

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Overview

Thailand is one of several countries in Southeast Asia that has a problem with tin residue. The waste piles resulting from tin mining contain high arsenic (as arseno-pyrite). After weathering and oxidation of the waste piles, arsenic may leach out and contaminates local surface and groundwater. The case had been discovered for decade at Ronphibun Sub-district, Nakorn Si Thammarat, a province in southern part of Thailand. Human health problem from drinking arsenic-contaminated water, in this area, is related to arsenic and include chronic arsenic poisoning and skin cancer, (ONEB, 1987; Nakorn Si Thammarat Province Health Office, 1988; Intarasoot, 1988; Choprapawon and Rodcline, 1997). Although, local people drink bottle water which is not contaminated by arsenic, most people still consume edible plants, fruits or vegetables growing in the area.

According to previous works, information of arsenic levels in soils and plants in this area is not sufficient to make an assessment of the risks. Our understanding of the arsenic contaminants in soils and edible plants grown in the area needs to be improved.

1.2 Arsenic contaminated in the environment

Arsenic (As), the third element in group V(A) of the periodic table with an atomic mass of 74.93 g/mol, is classified as a metalloid element. It is widely distributed in the environment, usually found to combine with other elements such as chloride, oxygen, sulfur and metal ions (i.e. copper, gold and iron) of which refer as “inorganic arsenic”. Arsenic combined with carbon and hydrogen is called “organic arsenic”.

Arsenic species	Formular	pK _a	Structure	
Arsenous acid (AsIII)	H ₃ AsO ₃	9.2	$\begin{array}{c} \text{OH} \\ \\ \text{HO}-\text{As}-\text{OH} \end{array}$	
Arsenic acid (As V)	H ₃ AsO ₄	2.3, 6.8, 11.6	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{As}-\text{OH} \\ \\ \text{OH} \end{array}$	2
MMA	HAsCH ₄ O ₃	3.6, 8.2	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{As}-\text{OH} \\ \\ \text{OH} \end{array}$	
DMA	AsC ₂ H ₇ O ₂	6.2	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\ \\ \text{OH} \end{array}$	
TMAO	AsC ₃ H ₉ O	4	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	
TMAI	AsC ₄ H ₁₂ I	N.A.	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{As}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right]^+ \text{I}^-$	
AsB	AsC ₅ H ₁₁ O ₂	2.18	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{As}^+-\text{CH}_2\text{COO}^- \\ \\ \text{CH}_3 \end{array}$	
AsC	AsC ₅ H ₁₄ OBr	N.A.	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{As}-\text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array} \right]^+ \text{Br}^-$	

Arsenic has two valency states, trivalent and pentavalent, which can form a vast range of compounds either in inorganic or organic forms. The most important inorganic arsenic forms are arsenite [As(III)] and arsenate [As(V)] ions. Organic arsenic compounds/ions in natural system mainly present as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine oxide (TMAO), arsenobetain (AsB), tetramethylarsonium ion (TMAI) and arsenocholine (AsC) (Yu *et al.*, 2003; Simon *et al.*, 2004). Some arsenic compounds and their chemical structures which are found in the environment is shown in Table 1-1.

Table1- 1 Some arsenic compounds and their chemical structure which are found in the environment

