A STUDY OF ARSENIC CONTENTS IN SOIL, FOOD AND BIOMATRIX BY NEUTRON ACTIVATION ANALYSIS TECHNIQUE

by

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I have gone through the contents of the thesis and present my evaluation as follows:

The thesis reports study of arsenic contents in top soils, food: rice and vegetables, water and sediment samples collected from different regions of Bangladesh, using neutron activation analysis technique. A systematic study of samples collected from various localities of Bangladesh known to be unaffected, moderately affected and highly affected with arsenic related problems is performed. The work includes sample collection from the field and preservation, preparation of sample for experiment, neutron irradiation, data collection, data reduction computation and determination arsenic concentration in the sample and statistical uncertainty in the measurement.

The thesis consists of six chapters and 4 appendices.

Chapter I gives introduction to chemistry of arsenic and its environment cycle, arsenic related health problems in the world, information about arsenic problem in Bangladesh and safety implementation to deal the problem. The chapter also describes effect of arsenic toxicity on the health of individual, arsenicosis and its socio-economic impact, uses of arsenic in various industries, mechanism of release of arsenic into ground water and food chain in general and in Bangladesh has been briefly discussed. Aim and objective of the work undertaken and reported in the thesis is described in the end of the chapter.

Chapter II describes principles of neutron activation analysis technique and methodology to compute elemental concentration. Various types of neutron activation analysis methods and determination of elemental concentration are described. Details of sample collection, sample preparation, its size, geometry and other parameters are given. Advantages of neutron activation analysis, its detection limit, accuracy and precision are also described.

Chapter III gives details of the irradiation and counting facilities used. The facilities of TRIGA Mark-II reactor at BAEC, Dhaka, Bangladesh and PARR-1 and PARR-2 at Islamabad, Pakistan have used for irradiating various samples. Details of the various irradiation facilities used for sample irradiation are given. A gamma spectrometer with HPGe detector with commercially available standard electronic modules (pre-amplifier, shaping amplifier, HV unit, PC based data acquisition and display system) have been used. Hypermet PC (Version 5.1) software is used for separating overlapped peaks in the gamma spectrum.

Chapter IV describes in detail the procedure of sample collection, sample preparation for irradiation, irradiation procedure, counting and analysis. The analysis of soils, sediments rice, husk, vegetables, human hair and two water samples collected from various areas of Bangladesh is presented. The sample collection has been done in three distinct areas identified as unaffected, moderately arsenic affected and highly arsenic affected. In addition the chapter also reports analysis of 18 water samples using Atomic Absorption Spectrophotometry. Certified reference material is analyzed in parallel with the sample to determine arsenic and other elements for sake of standardization and assess reliability of the experiment and the result. Both locally developed and commercially available software are used in elemental analysis. The data have been corrected for flux gradient, reaction interference effects

Chapter V presents the results abtained and discussion. The main findings are as follows.

Unaffected areas :

2 tubewell water samples Goainghat: As concentrations 10.70 ± 0.45 μg/L and 17.480 ± 0.73 μg/L.

Soils of Sylhet	As : 1.17 ± 0.14 to 5.73 ± 0.46 % Fe : 1.27 ± 0.14 to 4.07 ± 0.26 % strong correlation (R= 0.6869) between arsenic and iron concentrations.
Sediments of Savar, Dhaka: (7 samples)	As : 0.72 ± 0.03 to 6.82 ± 0.26 % Fe : 1.36 ± 0.02 to 3.38 ± 0.07 % Mn : 257 ± 14 to 2194± 116 ppm Correlation As vs. depth R= -0.6894 As vs Fe 0.9092
Rice of Goainghat (6)	As: 0.03 ± 0.001 to 0.12 ± 0.005 ppm
Husk (6)	< 0.07 ±0.003 to 2.00 ± 0.08 ppm
Rice of Sylhet (16)	As < 0.038± 0.004 and 0.112 ± 0.011
Husk (16)	< 0.194 ± 0.015 to 0.714 ± 0.034 ppm Correlation As in soil Vs As in rice R = 0.3162
Human hair Sylhet (12)	As <0.20±0.01 to 0.84±0.04 ppm.

Moderately affected areas: Companiganj upzilla, Sylhet

Water (18 samples)	As 6.90±0.51 to 87.23±0.75 μg/L Fe 0.46 ± 0.02 to 37.30 ± 0.15 ppm Mn 0.12 ± 0.09 to 1.14 ± 0.02 ppm
Soil	As 3.60 ± 0.14 to 7.95 ± 0.29 ppm Fe 4.48 ± 0.27 to 6.03 ± 0.25 %
Rice grain (5)	As < 0.038 ± 0.004 to 0.108 ± 0.010 ppm
Husk (5)	< 0.194 ± 0.015 to 0.566 ± 0.028 ppm
Vegetable (1)	0.110 ± 0.016 ppm
Human hair	< 0.32 ± 0.01 to 2.28 ± 0.09 ppm

Highly arsenic affected areas:

Sediments of kachua upzila(13) Depth 30 to 390 feet	As 0.65 ± 0.05 to 9.15 ± 0.35 ppm Fe 0.86 ± 0.01 to 4.56 ± 0.05 % Mn 178 ± 4 to 1646 ± 33 ppm Correlation As vs. Fe 0.9042. As vs Mn 0.111 As vs. depth -0.3549

Faridganj	Soil samples	As 3.22 ± 0.12 to 7.38 ± 0.26 ppm Fe 3.70 ± 0.16 to 5.46 ± 0.22 ppm Correlation R 0.7625
	Rice grain	As 0.148 ± 0.012 to 0.324 ± 0.014 ppm
	Husk	0.186 ± 0.008 to 0.369 ± 0.015 ppm No correlation in As in soil/ rice and As in rice/husk
	Vegetables	below detection limit of 0.110±0.004 ppm
	Hair samples	< 0.35 ± 0.07 to 3.45 ± 0.19 ppm (age group 15-30 yrs high concentrations)

16 rice samples; Comilla, Rajshahi, Rangpur, Dinajpur and Barisal districts	As 0.103 ± 0.021 and 0.717 ± 0.192 ppm

Damurhuda	Vegetable	As < 0.12 to 7.22 ± 0.43 ppm
	Hair sample	1.04 ± 0.06 to 48.52 ± 2.21 ppm
Dhaka Community Hospital	Hair samples (18)	1.87 ± 0.34 to 42.31 ± 2.55 ppm
Lohajang	Soil	As 5.15 ± 0.23 to 37.96 ± 1.35 ppm Fe 4.25 ± 0.19 to 5.32 ± 0.22 %
	Rice	As < 0.04 to 0.878 ± 0.035 ppm (highest value in rice grain)
	Hair	< 0.16 to 2.81 ± 0.12 ppm

Chapter VI summarizes the work carried out and gives conclusion.
The present study reveals following information,

1. Concentration of arsenic in soil is found to be much less than 20 ppm except at Lohajang (~38 ppm) which is a highly arsenic affected area.
2. Concentration of arsenic in rice grain is found to be less than 1 ppm which is permissible level for any food item. A maximum concentration of ~ 0.9±.04 ppm is observed from highly affected arsenic area, Lohajang. Even though the maximum As content of the soil is ~38 ppm, less than 1 ppm has reached the rice grain. The same trend is observed in rice samples from other places of highly affected areas.
3. All vegetables except arum contain arsenic below 1 ppm, arum sample Damurhuda shows ~ 7 ppm. NAA method gives only total As, which contains both inorganic and organic arsenic.
4. Considerable variation in As content in soil, grain and husk; no correlation is observed. This should be probably reinvestigated using large no. of samples from larger population (area).
5. As concentrations in hair samples vary from less than 1 ppm from unaffected area to a maximum of ~ 50 ppm in highly affected area of Damurhuda.
6. Bangladesh standard for As in drinking water is 50 μg/L .The As content in water samples of Goainghat (unaffected area) is found to be in the range 11 to 17 μg/L, whereas in Companiganj (moderately affected area) it is in the range 7 to 87 μg/L. 14 out of 18 water samples from this area were unfit for drinking. The As content in tube well water from Lohajang is as reported by British Geological Survey is 221.6 μg/L.

Overall comments on the work:

The sample collection from various arsenic level affected areas, sample preservation, neutron irradiation to predetermined fluence, activity data collection, reduction, and determination As, Fe and Mn concentration requires great effort, skill and expertise. Looking at the work reported in the thesis a great effort has been put in understanding arsenic problem in Bangladesh and using NAA technique for getting quantitative information. Even though the arsenic problem has been handled by many agencies using various techniques author has cleverly chosen NAA for the same and demonstrated better sensitivity and accuracy of the technique. This work is the major achievement of the thesis.

The results are well tabulated and interpreted. The diagrams are meticulously presented and discussed. The author's review of literature is up to date; however, references are not given in standard form. To summarize, the thesis is a well-prepared document on the arsenic problem in Bangladesh and its estimation and correlation with other elements. Author feels the experimental data will serve as a reference for As contents in soil, food and biomatrix due to its reliability and accuracy. The work may also promote other nations to look in to arsenic problem, a wishful thinking!!

However,

There are certain questions, doubts related to the work reported and typographical errors in the thesis are given on separate sheets, which candidate should attend to and make corrections in the thesis accordingly. Wherever doubts have been raised, the candidate should clear them to the examiner conducting viva voce.

After going through the thesis for its scientific contents, results presented and interpreted,

I recommend that the thesis submitted by Muhammad Abdul Hafiz be accepted for the award of the Degree of Doctor of Philosophy of the Bangladesh University of Engineering & Technology, Dhaka.

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At last I express my extreme gratefulness to Allah, the Almighty, the Merciful, for His constant blessings upon me.

The author

ABSTRACT

Neutron activation analysis (NAA) technique has been applied for the study of arsenic contents in soil, food (rice and vegetables) and human hair samples collected from different regions of Bangladesh. Some water and sediment samples were also analyzed. The samples were analyzed at Institute of Nuclear Science and Technology (INST), Savar, Dhaka, Bangladesh and Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan using TRIGA Mark-II, PARR-I and PARR-II research reactors. For the present work, the samples were collected from some unaffected, moderately affected and highly affected areas of Bangladesh. Selected unaffected areas are again some parts of Goainghat, Companiganj and Sylhet sadar upazilas of Sylhet district and Savar upazila, Dhaka. From unaffected areas samples of water, topsoil, sediment, rice and human hair were collected and analyzed. Companiganj upazila was found to be a moderately affected area. Eighteen water samples of this area were analyzed to find the level of arsenic pollution using atomic absorption spectrometry for convenience. Soil, rice, vegetables and human hair samples of these areas were also analyzed. Kachua and Faridganj upazilas under Chandpur district; Damurhuda upazila under Chuadanga district and Lohajang upazila under Munshiganj district were found to be highly arsenic affected areas. Thirteen undisturbed sediment samples of Kachua upazila were analyzed for arsenic, iron and manganese concentrations Soil, rice, vegetables and human hair of these areas were also analyzed. The unaffected (water arsenic below 50 μg/L), moderately affected (water arsenic greater than 50 μg/L and less than 100 μg/L) and highly affected areas (water arsenic greater than 100 μg/L) have been graded on the basis of limits given by some NGO's (NGO Forum, BRAC, Grameen Bank etc.) and other groups working in Bangladesh. Arsenic and iron were found to be positively correlated in all kinds of matrices. No correlation was found between arsenic and manganese; between water arsenic and hair arsenic, and also between soil arsenic and arsenic in rice grain. However, sometimes negative correlation was found between arsenic and manganese in sample matrices.

In the present investigation no evidence was found about arsenic pollution of rice beyond permissible level. Similarly, among vegetables only arum samples contain

arsenic, which contains both inorganic and organic arsenic. Some of organic species are less harmful for human health. Most of the soils of Bangladesh contain less than 10 ppm arsenic except Lohajang soil. People living in arsenic affected areas have arsenic concentration in hair as high as 50 ppm; whereas, hair arsenic in unaffected areas is less than 1 ppm.

DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Signature of the candidate:

Hafiz

(Muhammad Abdul Hafiz)
Session: October / 2001
Roll No.: P10011402P

LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrophotometer
AgDDC	Silver diethyldithiocarbamate
BAMWSP	Bangladesh Arsenic Mitigation Water Supply Project
BBS	Bangladesh Bureau of Statistics
BCAS	Bangladesh Center For Advanced Studies
BCSIR	Bangladesh Council for Scientific and Industrial Research
BGS	British Geological Survey
BWDB	Bangladesh Water Development Board
DCH	Dhaka Community Hospital
DFID	Department for International Development
DMA	Dimethylated Arsenic
DMAA	Dimethyl Arsenic Acid
DPHE	Department of Public Health Engineering
GOB	Government of Bangladesh
GSB	Geological Survey of Bangladesh
LGED	Local Government Engineering Division
MMI	Mott MacDonald International
NAA	Neutron activation analysis
TXRF	Total Reflection X-ray Fluorescence
UNDP	United Nations Development Programme
UNICEF	United Nations International Emergency Fund for Children
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

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Dedicated to my beloved
mother, wife, sons and
late father

CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

1.1 Arsenic as a chemical element

The name arsenic is derived from the Greek word *arsenikon,* means yellow orpiment. It is a chemical element in the nitrogen family (group VA of the periodic table), existing in both grey and yellow crystalline forms. Although some forms of arsenic are metal-like, it is best classified as metalloid and non-metal. It can be manufactured in three allotropic forms, the yellow (α) form, the black (β) form and the steel grey (γ) form. These have different physical properties. Apart from the elemental arsenic, where oxidation state by definition is 0, arsenic is stable in its states +5, +3 and -3. Table 1.1 shows some important properties of arsenic.

