PROJECT CODE: SUT7-715-44-12-28

SURANAREE UNIVERSITY OF TECHNOLOGY
RESEARCH REPORT

A PRELIMINARY STUDY ON THE STATUS OF ARSENIC CONTAMINATION IN SOUTHERN THAILAND

Dr. Ranjna Jindal

School of Environmental Engineering
Institute of Engineering
Suranaree University of Technology

Funded by Suranaree University of Technology 2001 Fiscal Budget

September 28, 2001

ACKNOWLEDGEMENT

The principal investigator of this study wishes to express her special thanks to the Suranaree University of Technology for funding this research. She is also greatly indebted to Mr. Abu Sayed Md. Kamal of Asian Institute of Technology for lending the field test kit and to Dr. Udomphon Puetpaiboon of Prince of Songkhla University and his students and staff for their help and assistance provided during the field visit to Ron Phibun district. The Environmental Research and Training Center (ERTC) is also acknowledged for providing some data and information.

Finally, her research assistant, Putong Ratanamalaya, deserves a very special thanks for her valuable help during this project. Assistance from Mrs. Rasame Ratanamalaya in accounting is also highly appriciated.

Ranjna Jindal

บทคัดย่อ

งานวิจัยนี้ทำการศึกษาการปนเปื้อนของสารหนู (arsenic) ในบริเวณภาคใต้ของประเทศไทย โดยทำการศึกษาถึงแหล่งกำเนิดของสารหนู กลไกการเคลื่อนที่ของสารหนูจากแหล่งกำเนิดมายังชุมชน และความเป็นพิษของสารหนู รวมทั้งรวบรวมวิธีการกำจัดสารหนู จากการศึกษาพบว่า แหล่งกำเนิดของสารหนูในพื้นที่ศึกษาอยู่ในบริเวณเหมืองแร่ดีบุกเก่าภายในตำบลร่อนพิบูลย์ อำเภอร่อนพิบูลย์ จังหวัดนครศรีธรรมราช มีสาเหตุมาจากกระบวนการออกซิเดชั่น (oxidation) ของสารหนูในดินทำให้น้ำใต้ดินเกิดการปนเปื้อนและสภาวะน้ำท่วมทำให้เกิดการแพร่กระจายของสารหนูในน้ำใต้ดินภายในบริเวณโดยรอบ ซึ่งทำให้ประชาชนในตำบลร่อนพิบูลย์ประสบปัญหาพิษสารหนู โรคมะเร็งผิวหนัง หรือ “ไข้ดำ” อย่างไรก็ตามยังไม่มีคำตอบที่แน่นอนเกี่ยวกับกระบวนการแพร่กระจายของสารหนู รัฐบาลและหน่วยงานวิจัยต่างๆ พยายามศึกษาเกี่ยวกับการปนเปื้อนของสารหนูมาเป็นเวลานาน แต่ก็ยังไม่มีข้อสรุปที่แน่นอนสำหรับการลดลงของการปนเปื้อนของสารหนู ดังนั้นความรู้เกี่ยวกับวิธีการกำจัดสารหนูในน้ำดื่มอย่างง่ายๆ จะมีประโยชน์ต่อประชาชนในร่อนพิบูลย์มาก วิธีการกำจัดสารหนูออกจากน้ำดื่มในราคาย่อมเยาสองวิธี คือ การกรองแบบคาลชิ (kalshi) ซึ่งใช้มากในประเทศบังกลาเทศ และกระบวนการกรองขนาดเล็กที่การปรับปรุงด้วยกระบวนการโคแอคกูเลชั่น (coagulation) ตามที่ได้มีการศึกษาโดยคณะวิจัยของมหาวิทยาลัยสงขลานครินทร์ในประเทศไทย

ABSTRACT

Arsenic contamination in southern Thailand was studied through source identification, mechanism of its transportation, and the severity of toxicity. A review of removal techniques reported in literature was also carried out. Sources of arsenic contamination in the Ron Phibun district were identified to be the previous tin mining acitivities around the area. Oxidation of arsenic in the soil caused contamination in groundwater and flooding spread out the contamination around the area. Villagers in Ron Phibun are suffering from chronic arsenic poisoning with skin cancer or "black fever." However, there is no clear answer about how arsenic was distributed in this region. Government agencies and research groups have had many studies conducted over the last few yeas, but no conclusion of the arsenic contamination mitigation in the area had been reported. Thus, any knowledge about the simple methods of arsenic removal from drinking water would be very helpful to the general public in Ron Phibun area. The two low-cost arsenic removal techniques for drinking water could be kalshi (pitcher) filtration used in Bangladesh and/or small-size water-filtering system enhanced with coagulation used by some researchers in Prince of Songkla University in thailand.

TABLE OF CONTENTS

Page No.

TABLE OF CONTENTS (contd.)

LIST OF TABLES

LIST OF FIGURES

Page No.

LIST OF BOXES

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Environmental impact of arsenic contamination is causing serious concerns in some countries such as Bangladesh, India, Taiwan, Thailand, Mexico, and Ghana in recent years. In 1968, a research group reported an association of arsenic in drinking water and skin cancer in a Taiwanese population (USNRC, 1999). Arsenic pollution has been creating serious social problems for affected people in some countries, e.g. Bangladesh. The affected people virtually become isolated from the society, as nobody wants contacts with them (Kamal, 1999). Severe problems of arsenic pollution have occurred in Ron Phibun District, Nakhon Si Thammarat Province in southern part of Thailand, where arsenic in groundwater was found as FeAsS and FeS_2 in the tin mining belt within that region.

According to a recent report, the Mekong Delta groundwater may not escape from an arsenic contamination problem. Apparently, this has not yet turned into a known major public health disaster such as in Bangladesh. No outbreak of arsenic related disease has been reported to the international health community, although that does not mean there is none, or they were not mistakenly dismissed as something else. The Mekong Delta may have a little more time than Bangladesh but certainly no time to waste either. The pressure of population growth and local economic development has led to rapid extraction of ground water going down, an identical path to Bangladesh and West Bengal. More importantly, the proposed diversion of 8.8 BCM (billion of cubic meters) of water from the Mekong River in Thailand and the planned development of 37 MW of hydropower reservoirs in China and Laos would exacerbate the arsenic problem into a catastrophe (Than and Long, 2000).

1.2 Background Information

Arsenic is a naturally occurring element present in the environment in both inorganic and organic forms and it is toxic and carcinogenic. Inorganic arsenic is considered to be the most toxic form of the element and is found in groundwater and surface water, as well as in many foods. A wide variety of skin and internal cancers, and cardiovascular and neurological effects, have been attributed to chronic arsenic exposure, primarily from drinking water (Smedley and Kinniburgh, 2001). Human exposure to inorganic arsenic occurs through inhalation, ingestion, or skin absorption. Occupational exposure may occur among smelter workers and the workers exposed in production and use of arsenic containing pesticides. Ingestion occurs mainly by drinking contaminated water. Most ingested arsenic is absorbed through the gastrointestinal tract and lungs and then into blood stream. It is distributed in lungs, liver, kidney, spleen, and intestine within 24 hours of ingestion and to skin, hair, and bone within two weeks. Harmful effects of arsenic on human health include acute and chronic toxicity. Acute toxicity occurs only from the ingestion of arsenic compounds. The symptoms of acute toxicity include severe vomiting and diarrhea, muscular cramps, facial edema, and cardiac abnormalities. An ingested dose of 70-180 mg of arsenic (III) oxide has been reported to be fatal in people. Symptoms may occur within few minutes of exposure if the arsenic compound is in solution but may be delayed for several hours if it is in solid form or taken with a meal. Chronic toxicity is manifested in the organ systems affecting the skin, nervous system, liver, cardiovascular system, and respiratory tract (Kamal, 1999).

In 1996, a subcommittee of US National Research Council (USNRC) was formed to review the arsenic toxicity database and to evaluate the scientific validity of USEPA's 1988 risk assessment for arsenic in drinking water. In its report, the subcommittee concluded that there is sufficient evidence from human epidemiological studies in Taiwan, Chile and Argentina, that chronic ingestion of inorganic arsenic causes bladder and lung cancer, as well as skin cancer. With minor exceptions, epidemiological studies for cancer are based on populations exposed to arsenic concentrations in drinking water of at least several hundreds micrograms per litter. Few data address the degree of cancer risk at lower concentrations of ingested arsenic. Noncancer effects resulting from chronic ingestion of inorganic arsenic have been detected at doses of 0.01 milligram per kilogram per day (mg/kg/d) and higher. Of the noncancer effects, cutaneous manifestations of exposure have been studied most widely. Developmental and reproductive effects resulting from chronic ingestion of inorganic arsenic have not been demonstrated in humans, although arsenic is known to pass through the placenta. Parental administration of inorganic and organic forms of arsenic are known to be tetratogenic in a number of mammalian species, and oral administration (e.g., 350-4,500 nanograms per gram (ng/g)) in the diet has been shown to affect growth and reproduction in minipigs, chicks, goats, and rats (USNRC, 1999).

Assessment of arsenic exposure via drinking water is often based on the measurements of arsenic concentration in drinking water and assumptions regarding the amount of water consumed. Such data are estimates, the uncertainty of which will depend on the method used.

1.3 Maximum Contaminant Level (MCL) and Guidelines

The current USEPA's interim maximum contaminant level (MCL) of 50 μg/L has been the standard for arsenic in drinking water in the United States since 1942 (USNRC, 1999). Under the 1996 SDWA (Safe Drinking Water Act) amendments, USEPA was required to propose a standard (an MCL) for arsenic in drinking water by January 2000 and finalize it by January 2001 (Smedley and Kinniburgh, 2001). The scientific controversies surrounding the current MCL for arsenic primarily involve the carcinogenic potency of arsenic, which has been evaluated by several USEPA or USEPA-sponsored groups over the past 20 years and to a lesser extent whether arsenic might be an essential nutrient. Based on a study in Taiwan in 1984, USEPA's Office of Research and Development estimated the potency of arsenic as a skin carcinogen in its health assessment document (HAD) for arsenic. The upper-bound estimate of potency suggested that the risk of skin cancer for individuals consuming 2 L of water with arsenic at 50 μg/L would be 2% (or 2/100). In 1988, USEPA's Risk Assessment Forum published a special report reviewing the carcinogenicity of arsenic and the data suggested that it might be an essential nutrient in birds and mammals. Using the same Taiwanese data, the forum estimated the risk of skin cancer associated with drinking 2 L of water containing arsenic at 50 μg/L on a daily basis over a lifetime to be 0.25 % (or 2.5/100). Using the same risk-assessment assumptions to lower the estimated risk to 1/10,000, which is the upper bound of what USEPA typically considers to be an "acceptable" risk, the forum concluded that the concentration of arsenic in drinking water would need to be lowered to 2 μg/L. In 1989, USEPA's Scientific Advisory Board (SAB) recommended that the agency revise its arsenic risk assessment to consider possible detoxication mechanisms that might substantially reduce cancer risks at low exposure level. SAB also concluded that available data are inadequate to conclude that arsenic is an essential nutrient for humans (USNRC, 1999).

The WHO guideline for As in drinking water was provisionally reduced in 1993 from 50 μg/L to 10 μg/L. The new recommended value is based largely on analytical capability. If the standard basis for risk assessment applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still. The USEPA limit was also reduced from 50 μg/L to 10 μg/L in January 2001 following prolonged debate over the most appropriate limit. The European Community's maximum admissible concentration (MAC) for As in drinking water is also to be reduced to 10 μg/L. The Japanese limit for drinking water is 10 μg/L and the interim maximum acceptable concentration for Canadian drinking water is 25 μ g/L (Smedley and Kinniburgh, 2001).

Whilst many national authorities are seeking to reduce theirs limits in the line with WHO guideline value, many countries and indeed all affected developing countries, still operate at present to the 50 μg/L standard, in part because of lack of adequate testing facilities for lower concentrations (Smedley and Kinniburgh, 2001).

1.4 Project Justification

After recognizing the alarming situation of arsenic contamination in southern Thailand, intensive surveilance and studies by various organizations, such as the Environmental Research and Training Center (ERTC), the Department of Environmental Quality Promotion (DEQP), the Pollution Control Department (PCD), the office of Environmental Policy and Planning (OEPP), the Department of Health (DOH), the Department of Mineral Resources (DMR), and the British Geological Survey (BGS), indicated that water resources in Ron Phibun were contaminated with arsenic, at concentration exceeding the World Health Organization's standards (the standard specifies a maximum value in portable water of 10 μg/L). The water in some shallow wells had arsenic levels 50-100 times higher than the standard value. In addition, it was found that serveral other sites in Ron Phibun were heavily contaminated. Old tin mines, and primary and secondary tin ore deposits, were suspected to be the source of arsenic contamination. Run-off from some areas of ore deposits, and tin dressing processes, were suspected to have caused soil contamination, this then passed through to shallow groundwater (JICA, 2000).

Although, studies of arsenic contamination of groundwater in the area have been carried out by various agencies, the source of the arsenic, and the contamination mechanisms, have not been yet studied in detail. In an early stage of tackling this problem, the Thai Government, through concerned agencies, have transported water from outside the area, and also provided water jars to local residents for collecting rainwater. In addition, recently, the government have constructed simple water pipelines; however these did not cover the entire area affected, and the water quality was not controlled according to Water Quality Standards set by the Ministry of Public Health.

Arsenic contamination in Ron Phibun has caused sickness, and seriously endangered public health. Contaminated water has been spread through groundwater, and residents drinking the groundwater have been exposed to arsenic contamination. An urgent study was therefore required in order to clarify the precise causes and contamination mechanisms. In addition, mitigation measures to remedy the contaminated areas needed to be devised and implemented.

1.5 Research Objectives

The overall aim of this research was to study the status of arsenic contamination in Southern Thailand. Specific objectives included:

a) source identification of arsenic contamination in the study area
b) assessment of arsenic concentration levels in the study area
c) review of low cost arsenic removal techniques

1.6 Scope of Research

Scope and limitation of this research included the following.

a) The study area of arsenic contamination in southern Thailand was distinguished to be the Ron Phibun district in Nakhon Si Thammarat province.
b) Sources of arsenic contamination in the study area were identified.
c) Samples collected from shallow wells, groundwater pumps, as well as surface water were analyzed for arsenic concentrations.
d) Arsenic concentration in drinking water was assessed.
e) Low cost arsenic removal techniques were reviewed.

1.7 End Users

The end users of the results of this study would be the general public and the concerned authorities in various fields, e.g., local and central environmental management administration, and the public health officials. The study was intended to increase awareness in government authorities and general public about arsenic contamination in southern Thailand.

The research results could be utilized to identify the potential risk areas for arsenic pollution in the southern part of Thailand, which has been the tin mining belt and so with the worse situation of arsenic contamination. The assessment of arsenic concentration levels in drinking water was done based on the results of the analysis of on-site samples as well as from the existing data available.

CHAPTER II

ARSENIC IN THE ENVIRONMENT

Arsenic is relatively scarce element in the earth crust and is found in the atmosphere, soils, rocks, and natural waters and organisms. It is mobilized in the environment through a combination of natural processes such as weathering reaction, biological activity and volcanic emissions, as well as through a range of anthropogenic activities. Most environmental arsenic problems are the result of mobilization under natural conditions, but man has had an important role through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants, and the use of arsenic as an additive to livestock feed, particularly for poultry (Smedley and Kinniburgh, 2001). There are various paths through which arsenic enters our environment and affects human health in very serious manner (USNRC, 1997).

2.1 Sources of Arsenic

Of the various sources of arsenic in the environment, drinking water probably poses the greatest threat to human health. Airborne arsenic, particularly through occupational exposure, has also given rise to known health problem in some areas (Smedley and Kinniburgh, 2001). The principal anthropogenic sources include: the application of arsenic containing insecticides, the addition of commercial fertilizers and manure, the discharge of municipal and industrial sewage and wastewater, and the fallout of aerosols from ore smelters and fossils fuel combustion plants (Kamal, 1999). Various forms of arsenic have been utilized in several industries. Arsenic compounds are also used as catalysts, animal feed additives, corrosion inhibitors, and in veterinary medicines and tanning agents. Arsenic trioxide (As_2O_3) has been used as a poison since ancient times. Organoarsenicals have been used as a herbicide, pesticide, and dipping agent for sheep. Various arsenates (Cu, Zn, Pb), in combination with chromate, are still used for preservation of wood. Some forms and sources of arsenic are summarized in Table 2-1.

Until recently, arsenic was often not on the list of constituents in drinking water routinely analyzed by national laboratories, water utilities, and NGOs and so the body of information about the distribution of arsenic in drinking water is not as well know as for many other drinking water constituents. In recent years, it has become apparent that both the WHO guideline value and current national standards are quite frequently exceeded in drinking water sources, and often unexpectedly so. Indeed, arsenic is now recognized as the most serious contaminant in drinking water on worldwide basis. In areas of high arsenic concentration, drinking water provides a potentially major source of arsenic in the diet and so its early detection is of great importance (Smedley and Kinniburgh, 2001).

Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers), and rainwater. These sources are very variable in terms of arsenic risk. Besides, obvious point sources of arsenic contamination, high concentrations are

Table 2-1 Types and Sources of Arsenic

Types	Forms	Sources
Inorganic arsenic compounds	Arsenic trioxide, Arsenic pentaoxide, Sodium & potassium arsenic, arsenate	Insecticides, rodenticide, fungicides, wood preservatives, and herbicides
Organic arsenic compounds	Mono and dimethyl arsenic acids	Seafood, etc.
Arsenic gas		Produced in metal smelting and refining, Galvanizing and etching, lead plating, and making of silicon microchips
Gallium arsenide		It is likely to become a significant replacement for silicon in: computer chips, satellite dish antenna, light emitting diodes, and many other semiconductor devices

Source: Kamal, 1999

Note: arsenic intake by humans is probably greater from seafood than drinking water.
Organic form of arsenic in nature (food) is less toxic compared to inorganic arsenic compounds.

mainly found in groundwater. Theses are where the greatest number of, as yet unidentified, sources are likely to be found (Smedley and Kinniburgh, 2001).

2.2 Arsenic Distribution in the Environment

Since arsenic is widely used in our environment and it is toxic, there are many ways of spreading and contaminating the surroundings. Some examples are as follows:

a) Water pollution by arsenic is attributed to both human activities and geohydrolithological phenomena.
b) Contamination by leaching of arsenic waste from mining operations, and industrial and agricultural processes have been found in some countries.
c) Soil is the principal sink for arsenic, and as most arsenic residues have low solubility and low volatility, they generally accumulate in the top soil layers
d) Arsenic in soils can be derived either naturally from weathering of arsenic containing rocks and minerals or through inputs of wastes from human activities
e) Air pollution by arsenic is caused through various industrial processes like smelting, and manufacturing of insecticides and drugs (Kamal, 1999).

Figure 2-1 shows the complete cycle of arsenic distribution in the environment (Kamal, 1999). In a closed organic cycle for the total environment, some form of arsenic is present in all phases of the ecosystem. Very few of the organic arsenicals have been identified, but a volatile arsine is suggested at present. The overall pathways of environmental movement of trace elements, which include arsenic, and a proposed cycle of toxic-element movement through the "geocycle," with arsenic from natural weathering processes available later to microorganisms, plants, and animals, are shown in Figure 2-2 (USNRC, 1997).

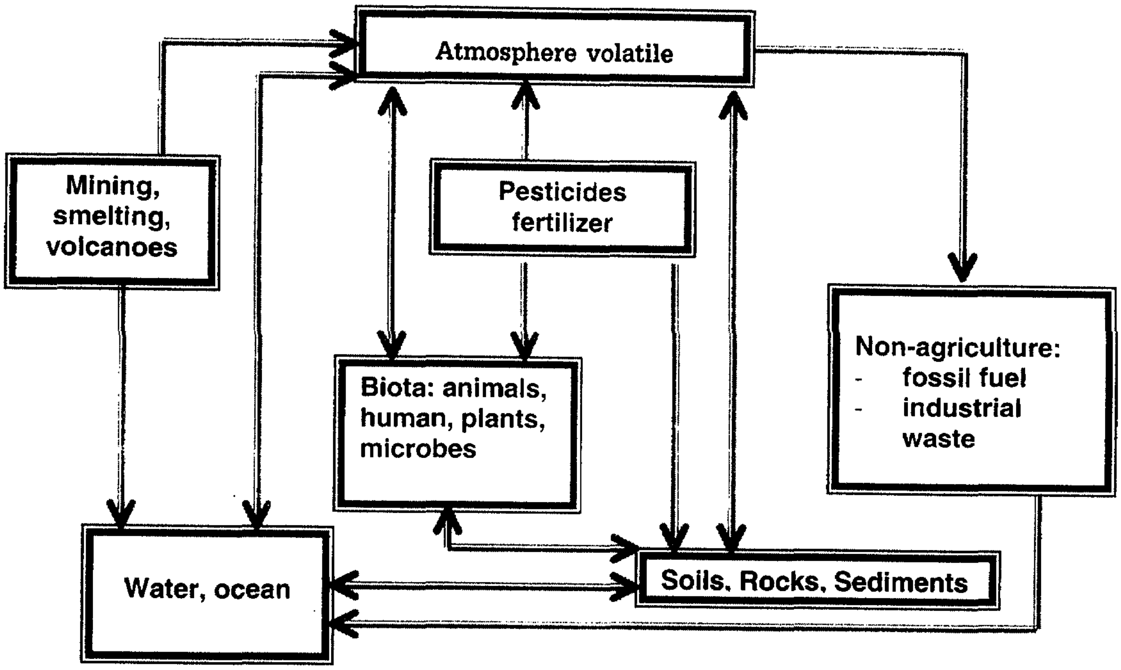
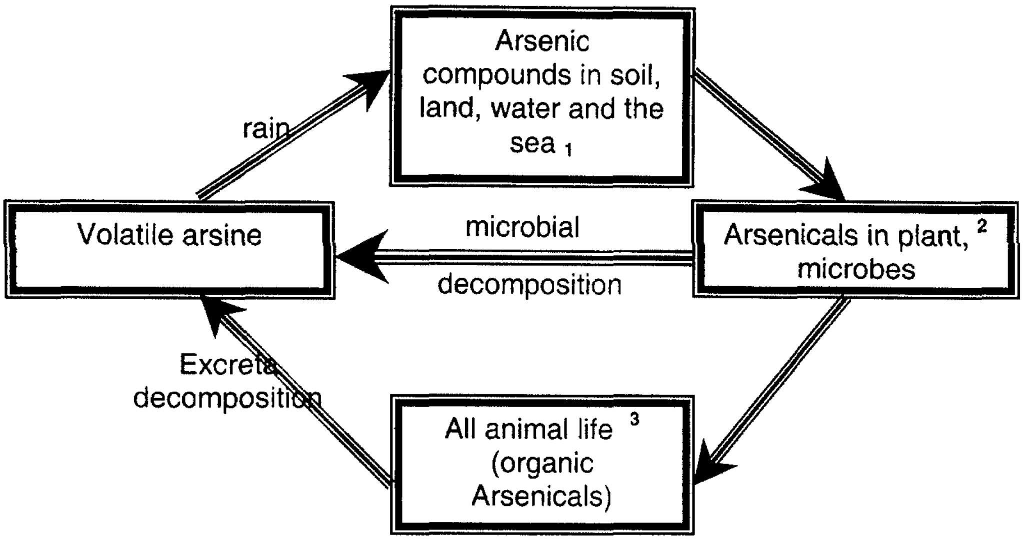


Figure 2-1 Transfer Cycle of Arsenic in the Environment (Source: Kamal, 1999)



1. the cycle in nature involves organic arsenicals; few identified
2. marine algae may contain arsenic at up to 9 ppm, land plants generally at less than 0.5 ppm
3. edible tissues of food animals contain, on average, below 0.5 ppm; fish, 0.5-3 ppm; and crustaceans, 3-100 ppm

Figure 2-2 Arsenic Cycle (Source: USNRC, 1997)

A model for arsenic cycle in agronomic ecosystem contains 12 possible transfers to and from a field for the organoarsenical herbicides. The model shows that arsenic transfer involved reduction to methylarsines, soil erosion, and crop uptake were the primary redistribution mechanisms in this model. Arsenic is mobile and nonaccumulative in the air, plant and water phases of the agronomic ecosystem. Arsenicals do accumulate in soil, but redistribution mechanisms preclude hazardous accumulations at a given site. This model is shown in Figure 2-3 (USNRC, 1997).

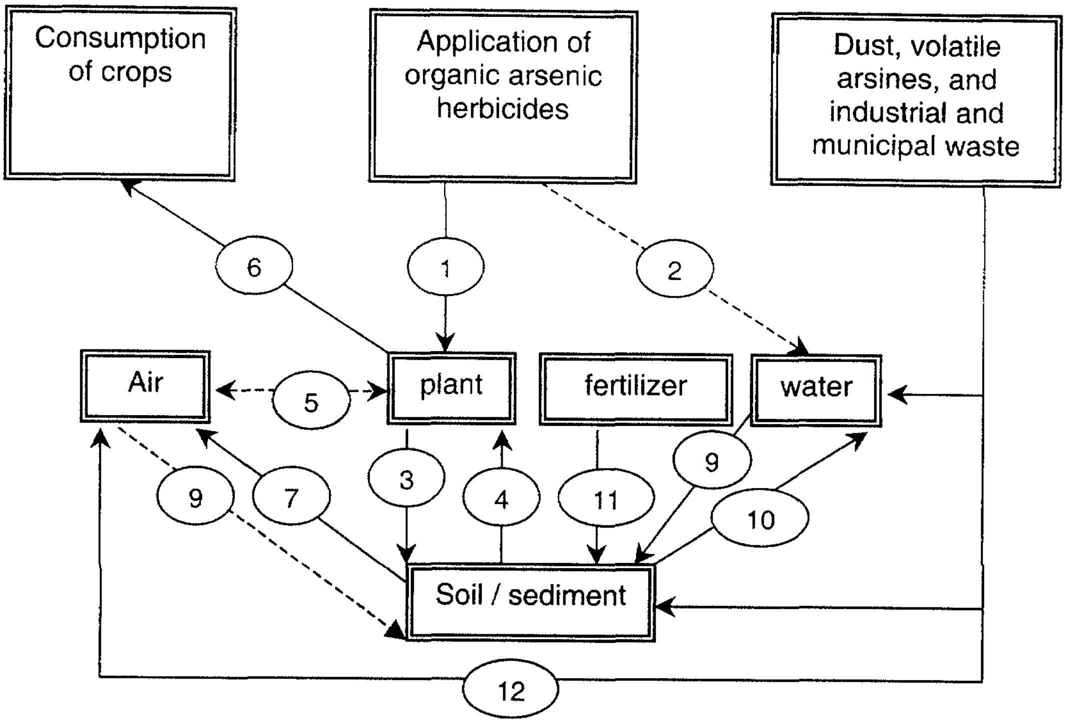


Figure 2-3 A Model for the Arsenic Cycle in an Agronomic Ecosystem. (Source: USNRC, 1997)

Inputs into the environment and a redistribution of arsenic in the terrestrial ecosystem are presented in Figure 2-4. Natural inputs are from volcanic action, decay of plant matter, and weathering of minerals within the soil, whereas man-made sources of arsenic are combustion of coal and oil, smelting of ores, and use of fertilizers and pesticides. The largest sink for man-made arsenic in the environment is soil. Man's activity does cause high environmental concentrations at some locations. Arsenic tended to be distributed continuously through the system as a function of temperature, and there is a definite tendency for concentration of arsenic in the lower temperature deposits in the combustion system (USNRC, 1997).

