6.98	754	378.2	3.3	482	nd
13	541972	1630669	Ban Nongpukwan	7.03	699	325.2	3.5	7.03	nd
14	535577	1629399	Kaow Hin Tung School	7.83	578	303.5	3.2	7.83	1

[#] nd – not detected, below the limit of detection, LDL 1 µg/L

4.1.3 Soil Texture

Particle size analysis determines the relative amounts of sand, silt and clay in a soil. These size fractions are the mineral component of a soil and together determine soil texture. Particle size analysis is a laboratory alternative to field texturing and offers a more reliable determination of particle size distribution. Soil textural classes are determined by the U. S. texture triangle (Soil Survey Staff, 1999) as shown in Figure 4.4. The texture of 39 top soil samples are mainly in sandy loam and loamy sand (in Table 4.7), and some points of sample are clay texture associated to sampling site nearby the stream.

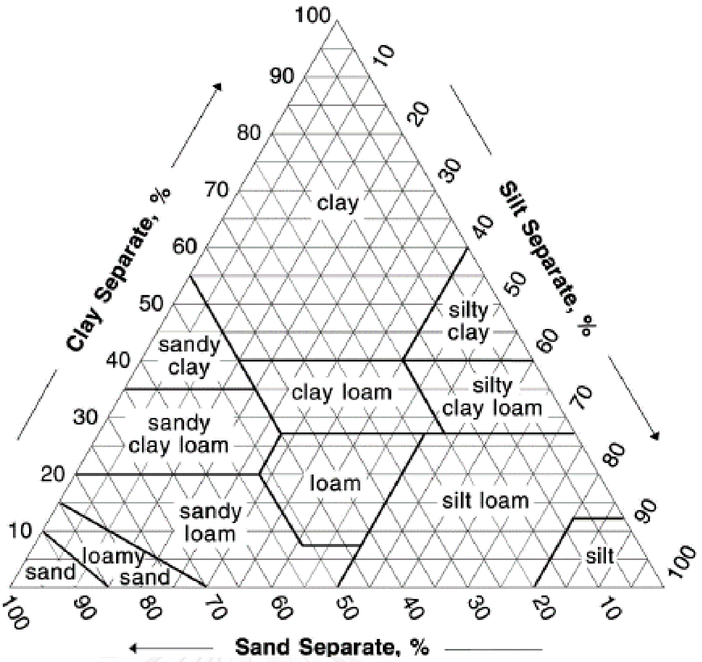


Figure 4.4 Soil textural classes in the U.S. texture triangle (Soil Survey Staff, 1999)

Table 4.7 Soil texture of the top soil sample

Point	Symbol	Texture	Point	Symbol	Texture
1	SL	Sandy loam	21	LS	Loamy sands
2	LS	Loamy sands	22	SL	Sandy loam
3	LS	Loamy sands	23	SL	Sandy loam
4	SL	Sandy loam	24	LS	Loamy sands
5	LS	Loamy sands	25	LS	Loamy sands
6	CL	Clay loam	26	C	Clay
7	SCL	Sandy clay loam	27	CL	Clay loam
8	SL	Sandy loam	28	SCL	Sandy clay loam
9	LS	Loamy sands	29	SCL	Sandy clay loam
10	SCL	Sandy clay loam	30	CL	Clay loam
11	SL	Sandy loam	31	SCL	Sandy clay loam
12	S	Sand	32	SCL	Sandy clay loam
13	LS	Loamy sands	33	CL	Clay loam

Point	Symbol	Texture	Point	Symbol	Texture
14	SL	Sandy loam	34	C	Clay
15	SL	Sandy loam	35	SL	Sandy loam
16	S	Sand	36	CL	Clay loam
17	SL	Sandy loam	37	C	Clay
18	SL	Sandy loam	38	SL	Sandy loam
19	SCL	Sandy clay loam	39	SCL	Sandy clay loam
20	SL	Sandy loam			

4.1.4 Soil sequential extraction

The five steps sequential extraction procedure to define the partitioning of *As* in the water soluble, extractable, reducible, oxidable and residual. The result of 39 samples is given in Table 4.8 .Also the value are marked with “nd” because of some fraction are below the limit of detection. and the summary of statistic are given in Table 4.9

Table 4.8 The five fraction and total *As* concentrations of soil sequential extraction

Point	Position		Arsenic in soil mg/Kg$^{\#}$					
	X	Y	EX1	EX2	EX3	EX4	EX5	TOTAL
1	537851	1644615	0.019	0.141	nd	0.379	17.136	17.675
2	537418	1643454	nd	0.058	nd	1.001	4.774	5.832
3	541283	1641743	nd	0.057	nd	0.213	21.030	21.299
4	543123	1641106	nd	0.064	nd	1.260	4.464	5.788
5	543605	1641073	0.004	0.066	nd	0.575	20.608	21.253
6	537761	1640942	nd	nd	2.000	7.500	43.580	53.080
7	537737	1640638	nd	nd	18.000	76.500	488.240	582.740
8	537965	1640331	nd	nd	23.000	74.000	480.430	577.430
9	538796	1640211	nd	nd	nd	nd	95.360	95.360
10	538816	1639896	nd	nd	23.500	79.500	967.420	1070.420
11	537642	1639755	nd	nd	7.500	20.500	246.690	274.690
12	539414	1639732	nd	nd	23.000	76.500	515.050	614.550
13	538640	1639711	nd	nd	nd	8.500	85.710	94.210
14	537475	1639486	nd	nd	nd	11.000	91.230	102.230

Point	Position		Arsenic in soil mg/Kg[#]					
	X	Y	EX1	EX2	EX3	EX4	EX5	TOTAL
15	537985	1639348	nd	nd	6.500	27.000	362.770	396.270
16	539014	1638925	nd	nd	22.000	32.500	513.600	568.100
17	538277	1638694	nd	nd	nd	nd	149.820	149.820
18	538584	1638116	nd	nd	2.500	13.500	36.120	52.120
19	538151	1637908	nd	nd	8.500	38.000	453.580	500.080
20	538517	1637865	nd	nd	3.500	nd	109.890	113.390
21	536791	1636634	0.039	0.129	0.488	0.603	3.585	4.844
22	537078	1636407	0.072	0.515	0.668	1.490	8.807	11.551
23	537522	1635808	0.053	0.277	0.940	1.434	5.313	8.017
24	538396	1634629	0.196	0.806	1.486	2.557	10.389	15.435
25	539233	1633289	0.300	0.464	11.792	5.811	28.832	47.199
26	542621	1633188	0.011	0.057	0.083	0.372	13.039	13.561
27	531377	1634299	0.055	0.264	0.297	1.743	66.353	68.712
28	532098	1633799	nd	0.046	nd	0.868	31.827	32.741
29	534459	1632992	0.024	0.306	nd	0.654	34.995	35.979
30	537526	1632774	0.099	0.110	nd	1.449	183.029	184.686
31	534872	1632497	nd	0.122	nd	0.582	28.347	29.051
32	533755	1632322	nd	0.039	nd	0.185	7.985	8.209
33	537583	1632088	0.056	0.081	0.027	2.764	260.368	263.295
34	537537	1631433	0.300	0.621	0.246	2.565	224.091	227.824
35	533742	1630152	0.426	1.371	1.216	5.844	239.943	248.800
36	536707	1630091	nd	0.045	nd	0.454	14.743	15.241
37	537467	1629503	0.059	0.475	0.012	1.201	63.741	65.489
38	535641	1629420	nd	0.052	nd	0.758	19.153	19.963
39	536310	1629409	0.081	0.839	0.148	0.804	80.734	82.606

[#]nd – not detected, below the limit of detection, LDL 0.005 mg/L of fraction solutions

Table 4.9 Summary of descriptive statistics for *As* in soil

Arsenic in soil						
Number of samples, N	39					
	Total	soluble	extractable	reducible	oxidable	residual

Mean (mg/kg)	171.783	0.046	0.180	4.036	12.835	154.687
Median (mg/kg)	65.489	0.000	0.057	0.148	1.449	63.741
Std. Deviation (mg/kg)	238.49	0.10	0.30	7.47	23.66	211.00
Maximum (mg/kg)	1070.42	0.426	1.371	23.500	79.500	967.420
Minimum (mg/kg)	4.844	0.000	0.000	0.000	0.000	3.585

4.1.4.1 Spatial distribution of *As* in soils

The map of *As* distribution in top soils of Dan Chang is shown in Figure 4.5 and spatial distribution maps are shown in Figures 4.6 to Figure 4.11. The soil samples of the old mine fall under toxic and alert categories with respect to arsenic as some of the samples exceed and some are approaching the WHO guideline value of 0.01 ppm. It has also been observed that groundwater samples adjoining to foothills contain arsenic at a toxic level. *As* the study area lies within an alluvial basin, the most probable natural sources of arsenic in groundwater may be heavy deposition of sediments due to surface erosion from surrounding hills and creating aquifers. However, it can be claimed that the study area is undisturbed by anthropogenic sources compared to industrialized countries, where river basins are generally affected by industrial activities. Soil quality standards for Habitat and Agriculture Not exceed 3.9 mg/kg, for Other Purposes not exceed 27 mg/kg.

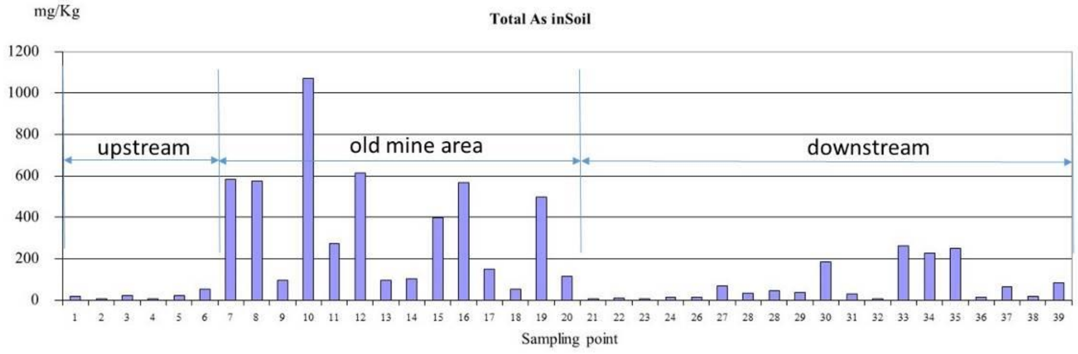


Figure 4.5 Comparison of *As* in soil sample

Mean concentrations of total *As* in soils (Table 4.9) are exceeded 30 mg/kg [the mean value of *As* in Thailand (Orathai et al., 2009)] especially in samples from old mine area are in higher than 1000 mg/kg. The distribution map of *As* contaminated areas was rasterized by IDW and distribution map of total *As* showing that *As* is not evenly distributed (Figure 4.6); The higher *As* concentrations are mainly located in the old tin mine area.

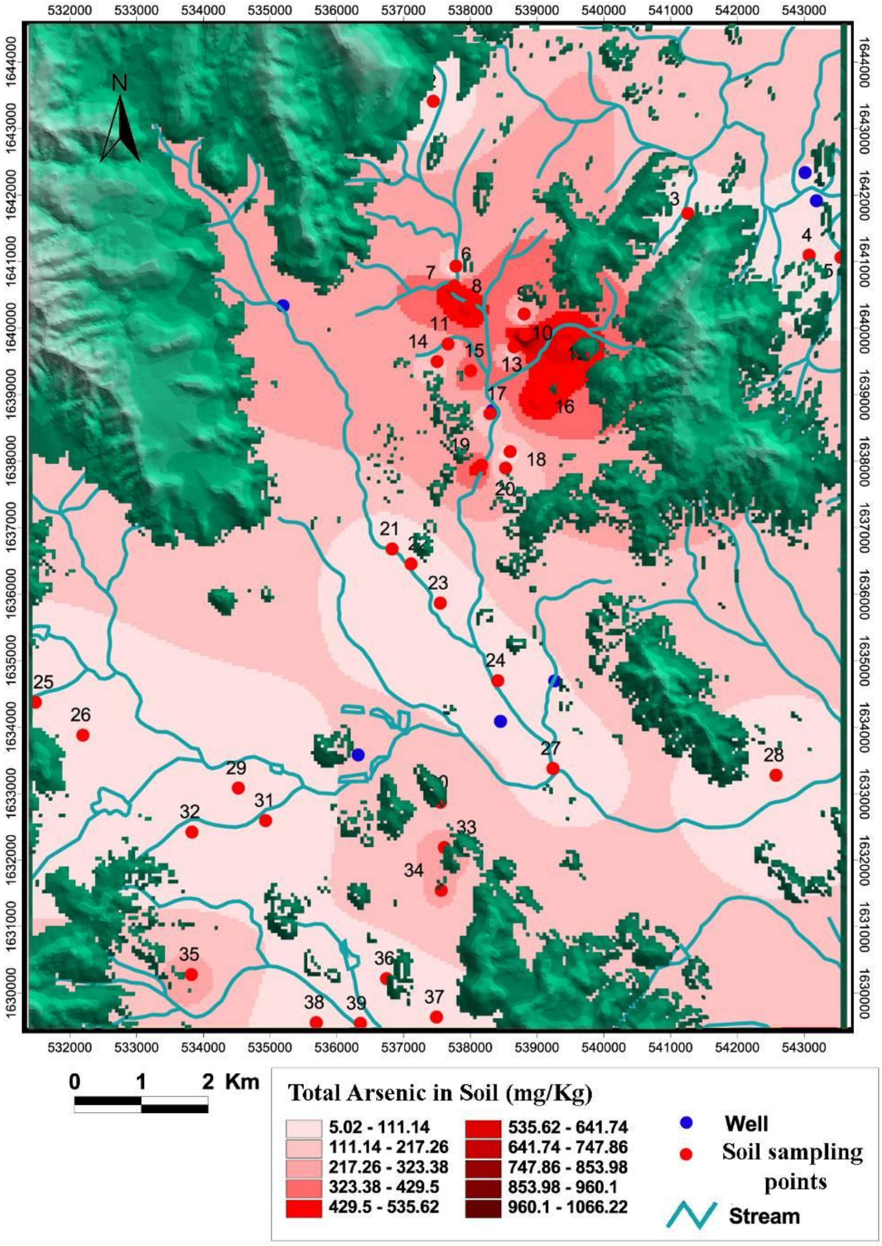


Figure 4.6 The distribution map of total *As* in soils

The distribution of soluble *As* is mainly in the downstream, form the highest south site as Ban Sambat Charern (Figure 4.7) and there are not evenly distributed over the area because many point are zero value.