TABLE 1.1

Properties of arsenic (Encyclopedia Britannica, 1994)

Parameter	Value
Atomic number	33
Atomic weight	74.92158
Melting point (grey form)	814°C at 36 atm
Boiling point	616°C (sublimes)
Density: Grey form Yellow form	5.73 g/cm^3 at 14°C 2.03 g/cm^3 at 18°C
Electronic configuration	2-8-18-5 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$

Arsenic has been called *the poison of the kings and the king of the poisons.* It has a long history of use as a poison to commit murder or of adverse health effect in those working with or exposed to arsenic containing products. Arsenic has six specific characteristics (Azcue and Nriagu, 1994):

- It is a virulent poison on acute ingestion, 76 mg arsenic (III) is considered to be lethal to adults.
- It is extremely toxic on long-term exposure to very low concentrations. The WHO acceptable skin cancer risk is calculated to be 0.17 μg arsenic/L of water (WHO, 1996).
- It is not visible in water and food. Even heavily contaminated water may be clear and colorless.
- It has no taste. Even heavily contaminated water may have a pleasant taste.
- It has no smell, even at deadly concentrations.
- It is difficult to analyze, even when occurring in water in concentrations twice as high as the WHO guideline.

Arsenic is found everywhere in the environment. It is found in atmosphere, biosphere, hydrosphere, pedosphere and geosphere and transferred from one to another by natural processes or human activities (Ahmed, 2003). Environmental cycle of arsenic is shown in Figure 1.1.

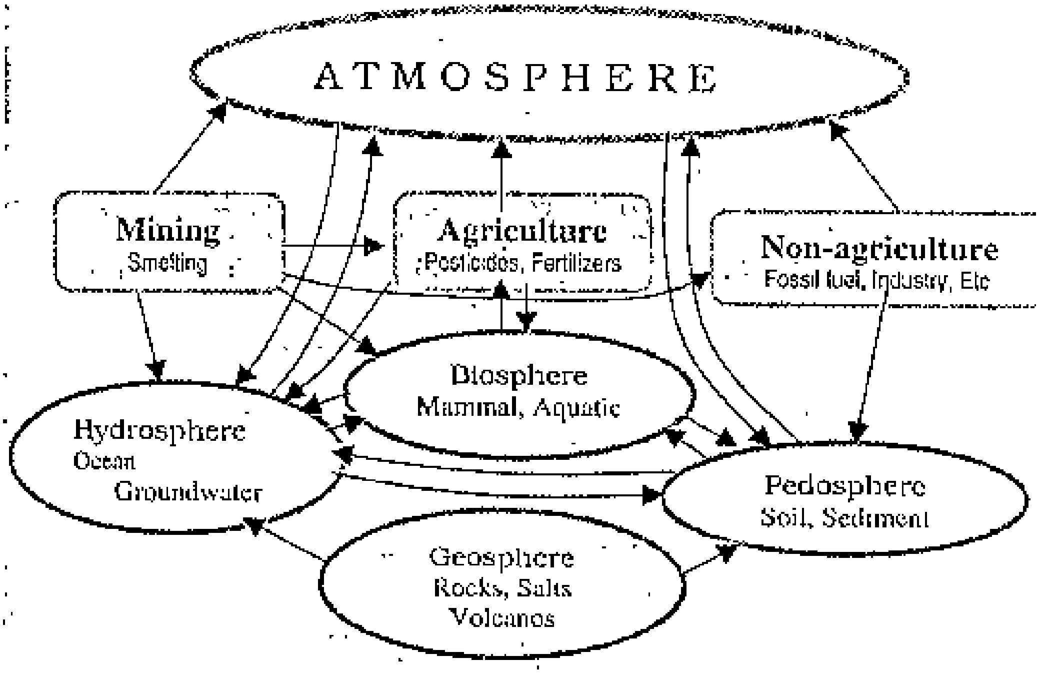

Figure 1.1 The environmental cycle of arsenic (Bhumbla and Keefer, 1994)

Arsenic is a component of more than 245 minerals (Azcue and Nriague, 1994). Some common arsenic minerals are arsenopyrite (FeAsS), realger (AsS), orphiment (As_2S_3), arsenolite (As_2O_3), etc. It is estimated to be the 20th and 12th most abundant element in earth crust and biosphere, respectively (Katrinen and Martin, 1995). It may be seen that rocks and minerals are the main reservoirs of arsenic, which is mobilized in the other compartments of environment by natural weathering processes, biological activity, volcanic eruption and anthropogenic activities.

1.2 Spread of arsenic problem

Elevated concentrations of arsenic of natural origin have been reported in groundwater in many parts of the world. Arsenic poisoning due to excessive exposure to natural and anthropogenic arsenic in drinking water has been documented in Argentina, China, Taiwan, Thailand, India, Mexico, USA, Ghana, Hungary, United Kingdom, Chile, New Zealand, Russia and Bangladesh. It is estimated that about 29 million people in Bangladesh are exposed to an arsenic concentration in drinking water exceeding 50 μg/L (Ahmed, 2003).

In the Indian subcontinent arsenic pollution was first detected in West Bengal, India. Over the period of a decade it has been recognized that there is a serious health hazard originating from arsenic in underground drinking water in West Bengal, India, which was possibly noticed in 1978. But the first official report of arsenic study was presented in July, 1983 by Dr. K C Saha, retired Professor and Head of Dermatology, School of Tropical Medicine, Calcutta. At the same time, chronic arsenic toxicity from drinking water was reported by a survey team of Jadavpur University, West Bengal. Arsenic in ground water has been found in excess of 50 μg/L (BCAS, 1999).

Arsenic dermatosis patient was first identified in Gangaram village of 24-Parganas in 1983. At the first stage doctors could not identify the actual cause of the peculiar skin disease. When similar patients with skin disease came to Calcutta from that area for treatment, an expert team wanted to analyze some tubewells water of Gangaram village and found high level of arsenic in water. After getting confirmation, dermatologists started analysis of hair, nail, urine and skins of those patients and found significant level of arsenic in these biological tissues (Das et al., 1994). Six districts of West Bengal are arsenic affected. About 1.0 million people are drinking arsenic-contaminated water and about 200,000 people have arsenical skin lesions (Das et al., 1996).

In 1990, the School of Environmental Studies, Jadavpur University, West Bengal, reported in daily newspaper that as the southeastern parts of West Bengal are arsenic contaminated, some southwestern regions of Bangladesh might also be contaminated by arsenic. Meanwhile, several patients from Bangladesh went to Calcutta for the treatment of similar type of skin disease. The Director of the school of Environmental Studies felt that problem of arsenic contamination in Bangladesh border adjacent areas might be more serious than West Bengal.

1.3 Arsenic in Bangladesh

In 1993 the Department of Public Health Engineering (DPHE) collected 34 shallow tubewell water samples from Barogharia union of Chapai Nawabganj district. The samples were tested at the Atomic Energy Commission laboratory, Dhaka and 5 of the samples were found to be highly contaminated by arsenic (BCAS, 1999).

In Bangladesh allowed concentration level of arsenic in drinking water is 50 μg/L. Drinking water standards are mostly defined on the basis of the advice from agencies such as the World Health Organization. In 1993, WHO made a provisional guideline value of 10 μg/L for arsenic in drinking water. which is associated with a lifetime excess skin cancer risk of about 6 per 10,000 population. The Bangladesh standard of 50 μg/L (GOB, 1997) is associated with a higher risk of 30 per 10,000 population. Table 1.2 shows the currently accepted national standards of some selected countries for arsenic in drinking water (Yamamura, 2002).

National standards are adopted considering environmental, social, economic and cultural conditions of the region. In Bangladesh, the adoption of the WHO guideline value (10 μg/L) as the national standard for arsenic is much more difficult because of the following reasons

- An estimated 46% of the tubewell will have to be declared unsafe for drinking water supply;
- The low-cost coagulation based water treatment options and existing natural iron based water treatment facilities established in few urban centers are to be abandoned;
- Alternate water supply systems are to developed for 49 million people exposed to arsenic higher than 10 μg/L;
- The existing arsenic testing facility by field kit at local level to be discontinued because of its low accuracy at 10 μg/L level and replaced by costly laboratory methods (Ahmed, 2003).

TABLE 1.2

National standards of some selected countries for arsenic in drinking water

Country	Standard, mg/L	Country	Standard, mg/L
Australia (1996)	0.007	Bahrain	0.05
European Union (1998)	0.01	Bangladesh (1997)	0.05
Japan (1993)	0.01	Bolivia (1997)	0.05
Jordan (1991)	0.01	China	0.05
Laos (1999)	0.01	Egypt (1995)	0.05
Mongolia (1998)	0.01	India	0.05
Namibia	0.01	Indonesia (1990)	0.05
Syria (194)	0.01	Oman	0.05
USA (2001)	0.01	Mexico	0.05
Canada	0.025	Philippines (1978)	0.05
Vietnam (1989)	0.05	Saudi Arabia	0.05
Zimbabwe	0.05	Sri Lanka (1983)	0.05

1.4 Arsenic sample testing

Various organizations and agencies started water sample testing from 1995 using field kits and laboratory methods. Among them DPHE, UNICEF, WHO, BAEC, Jahangirnagar University (Safiulla, 1998), Dhaka community Hospital, BUET and BCSIR (M F Ahmed et al., 1997; MMI, 1998) may be especially mentioned.

The study conducted by British Geological Survey (BGS), DPHE and Mott MacDonald Limited (MML) in two phases examined 3534 distributed water samples from 61 districts (DPHE, BGS and MML, 1999, BGS and DPHE, 2001). It should be noted that there are about 8.61 million hand-tubewells in Bangladesh. In the BGS laboratories arsenic was measured mainly by atomic fluorescence spectrometry with hydride generation (HG-AFS). The survey has shown that in a national scale water from 27% of the shallow tubewells (depth < 150 m) exceeded the Bangladesh standard for arsenic in drinking water, 50 µg/L (GOB, 1997) and 46% exceeded the WHO guideline value of 10 µg/L. Figures for deep wells (depth > 150 m) were 1% and 5%, respectively. They observed that although 27% of shallow tubewells are contaminated in the national scale, in many areas more than 90% of shallow tubewells are contaminated. The district-wise average arsenic concentration was found to vary from 1 µg/L in Thakurgaon to 366 µg/L in Chandpur.

Recent large scale national tubewell screening program has been conducted by DPHE under Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP). The results of the screening were reported in June 2003. DPHE selected 270 affected upazilas as indicated in the previous study for screening. Some results of this screening program are mentioned in Tables 1.3-1.4 and Figure 1.2.