2.3 Arsenic in Groundwater

Several processes have been proposed to explain the release of sedimentary arsenic into ground water and the main reactions of arsenic in ground water. These include:

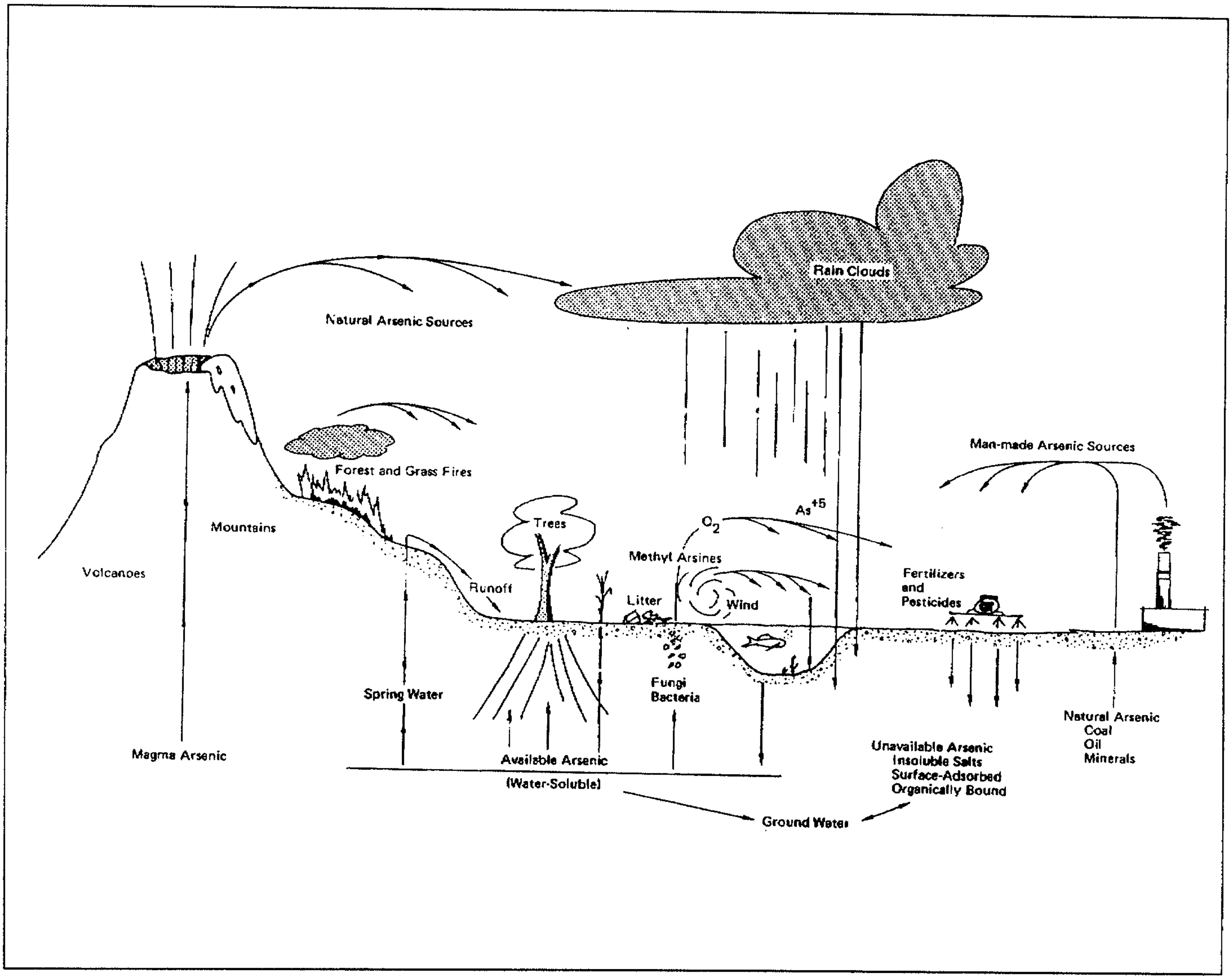


Figure 2-4 Environmental transfer of arsenic (source: USNRC, 1997)

a) Oxidation of Iron Pyrite and Arsenopyrites by Air

Charkraborti and his colleagues studied and confirmed the presence of arsenic in iron pyrite sediments. They suggested that the high volume extraction of ground water in West Bengal has exposed the deltaic sediments to air, which through oxidation reaction causes the decomposition of iron pyrites to ferrous sulfate ($FeSO_4$), ferric sulfate ($Fe_2(SO_4)_3$) and sulfuric acid (Than and Long, 2000). The process frees up arsenic, which is then oxidized into arsenite and arsenate, both of which are soluble in ground water. The equations are (Kamal, 1999):

$$\underset{\text{Arsenopyrite}}{\mathrm{FeAsS}} \xrightarrow{\text{Oxidized in air}} \underset{\text{Arsenic trioxide}}{\mathrm{As_2O_3}} + \mathrm{H_2O} \rightarrow \underset{\text{Arsenous acid}}{\mathrm{H_2AsO_3}}$$

$$\underset{\text{Arsenopyrite}}{FeAsS} \xrightarrow{\text{Oxidized in air}} \underset{\text{Arsenic pentaoxide}}{As_2O_5} + H_2O \longrightarrow \underset{\text{Arsenic acid}}{H_2AsO_4}$$

In the last two decades, the Green Revolution at Bengal had lowered the ground water level and thus the release of arsenic.

b) Reduction Reaction of Arseniferrous Iron-oxyhydroxides

The oxidation theory however fails to explain the increase in arsenic level in deeper wells and anoxic condition. Ross Nickson of the University College London suggested that in deep wells, arsenic is released when arseniferous iron-oxyhydroxides are reduced in anoxic water. Nickson observed that arsenic-rich ground water is mostly restricted to the alluvial aquifers of the Ganges Delta and concluded that the source of arsenic must lie in the Ganges source region upstream of Bangladesh (Than and Long, 2000).

c) Microorganisms

Le Blanc's analyses of surface water samples taken from around Montpellier (France), a region with large heavy metal deposits. Le Blanc's data indicated that the pH's fall in the range from 2.5 to 3.5, and arsenic contents fall in the range of 100 to 300 mg/L. The presence of a group of microorganism, the stromatolytique was found which Le Blanc considered the main cause of the high level of arsenic content in water. Le Blanc explained that the microorganism acts as catalyst and provides oxygen for the oxidation of metal sulfides producing sulfuric acid and metals. The acid then attacks on the metals to produce metal sulfate and release soluble arsenic in water (Than and Long, 2000).

Mining and mineral processing is the most commonly reported anthropogenic source of arsenic contamination in groundwater as has been observed in a number of countries with affected areas being characterized by their close proximity to mining operations. Contamination is particularly likely to occur from rainwater percolation through the piles of mining waste, and many pollute both surface and groundwater. Industrial waste disposal can cause localized but serious arsenic contamination in groundwater (Smedley and Kinniburgh, 2001).

d) Oxidation and Reduction

Unconfined aquifers subjected to oxidation and reduction, and underlain by peaty clay and/or clay layer is responsible for arsenic contamination. The continued abstraction of water from unconfined aquifer releases pentavalent arsenic and is transformed into trivalent arsenic on reduction to become soluble and mobile in water (Kamal, 1999).

2.4 Arsenic in Natural Water – Aqueous Speciation

Arsenic is problematic in a number of major aquifers as a result of its relatively high mobility under the pH-redox conditions of most natural groundwater and its high toxicity. High concentrations are found under both oxidizing and reducing conditions. Most problems are found in young aquifers with slow rates of groundwater flow such that aquifer flushing, and hence arsenic removal, has been restricted (Smedley and Kinniburgh, 2001).

According to United Nations Synthesis Report on Arsenic in Drinking Water, arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements *in its sensitivity* to mobilization at pH value typically found in groundwater (pH 6.5-8.5) and under both oxidizing and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3, 0,+3, +5) but in natural waters is mostly found in inorganic form as oxidation of trivalent arsenite, As (III) or pentavalent arsenate, As(V). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollution (Smedley and Kinniburgh, 2001).

Most toxic trace metals occur in solution as cations, which generally become increasingly insoluble as the pH increases. At the near-neutral pH typical of most groundwater, the solubility of most trace-metal cations is severely limited by precipitation as, or coprecipitation with, an oxide, hydroxides, clay or organic matter. In contrast, most oxyanions including arsenate tend to become less strongly sorbed as the pH increases. Under some conditions at least, the anions can persist in solution relatively high concentrations (tens of µg/L) even at near-neutral pH values. Therefore the oxyanion-forming element, As, is some of the most common trace contaminants in groundwater. Arsenic is unique in being relatively mobile under reduced condition. It can be found at concentration in the mg/L range when all other oxyanion-forming metals are present in the µg/L range (Smedley and Kinniburgh, 2001).

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing condition, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HasO_4^{2-}$ becomes dominant ($H_3AsO_4^0$ and AsO_4^{3-} may be present in the extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about 9.2, the unchanged arsenite species $H_3AsO_3^0$ will predominate (Figure 2-5).

Affected oxidizing aquifers are typically in arid or semi-arid zones where recharge is low. In these, pH and salinity are often high, arsenic is dominated by As (V) and may be associated with high concentrations of other anions and oxyanions (F, HCO_3, V, Mo, Se, U, B, Be). Arsenic mobilization is probably a result of desorption from oxide minerals under the high-pH conditions. Examples include the Quaternary volcanic and sedimentary aquifers of the central Argentina, northern Chile, north central Mexico and parts of southwest USA (Smedley and Kinniburgh, 2001).

Affected reducing aquifers are typified by groundwater with high Fe, Mn and NH_4 concentrations and often show evidence of sulfate reduction. Arsenic (III) forms a high proportion of the total arsenic present. Mobilization of arsenic is likely to be dominantly by reductive desorption from, and dissolution of, iron-oxide minerals.

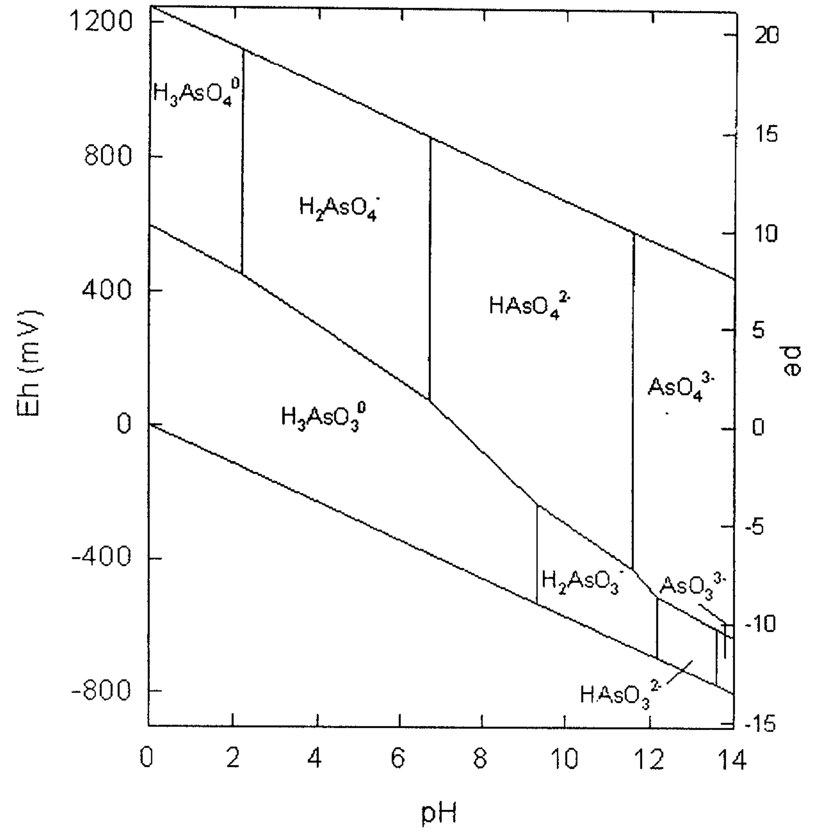


Figure 2-5 Eh-pH Diagram of Aqueous Arsenic Species in the System As-O_2-H_2O at 25 °C and 1 bar Total Pressure (Source: Smedley and Kinniburgh, 2001)

Examples include the Quaternary aquifers of Bangladesh and West Bengal, Inner Mongolia, Taiwan, Hungary and parts of southwest USA (Smedley and Kinniburgh, 2001).

Arsenic is widely distributed in the environment, where its source, mobility, and fate can be understood in the context of ubiquitous redox reactions that involve oxygen, sulfur, iron, and organic matter. Arsenic in soil and rock is commonly associated with either iron oxyhydroxides (FeOOH) or iron sulfides (FeS_x). In oxidizing environments, weathering of sulfides may source arsenic and this mechanism explains pollution of surface waters with arsenic. Such a mechanism cannot explain the widespread occurrence of arsenic in anoxic environments that are characteristic of confined and deep unconfined aquifers, where reduction of FeOH is the common source of dissolved arsenic in groundwater (Smedley and Kinniburgh, 2001).

CHAPTER III

HEALTH EFFECTS OF ARSENIC AND ITS TOXICITY

A review of the evidence of health effects in humans resulting from ingestion of inorganic arsenic reported in the large majority of the studies concluded that the source of exposure is drinking water contaminated with inorganic arsenic from natural sources. A few studies involve other sources of exposure, however, such as industrially contaminated drinking water, medicinal use of arsenic and arsenical pesticides.

3.1 Toxicity of Arsenic

Exposure to environmental contaminants including arsenic can occur through one or more of three pathways, inhalation, ingestion and dermal absorption. In the case of arsenic, available evidence suggests that non-occupational exposure occurs primarily through the ingestion of food and water, with the inhalation pathway playing only a minor role. Food is more commonly the main contributor to total intake but in areas where drinking waters contain relatively high levels of arsenic, drinking water may be the most important source of arsenic intake. Intake via dermal absorption is believed to be negligible (Abernathy and Morgan, 2001).

a) Exposure

Human exposure to inorganic arsenic occurs through inhalation, or skin absorption. Inhalation usually occurs occupationally or during cigarette smoking. In unpolluted areas the amount of arsenic inhaled is about 0.05 mg/day or less. Depending on the amount of arsenic in tobacco, an average smoker may inhale 20 μ g/day. Skin exposure may occur among smelter workers and workers exposed in production and use of arsenic containing pesticides. In most food stuffs arsenic mainly occurs in the organic form and concentrations are usually less than 1 μg/kg. However, marine fish may contain arsenic up to 5 μg/kg. Ingestion occurs mainly by drinking contaminated water.

b) Mechanisms

Reactions of arsenic in human body are absorption, excretion and retention. All is influenced by the amount and chemical forms in which it is ingested. Most ingested arsenic is absorbed through the gastrointestinal tract and lungs into blood stream. It is distributed in the lungs, liver, kidney, spleen, and intestine within 24 hr of ingestion and to skin, hair and bone within 2 weeks. Inorganic arsenic entering the body undergoes methylation, which is a detoxification mechanism. First monomethylarsonate (MMA) is produced, which is then methylated to dimethylarsinate (DMA). The metabolites are less toxic than inorganic arsenic and bind less to tissues. In human body, trivalent arsenic is oxidized to the pentavalent state. The opposite can also take place. Arsenic (III) in the body combines with sulphydryl containing substances and inhibits the activity of many enzymes. It interferes with cell enzymes, cell respiration and mitosis (Kamal, 1999).

Toxicity of As (III) is explained in terms of its great affinity for thiol group (S-H) in enzymes and proteins. Enzymes and protein are then inhibited (Kamal, 1999). The mechanism is shown in Figure 3-1.

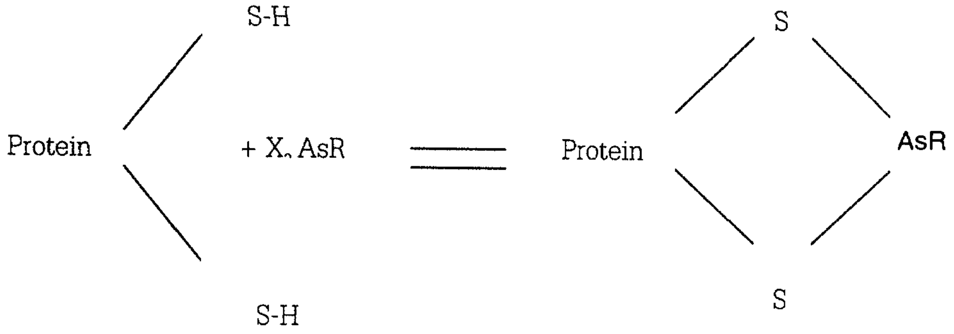


Figure 3-1 Affinity of As (III) for Thiol Group in Emzymes and Proteins (Kamal, 1999)

Arsenic affects all the organs and systems of the body. The toxicity of arsenic compounds depends on the chemical and physical forms of the compound, the route by which it enters and the age and sex of the exposed individuals. Arsenite (III) is more toxic than arsenate (V). Arsenic in solution is more toxic than undissolved arsenic. Toxicity in order can be represented as follows (Kamal, 1999):

Arsine > inorganic arsenic (III) > organic arsenic (V) > Arsonium compounds and elemental arsenic

C) Excretion

Among ingested arsenic, 5-10 % is excreted in feces and 90-95 % in urine. Small amounts are recovered in bile, feces, saliva, and breast milk. The major metabolites found in the urine are methylarsenic acid and dimethylarsenic acid. A portion of the absorbed arsenic is deposited in the skin, hair and nails where it is firmly bound to keratin. Storage in these metabolically dead tissues is responsible for the slow elimination rate of arsenic. Arsenic in urine, hair and nails has been used as an index for monitoring the exposure of victim and urinary arsenic is generally reported as the most reliable indicator of recent exposure to inorganic arsenic. Blood arsenic is not considered a good indicator because it is cleared within a few hours of absorption. After administration, arsenic appears in urine within 2 to 8 hours. Approximately 10-30% of the ingested arsenic is directly excreted as the inorganic form, 10-20% as methylarsenic acid and 60-80% as dimethylarsenic acid. Unexposed people show arsenic concentration in urine 0.01-0.05 mg/L, in hair usually below 1 mg/kg, and in blood 0.0015-0.0025 mg/L (Kamal, 1999).

3.2 Health Effects of Arsenic

Arsenic has long been associated with toxic effects, producing marked impacts on health after both oral and inhalation exposure. Effects range from acute lethality to chronic effects, such as cancer and diseases of the vascular system. Studies in laboratory animals have demonstrated that the toxicity of arsenic is dependent on its form and its oxidation state. It is generally recognized that the soluble inorganic arsenicals are more toxic than the organic ones, and the trivalent forms (AsIII) are more toxic than the pentavalent ones (AsV). There are multiple end-points, with several different organ systems being affected, including the skin and the respiratory, cardiovascular, immune, genitourinary, reproductive, gastrointestinal and nervous systems (Abernathy and Morgan, 2001).

Arsenic can cause acute and chronic toxicity. Acute toxicity occurs only from the ingestion of arsenic compounds; symptoms include severe vomiting and diarrhea, muscular cramps, facial edema and cardiac abnormalities. Ingestion dose of 70-180 mg of arsenic (III) oxide has been reported to be fatal in people. Symptoms may occur within a few minutes of exposure if the arsenic compound is in solution but may be delayed for several hours if it is solid or taken with a meal. Chronic toxicity is best discussed in terms of organ systems affected, e.g., the skin, nervous system, liver, cardiovascular system, and respiratory tract. Chronic effects develop very insidiously after six months to 2 years or more, depending on the amount of arsenic ingested, the length of exposure, and the immunity level of the person (Kamal, 1999).

Clinical manifestations stages:

- Initial stage
    - Skin color becomes black
    - Skin become rough and tough
    - Eyes become red-conjunctivitis
    - Pain in inhaling-bronchitis
    - vomitting and diarrhea-gastroenteritis
- Middle stage
    - Black and white spots on the skin-Leukomelanosite
    - Palm and sole are affected by hard nodules
    - Swelling of legs-non pitting edema
    - Peripheral neuropathy
    - Complications of kidney and liver
- Final stage
    - Infectious of lateral organs-Gangrene
    - Cancer in lungs, kidney and uterus
    - Total liver damage
    - Total kidney damage

a) Short-term Effects

Ingestion of large doses of arsenic usually results in symptoms within 30 to 60 minutes, but may be delayed when taken with food. Acute arsenic poisoning usually starts with a metallic or garlic-like taste, burning lips and dysphagia. Violent vomiting may ensue and may eventually lead to hematemesis. These gastrointestinal symptoms are the result of intestinal injury caused by dilatation of splanchnic vessels leading to mucosal vesiculation. These vesicles rupture causing bleeding, diarrhoea, and protein wasting. Gastrointestinal symptoms often result in dehydration and electrolyte imbalance, and may lead to the development of hypotension and hypoxia. After the initial gastrointestinal problems, multiorgan failures may occur, followed by death.

Survivors of acute arsenic poisoning have been shown to develop hepatomegaly, melanosis, bone marrow suppression, hemolysis, and polyneuropathy resulting from damage to the peripheral nervous system (Abernathy and Morgan, 2001).

b) Chronic Arsenic Exposure

Chronic exposure to lower levels of arsenic has long since been linked to adverse health effects in human populations. The earliest reports date back to the latter part of the 19th century when the onset of skin effects (including pigmentation changes, hyperkerotosis and skin cancers) were linked to the consumption of arsenic in medicines and drinking water. In the early 1900s, numerous reports of skin disorders in Argentina, Chile, Mexico and Taiwan, which were attributed to arsenic exposure via drinking water, were published. In the 1940s the discovery of a case of lung cancer, believed to be the result of exposure to arsenical dust in a British factory, sparked a series of more detailed investigations into the matter. These in turn revealed unexpectedly high lung cancer rates in a number of different occupational exposure situations (Abernathy and Morgan, 2001).

Vascular Diseases:

Exposure to arsenic has been linked to various vascular diseases affecting both the large and small blood vessels. Much of the early work on arsenic and vascular disease focused on effects in small vessels (i.e. BFD and other peripheral vascular diseases), while later research has been directed primarily at effects in larger vessels (cardiovascular and cerebrovascular diseases). Some work has also been done on the possible link between arsenic exposure and hypertension (a known vascular disease risk-factor) (Abernathy and Morgan, 2001).

Peripheral Vascular Diseases

As mentioned above, arsenic has been linked to development of the peripheral artery disease, Blackfoot disease (BFD) that is endemic in parts of Taiwan. The condition is characterized by an insidious onset of coldness and numbness in the feet, followed by ulceration, black discoloration and subsequently dry gangrene of the affected parts (Abernathy and Morgan, 2001).

Cardio- and Cerebrovascular Diseases

Studies linking exposure to arsenic and mortality from cardiovascular diseases are also summarized in Table 3-1. Whereas studies in Taiwan involving BDF-patients have shown significant associations, including exposure-response relationships between arsenic concentrations in well waters and death rates from cardiovascular disease, drinking water studies conducted in other world regions, albeit at lower exposure levels, have been less conclusive (Abernathy and Morgan, 2001).

In contrast, there is only limited evidence for an association between arsenic exposure and cerebrovascular diseases. A few Taiwanese studies have shown an elevated risk of death from cerebrovascular disease with increasing arsenic exposure. Other studies in this region have, however, not produced similar findings; elevations

Table 3-1 Effects of Arsenic on Vascular System

Study Population	Source and level of arsenic exposure	Health effects, metric of exposure and and measure of association				Comments
241 BFD patients and 759 age-sex-residence matched controls	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Exp. time yrs	Peripheral vascular disease OR			OR adjusted for nutritional factors, family history of BFD, education, and evidence of skin lesions
		<1	1.0			
		1-29	3.0			
		>30	3.4 $p<0.001$ for trend			
789 BFD patients	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	End point	$SMR_{national}$	SMR_{local}		No adjustment for potential confounders
		Periph. vasc. Disease	1243***	351***		
		Cardio-vasc. Disease	209***	160**		
		Cerebrovasc. Accid.	118 NS	107 NS		
		*** $p < 0.001$; ** $p<0.01$				
Mortality and population data for 1973-1986 in 42 villages in Taiwan	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Age adjusted mortality rates per 100,000 As exposure				
			< 0.30	0.30-0.59	≥0.60ppm	No increase in cerebrovascular accidents in either males or females at any exposure dose.
		All vascular diseases				
		Males	364	421	573	Used published Taiwan data from 1964 to 1966; The Natelson method was used (Tseng et al, 1968; Kuo, 1964).
		females	278	371	386	
		peripheral vascular diseases				
		males	23	58	60	
		females	18	48	35	
		cardiovascular diseases				
		males	126	154	260	
		females	1	153	145	
382 men and 516 women residing in villages in BFD-endemic area	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Hypertension				Exposure determined from residential history and village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages, Natelson method).
		Cum expos. mg x L^{-1}yr	OR			ORs adjusted for age, sex, disease status of diabetes, proteinuria, body mass index, fasting serum triglyceride levels
		0	1.0			
		0.1 - 6.3	0.8 (0.2 – 3.2)			
		6.4 - 10.8	2.3 (0.8 – 6.8)			
		10.9 - 14.7	3.4 (1.2 – 9.2)			
		14.8 - 18.5	3.8 (1.4 – 10.3)			
		>18.5	2.9 (1.1 – 7.3)			
		unknown	1.5 (0.6 – 4.2)			

Source: Abernathy and Morgan, 2001

Table 3-1 Effects of Arsenic on Vascular System (contd.)