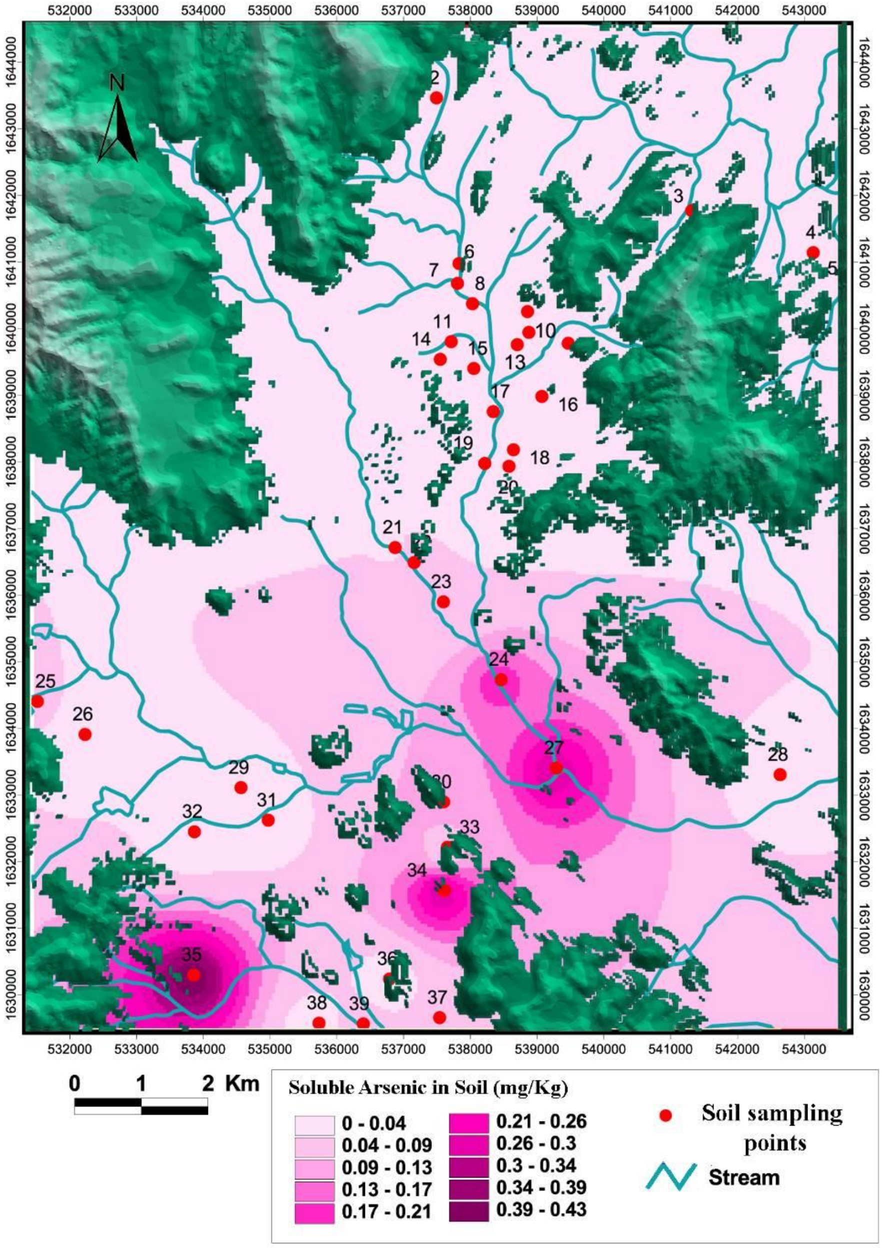


Figure 4.7 The soluble *As* (1st extracted) distribution map

The distribution of extractable *As* (Figure 4.8) is similar to that of soluble arsenic because the soil sample that have been detected with soluble arsenic also contain detected extractable arsenic too.

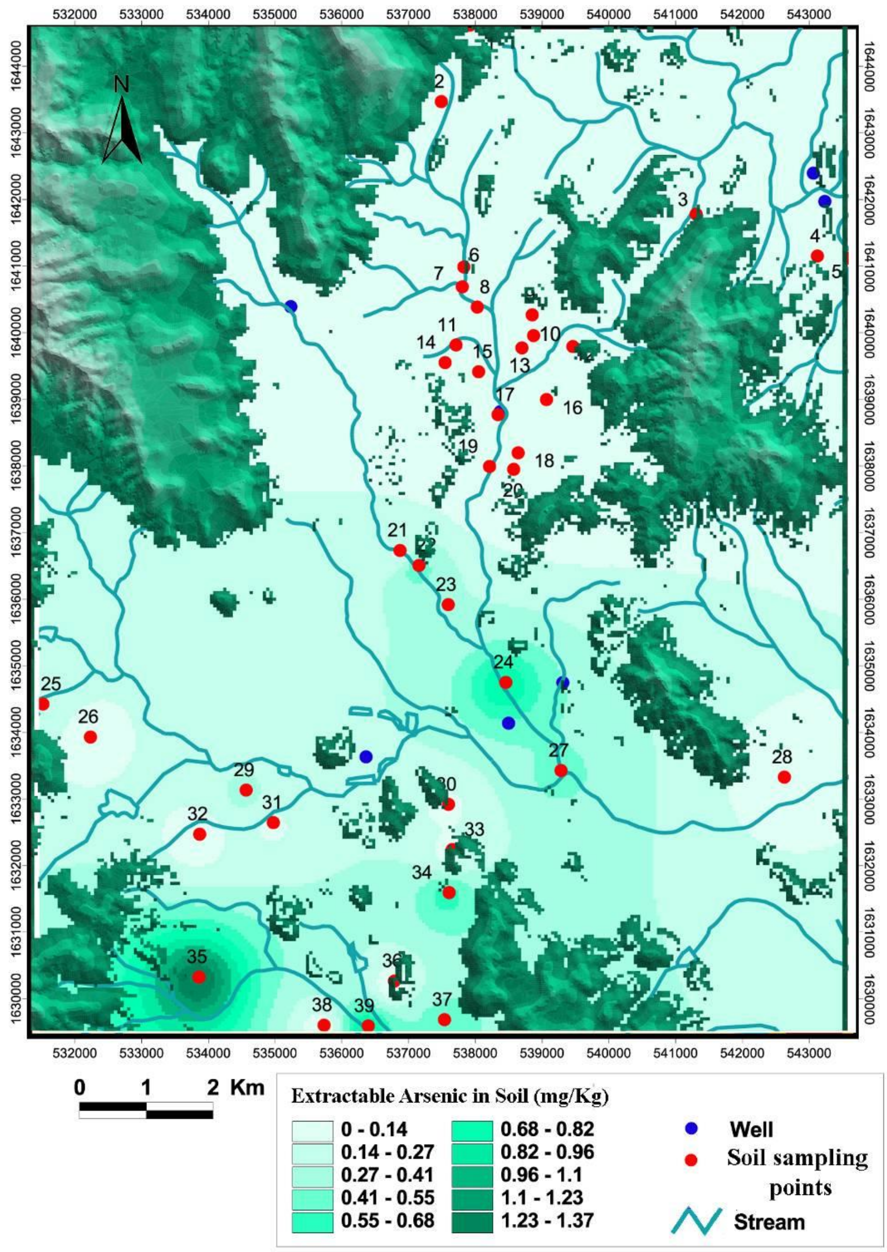


Figure 4.8 The extractable *As* (2^{nd} extracted) distribution map

For the reducible As, arsenic is not evenly distributed (Figure 4.9) and it shows fairly high As concentration at the old tin mine area, but not exceeding the mean value.

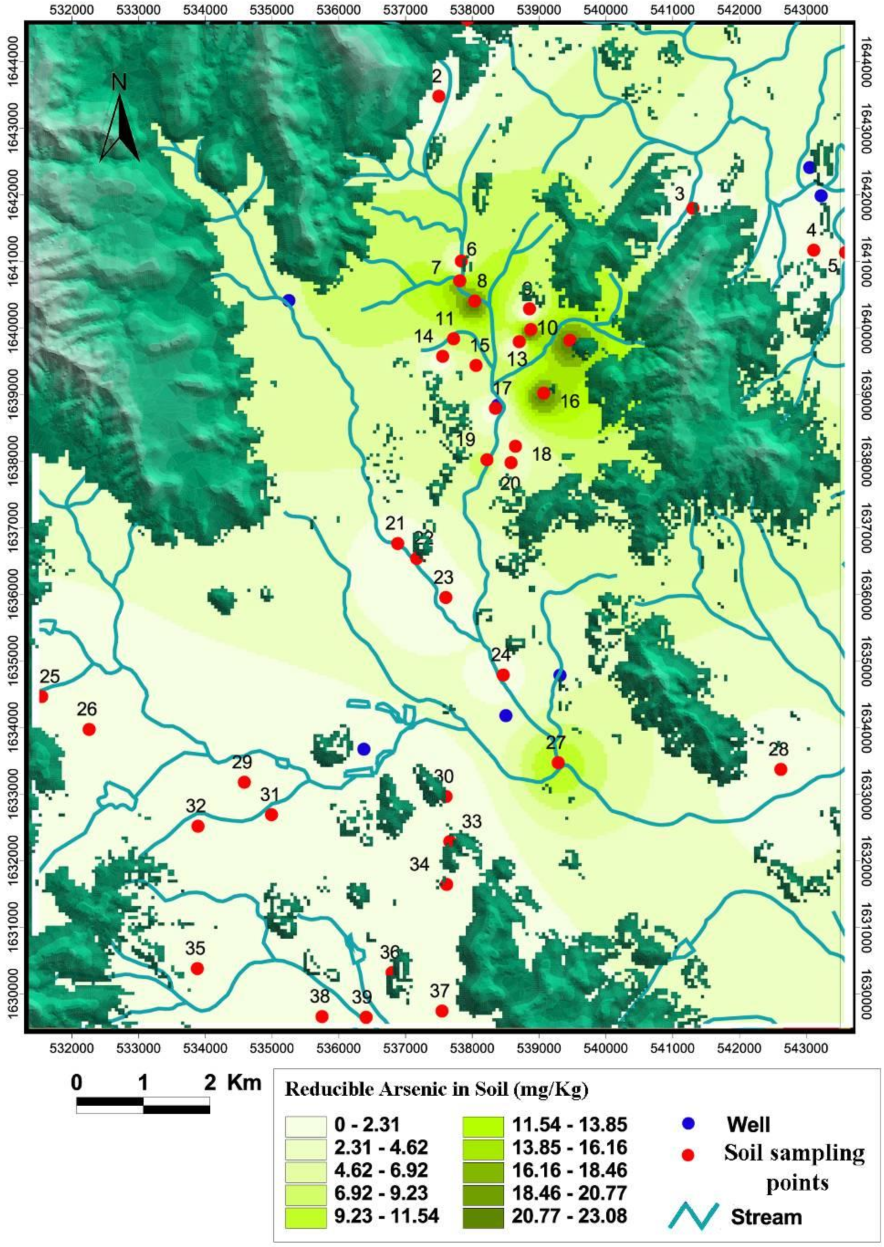


Figure 4.9 The reducible *As* (3^{rd} extracted) distribution map

The oxidable *As* distribution arsenic is not evenly distributed (Figure 4.10) and it is high at the old mine area; the high value exceeds mean up to 79.50 mg/kg.

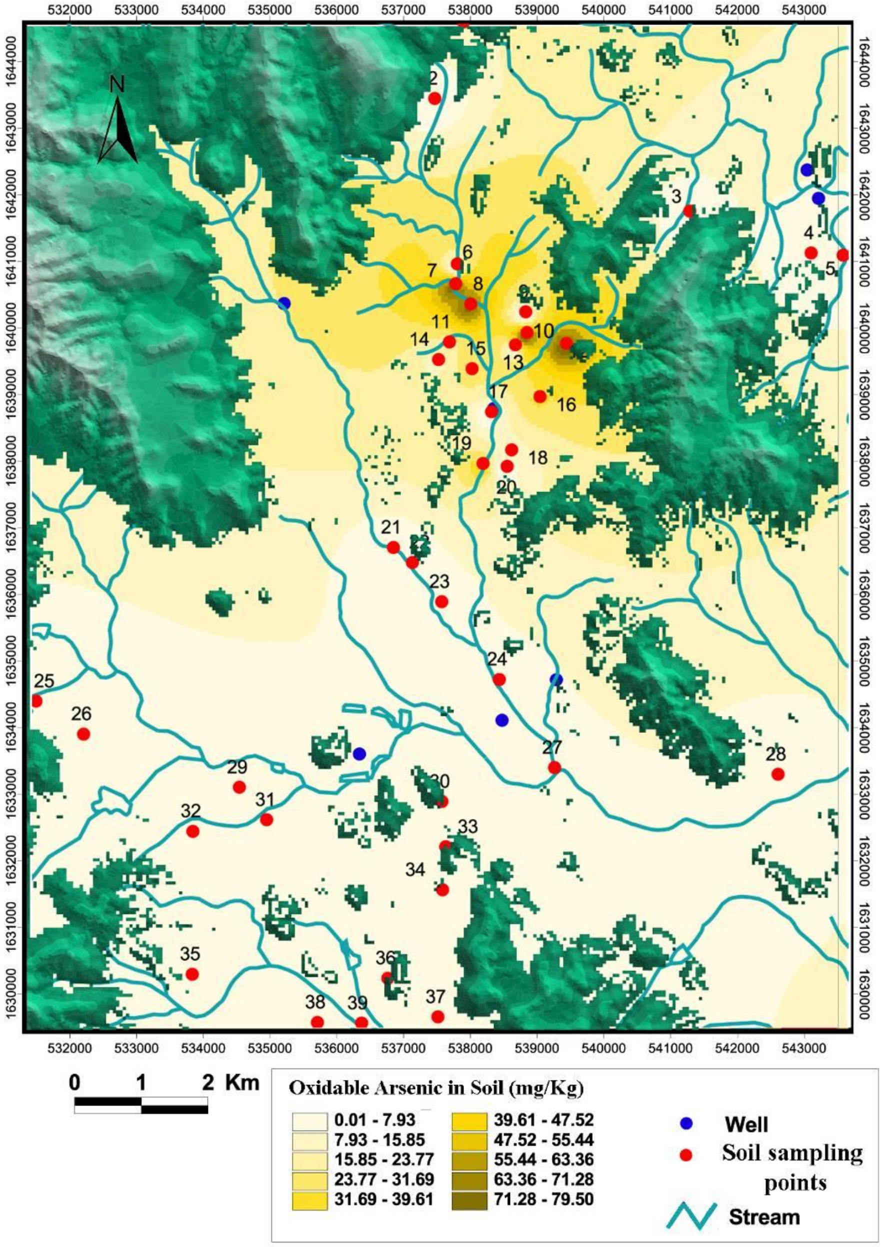


Figure 4.10 The oxidable *As* (4th extracted) distribution map

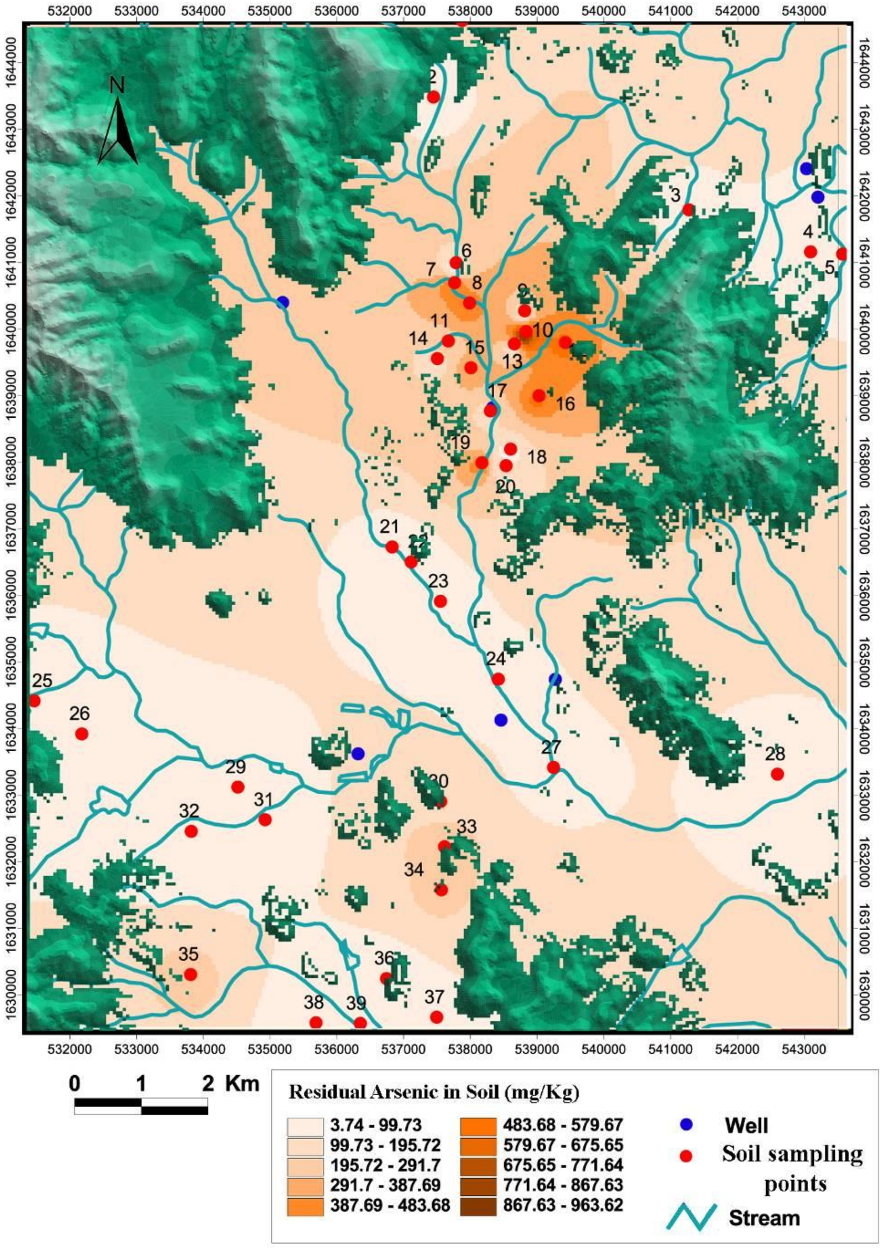


Figure 4.11 The residual *As* (5^{th} extracted) distribution map

The distribution of residual arsenic, the final fraction of sequential extraction (Figure 4.11) is similar to the distribution of total arsenic because the value of total arsenic content is mainly from the value of residual arsenic.