TABLE 1.3

National summary of the screening program

Total upazilas screened	270
Total operative tubewell	50.70 lac
Contaminated tubewell (>=0.05mg/l)	14.40 lacs
Contaminated (%)	29.12%
Population surveyed	6.57 Crore
Patients	38,118

TABLE 1.4

Top 10 arsenic contaminated upazilas

Rank	Upazila	District	% contaminated TW
1	Shahrasti	Chandpur	98.62
2	Faridganj	Chandpur	98.53
3	Hajiganj	Chandpur	98.25
4	Kachua	Chandpur	97.93
5	Kalaroa	Shatkhira	94.77
6	Gopalganj sadar	Gopalganj	93.72
7	Muradnagar	Comilla	93.25
8	Lohajang	Munshiganj	90.94
9	Faridpur	Bhanga	90.87
10	Begumganj	Noakhali	90.37

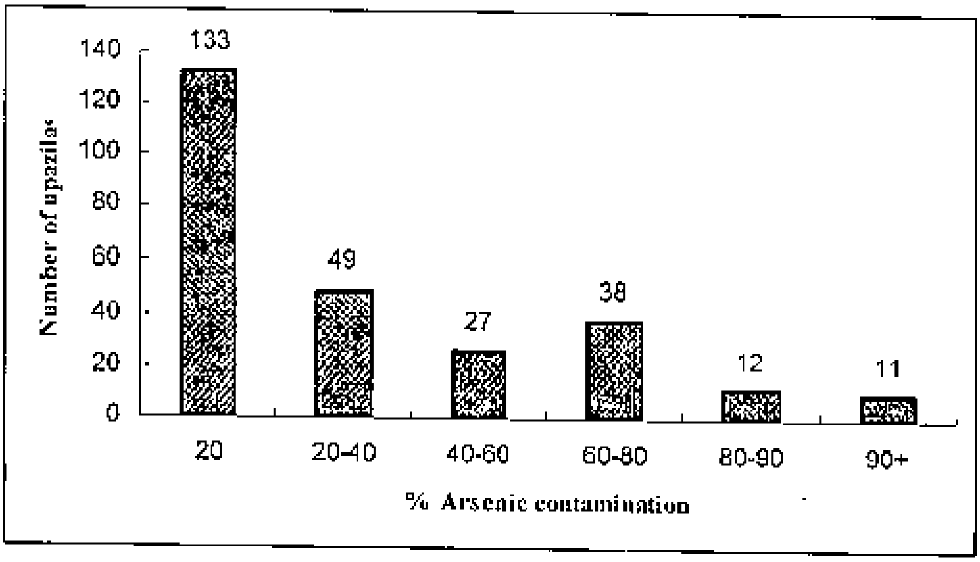

Figure 1.2 Number of upazilas with different contamination status

1.5 National policy for arsenic mitigation, 2004

- Technology options are area dependent
- No single option can serve the people having diverse socio-economic background
- Mitigation program for water supply must promote a range of technology option
- Give preference to surface water over ground water as source of water supply

Alternative water supply options

- Dug well
- Pond/river sand filter (PSF/RSF)
- Large scale surface water treatment
- Deep hand tubewell
- Rainwater harvesting
- Arsenic removal technology

Policy statements

Access of safe water for drinking and cooking shall be ensured through implementation of alternative water supply options in all arsenic affected areas. All arsenicosis cases shall be diagnosed and brought under an effective management system. Impact of arsenic on agricultural environment shall be assessed and addressed.

1.6 Arsenic toxicity

The primary impact of arsenic exposure is on the health of the individual who ingests it through any media. Depending on the period and level of exposure, people in the affected area face different stages of arsenicosis. Manifestation of the disease occurs after quite a long period of exposure. How soon the symptoms will appear depends on the age of the individual, his or her nutritional status and amount of arsenic ingested during the period. Figure 1.3 (Dahi. 1997; Ali and Ahmed, 2003) shows a qualitative scale indicating that the toxicity of arsenic compounds varies to a large extent depending upon their chemical form.

(Highest toxicity)
Arsine gas
↑
Inorganic As (III)
↑
Organic As (III)
↑
Inorganic As (V)
↑
Arsonium compounds
↑
Elemental As
(Lowest toxicity)

Figure 1.3 Arsenic toxicity scale

1.7 Arsenicosis and its socio-economic impact

Arsenicosis is defined as a chronic condition arising from prolonged ingestion of arsenic above safe dose for at least six months, usually manifested by characteristics skin lesions of melanosis and keratosis with or without involvement of internal organs (WHO). In chronic low doses, it accumulates in lipid-rich tissues. High concentrations of arsenic are present in hair, nail and skin of an affected person (Zinatunnessa, 2001). Early signs of arsenic poisoning appear as dark pigmentation on the skin (melanosis). Then hard blisters appear on the palms and soles (keratosis). Arsenic may lead to skin cancer. Internal organs such as the liver, the kidneys and the lungs are also affected. As the health of the affected person deteriorates, he cannot undertake any physical labor and he becomes jobless. He cannot support his family. Even if an affected individual is able to work, nobody likes to hire him.

The disease is thought to be contagious and the neighbors shun him. There have been cases where the spouse had left her/his partner in fear of being affected by the person. Arsenic affected girls of marriageable age could not get married, as nobody wanted to marry them. The socio-economic impact of arsenicosis is shown in Figure 1.4 (Zinatunnessa, 2001).

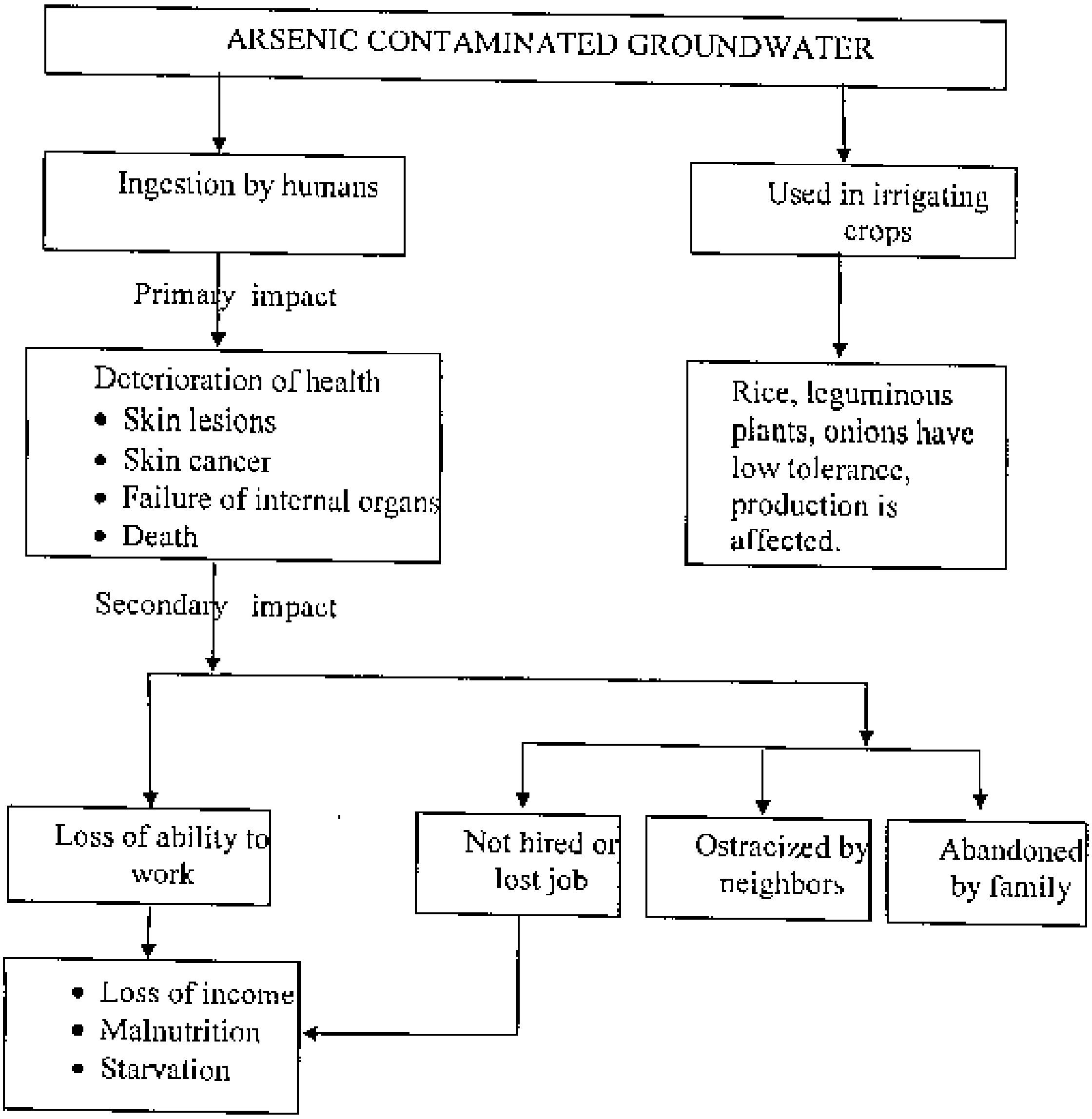

Figure 1.4 Socio-economic impact of arsenicosis

1.8 Uses of arsenic compounds

Arsenic has many uses. Arsenic compounds are mainly used in agriculture, livestock, medicine, electronics, industry, metallurgy etc., which are shown in Table 1.5.

TABLE 1.5

Main uses of arsenic compounds (Azcue & Nriagu, 1994)

Sector	Uses
Agriculture	Pesticides, insecticides, defoliants, wood preservatives, debarking trees, soil disinfectant.
Livestock	Feed additive, Disease prevention (swine dysentery, heartworm infection), cattle and sheep dips, algaecides.
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dyes, soap.
Medicine	Homeopathic medicine, antisyphilic drugs, anti amoebiasis drugs.
Electronics	Solar cells, opto-electronic devices, semiconductor applications, light emitting diodes in digital instruments.
Metallurgy	Alloys e.g. automotive body solder and radiators, battery plates as hardening agent.

For these widespread uses of arsenic the following anthropogenic hypotheses for its pollution have been proposed:

- Agrochemicals, either as an active elements in pesticides or as impurities in fertilizers;
- Wood preservatives, mainly in electric poles;
- Industrial sources;
- Mineral processing;
- Acid mine drainage;
- Enhanced leaching beneath irrigated lands;
- Burning of fossil fuels;
- Other miscellaneous sources.

None of these can account for the extent and mode of occurrence of arsenic in Bangladesh and West Bengal, India. Alternate hypotheses have been proposed to explain the origin of arsenic in Bangladesh drinking water. Among these, two theories namely 'pyrite oxidation' and 'oxyhydroxide reduction' are most successful to describe geological origin and can account for the widespread distribution of arsenic.

1.9 Mechanism of release of arsenic to groundwater

a. Mechanism of release of arsenic to groundwater - pyrite oxidation hypothesis

The role of pyrite (pyrite-FeS_2, arsenopyrite-FeAsS) oxidation as an explanation for both surface and groundwater pollution has been demonstrated in many mining areas around the world (Welch et al., 1988). Arsenic is assumed to be present in certain sulphide minerals that are deposited within the sediment under reducing conditions. In response to pumping there is a decline in the water table, air penetrates deeper into the ground, leading to the decomposition of the sulphide minerals and the release of arsenic into the pore water. During a subsequent rise of the water table, the pore water containing the dissolved arsenic mixes with the rising groundwater leading to an arsenic-rich shallow groundwater. The mechanism has been elaborated by Mandal et al. (1996), Acharyya (1997), Sinha Ray (1997) and others.

b. Mechanism of release of arsenic to groundwater - oxyhydroxide reduction hypothesis

A number of workers have found that the field evidence in Bangladesh is not consistent with the theory of pyrite oxidation. An alternative explanation has been proposed in which it is believed that arsenic is adsorbed onto fine-grained iron or manganese oxides, especially onto iron oxyhydroxide (FeOOH) which, after burial, slowly break down as the pore water of the sediments becomes more reducing over time.

Bhattacharya et al. (1997) and NRECA (1997) note that most arsenic-rich waters were high in ferrous ions and low concentrations of sulphate, which indicate that oxidation of pyrite is unlikely. The studies also established that high arsenic concentrations are strongly correlated with highly reducing conditions. Mineralogical and sedimentological studies (Ahmed et al., 1998 and DU/BWDB, 1998) of core samples from contaminated aquifers revealed insignificant amounts of pyrite present in the aquifer sand. The studies conclude that the arsenic adsorbed on these coatings is most likely the source of arsenic in Bangladesh aquifers.

1.10 Entrance of arsenic into the food chain

In the absence of adequate surface water in the dry season, irrigation is mainly dependent on groundwater. Area under irrigation has been increased significantly to raise food production for the need of the nation. Much of this increase has been accomplished through utilization of shallow tubewell. Area under irrigation by surface water has remained more or less static since early eighties; while the area under irrigation by shallow tubewells has increased by a factor of about five. During each irrigation season, an estimated 27209 Mm^3 of water is extracted through shallow tubewells. This quantity is much higher than the amount of groundwater extracted for domestic use throughout the year (Ali, 2003). In fact, 86% of total groundwater withdrawn is utilized in agricultural sector.

In Bangladesh, *boro* rice (dry season rice) is the major recipient of irrigation water. Wheat and a range of other crops and vegetables cultivated in the dry season also need irrigation. Figure 1.5 shows total irrigation coverage along with contribution from Flood Control Drainage and Irrigation (FCDI) coverage. In Bangladesh, total irrigation coverage accounts for over 60% of the net cultivated area. This figure shows that during 1973-94, *boro* registered a very high production growth, by a factor of over three. Currently *boro* rice accounts for about 37% of the total rice production in Bangladesh. Rice (*Oryza sativa* L.) as the staple food provides 73% of calorific intake for Bangladeshi's (Ninno, C. and Dorosh, P. A., 2001). If arsenic concentration in irrigation water is 100 µg/L and if 1000 mm of irrigation water is needed in a dry season, then this adds 1 kg of arsenic per hectare of irrigated land each year (Ali, 2003). Possibility of introduction of arsenic in food chain and long-term implications (e.g., reduced yield) of arsenic in the agricultural fields are considered seriously. Approximately, 20% crop loss has been reported due to high arsenic content in growth medium. The level of arsenic in soil having above 20 ppm may affect rice yield (Shah et al., 2004).