N.A. = Not available

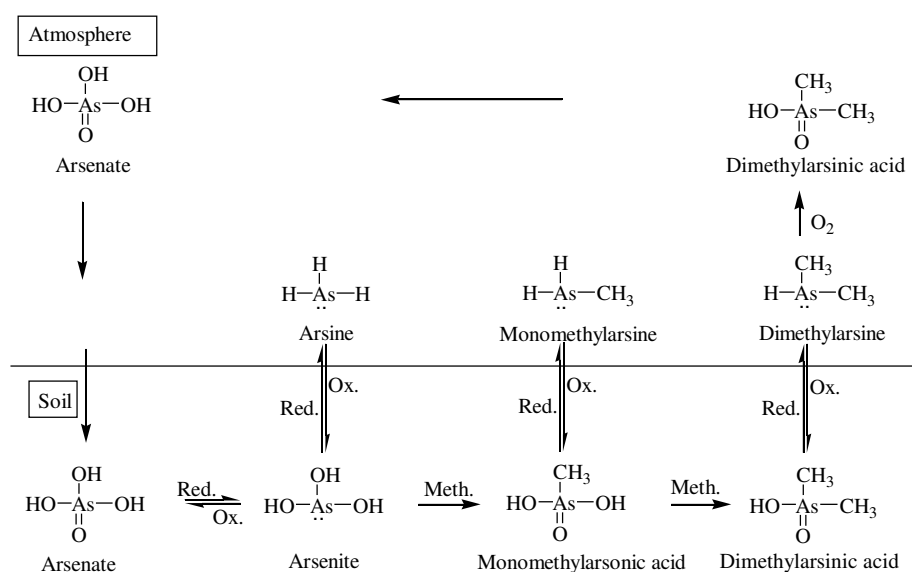
Source: Yu *et al.*, (2003)

Biochemical and toxicological behavior of different forms arsenic vary widely. Inorganic forms such, as arsine (AsH₃), As(III) and As(V), are more toxic than organo-arsenical. The arsenobetain and arsenocholine are apparently found to be non-toxic to living cells. The toxicity of different species of arsenic can be

arranged in a decreasing order as $\text{AsH}_3 > \text{As(III)} > \text{As(V)} > \text{MMA} > \text{DMA} > \text{TMAO}$ (Samanta *et al.*, 1999).

1.2.1 Arsenic in soil

The normal level of arsenic which is found in soil is about 5-6 mg/kg (Lioa *et al.*, 2005), while an average toxic level of arsenic is reported at 40 mg/kg dry soil (Sheppard, 1992). Arsenic in soils exists mostly as inorganic form while an organic form is occasionally found. The existence of organoarsenic species in soil depends on microbial-mediated methylation processes of inorganic arsenic. Biomethylation is a significant process in a biochemical cycle of arsenic. Redox conditions, pH, biological activities and adsorption reaction usually control solubility of arsenic (Pongartz, 1998). The chemical forms and their transformations in the soils are shown in Figure 1-1.



Source: Pongartz, 1998

Figure 1-1 Biological transformations of arsenic

Under anaerobic conditions, arsenate is reduced to arsenite via microbial activity (Figure 1-1). Further transformations are performed by methylation to form MAA and then to DMA. The formed compounds can be reduced to the corresponding arsines by anaerobic micro-organisms. These arsines, which are highly

volatile, are transferred from the soil to the atmosphere where an oxidation process follows. As a consequence the arsines are transformed to inorganic arsenic. The cycle is completed because atmospheric arsenate returns to the soil via dry or wet deposition (Pongratz, 1998). The normal range of arsenic concentrations and distribution of arsenic in soil from various countries are given in Table 1-2.

Table1- 2 Arsenic contents in the soil of various countries

Country	Type of soil/ sediment	N	Range (mg kg ⁻¹)	Mean (mg kg ⁻¹)	References
West Bengal, India	Sediments	2235	10-196	-	Chakraborti <i>et al.</i> (2001)
Bangladesh	Sediments	10	9.0-28	22.1	Nickson <i>et al.</i> (2000)
Argentina	All types	20	0.8-22	5	Mandal and Suzuki. (2002)
China	All types	4095	0.01-626	11.2	Mandal and Suzuki (2002)
France	All types	-	0.1-5	2	Mandal and Suzuki (2002)
Italy	All types	20	1.8-60	20	Mandal and Suzuki (2002)
Japan	All types	358	0.4-70	11	Mandal and Suzuki (2002)
	Paddy	97	1.2-38.2	9	Mandal and Suzuki (2002)
Mexico	All types	18	2-40	14	Whetstone <i>et al.</i> (1942)
South Africa	-	2	3.2-3.7	3	Mandal and Suzuki (2002)
United Stated	-	52	1.0-20	7.5	Stater <i>et al.</i> (1937)
	Tiller	1215	1.6-72	7.5	Mandal and Suzuki (2002)
General information					
Normal range in various countries	Soil	-	0.1-40	6	Lioa <i>et al.</i> , (2005); Mandal and Suzuki (2002); Sheppard, (1992)
High risk to health	Soil	-	>40-100	-	Sheppard (1992)
Toxic level	Soil	-	>100	-	Sheppard (1992), Lioa <i>et al.</i> (2005)