4.2 DRASTIC vulnerability map

The vulnerability map is based on the DRASTIC index (Di) which is computed as the weighted sum overlay of the seven layers using the following equation:

$$\text{DRASTIC Index } (D_i) = D_rD_w + R_rR_w + A_rA_w + S_rS_w + T_rT_w + I_rI_w + C_rC_w$$

1. Depth to water
2. Net Recharge
3. Aquifer media
4. Soil media
5. Topography
6. Impact of the vadose zone
7. Hydraulic Conductivity

4.2.1 Depth to water

Depth to water refers to the depth to the water surface in an unconfined aquifer. Deeper water table levels imply lesser chance for contamination to occur.

Table 4.10 Depth to water index

Depth to water w = 5	Ranges (ft)	Ratings (Dr)	Index (Di)
	5-15	9	45
	>15-30	7	35
	>30-50	5	25
	>50-75	3	15

The depth of water in the study area varies between 2.03 m to 16.52 m below the ground surface. The rating scores ranges between 3 and 9 were presented in Table

4.10 and the spatial variation is shown in Figure 4.12 Depth to water table in study area is high rating in the plain area between mountain range.

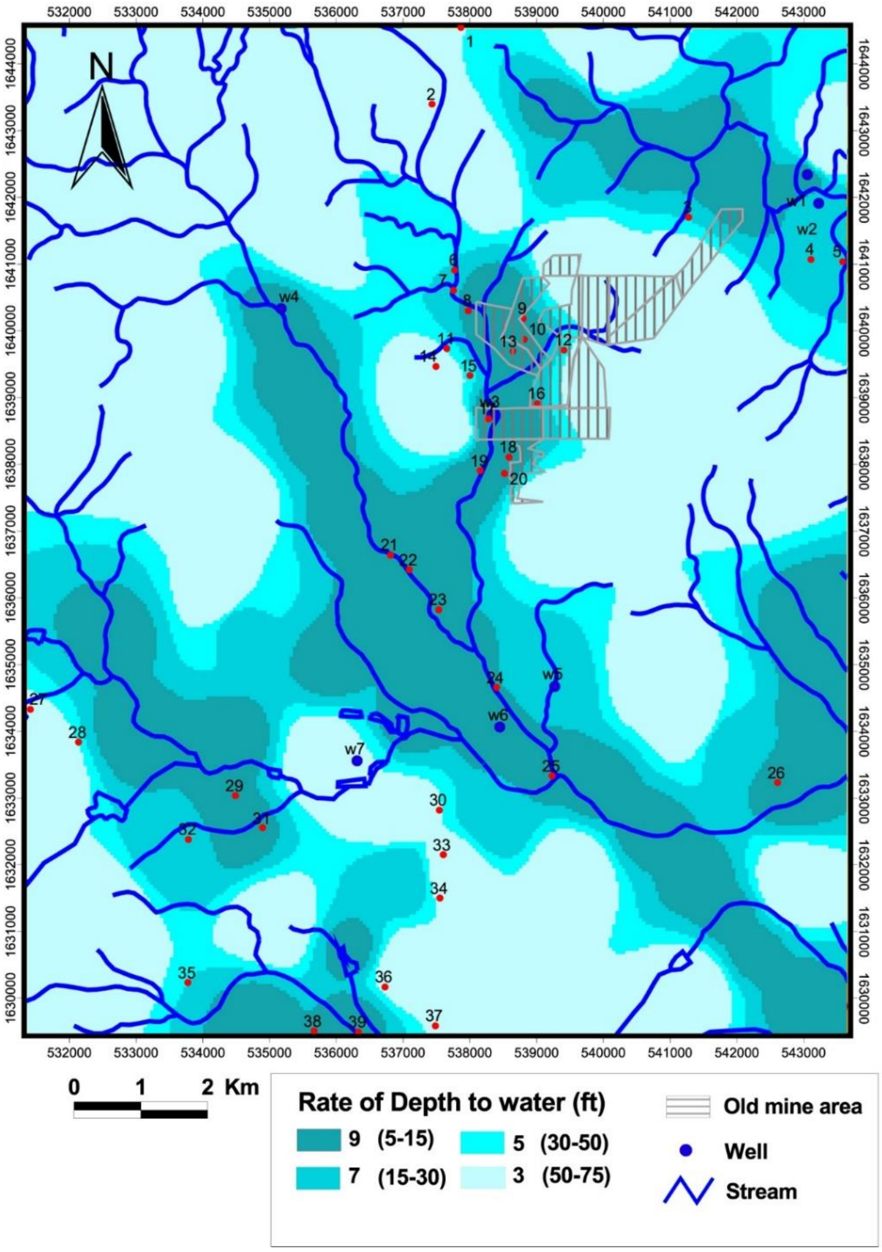


Figure 4.12 Depth to water table map

4.2.2 Recharge

Recharge indicates the amount of water per unit area of land which penetrates the ground surface and reaches the water table. Recharge water is available to transport a contaminant vertically to the water table, horizontal with in an aquifer.

Net recharge data were not available for the study area. Therefore, it is calculated through a combination of slope, soil permeability and rainfall following the method of Piscopo (Kamlesh and Shukla., 2014; M. Al-Rawabdeh Abdulla et al., 2013; Piscopo, 2001). Recharge was calculated using the formula:

$$\text{Recharge value} = \text{Slope (\%)} + \text{Rainfall} + \text{Soil permeability}$$

The data of average annual rainfall in Suphan Buri and Kanchanaburi, 9 stations (Table 4.11) around the study area was obtained from Meteorological Department, Thailand. By the data interpolation of rainfall, the rainfall are distributed from northeast to southwest in range of 830-1070 mm (Figure 4.13)

Parameter and recharge value for the study area was measured using data given in Table 4.12 and Table 4.13

Table 4.11 Average annual rainfall in Suphan Buri and Kanchanaburi

No	Station Code	Average annual rainfall (mm)	Duration	Station description
1	410002	1346	1985-2014	Banrai District Uthai Thani
2	425008	834	1985-2012	Dan Chang Agriculture Office. Suphan Buri
3	425009	846	1985-2012	Nong Ya Sai Agriculture Office. Suphan Buri
4	425011	1216	1992-2014	Nikhom Krasieo, Dan Chang District
5	450005	504	1986-2013	Si Sawat District Kanchanaburi
6	450006	807	1985-2014	Lao Khwan District Kanchanaburi
7	450023	1168	1985-2014	Bankaolek Si Sawat District Kanchanaburi
8	450027	812	1989-2013	Banpai-Na-Saun Si Sawat District Kanchanaburi
9	450028	489	1988-1996	Nongree Agriculture Office. Kanchanaburi

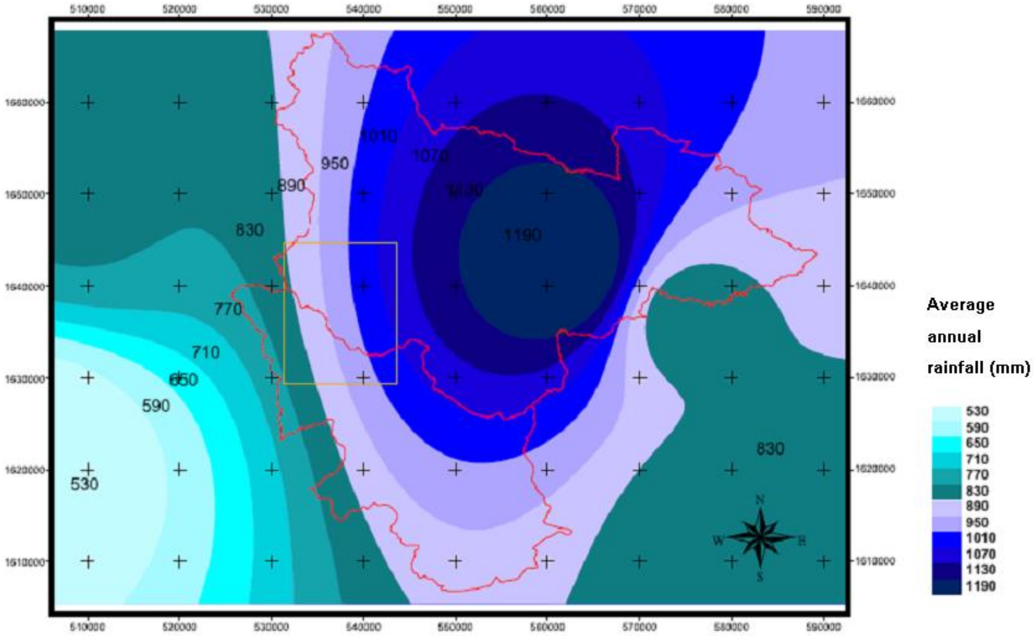


Figure 4.13 Average annual rainfall

Table 4.12 Data used for estimating of net recharge in the study area

Rainfall (mm) (1985-2014 data)		Slope (%)		Soil Permeability	
Range	factor	Range	Factor	Range	Factor
1070-850	4	<2	4	High	5
< 850-700	3	2-10	3	Mod-high	4
		10-33	2	Moderate	3
		>33	1	Slow	2
				Very slow	1

Table 4.13 Recharge value and Net recharge index

Recharge value W=2	Rating (Rr)	Index (Ri)
5–7 mm	3	6
> 7–9 mm	5	10
> 9–11mm	8	16
> 11–13 mm	10	20

Net recharge range and rating shown in Figure 4.14. The high rating of net recharge is in plain area.

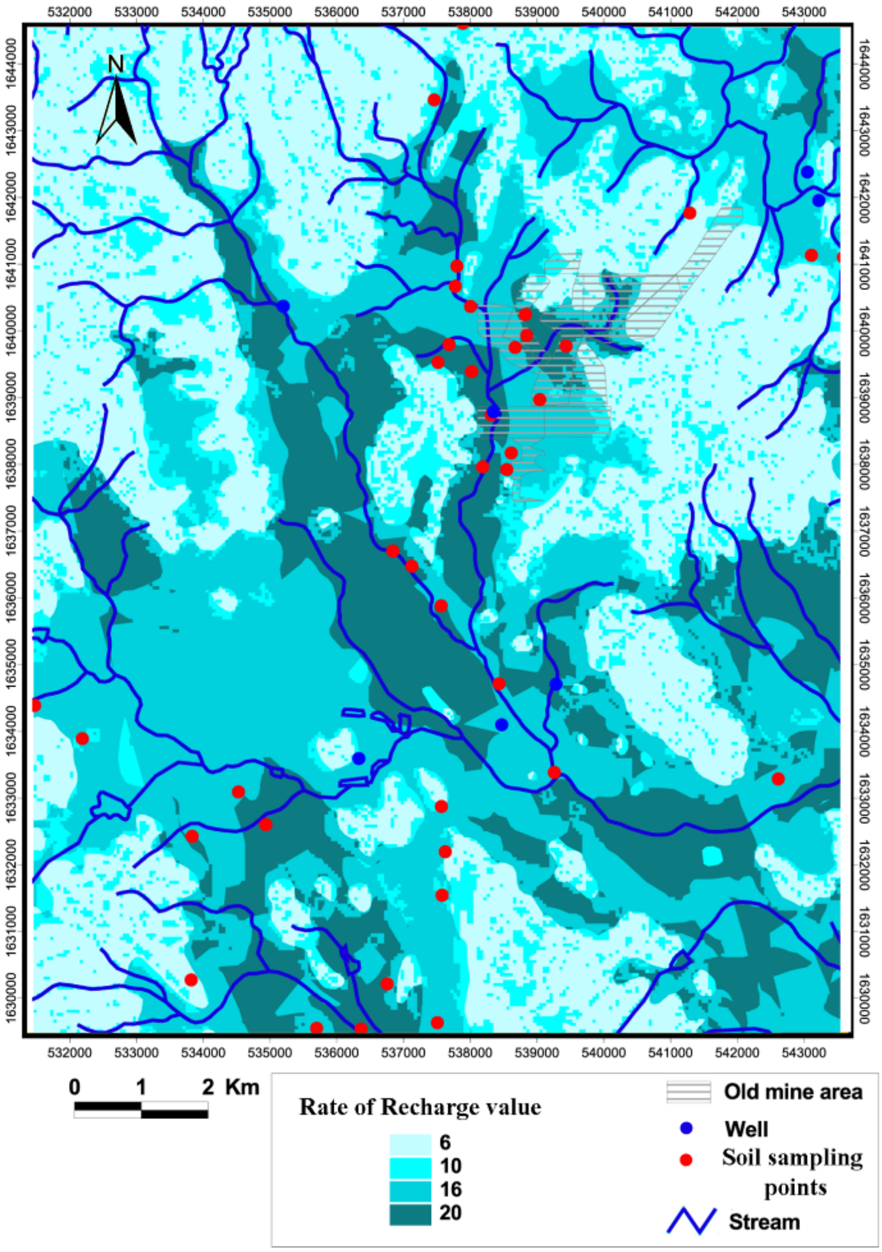


Figure 4.14 Rate of recharge value

4.2.3 Aquifer media

Aquifer media refers to the consolidated or unconsolidated medium which serves as an aquifer. The larger the grain size and more fractures or openings with in an aquifer, leads to higher permeability and lower attenuation capacity, hence greater the pollution potential. The high rating of aquifer media in study area are related to unconsolidated aquifer as terrain and colluvium aquifer (Table 4.14), In the map shown in Figure 4.15. The central of study area is greater in terms of the pollution potential.