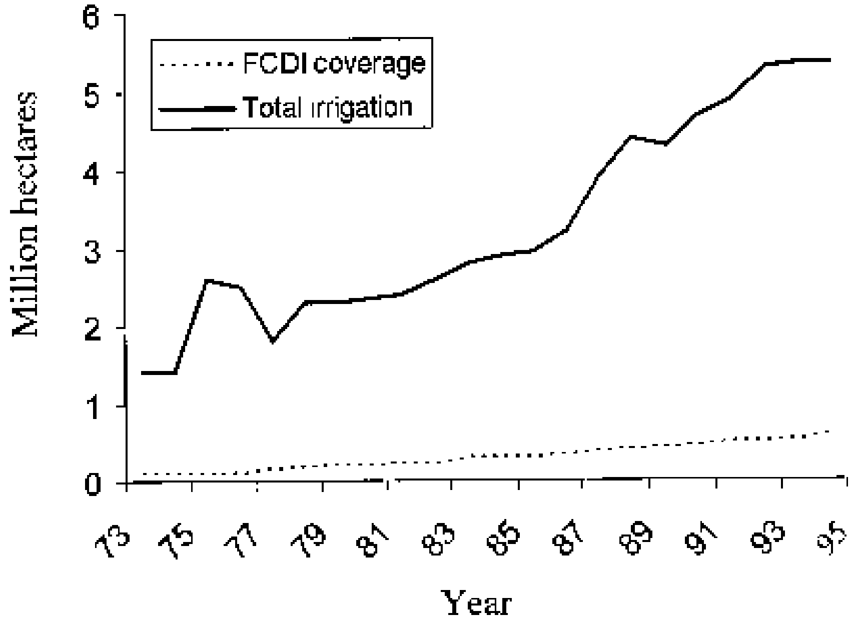

Figure 1.5 Growth in irrigation coverage in Bangladesh
(Source : Chowdhury et al., 1997; Ali, 2003)

The increased concentration of arsenic in irrigation water and in topsoil in the plant-roots zone is likely to result in increased concentration in plant and food grains. The preliminary findings of UNDP/FAO studies in Bangladesh showed that arsenic content in rice produced by irrigation with contaminated water is higher but relative increase is not significant. The highest concentration was found in the roots of the rice plant, and then comparatively a lower concentration in stem and leaves and the lowest concentration was found in rice grain.

Groundwater abstracted for public water supplies and irrigation results in a huge quantity of arsenic cycled through the environment each year with major implications on public health and environment (Ali et al., 2003). In dry season 75% of the total cropped area is used for rice cultivation (Dey et al., 1996). According to a report (Ullah, S. M., 1998). in areas irrigated with contaminated water, soil arsenic level can reach up to 83 μg g^{-1} arsenic. Amount of arsenic ingested by the inhabitants of the contaminated regions could be considerably more than previously thought (Meharg et al., 2003). Food surveys in the United States and Europe showed rice as a major dietary source of arsenic. In countries that have a rice subsistence diet, the importance of dietary exposure to arsenic through rice could be considerable, as shown by the study of Schoof et al. (1999). Rice grain grown in some regions of Bangladesh where arsenic is building up in soil has high arsenic concentrations, with levels above 1.7 μg g^{-1} (Meharg et al., 2003). Levels of arsenic in rice grain are typically 0.05-0.4 μg g^{-1} for North America, Europe, and Taiwan (Robberecht et al., 2002; Schoof et al., 1999; Tao et al., 1998; Scoof et al., 1998).

Arsenic pumped with tubewell water can (i) undergo transformation (e. g., through redox or microbial processes), (ii) volatilize into the atmosphere, (iii) undergo adsorption-desorption and thus become retained onto soil, (iv) washed away by surface runoff or leached into the groundwater, and (v) be taken up by plants, and subsequently enter into the food chain (Ali et al., 2003) Studies by Meharg et al. (2002) and Huq et al. (2001) demonstrate significant uptake of arsenic by rice and a range of vegetables commonly grown in Bangladesh. Tobacco plants have capacity to accumulate arsenic from soil. Numerous greenhouse studies have revealed that an increase in arsenic in cultivated soils lead to an increase in the levels of arsenic in edible vegetables (Burlo et al., 1999; Carbonnel-Barrachina et al., 1999). More studies are needed to develop a reliable database on the presence of arsenic in irrigated soil and plant materials (rice, vegetables) and to assess their interrelationships. Since rice straw is widely used as cattle feed in Bangladesh and India, high arsenic in rice stem and leaf may result in adverse health impacts on cattle and increased human arsenic exposure via plant-animal-human pathway. A simplified block diagram of arsenic in food chain is shown in Figure 1.6.

Toxicity of arsenic depends on its accumulation in the body. A fraction of arsenic is deposited in the skin, hair and nails where it is firmly bound to keratin. Among these, hair is the most suitable indicator of arsenic accumulation in the body. Hair indicates long time exposure of arsenic. Hair is easy to clean, collect and store before analysis. Arsenic concentration data on hair are essential for the assessment of the degree of contamination of the patient and consequently will be useful for his/her proper treatment.

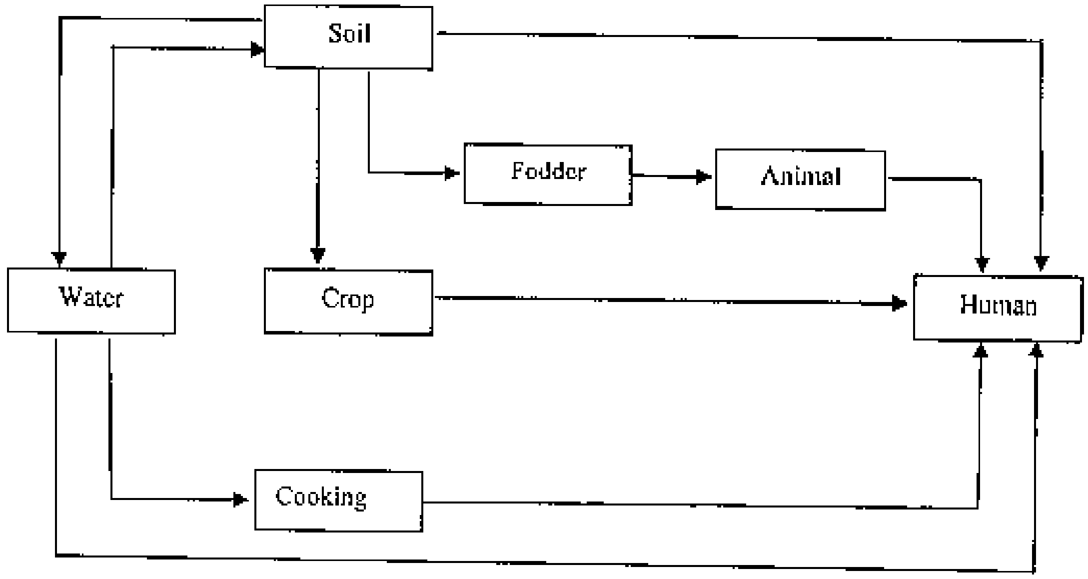

Figure 1.6 Arsenic in the food chain – a simplified block diagram

1.11 Rationale of the present work

In a recent published work Islam and Uddin (2002) emphasized on the research in the fields of

[1] Systematic work on the analyses of the aquifer sediments undertaken,

[2] Release mechanism of arsenic in groundwater should be investigated,

[3] Research on effect of arsenic contaminated irrigation water on crops should be undertaken in a systematic way,

[4] Research should be undertaken on risk of arsenic in food chain in relation to livestock/humans, and

[5] Research should be undertaken on impact of arsenic contaminated water on soil quality.

As mentioned earlier, arsenic concentration in tubewell water was determined extensively in Bangladesh using field kits and laboratory methods like atomic absorption spectrophotometer (AAS). But only water arsenic data can give an incomplete picture, because it has already been stated that arsenic has entered all compartments of the environment and food chain. To analyze soil, food and biomatrix in AAS method, it is required to dissolve the sample in acidic solution which is somewhat difficult in many cases. Present work intends to undertake some of the above research themes by implementing the study of arsenic concentrations mainly in soil, rice, vegetables and human hair samples using neutron activation analysis (NAA) technique. This method is especially suitable for solid matrices because there is no need for dissolving the sample. Samples are dried in an oven, irradiated in the research reactor, allowed to decay for sufficient time and then counted by using high purity Ge (HPGe) detector. It is relevant to analyze sediment samples of affected and unaffected sites. For this reason some sediment samples were also analyzed for As, Fe and Mn. The present work also aims at exploring the possibility of any correlation among arsenic concentrations in the sample matrices.

1.12 Activation as a multielemental analytical technique

Activation process was discovered by Joliots in 1934. He observed that Al, B and Mg became radioactive upon alpha bombardment. Hilde Levi and Gerge Hevesy (1936) are credited with the first use of neutron activation analysis (NAA). They were awarded the Nobel Prize in 1943 for their contributions to the use of radioisotopes as tracers and development of neutron activation analysis technique.

NAA is one of the most powerful multielemental nuclear analytical techniques. It is a sensitive, selective and accurate method. It is often called a "referee method" because of its extensive use in analytical quality control purposes. New analytical methods are routinely verified using NAA. With the recent advances in nuclear reactors and high-efficiency high-resolution semiconductor (HPGe) detectors, NAA has become an excellent tool for elemental analysis. The method's characteristics can be summarized as follows:

[1] Very low detection limits for 30 - 40 elements,

[2] Significant matrix independence,

[3] The possibility of non-destructive analysis (instrumental NAA or INAA),

[4] The use of radiochemical separation to overcome interference in complex

gamma-ray spectra (radiochemical NAA or RNAA),

[5] An inherent capability for high levels of accuracy compared to other trace element analysis techniques.

It is hardly possible to provide a complete survey of current NAA applications, however, some trends can be identified. It follows from various reviews that NAA has been applied for determining many elements, usually trace elements, in the following fields:

(1) Archaeology
(2) Biomedicine
(3) Environmental science and related fields
(4) Forensics
(5) Geology and geochemistry
(6) Industrial products
(7) Nutrition
(8) Quality assurance of analysis and reference materials

1.13 Aim and objectives of the work

NAA technique has been adopted in the present work for the determination of arsenic contents in soil, food (rice and vegetables) and biomatrix (human hair) of unaffected, moderately affected and highly affected areas. The samples were collected from 8 upazilas of Bangladesh. The objectives of the work are mentioned below:

a. Apply the NAA technique for the investigation of arsenic contents in the sample matrices,
b. Compare the measurements at INST, Savar and PINSTECH, Islamabad, and
c. Establish interrelationship of the arsenic data among the sample matrices.

Arsenic concentration data on soil, food and biomatrix obtained in the present work will serve as the reference for researchers working with field kits and other non-nuclear laboratory methods.

1.14 Layout of the dissertation

The planning of the dissertation has been done in the following way. Theoretical aspects concerning the work have been discussed in Chapter II. Irradiation and counting facilities are described in Chapter III. Chapter IV contains experimental details of the analysis of each kind of the samples. A discussion on the results obtained in the work has been accommodated in Chapter V. Summary of the work and conclusions extracted in the investigation are provided in Chapter VI of the dissertation.

CHAPTER II

PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS

CHAPTER II

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2.1 Neutron activation

Neutron activation is a nuclear reaction phenomenon. When a neutron interacts with a target nucleus, a compound nucleus is formed. The compound nucleus has a finite lifetime (10^{-13} - 10^{-15} s) during which it remains in a highly excited state (symbol *) due to the high binding energy and kinetic energy of the neutron in the nucleus. De-excitation of the compound nucleus can occur in different ways that are independent of the way the compound nucleus is formed. Each of these processes (shown in Figure 2.1) has a certain probability, depending on the nuclear cross section of each mode, which is related to the excitation energy of the compound nucleus.

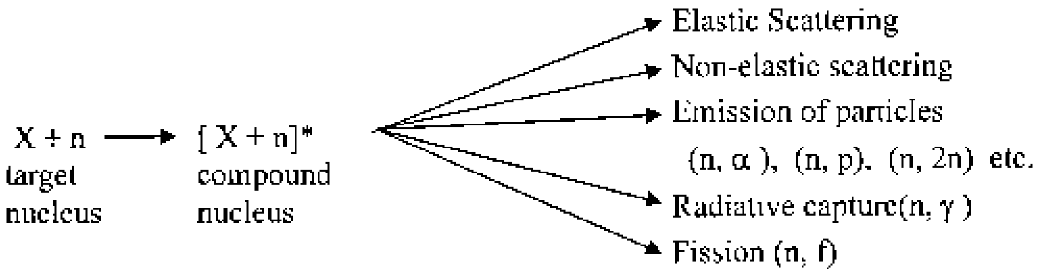

Figure 2.1 Decay of compound nucleus

In elastic scattering the resulting nucleus is identical with the target, whereas in non-elastic scattering a radioactive isomer may be formed. In the emission of particle(s) the resulting nucleus is usually radioactive and differs from the target nuclide in atomic or mass number, or both. The most favorable and important nuclear reaction in NAA is radiative capture (n,γ), in which the excited nucleus passes to a lower energy state by the emission of one or more γ-rays. The resulting nucleus is usually radioactive.