N = Number of samples

All type = soil and sediment

1.2.2 Arsenic in plants

Arsenic is chemically similar to phosphorus, an essential plant nutrient. It behaves like phosphate in the plant-soil system (Haung, 1994). Some plants can show a great ability of withstand and accumulate high concentration of toxic metals

and chemicals (Visoottiviseth *et al.*, 2002). Furthermore, the accumulation of some kinds of plant species with toxic metals shows the high concentrations that are referred as hyperaccumulators (Brooks *et al.*, 1997; Visoottiviseth *et al.*, 2002). Arsenic content in plants, in general, is in descending order from root to stem and leaf (Lui, *et al.*, 2005). Arsenic uptake is largely species specific and the concentrations in plant tissues generally can not be related to those in the soils (O'Neill, 1995). Arsenic can accumulate to high levels in some crops even when the levels of arsenic in the soil are relatively low (Huang, 1994).

1.2.3 Arsenic in water

The arsenic is found at low concentration in natural water. The unpolluted fresh water has a level of arsenic ranges from 1-10 $\mu\text{g L}^{-1}$, rising to 100-5000 $\mu\text{g L}^{-1}$ in sulfide mineralization and mining area (William *et al.*, 1996; Mandal and Suzuki, 2002). At moderate or high redox potentials, arsenic may be stable as pentavalent (arsenate) oxyanions, (H_3AsO_4 , H_2AsO_4^- , $\text{H}_2\text{AsO}_4^{2-}$ and AsO_4^{3-}). Under reducing condition and low redox potential, the trivalent arsenite species (H_3AsO_3) is a predominant species (Mandal and Suzuki, 2002). The maximum permissible concentration of arsenic in drinking water is 50 $\mu\text{g L}^{-1}$ and recommended value is 10 $\mu\text{g L}^{-1}$ by WHO (2001).

1.3 The analytical techniques for arsenic analysis

Several techniques have been developed to determine the presence of the arsenic compounds such as spectrometric techniques, graphite furnace atomic absorption spectrophotometric technique (Hata *et al.*, 1999), hydride generation technique coupled with inductively coupled plasma techniques (Feng *et al.*, 1998), neutron activation analysis (Sun and Yang, 1999), electrochemical methods (Adeloju *et al.*, 1999) and commercially available sensors (Kinniburgh and Kosmus, 2002). The summary of different techniques which are widely used for arsenic determination is given in Table 1-3. It can be seen from Table 1-3 that all of the analytical techniques are suitable for arsenic determination in environmental sample, due to high precision and sensitivity, low detection limit and can be used with many kinds of environmental sample. However, it seems to be that atomic absorption

spectrophotometry coupled with hydride generation (HG-AAS) is widely used for arsenic determination when compared with those techniques. For example, flame atomic absorption (F-AAS) technique lacks the sensitivity required for most environmental applications, graphite furnace atomic absorption (GFAAS) has a problem with salt matrix of sea water, when sample is injected as liquid form, fraction collection or sophisticated interface being required (Gonzalez *et al.*, 2003). The ICP-MS detector gives high sensitivity and can be set on-line with other techniques, however, the high operating cost and not yet standard equipment in general laboratories, are still being the main problems. Electrochemistry technique is the one of the best technique for arsenic determination due to a high sensitivity and that it is easy to perform, however, analyzing rate is still being a problem, in case of large numbers of samples.