Table 4.14 Aquifer media index

Aquifer media w = 3	Aquifer Media	Ratings (Ar)	Index (Ai)
	Granitic, Gr	4	12
	Ordovician Limestone,Ols	6	18
	Permian Carboniferous Metasediments, PCms	6	18
	Colluvial Deposits, Qcl	8	24
	Terrace Deposits, Qt	8	24
	Silurian-Devonian Metamorphic Rock, SDmm	4	12

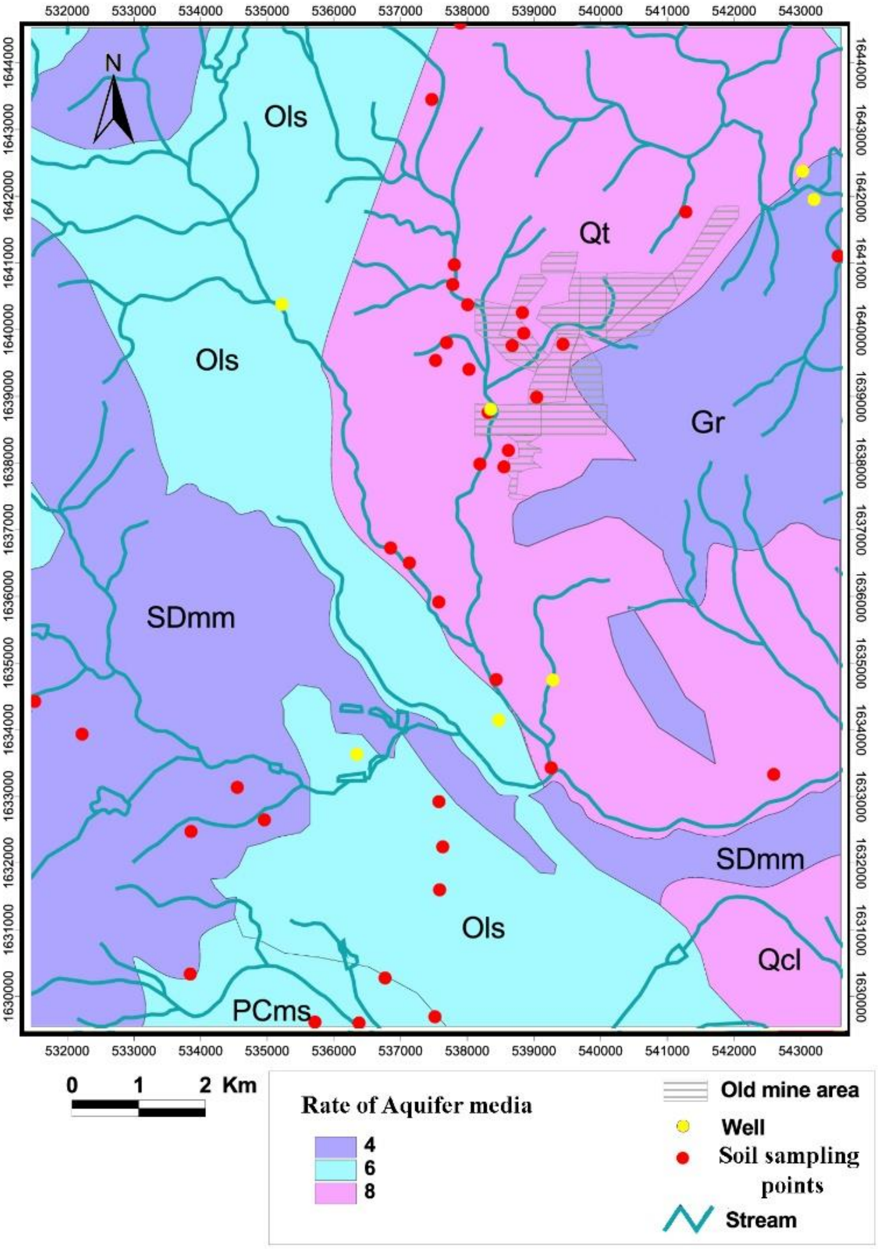


Figure 4.15 Rate of aquifer media map

4.2.4 Soil media

Soil media refers to the uppermost weathered portion of the vadose zone characterized by significant biological activity. Soil has a significant impact on the amount of recharge which can infiltrate into the ground. Rating of soil media in study area give in Table 4.15 and soil media map shown in Figure 4.16.

Table 4.15 Soil media index

Soil media w = 2	Soil group	Ranges	Permeability*	Ratings (Sr)	Index (Si)
	37	Loamy sand	Mod-high	9	18
	35,36,40,48	Sandy loam	High	6	12
	56	Loam-Sandy loam	Mod-high	6	12
	38	Loam-Fine sandy loam	Mod-high	6	12
	33	Silt loam	Mod-high	4	8
	47	Clay-Loam	Mod-high	3	4
	29,31,55	Clay	Moderate	1	2
	62	Complex slope	Low	1	2

*(Office of Soil Survey and Land Use Planning, 2005)

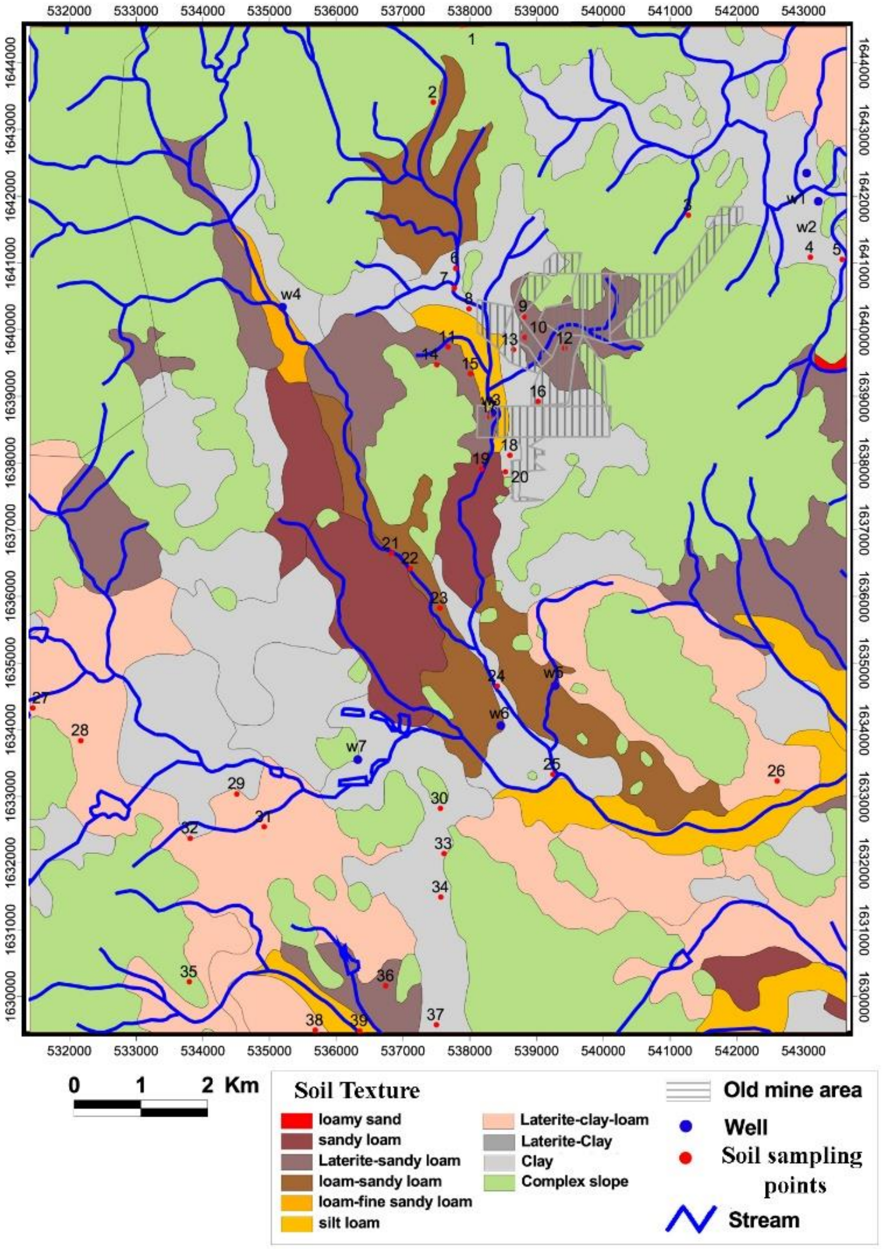


Figure 4.16 Soil media map

Rate of soil type map shows that the high rate area are vicinity of stream (Figure 4.17) and low rate area related with soil group 62, there are complex slope in mountain and forest areas.

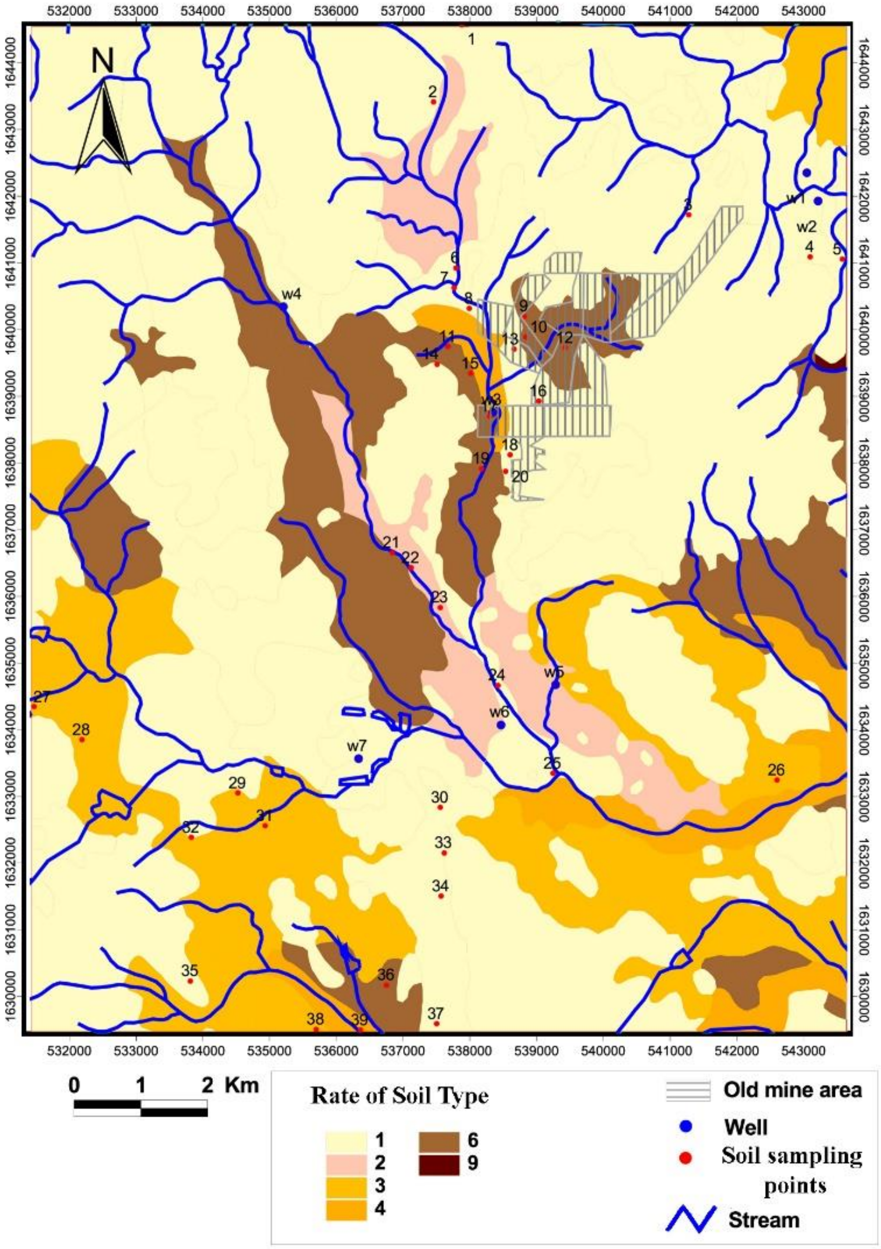


Figure 4.17 Rate of soil type map

4.2.5 Topography

Topography refers to the slope of the land surface. It helps whether a pollutant were moved by runoff or remained on the ground surface in an area long enough to infiltrate it.

The slope indexderived from the DEM. The ratings assigned in the study are presented in Table 4.16 and spatial distributions of slope were presented Figure 4.18.

Table 4.16 Topography index

Topography w = 1	Slope Ranges	Ratings (Tr)	Index (Ti)
	0-2	10	10
	2-6	9	9
	6-12	5	5
	12-18	3	3
	>18	1	1

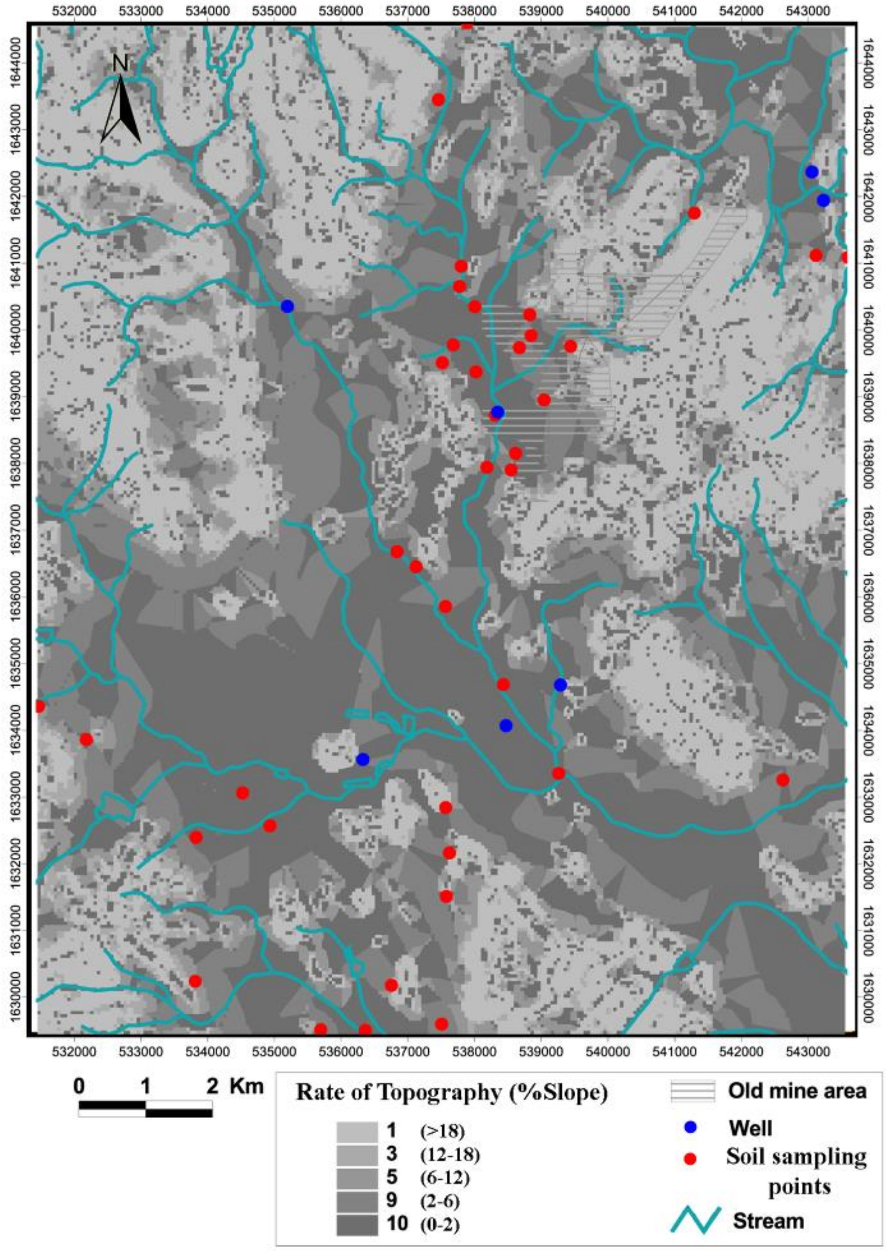


Figure 4.18 Topography (slope) map

4.2.6 Impact of the vadose zone

Impact of the vadose zone is defined as unsaturated zone material. The significantly restrictive zone above an aquifer forming the confining layers is used in a confined aquifer, as the type of media having the most significant impact.