Study Population	Source and level of arsenic exposure	Health effects, metric of exposure and and measure of association	Comments
582 residents of BFD-endemic area	Drinking water As range 1 to 1097 µg/L, 50% between 300 and 700 µg/L	Exposure category mg/l years — Periph. vasc. dis. OR (CI 95%) 0 — 1 1 - 19 — 3.1 (0.9 – 10.4) > 20 — 4.8 (1.4 – 16.7)	142 water samples from 114 well analysed for As Used ratio of ankle and brachial systolic arterial pressure as indicator of PVD. Measurement by Doppler ultrasound. Those with ABI of >1.20 excluded due to possible misclassification of peripheral vascular disease. Adjusted for age, sex, body mass index, cigarette smoking, diabetes mellitus, hypertension, plasma lipids
Residents of 60 villages in arsenic endemic area in Taiwan. 1,355,915 person years	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Cumulative mortality from birth to age 79 from ischemic heart disease (1973-1986) Exposure category As mg/L — cumulative mortality % < 0.10 — 3.4 0.10-0.34 — 3.5 0.35-0.59 — 4.7 ≥0.60 — 6.6	Exposure determined from village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages).
263 BFD patients and 2293 referents from the 60 villages above	Same as above	Expo category mg•l^{-1} •yrs — Relative risk of isch. heart disease (CI) 0 — 1.00 <10 — 2.2 (0.46-10.2) 10.0-19.9 — 3.3 (0.83-13.4) 20 + — 4.9 (1.4-17.7)	Exposure determined from village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages). Small number of deaths. Cox proportional hazard model adjusted for age, sex, smoking, body mass index, serum cholesterol, serum triglyceride level, hypertension, diabetes mellitus black foot disease. Relative risk of BFD patients vs non-BFD, 2.48 (1.1.4-5.4)
74 cases of ISHD and 193 referents from the population of the Chen et al, 1995 study	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Duration of drinking As containing water, yr — IHD — OR (CI) >13 — 1.0 13-29 — 2.6 (1.0 - 6.4) ≥ 30 — 2.9 (1.0 - 8.3)	Exposure determined from village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages). OR Age- and sex adjusted No significant association with cumulative arsenic exposure

Source: Abernathy and Morgan, 2001

Table 3-1 Effects of Arsenic on Vascular System (contd.)

Study Population	Source and level of arsenic exposure	Health effects, metric of exposure and and measure of association	Comments
4058 members of The Church of Jesus Christ of Latter Day Saints in Millard Co., Utah	Range of exposure from 3.5 µg/L to 620 µg/L; median exposures range from 14 to 166 µg/L depending on location.	Males SMR(CI) / Females SMR(CI) Cerebrovasc. Dis. 79 (62-99) / 87 (71-106) All heart dis. 80 (73-88) / 81 (72-91) Isch. heart dis. 76 (67-85) / 64 (53-76) Dis. of arter. & capill. 93 (61-135) / 86 (52-132) Arteriosclerosis 124 (69-204) / 118 (68-188) Aortic aneurysm 76 (35-144) / 48 (6-173) Hypert. heart dis. 220 (136-336) / 173 (111-258) Other heart dis. 94 (71-122) / 143 (111-180)	for 2073 cohort members, "most" had at least 20 years history of exposure in their respective towns. The balance of the cohort (n = 1985) were included if they had spent any lenght of time in the arsenic-affected community. Existing and historic arsenic concentrations used. Death rates for the state of Utah for the years 1960 to 1992 were used to generate the expected deaths. No indication of exposure-response relationship for any of the vascular health effects. Exposure for the highest exposure group likely to be overestimated because of introduction of low-arsenic water into one community, which was not considered in the analysis
1595 people from 4 villages in Bangladesh. 1481 exposed to arsenic and 114 non exposed controls	Arsenic in drinking water. For 39, 36, 18, and 7%, the exposure was <0.5, 0.5 - 1, and >1 mg/L, and unknown, resp.	Expo category mg/L yrs — PR* for hypertension (CI) 0 — 0.8 (0.3 – 1.7) < 5 — 1.5 (0.7 – 2.9) 5 - 10 — 2.2 (1.1 – 4.4) >10 — 3.0 (1.5 – 5.8)	Used existing arsenic water measurements (measured by flow-injection hydride generation AAS). Hypertension defined as >140 mmHg systolic BP together with >90 mmHg diastolic BP Study limited to the 1595 individuals out of 1794 eligible, who were at home at the time of the interview. 114 persons were considered unexposed and were used as the reference group. *PR = Mantel-Haenszel prevalence ratio adjusted for age, sex and BMI
478 patients treated with Fowler's solution for 2 weeks - 12 years in 1946-60 and followed until 1990	Cumulative dose <500 mg, 500-999 mg, 1000-1999mg; ≥2000 mg	Mortality from vascular diseases SMR — CI Cardiovacular disease 91 — 74 – 110 Ischemic disease 85 — 60 – 110 Cerebrovascular disease 72 — 40-110	The SMR's for the whole group. No dose-response relationship observed, but the numbers were small.

Source: Abernathy and Morgan, 2001

Table 3-1 Effects of Arsenic on Vascular System (contd.)

Study Population	Source and level of arsenic exposure	Health effects, metric of exposure and and measure of association	Comments
2802 men who worked in the smelter for ≥ 1 yr during 1940 -64, vital status followed 1941-1986	Ambient air in a smelter	Cum. exp. mg•m^{-3}•yr — Isch. Heart dis SMR — Cases < 0.75 — 108 — 55 0.75 - — 103 — 67 2.0 — 107 — 74 4.0 — 122 — 87 8.0 — 128 — 91 20 — 132 — 46 ≥45 — 90 — 8	Exposure assessed from industrial hygiene data (available from 1938) and extrapolation from urinary arsenic concentrations
2802 men who worked in the smelter for ≥ 1 yr during 1940-64, vital status followed 1940-1976 (same cohort as in Enterline et al., 1995, but a shorter follow-up time)	Ambient air in a smelter	Cum. exp. mg•m^{-3}•yr — Isch. Heart dis RR — CI < 0.75 — 1.0 0.75 –1.999 — 0.9 — 0.64-1.3 2.0-3.999 — 1.1 — 0.78-1.6 4.0-7.999 — 1.4 — 0.98-2.0 8.0-19.999 — 1.7 — 1.2-2.5 >20 — 1.5 — 0.95-2.5	20-year lag and work status imcluded in the model No effects found for cerebrovascular disease.
8104 white males employed for ≥ 1 yr before 1957. Vital status followed 1938 - 1987.	Ambient air in a smelter	Arteriosclerosis and coronary heart disease SMR 105 (CI 99-110; Cerebrovascular disease SMR 103 CI (93-115)	
3916 men who worked ≥ 3 mo in the smelter in 1928-1967. Vital status followed until 1981	Ambient air in a smelter. Categories for cumulative exposure < 0.25, 0.25 - 15, 15-100 and ≥ 100 mg m^{3} yr	Ischaemic heart disease SMR 107 (CI 97-117); Cerebrovascular disease SMR 106 (CI 88-126)	In an earlier report (Axelson et al, 1978), a two-fold increase in mortality from cardiovascular disease
839 copper smelter workers	Ambient air in a smelter	7 Deaths from heart diseases vs 14.9 expected	
1974 gold miners	Air-borne exposure to arsenic, radon, silica	Ischaemic heart disease SMR 103 (173 expected cases)	

Source: Abernathy and Morgan, 200

in mortality rates due to cerebrovascular diseases, if present at all, are only small compared with those for cardiovascular disease. Furthermore, studies from other countries provide only very limited support for the Taiwanese findings (Abernathy and Morgan, 2001).

Hypertension

Evidence for an association between long-term exposure to arsenic and the prevalence of hypertension is limited to only a few studies, two environmental and one occupational. Nevertheless, all three studies found elevations in blood pressure with arsenic exposure (Abernathy and Morgan, 2001).

Cancer Effects:

The carcinogenic role of arsenic compounds was first noted over 100 years ago in one observation that an unusual number of skin tumors develop in patients treated with arsenicals. In 1980 review of arsenic, the International Agency for Research on Cancer (IARC 1980) determined that inorganic arsenic compounds are skin and lung (via inhalation) carcinogens in humans. Data suggesting an increased risk for cancer at other sites were noted to be inadequate for evaluation. Since 1980, several addition studies of cancer and exposure to arsenic in drinking water have been completed (Abernathy and Morgan, 2001).

The earliest indications that exposure to arsenic and cancer were related date back to the late 1930s and early 1940s. In the seminal investigation of 1948, a remarkably elevated relative cancer mortality rate from lung and skin cancer was observed amongst workers at a sheep-dip factory that manufactured sodium arsenite. Original suspicions that ingested arsenic could cause lung cancer were provided by a study in the Argentine province of Cordoba, where mortality records for all deaths occurring between 1949 and 1959 in areas with high arsenic level in drinking water (weighted average approximately 600 µg/L) were compared with cause-specific mortality rates from the entire province. Thirty five percent of all cancer deaths were related to respiratory organs (Abernathy and Morgan, 2001).

Detailed investigations into elevated cancer risks amongst copper smelter workers exposed to arsenic in the air were initiated in the 1960s; these studies were primarily concerned with the development of respiratory cancers, in particular lung cancers. Over the past 20-30 years, research effort has also focused on the likely relationship between various types of cancers and exposure to arsenic through the consumption of drinking water. Much of this type of work has centred on populations in the BFD-endemic parts of Taiwan, but there are reports of elevated cancer risks at multiple sites (notably lung, skin, bladder, kidney and liver) from other parts of the world including Japan, Chile and Argentina where subsets of the population are exposed to arsenic-contaminated drinking water. A considerable body of scientific research work has accumulated on the subject and several comprehensive reviews have been published in recent years (Abernathy and Morgan, 2001).

Cancers of the Lung, Bladder and Kidney

Exposures via Drinking Water:

The link between cancers of the lung, bladder and kidney and arsenic exposure in drinking water has been most thoroughly studied in Taiwan. Here, studies of differing design have consistently shown high mortality risks from lung, bladder and kidney cancers among populations exposed to arsenic via drinking water. Moreover, where exposure-response relationships have been investigated, the risk of cancer for these sites increases with increasing exposure. Reports of increased cancer risk from exposure to arsenic in drinking water are not confined to Taiwan; studies from Argentina, Chile Japan and Finland have also demonstrated positive associations (Abernathy and Morgan, 2001).

Increased mortality from lung and bladder cancers was also found to be linked to increased drinking water arsenic concentrations in the eastern region of the Cordoba province in Argentina (Abernathy and Morgan, 2001).

Not all studies of populations exposed to arsenic via drinking water have conclusively shown positive findings for increased, lung, bladder and kidney cancer. Several mortality studies from the USA, for example, have not shown positive associations between ingested arsenic and lung cancer. An ecological study based on records of average drinking water arsenic concentration at the county level found no significant excess county lung cancer mortality (Abernathy and Morgan, 2001).

Studies in Belgium and Australia have also failed to find conclusive evidence of a link between arsenic exposure in drinking water and cancers of the lung, bladder and kidney. One study reported that mortality ratios did not support an association of cancer with drinking water exposures in a population living in the vicinity of a conglomeration of non-ferrous smelters. Arsenic concentrations were again relatively low, the area of highest exposure having measured concentrations in the range 20-50 µg/L (Abernathy and Morgan, 2001).

Exposures via Inhalation:

Studies on populations occupationally exposed to arsenic, such as non-ferrous metal smelter workers, pesticide manufacturers and miners, have consistently demonstrated an excess lung cancer risk among those exposed. Dose-response relationships have been investigated in those populations where there is sufficient information on the levels of exposure. The most important studies of this type are based on data obtained from three copper smelters, in Tacoma (Washington, USA), Anaconda (Montana, USA) and Rönnskär (Sweden). In all three cohorts, a statistically significant increase in lung cancer risk with increasing exposure has been demonstrated (Abernathy and Morgan, 2001).

Increased lung cancer risks have also been observed in workers employed at pesticide manufacturing plants and amongst tin miners in the UK and China and gold miners in France, Canada and Australia. Furthermore, several studies have reported an increased mortality from lung cancer in populations residing in areas close to arsenic-emitting industries, including for example, non-ferrous metal smelter complexes and factories producing arsenical pesticides (Abernathy and Morgan, 2001).

In contrast to the situation for lung cancers, kidney or bladder cancer risks are not consistently elevated in studies among people occupationally exposed to arsenic. Although early autopsy series on wine growers have linked exposure to arsenic to hepatic angiosarcoma, later studies have failed to provide conclusive evidence for such a link. This difference between the occupational and environmental studies may reflect lower systemic concentrations of arsenic after inhalation exposure (Abernathy and Morgan, 2001).

Skin Cancer and Precancerous Lesions of the Skin

Several early case reports have suggested that arsenic from medicinal use, drinking water and occupational exposure may be related to skin diseases, including cancer. Exposure to arsenic via drinking water has since been shown to be associated with an increased risk of skin cancer and other skin diseases (Abernathy and Morgan, 2001).

Skin cancer often arises from a keratotic change, the developed forms of which are classified as Bowen's disease; keratosis in turn may be preceded by disturbances in the skin pigmentation (hyper- and/or hypopigmentation). Arsenical skin cancers are usually squamous or basal in histologic type and arise primarily on unexposed areas of the body, including the palms and feet. It has been hypothesized that arsenic combines with sulphydryl groups in body tissues and interferes with pyruvate-oxidase activity, both mechanisms that are associated with cancers of the skin (Abernathy and Morgan, 2001).

A series of studies from BFD-endemic parts of Taiwan have clearly demonstrated the existence of an exposure-response relationship between the magnitude of arsenic exposure and incidence of skin cancer and other manifestations including keratosis and hyperpigmentation (Abernathy and Morgan, 2001).

Evidence for the link between skin cancers and arsenic is further supported by the results of studies conducted in other world regions including Argentina, Chile, and Mexico. Recent studies from West Bengal, India and Bangladesh in populations with a history of exposure to arsenic-contaminated drinking water, have documented similar findings. In contrast, studies carried out in the USA have not shown any excess of skin disorders (Abernathy and Morgan, 2001).

Exposure to arsenic via other exposure routes have also been linked to dermal effects. Although an early study linked excess skin cancer mortalities to occupational arsenic exposure, more recent occupational studies involving arsenic exposure do not support this finding. Isolated reports of other dermal effects have, however, been found in the literature. For example, one report in 1980 concluded that arsenite (As_2O_3) can induce an irritative contact dermatitis following occupational exposure. Three Swedish glass workers suffered cutaneous lesions, including pruritic maculopapules, pustules and folliculitis, that were localized primarily in exposed and moist areas. Patch tests of the powders the workers were exposed to were positive, and there was a weak positive response to a 5% concentration of As_2O_3 in petrolatum.

A change in work practices by the workers alleviated the skin conditions. Another research group reported on a case of contact hypersensitivity to arsenic in a crystal factory employee, who had no previous history of skin disorders. A patch test was done with various diluted compounds and sodium arsenate was the only chemical that tested positive. The skin disorder healed after treatment and reassignment to another position (Abernathy and Morgan. 2001).

Cancer at other sites

Several studies in Taiwan have suggested that arsenic may be related to cancers of the oesophagus, stomach, small intestine, colon, nose, larynx, bone and prostate, as well as lymphoma and leukaemia. In several studies, an elevated mortality from liver cancer was associated with high exposures to arsenic via drinking water. Increased rates of prostate cancer with increasing exposure to arsenic have also been noted (Abernathy and Morgan, 2001).

Links between arsenic exposure and cancer at sites other than skin, lung, bladder and kidney have not been investigated in any great detail in countries outside of Taiwan. Of the studies available, results are generally mixed. In one of two studies in Chile, mortality from liver cancer was positively associated with drinking water arsenic exposure. One study in Argentina, however, found no such relationship. Furthermore, one study in the USA and another in Australia, neither of which showed a clear cut increase in the risk of lung, bladder or kidney cancer, found evidence of a moderately elevated mortality of cancer of the prostate (Abernathy and Morgan, 2001).

Similarly, occupational studies of arsenic exposure have not revealed any consistent relationship between cancer incidence at sites other than the lung. A significant relationship was observed between arsenic exposure and the incidence of cancers of a large category of "digestive organs " in a Swedish cohort (Abernathy and Morgan, 2001).

There was a statistically significant association between arsenic exposure and cancer of the buccal cavity and pharynx in the Tacoma cohort, but not in the Anaconda cohort in 1964-1977 or in the US pesticide producer cohort. Similarly, no excess of stomach cancer was observed in the Japanese smelter cohort. However, in UK tin miners, two deaths from stomach cancer were observed (0.2 expected, SMR 890, $p<0.05$). In the Tacoma cohort, there was an increase in the cancer of large intestine ($p < 0.01$) but not a significant excess of rectal or bone cancer. An excess of rectal cancer was observed in the French gold miner cohort and of cancer of the large intestine (except rectum) in the Japanese smelter cohort (Abernathy and Morgan, 2001).

Genotoxicity and Related End Points:

Genotoxicity studies in relation to arsenic exposure have included exposed and unexposed individuals from several populations, and have based their analyses on various tissues, including blood, buccal and bladder cells as well as sections from tumour sections or Bowen's disease. Despite some negative findings, the weight of evidence indicates that arsenic can cause clastogenic damage in a variety of cell types, with differing end points, in exposed individuals (Abernathy and Morgan, 2001).

Diabetes Mellitus:

Diabetes mellitus has also been linked with drinking water arsenic exposure. One research assessed the relationship between ingested inorganic arsenic and prevalence of diabetes mellitus in 891 adults residing in southern Taiwan. Their study found that residents in the BFD-endemic areas had a two-fold increase in the prevalence of diabetes mellitus (after adjustment for age and sex) when compared to residents in Taipei and the entire Taiwan population. The authors also described a dose-response relationship between the level of arsenic in water and the prevalence of diabetes after adjusting for age, sex, body mass index and activity level. Positive associations were also demonstrated in two further studies from Taiwan (Abernathy and Morgan, 2001).

A positive association with diabetes has also been found in Bangladesh. However, in the US, diabetes is a condition with a low-case fatality rate, so an association with diabetes mellitus may not be observed. More work is needed prior to deciding whether there is an association in the US between diabetes and drinking water arsenic. Two occupational studies have found an association between arsenic exposure and diabetes mellitus. In both cases, however, the results were of borderline significance. Based on a case-referent analysis involving Swedish glass workers, found a slightly elevated risk for diabetes among those glasswork employees considered to be exposed to inhaled forms of arsenic. In a smaller (12 exposed cases) case- referent study in the Rönnskär Swedish cohort, a slightly elevated risk of diabetes mellitus associated with arsenic exposure was also observed (Abernathy and Morgan, 2001).

Neurological Effects:

It is generally accepted that acute arsenic poisoning causes neurological effects in humans, especially in the peripheral nervous system. To date, however, little work has been done on the possibility that lower-level, long-term exposure to arsenic may also lead to neurological effects. Of the limited number of available studies on this topic, several have described the onset of various neurological symptoms in subjects exposed to arsenic. One research group, for example, reported a positive association between electromyography (EMG) abnormalities and arsenic levels in drinking water and hair samples in residents of Waverley, Nova Scotia, Canada. Among those using water with more than 1 mg/L arsenic, the frequency of ENG abnormalities was 50% (Abernathy and Morgan, 2001).

In a study in 1979, workers at a copper smelting plant exposed to arsenic trioxide were examined for peripheral neuropathy. A total of 70 factory workers and 41 non-arsenic workers were evaluated. The data suggested an association between exposure to arsenic and a higher number of peripheral neuropathological disorders (sensory and motor neuropathy) and electrophysiological abnormalities (reduced nerve conduction velocity and amplitude measurements) among the exposed workers. Not all studies have found evidence of positive associations; in a cross-sectional study of 211 residents of Fairbanks, Alaska could find no evidence of neurotoxicity amongst the exposed population(Abernathy and Morgan, 2001).

On balance therefore, the evidence for a link between exposure to arsenic and neurological effects remains weak. Although a handful of studies have suggested that changes in nerve function may occur following exposure to arsenic, such studies are typically limited by their small sample populations, differing end-points and methods of measurement and probable coexposure to other known neurotoxins (Abernathy and Morgan, 2001).

Reproductive effects:

In addition to the health effects already mentioned, arsenic has also been linked to adverse reproductive outcomes. A number of studies have attempted to investigate this possible connection, the results of which suggest increased foetal, neonatal and postnatal mortalities, and elevations in low birth weights, spontaneous abortions, stillbirths, pre-eclampsia and congenital malformations (Abernathy and Morgan, 2001).

However, there does not appear to be consistent evidence linking any one particular reproductive outcome to arsenic exposure, and at the present time it is generally accepted that there is insufficient evidence to support the notion that arsenic causes reproductive effects in humans (Abernathy and Morgan, 2001).

Supporting evidence from experimental studies in animals

A number of animal carcinogenicity studies on arsenic have been carried out, the results of which are reviewed by IARC and most recently by WHO. Results are inconclusive owing to the fact that the majority of such studies are considered to suffer from limitations of one sort or another, e.g., either high dose levels, relatively short exposure times and small sample sizes. Furthermore, some studies have been conducted using strains of animals that are believed to have a high background number of tumors(Abernathy and Morgan, 2001).

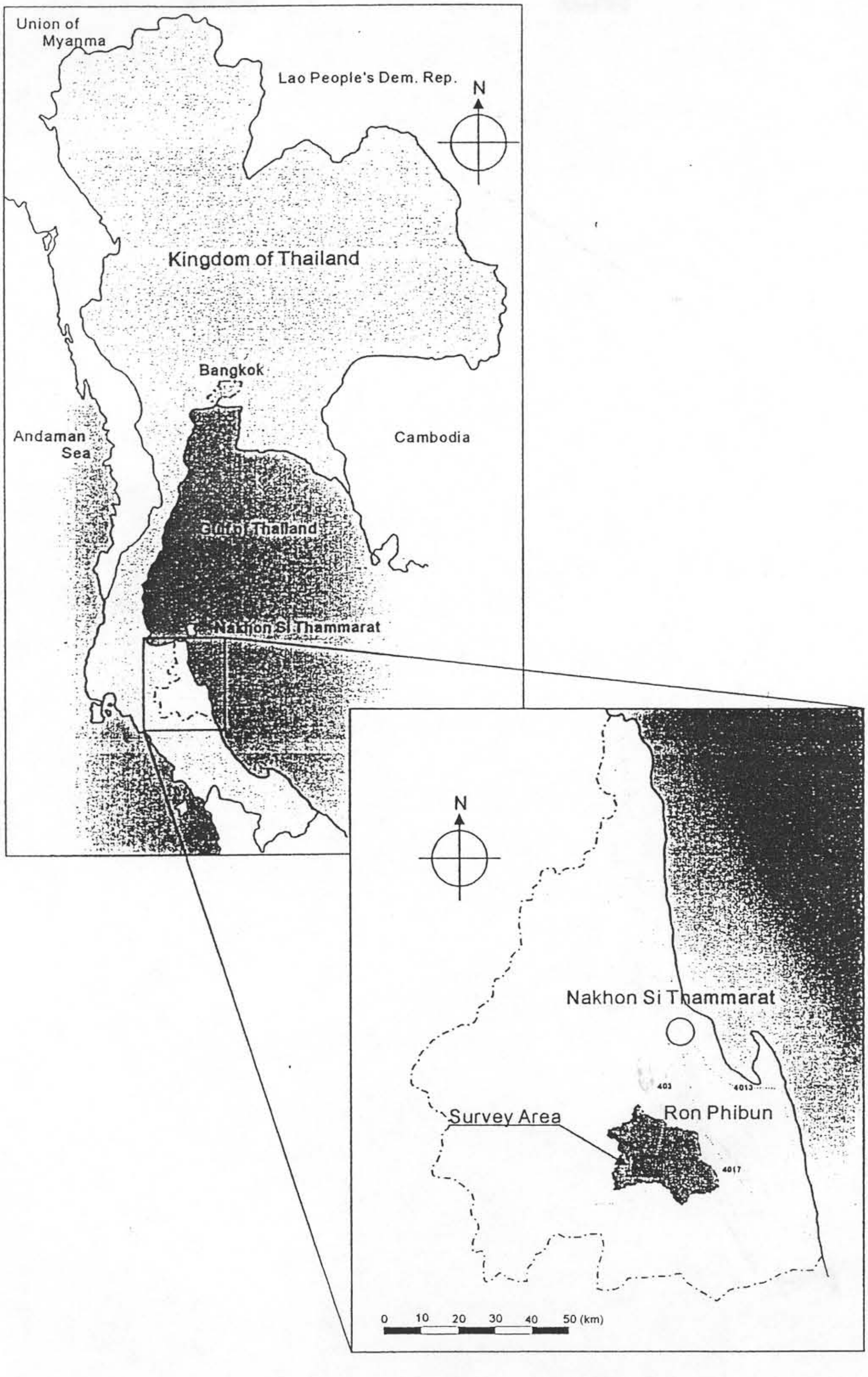


Figure 4-1 Regional setting of Ron Phibun District (Source: JICA, 2000)

contamination. Along the Ron Phibun route, near Num Khun canal, a layer of clay one meter thick had been brought to cover the laterite soil. This resulted in a noticeable increase in measured contamination; (laterite under such reducing conditions causes arsenic to be released into the groundwater). The site along the Ron Phibun – Khao Chum Thong route was covered by a two-meter thick layer of landfill material, which might have been contaminated by arsenic. Here, under chemically reducing conditions created by the landfill, and some domestic sewage, laterine may have released arsenic (JICA, 2000).

c) Water Supply in Ron Phibun

Currently, water supply in Ron Phibun District is mainly provided by 2 agencies, the Provincial Waterworks Authority (PWA) and the Ministry of Health (MOH). Water is also supplied partly through the use of deep wells (JICA, 2000).

PWA Water Services:

PWA waterworks covers villages 2, 12, 13, 15 and 7, a total of 1,056 households, using a source in Huai Nong Pet. This waterworks was established 20 years ago in Ron Phibun town and formerly made use of Khao Ron Na to provide water to its service population. The facilities consisted of a slow sand filter and a reservoir pond. In 1990, a different water source was developed and a new facility was constructed. Presently, PWA uses a coagulation/sedimentation tank and a rapid sand filtration tank and discharges the treated water into a reservoir pond. Water analysis is regularly carried out once a year. Simple tests and water quality monitoring activities are also carried out once a month. Current arsenic level in the water is 0.002 mg/L, lower than the level designated for drinking water in the nation (JICA, 2000).

MOH Water Services:

The MOH waterworks provides water using the Klong Thaloeng, which is located in the northern part of Ron Phibun. Although this source has abundant water, it has been affected by water extraction for alluvial mining concentration activities at the area directly upstream. This water service was established about 60 years ago; the weir was old and the iron pipe leaked seriously. Since most mining activities are suspended, the water is only used at one refining plant. The weir of MOH waterworks was constructed by the Royal Irrigation Department (RID) in 1995, while the treatment plant was built by MOH in 1996. RID was in charge of the installation of conveyance pipelines from the water source up to the treatment plant, while MOH was responsible for the treatment plant, water supply tank and secondary distribution pipelines. The distribution of water to each household is the responsibility of the residents. MOH water services cover village 2, 12, 15, 1, 3, 9 and 16. This waterworks is not operating at present because the water services cover a wide area with little water to supply; some of the residents have been using river water free of charge to irrigate their orchards; and the lack of consensus on the payment of a water fee and the rampant stealing of water (JICA, 2000).

Deep Wells:

Through the Accelerated Rural Development Department (ARD), the Department of Mineral Resources (DMR), the Public Works Department (PWD), and the military, every village has the construction of water supply facilities (deep wells, elevated tanks, distribution pipelines). Although numerous tube wells have been drilled in these areas, some are not used at all. The deep wells were registered in the well inventory. The residents are in charge of maintenance of each deep well (JICA, 2000).