Therefore, AAS combined with HG technique has been frequently used for the direct determination of arsenic in environmental samples because of simple use, quick operation, high sensitivity, low running costs, no interference effect
a n d l o w d e t e c t i o n l i m i t .

Table1- 3 Analytical method used for arsenic determination

Method	Sample media	Form detected	Linearity rang ($\mu\text{g L}^{-1}$)	DL ($\mu\text{g L}^{-1}$)	%RSD	% Recovery	Sampling rate Sample/hr.	References
Spectrometric								
HG-AAS	Water	As(III)	0.01-0.1	0.3	2.3 _{N=10}	96-108	120	Coelho <i>et al.</i> (2002)
		As(V)	0.01-0.1	0.5	2.0 _{N=10}	97-100		
HG-AFS	D r i n k i n g water	As(III)	0.1-10.0	0.37	1.1 _{N=10}	-	180	Nielsen and Hansen (2000)
		As(V)	0.1-10.0	0.03	1.3 _{N=10}			
HG-AAS	C h i n e s e medical herb	As(Total)	Upto- 22	0.13	2.1 _{N=8}	93.8-96.1	-	Lui <i>et al.</i> (2005)
		As(III)	0.05-2.5	0.02	-	-	102	
GF-AAS	Soil	As(V)	-	0.11	1.43 _{N=11}	89.3-118	-	Lopez-G <i>et al.</i> (2006) Shi <i>et al.</i> (2005)
		As(V)	-	0.07	-	80.4-111		
	Sea water	As(III)	-	0.02	-	97.1-103.4	-	Zhang <i>et al.</i> (2004)
		As(V)				96.6-99.4		
ICP								
HG-ICP-MS	River water	As(III)	0.5-10	0.12	-	91-96	-	Feng <i>et al.</i> (1998)
		As(V)	0.5-10	0.40		108-121		
HG-ICP-AES	Freshwater	As(III)	-	0.1	3 _{N=5}	93-109	-	Jitmanee <i>et al.</i> (2005)
		As(V)		0.1	5 _{N=5}	96-104		
Electrochemistry								
CCAS	River water	As(III)	-	3	-	90-96	-	Svancara <i>et al.</i> (1997)
		As(V)		0.5		90-96		
ASV	Sea water	As(Total)	-	0.19	2 _{N=5}	97-101	-	Sun <i>et al.</i> (1997)
	River water	As(III)			8 _{N=11}		-	Li and Smart (1996)
	Sea water							
Nuclear								
NAA	Nature water	As(III)	-	0.001	2 _{N=5}	100-101	-	Sun <i>et al.</i> (1999)
		As(V)		0.001		96.1-103.5		

AAS = Atomic absorption spectrometry,
MS = Mass spectrometry,
CCAS = constant current stripping analysis,

HG = Hydride generation ,
AFS = Atomic fluorescence spectrometry,
NAA= Neutron activation analysis,

GF = Graphite Furnace,
AES = Atomic emission spectrometry,
ASV= Anodic stripping voltametry

ICP= Inductively coupled plasma

1.4 Health Effects of arsenic on human

One of many source potentials of carcinogen and incidences of populations referring to blackfoot disease due to long term exposure to arsenic concentrations ($0.1-0.9 \text{ mg L}^{-1}$). The most common symptoms of this long-term of arsenic exposure are presented as type of skin pigments, hyperkeratosis, and ulcerations (Sharma *et al.*, 2003). Arsenic can cause cancer in kidney, bladder, skin, lung, and liver. However, the most important effect on human is to the skin. The level of arsenic toxicity to each individual human depends on genetic variety, nutrition level, exposure time and expose level (Brown and Chen, 1995; Pontius *et al.*, 1994). The pictures of various skin cancer related to arsenic poisoning are shown in Figure 1-2.