According to the DRASTIC ratings, the value for impact of vadose zone is shown in Table 4.17 and spatial variations are presented in Figure 4.19. The characteristics of the material, including the rock above the water table, are gravel, silt, clay, laterite, metamorphic and granite.

Table 4.17 Impact of the vadose zone index

Impact of the vadose zone w = 5	Material	Ratings (Ir)	Index (Ii)
	terrace deposits, Gravel, silt, clay and laterite.; Quaternary	6	30
	colluviam deposits, Gravel, silt, clay and laterite; Quaternary	6	30
	limestone Argillaceous Limestone; Ordovician	6	30
	Granite, Quartz monzonite, Monzonite; Mesozoic	5	25
	Quartzite, Quartzschist, Phyllite, Carbonaceous-Phyllite; Silurian-Devonian	5	25

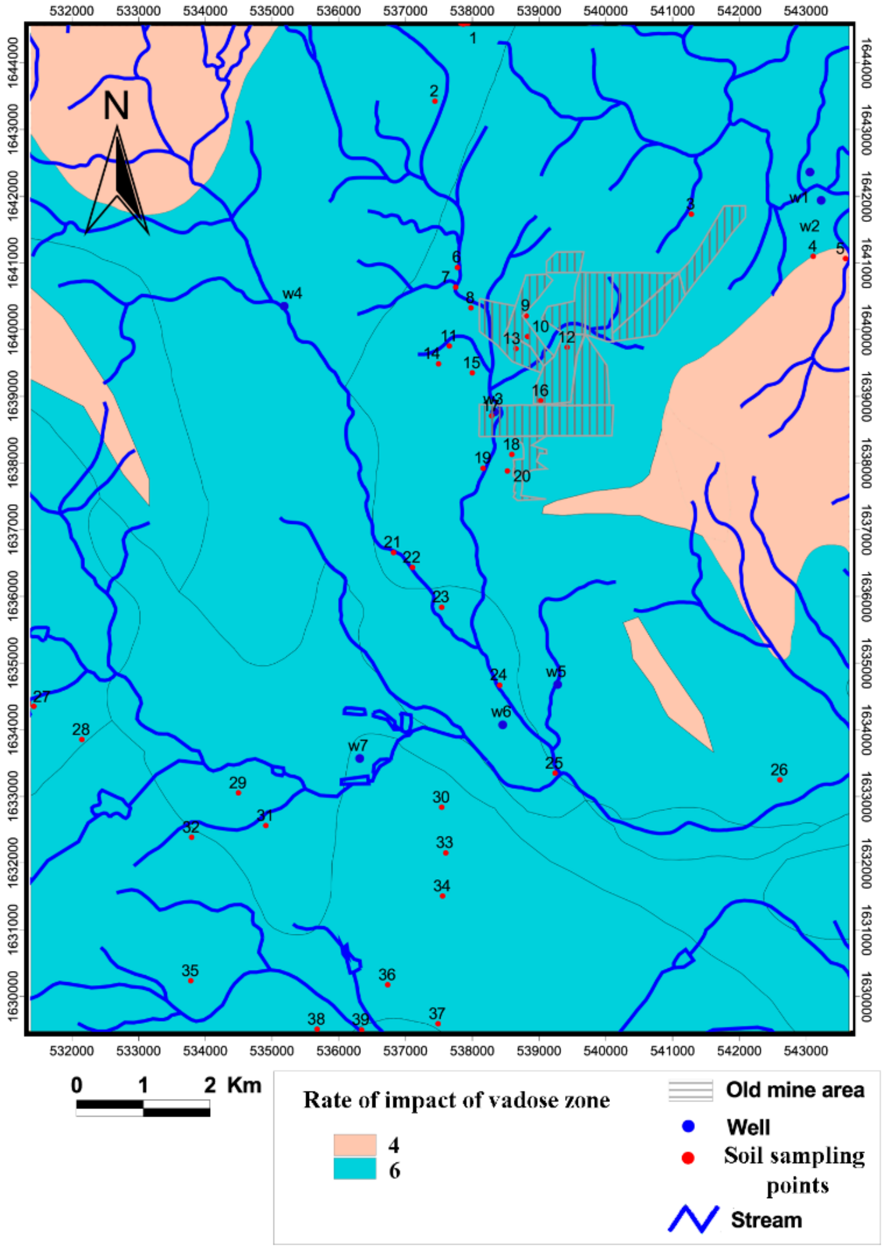


Figure 4.19 Rate of impact of vadose zone

4.2.7 Hydraulic Conductivity

Hydraulic Conductivity refers to the ability of an aquifer to transmit water, controlling the rate at which groundwater flows under a given hydraulic gradient.

The hydraulic conductivity ranges between 0.00001 m/day to 10.89 m/day in the study area. The ratings based on hydraulic conductivity are shown in Table 4.18

the hydraulic conductivity map and spatial distribution are shown in Figures 4.20 and 4.21, respectively.

Table 4.18 Hydraulic Conductivity index

Hydraulic Conductivity w = 3	Aquifer Type	K (m/day)	Ratings (Cr)	Index (Ci)
	Granitic, Gr	0.078-1.26	1	3
	Ordovician Limestone,Ols	0.00001-10*	2	6
	Permian Carboniferous Metasediments, PCms	0.0694-0.450	1	3
	Colluvial Deposits, Qcl	0.0234-4.49	1	3
	Terrace Deposits, Qt	0.037-10.89	2	6
	Silurian-Devonian Metamorphic Rock, SDmm	0.0756-7.15	2	6

* The value dervied from DGRM CR 2000-2550 Risk Assessment for Groundwater Resource Contamination (Khon Kaen University, 2007).

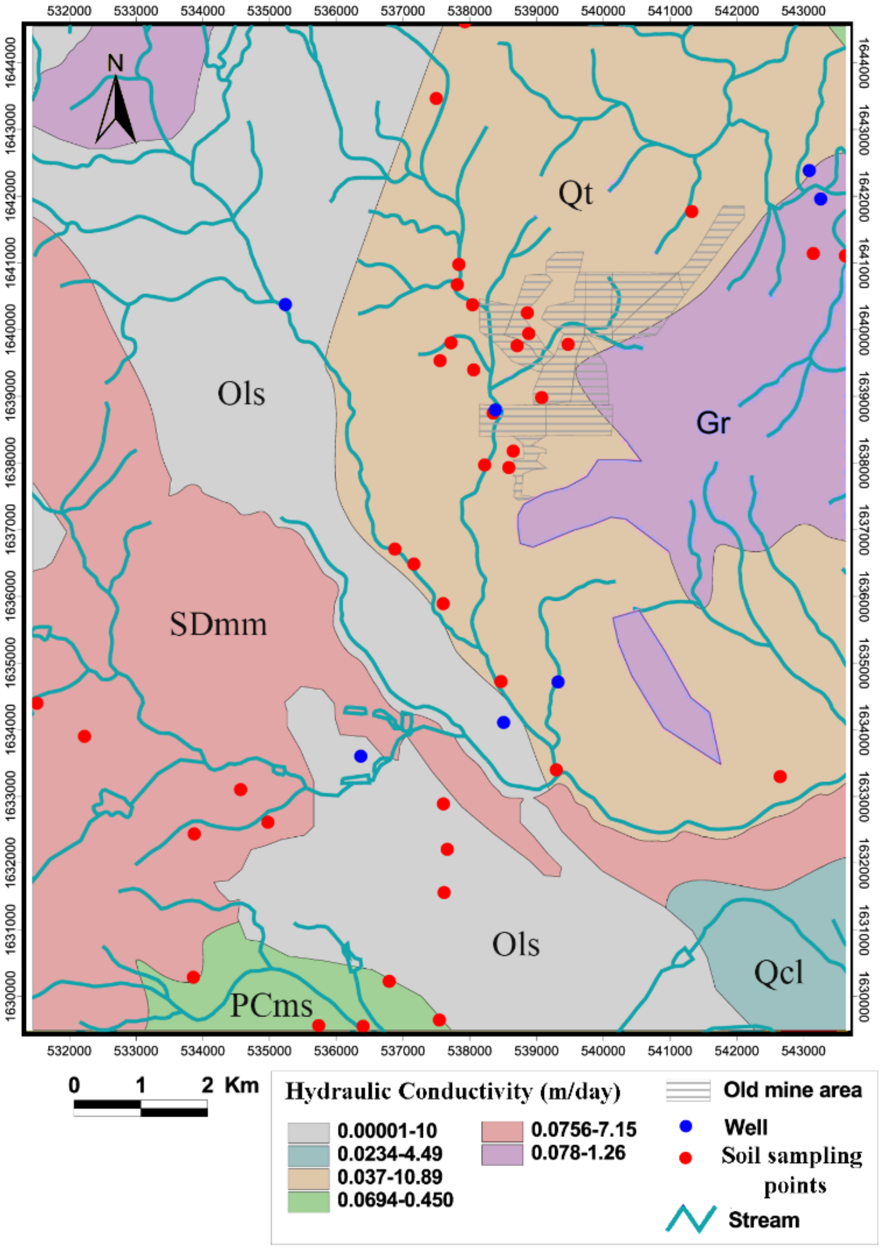


Figure 4.20 Aquifer and hydraulic conductivity

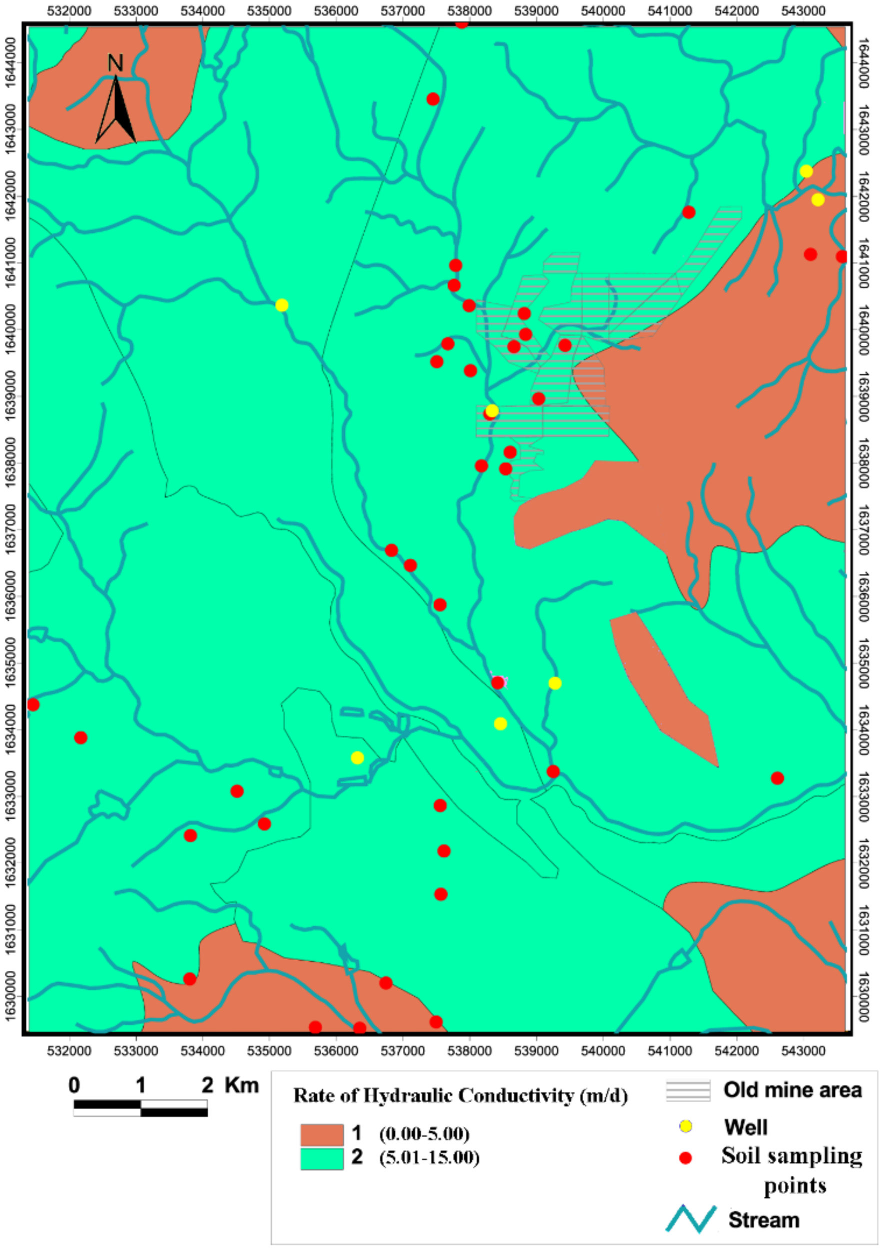


Figure 4.21 Rate of hydraulic conductivity

4.2.8 DRASTIC vulnerability map

The index score of groundwater vulnerability assessment ranged from 59 to 147 . According to groundwater vulnerability, this study area was divided into three zones: low (index score <100); moderate (index score 100–130) and high (index score > 130). Around 18.65% of the area showed high vulnerability and around 34.88 % showed moderate vulnerability and 46.47 % of the area showed low vulnerability. The high, medium and low vulnerability have been assigned in Table 4.19. The highly vulnerable areas is located along the creek or waterway while the plain area is moderate in the vulnerability and the mountain area is low in the vulnerability (Figure 4.22).