A radioactive nuclide has a characteristic half-life ($T_{1/2}$) mode of decay and energy of emitted radiation(s) during the decay process. Depending on the energy considerations (Q value), a radionuclide can decay to a daughter product (usually stable) by various ways, as shown in Figure 2.2 (a). In Figure 2.2 (b) partial decay scheme of ^{76}As is shown.

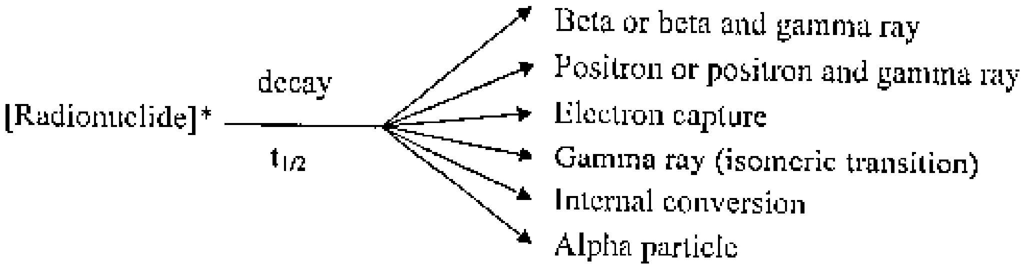

Figure 2.2 (a) Decay of radionucleus

^{75}As + n = ^{76}As + γ (Prompt)

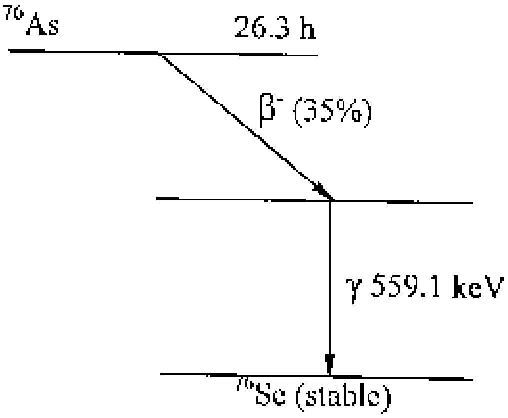

Figure 2.2 (b) Partial decay scheme of ^{76}As

In general, the majority of the (~90%) radionuclides formed by the radiative capture (n,γ) process undergo beta decay, and in most cases beta decay is associated with emission of one or more γ-rays. In fact, very few radionuclides undergo pure beta decay (^{3}H, ^{14}C, ^{32}P, ^{35}S and ^{204}Tl). Positron decay and electron capture are favourable in radionuclides that have an excess number of protons. Electron capture and internal conversion result from interaction of the nucleus with orbital electrons of the atom, and these processes in general lead to the emission of X-rays. In contrast γ-ray emission results from nucleon configurational changes within the nucleus. However, the electron capture decay of some radionuclides is accompanied by γ-ray emission along with X-ray emission. Alpha-particle emission is favourable only in elements with a high mass number (Z>83) and, although it is frequently accompanied by γ-ray emission, the detection of alpha particles in NAA is extremely limited because of their very short range, which causes serious absorption losses in a sample matrix. Overall, most of the radionuclides that undergo decay by alpha, beta or positron emission and by electron capture also emit γ-rays as a result of readjustment of energy content in the radionuclides from excited states to more stable states (Laul, 1979 and Wang et al., 1975).

The X- and γ-ray photon energies are discrete and characteristics of the radionuclides. Because of this hallmark property γ-ray and X-ray measurements are widely used in multielemental neutron activation analysis (NAA). Gamma-ray measurements have, in general, much wider applications in NAA than X-ray measurements because γ-rays emitted from most radionuclides have a wider range of energies (40 - 3000 keV) and have greater penetrating range than X-rays (2 - 90 keV) and thus are subject to minimal loss by absorption in a sample matrix during there measurements. This property, coupled with the recent developments in high-resolution and high-efficiency semiconductors such as HPGe detectors and the availability of high-flux reactors, makes NAA-gamma spectrometry a powerful mutielemental technique in analyzing various types of materials.

2.2 Determination of elemental concentration

The elements to be determined in a sample are made radioactive by irradiating the sample with neutrons, and the radionuclides are formed which are characterized by their half-lives and characteristic gamma energy radiated. The number of detected γ-rays of a particular energy is directly proportional to the disintegration rate of the radionuclide, which in turn is directly proportional to the amount of its parent isotope in the sample. The basic equation for NAA for an element x is as follows:

$$DPS = \frac{WN_A F}{M} \sigma\phi(1 - e^{-\lambda_x * T})e^{-\lambda_x * t} \qquad (1)$$

From gamma spectrometric measurement,

$$DPS = \frac{CPS}{I_G \times \varepsilon} \qquad (2)$$

Where,

DPS = disintegrations/s of a radionuclide x* at time t after the end of irradiation

CPS = count rate of a radionuclide x* at time t

N_A = Avogadro's number

W = weight of an element x irradiated, in grams

F = fractional isotopic abundance of target element

M = atomic weight of the element x

σ = nuclear reaction cross section in cm^2

φ = flux of neutrons ($cm^{-2}.s^{-1}$)

λ_x = decay constant ($0.693/t_{1/2}$) of the radionuclide

T = irradiation time

t = decay time after the end of irradiation

ε = detector efficiency

I_G = gamma-ray intensity.

When $T >> t_{1/2}$, then $1 - e^{-\lambda T}$ is reduced to about 1. This is a case of 'saturation activity'. When $T << t_{1/2}$ then $1 - e^{-\lambda T}$ can be reduced to λT. When we combine equations (1) and (2) the only unknown W is determined (Laul, 1979).

2.2.1 Elemental concentration by absolute method

The concentration of an element in a sample can be calculated from the NAA equations (1) and (2) by knowing the neutron flux (measured by a flux monitor using elements such as Au, Co, Fe and Sc), the counting efficiency of the radiation detector, σ, λ, and the decay scheme of a radionuclide. If these nuclear properties are precisely known, then this absolute single-standard method can yield accurate concentrations of other elements in a sample. If there is an uncertainty in any of above parameters, this can easily affect the accuracy in determining the absolute concentration of an element.

2.2.2 Elemental concentration by comparative method

A very important approach to determine the concentration of an element is the comparative method, which is the most simple and accurate way of quantifying the concentration of an element. In the comparative method an element x in a sample and a known amount of the same element x as a standard are irradiated together, and both the sample and standard are counted under exactly the same conditions by the same detector. This procedure eliminates any uncertainty in the parameters σ, φ, λ, and in the decay scheme and detection efficiency. The NAA equation by the comparative method is thus reduced to a simple form, as shown below:

$$\frac{\text{Weight of element x in sample}}{\text{Weight of element x in standard}} = \frac{\text{Decay corrected CPS in sample}}{\text{Decay corrected CPS in standard}}$$

Knowing the activities of x* in sample and standard, the sample and standard decay times and the weight of element x in the standard, the weight of element x in the sample is calculated (Laul, 1979). Concentration of an element in the sample in ppm is determined by

$$\text{Concentration} = \frac{\text{Weight of element x in the sample}}{\text{Weight of the sample}} \times 10^6 \text{ ppm.}$$

2.3 Various forms of neutron activation analysis

2.3.1 Instrumental neutron activation analysis (INAA)

Instrumental neutron activation analysis (INAA) is often referred to as non-destructive NAA or as NAA without post-irradiation radiochemical separation. It is a multielemental method whereby γ-ray spectrometry is applied to radioactivity measurements. INAA promises reliable analytical results, because the possible error due to contamination and element loss can be easily avoided. INAA is capable of analyzing large samples varying from a several grams to several kilograms (Bode, 1998).

2.3.2 Radiochemical neutron activation analysis (RNAA)

RNAA involves a post-irradiation radiochemical separation procedure to isolate one or a group of elements, or eliminate interfering nuclides. Application of a carrier makes chemical separation much more convenient. The chemical yield can be calculated from re-determination of the added carrier when it is a stable isotope. When the carrier is a radioactive one, chemical yield can be obtained directly from the sample γ-ray measurement.

2.3.3 Epithermal neutron activation analysis (ENAA)

In ENAA, a sample is irradiated in an epithermal neutron flux by covering it with cadmium foil or putting it in a borated capsule. Q_0 is defined as the resonance-to-thermal cross section ratio. ENAA is mainly used to determine a high Q_0 nuclide when a low Q_0 nuclide is the interference. When irradiated in an epithermal neutron flux, a high Q_0 nuclide like ^{114}Cd ($Q_0 = 39.6$) will be more activated than a low Q_0 nuclide like ^{23}Na ($Q_0 = 0.59$) if compared to the activation in normal NAA. In this way detection limits of many elements including arsenic are improved using cadmium or born filters.

2.3.4 Prompt gamma-ray neutron activation analysis (PGNAA)

In PGNAA, the prompt γ-rays emitted during the nuclear reaction are measured. It is a non-destructive and multielemental method (Lindstorm et al., 1993: Molnar et al., 1997). PGNAA may provide elemental contents and depth profiling for elements H. B. C. N, P, S, Cd, Pb and some rare earth elements, especially Sm and Gd. Most of these elements camıot be (or cannot be easily) determined with normal NAA, so PGNAA is a complimentary method. To carry out PGNAA, a neutron beam guide and a γ-ray detector assembly are used.

2.3.5 Cyclic neutron activation analysis

In this method, a sample is repeatedly activated, and the γ-ray spectra after each irradiation are summed (Spyrou, 1981). The repetition can continue till the accumulated activity from long-lived nuclides is too high. The main advantage of cyclic activation is that short-lived radionuclides (second to minutes half-lives) are easily measured whereas the activities of medium and long-lived radionuclides are built up gradually and thus do not mask the short-lived activities.

2.4 NAA procedure

Neutron activation analysis procedure (IAEA, 2001) may involve some or all of the following steps:

(1) Sampling:
(2) Pre-irradiation sample treatment (such as cleaning, drying or ashing, pre-concentration of elements of interest or elimination of interfering elements, sub-sampling and packing);
(3) Irradiation (and prompt γ-ray counting in PGNAA);
(4) Radiochemical separation (only in RNAA)
(5) Radioactivity measurement;
(6) Elemental concentration calculation;
(7) Critical evaluation of results and preparation of the NAA report.

2.4.1 Sample collection

2.4.1 Sample collection

The main problems are to attain a representative sample and avoiding external contamination on collection of sample. Heterogeneity is a problem common to all fields of study and it is important to obtain a representative sample for analysis. The size of sample initially required and the size of the sub-sample necessary for analysis are defined by the sampling constant, a term which was defined for geochemical use by Ingamells and Switzer (1973) and has been applied to biological material by Heydorn and Damsgaard (1987). Taking a small sample from the bulk material is done carefully. Even after careful preparation it is possible to see heterogeneities in material where distribution of the elements is not uniform.

2.4.2 Sample preparation

The quality of analysis is strongly dependent on the amount of care taken during the preparation of the sample. Unless the sample provided is representative of the material to be examined the results may be meaningless. The requirement for representative analysis may mean that a large sample will be homogenized before subsampling and then some form of preconcentration may be necessary before the elements of interest may be determined.

2.4.3 Sample size

In theory amount of samples required is dictated by the sensitivity of the method for a particular element but in practice the background effects will be the main limitation. There are in fact several problems associated with analyzing samples weighing more than one gram: the amount of activity produced may present a radiation hazard; neutron self-shielding may reduce the activity in matrices with high neutron cross sections; gamma ray attenuation may reduce the apparent activity in the sample; there may be difficulty in reproducing the geometry of a large sample in a standard. Consequently the sample size is usually kept below one gram.

2.4.4 Sample geometry

Regardless of the form of the sample, whether it is solid or liquid, a reproducible geometry is most important. The neutron flux distribution in the reactor irradiation site can be quite large and so there are advantages in keeping the samples and standards and monitors as close as possible. The sample should not have too long a profile in the flux; otherwise there may be a significant neutron flux gradient across the sample itself. At the time of counting, the smaller the sample, the closer it is to the detector and therefore the sensitivity will be greater. A tall thin sample will give fewer counts than an equivalent short fat sample.

Soil and sediment samples are normally homogenized for sampling. Liquid samples are taken in a fixed volume. Air filter paper samples are folded in a fixed geometry. Reduction of size may be required because of limitations in the irradiation site, particularly for plant material. Small samples are more convenient and it is possible to compact plant and filter paper samples by pelletizing or ashing and pelletizing. Pelletized samples can present an extremely reproducible geometry.