Arsenic poisoning or arsenicosis



Keratosis on hand



Arsenic lesions on feet



Arsenic lesions on hand, cancer



Skin cancer

Figure1- 2 Illustration of skin cancer caused by arsenic

1.5 Source and value of exposure

Arsenic could enter human body from food, water, air and soil. Table 1-4 presents a general figure of a daily arsenic intake via various media.

Table1- 4 Estimated daily intake of arsenic for each individual

Routes	Daily intake ($\mu\text{g day}^{-1}$)	References
Air		
General' s public intake	0.04-0.09	Pontius <i>et al.</i> (1994)
Food		
United States	12–14	Yost <i>et al.</i> (1998)
Belgium	45	Buchet <i>et al.</i> (1983)
Canada	7 (inorganic)	Hughes <i>et al.</i> (1994)
Japan	182	Sharma <i>et al.</i> (2003)
Netherlands	5 – 950	Sharma <i>et al.</i> (2003)
France	109	Leblanc <i>et al.</i> (2000)
England	63	Ysart <i>et al.</i> (1999)
Soil	0.14 - 0.28	Hughes <i>et al.</i> (1994)
Water	<1 – 10	Sharma <i>et al.</i> (2003)
Smoker (20 cigarettes/day)	0.7 - 2.1	Hughes <i>et al.</i> (1994)

Food item is probably the most significant source of arsenic entering human body. The daily intake of arsenic from food, as shown in Table 1-4, is generally between 5-950 μg per day for each individual (Sharma *et al.*, 2003). However, the arsenic intake value from food is widely varying depending on types of food. However, inorganic arsenic is considered to be toxic to human. Thai standard value of arsenic in food was established by Food and Drug Administration (FDA), Ministry of Public Health since 1979 at the value of $<0.1 \text{ mg kg}^{-1}$ (body weight) per day.

1.6 Arsenic contamination in Ronphibun Sub-district

1.6.1 Background information of arsenic contamination

Ronphibun Sub-district (Figure 1-3) around the Sruangchan and Ronna mountain ranges where tin-mining activities had existed for more than 50 years, has been recognized in facing arsenic contamination problem. The problem was first recognized in 1987 following a diagnosis of arsenical skin cancer (ONEB, 1987; Nakorn Si Thammarat Province Health Office, 1988). The area has an extensive history of bedrock and alluvial mining. Minerals of the area comprise of cassiterite (SnO_2), wolframite ($(\text{Fe,Mn})\text{WO}_4$), arsenopyrite (FeAsS) and pyrite (FeS_2) occurring in pegmatites and greisenized quartz-vein margins throughout Khao Luang batholiths. Ore-bearing veins, grading 5-10% cassiterite with 1% arsenopyrite, typically extend

for distances of 10-40 m, averaging 10-20 m deep and 3-35 cm wide. Vein orientations are characteristically East-West (Williams *et al.*, 1996; Sirinawin and Sompongchaiyakul, 2004). The waste from tin mines is typically rich in arsenopyrite and related alteration products.