Stream Water:

Villages 2, 3, 8, 10 and 11 draw water from streams, using the flowing surface water directly without any prior treatment (JICA, 2000).

Water Use Conditions:

Water supplied by the waterworks is mostly used for laundry, bathing and other miscellaneous purposes, hardly for drinking and cooking. Rainwater is used for drinking and cooking. The results of water use survey carried out by the Pollution Control Department (PCD) by interviewing 307 households in Ron Phibun subdistrict are shown in Table 4-1.

Table 4-1 Water Use in Ron Phibun Subdistrct

Water source	No. of households	% usage
Rainwater	262	85
Waterworks	144	47
Shallow wells	129	42
Surface water	14	5
Bottled water	15	4

Source: JICA, 2000.

Figure 4-2 shows the water service network in Ron Phibun District; Figure 4-3 and 4-4 show water storage for Ron Phibun Community area.

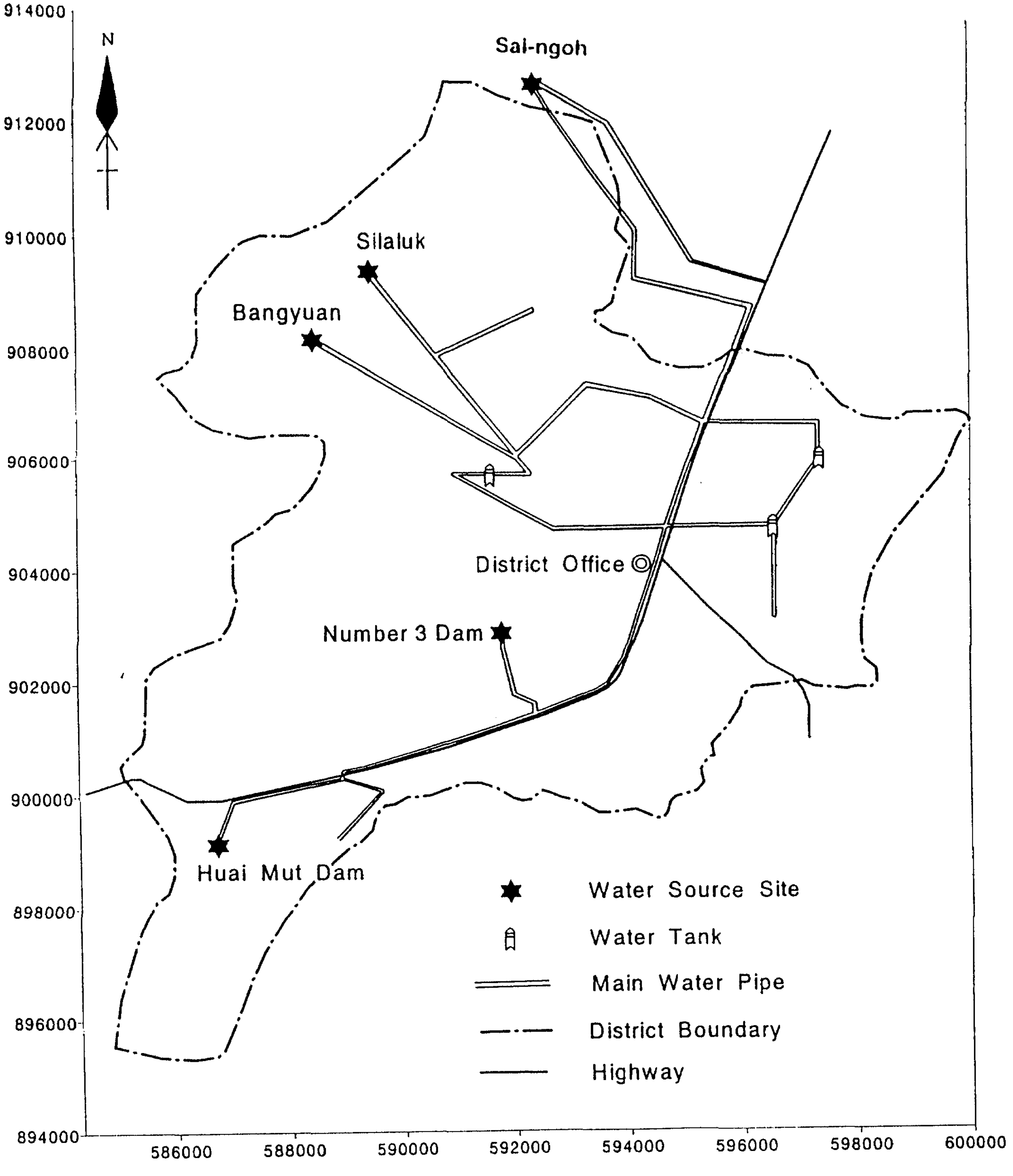


Figure 4-2 Water Service Network in Ron Phibun District (JICA, 2000)

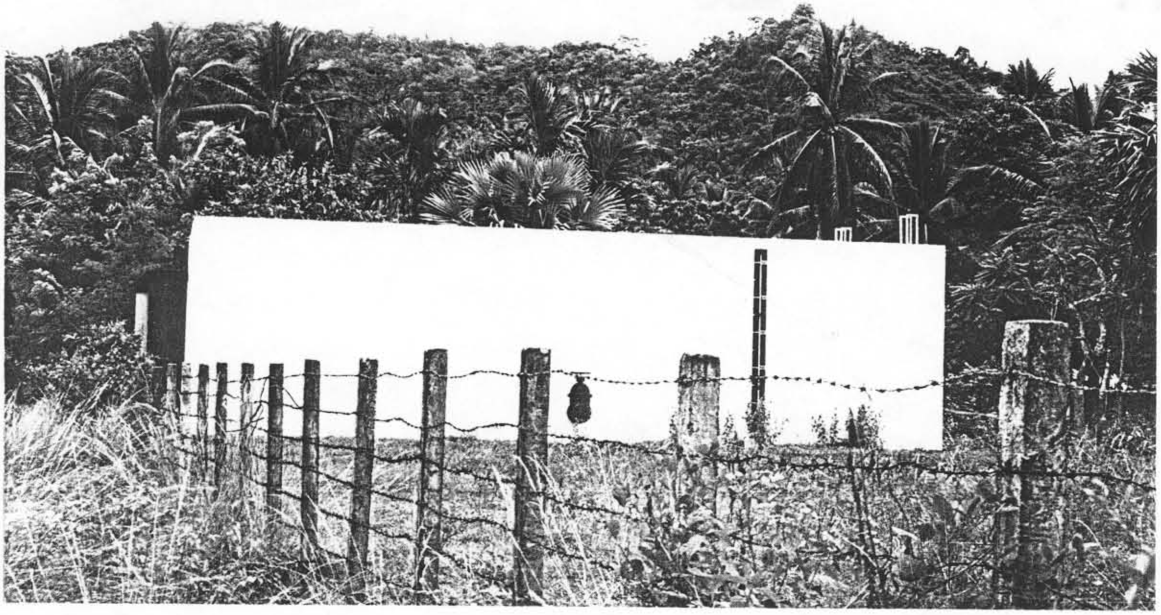


Figure 4-3 Water storage for Ron Phibun Community Area

Figure 4-4 Water Storage for Ron Phibun Community Area

4.2 Identification of Contamination Sources

From Khao Suan Chan Mountain and Khao Ron Na Mountains to Pak Panung River, there have been tin-mining activities in Ron Phibun District, Nakhon Si Thammarat Province for more than 100 years. Considering the arsenic load to the Ron Phibun sub-district, a primary ore deposit or mineralized zone, in nature, contributes very little to the arsenic contamination of area (JICA, 2000, Maharachpong, 1997, Paijitprapaon, *et al.*, 1995, Vitayavirasuk and Thongboriboon, 1997, Williams, *et al.*, 1996, and Wittayawarawat, 1994).

On the other hand, it is recognized that roasting process, in which arsenic was removed from tin crude concentrates, existed in the concentrator ruins in the study area. Ore dressing waste containing arsenic in sulfide form (arsenopyrites), oxide form (as As_2O_3), and sulfate form, was generated during their operation. Some part of these wastes has remained inside and/or along circumference of old concentrator. Large amount of them might have been dumped at some places within Ron Phibun district (JICA, 2000, Maharachpong, 1997, Paijitprapaon, *et al.*, 1995, Vitayavirasuk and Thongboriboon, 1997, Williams, *et al.*, 1996, and Wittayawarawat, 1994).

Although most of the mines ceased operation in the late 1980's, the release of arsenopyrite (FeAsS) from the tin ore has left a legacy of extensive arsenic contamination in many areas of Ron Phibun District. Groundwater and many shallow wells are contaminated. The long-term use of contaminated water for agriculture and/or direct consumption poses a serious risk of chronic arsenic poisoning among the local population. Arsenical skin lesions, including hyperpigmentation and hyperkeratosis, are common among the residents of Ron Phibun District. There is evidence that chronic arsenic poisoning also causes damage to many other organs systems, and may result in the development of various forms of cancer (Boriboon, 2000).

Five identified arsenic contaminated areas were reported by a recent study as indicated below (JICA, 2000):

i. **Around the foothill concentrator and its downstream**: The concentrator waste has transported by flood and spread in the area.
ii. **Around the town concentrator**: The concentrator waste might have been dumped to the dredging pond west of the town concentrator
iii. **The area of laterite soil**: Clay of one meter thick was brought to cover the area and laterite soil was made to be in a reduction condition. Laterite under a reduction condition released arsenic into groundwater.
iv. **Landfill site**: The site is covered with two-meter thick landfill material. The landfill material might be contaminated by arsenic, like the concentrator waste. Laterite may release some arsenic because of reduction condition created by the landfill and some domestic waste.
v. **New and old waste dump**: Contamination might have been caused by reduction condition created by organic domestic waste and some concentrator waste might be mixed with domestic waste.

4.3 Mechanism of Arsenic Release from a Contaminant Source

a) Geochemical Phase of Arsenic

When arsenic is concentrated in the sedimentary strata, generally, it is in the form of sulfide such as arsenopyrite or co-precipitated with or adsorbed onto oxide/hydroxide of Fe and Mn. Conventional elution test of soil can detect As_2O_3 included in the roasting waste but it cannot easily detect arsenic in sulfide or oxide/hydroxide of Fe and Mn. That means the elution test alone may not be able to identify the contamination source and even if it could, it is difficult to clarify mechanism of arsenic release. From this viewpoint, sequential extraction of soil sample should be carried out to find the geochemical phase of arsenic to identify the contamination source and clarify the arsenic release mechanism (JICA, 2000).

b) Physical and Chemical Conditions

Release of arsenic From Fe oxide or hydroxide was controlled by the oxidation-reduction potential. Fe (II) ion co-precipitates with arsenic in water in oxidizing condition and forms hydroxide. Fe oxide and hydroxide also adsorbs arsenic very well in the oxidation condition. However arsenic co-precipitated with Fe, and arsenic adsorbed onto Fe oxide will be released into the environment from the Fe (II) ion under the reducing condition. On the other hand, the possibility of arsenic release from sulfide is considered small because arsenopyrite is relatively stable under normal conditions (JICA, 2000).

c) Arsenic Species Analysis and Behavior

Arsenic is the element whose toxicity is changed by its chemical speciation. There is over several hundreds to thousands differences in toxicity between inorganic arsenic in water and organic arsenic in an aquatic organism. Even within inorganic arsenic, trivalent arsenic and pentavalent arsenic have several times difference in toxicity. As (III) is more toxic than As (V). Furthermore, behavior in soil and groundwater changes by its speciation. As (III) is near neutral in terms of its electric charge and hardly adsorbed, while As (V) is positively charged and easily adsorbed. Therefore, arsenic speciation is important in study of arsenic pollution (JICA, 2000).

CHAPTER V

ARSENIC MEASUREMENT

The Safe Drinking Water Act (SDWA) directs the U.S. Environmental Protection Agency (USEPA) to publish a Maximum Contaminant Level Goal (MCLG) and promulgate a national primary drinking water regulation for arsenic. A primary drinking water regulation is set at an MCL if "it is economically and technologically feasible to ascertain the level of such contaminant in water in public water systems....", including quality control and test procedures to insure compliance. USEPA is to set the Maximum Contaminant Level (MCL) as close to the MCLG as is feasible with the best available technologies. Determination of the MCL will also be dependent on the ability of laboratories to reliably measure the contaminant at the MCL, the health risks, and the cost and benefits associated with arsenic at the proposed MCL level (USEPA, 2001-a).

In considering analytical methods for use in compliance monitoring, USEPA evaluates the overall sensitivity of the techniques. In previous regulations, USEPA used two measures of analytical capability, the Method Detection Limit (MDL) and the Practical Quantitation Level (PQL). The MDL is a measure of an individual laboratory's sensitivity and is defined as "the minimum concentration of a substance that can be reported with 99% confidence that the analyte concentration is greater than zero." MDLs can be operator, method, laboratory, and matrix specific. Because MDLs are derived under research-type conditions, they are not necessarily reproducible within a laboratory or between laboratories due the day-to-day analytical variability that can occur (USEPA, 2001-a).

In an effort to integrate this analytical chemistry data into regulation development, the Agency uses the PQL to estimate or evaluate the minimum, reliable quantitation level that most laboratories can be expected to meet during day-to-day operations. The Agency has defined the PQL as "the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions (November 13, 1985 Federal Register Notice (50 FR 46906))." A PQL is either determined through the use of interlaboratory studies or, in absence of sufficient information, through the use of a multiplier of 5 to 10 times the MDL. USEPA has conducted water supply (WS) performance evaluation (PE) studies twice a year to certify drinking water laboratories, provide large-scale evaluation of analytical methods, a database for method validation, demonstrate method utilization by a large number of laboratories, and to provide PQL data. Using graphical or linear regression analysis of the WS data, the Agency sets a PQL at a concentration where at least 75% of the laboratories (generally USEPA and State laboratories) could perform within an acceptable level of precision and accuracy. This method of deriving a PQL was used in the past for inorganics such as antimony, beryllium, cyanide, nickel and thallium (USEPA, 2001-a).

5.1 Arsenic Measurement Methods

The Agency has approved several analytical methods to support compliance monitoring of arsenic at the current MCL of 50 µg/L. Spectroscopy is the foundation of these analytical methodologies for determining arsenic in drinking water. These analytical methodologies all report "total" arsenic, which is defined as the concentration of arsenic present in the dissolved (or filtered) and suspended fractions of the water sample. The arsenic is oxidized and analyzed without regard to the chemical form (i.e., organic or inorganic) or oxidation state (i.e., As (III) and As (V)) of the arsenic. These analytical methodologies, written by USEPA, the American Society of Standards and Methods (ASTM), and the American Public Health Association (for Standard Methods), include guidance on sample preservation, sample digestion and instrumental parameters. The USEPA approved methodologies, the MDLs, some of the advantages and disadvantages of each method and the estimated cost of analysis are shown in the Table 5-1 (USEPA, 2001-a):

Development of the PQL for Arsenic

As stated earlier, the PQL is used by USEPA to determine the lowest level of arsenic in drinking water that can be reliably measured with some degree of accuracy and precision on a routine basis. In 1994, USEPA evaluated data from a number of Water Supply (WS) studies. Evaluating the graphical results of these WS studies, the Agency determined the PQL for arsenic to be 2.0 µg/L at an acceptance limit of ± 40%. In February of 1994, the American Water Works Association (AWWA) sponsored a study of eight commercial laboratories and 14 utilities ["An Evaluation of the Practical Quantitation Level (PQL) for Arsenic"]. The AWWA study used arsenic spiked water samples for several matrices which included reagent water, high total organic carbon (TOC) / high total dissolved solids (TDS), low TOC/low TDS, and high TOC/low TDS. Using USEPA and Standard Method (SM), graphite furnace atomic absorption (GFAA) and gaseous hydride atomic absorption (GHAA) techniques to analyze the spiked water samples, the AWWA study graphically supported a PQL of 4 µg/L with an acceptance limit of ±30% for all matrices. The USEPA Science Advisory Board (SAB) recommended in its July 1995 final report that it set the PQL for arsenic using acceptance limits similar to those used for other inorganics (± 20% or ± 30%) (USEPA, 2001-a).

Graphical and statistical analyses indicate a PQL of 3 µg/L would be reached at acceptance limits of ± 25% or ± 30%. Preliminary estimates of a private laboratory capacity at this PQL appear to be sufficient, based on the number of voluntary non-regulatory agency laboratories that participated in the low-level arsenic studies. All approved methodologies with the approved modifications should be able to meet this performance level. Before making a final decision, the Agency plans to have the 1999 report for the derivation of the arsenic PQL reviewed by external peer reviewers (USEPA, 2001-a).

5.2 Atomic Absorption Spectrophotometer Method

A spectrophotometer is a spectrometer equipped with a photoelectric detector. These sectrometers are single channel devices in which each element of the spectrum

Table 5-1 Approved Analytical Methods (and Method Updates) for Arsenic (CFR 141.23)

Methodology	MDL (μg/L)	Advantages	Disadvantages	Estimated Cost of Analysis
Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)	8 5	Multi-analyte	Not widely used Higher MDL than other methods	$15 to 25
Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)	1.4 (0.1)[1]	Multi-analyte Low MDL Demand Increasing	High capital cost	$ 10 to 15
Stabilized Temperature Platform Graphite Furnace Atomic Absorption (STP- GFAA)	0.5 (0.1)[2]	Widely Used Low MDL	Single analyte	$ 15 to 50
Graphite Furnace Atomic Absorption (GFAA)	1 5	Widely Used Low MDL	Single Analyte	$15 to 50
Gaseous Hydride Atomic Absorption (GHAA)	0.5 1	Low MDL	Single Analyte	$15 to 50

[1] In 1994, USEPA approved the use of selective ion monitoring with ICP-MS. ICP-MS with this modification is capable of achieving a method detection limit of 0.1 μg/L ("Methods for the Determination of Metals in Environmental Samples - Supplement I," USEPA/600/R-4/111, USUSEPA, 1994). Advantages include a short analysis time, lower detection limits and multi-analyte capabilities. However, instrument acquisition can be costly and the analysis for arsenic is subject to interference from the formation of an argon chloride in high chloride water samples.

[2] In 1994, USEPA approved the use of multiple depositions with STP-GFAA. The use of multiple depositions with STP-GFAA is capable of attaining a method detection limit of 0.1 μg/L ("Methods for the Determination of Metals in Environmental Samples - Supplement I," USEPA/600/R-4/111, USUSEPA, 1994). GFAA instrumentation is widely available; however analysis time is longer using multiple injections.

Source: USEPA, 2001-a

is viewed serially, not simultaneously. Spectrophotometers are employed for absorbance measurements in the ultraviolet, visible, and infrared regions (Skoog and Leary, 1992).

Hydride Generation:

This method is applicable for the determination of arsenic by conversion to its hydride by sodium borohydride reagent and aspiration into an atomic absorption atomizer. Arsenous acid, the arsenite (As (III)) oxidation state of arsenic, is instantaneously converted by sodium borohydride reagent in acid solution to its volatile hydride. The hydride is purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of hydride by the carrier gas and provides rapid, sensitive determinations of arsenic. At room temperature and solution pH value of 1 or less, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As (III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before its reaction with sodium borohydride (Clesceri, et al., 1990).

Electrothermal Method:

This method is suitable for determination of micro quantities of arsenic. An electrically heated device with electronic control circuitry is designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest (Clesceri, et al., 1990).

5.3 A Novel Soil Gas Technique Applied to an Arsenic Contaminated Area

A novel soil gas technique was applied to detect and determine the subsurface arsenic contamination at Ron Phibun district, Nakhon Si Thammarat province of Southern Thailand. This technique was tested for the first time in this type of geochemical environment in order to detect volatile forms of arsenic. Arsenic is an element, which may volatilize from contaminated waters, from soils and sediments by anaerobic bacteria as arsine, or one of the methylated forms such as trimethylar-sine. The study consisted of:

1) comparing soil-gas from a known area of arsenic contamination against an area with background concentrations of arsenic
2) comparing soil-gas with arsenic concentrations in shallow groundwater.

Preliminary interpretation of the soil gas data indicated a sharp contrast between the contaminated area and background area. There was a fair correlation between soil gas arsenic concentration and arsenic content of shallow groundwater (Wongsanoon, 1997).

5.4 Field Test Kit

ANN (Asia Arsenic Network) Field Test Kit modified by NIPSOM (National Institute of Preventive and Social Medicine), Mohakhali, Dhaka (Ahmad et al., 1997) was utilized in Ron Phibun field trip. Modified Arsenic Field Test Kit (as shown in Figure 5-1), is a cheap and easy device for detection of arsenic in water. This improved field kit technique offers a user friendly and simple way of testing a large number of samples at the community level to screen out the contamination of the tubewell water. The results can be obtained within 5 minutes and it can detect arsenic from 0.01 mg/L to 0.5 mg/L or higher. The field kit method is based on the principle of Gutzeit reaction (Eq. 5-1), which is a qualitative or roughly quantitative method; it is sensitive to as little as 0.001 mg As and provides an accuracy of ± 0.005 mg.

Gutzeit Reaction:

$$\underset{\text{(mercuric bromide)}}{AsH_3 + 2HgBr_2} \rightarrow \underset{\text{(arseno mercuric bromide)}}{AsH(HgBr)_2} + 2HBr \qquad (5\text{-}1)$$

In this method, arsenic gas is liberated from an arsenic containing water sample; arsenic gas produces color on filter paper treated with mercuric bromide. A range of colours from faint yellow to dark brown may appear on the filter paper, which can be translated into the corresponding arsenic concentration from a precalibrated chart provided with the kit (Figure 5-2).

In ground water, arsenic usually occurs as arsenite (As(III)) and arsenate (As (V)). To determine the arsenic in water, arsenate is reduced to arsenite by the reducing agents (Potassium iodide and Stannous chloride). As(III) is then reacted with Zinc and HCl to produce arsine gas, as shown in Eqs. (5-2)-(5-4).

Reduction:

$$As^{5+} \xrightarrow[KI,SnCl_2]{} As^{3+} \qquad (5\text{-}2)$$

$$Zn + HCl \rightarrow ZnCl_2 + H_2 \qquad (5\text{-}3)$$

$$As^{3+} + H_2 \rightarrow AsH_3 \qquad (5\text{-}4)$$

Color change (yellow to reddish brown) produced on the disc paper by reaction of arsine gas with modified mercury bromide indicates the presence of arsenic in water. When no color appears on the disc paper, it indicates absence of arsenic or the concentration to be below detectable limit. To avoid interference with hydrogen sulphate, cotton ball impregnated with lead acetate solution may be used.

The materials and chemicals required for the Arsenic Test Kit are as follows:

1) Flanges
2) Clip
3) test tube
4) small spoon
5) small plastic forceps
6) Zinc
7) Potassium iodide
8) Stannous chloride
9) Hydrochloric acid (1:1)
10)Disc paper
11)Color scale
12)Tissue paper
13)Test tube holder
14)Carrying box

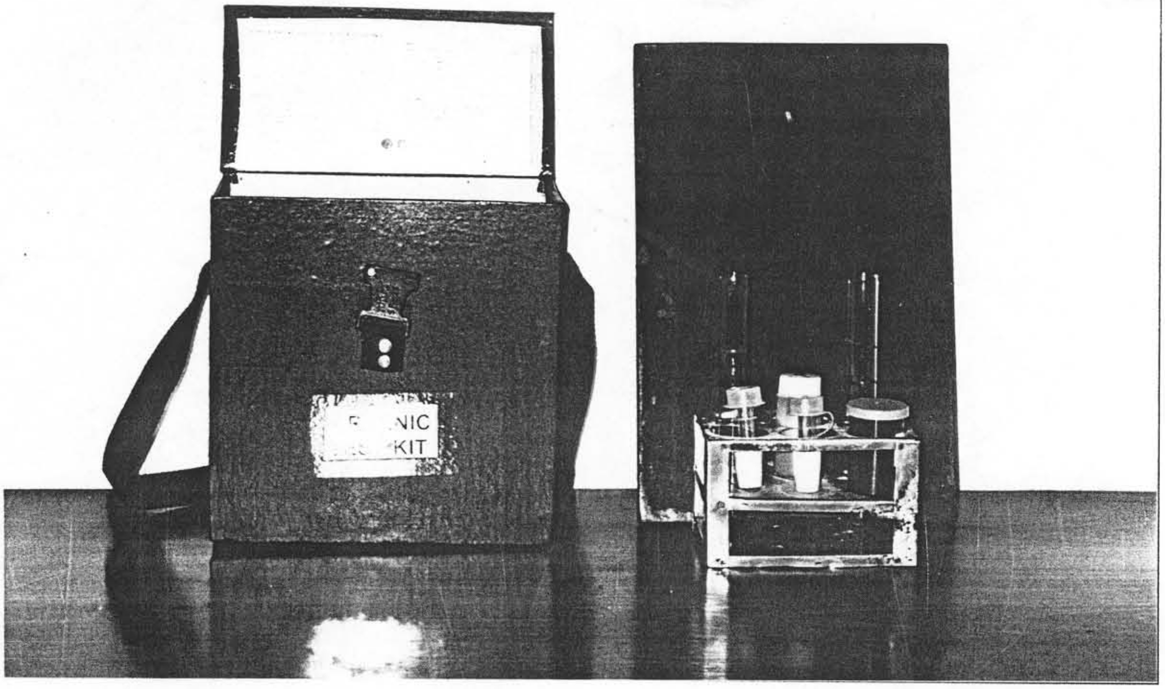


Figure 5-1 Field Test Kit

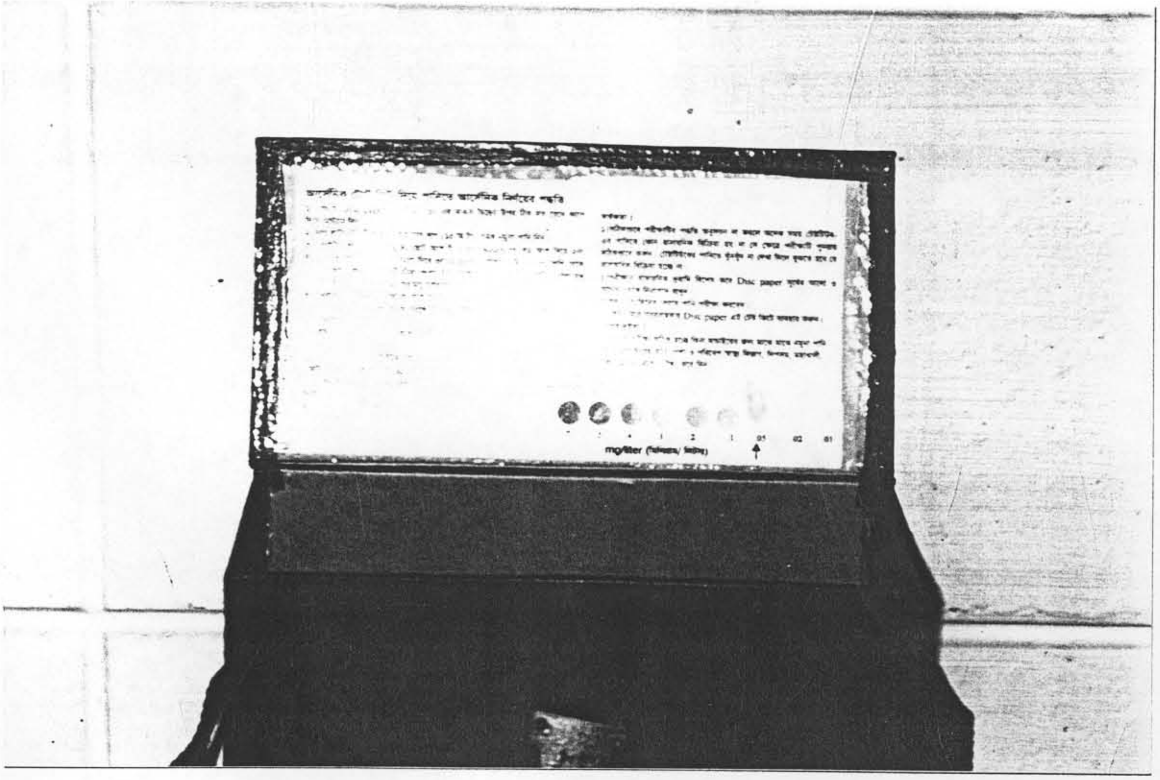


Figure 5-2 Field Test Kit Colour Chart

Procedure:

1) place the disc paper between the flattened surfaces of two flanges with the help of the forceps and secure the flanges with the clip
2) take 15 ml of water sample in the test tube (up to the lower mark)
3) add approximately 0.1 g of potassium iodide, 0.5 g of zinc and 0.1 g of stannous chloride to the water sample taken in the test tube
4) add 4 ml of 1:1 hydrochloric acid into the test tube (up to the higher mark) and insert the appropriate end of the flange into the test tube
5) knock gently the lower end of the test tube for few seconds
6) allow the test tube to stand for 5 minutes; by this time the expected reactions should have taken place
7) remove the secured flanges from the test tube, separate the flanges and bring out the disc paper
8) compare the color change obtained on the disc paper with the color chart and record the arsenic content in the water sample

Precautions to be taken:

a) if the bubbles (indication of reaction) are not generated after addition of HCl, repeat the test
b) the chemicals and disc papers should be kept away from direct sunlight and moisture

CHAPTER VI

ASSESSMENT OF ARSENIC CONCENTRATION IN SOUTHERN THAILAND

6.1 Previous Studies

A major cause of food contamination is the pollution of air, water, and soil. In recent year, it has been found that arsenic is present in our environment particularly in well water. A number of reports indicated a high level of arsenic in drinking water such as 0.1-1.18 ppm (1180 μg/L) in Taiwan and 2.47 ppm (2470 μg/L) in Thailand in Ron Phibun well water. One of effects of arsenic on human health is black foot disease. Black foot disease was found among 495 out of 2,216 people of the Ron Phibun area. Maximum arsenic content in agricultural products in Ron Phibun was 1.2 mg/kg, which is less than 2 ppm (legislation limit) (Boribbon, 2000).

a) Emerging Chemical Food Problems

A survey of the dietary intake of arsenic in the contaminated area of Ron Phibun district was conducted by the Department of Medical Sciences of Thailand. The results showed the level of arsenic intake to be 35.89-15,312.07 μg/day/person from 90 households. Sixty-five percent of population of Ron Phibun showed arsenic intake over ADL (acceptable daily intake), of 128 μg/day/person. Arsenic in ready-to-eat food ranged from 0.015-1.54 μg/kg, and in drinking water, ranged from 0.001-3.16 μg/L. Chicken is one source of arsenic contaminated food. Arsenic compounds were used in chicken farming as a growth promoter. The arsenic detected in chicken averaged 0.49 mg/kg in 128 samples. Table 6-1 shows the results of the survey of arsenic in Thai food (Boriboon, 2000).