Table 4.19 Classes of DRASTIC Vulnerability Index

DRASTIC vulnerability index		
Low	< 100	46.47 %
Moderate	100-130	34.88 %
High	> 130	18.65 %

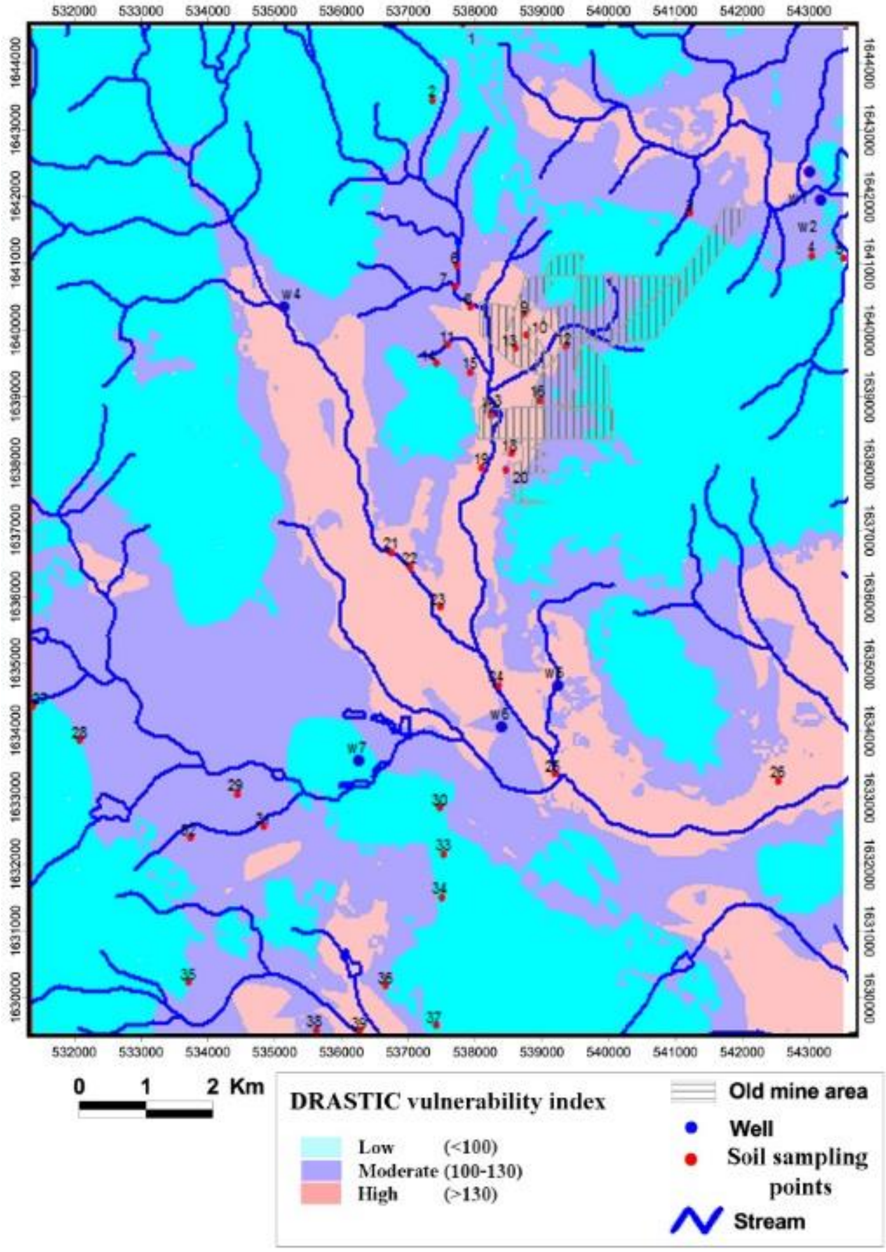


Figure 4.22 DRASTIC vulnerability map

CHAPTER V
DISCUSSION AND CONCLUSIONS

Risk assessment of *As* contaminated soil, old Tin mine used practically method as sequential extraction of arsenic in soil with effective vulnerability method as DRASTIC. The 39 soil samples were analyzed the total arsenic and sequential extraction, the concentration of total arsenic and each fraction were apply to spatial distribution maps. Risk map is the result of considered arsenic distribution map with DRASTIC vulnerability map.

5.1 Ground water analysis

The chemical parameters of groundwater and piper-diagram plot show the water type is mainly Ca-HCO_3 waters. The Ca-HCO_3 water type indicate areas of fresh recharge (Olobaniyi et al., 2007) and may originate from CO_2-charge rainstorm which produce weak carbonic acid that later dissociates into hydrogen ions and bicarbonate ions (Tijani et al., 2005). Also, Acidic groundwater in this area with the oxidation potential in range of 270 – 390 mV lead to form of arsenic be probable in ionized Arsenate ($HAsO_4^{2-}$, $H_2AsO_4^{-}$) form as shown in Figure 5.1

The highest arsenic concentration in groundwater of shallow ring-well was found in well No.3 in both season, wet and dry season at 6 μg/L and 14 μg/L, respectively. The result show that the concentrations of arsenic in dry season were higher than that in wet season in study area, similarily, Buragohain (Buragohain et al., 2010) in India and the reason might be due to concentration effects and probably due to dilution by rainwater as recharge in wet season which influences concentration.

But it is different from the result reported by Munk et al. (Munk L.A. et al., 2011) and Keshavarzi et al. (Keshavarzi B. et al., 2011) also observed that, the mean concentration of arsenic in groundwater in wet season were higher than that in dry season in Anchorage (USA) and west of Iran. One of the possible reasons that the concentrations of arsenic in wet season were generally higher than that in dry season, indicating that arsenic in surface might be one of the main sources for arsenic in shallow groundwater. Therefore , arsenic in shallow groundwater at dry event are higher than wet event, higher recharge during wet periods can, in turn, dilute shallow mineralized and contaminate waters.

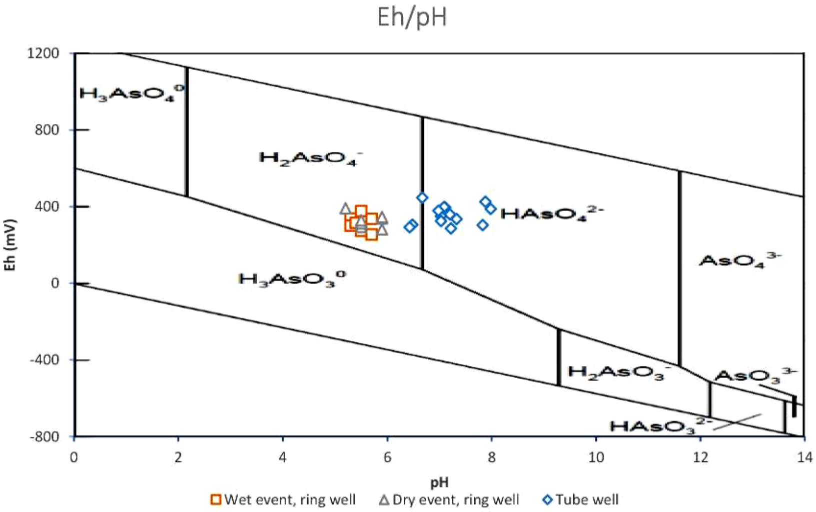
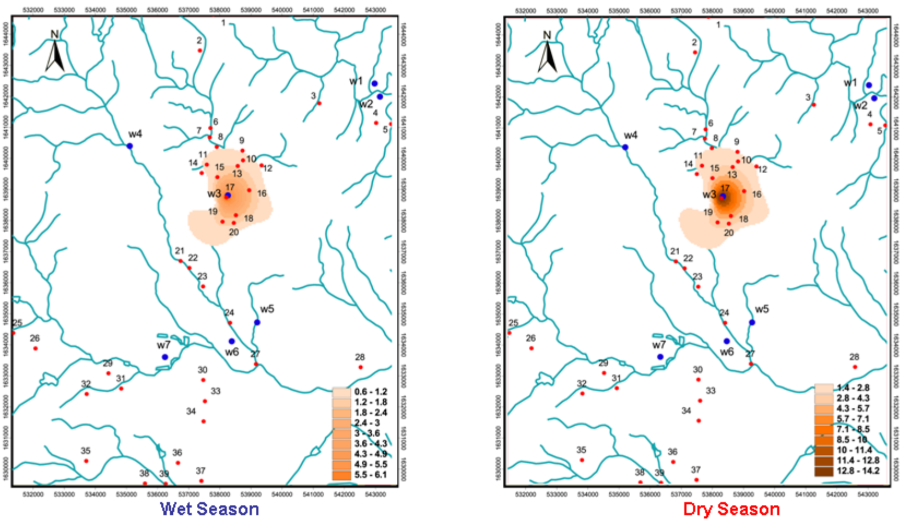


Figure 5.1 Arsenic forms of GW sample with Eh–pH condition

The spatial distribution of arsenic in shallow groundwater during wet and dry event, there are show the same distribution patterns (Figure 5.2). On the other hand, The result of arsenic in tube well (deep) are high concentrate at the southeast of study area, at point 11 and 12, while the relatively lower and non-detect are in the north of study area (Figure 5.3). Contrasting arsenic in shallow and deep aquifers of study area are



Wet Season

Dry Season

Figure 5.2 Comparison of arsenic concentration of shallow groundwater at wet and dry event

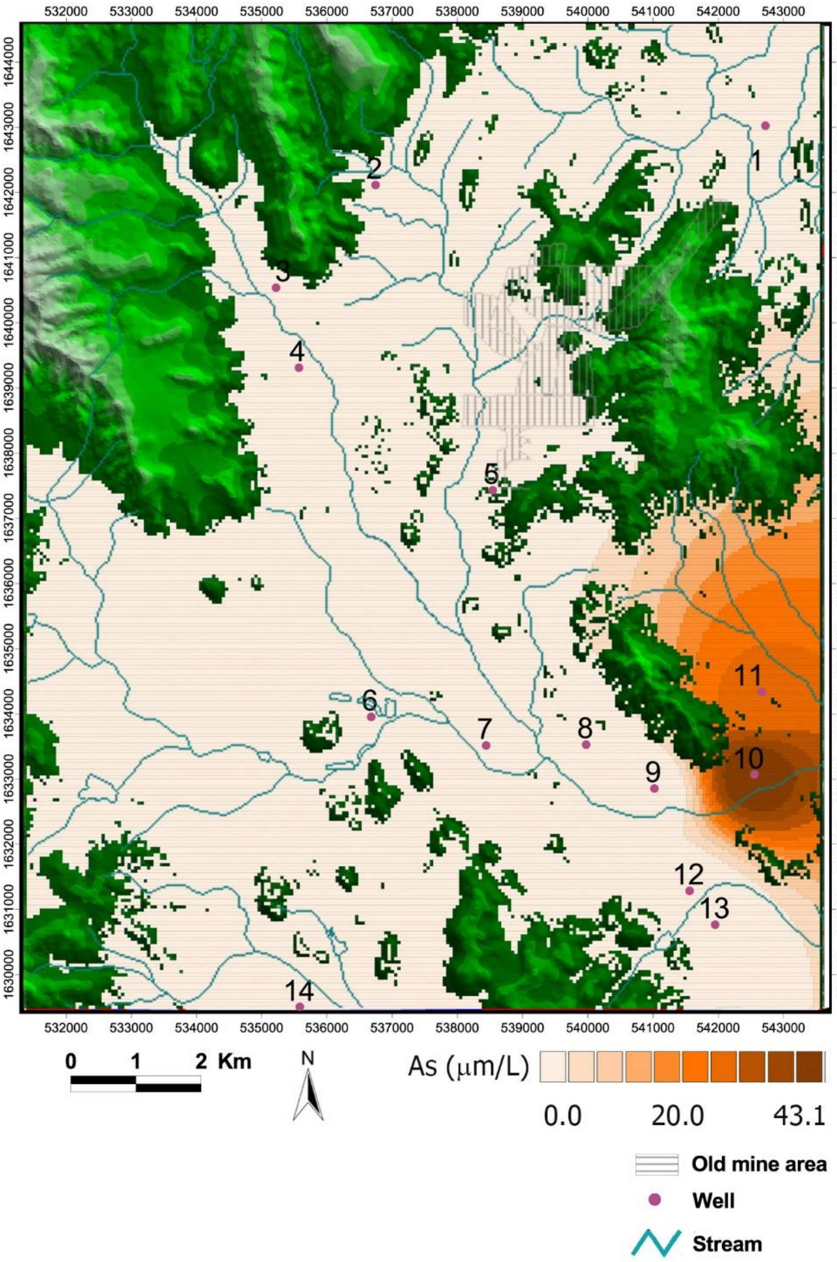


Figure 5.3 Distribution map of *As* concentration of tube well groundwater

Contrasting arsenic in shallow and deep aquifers of study area as may be in different groundwater system. Especially, the deep aquifer of southeast area at covered by layer of clay

5.2 Soil analysis

The 39 soil samples were analyzed the total arsenic and sequential extraction, the concentration of total arsenic is in soil at old Tin mining area is 4.8 – 1070.4 mg/kg , and found that the value of *As* contamination is not normally distributed (Figure 5.4). Previous work in this area by Orathai (Orathai et al., 2009) after the last mine were abundance for 5 years reported the total arsenic in soil are in range of 8.96 - 92.35 mg/kg. Also another old tin mine in Thailand at Amphoe Ron Phibun, Nakhon Si Thammarat has the total arsenic in soil are in range of 2.53 - 151 mg/kg.

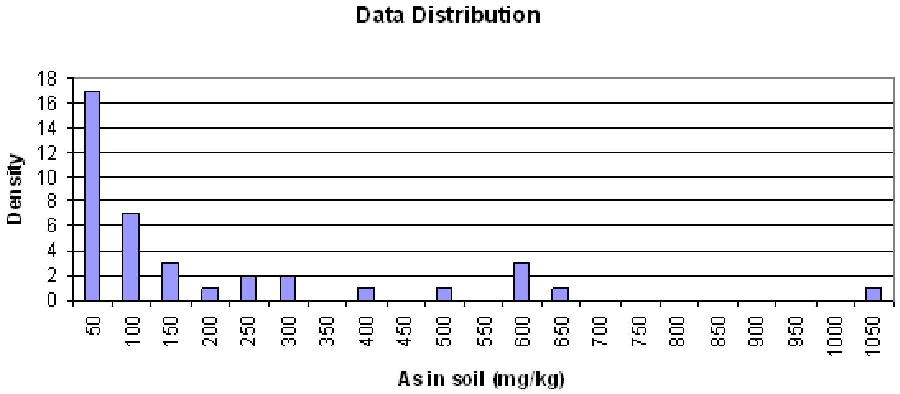


Figure 5.4 Distribution of arsenic in soil

and the results of sequential extraction are mostly in oxidable and residual fraction as shown in Figure 5.5. The mobility factor of this area is relatively high in southern, out of old mine (Figure 5.6) which separated to other subwatershed of old mine are shown distribution map in Figure 5.7. The old mine area are very low mobility factor. Therefore, the fraction have a high ratio of immobilized form.