2.4.5 Homogenization

Homogenization is considered to serve two purposes. The first is to provide a uniform source of material from which a small aliquot may be taken that will be representative of the material. In activation analysis the size of the sample taken may be very small and it is important to ensure that it is representative. The second reason for homogenizing a sample is to ensure that the actual sample to be irradiated and counted is uniform throughout. In other comparable analytical techniques for trace element analysis the final sample is usually in liquid form and so by nature is uniform. If a solid is used it must be homogeneous. Homogenization is achieved by processing all the material collected. In general solid samples are ground to a fine powder. Plant material and biological tissue are also ground down to a fine powder after drying. The samples themselves have to be dried before homogenization using low temperatures to avoid loss of trace elements.

2.4.6 Preconcentration

A sample may be considered to be preconcentrated if part of it is removed prior to irradiation. The reduction of volume will automatically improve the sensitivity of counting on the detector due to the improved geometry. It is also necessary to reduce the size so that it will fit into the irradiation site. Preconcentration techniques can also include removal of unwanted elements in the matrix of the sample (Parry, 1991).

2.5 Advantages of NAA technique

There are many advantages of NAA method. They are:

- sensitivity and applicability for minor and trace elements in a wide range of matrices
- the virtual absence of an analytical blank
- the relative freedom from matrix and interference effects
- the possibility to perform analysis nondestructively using so-called instrumental neutron activation analysis (INAA)
- high specificity based on the individual characteristics of the induced radionuclides
- the capability of INAA for multi-element determination, often allowing 30 to 40 elements to be determined in many matrices
- an inherent potential for accuracy compared to other analytical techniques. Since the theoretical basis of INAA is simple and well understood, the sources of uncertainty can be modelled and well estimated
- the totally independent principle as a nuclear-based property in contrast to the electronic nature of most other analytical techniques
- the isotopic basis which often offers a choice of analytically independent routes for element determination
- in cases where the induced radionuclides of trace elements are masked by matrix activity, radiochemical separation provides interference-free detection limits close to the theoretical ones. Thus, in the radiochemical mode of NAA (RNAA), the technique has other advantageous features
- trace and ultratrace (radio) chemistry can be performed under controlled conditions by inactive carrier additions

- the chemical yield of separation can be obtained simply using carrier budgeting or the radiotracer method

No other analytical technique has the capability to provide multielement data non-destructively, often with good detection limits and in a virtually matrix independent manner. This is largely due to: (i) neutron, being a non-charged particle, easily penetrates the sample and reacts with nuclei; (ii) the gamma rays emitted by the induced nuclides with energies above 100 keV have also a high penetrating power. Both its inherent potential for accuracy and totally independent principle as a nuclear-based property make NAA invaluable as a reference or referee method. The possibility of determining a particular element using various isotopes, together with the possibility to perform the analysis by INAA and RNAA and to perform other additional checks on the consistencies of the results, form the basis for a unique ability to verify the analytical data produced by the technique (IAEA-TECDOC-1121, 1999).

2.6 Detection limits

The detection limit represents the ability of a given NAA procedure to determine the minimum amounts of an element reliably. It is often calculated using Currie's formula (Currie, 1968):

$$D_L = 2.71 + 4.65\sqrt{B}$$

where D_L is the detection limit and B is the background under a γ-ray peak. It is valid only when the γ-ray background (counting statistics error) is the major interference.

However, practically, the INAA detection limit depends on:

(a) *The amount of material to be irradiated and to be counted.* This is often set by availability, sample encapsulation aspects and safety limits both related to irradiation and counting, and possibly because of neutron self-shielding and gamma-ray self-absorption effects. For these reasons practically the sample mass is often limited to approximately 250 mg

(b) *The neutron fluxes.* These are clearly set by the available irradiation facilities.

(c) *Irradiation time.* This is set by practical aspects, such as the limitations in total irradiation dose of the plastic containers. The maximum irradiation time for polyethylene capsules is usually limited to few hours, for instance 5 hours at 5×10^{13} n $cm^{-2}s^{-1}$.

(d) *The total induced activity that can be measured* is set by the state-of-the-art of counting and signal processing equipment, with additional radiation dose and shielding consideration. As an example, the maximum activity at the moment of counting may be limited to approximately 250 kBq.

(e) *Counting time.* A very long counting time may set limits to the number of samples processed simultaneously in case the radioactivity decays considerably during this counting time.

(f) *Total turn-around time.* Although sometimes better detection limits may be obtained at long decay times, the demands regarding the turn-around time often imply that a compromise has to be found between the longest permissible decay time and experimenter's ease.

(g) *Detector size, counting geometry and background shielding.* Detector's characteristics may be set in advance by availability but several options exist (IAEA, 2001).

2.7 Accuracy and precision

Error is defined as the difference between the true value and the measured value. Therefore, least error means greater accuracy in a measurement. Precision is an evaluation of the random errors in an experiment and thus it is a measure of the reproducibility of a value. Random errors can be caused by counting statistics, sampling, instrumental fluctuations, weighing, random contamination and irreproducible chemical reactions (Alfassi, 1994).

In NAA, counting statistics is the dominant factor for the precision of the analytical results. The uncertainty of a single measurement is usually denoted by the counting statistics at the 68% confidence limit, whereas the precision of a mean value obtained by the NAA method is measured by the replicate analysis of a homogeneous sample. Precision can thus be reported as 1σ, 2σ or 3σ representing 68%, 95% and 99% confidence limit. Standard deviation equation is as follows:

$$\sigma_x = \left[\frac{\sum (X_i - \overline{X})^2}{N-1} \right]^{\frac{1}{2}}$$

where σ_X = standard deviation of an individual measurement of X at the 68% confidence limit

X_i = individual measurement

$\overline{X}$ = mean value, $\Sigma X_i/N$

N = number of measurements

As in other chemical techniques, there are numerous pitfalls which can hamper reliable measurements. An estimate of accuracy of the measurement is achieved by analyzing certified reference materials. This indicates how good one's techniques and methods are when the results are compared with known concentrations of major, minor, and trace elements in similar or other matrices.

There are several factors which can limit the accuracy of NAA. including:

(1) changes of neutron flux profile which are not carefully monitored;

(2) inaccurate placements of sample in front of detectors including volume variations between standards and sample. Radiation from the sample to the detector decreases at $1/r^2$, where r is the distance of the source and detector. This is particularly significant when counting is done at short distances from the detector. Sample position is crucial. every effort should be made to retain a nearly identical geometry between the samples and standards;

(3) unknown changes in relative natural abundances of certain elements such as boron. sulfur, and lead;

(4) inaccurate correction for deadtime losses and pulse pile-up by either software or hardware methods;

(5) poor deconvolution of overlapping peaks by computer programs;

(6) unforeseen nuclear or spectral interference;

(7) human factor errors, including incorrect reading of irradiation, decay or counting times and sample weights. Exact times for short irradiations are crucial;

(8) trace impurities in counting vials which have been activated along with the samples (this is particularly crucial for biological and some environmental samples);

(9) volatilization of certain elements such as mercury during irradiation;

(10) incorrect drying procedures for bioenvironmental samples which have high moisture content.

CHAPTER III

IRRADIATION AND COUNTING FACILITIES

CHAPTER III

IRRADIATION AND COUNTING FACILITIES

Neutron activation analysis is a nuclear analytical technique (NAT). In this method the samples are usually irradiated in a research reactor. Then radioactivity of the irradiated samples is measured by gamma spectrometer. In this chapter, description of reactor and gamma spectrometer is provided.

3.1 The research reactors

For neutron irradiation Bangladesh Atomic Energy Commission TRIGA Mark-II and PARR-1 and PARR-2 research reactors of Pakistan have been utilized. The 3 MW TRIGA research reactor is situated at Savar, Dhaka, Bangladesh and is the only nuclear reactor in the country. It is a research reactor having a tank type construction and is used for training, research and isotope production. (**T**raining, **R**esearch, **I**sotope production, **G**eneral **A**tomics = **TRIGA**). The reactor is of US origin and has been designed and constructed by the General Atomics, San Diego, California, USA. The reactor was tested and commissioned at its full power of 3 MW at the end of October 1986. The TRIGA Mark-II research reactor is a light water cooled and graphite reflected reactor designed for steady state and square wave power level of 3 MW (thermal). The reactor is also operated in pulsing mode with a maximum reactivity insertion of up to \$2.00 (0.14% δk/k). The corresponding peak power achieved is about 852 MW with a half-maximum pulse width of nearly 18.6 milliseconds. The reactor core is located near the bottom of the reactor tank and consists of 100 fuel elements (including 5 fuel follower control rods and two instrumental fuel elements).

PARR-1 and PARR-2 are two research reactors situated in the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan. The main features of the TRIGA Mark-II research reactor have been presented in Table 3.1 (BAEC, 2002); and those of PARR-1 and PARR-2 research reactors are presented in Table 3.2.

TABLE 3.1

Main features of the BAEC TRIGA Mark-II research reactor

Fuel-moderator material	Uranium = 20.00 wt% ZrH$_{1.6}$ = 79.53 wt% ^{167}Er = 0.47 wt%
Uranium enrichment	19.70 wt%
Fuel element dimensions (overall)	Diameter = 03.73 cm (01.47 in) Height = 75.18 cm (29.60 in)
Cladding	Material = type 304 stainless steel Thickness = 0.5 mm (0.02 in)
Active core volume	Diameter = 55.25 cm (21.75 in) Height = 38.1 cm (15 in)
Core loading	Fuel elements = 93 IFE* = 02 FFCR** = 05
Control rod	Material = Boron carbide (B$_4$C) No of control rods = 06
Reflector	Material = Graphite with aluminum cladding Radial thickness = 19 cm (7.5 in) Height = 52.7 cm (20.75 in)

IFE* =Instrumented fuel elements; FFCR**= Fuel follower control rod

TABLE 3.2

Main features of PARR-1 and PARR-2 reactors

	PARR-1	PARR-2
Reactor type	POOL	Miniature Neutron Source Reactor (MNSR)
Thermal power, steady	9 MW	30 kW
Max flux, Thermal, n cm^{-2} s^{-1}	9.0E13	1.0E12
Max flux, Fast, n cm^{-2} s^{-1}	2.6E14	3.2E11
Moderator	Light water	Light water
Coolant	Light water	Light water
Reflector	Light water +Graphite	Beryllium + water
Control rod number	5	1

3.2 Irradiation facilities used for NAA works

Irradiation facilities most frequently used for neutron activation analysis research are

a. Pneumatic transfer system
b. Rotary specimen rack
c. Dry central thimble

3.2.1 Pneumatic transfer system

Very-short-lived radioisotopes are produced with the aid of a pneumatic transfer system, which rapidly conveys a specimen to and from the reactor core. The system consists of the following major components:

a. Specimen capsule ("rabbit")
b. Blower and filter assembly
c. Valve assembly
d. Terminus assembly
e. Receiver-sender assembly
f. Control assembly

The system is controlled from the receiving area and may be operated either manually or automatically, i.e., with an electric timing device incorporated into the system so that the specimen capsule is automatically ejected from the core after a predetermined time span.

A solenoid-operated valve controls the airflow. The system operates on a pressure differential, drawing the specimen capsule in and out of the core by vacuum. Thus the system is always under negative pressure, so that any leakage is always into the tubing system. All the air from the pneumatic system is passed through a filter before being discharged. The specimen capsule, or rabbit, is made of polyethylene and is designed to pass freely in a tube with a curved section no smaller than 2 ft in radius and an inside diameter no smaller than 1.08 inch.

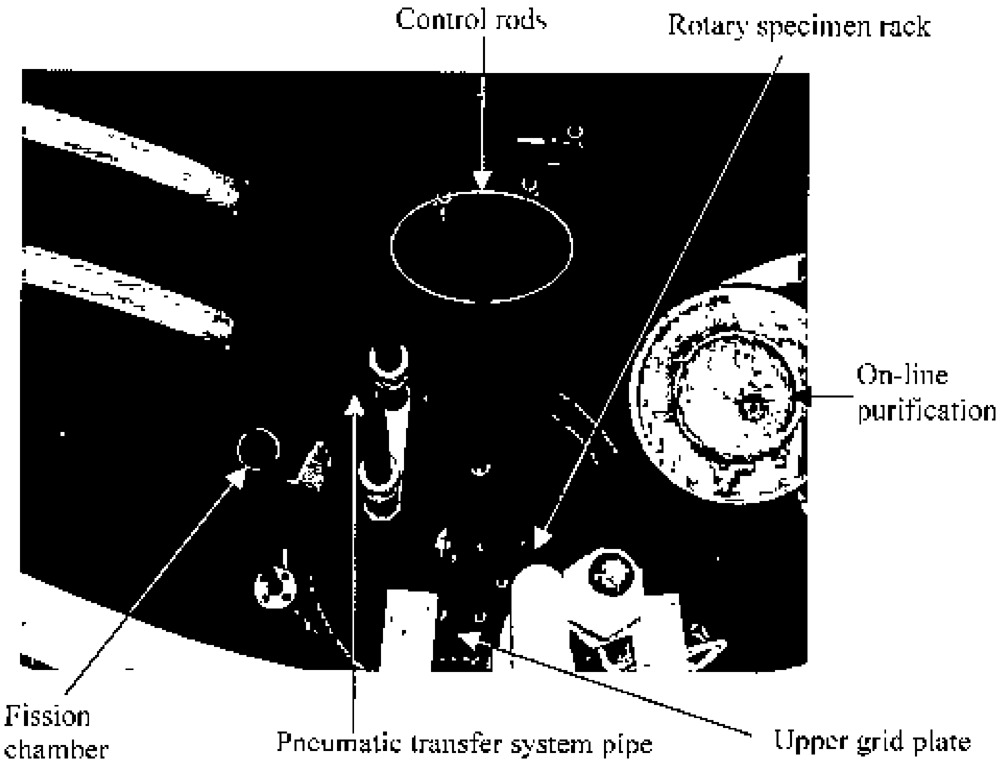

Figure 3.1 Top view of the pool-type BAEC TRIGA Mark-II research reactor. Upper grid plate, central thimble, control rods, rabbit terminus, fission chambers and other accessories are seen in the photograph.