Table 6-1 Arsenic Contamination in Thai Food in 1998

Categories	Number of sample	As (mg/kg)
Vegetable	219	0.09
Fruit	67	0.08
Meat	25	0.13
Aquatic animal	148	0.17
Miscellaneous	104	0.16

Source: Boriboon, 2000

b) Arsenic Contamination in Ron Phibun

Various studies on arsenic contamination in southern Thailand had been conducted, especially in Ron Phibun District, Nakhon Si Thammarat. Many research groups spent years of studying on arsenic concentrations in the area. The occurrence of human health problems resulting from arsenic contamination of domestic water supplies in Ron Phibun District was first recognized in 1987. The area has an extensive history of bedrock and alluvial mining, the waste from which is typically rich in arseno-pyrite and related alteration products. In 1994 a collaborative study was instigated involving Thai and British government authorities to establish the distribution and geochemical form of As in surface drainage and aquifer systems in the affected area, the probable sources of As contamination, and the potential for problem alleviation. Hydrochemical analyses of surface and groundwater have confirmed the presence of dissolved As at concentrations exceeding WHO potable water guidelines by up to a factor of 500. Contamination of the shallow alluvial aquifer system is systematically more severe than the underlying carbonate-hosted aquifer. Deep bore holes may therefore provide the best available potable water source for the local population. The presence of up to 39% of total As as arsenite (H3AsO3) within the carbonate aquifer may, however, constitute a "hidden" toxicological risk, not evident in the shallow groundwater (in which arsenate species account for > 95% of total As). Mineralogical investigations of As-rich tailings and flotation wastes were undertaken to evaluate their likely impact on water quality. The results indicate that although some flotation wastes contain up to 30% As, the rate of leaching is extremely low. Consequently the As loading of drainage emanating from such waste is below the subregional average (William, et al, 1996).

Analyses of the silty alluvium that covers much of the central sector of the study area have highlighted As concentrations of up to 5000 mg kg-1, probably carried by disseminated arsenopyrite. Following sulfide dissolution, the mobility of As in this material may be high (with resultant contamination of shallow groundwater) due to the low Fe content of the soil. On the basis of the data acquired, a range of pollution (William, et al, 1996). Figures 6-1 – 6-4 show the drainage networks and the potential arsenic contamination sources, arsenic concentrations in surface waters, shallow groundwaters, and carbonate aquifer waters of Ron Phibun area, respectively.

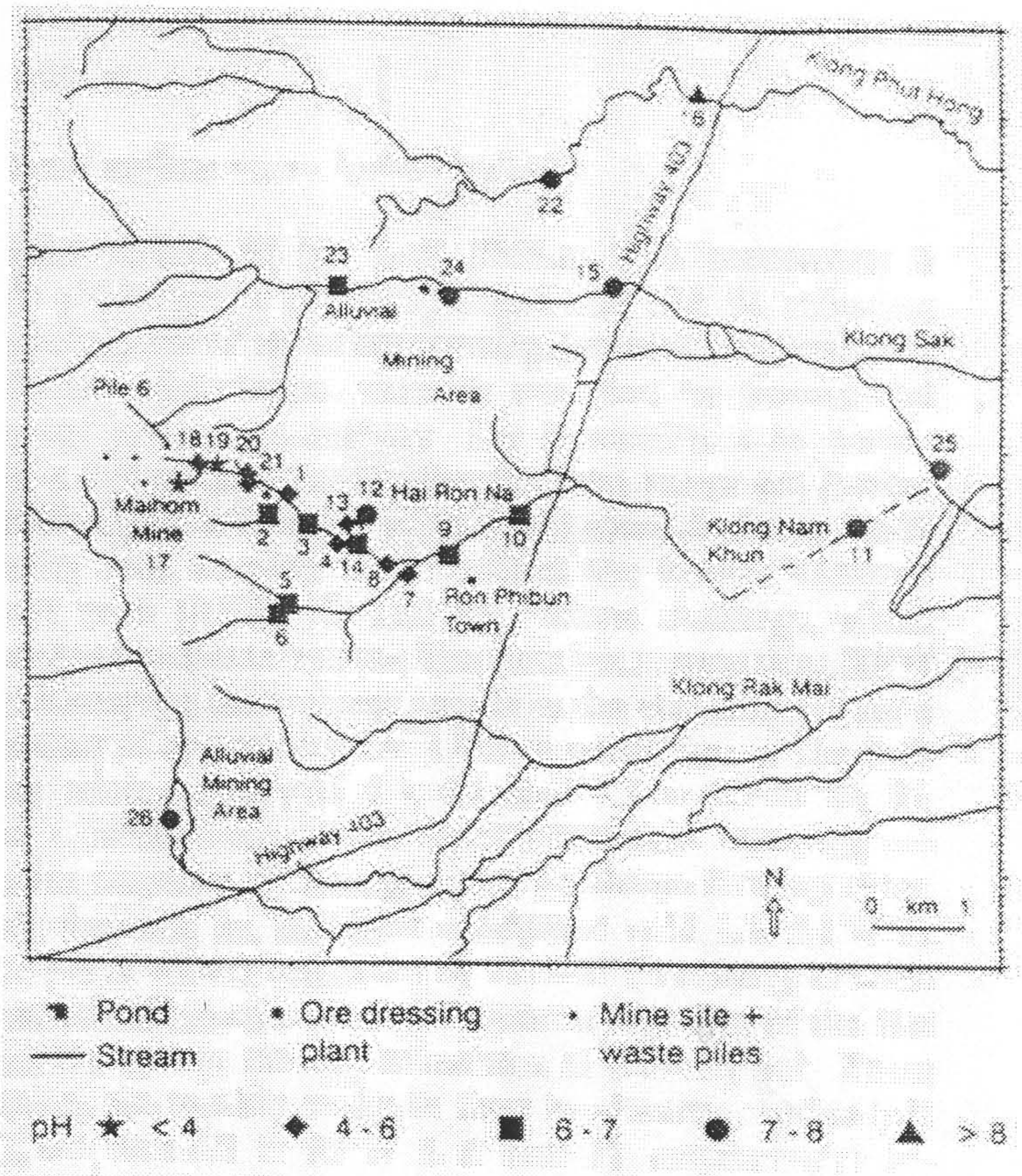


Figure 6-1 The Drainage Networks and the Potential Arsenic Contamination Source (Source: William et al., 1994)

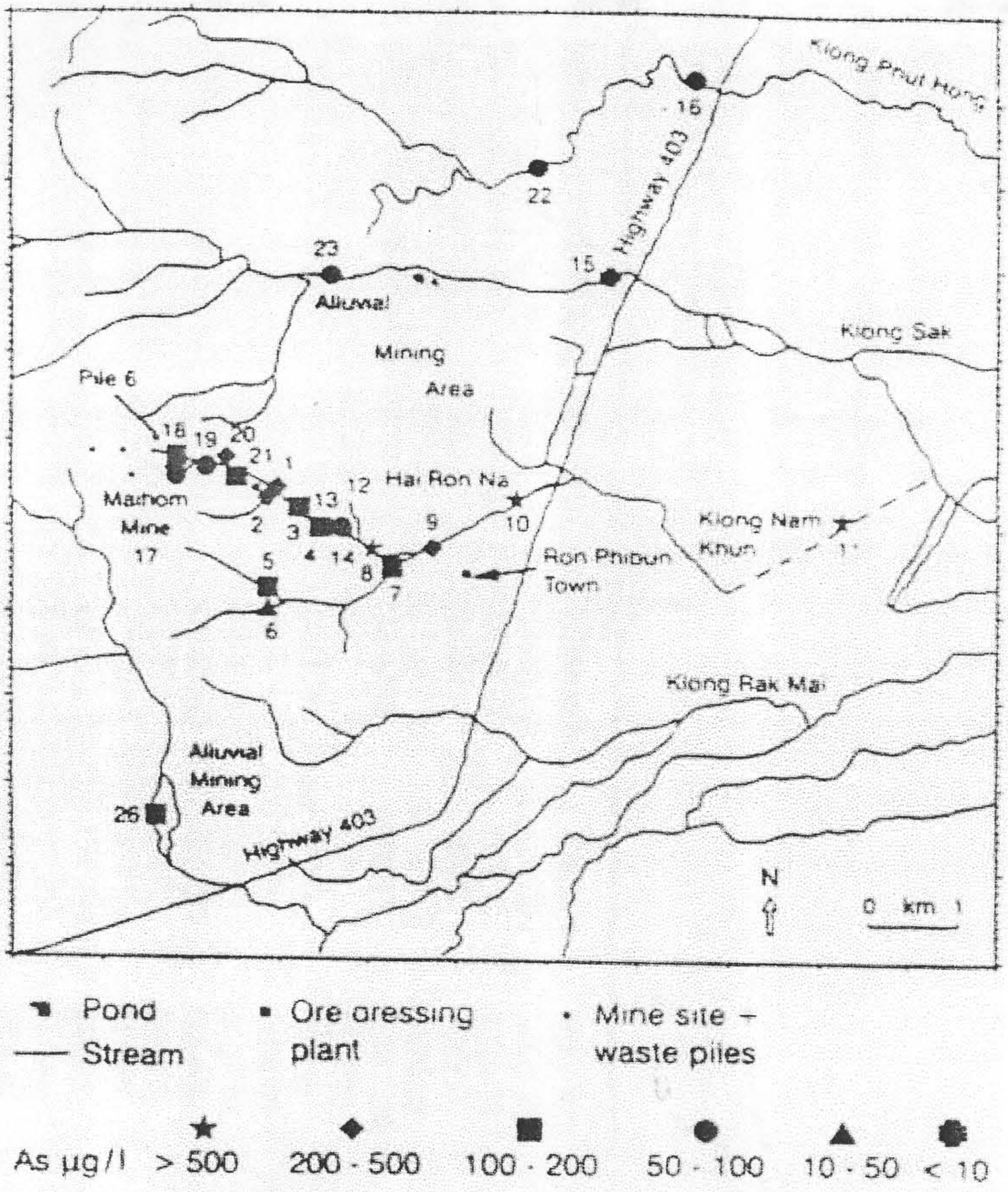


Figure 6-2 Arsenic Concentrations in Surface Waters of Ron Phibun District
(Source: William, et al., 1994)

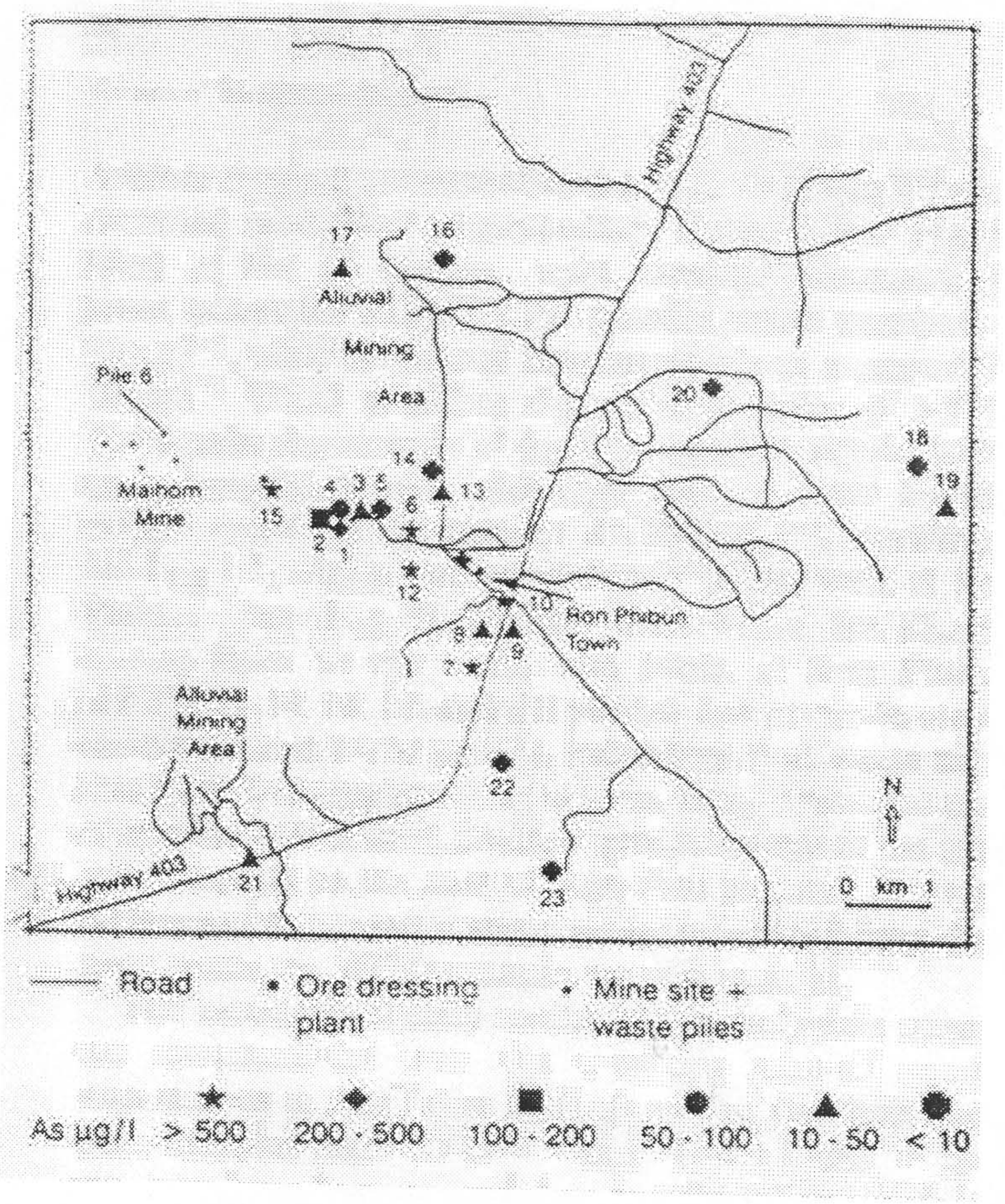


Figure 6-3 Arsenic Concentrations in Shallow Groundwaters of Ron Phibun District (Source: William, et al., 1996)

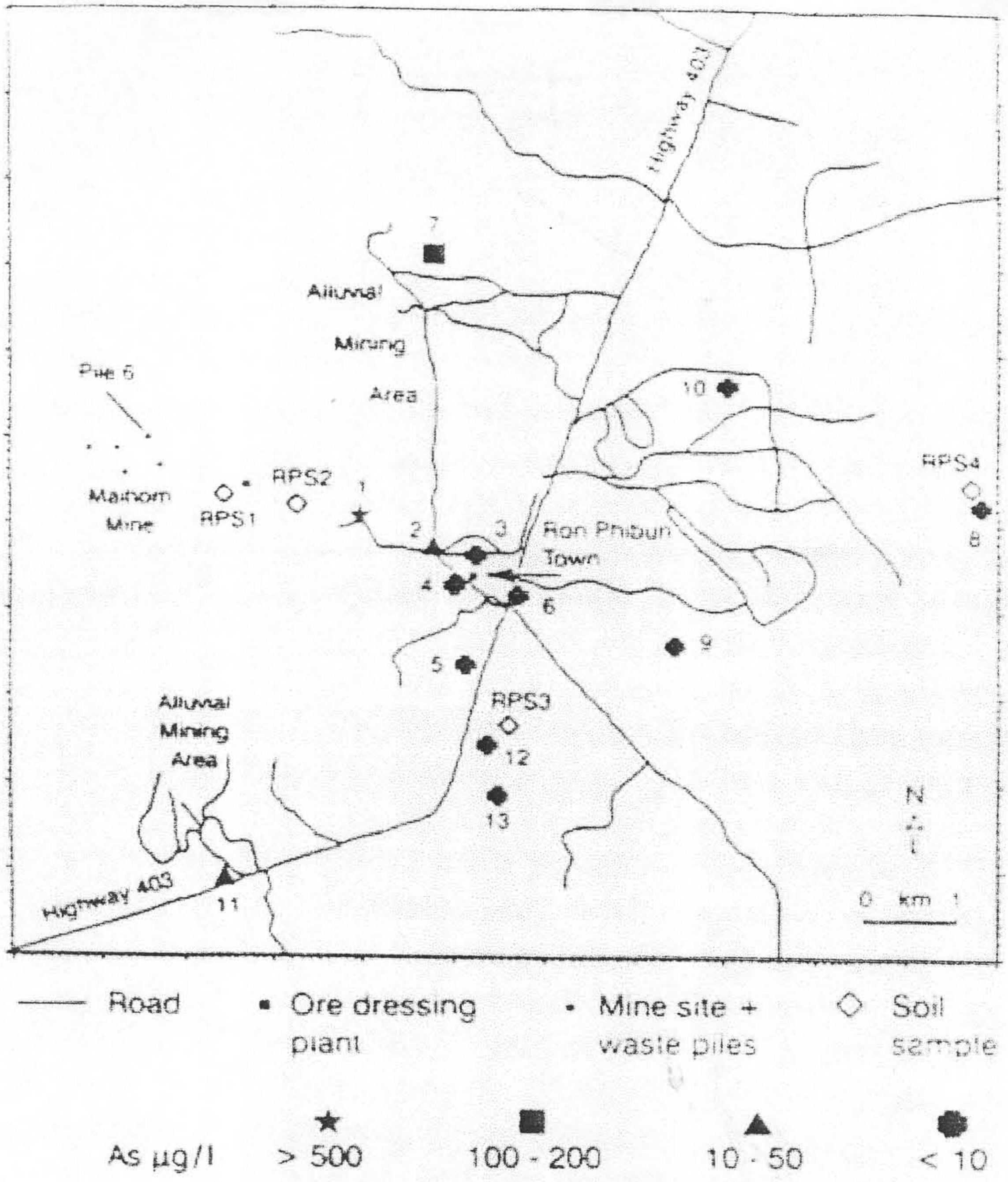


Figure 6-4 Arsenic Concentration in Carbonate Aquifer Waters, Ron Phibun District (Source: William et al., 1994)

A summary of previous studies on arsenic contamination status in Ron Phibun area is presented in Table 6-2.

Table 6-2 Summary of Arsenic Status in Ron Phibun Area

Time Period/ Research Group	Location	Samples	NO. of samples	Method	Concentration/Affected Population
1988 by the Ministry of Public Health	Ron Phibun District, Nakhon Si Thammarat	Arsemnic-induced skin disorders			1000 cases of Arsenic related illness
		Skin cancer			20 cases of Arsenic related illness
May 1990-March 1991	Ron Phibun District, Nakhon Si Thammarat	Water source	400	AA	0.055-5.560 mg/L (55-5560 µg/L) higher than drinking water standard
		Vegetable & fruit	40		Lower than the standard of Ministry of Public Health
		Hair	40		7.45 mg/kg (0.26-19.70 mg/kg) for high-risk villages
					3.14 mg/kg (0.10-13.50 mg/kg) for low-risk villages
April-May 1993-January 1994	Pak Phanang river basin, Nakhon Si Thammarat	Stream water			21.02-427.07 µg/L
		Sediment			6.89-381.24 mg/kg
		Soil			2.85-5.80 mg/kg
		Iron & manganeses oxides species			10-30 %
		Floatation waste			30 % arsenic
		Silty alluvium			5000 mg/kg
1994 by UK & the Government of Thailand Department of Mineral Resources	Ron Phibun District, Nakhon Si Thammarat	Alluvial soil			Up to 5000 mg/kg
		Aquifer groundwater			2-5115 mg/L
		Deep groundwater			39 % of arsenite
		Shallow groundwater			95 % of total arsenic
1996-1997	Ron Phibun Sub district, Nakhon Si Thammarat	Shallow groundwater		AAS with graphite furnance and Zeeman background correction	Undetectable – 3.34 mg/L
		Stream water			1.3-245.5 g/L
		Stream sediment			193.3-1854.8 mg/kg dry weight
		Aquatic plants			0.86-2.97 mg/kg wet weight water hyacinthes
		Aquatic animals			0.53-2.45 mg/kg wet weight bitter snails

Sources: Williams,et al., (1996), Chiangmai, (1991), Wittayawarawat, (1994), and Vitayavirasuk and Thongboriboon, (1997)

6.2 Field Observations and On-site measurement

A field visit was made to the study area for an overall survey to locate the potential risk arsenic contamination sites and to do on-site measurements of arsenic levels on the samples collected. The field samples were collected from the following sources:

1) surface water - shallow stream
2) shallow well
3) groundwater
4) soil

Field test kit (describe in 5.3) was used for on-site determination of arsenic concentration in water samples. Interviewing the locals was conducted to observe the overall current status of the severity of the arsenic contamination in the area. Figure 6-5 - 6-11 show the field test kit measurement and the points of water sample collections from surface water, a well pump and a shallow well. Figure 6-12 and 6-13 show the points of soil sample collections.

6.3 Results of the On-site Measurement for Arsenic Contamination

Based on the results of the on-site measurements in Ron Phibun town, on 2nd May 2001, arsenic concentrations in the shallow stream, shallow groundwater, and shallow well pumps in study area were exceeding the USEPA and WHO's drinking water standards as mentioned in section 1.3. Table 6-3 shows the overall results of the on-site measurement.