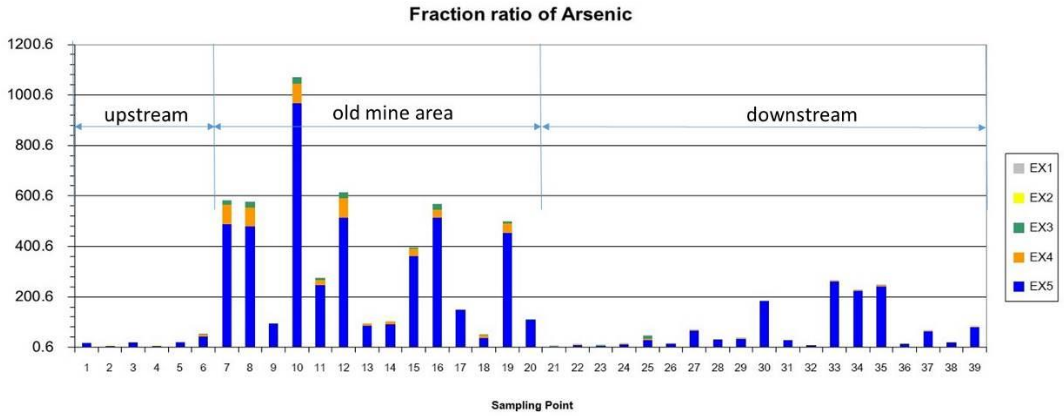


Figure 5.5 Arsenic in soil and distribution related with zone of area

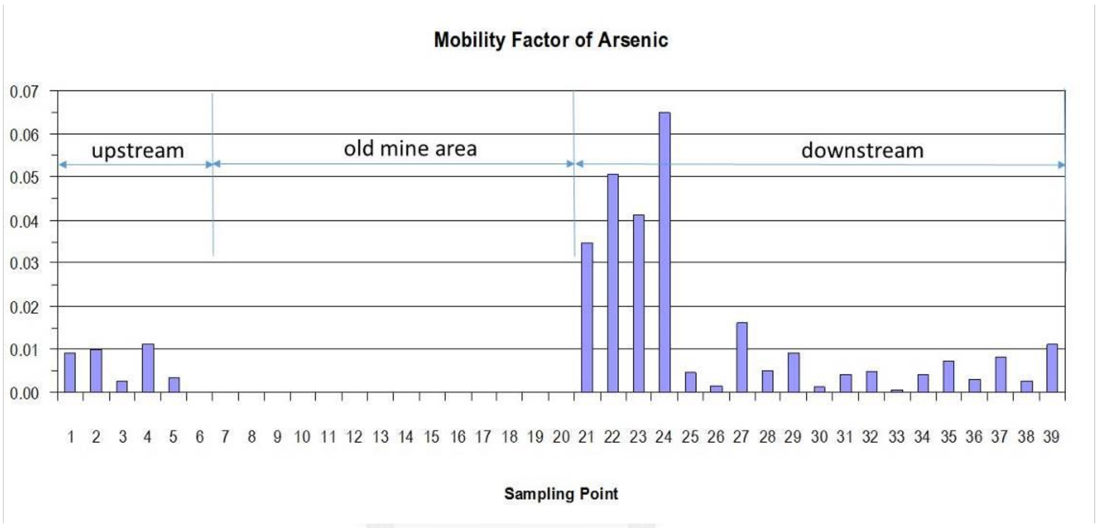


Figure 5.6 Mobility factor of As from 39 samples

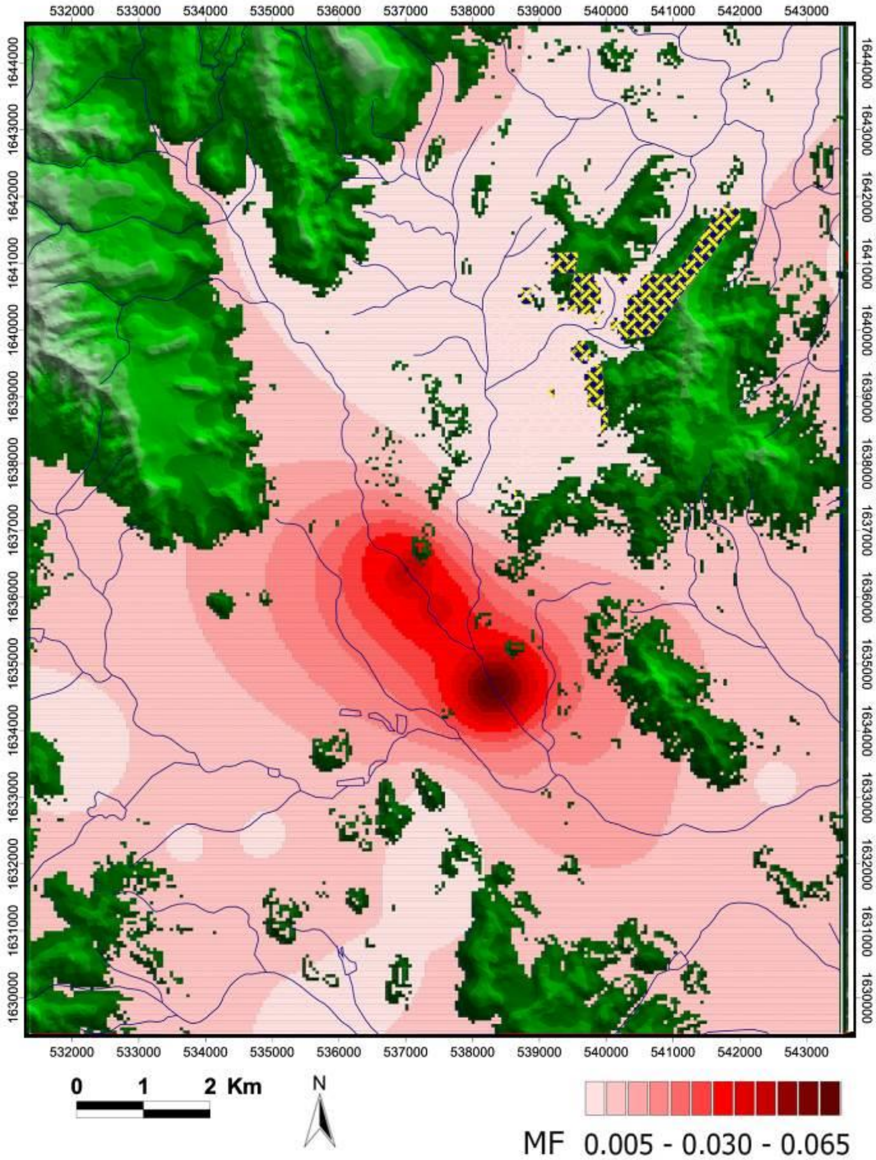


Figure 5.7 Mobility factor map of arsenic from 39 samples

The other fraction of soil extraction as soluble, extractable and reducible, are not over national limited value at 3.9 mg/kg.

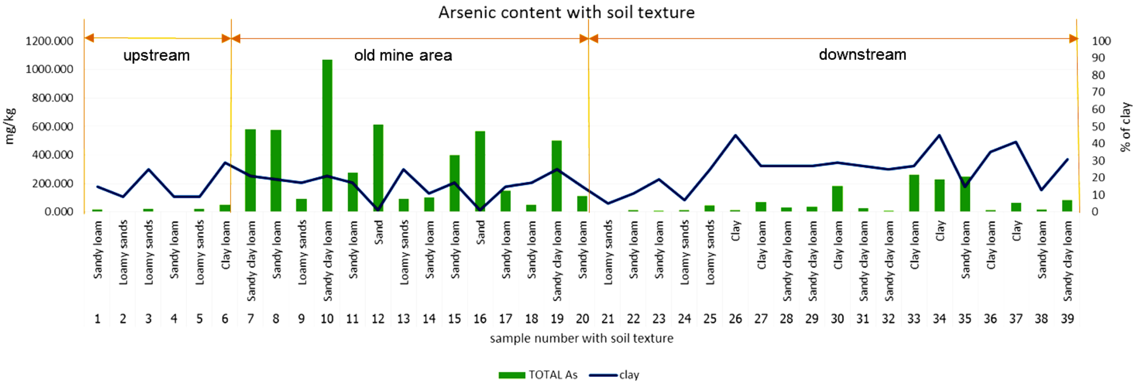


Figure 5.8 *As* concentration with soil texture

Soil texture is another important factor that can influence arsenic mobility (Fitz and Wenzel, 2002; Quazi et al., 2011). In general, clay or finer texture soils have much more surface area than coarse or sandy soils. Sand (quartz) is expected to facilitate greater arsenic leaching or loss with runoff. So, the soil with high amount of clay such as clay, clay loam and sandy clay loam can be able to adsorb an arsenic. However, some sample with low amount of clay have high arsenic content as sample number 12 and 16 are sandy soil, which is a sample of mine area. Also, Zulfahmi et al were analyzed tailing sand by XRD indicated the presences of arsenopyrite realgar, chalcopyrite, pyrite, hematite and quartz minerals (Zulfahmi et al., 2012).

The *As* from sequential extraction has a different form in each fraction propose by S. Van Herreweghe et al. (Van Herreweghe et al., 2003) that show in Table 5.1

Table 5.1 Form of *As* with the extract condition

Form of Arsenic	Extract Condition
$Na_2HAsO_4.7H_2O$ (sodium arsenate)	soluble
$Ca_3(AsO_4)_2.xH_2O$ (calcium arsenate)	Extractable
$FeAsO_4.xH_2O$ (scorodite)	Reducible
AsS (realgar) and As_2S_3 (orpiment)	Oxidable (H_2O_2)
$FeAs_2$ (Lollingite)	Residual form

Contamination factor (C_f) was used for indicate degree of environmental contamination (Abrahim and Parker, 2008), the C_f of *As* contaminated in soil sample divided by Shale values are 6.6 mg/kg as a background value of *As*. The C_f of study area are in range of 0.73 – 162.18 and the spatial distribution shown in Figure 5.9.

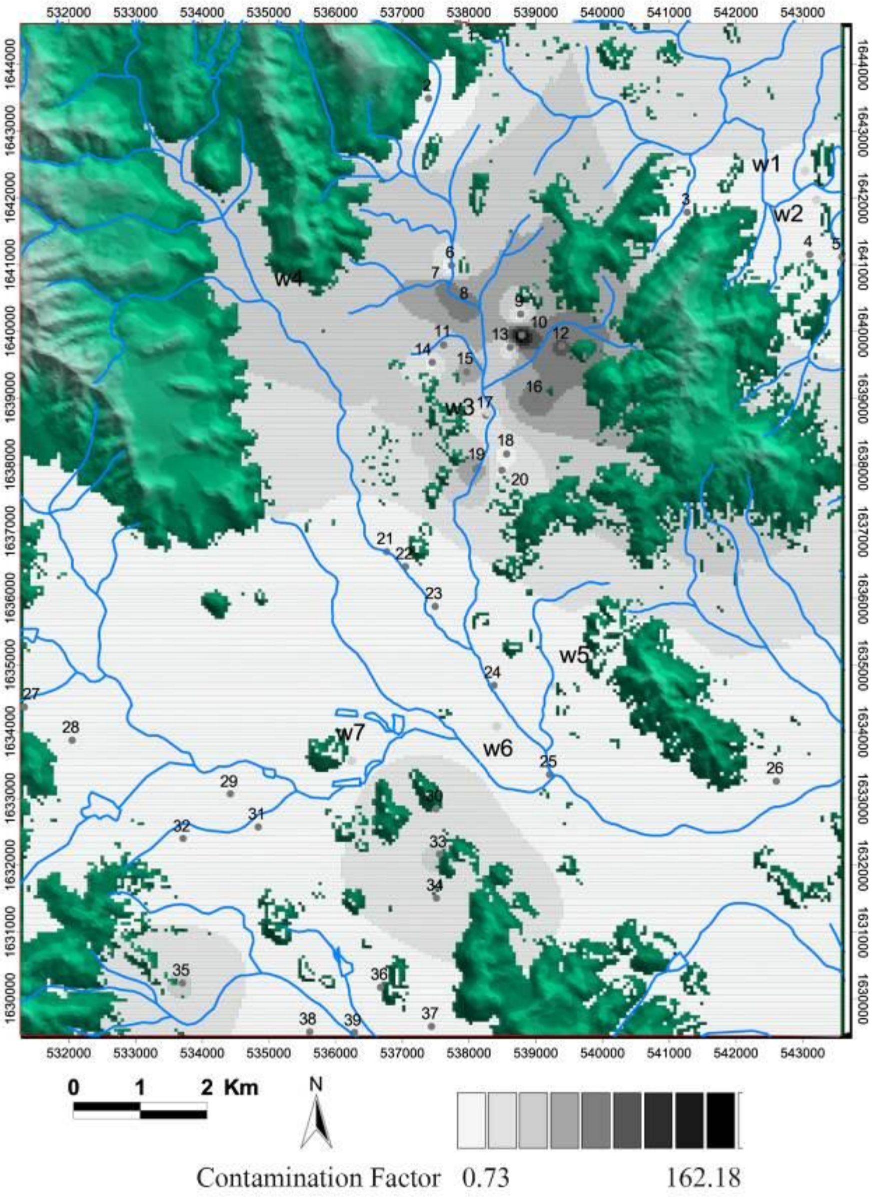


Figure 5.9 Contamination Factor of *As*

C_f values were interpreted as suggested by Hakanson (Hakanson, 1980), where: $C_f < 1$ indicates low contamination; $1 < C_f < 3$ is moderate contamination; $3 < C_f < 6$ is considerable contamination; and $C_f > 6$ is very high contamination. Therefore, the values showed mostly area are very high contamination for *As* according to Hakanson's C_f classification

5.3 Drastic map and risk assessment

The Index of DRASTIC vulnerability, summary of 7 parameters, as shown in Figure 4.21, the weakened zones distributed as a spot along the plain area. Especially, part of tailing have a score of DRASTIC in range of high vulnerable. Moreover, considerate with sampled wells and vulnerability map in order to see well with high concentration of total *As* is found in high vulnerable zones. The location and distance of village adjacent to old Tin mine are shown in the risk maps (Figure 5.10 and 5.11) and Table 5.2

Table 5.2 Village adjacent to old Tin mine

No	Village name	Distance to old Tin mine (km)
1	Ban Lawa Wung Kwai	3.9
2	Ban Numtok Saitong	5.0
3	Ban Kok Chang	3.2
4	Som Det Charoen village	6.7
5	Ban Khao Yai	7.4
6	Ban Muang Tao	8.4

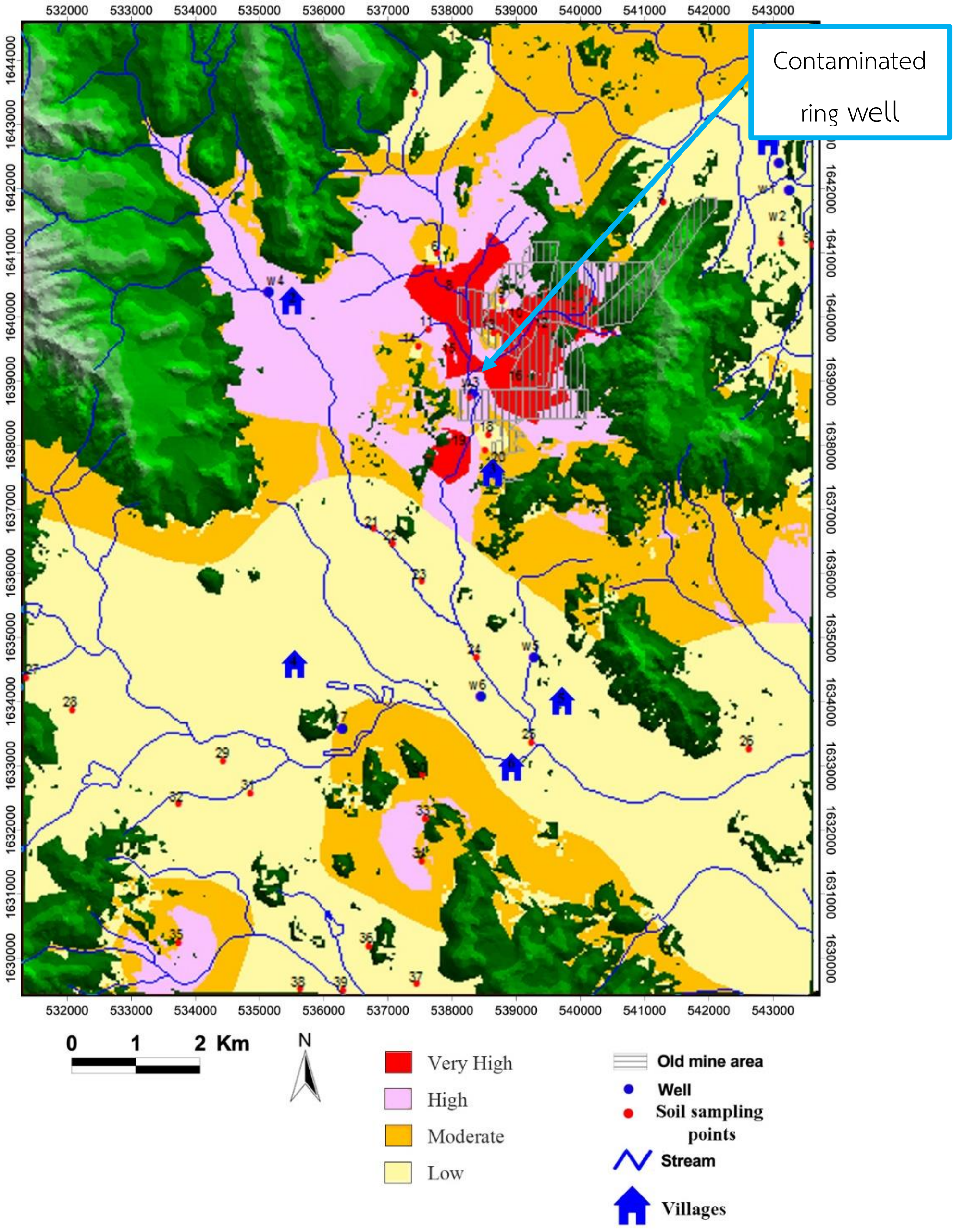


Figure 5.10 Risk map by contamination factor

In order to evaluate the risk pollution, the integrated and overlay the map of the contamination factor or mobility factor of *As* with the vulnerability map. In fact, the risk map using contamination factor and DRASTIC map shows zone of moderate, high and very high risk in the area of old mine area, as shown in Figure 5.10. In contrast, the risk map using mobility factor and DRASTIC map shows high and very high risk in the center of study area (Figure 5.11).