3.2.2 Rotary specimen rack ("lazy susan")

The lazy susan assembly consists of a stainless steel rack that holds specimens during irradiation and a ring-shaped seal-welded aluminum housing. The rack can be rotated inside the housing and supports 41 evenly spaced aluminum tubes. These tubes serve as receptacles for the specimen containers.

Three types of irradiation specimen containers are routinely used in TRIGA reactors. Two of these containers, C10 and C20, are used in rotary specimen rack, which accepts two such containers in each of the 40 positions. An inner plastic vial is always used in conjunction with the polyethylene specimen container to protect the container from contamination and damage. The polyethylene container is suitable for experiments of short duration. For longer-term experiments, use of aluminium containers is preferable.

3.2.3 Central thimble

The central thimble is located in the center of the core. It provides space for irradiation of small samples at the point of maximum flux. It also makes possible the extraction of a highly collimated beam of neutron and gamma radiation.

3.3 Neutron flux

Thermal and epithermal neutron fluxes at 3 MW power level were measured in the irradiation locations of the TRIGA reactor core using cadmium ratio foil activation technique and presented in Table 3.3. Measurement was done at 50 W and extrapolated to 3 MW. The value of the cadmium ratio in the irradiation site varied from 3.922 to 4.314 and the thermal to epithermal flux ratio was in between 18.64 to 21.14. In the calculation of the neutron fluxes, self-shielding factors for thermal and epithermal neutrons were introduced. For this purpose pure gold foils of 25μm thickness were used whereas thickness of the cadmium foils was 1 mm.

TABLE 3.3

TRIGA reactor irradiation facilities and corresponding neutron fluxes at 3 MW

Irradiation facility	Thermal flux, n cm^{-2} s^{-1}
Dry central thimble (DCT)	$\sim 7.46 \times 10^{13}$
Pneumatic transfer system ("Rabbit")	$\sim 3.05 \times 10^{13}$
Rotary specimen rack ("Lazy Susan")	$\sim 1.37 \times 10^{13}$

3.4 Specimen lifting device

The specimen lifting device, a specially modified fishing pole, is used for inserting specimen containers in, and removing them from, the rotary specimen rack and dry central thimble. This pole enables the operator to keep specimens at a distance that permits safe handling of most isotopes and provides maximum flexibility during handling. An electric cable attached to the reel serves as a hoisting cable for the specimen containers and as a power conductor for actuating the specimen pickup tool. This pickup assembly is a small, solenoid-operated. scissors-type device which fits into the upper end of the specimen container. To release a container from the mechanism, the pickup solenoid is actuated from a button on the reel.

3.5 Radiation protection

After irradiation the samples are withdrawn from the core under the presence of a health physics personnel. Samples are removed from the core at least 1 hour after the end of irradiation. Radioactivity at the time of removal depends on many factors such as irradiation time. neutron flux, cross section of the target elements, half-life of the product and sample weight. Radiation dose is measured at the time of removal and the sample containers are then kept in a lead cask of wall thickness 1.3 cm, outside diameter 14 cm and height 14 cm. Then radiation dose is measured at the surface and 1 m from the surface of the closed cask. If the dose level is considered to be safe then the cask is transported from the reactor hall to the activation lab using a trolley. After allowing sufficient decay time the dose level at the surface of the specimen containers are measured again. If the dose is sufficiently low the irradiated samples are opened from the specimen containers while the workers stay behind a lead glass shield. The working personnel use thermo luminescence dosimeter (TLD) for radiological monitoring. Samples are then counted for gamma photons in a HPGe detector if radiation level and hence dead times are permissible. Lead and cast iron of thickness 10 centimeters is used as shielding at all sides and the top of the detector. This shielding protects working personnel in the lab from radiation emitted from the irradiated samples.

3.6 The counting facility and spectrometry equipment

3.6.1 The detector

3.6.1.1 Detector overview

The choice of a particular detector for an application depends upon the gamma energy range of interest and resolution and efficiency requirements. Additional considerations include count rate performance, the suitability of the detector for timing experiments, and of course, price. The detector must have sufficient material to absorb incident gamma-ray energy. Thus a gas-filled proportional counter is suitable for 14.4 keV gamma rays or for X-rays, but would not "see" 1 MeV gamma rays because the probability of absorption of the gamma-ray energy is too low.

Semiconductor detectors are the newest types available, consisting of large crystal of very pure germanium or silicon or compound crystals. The superior resolution of these detectors has revolutionized data gathering for X-ray and gamma-ray measurements.

3.6.1.2 High Purity Germanium (HPGe) detector

The group IV elements silicon and germanium are by far the most widely used semiconductors, although some compound semiconductor materials are finding its use in special applications as development work on them continues. Table 3.4 gives some key characteristics of various semiconductors as detector materials.

TABLE 3.4

Characteristics of various semiconductors as detector materials (Canberra, 1991)

Material	Z	Band Gap (eV)	Energy/e-h pair (eV)
Si	14	1.12	3.61
Ge	32	0.74	2.98
CdTe	48-52	1.47	4.43
HgI_2	80-53	2.13	6.5
GaAs	31-33	1.43	5.2

The conventional coaxial germanium detector is often referred to as Pure Ge, HPGe, or Hyperpure Ge. Regardless of the superlatives used, the detector is basically a cylinder of germanium with an n-type contact on the outer surface and p-type contact on surface of an axial well. The n and p contacts, or electrodes, are typically diffused lithium and implanted boron, respectively. The outer n-type diffused lithium contact is about 0.5 mm thick. The inner p-type contact is about 0.3 μm thick. The useful energy range of the coaxial germanium detector is 50 keV to more than 10 MeV. Some important dimensions of a typical closed end vertical dipstick detector are mentioned below.

Diameter	: 4.1 cm
Length	: 5.5 cm
Active area facing the window	: 17.50 cm^2
Distance from the window	: 0.5 cm

Cross section of a coaxial germanium detector is shown in Figure 3.2. The germanium has a net impurity level of around 10^{10} atoms/cc so that with moderate reverse bias, the entire volume between the electrodes is depleted, and an electric field extends across this active region. The depletion depth is inversely proportional to net electrical impurity concentration and extremely pure material is required. In this way large sensitive detector volume is achieved for high counting efficiency.

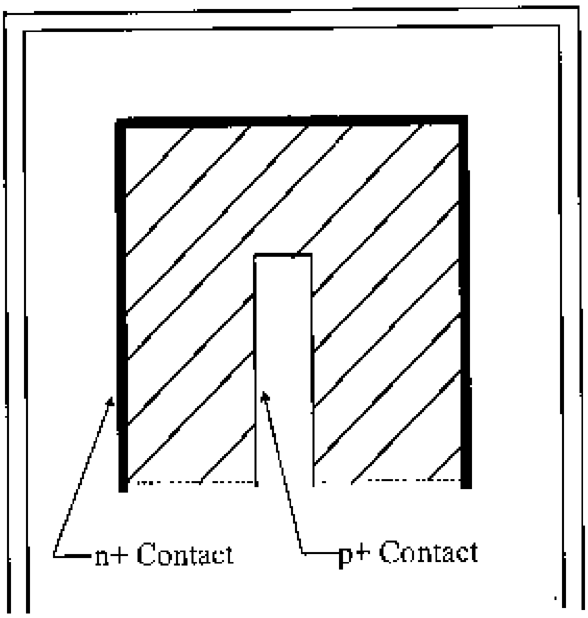

Figure 3.2. Coaxial Ge detector cross section (Canberra, 1991). The hatched region indicates active volume for gamma ray interaction.

When photons interact within the depletion region, charge carriers (holes and electrons) are freed and are swept to their respective collecting electrodes by the electric field. The resultant charge is integrated by a charge sensitive preamplifier and converted to a voltage pulse with amplitude proportional to the energy deposited in the detector.

An ideal detector converts all of the energy of the gamma ray into an electric pulse that is directly proportional to the gamma-ray energy. Compton scattering often results in only a fraction of the energy being deposited because the γ-ray can scatter and then escape from the crystal without further interaction. The full energy peak can be produced by a photoelectric absorption, or one or more Compton scattering followed by photoelectric absorption.

If pair production occurs, the positron slows down in the material and then annihilates, producing two 511 keV gamma rays. Each of these may escape from the detector totally, or leave part of their energy by Compton scattering. If one or both totally escape, the deposited energy is the full energy minus 511 or 1022 keV, leading to designation of these peaks as "single escape" and "double escape" peaks.

The band gap figures in Table 3.4 signify the temperature sensitivity of the materials and the practical ways in which these materials can be used as detectors. Just as germanium transistors have much lower maximum operating temperatures than silicon devices, so do germanium detectors. As a practical matter both Ge and Si photon detectors must be cooled in order to reduce the thermal charge carrier generation (noise) to an acceptable level. The common medium for detector cooling is liquid nitrogen. The detector element and in some cases preamplifier components are housed in a clean vacuum chamber which is attached to or inserted in a LN_2 Dewar. The detector is in thermal contact with liquid nitrogen which cools it to around 77^{o}K or -196^{o}C. At these temperatures, reverse leakage currents are in the range of 10^{-9} to 10^{-12} amperes.

Semiconductor detectors provide greatly improved energy resolution over other types of radiation detectors for many reasons. Fundamentally, the resolution advantage can be attributed to the small amount of energy required to produce a charge carrier and the consequent large output signal relative to other types for the same incident photon energy. The charge multiplication that takes place in proportional counters and in electron multipliers associated with scintillation detectors, resulting in large output signals, does nothing to improve the fundamental statistics of charge production.

The average energy necessary to create a hole-electron pair in germanium is ~2.98 eV. This average energy is about four times the forbidden gap energy (~0.74 eV) because most electrons are promoted from deep in the valence band to the high in the conduction band. The HPGe detector that has been used in INST for the present work has energy resolution of 1.8 keV (FWHM) at 1332.51 keV line of ^{60}Co and relative efficiency of 15%. In PINSTECH, resolution of the detector was 1.9 keV at the same energy with relative efficiency of 25%.

3.7 Electronics associated with gamma spectrometry

Most radiation detectors produce an electrical signal, which must be processed in order to give meaningful information about the radiation being detected. This signal processing usually consists of some combination of three basic operations:

1. Amplification - making the signal bigger in magnitude
2. Shaping - changing the "shape" of the electrical signal. A detector's electrical signal consists of an electrical charge that increases and then decreases with time. Pulse shaping changes the time behavior of the signal.
3. Analysis - sorting of the pulses by their height or area, and so forth.