Table 6-3 Results of the On-site Measurement for Arsenic Contamination

Location No.	**Samples**	**Concentration (µg/L)**	
		Sample 1	**Sample 2**
1	Surface water – shallow stream (near the bridge)	20	150
	Shallow groundwater (near the bridge)	> 700	> 700
	2 soil samples collected	-	-
2, 3, 4	Mud and a few soil samples collection only	-	-
5	Shallow well, house # 245, Village 12	10	< 10
	2 soil samples collected	-	-
6	Shallow well pump	10	< 10

Note: Location # 1, 2, 3, 4, 5, and 6 are shown in figure 6-5

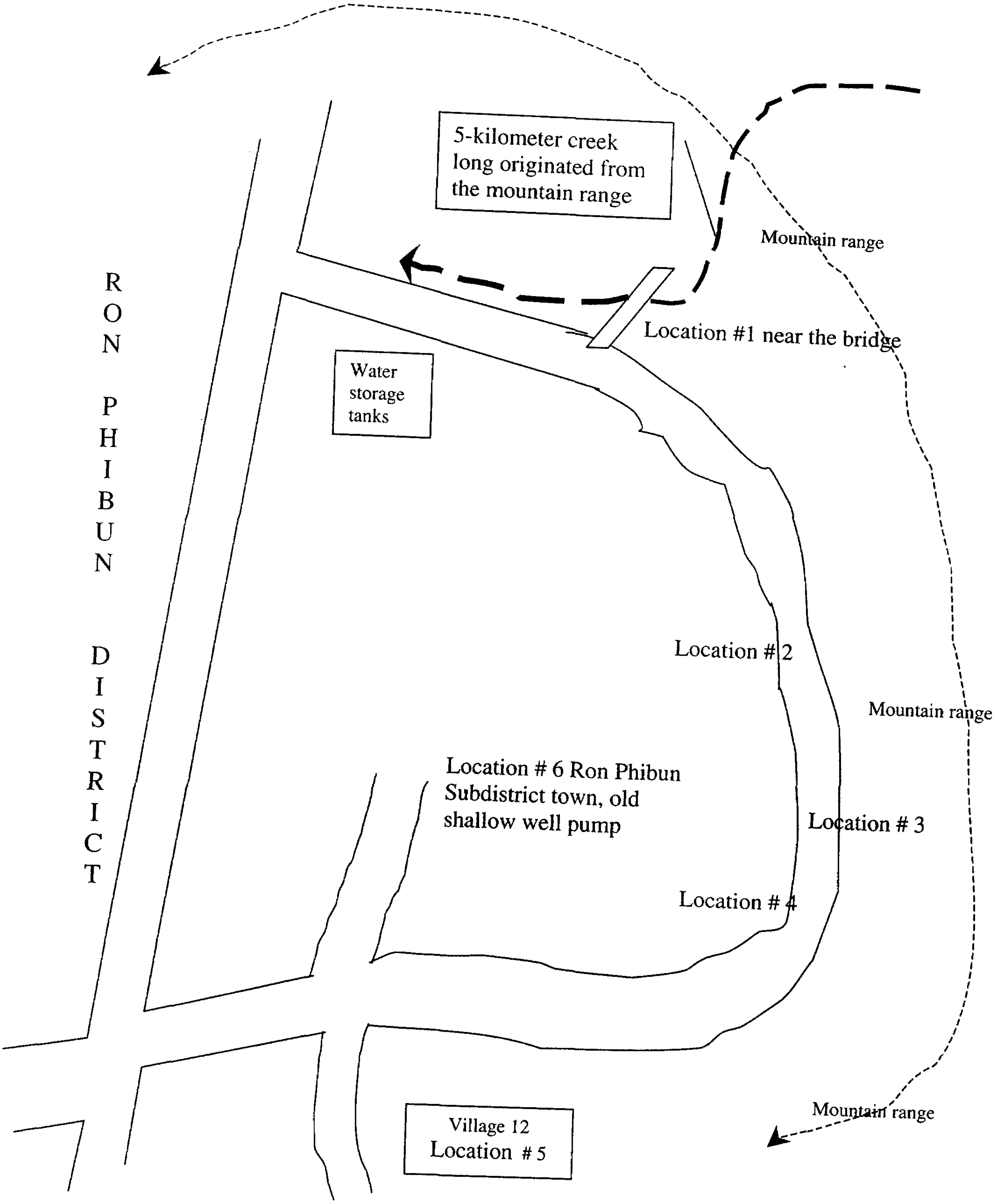


Figure 6-5 Sampling Location Map According to the Availability

Figure 6-6 Field Test Kit Measurement

Figure 6-7 Public Water Source Sample Collection and Measurement

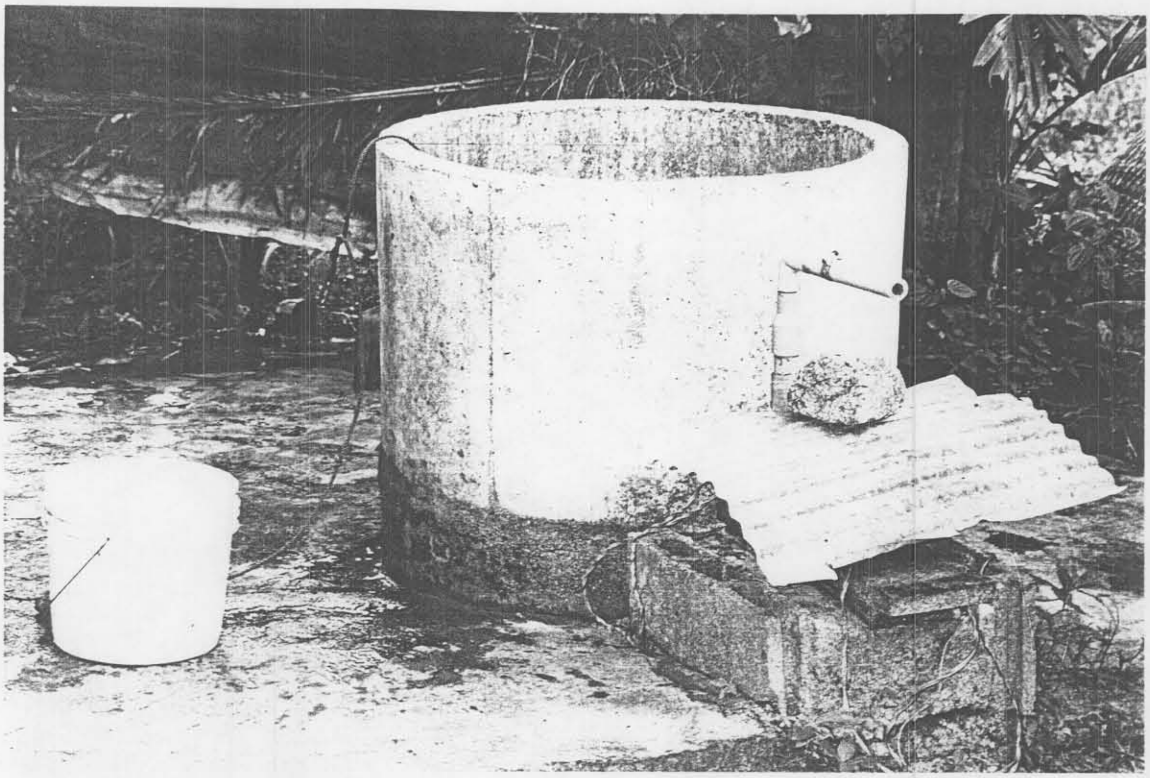


Figure 6-8 Shallow Well Water Source Utilized as Washing

Figure 6-9 A Water Puddle in the Community

Figure 6-10 A Swamp in the Community

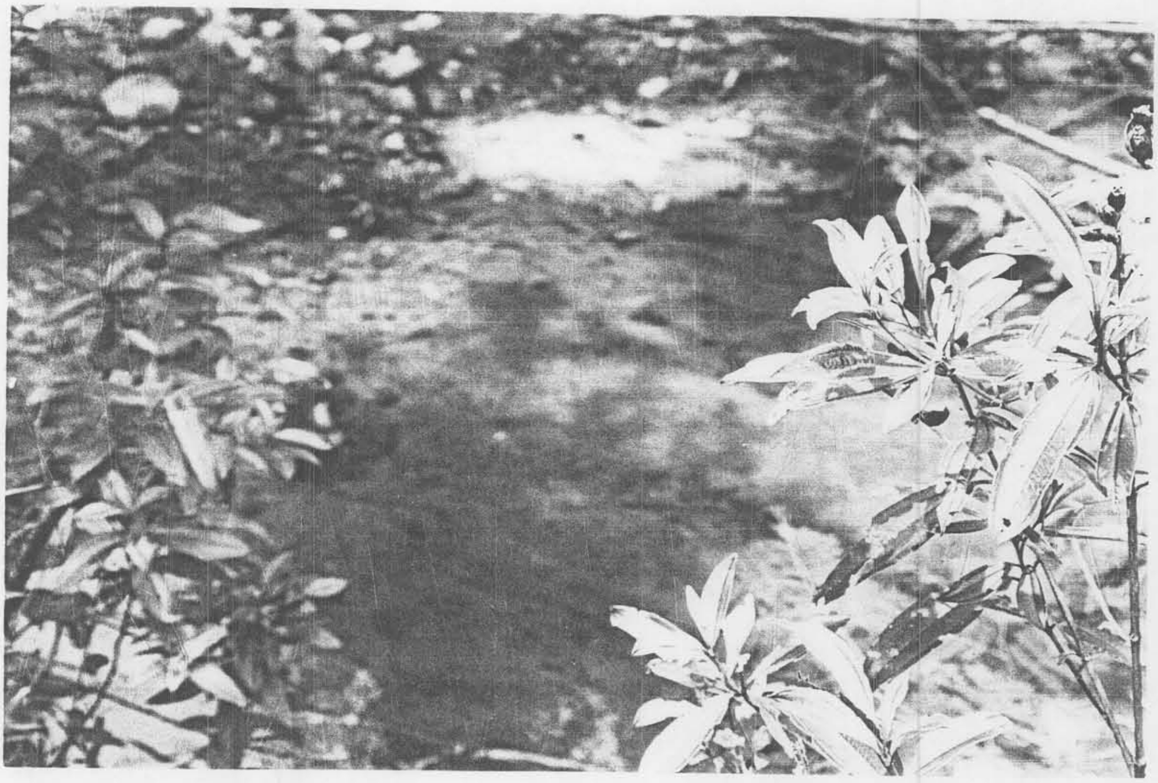


Figure 6-11 The Shallow Stream from Khao Suan Chan Mountain

Figure 6-12 Surface Water Sample Collection

Figure 6-13 Soil Sample Collection

Figure 6-14 Mud Sample Collection

CHAPTER VII

EFFECT OF ARSENIC IN SOUTHERN THAILAND

7.1 Arsenic and Health Effect on People in the Study Area

Several studies by various agencies indicated that more than 1,000 inhabitants in Ron Phibun area were suffering from various stages of arsenic poisoning, or so-called "Black Fever". In addition, arsenic was found in the hair and nails of more than 80% of school pupils. In 1992, it was also found that more than 22 % of pupils had skin symptoms of arsenic poisoning. Investigations indicated that the disease was caused by long-term consumption of arsenic-contaminated water (JICA, 2000).

Based on the field survey of the study area in May 2001, Figures 7-1 and 7-2 show one villager affected by chronic arsenic poisoning symptoms on skin.

Figure 7-1 One Lady Showing Where Her Skin is Affected by Arsenic

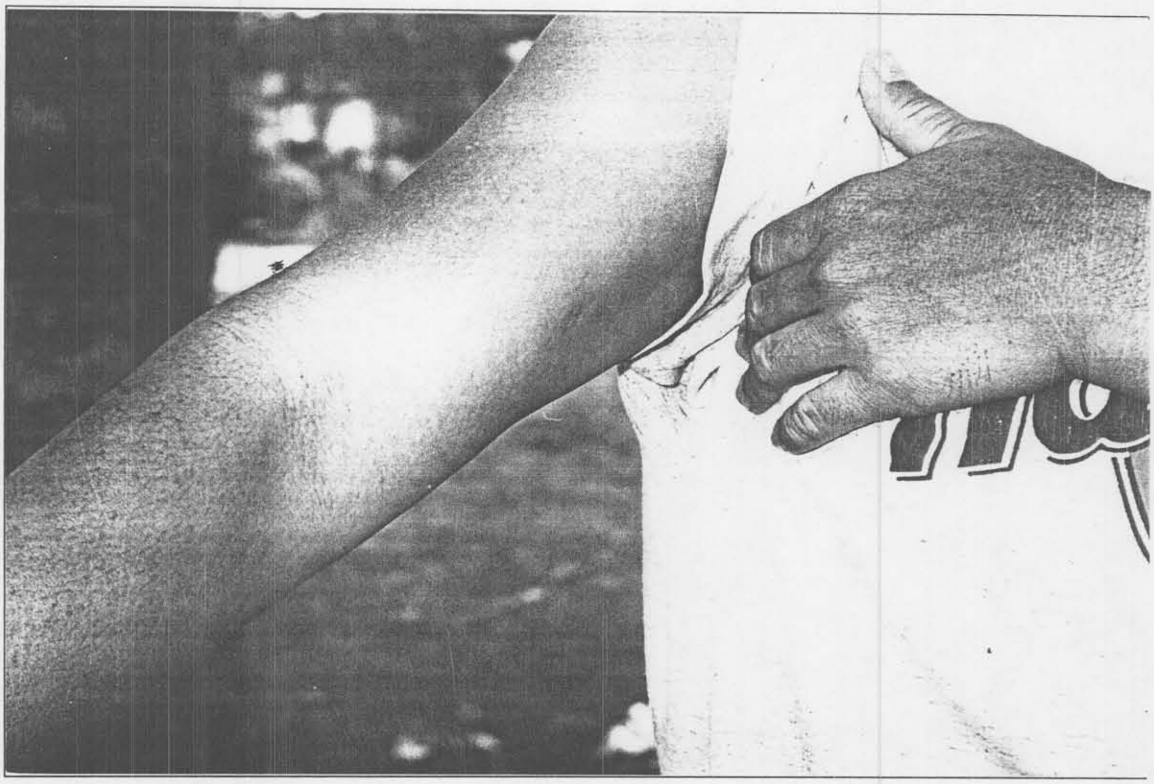


Figure 7-2 Black and White spots on the Arms due to Arsenic Poisoning

7.2 Social Impact of Arsenic Contamination

a) Attitude and Practice among Villagers in Ron Phibun District

A study was carried out in Ron Phibun during July 1988 by interviewing a total of 410 villagers in the area. Two hundred and six were indentified as in a high risk group and the rest (204) were in a low risk group. People in both groups appeared to understand what arsenic poisoning was and knew the cause of disease. The high-risk group had better general knowledge and attitude about the nature of disease but worse knowledge about the harmfulness when compared with the low risk ones. Sixty-six percent of villagers, whose well water had high level of arsenic (0.05 mg/L or 50 μg/L) went for physical examination, and the disease was found to occur in higher proportion in this group than in those in the low risk group. The reasons, why some villagers had no physical examination, were the absence of symptoms and their not having water from a contaminated well. The high risk group tended to abandon their wells and use rain water instead. Tap water and water from artesian well will be also used. Most of them expected that there would be sufficient water for drinking year round. Tap water was used only in high risk area (Bridhikitti et al., http://www.psu.ac.th/epidemiology).

Currently, people in Ron Phibun area don't seem to pay much attention because it is a chronic affect, and the skin symptoms appearance was very normal for them. They continue living as if there was no contamination of arsenic. The live stocks are fed naturally, as seen in Figure 7-3.

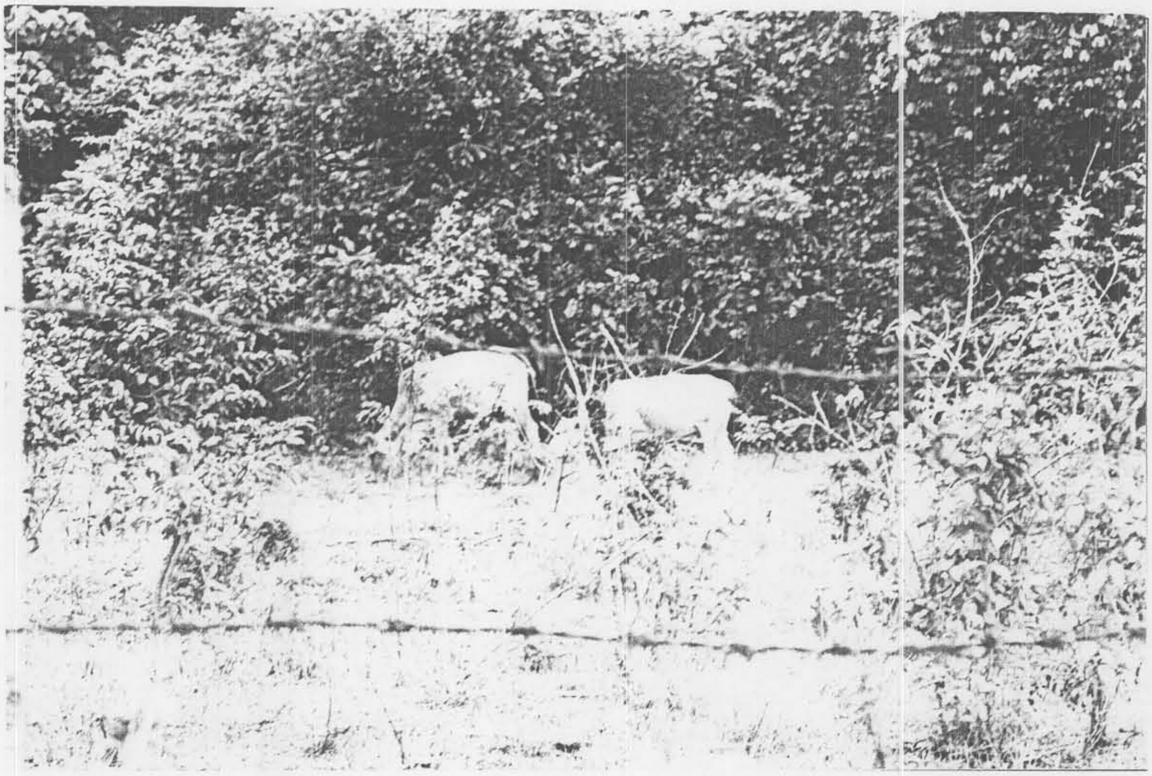


Figure 7-3 Cattle Eating Grass Grown in the Contaminated Soil

b) Attitude of the Locals towards Researchers

While interviewing people in the study area, during the field visit of this work, most were very cooperative and helpful. However, some people were irritated and disturbed by a large number of researchers going through Ron Phibun again and again in the past few years. Most researchers who went to Ron Phibun, asked the same questions and went through the same sample collection processes. Figure 7-4 shows the interviewing one helpful local, who led the research team of this study to the points of survey by previous research groups and also suggested where to collect samples from some public groundwater sources. Figure 7-5 shows the point of water sample collection from tube well during a previous study by JICA research team.

Figure 7-4 Interviewing One of the Locals

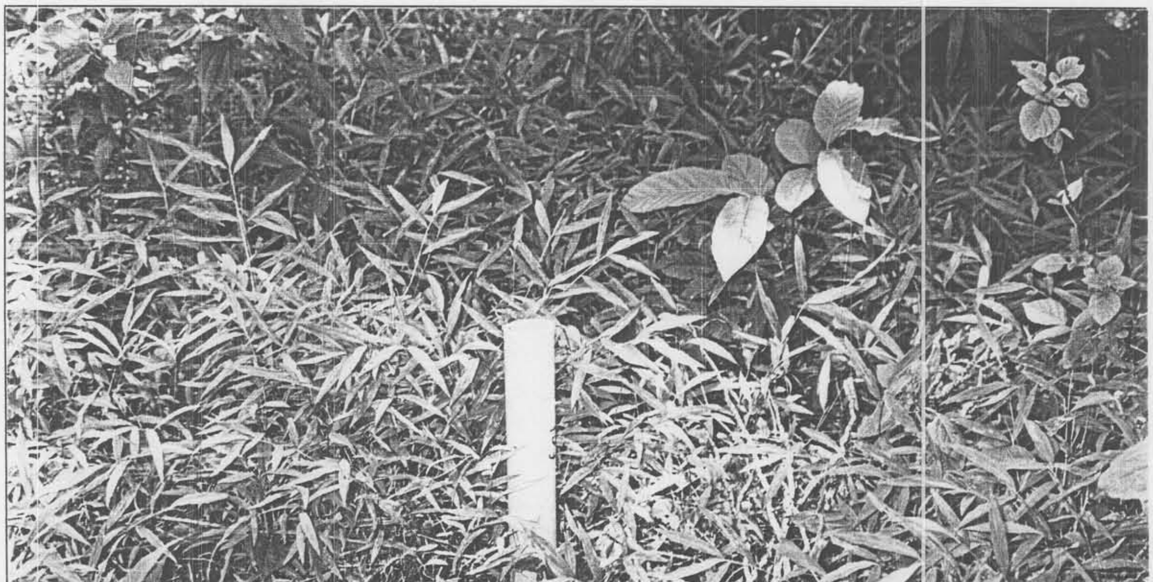


Figure 7-5 Tube Well Monitoring Station from JICA Project

CHAPTER VIII

REVIEW OF AVAILABLE REMOVAL TECHNIQUES

Previous chapters have documented the serious health effects that are posed by ingestion of arsenic through drinking water. While some palliative treatment of arsenicosis patients is possible, it is clear that the first step in treating patients, and preventing others from falling sick, is to identify safe sources of water for drinking and cooking in arsenic-affected areas. This chapter will present a brief overview of safe drinking water supply technologies that can provide arsenic-free drinking water, either through identifying an arsenic-free source or by removing arsenic from contaminated water. The main focus of this chapter is on rural and peri-urban settings, though many of the technologies discussed are applied in central water supply systems as well, and a few examples of centralized arsenic removal are given (USEPA, 2001-b).

8.1 Removal Treatment Technologies

In water, the most common valence states of arsenic are As(V), or arsenate, which is more prevalent in aerobic surface waters and As(III), or arsenite, which is more likely to occur in anaerobic ground waters. In the pH range of 4 to 10, the predominant As (III) compound is neutral in charge, while the As (V) species are negatively charged. Removal efficiencies for As(III) are poor compared to removal As(V) by any of the technologies evaluated due to the negative charge (USEPA, 2001-b).

> In September, 1993, USEPA developed, with contractor support, a document entitled "Treatment and Occurrence-Arsenic in Potable Water Supplies". This document summarized the results of pilot-scale studies examining low-level arsenic removal, from 50 parts per billion (ppb or µg/L) down to 1 ppb or less. USEPA convened a panel of outside experts in January 1994 to review this document and comment on the ability of the technologies to achieve maximum contaminant levels (MCLs) under consideration. Key findings of this report are summarized below. USEPA is in the process of gathering new information with contractor support on the technologies to update the report since it was created. Information on prospective technologies were obtained from more recent studies and the results of the studies are also summarized below (USEPA, 2001-b).

Technologies (USEPA, 2001-b):

The technologies under review perform most effectively when treating arsenic in the form of As(V). As (III) may be converted through pre-oxidation to As(V). Data on oxidants indicate that chlorine, ferric chloride, and potassium permanganate are effective in oxidizing As(III) to As(V). Pre-oxidation with chlorine may create undesirable concentrations of disinfection by-products. Ozone and hydrogen peroxide should also oxidize As(III) to As(V), but no data are available on performance.

Coagulation/Filtration (C/F) is an effective treatment process for removal of As(V) according to laboratory and pilot-plant tests. The type of coagulant and dosage used affects the efficiency of the process. Within either high or low pH ranges, the efficiency of C/F is significantly reduced. Alum performance is slightly lower than ferric sulfate. Other coagulants were also less effective than ferric sulfate. Disposal of the arsenic-contaminated coagulation sludge may be a concern especially if nearby landfills are unwilling to accept such a sludge.

Lime Softening (LS), operated within the optimum pH range of greater than 10.5, is likely to provide a high percentage of As removal for influent concentrations of 50 µg/L. However, it may be difficult to reduce consistently to 1 µg/L by LS alone. Systems using LS may require secondary treatment to meet that goal.

Activated Alumina (AA) is effective in treating water with high total dissolved solids (TDS). However, selenium, fluoride, chloride, and sulfate, if present at high levels, may compete for adsorption sites. AA is highly selective towards As (V); and this strong attraction results in regeneration problems, possibly resulting in 5 to 10 percent loss of adsorptive capacity for each run. Application of point-of-use treatment devices would need to consider regeneration and replacement.

Ion Exchange (IE) can effectively remove arsenic. However, sulfate, TDS, selenium, fluoride, and nitrate compete with arsenic and can affect run length. Passage through a series of columns could improve removal and decrease regeneration frequency. Suspended solids and precipitated iron can cause clogging of the IE bed. Systems containing high levels of these constituents may require pretreatment.

Reverse Osmosis (RO) provides removal efficiencies of greater than 95 percent when operating pressure is at ideal psi. If RO is used by small systems in the western U. S., 60% water recovery will lead to an increased need for raw water. The water recovery is the volume of water produced by the process divided by the influent stream (product water/influent stream). Discharge of reject water or brine may also be a concern. If RO is used by small systems in the western U. S., water recovery will likely need to be optimized due to the scarcity of water resources. The increased water recovery can lead to increased costs for arsenic removal.

Electrodialysis Reversal (EDR) is expected to achieve removal efficiencies of 80 percent. One study demonstrated arsenic removal to 3 µg/L from an influent concentration of 21 µg/L.

Nanofiltration (NF) was capable of arsenic removals of over 90%. The recoveries ranged between 15 to 20%. A recent study showed that the removal efficiency dropped significantly during pilot-scale tests where the process was operated at more realistic recoveries. If nanofiltration is used by small systems in the western U. S., water recovery will likely need to be optimized due to the scarcity of water resources. The increased water recovery can lead to increased costs for arsenic removal.

Point of Use/Point of Entry (POU/POE), POU and POE devices can be effective and affordable compliance options for small systems in meeting a new arsenic MCL. A Federal Register notice is being prepared by EPA to delete the prohibition on the use of POU devices as compliance technologies. Because of this prohibition, few field studies exist on the application of POU and POE devices. One such case study was performed by USEPA, in conjunction with the Village of San Ysidro, in New Mexico (Rogers 1990). The study was performed to determine if POU Reverse Osmosis (RO) units could satisfactorily function in lieu of central treatment to remove arsenic and fluoride from the drinking water supply of a small rural community of approximately 200 people. A RO unit, a common type of POU device, is a membrane system that rejects compounds based on their molecular properties and characteristics of the reverse osmosis membrane. The RO units removed 86% of the total arsenic.

8.2 Prospective Technologies

Ion Exchange with Brine Recycle. Research recently completed by the University of Houston (Clifford) at McFarland, CA and Albuquerque, NM has shown that ion exchange treatment can reduce arsenic (V) levels to below 2 µg/L even with sulfate levels as high as 200 mg/L. Sulfate does impact run length, however; the higher the sulfate concentration, the shorter the run length to arsenic breakthrough. The research also showed that the brine regeneration solution could be reused as many as 20 times with no impact on arsenic removal provided that some salt was added to the solution to provide adequate chloride levels for regeneration. Brine recycle reduces the amount of waste for disposal and the cost of operation (USEPA, 2001-b).

Iron (Addition) Coagulation with Direct Filtration. The University of Houston (Clifford) recently completed pilot studies at Albuquerque, NM on iron addition (coagulation) followed by direct filtration (microfiltration system) resulting in arsenic (V) being consistently removed to below 2 µg/L. Critical operating parameters are iron dose, mixing energy, detention time, and pH (USEPA, 2001-b).

In conventional Iron/Manganese (Fe/Mn) removal processes, iron coagulation/filtration, and iron addition with direct filtration methods are effective for arsenic (V) removal. Source waters containing naturally occurring iron and/or manganese and arsenic can be treated for arsenic removal by using conventional Fe/Mn removal processes. These processes can significantly reduce the arsenic by removing the iron and manganese from the source water based upon the same mechanisms that occur with the iron addition methods. The addition of iron may be required if the concentration of naturally occurring iron/manganese is not sufficient to achieved the required arsenic removal level (USEPA, 2001-b).