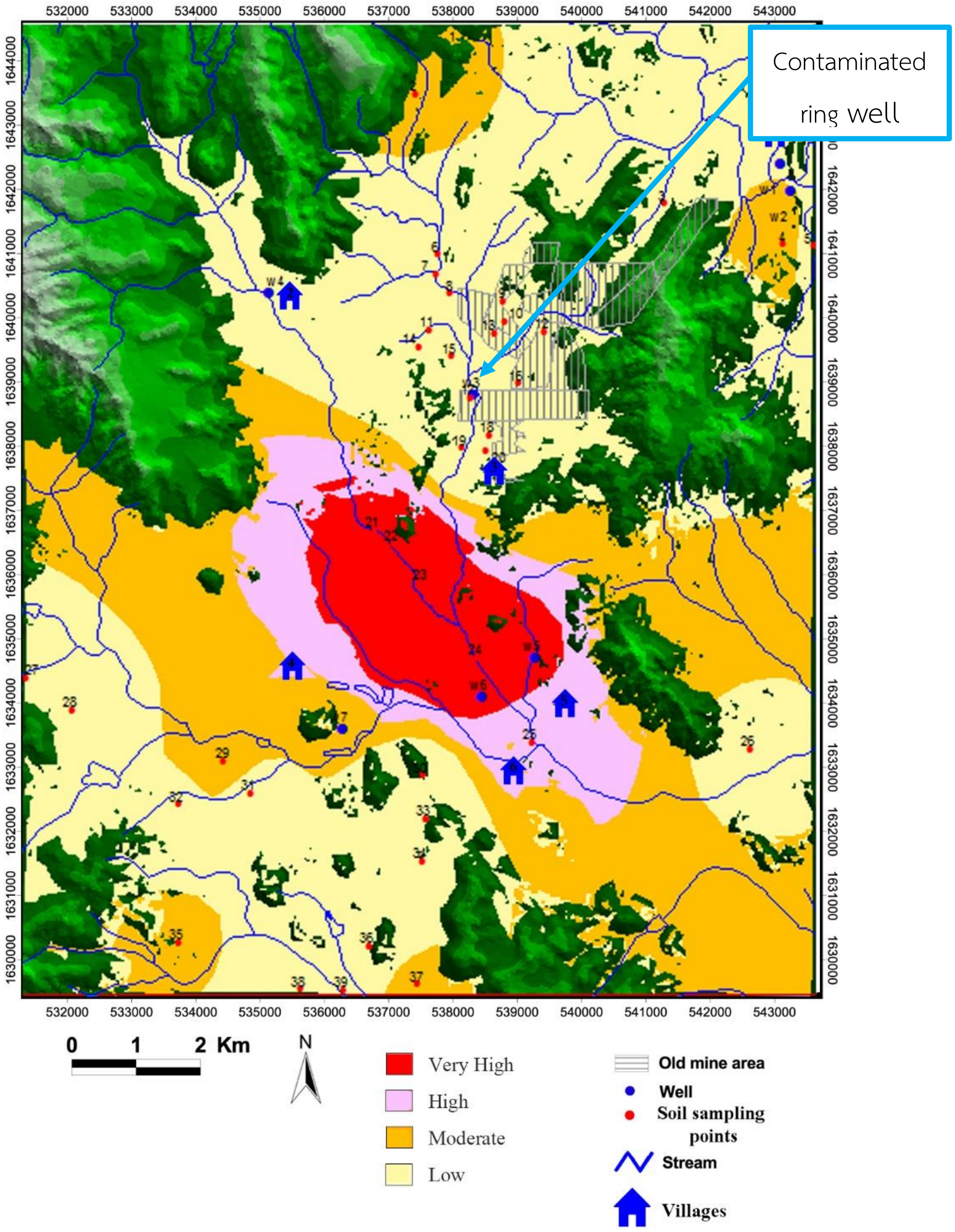


Figure 5.11 Risk map by mobility factor

Although, the risk map with contamination factor show a low risk of area which has contaminated groundwater, it shows shorter distances from risk zone and reasonable of contamination with groundwater flow.

5.4 Conclusion

Risk of arsenic from contaminated soils to shallow groundwater is depended on vulnerability and potential of arsenic in soil. The tailing area have high vulnerability but the potential are low because *As* mostly in oxidable and residual fraction.

Two risk maps are created by overlaying DRASTIC map with mobility factor and contamination factor, respectively. The both methods show a low risk of groundwater to contamination at mine area. Although, the area of high contaminated soil are low mobility factor. The risk map made from contamination factor shows that higher correlation with *As* in groundwater than that of the risk map from mobility factor. Otherwise. In this case, total arsenic in contaminated soil had an effect on shallow aquifer more than mobility factor from sequential extraction method.

Although the results of this research show the relationship between the contamination of groundwater with the contamination factor. However, the risk map from mobility factor is also important to indicate the contaminated areas where *As* is distributed in to the other phase, such as surface water and plants, which may affect health.

Moreover, the high vulnerability of the area with high arsenic content in soil will be risk, if the area are activate.

5.5 Recommendation

For the contamination factor, using the background of *As* in granite for calculation of the contamination factor will make the results more reasonable.

In addition, further studies of spatial distribution and vertical variation of arsenic in soils will be indicating the contamination and distribution of *As* dependent on bedrock or anthropogenic inputs. Especially, the old Tin mine area have been turned to agriculture area may be another sources of arsenic.

Should be studied arsenic in crops, because the top soil with high arsenic may have contaminated the crops.

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APPENDIX

Table 1A Soil texture of the top soil sample

Point	Position		Weight % of Particles			Symbol	Texture
	X	Y	Sand	Silt	Clay		
1	537851	1644615	64	21	15	SL	Sandy loam
2	537418	1643454	80	11	9	LS	Loamy sands
3	541283	1641743	30	45	25	LS	Loamy sands
4	543123	1641106	78	13	9	SL	Sandy loam
5	543605	1641073	82	9	9	LS	Loamy sands
6	537761	1640942	42	29	29	CL	Clay loam
7	537737	1640638	56	23	21	SCL	Sandy clay loam
8	537965	1640331	58	23	19	SL	Sandy loam
9	538796	1640211	52	31	17	LS	Loamy sands
10	538816	1639896	56	23	21	SCL	Sandy clay loam
11	537642	1639755	54	29	17	SL	Sandy loam
12	539414	1639732	92	7	1	S	Sand
13	538640	1639711	44	31	25	LS	Loamy sands
14	537475	1639486	78	11	11	SL	Sandy loam
15	537985	1639348	54	29	17	SL	Sandy loam
16	539014	1638925	94	5	1	S	Sand
17	538277	1638694	62	23	15	SL	Sandy loam
18	538584	1638116	60	23	17	SL	Sandy loam
19	538151	1637908	54	21	25	SCL	Sandy clay loam
20	538517	1637865	54	31	15	SL	Sandy loam
21	536791	1636634	88	7	5	LS	Loamy sands
22	537078	1636407	74	15	11	SL	Sandy loam
23	537522	1635808	64	17	19	SL	Sandy loam
24	538396	1634629	82	11	7	LS	Loamy sands
25	539233	1633289	44	31	25	LS	Loamy sands

Point	Position		Weight % of Particles			Symbol	Texture
	X	Y	Sand	Silt	Clay		
26	542621	1633188	30	25	45	C	Clay
27	531377	1634299	40	33	27	CL	Clay loam
28	532098	1633799	50	23	27	SCL	Sandy clay loam
29	534459	1632992	48	25	27	SCL	Sandy clay loam
30	537526	1632774	40	31	29	CL	Clay loam
31	534872	1632497	50	23	27	SCL	Sandy clay loam
32	533755	1632322	54	21	25	SCL	Sandy clay loam
33	537583	1632088	46	27	27	CL	Clay loam
34	537537	1631433	28	27	45	C	Clay
35	533742	1630152	66	19	15	SL	Sandy loam
36	536707	1630091	44	21	35	CL	Clay loam
37	537467	1629503	36	23	41	C	Clay
38	535641	1629420	68	19	13	SL	Sandy loam
39	536310	1629409	50	19	31	SCL	Sandy clay loam

Table 2A Log data of cross section line A-A’

No	well no	N	E	Elev(m)	Depth from	Depth to	Rock
1	TP395	536794	1642119	355.00	0.00	6.00	laterite
					6.00	42.00	limestone
					42.00	48.00	
					48.00	56.00	
2	MD457	537997	1639947	291.00	0.00	1.52	clay
					1.52	10.67	gravel
					10.67	28.96	limestone
3	TY42	539400	1638332	303.00	0.00	1.52	clay
					1.52	6.10	laterite
					6.10	15.24	weathered granite
					15.24	54.88	granite

No	well no	N	E	Elev(m)	Depth from	Depth to	Rock
					91.46	91.46	
4	TY110	542871	1633784	226.00	0.00	1.52	clay
					1.52	16.77	weathered granite
					16.77	38.11	

Table 3A Log data of cross section line B-B'

No	well no	N	E	Elev(m)	Depth from	Depth to	Rock
1	TY106	537240	1635567	254.00	0.00	3.05	rock
					3.05	6.10	clay
					6.10	12.20	limestone
					12.20	25.91	clay
					25.91	30.49	limestone
					30.49	36.59	clay
					36.59	50.30	limestone
2	TY113	538022	1637290	262.00	0.00	4.57	clay
					4.57	15.24	
					15.24	18.29	weathered granite
					18.29	73.17	
					73.17	122.00	
3	TY105	538518	1638108	277.00	0.00	3.05	clay
					3.05	38.11	weathered granite

Table 4A Log data of cross section line C-C'

No	well no	N	E	Elev(m)	Depth from	Depth to	Rock
1	TY106	537240	1635567	254.00	0.00	3.05	rock
					3.05	6.10	clay
					6.10	12.20	limestone

No	well no	N	E	Elev(m)	Depth from	Depth to	Rock
					12.20	25.91	clay
					25.91	30.49	limestone
					30.49	36.59	clay
					36.59	50.30	limestone
2	TY107	539960	1633536	236.00	0.00	6.10	weathered granite
					6.10	32.01	
3	TY108	540953	1632942	223.00	0.00	4.57	clay
					4.57	9.15	
					9.15	32.01	weathered granite

Table 5A Assigned Weights for DRASTIC Features (Aller et al. 1986)

Feature	Weight
Depth to Water	5
Net Recharge	4
Aquifer Media	3
Soil Media	2
Topography	1
Impact of Vadose Zone	5
Hydraulic Conductivity of the Aquifer	3

Table 6A Ranges and Ratings for Depth to Water (Aller et al. 1986)

Range (feet)	Rating
0-5	10
5-15	9
15-30	7
30-50	5
50-75	3
75-100	2
100+	1

Table 7A Ranges and Ratings for Net Recharge (Aller et al. 1986)

Range (inches)	Rating
0-2	1
2-4	3
4-7	6
7-10	8
1 0+	9

Table 8A Ranges and Ratings for Aquifer media (Aller et al. 1986)

Range	Rating	Typical Rating
Massive Shale	1-3	2
Metamorphic/Igneous	2-5	3
Weathered Metamorphic/Igneous	3-5	4
Thin Bedded Sandstone, Limestone, Shale Sequences	5-9	6
Massive Sandstone	4-9	6
Massive Limestone	4-9	6
Sand and Gravel	4-9	8
Basalt	2-10	9
Karst Limestone	9-10	10

Table 9A Ranges and Ratings for Soil Media (Aller et al. 1986)

Range	Rating
Thin or Absent	10
Gravel	10
Sand	9
Peat	8
Shrinking and/or Aggregated Clay	7
Sandy Loam	6
Loam	5
Silty Loam	4
Clay Loam	3
Muck	2
Nonshrinking and Nonaggregated Clay	1

Table 10A Ranges and Ratings for Topography (Aller et al. 1986)

Range (percent slope)	Rating
0-2	10
2-6	9
6-12	5
12-18	3
18+	1

Table 11A Ranges and Ratings for Impact of Vadose Zone Media (Aller et al. 1986)

Range	Rating	Typical Rating
Silt/Clay	1-2	1
Shale	2-5	3
Limestone	2-7	6
Sandstone	4-8	6
Bedded Limestone, Sandstone, Shale	4-8	6
Sand and Gravel with significant Silt and Clay	4-8	6

Range	Rating	Typical Rating
Metamorphic/Igneous	2-8	4
Sand and Gravel	6-9	8
Basalt	2-10	9
Karst Limestone	8-10	10

Table 12A Ranges and Ratings for Hydraulic Conductivity (Aller et al. 1986)

Range (GPD/ft^2)	Rating
1-100	1
100-300	2
300-700	4
700-1000	6
1000-2000	8
2000+	10

Table 13A Soil permeability class (USDA , 1994)

Texture class	Texture	Permeability rate	Permeability class
Coarse	Gravel, coarse sand Sand, loamy sand	> 20 inches/h 6–20 inches/h	Very rapid Rapid
Moderately coarse	Coarse sandy loam, sandy loam, fine sandy loam	2–6 inches/h	Moderately rapid
Medium	Very fine sandy loam, loam, silt loam, silt	0.60–2 inches/h	Moderate
Moderately fine	Clay loam, sandy clay loam, silty clay loam	0.20–0.60 inches/h	Moderately slow
Fine	Sandy clay, silty clay, clay (<60%)	0.06–0.20 inches/h	Slow

Texture class	Texture	Permeability rate	Permeability class
Very fine	Clay (>60%), clay pan	< 0.06 inches/h	Very slow

Table 14A Net recharge ratings (Piscopo G., 2001)

Range	Rating
6–8	1
8–10	3
10–12	5
12–15	8
15–17	10

The pictures of well in the study areas

Shallow ring wells

Ring-well 1

Ring-well 2

Ring-well 3

Ring-well 4


Ring-well 5


Ring-well 6


Ring-well 7

Deep tube wells

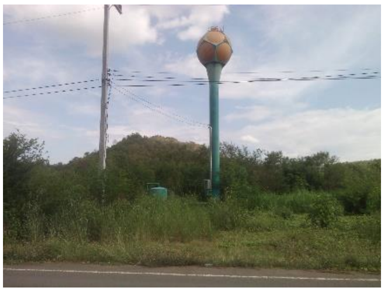

Tube-well 1


Tube-well 2


Tube-well 3


Tube-well 4


Tube-well 5


Tube-well 6


Tube-well 7


Tube-well 8


Tube-well 9


Tube-well 10


Tube-well 11


Tube-well 12


Tube-well 13


Tube-well 14

The pictures of soil sampling sites


Soil No 1


Soil No 2


Soil No 5


Soil No 6


Soil No 9


Soil No 10

Soil No 11

Soil No 12

Soil No 17

Soil No 18

Soil No 21

Soil No 22

Soil No 23

Soil No 24

Soil No 27

Soil No 28

Soil No 30

Soil No 32

Soil No 35

Soil No 36

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