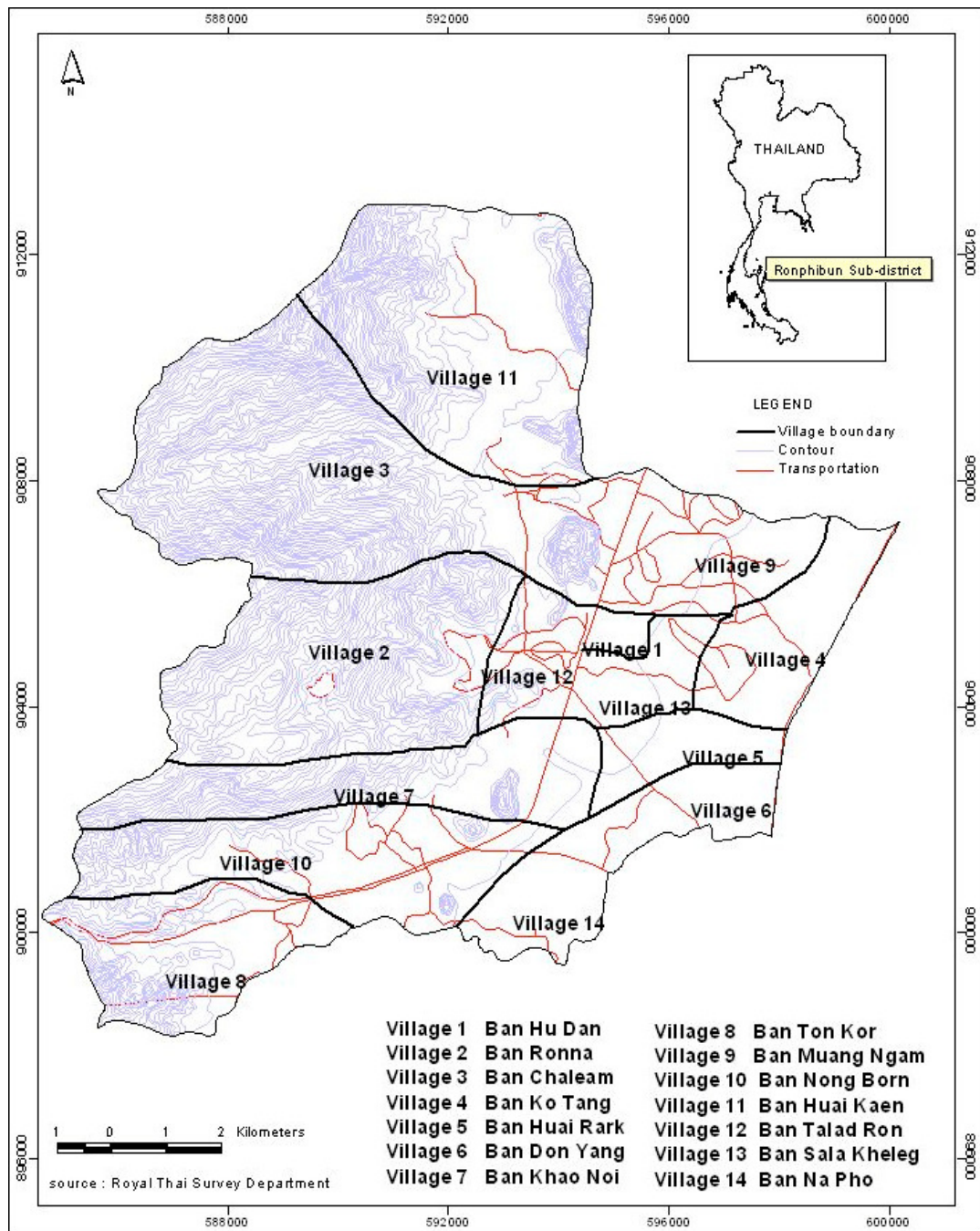


Figure1- 3 Map of Ronphibun Sub-district, Nakhorn Si Thammarat Province

1.6.2 Distribution of arsenic in Ronphibun Sub-district

Arsenic contamination in various environmental media in Ronphibun Sub-district was extensively reviewed by Sirinawin and Sompongchaiyakul, (2004) and is presented in Table 1-5.

Table1- 5 Arsenic concentration from various environmental media in Ronphibun Sub-district