8.3 EPA Research Activities

EPA' s Office of Research and Development (ORD) is in the process of funding three arsenic treatment research activities. First, a field study will be conducted to evaluate the effectiveness of eight full scale drinking water treatment plants to remove arsenic from their source water on a sustained basis for six to twelve months. The processes included in this field study will be two large system technologies, conventional coagulation/ filtration, and lime softening, and two small system technologies, ion exchange and the iron/manganese, and oxidation/filtration process. These evaluation studies will also include characterization and quantification of the residuals produced by each process. A second project will consist of laboratory and pilot plant studies to characterize the kinetics of oxidation of arsenic III to arsenic V by various oxidants and oxidation processes. And finally, a workgroup meeting is being planned for February, 1998 to review the state of the science of existing and developing drinking water treatment technologies effective for arsenic removal. Future work will entail additional full scale field studies on other small system treatment alternatives, such as activated alumina treatment, residuals characterization and management studies, and treatment cost and evaluation studies (USEPA, 2001-b).

a) **Issues Concerning Arsenic Removal Techniques** (USEPA, 2001-b)

Some important issues concerning the arsenic removal technologies are summarized as follows:

Coagulation/Filtration and Lime Softening:

- Not appropriate for most small systems--high cost, need for well trained operators, and variability in process performance
- CF & LS alone may have difficultly in consistently meeting a low-level MCL. IE may be useful as a polishing step.
- Disposal of sludge may be a problem

Activated Alumina:

- Lack of availability of F-1 alumina. Testing of substitute not yielding same results.
- Chemical handling requirements may make this process too complex and dangerous for many small systems
- AA may not be efficient in the long term, as it seems to lose significant adsorptive capacity with each regeneration cycle
- Highly concentrated waste streams-disposal of brine may be a problem

Ion Exchange:

- Highly concentrated waste by-product stream- disposal of brine may be a problem. Brine recycling might reduce the impact.
- Sulfate levels affect run length
- Recommended as a BAT primarily for small, ground water systems with low sulfate and TDS, and as the polishing step after filtration for low-level options

Reverse Osmosis/Nanofiltration:

- Extensive corrosion control could be required for low-level option--ability to blend would be limited
- Water rejection (about 20-25 percent of influent) may be an issue in water-scarce regions

Electrodialysis Reversal:

- Water rejection (about 20-25 percent of influent) may be an issue in water-scarce regions
- May not be competitive with respect to costs and process efficiency when compared with RO and NF, although it is easier to operate

Point of Use/Point of Entry:

- Adopting a POU/POE treatment system in a small community requires more record keeping to monitor individual devices than does central treatment.
- POU/POE systems require special regulations regarding customer responsibilities, water utility responsibilities, and the requirement of installation of the devices in each home obtaining water from the utility.

Waste Disposal:

Disposal of the arsenic-contaminated coagulation sludge from the C/F and LS technologies may be a concern. For large treatment plants, a large body of water would likely be needed to discharge the contaminated brine stream from the RO/NF technologies. Inland treatment plants would possibly need either some pretreatment prior to discharge or would need to discharge to the sanitary sewer due to the increase in salinity. Discharge to sanitary sewers may require pretreatment to remove high arsenic levels. The waste stream produced by IE/AA technologies is a highly concentrated brine with high TDS. These brine streams may require some pretreatment prior to discharge to either a receiving body of water or the sanitary sewer.

b) Questions of Significance

Some questions of significance related to arsenic removal technologies include the following (USEPA, 2001-b):

- Are there other feasible candidates for treatment technologies for removal of arsenic from drinking water?
- What are the best technology options for small ground water systems?
- How cost effective and efficient are point-of-use and point-of-entry treatment units for arsenic?
- Are other field studies available on the application of POU or POE devices for arsenic removal?
- What new treatment technology performance data are available, especially for achieving arsenic concentrations in finished water below 5 µg/L?

8.4 Arsenic Removal in Various Countries

Arsenic removal technologies are less well documented in standard water supply texts, though a large and growing literature exists in technical journals. In addition, many other valuable papers are found in seminars and conferences proceedings, particularly in Latin America and Asia. Since many of these resources are less accessible, this section presents some review of arsenic removal technologies in various countries.

Safe drinking water options to address the natural/human disaster of arsenic contamination of groundwater in Bangladesh, West Bengal in India, and other emerging economies, include:

- well-water treatment
- surface water treatment
- rain water collection
- construction of deeper wells
- groundwater treatment/aquifer recharge

One such review study, conducted in 1999, provided a comprehensive review of low-cost, well-water treatment options, based on actual laboratory, pilot and full-scale experiments and applications. Twenty-two specific technologies were presented under the general categories of oxidation, coagulation/precipitation, sedimentation, filtration, adsorption, solar distillation and membrane processes (Murcott, 2000).

Three case studies from the above review are presented here.

1) Hungary

In Hungary it was well known that 20 years ago more than 80 settlements with 400,000 inhabitants were served with tap water containing As-ions >50 mg/L concentration. This contamination arises from natural leaching of arsenic rocks by the percolating water. Arsenic ions are accompanied by high amounts of ammonium-, Fe-, and Mn-ions, as well as humic acids (about 10-15 mg/L), dissolved gases, and has high temperature, >30 °C. The new regulation of European Union sets a limit of 10-mg As/L. Today more than 1.3 million inhabitants on 400 settlements are served with tap water containing higher arsenic content than 10-mg/L in Hungary. To keep this new standard, a huge effort has to be done. Solution of this problem needs a concentrated research since the 400 wells are well scattered over the country. Research activities included:

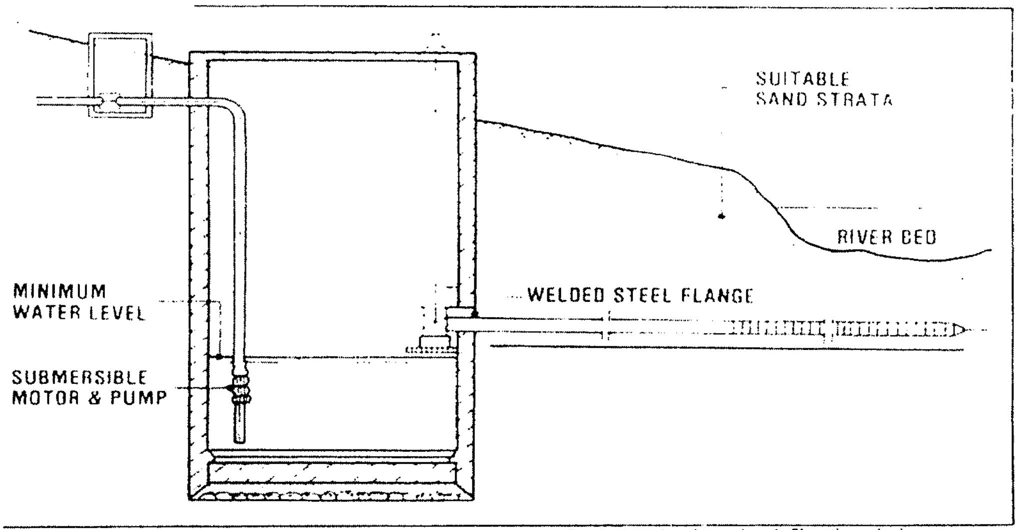
i. evaluation of existing and widely applied arsenic removal technologies,
ii. development of new efficient arsenic removal technologies to provide the 10 g As/L level. From environmentally friendly raw materials new absorbents were developed.

Main features of absorbents were determined: the pH value belong to the zero point of charge of the adsorbent was determined in equilibrium solutions in the presence As (III)- and As (V)-ions, (pHiep), the amount of surface charged groups, surface charge, surface potential, stability constants of compounds formed on the surface of the adsorbent and the effect of pH to the adsorbed amount of arsenic ions.

The adsorbent/solution ratios, the ionic strength, the initial pH of the solution and arsenic concentration were changed for the characterization. Results were evaluated by chemical and electrical double layer models. (Hlavay and Polyak, 2000)

Box 8.1: Bank infiltration in Hungary

Hungary has developed what is probably the largest bank infiltration system in Europe. The municipal water works in the capital, Budapest, has installed a network of shallow wells (typically 6-10 meters deep) on two large islands in the Danube river. Supply wells are most often sited 100-300 m from the shore, but in some cases are as close as 30 meters. Isotopic tests have shown that the abstracted water is very young, and almost entirely derived from the river. However, bacteriological quality is good, and the water requires little treatment - only iron and manganese removal from some wells, and safety chlorination in all cases to provide a residual for distribution. Underground tunnels deliver the water to the capital and surrounding areas, meeting the needs of some 4.5 million inhabitants, or about 45% of the country's population. Similar bank infiltration systems supply water to most major settlements on the Danube. Bank river intake using infiltration drain is shown in the figure below.



Bank river intake using infiltration drains

Source: Johnston, et al., 2001

2) Bangladesh

A simple three-pitcher (locally known as '3-kalshi') filtration assembly, made entirely from readily available local materials, has been tested for its efficacy in removing arsenic from the groundwater of Bangladesh. In this set up, the first kalshi at the top contains iron chips and coarse sand; the second kalshi has wood charcoal and fine sand, while the third kalshi collects filtered water. About 240 L of arsenic contaminated groundwater and groundwater samples spiked with high concentrations of both As (III) and As (V) were filtered through the system. Analytical measurements were performed by using anodic stripping voltammetry (ASV). The techniques of atomic absorption spectrophotometry and inductively coupled plasma atomic emission spectrometry (ICPAES) were employed to validate measurements of arsenic and 24 other metals before and after filtration. Total Fe, ionic conductivity, Eh, pH, temperature, and flow rates were measured during various stages of the filtration process. The arsenic (total) was removed to below 10 ppb level for most samples even at the highest input concentration of 1100 ppb arsenic. The dissolved iron concentration decreased from an average 6000 ppb to 200 ppb after filtration. With a fixed input of dissolved iron, the arsenic removal capacity increases linearly with each filtration. A decrease in conductivity by 35% of the original value indicates substantial removal of dissolved ions. The daily capacity of the 3-kalshi system varied from 42 -148 L/day. The final water quality meets, and in some cases, exceeds the guideline values recommended by USEPA, World Health Organization, and Bangladesh. This simple setup could make potable water in rural Bangladesh. (Mohammad et al., 2000)

Box 8.2 Deep Aquifer in Bangladesh

In Bangladesh, the most serious arsenic contamination is seen in shallow tubewells, while only a few deep tubewells have been shown to contain high levels of arsenic. A major hydrogeological survey found that in surveyed areas, while over 40% of wells less than 100 m deep (n=1662) exceeded the Bangladesh drinking water standard of 50 µg/L, less than 1% of the wells deeper than 150 m (n=317) exceeded the limit. The deeper wells are less prone to arsenic contamination because they are screened in a pre-Pleistocene aquifer. These aquifer sediments are millions of years old, and any arsenic present has probably been flushed out, or is present in a stable solid form. The shallow wells, in contrast, are screened in Holocene aquifers that are only thousands of years old, and have not been completely flushed since deposition. These shallow sediments are rich in organic matter, which creates the reducing conditions that encourage mobilization of arsenic, as well as elevated iron levels (Figure 8-1).

Source: Johnston, et al., 2001

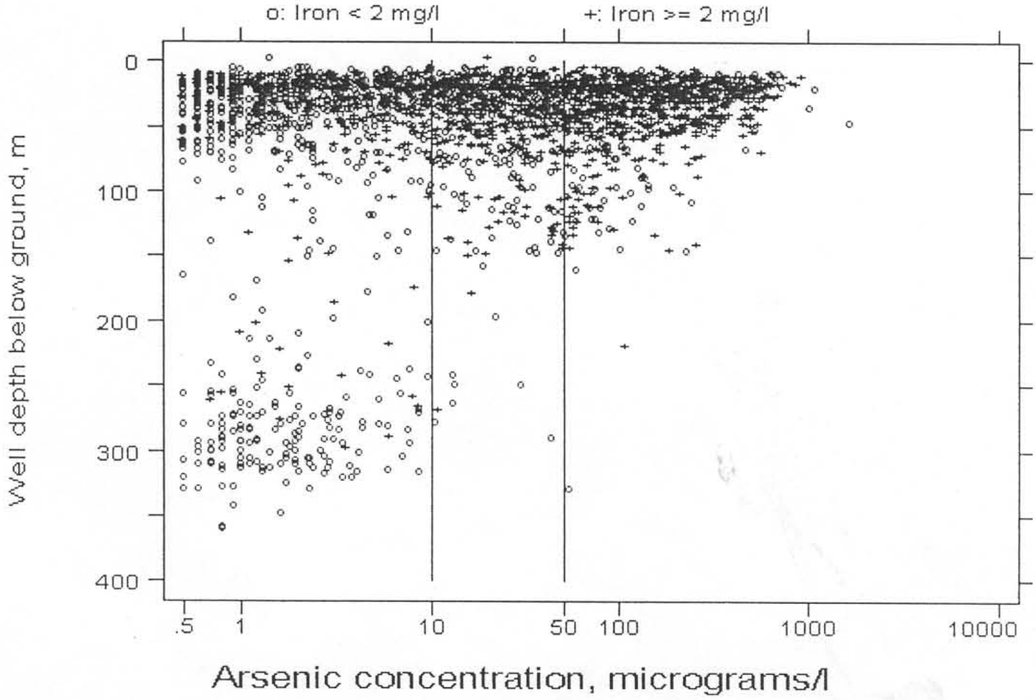


Figure 8-1 Arsenic and Well Depth in Bangladesh (source: Johnston, et al., 2001)

Note: vertical lines at 10 and 50 µg/l represent the WHO Guideline Value and Bangladesh Standard, respectively.

Box 8.3 Three Kalshi Filter in Bangladesh

A simple arsenic removal system has been developed in Bangladesh, based on a traditional sand filtration water purification system. Three 18-L clay pitchers (called kolshi) are stacked vertically in a metal rack. The top pitcher contains coarse sand and metal iron filings, the second pitcher wood charcoal and fine sand, and the third serves as storage. Arsenic-rich groundwater is poured into the top pitcher, and trickles through small holes into the second and third pitchers. One unit costs about $5, and flow rates average 2.6 to 2.9 liters per hour.

Laboratory tests show that the three kalshi filter can remove arsenic from groundwater containing a wide range of arsenic concentrations (80 to over 1000 µg/L). Arsenite proportions in the groundwater ranged from 40% to near total, and were typically greater than 70%. Filtered water generally contained from 5-30 µg/L arsenic, all as arsenate. In some cases arsenic removal exceeded 99%.

Field testing of two hundred units confirms this impressive finding: after one week of operation, 90% of the filters produced water in which no arsenic could be detected using field kits, and 7% produced water with significantly reduced but detectable arsenic levels. Iron levels were also dramatically reduced, in some cases from over 1 mg/L to below 0.1 mg/L. After four months of operation, the filters were still operating efficiently.

This system shows great promise in that it is highly effective, inexpensive, easy to operate, and is similar a traditional water treatment method. A significant drawback of the three kolshi filter is that treated water can easily become contaminated with faecal bacteria, either during transport of the water from the well, or storage in the household. Bacteria may also be present in the media, if it is not sterilized. Field tests showed that some slight contamination occurred before filtration (15% of samples showed some contamination, with a maximum of 130 TC/100 ml), but that bacteria counts increased dramatically during filtration and storage: nearly two thirds of treated samples showed counts higher than 100 TC/100 ml, and a fifth had levels above 10,000 TC/100 ml. It may be possible to reduce the risk of bacterial contamination by sterilizing the media before filter construction.

Source: Johnston, et al., 2001

3) USA

Since 1993, Southern Company Services, Inc., cofunded by the Electric Power Research Institute (EPRI), has developed and tested a number of technologies to clean soil and groundwater contaminated with arsenic. These technologies include:

- solidification/stabilization (S/S) with Portland cement and chemical additives
- soil flushing (in situ soil washing)
- iron coprecipitation combined with cross-flow
- ceramic membrane filtration
- electroremediation or electrokinetics
- phytoremediation
- in situ chemical fixation

- natural attenuation modeling

Two sites were treated with the S/S method. In another study, a number of soils flushing reagents were tested. With this application, iron coprecipitation and ceramic membrane filtration were selected as water treatment technologies. These water treatment processes cleaned arsenic from influent concentrations of about 0.5 to 1 mg/L (500 µg/L to 1000 µ/L) to below the drinking water standard (0.05 mg/L or 50 µg/L) or lower (< 0.005 mg/L or < 5 µg/L).

In electroremediation, contaminants are moved under the influence of a direct current between electrodes in the ground. Successful electroremediation treatability studies were performed in the laboratory, and a field demonstration at an arsenic-contaminated site underway. In the phytoremediation studies, two native plants were demonstrated to take up arsenic, with the potential for stabilizing or remediating arsenic-contaminated soils. Treatability studies for in situ fixation, where a liquid chemical reagent is applied to fix the arsenic in place in a less leachable form, underway. In 1999, Southern Company tested several computer models designed to predict fate and transport of contaminants. Best simulated observed conditions at arsenic-contaminated sites. (Redwine, 2000)

8.5 Arsenic Removal in Thailand

Arsenic from contaminated drinking water is one of the causes of arsinosis at Ron Phibun District, Nakhon Si Thammarat Province. A preliminary study on a small-size water-filtering system to remove arsenic from shallow-well water often used for drinking and cooking were conducted in 1997. As (III) was oxidized to As (V) by chlorinating. Ferric chloride was used to precipitate arsenic at a ratio of Fe/As > 4/1. Enhanced flocculation occurred when the pH was raised to 7, when more than 90 % of arsenic precipitated out. Complete removal of arsenic was achieved by filtering through a column packed with Fe (II) treated activated carbon. This system could reduce arsenic to less than <0.01 mg/L (< 10 µg/L), which is the limit suggested by WHO. (Arrykul et al., 1997)

8.6 Strategy to deal with Arsenic Contamination Problem

a) Source Substitution:

Three main sources of water can be considered as substitutes for contaminated water: groundwater, rainwater, and surface water (Johnston, et al., 2001).

Groundwater is largely free from harmful bacteria and fecal contamination, though a poorly designed or constructed well can become contaminated from surface water. To prevent this, wells should be grouted around the borehole, and finished at the surface with a concrete platform, with good drainage away from the well. Most commonly, groundwater is reached through boreholes, drilled either by hand or machine. When drilling in arsenic-affected areas, precautions should be taken to make sure that safe aquifers do not become contaminated. If a borehole must penetrate a contaminated aquifer to reach safe water below, the borehole should be grouted after drilling is completed. In some areas, groundwater can have naturally occurring water quality problems aside from arsenic, such as high levels of iron, manganese, nitrate, chloride, or fluoride. Before promoting new sources of groundwater, the chemical quality should be tested in laboratories (Johnston, et al., 2001).

Rainwater is free from arsenic, and if properly collected, can provide a safe drinking water source. Bacterial contamination is a concern, but this can be minimized by collecting rain from a roof (galvanized metal makes a good collection surface). Tree branches should not overhang the roof, and the roof should periodically be cleaned. Water can be collected through gutters, and piped into a storage tank. Tanks can be built of many materials, but ferrocement (cement with wire reinforcement) is strong and inexpensive, and also can keep the water pH near neutral. When rain first begins to fall, especially at the end of a dry season, roof water should be allowed to run off for 10-15 minutes before collection, to clean the roof. Close to urban areas, and when metal roofs are used, collected rainwater can contain unsafe levels of lead and zinc, and possibly other metals. Typically, collected rainwater contains low levels of bacteria (fecal and total coliform counts average 5-15 and 25-75 per 100 ml, respectively). Water quality testing should be done to ensure that collected water meets relevant standards. In some cases, rainwater may be the safest source of drinking water available, even if low levels of bacteria are present. Often, rainfall is seasonal, and large storage tanks would be required to bridge the dry season. While water can be safely stored for long periods, the large tanks may be too expensive. In such cases, small storage tanks provide an inexpensive and convenient water source during the rainy season, and other sources should be found for the dry season as shown in Figure 8-2 (Johnston, et al., 2001).

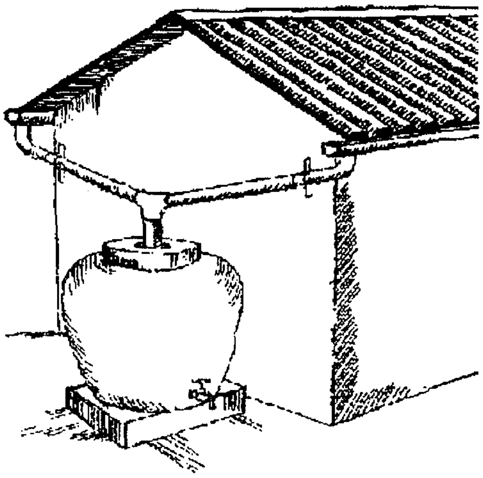


Figure 8-2 Rooftop Catchment with Tank (Source: Johnston, et al., 2001)

Surface water requires more treatment than groundwater or rainwater, since it usually has very high bacterial contamination. In order to ensure that treatment is always effective, it is important to include multiple barriers to contamination. The most effective treatment appropriate at the rural, community level, is slow sand filtration, followed by a safety dose of chlorine, as shown in Figure 8-3.

In slow sand filtration, surface water passes through prefilters, and is then filtered through 80-100 cm of sand. A bio-layer develops near the surface of the sand, which can effectively destroy most pathogens. Operation of the slow sand filter may be improved through pretreatment with bank infiltration, sedimentation or roughing

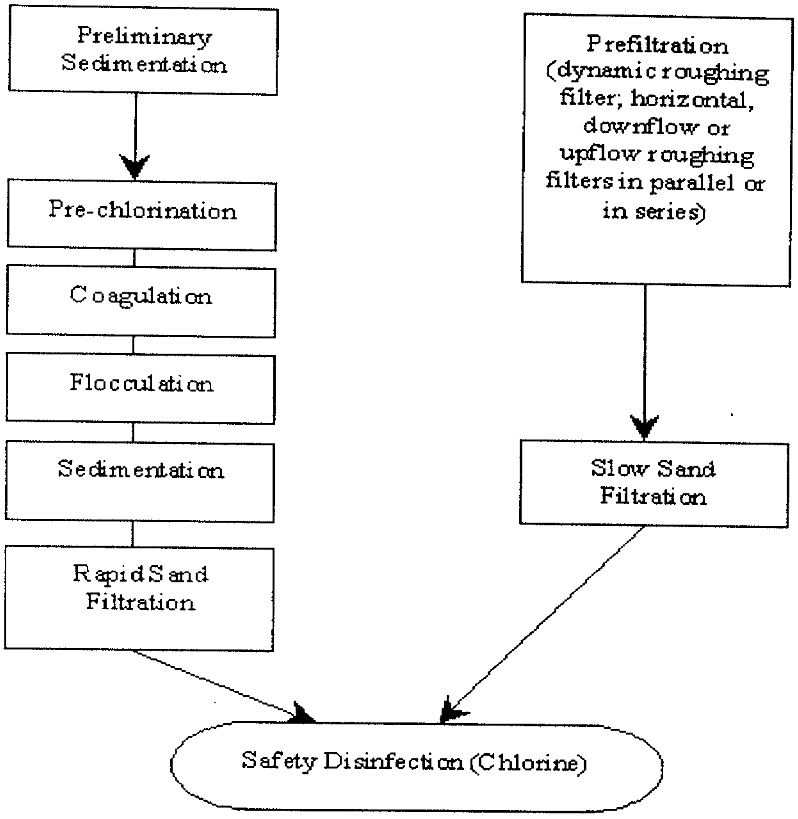


Figure 8-3 Multiple Barriers to Microbiological Contamination in Surface Water Treatment (Source: Johnston, et al., 2001)

filtration. The use of roughing filters, in particular, permits effective treatment of water containing higher levels of turbidity, color, and pathogens. This 'multi-stage filtration' (Figure 8-4) is a robust and reliable treatment method in rural communities, and for small and medium size municipalities.

Slow sand filtration will not efficiently remove arsenic or agricultural chemicals such as pesticides. It is important to test the water quality of the unfiltered water to make sure that arsenic and pesticides are not present. Likewise, for bacteria, the cleaner the source water, the cleaner the treated water will be. Ponds and other surface water sources used for slow sand filtration should be protected: latrines should not be located near the water, and people and animals should not bathe nearby.

Slow sand filters must be regularly cleaned, and the top few centimeters of sand in the filter should be scraped off. After cleaning, the filter will need several days to 'ripen', and treat water effectively. During this ripening period, filtered water should be disinfected before drinking. Solar disinfection, or SODIS, is a promising new technology that uses clear plastic bottles to purify water. Bottles are filled with clear water and left in the sun for several hours. The combination of ultraviolet radiation and high temperature is able to destroy most pathogens. SODIS will not improve the chemical quality of water, but it can provide an inexpensive, easy way to improve microbiological quality. Surface water may also be purified by drawing the water from shallow wells located close to the surface water body. This 'bank infiltration' can improve the chemical as well as microbiological quality of water, and is becoming more popular in Europe (Johnston, et al., 2001).

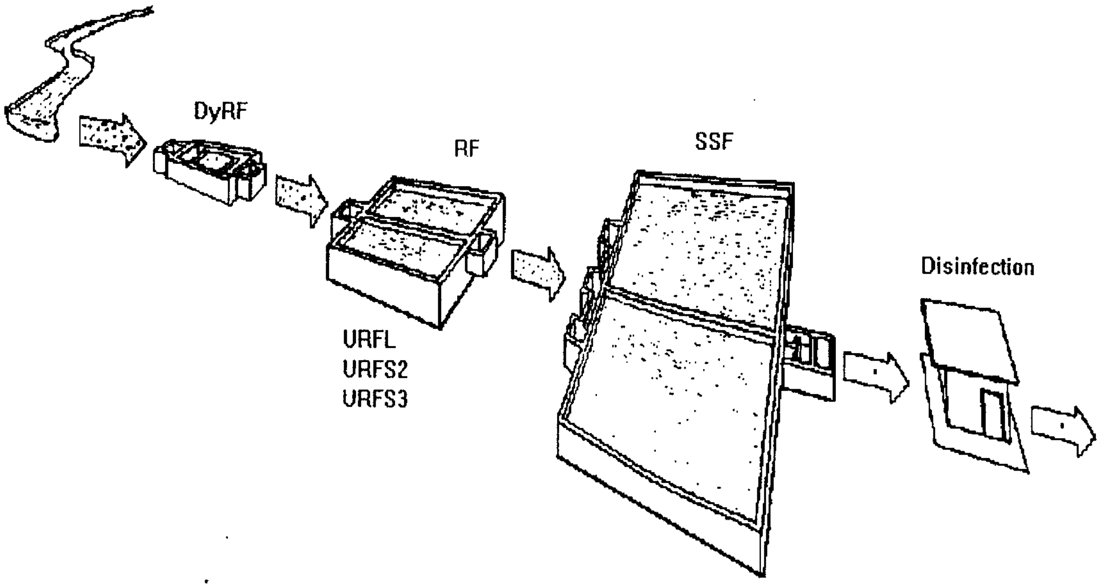


Figure 8-4 Multi-stage Filtration (Source: Johnston, et al., 2001)

b) Arsenic Removal

In some areas source substitution may be impossible during part or all of the year, or may be very expensive. Arsenic removal may be more appropriate in these situations.