Sources of Arsenic	Concentration Range		References
Mine tailing	21 – 14,000	mg kg ⁻¹	Visoottiviseth <i>et al.</i> (2002)
Mine tailing	Up to 11,100	mg kg ⁻¹	Francesconi <i>et al.</i> (2002)
Soil in HRA	7.5 - 510.9	mg kg ⁻¹ dry wt	Rakwong (1999)
Soil in LRA	1.7 - 88.6	mg kg ⁻¹ dry wt	Rakwong (1999)
Soil	51 - 1,860	mg kg ⁻¹	Francesconi <i>et al.</i> (2002)
Soil	50- 5,000	mg kg ⁻¹	Suwanmanee (1991)
Soil gas	0.26-12.7	µg l ⁻¹	Wongsanoon <i>et al.</i> (1997)
Silty alluvium	Up to 5,000	mg kg ⁻¹	Williams <i>et al.</i> (1996)
Fruits and Vegetables	<0.002 - 0.207	mg kg ⁻¹	Rakwong (1999)
Aquatic plants	0.23 - 2.97	mg kg ⁻¹ wet wt	Tongboriboon (1997)
Fern	88 - 8,350	mg kg ⁻¹ dry mass	Francesconi <i>et al.</i> (2002)

Source: Sirinawin and Sompongchaiyakul, (2004)

Na Chiengmai (1991) and Rakwong (1999) concluded that Village No. 1, 2, 12 and 13 appeared to have higher risk than Village No. 3, 6, 7, 8, 9, and 14. Rakwong (1999) reported that Village No. 2 has the highest risk of cancer. Francesconi *et al.* (2002) focused on arsenic speciation. They reported arsenic in aqueous extracted soils collected from high-contaminated area in Ronphibun Sub-district as arsenate 97-98% and as arsenite 2-3%. The same study was found that arsenic species (both inorganic and organic) which were present in different parts of *Pityrogramma calomelanos* plant were vary. Large amounts of inorganic species and small amounts of methylarsenate and dimethylarsenate were found. However, there was no clear relationship between arsenic concentrations in the soil and the plant tissues.

1.6.3 Risk assessment studies

The potential of risk from drinking water was found in the order of Village No. 2>1>12>3>14>13>6>8>9>7, while risk from soil was found in the order of Village No. 2>1>12>13>7>3>14>8>9 (Na Chiengmai, 1991 and Rakwong, 1999). Zhang *et al.* (2001) conducted an arsenic risk assessment study in four villages based on the arsenic exposure from drinking water, it was found that Village No. 12 had the highest risk due to arsenic consumption. It was found that 31% of arsenic chronic patients, out of 334 cases in 1997, lived in Village No. 12 and 22% lived in Village No. 13 (JICA, 2000).

After mining and ore processing was prohibited in 1994, arsenic concentration in water showed a significant decline (Pajitpraporn and Thongrak, 2001; Sirinawin and Sompongchaiyakul, 2004). Over the past decades, clean water supplies, utilisation and consumption have been introduced to the area. The chronic arsenic poisoning might be under control as indicated by the stable prevalence of skin cases compared with the previously reported since the populations have switched to arsenic-free water. However, there was a report in 1999 that a medical personnel at Ronphibun Hospital, who had never drank well water and had only one meal containing locally grown vegetables, developed noticeable pin-head-sized papules and slightly increased arsenic level in hair after 1 year of working (Piampongsant, 1999).

Chantaravijit *et al.* (2000) identified and evaluated the magnitude risk factors of arsenic in Ronphibun district. It was reported that a major exposure pathway was accidental soil ingestion. There were 446 cancer cases in Ronphibun district that caused by this factor. The second largest risk factor was a consumption of vegetables and fruits contaminated with arsenic, 90 cancer cases found. The third risk was drinking water from shallow well; 20 skin cancer cases found. The fourth risk was from consuming fishes and other aquatic animals, 17 cancer cases found. Beside water consumption, arsenic exposure via accidental soil ingestion and food consumption should also be included in strategic plan to solve arsenic problem in Ronphibun district.

1.7 Objectives

The objectives of this study were (i) to determine total arsenic in soils and to estimate total arsenic accumulated in edible plant samples, which were collected from the same location as soil samples; and (ii) to assess the risk from the contaminated edible plants growing in such area.

1.8 Anticipation outcome

To improve the information concerning arsenic levels in soils and edible plants from the 8 villages which are located in low and high risk areas. The results will be used to assess the risks that local people incur when they eat edible plants growing in the arsenic contaminated areas.