Coagulation and filtration is the most common arsenic removal technology. By adding a coagulant such as alum, ferric chloride, or ferric sulfate to contaminated water, much of the arsenic can be removed. If arsenic is present as arsenite, the water should be oxidized first, using chlorine, permanganate, ozone, or other oxidants. After adding the coagulant, the water should be stirred, allowed to settle, and filtered for best results. Coagulation improves parameters such as turbidity and color, and can reduce levels of organic matter, bacteria, iron, manganese, and fluoride, depending on operating conditions (Johnston, et al., 2001).

Coagulation with ferric salts works best at pH below 8. Alum has a narrower effective range, from pH 6-7. If pH is above 7, removal may be improved by adding acid to lower pH. In general, the higher the coagulant dose, the better the arsenic removal. Typical doses are 5 to 30 mg/L ferric salts or 10 to 50 mg/L alum. If the source water has high levels of phosphate or silicate, coagulation may be less effective. However, sulfate, carbonate, and chloride have little effect on removal rates.

Ion exchange resins are commercially produced, synthetic materials that can remove some compounds from water. Most commonly they are used in water softening, but some resins are very good at removing arsenic. These resins only remove arsenate, so if the raw water contains arsenite, it should be oxidized first. Other compounds, including sulfate, nitrate, nitrite, and chromate, are also removed to some degree by most arsenic removal resins (Johnston, et al., 2001).

Ion exchange resins usually come as sand-like grains, and are used in packed beds or columns, most often with an Empty Bed Contact Time (EBCT) of 1.5 to 3 minutes. A bed can typically treat several hundred to a thousand bed volumes before the resin must be regenerated. The amount of water a bed can treat is largely independent of arsenic concentration and pH. Instead, run lengths are largely determined by sulfate levels, since sulfate can quickly saturate the resin. For this reason, ion exchange resins are only appropriate in waters with under 120 mg/L sulfate, and work best with waters with under 25 mg/L sulfate. High levels of dissolved solids (TDS > 500 mg/L) will also shorten run times.

Resins will not adsorb iron, but if the raw water contains high levels of dissolved iron, the iron can precipitate out and clog the filter. When the resin is saturated, it can easily be regenerated with a simple brine solution. Regenerated resin can be used over and over again (Johnston, et al., 2001).

Activated alumina, like ion exchange resins, is commercially available in coarse grains. Activated alumina is used in packed beds, with longer EBCTs (about 5 to 8 minutes) than ion exchange resins. Activated alumina beds usually have much longer run times than ion exchange resins, typically several tens of thousands of beds can be treated before arsenic breakthrough. Activated alumina works best in slightly acidic waters (pH 5.5 to 6) – above pH 7 removal efficiency drops sharply. The main factors controlling bed run length are pH and arsenic concentration. Concentrations of other solutes have a relatively small effect (Johnston, et al., 2001).

For best results, raw water containing arsenite should be oxidized before treatment. Phosphate, sulfate, chromate and fluoride are also removed by activated alumina, but nitrate is not. Saturated activated alumina can be regenerated with flushing with strong base followed by strong acid. Regenerated media loses some volume and eventually must be replaced. Like ion-exchange resins, activated alumina beds can be clogged by precipitation of iron.

Membrane methods for arsenic removal include reverse osmosis and nanofiltration, as shown in Figure 8-5. These make use of synthetic membranes, which allow water through but reject larger molecules, including arsenic, chloride, sulfate, nitrate, and heavy metals. The membranes must be operated at high pressures, and usually require pretreatment of the raw water. Household level membrane units usually only treat about 10% of the water, resulting in a large waste stream. Municipal membrane units can achieve higher total recovery rates by using membranes in series. Currently available membranes are more expensive than other arsenic removal options, and are more appropriate in municipal settings, where very low arsenic levels are required. However, membrane technology is advancing rapidly, and it is conceivable that future generations of membranes could be used effectively in rural settings (Johnston, et al., 2001).

Other techniques exist for arsenic removal, but are less well documented. When arsenic-rich water also contains high levels of dissolved iron, iron removal will also remove much of the arsenic. Many new materials are being tested for arsenic removal, including low-tech iron-coated sand and greensand, novel iron-based sorbents, and specially engineered synthetic resins. Some of this research is promising, but these technologies are still under development. All arsenic removal technologies generate some kind of arsenic-rich waste. These wastes are generally not hazardous to handle, but special care must be taken in disposing of them, especially at centralized plants. At the community or household level, the volume of waste generated is usually not enough to have a major environmental impact, and stabilized wastes can be disposed of with other solid wastes, solidified in concrete, buried, or discarded in sanitary latrines (Johnston, et al., 2001).

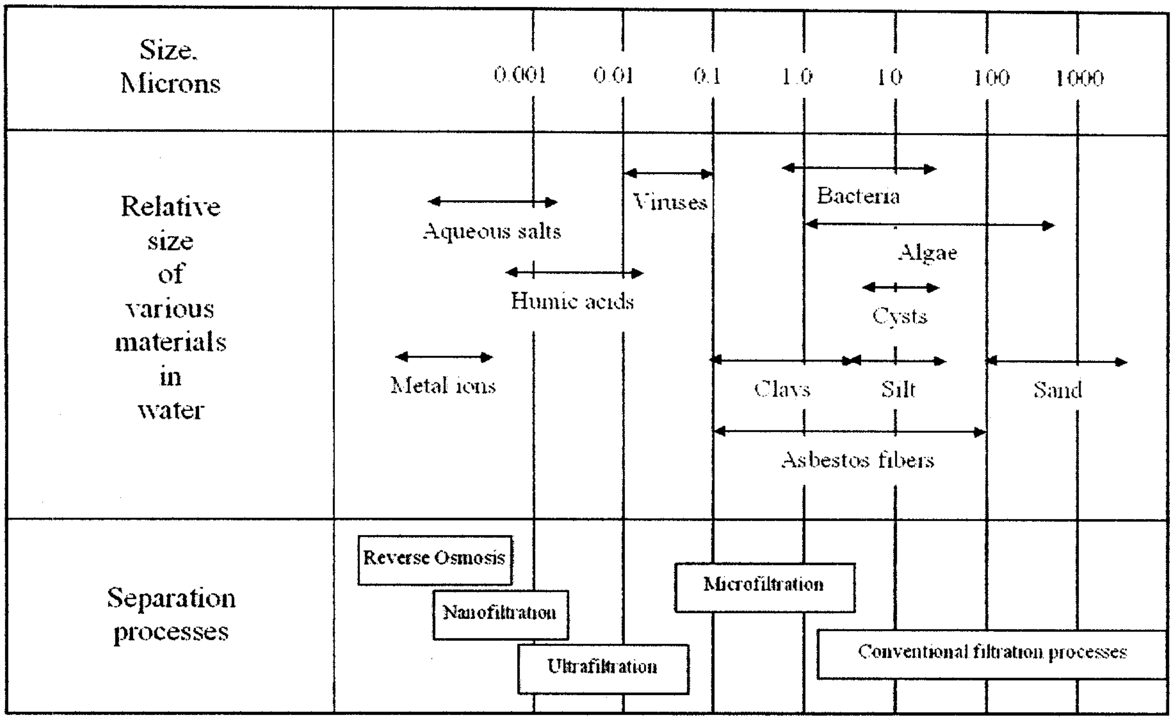


Figure 8-5 Pore Size of Various Membranes, and Size of Materials Subject to Filtration (Source: Johnston, et al., 2001)

CHAPTER IX

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

9.1 Summary and Conclusions

Arsenic contamination in southern Thailand was studied through source identification, mechanism of its transportation, and the severity of toxicity. A review of removal techniques reported in literature was also carried out. Sources of arsenic contamination in the Ron Phibun district were identified to be the previous tin mining acitivities around the area. Oxidation of arsenic in the soil caused contamination in groundwater and flooding spread out the contamination around the area. Villagers in Ron Phibun are suffering from chronic arsenic poisoning with skin cancer or "black fever." However, there is no clear answer about how arsenic was distributed in this region. Government agencies and research groups have had many studies conducted over the last few yeas, but no conclusion of the arsenic contamination mitigation in the area had been reported. Thus, any knowledge about the simple methods of arsenic removal from drinking water would be very helpful to the general public in Ron Phibun area. The two low-cost arsenic removal techniques for drinking water could be kalshi (pitcher) filtration used in Bangladesh and/or small-size water-filtering system enhanced with coagulation used by some researchers in Prince of Songkla University in thailand.

9.2 Path of Tackling Arsenic Problem

In both developing and industrialized countries, that have faced arsenic contamination of drinking water resources, source substitution, where possible, has been the preferred alternative. However, in some areas, arsenic removal may be a more practical, economically feasible strategy, at least for short-term supply of safe drinking water. Contaminated sources can still be safely used for purposes other than drinking and cooking, and should not be sealed unless safe water is conveniently available in the quantities required for all purposes (Johnston, et al., 2001).

Conventional systems for drinking water supply are well-documented, and those striving to develop safe sources of drinking water in areas affected by arsenic can, turn to a rich library of manuals, texts, and journal articles. Locally, research may be needed to determine what water resources are available, but once inventoried, conventional systems for water supply are relatively well understood (Johnston, et al., 2001).

The situation is slightly different regarding arsenic removal technologies. Some systems are fairly well documented. Conventional coagulation, notably, has been extensively reviewed in the literature in recent years. Arsenic removal under varying geochemical conditions has been investigated, and the effects of coagulant dose, influent arsenic concentration, pH, and the presence of competing co-solutes have been described in some detail. While some details, such as the mechanisms of arsenite adsorption onto HFO and effects of competition from phosphate, are not yet quantitatively documented, enough is known about the mechanisms of arsenic removal through coagulation to design effective removal systems, at least to reduce arsenic levels below 50 μg/L (Johnston, et al., 2001).

For the newly emerging technologies, such as semi-permeable membranes and various sorptive media, less is known about the effects of dose and pH, and even less about the effects of competing solutes. Global interest in improved methods of arsenic removal has led to a rich period of experimentation, in which novel sorbents have been essayed, and existing technologies for arsenic removal have been modified and/or combined to yield substantially different systems. These novel systems have typically been evaluated only by a handful of researchers, under a narrow range of environmental conditions, for short periods of time. In many cases advances in removal of arsenic, particularly of arsenite, has been demonstrated, but mechanisms are still poorly understood . Much more research needs to be conducted to identify those technologies that can effectively remove arsenic under real-world conditions, and consistently do so for extended periods of time (Johnston, et al., 2001).

With regard to arsenic removal in rural settings, more research needs to be done on the safe handling and disposal of arsenic-rich wastes. Experiments in the US have shown that coagulant sludge is generally safe for disposal in municipal landfills. However, in developing countries sanitary landfills are usually nonexistent, and solid waste often ends up simply dumped into rubbish heaps. The stability of arsenic waste streams under such environmental conditions has not been investigated. Simple burial, biomethylation, and stabilization of wastes into cement or bricks have all been proposed, but not thoroughly researched (Johnston, et al., 2001).

Numerous technical questions remain unanswered. Nonetheless, based on the technology available, it is certainly possible to design arsenic removal systems that can reduce even highly contaminated influents to below 50 μg/L. Centralized arsenic removal plants in various countries have proven that such plants can be effective under a wide range of environmental and economic conditions. However, the great majority of people exposed to arsenic in drinking water globally live in rural, generally poor areas, where centralized arsenic removal is not practicable. Arsenic mitigation interventions in these areas must make use of source substitution, decentralized arsenic removal, or a combination of both(Johnston, et al., 2001).

Experiences with decentralized arsenic mitigation remain scarce, and are generally limited to a handful of pilot studies that are heavily donor-dependent. Accordingly, there is a great need for operations research, to determine how the technologies (both conventional water supply and arsenic removal) can be effectively applied as arsenic mitigation interventions in rural settings. The limited experiences available indicate that effecting change in water use practices in arsenic-affected areas requires much more than telling users not to use a specific source. Affected communities are often ignorant both of the threat posed by arsenic in their water supply, and of potential sources of arsenic-free water. Until water users understand the problem of arsenic contamination and its impact on their health, and have reliable information about safe alternatives, they will be unwilling and unable to make an informed choice to change their water use patterns. The biggest challenges ahead lie in adapting the technologies for application in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking (Johnston, et al., 2001).

9.3 Action Plan in Thailand

In 1987, the skin manifestation of chronic arsenic poisoning was first diagnosed among the residents of Ron Phibun District, Nakhon Si Thammarat Province of Southern Thailand. A case study was conducted, which reported that more than 1500 people, between age ranging from 4 months to 85 years, were affected. Among those, there were 6 with proven skin cancer. In some schools, over 80% of the students showed excess arsenic levels in their hairs and nails. The Department of Geology investigated the source of contamination and found high level of arsenic in the shallow wells which were the main sources of drinking water in that area. Poisoning resulted from chronic exposure to contaminated water that drained from tin mine. Presumably, the processes involved in mining and extraction of tin changed the insoluble arsenic compounds to a more soluble arsenate salts (arsenopyrite). At many sites, the arsenic content of water exceeded by 8-100 times the 0.05 ppm (50 μg/L), concentration that is the accepted safety level for occasional exposure. During 1987-1988, chronic arsenic poisoning turned to be political issue and made lots of confusion in many sectors: the people, the media, the government officers, and the NGOs, etc. This has led to ignorance of the villagers and the local government. None of the interventions could solve the problem. Even worse, the bureaucratic system has high resistance to the movement of both the technical and community groups. Since the discovery of the epidemic, there was no systematic epidemiological study conducted in the field until late 1994. The prevalence survey in late 1994 found that the overall rate of skin manifestation in Ron Phibun sub-district is 30%, highest in 3 villages with the prevalence of 50%. In addition, high level of arsenic content in hair of people in this area is 60%, highest in the age group of 0-5 years (79%). (Paijitprapaon, et al., 1995)

Arsenic contamination has caused harmful effects on the public health, especially, the danger due to skin cancer in over 1,500 people in Ron Phibun district since 1987. The existing resolution plan taken by the Thai Government included the following measure:

- stop the mining in Ron Phibun area
- dispose mineral waste and residue to landfill
- clean water supply management
- patients treatment
- public awareness about arsenic contamination

Ron Phibun area still has arsenic contamination in both surface water and groundwater, as well as, in the old mining area. During 1997-1998, one PCD survey showed that arsenic contamination in surface water and groundwater in villages 1, 2, 7, 9, 12, and 13 in Ron Phibun District exceeded the standard.

Short-term Action Plan:

- providing clean water and surface water source that is not contaminated by arsenic within the area
- improve water supply system and expand water supply pipeline to cover the whole area
- recover the old mine area and turn it into the village reservoir.

Long-term Action Plan:

- monitoring arsenic contamination in surface water, groundwater and agricultural products
- mining waste and mineral residue management
- investigation of epidemics (PCD, 1999).

REFERENCES

Abernathy, C. and Morgan, A.. 2001. "Exposure and health effects". United Nations Synthesis Report on Arsenic in Drinking Water. Available at http://www.who.int/water_sanitation_health/Arsenic/ArsenicUNRep3.htm.

Ahmad, S.A., Sayed, M.H.S.U., Hadi S.A., Khan A.W., 1997. "Modified Arsenic Filed Test Kit: A Cheap and Easy Device for Detection of Arsenic in Water." Journal of Preventive and Social Medicine 16 (2): 143-150.

Arrykul, S., Maharatchapong, N., Kooptarnon, K., Bunnaul, P., 1997. Arsenic Removal from Potable Water, Toxic metal studies of Pak Panang and Pattani river basins, Oct, 1997, research and Development Office, Prince of Songkla University. Also available at http://www.psu.ac.th/epidemiology.

Boriboon, P., 2000. "Emerging Chemical Food Problems." Journal of Environmental Medicine, Vol. 2, No. 1: 78-86.

Bridhikitti,V., Varinsatein, P., Tipmontein, B., Tiemthong. S., unknow. Knowledge, attitude and practice among villagers in Tambon Ronpiboon, Nakorn Sri Thammarat Province. available at http://www.psu.ac.th/epidemiology.

Chiangmai, N.N., 1991. Arsenic concentration in water, vegetables, fruits and hair of Amphoe Ron Phibun, Nakhon Si Thammarat Province Songklanagarind Medical Journal 1-2, vol 13:59-67. Also available at http://www.psu.ac.th/epidemiology

Clesceri, L.S., Greenberg, A.E., and Trussell R.R., 1990. Selected Physical and Chemical Standard Methods for Students: Based on Standard Methods for the Examination of Water and Wastewater. 17th edition. APHA-AWWA-WPCF.

Hlavay, D.Sc.J., Ph.D., Polyak, K., Ph.D., 2000. ADVANCED ARSENIC REMOVAL PROCESSES FOR DRINKING WATER PURIFICATION, available at http://phys4.harvard.edu/~wilson/SanDiego2000/Abstracts8.html.

Johnston, R., Heijnen, H., and Wurzel, P., 2001. "Safe Water Technology". United Nations Synthesis Report on Arsenic in Drinking Water. Available at http://www.who.int/water_sanitation_health/Arsenic/ArsenicUNRep6.htm.

Japan International Cooperation Agengy (JICA), The Kingdo of Thailand, and The Ministry of Science, Technology and Environment, 2000. Final Report (Summary) on the Environmental Management Planning Survey for Arsenic Contaminated Area of the Nakhon Si Thammarat Province in the Kingdom of Thailnad. Misui Mineral Develoment Engineering Co., Ltd. And Kokusai

Kogyo Co., Ltd.

Kamal, A.S.Md.1999. A Preliminary Study on Source Identification of Arsenic Contamination in Hizla Bangladesh. Master of Science Thesis. Asian Institute of Technology.

Maharachpong, N., 1997. Treatment of arsenic contaminated water from Ampher Ronpiboon, Changwat Nakhon Sir thammarat, Toxic metal studies of Pak Panang and Pattani river basins, Oct, 1997, research and Development Office, prince of Songkla University. Also available at http://www.psu.ac.th/epidemiology.

Mazumder, D.N.G., 2001. "Diagnosis and treatment of chronic arsenic poisoning". United Nations Synthesis Report on Arsenic in Drinking Water. Available at http://www.who.int/water_sanitation_health/Arsenic/ArsenicUNRep4.htm.

Mohammad Alauddin., Ph.D., Abul Hussam., Ph.D., Amir H. Khan, Ph.D., 2000. CRITICAL EVALUATION OF A SIMPLE ARSENIC REMOVAL METHOD FOR GROUNDWATER OF BANGLADESH, available at http://phys4.harvard.edu/~wilson/SanDiego2000/Abstracts8.html.

Murcott, S., 2000. A COMPREHENSIVE REVIEW OF LOW-COST, WELL-WATER TREATMENT TECHNOLOGIES FOR ARSENIC REMOVAL http://phys4.harvard.edu/~wilson/SanDiego2000/Abstracts8.html.

Paijitprapaon, A., Charoenchaisri, P., and Williams, M., 1995. Chronic arsenic poisoning in Ronpibool District, Nakorn Srithammarat Province, Southern Thailand: how should we balance between economics and health? Second international conference on arsenic exposure and health effects : June 12-14, 1995, San Diego, CA. Also available at http://www.psu.ac.th/epidemiology.

PCD (the Pollution Control Department), 1999. The Action Plan on Arsenic Contamination Remediation in Ronphibul District Area. Environmental news No. 25/2542. Available at www.pcd.go.th/Public/News/GetNews.cmf?id=37

Redwine, J.C.Ph.D., 2000. INNOVATIVE TECHNOLOGIES FOR REMEDIATION OF ARSENIC IN SOIL AND GROUNDWATER, available at http://phys4.harvard.edu/~wilson/SanDiego2000/Abstracts8.html.

Skoog, D.A., and Leary, J.J., 1992. Principles of Instrumental Analysis. 4th edition. Saunders College Publing.

Smedley, P.L. and Kinniburgh, D.G., 2001. "Source and behaviour of arsenic in natural waters". United Nations Synthesis Report on Arsenic in Drinking Water., available at http://www.who.int/water_sanitation_health/Arsenic/ArsenicUNRep1.htm.

Thanh, M.T., Ph.D. and Long, P.P.P.E., 2000. Groundwater Arsenic Contamination: Can it happen in The Mekong Delta? A Vietnamese Perspective. Available at http://www.mekongforum.org/long4e.html.

USEPA, 2001-a. Arsenic in Drinking water, Analytical Methods. Available at http://www.epa.gov/safewater/ars/ars7.html.

USEPA, 2001-b. Arsenic in Drinking water, Treatment Technologies: Removal. Available at http://www.epa.gov/safewater/ars/treat.html.

USNRC (United States National Research Council), 1999. Arsenic in Drinking Water. National Academy Press. Also available at http://www.nap.edu.

USNRC (United States National Research Council), 1997. Arsenic: Medical and Biological Effects of Environmental Pollutants. National Academy Press. Also available at http://www.nap.edu.

Vitayavirasuk B., Thongboriboon, T., 1997. Arsenic contamination in shallow groundwater and surface water environment in Ron Phibun Subdistrict, Ron Phibun district, Nakhon Si Thammarat Province, Southern Thailand. Toxic metal studies of Pak Panang and Pattani river basins, Oct, 1997, research and Development Office, prince of Songkla University. Also available at http://www.psu.ac.th/epidemiology.

Williams, M., Fordyce, F., Paijitprapapon, A., and Charoenchaisri, P., 1996. Arsenic contamination in surface drainage and groundwater in part of the southeast Asian tin belt, Nakhon Si Thammarat Province, southern Thailand. Environmental Geology, 27. 16-33. Also available at http://www.psu.ac.th/epidemiology/inpub/william.htm.

Wongsanoon, J., Boonchalermkit, S., Srilachai, S., Fukuda, M., Nakamura, S., Klusman, R., 1997. A novel soil gas technique applied to an arsenic contaminated area of Ron Phiboon, Southern Thailand. Toxic metal studies of Pak Panang and Pattani river basins, Oct, 1997, research and Development Office, prince of Songkla University. Also available at http://www.psu.ac.th/epidemiology.

Wittayawarawat, W., 1994. Contamination of arsenic, cadmium and lead in Pak Phanang river basin, Changwat Nakorn Si Thammrat Environmental Management, Prince of Songkla University. Also available at http://www.psu.ac.th/epidemiology.

CURRICULUM VITAE

1. *Name:* Dr. Ranjna Jindal

2. *Current position:* Lecturer
School of Environmental Engineering
Institute of Engineering
Suranaree University of Technology

3. *Education background:*

Degree / year	Major	University
B.Sc. (Hons.) 1970	Physics, Mathematics, Statistics	Meerut University, India
M.Sc. 1973	Nuclear Physics	Meerut University, India
M.Sc. 1982	Environmental Engineering	Asian Institute of Technology Bangkok, Thailand
D.Tech.Sc. 1995	Environmental Engineering	Asian Institute of Technology Bangkok, Thailand

4. *Fields of specialization:*

- Water and wastewater Engineering
- Solid waste management
- Air pollution control

5. *List of Publications:*

Jindal, R. and P. Pimpan (2001). “Rock-bed Filtration Performance Evaluation for Wastewater Treatment”, Suranaree J. Sci. Technol. Vol. 8, No. 1-2, Suranaree University of Technology, Nakhon Ratchasima, Thailand. pp. 42-49.

Jindal, R. and S. Fujii (1999). " Pilot-plant Experiments on Rock-bed Filtration for improving canal water quality." Environmental Technology . Vol. 20, pp. 343-354.

Jindal, R. and S. Fujii (1998). "Modelling of Rock-bed Filtration Process." Environmental Technology Vol. 19, pp. 273-281.

Jindal, R., H. Harada, and S. Shikura (1997). “Solid Waste Management in Some Asian Countries A State- of the-Art Review.” Environmental Sanitation Reviews No. 42/43, Asian Institute of Technology, Bangkok, 126p.

Jindal, Ranjna (1995). "Development and Modelling of a Water Treatment System Using the Rock-bed Filtration Method." D.Tech.Sc. Dissertation, No. EV-95-2, Asian Institute of Technology, Bangkok, Thailand.

Lohani, B. N., G. Todino, and R. Jindal (1984). "Recycling of Solid Wastes." Environmental Sanitation Reviews No. 13/14, Asian Institute of Technology, Bangkok, 140p.

Rabbani, K.R., R. Jindal, and H. Kubota (1983). "Composting of Domestic Refuse." Environmental Sanitation Reviews No. 10/11, Asian Institute of Technology, Bangkok, 107p.

Jindal, Ranjna (1982). "A statistical analysis of some sediment components accumulated in the reservoirs and lakes." M.Sc. Thesis No. EV-82-28, Asian Institute of Technology, Bangkok, Thailand.

Rani, Ranjna, P.S. Mahesh and Sneh (1975). "Vibrational properties of CsCl by Shell Model." *Indian Journal of Pure and Applied Physics*, Vol. 13, pp. 823 - 825.

6. *List of presentations:*

Jindal, R. and S. Fujii (2001). "Experimental Evaluation of a Rock-Bed Filtration Model." *Proceeding of The Sixth International Symposium on In Situ and On-Site Bioremediation*, San Diego, CA, USA.

Jindal, R. and P. Pimpan (2001) "Rock-bed Filtration for Domestic Wastewater Treatment." *The Seventh National Convention of Civil Engineers*, Bangkok, Thailnad.

Jindal, R., U. Weesakul, C. Sripadungtham, and P. Soparat (1997). "Wastewater Treatment by Rock-bed Filtration." Presented at The Third National Convention on Civil Engineering. 12-14 November. Phuket, Thailand.

Jindal, R., S. Fujii, C. Niwa, and M. Mouri (1995). "Pilot-plant Experiments for Improvement of Polluted Canal/Klong Water by Rock-bed Filtration Method." Proc. of the IAWQ Asian Regional Conference on Water Quality and Pollution Control held in Manila, Philippines during 7-9 February 1995, pp. 707-730.

Rani, Ranjna and P.S. Mahesh (1975). "Debye-Waller factors of Molybdenum by Kreb's model." Paper presented at the 44th Annual Symposium of National Academy of Sciences held at the Bhagalpur University, Bhagalpur, India.

7. *List of Reports/Articles:*

Joshi, D.L., Chaisak Sripadungtham, and R. Jindal (1998). "Investigation of Canal Water Quality in Bangkok Area." A project report submitted to the Sumitomo Heavy Industries Ltd., Japan (The UNITWIN/UNESCO Chairs Programme).

Chaisak Sripadungtham and R. Jindal (1997). " Rock-bed Filtration - A new Technique for Wastewater Treatment." A project report submitted to the Sumitomo Heavy Industries Ltd., Japan (The UNITWIN/UNESCO Chairs

Programme).

Jindal, R. (1996). "Application of rock-bed filtration for canal water treatment: A pilot-plant study in Thailand." ENFO News (ENSIC, AIT, Bangkok), Vol. 18, No.3, pp.2-3.

Jindal, R. And S. Fujii (1995). "Pilot-plant Experiments on Application of the Rock-bed Filtration for Canal Water Quality Improvement for a Bangkok Canal." A project report submitted to the Shimidzu Corporation, Ltd., Japan.