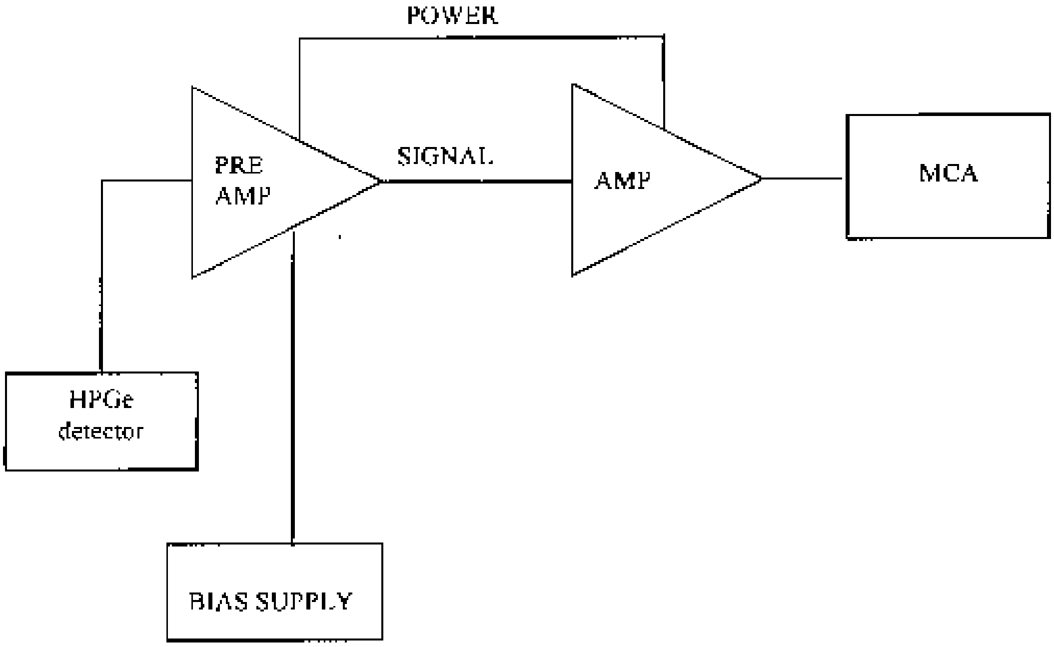

Figure 3.3 Gamma spectrometry system

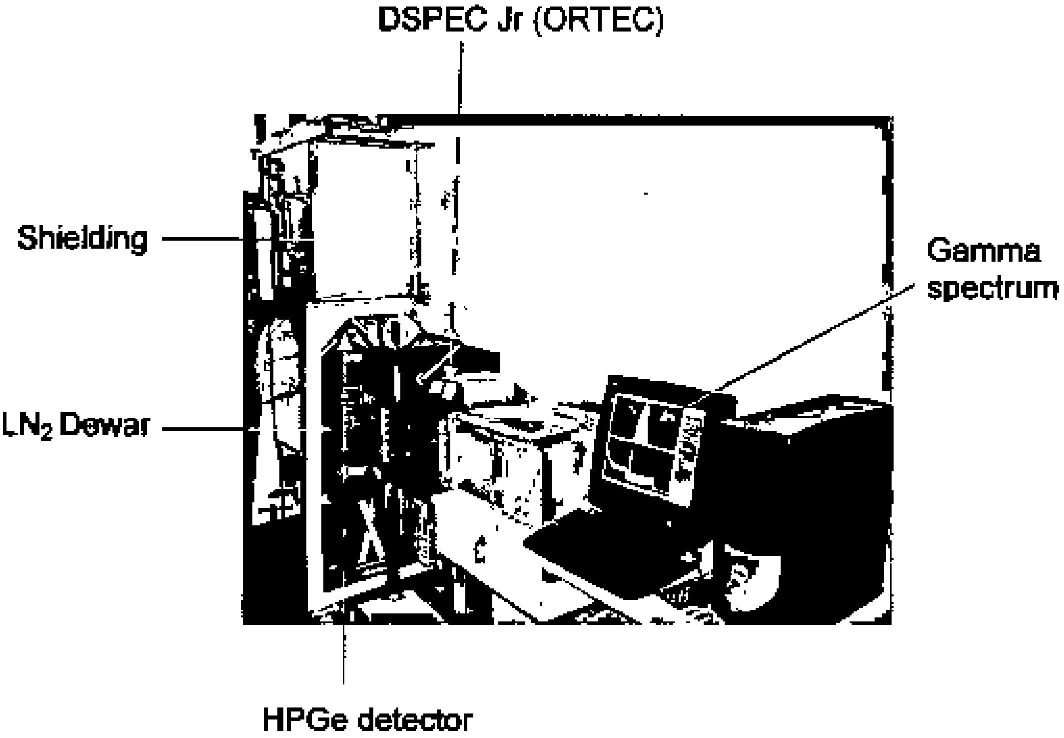

Figure 3.4 Partial view of the gamma spectrometry lab. HPGe detector, detector shielding, DSPEC jr, nuclear instrumentation modules (NIM), oscilloscope and data acquisition computer are seen in the photograph.

This amplification, shaping, and analysis of the detector's signal are done by electronic circuitry. All the electronic equipment that extracts information from the detector signal is classified into certain general types by the function it performs. In Figure 3.3 electrical signals from the *detector* pass to a *preamplifier*, where a preliminary shaping and amplification take place. From the preamplifier, the signals go to an *amplifier*, where final shaping and amplification are done. On leaving the amplifier, the signals go to a *pulse height multichannel analyzer*, where they are sorted in groups by height and the number of pulses in each group is recorded.

3.7.1 The preamplifier

The preamplifier associated with semiconductor detectors performs four essential functions:

1. Conversion of charge to voltage pulse
2. Signal amplification
3. Pulse shaping
4. Impedance matching

The detector is basically a device that senses the ionization created in the detector and converts it into a pulse of electrical charge, q. (The charge q changes as a function of time and thus is most properly denoted as q[t]). The magnitude of the charge, q(t), is in the range 10^{-10} to 10^{-15} coulomb/pulse (Wang et al., 1975). For absorption of a 1 MeV particle, charge generation is

$$Q = \frac{10^{6}\ \text{eV (photon energy)}}{2.98\ \text{eV/ e-h pair}} \times [1.6 \times 10^{-19}\ \text{C}](\text{Charge/e-h pair})$$

$$= 5.4 \times 10^{-14}\ \text{coulombs}$$

The preamplifier produces a voltage signal V(t) by passing the electrical charge from the detector q(t) to a capacitor C. It is known that

$$V(t) = \frac{q(t)}{C}$$

where V(t) is the voltage in volts, q(t) the charges in coulombs, and C the capacitor in farads.

The Canberra Model (2001) represents the latest advance in charge sensitive preamplifiers. The preamplifier converts the ionization charge developed in the detector during each absorbed nuclear event to a step function pulse output whose amplitude is proportional to the total charge accumulated in that event. The pulse decays exponentially with a time constant of 50 microseconds (nominal) to segregate successive events in high count rate applications.

A germanium detector represents an extremely high source impedance (~10 gigaohms) and appreciable capacitance (10 - 50 pF). The design of the model 2001 includes a FET input circuit optimized to the ultra-high source impedance characteristics of Ge detectors. The noise level is equivalent to less than 600 eV FWHM (Ge) with a source capacitance of 0 pF, using 2 microsecond near Gaussian pulse shaping, and degrades at less than 17 eV/pF. The count rate capability has been demonstrated in excess of 200,000 counts per second using ^{60}Co source (1.33 MeV peak). The fast rise time is maintained over a wide range of detector source capacitance: less than 40 ns with C_{source} =0 pF, and less than 50 ns with C_{source} =100 pF (Canberra, 1979). Energy sensitivity is 100 or 500 mV/MeV as selected by jumper plug on printed circuit board internal to the unit.

The preamplifier is usually located very close to the detector and is connected to it by a short, electrically shielded cable. The reason for this arrangement is to minimize the distortion of the signal entering the preamplifier by electrical noise in the cable. Electrical noise is broadly defined as any signal in the equipment not due to nuclear radiation and its interaction with the detector. Some common sources of noise include input capacitance of the leads connecting the preamplifier to the detector, vibration of circuit components, random thermal agitation of electrons in the circuits, and unwanted discharge of electrons by various circuit components. Detector bias voltage is supplied through the preamplifier and the range of the detector bias voltage is 0 to ± 5000 VDC. For the present experiment +4000 VDC was used.

3.7.2 Spectroscopy amplifier

The amplifier acts on the signal from the preamplifier to change further its shape and size. The purpose of this additional amplification and shaping is twofold. First, further amplification improves the signal-to-noise ratio. Further shaping acts to prevent pulse pileup. Since pulses from the radiation detectors occur randomly, one pulse from the detector may begin before the preceding detector pulse has terminated. By shortening the time duration of each pulse ("clipping" the pulse), pulse overlap can be minimized. The amplification achieved in the amplifier is specified by the gain of the amplifier, which is formally defined as the ratio of the output pulse height to the input pulse height. The gain of an amplifier is usually same for all pulses entering the amplifier, regardless of size. When the output pulse height is linearly proportional to the input pulse height, the amplifier is linear.

In any counting system operating at count rates of greater than 100 counts per second, when choosing the amplifier pulse shape, there is always a conflict between increasing the signal-to-noise ratio and preventing pulse pileup. For semiconductor detectors, semi-Gaussian pulse shaping is best because one achieves ~18% better energy resolution with semi-Gaussian shaping than with RC pulse shaping. The main features of Model 2022 Spectroscopy Amplifier (Canberra, date not mentioned) are:

- Gain range - Continuously variable from ×3 to ×3900, product of COARSE and FINE GAIN controls.
- Operating temperature - 0 to 50°C
- Gain drift - Less than or equal to ±0.0075%/°C
- Six shaping time constants: 0.5. 1, 2. 4, 8, and 12 μs
- Active baseline restorer for optimum performance

3.7.3 Multichannel pulse height analyzer

The heart of the multichannel analyzer is the analog-to-digital converter (ADC), which converts the incoming analog amplifier signal to a group of standard-shaped pulses. If the incoming pulse is 4 volts, the ADC might produce 400 standard pulses; or if the incoming pulse was 3 volts, 300 pulses would be produced. In this way, analog information (the signal height) is converted to digital information (the number of pulses).

The most commonly used ADC design is that of Wilkinson. First, the input signal is given flat-top, using a pulse-stretching network. When the input signal reaches its peak amplitude, an oscillator is turned on, thereby producing a train of standard pulses, and a linearly rising voltage is also turned on. When the voltage of the input signal and the linearly rising signal become equal, the oscillator is turned off. Consequently, the bigger the initial signal voltage, the longer it will take for the linearly rising voltage to equal the input signal amplitude; and the oscillator will produce more pulses. The pulses from ADC are counted by the address scaler, and the resultant number is said to be the address (channel number) of that signal. At each memory location or channel, a counter records the number of occurrences of the incoming signal.

PC based System 100 MCA boards and software were used for data acquisition and display in the early phase of the present work. The System 100 MCA has a full 16K channels of data memory, which can be configured as 4K (4096 channels), 8K (8192 channels), or the entire 16K (16384 channels). Some features of S 100 MCA are

- Vertical axis in linear or log scale
- Built-in energy calibration function
- Built-in peak analysis function
- Built-in live time correction function
- Read out of dead time in percentage

In the second phase of the work, DSPEC jr and Maestro-32 were used for data acquisition and display. DSPEC jr is an integrated device containing the amplifier, high voltage unit and ADC.

3.8 Gamma spectrum evaluation software

Hypermet PC (version 5.1) gamma spectrum evaluation software is used in the INST lab for separating overlapping peaks. Main gamma-ray peak of ^{76}As is observed at 559.1 keV. Gamma-ray peaks of ^{82}Br and ^{122}Sb are observed at 554.31 and 564.1 keV, respectively. Contributions of these two peaks are easily separated with the help of Hypermet PC software.

3.9 Detector shielding

Because of the cosmic radiation that continuously bombards the earth's atmosphere and the existence of natural radioactivity in the environment, all radiation detectors record some background signal. The nature of this background varies greatly with size and type of detector and with the extent of shielding that may be placed around it. Because the magnitude of the background ultimately determines the minimum detectable radiation level, it is most significant in those applications involving radiation sources of low activity. However, background is often important enough in routine usage so that the majority of radiation detectors are provided with some degree of external shielding to cause a reduction in the measured level. A second purpose of detector shielding is to provide a degree of isolation in laboratories where other radiation sources may be used or moved during the course of measurement.

Sources of background

Background radiations are conveniently grouped into five categories:

1. The natural radioactivity of the constituent materials of the detector itself.
2. The natural radioactivity of the ancillary equipment, supports, and shielding placed in the immediate vicinity of the detector.
3. Radiations from the activity of the earth's surface (terrestrial radiation), walls of the laboratory, or other far-away structures.
4. Radioactivity around the air surrounding the detector.
5. The primary and the secondary components of cosmic radiation.

In gamma-ray detector without shielding, the cosmic-ray component is normally dominant. When significant shielding is provided, both the cosmic flux and the background due to ambient sources of gamma rays are decreased, and the radioactive contamination of structural and shielding materials around the detector becomes an important fraction of remainder. A typical background is made up of a 30% contribution from cosmic radiation, 60% from radioactive contamination of shielding materials, and 10% from radioactivity within the detector and unidentified sonrces.

CHAPTER IV

ANALYTICAL TECHNIQUES

CHAPTER IV

ANALYTICAL TECHNIQUES

Soil, sediment, rice, husk, vegetables, human hair and two water samples were analyzed using neutron activation analysis (NAA) technique. In addition, 18 water samples were also analyzed using Atomic Absorption Spectrophotometry (AAS). All samples were collected from different areas of Bangladesh and analyzed in INST, Savar, Dhaka and PINSTECH, Islamabad, Pakistan. In this chapter, analysis technique for each of the sample types has been described in details.

4.1 Analysis of water samples

4.1.1 *Measurement of arsenic in water using preconcentration by drying*

Water samples were analyzed to find the level of arsenic pollution of the area. The samples were collected in pre-cleaned. acid washed polyethylene bottles (500 mL each) after withdrawing water by pressing the tubewells for 10 minutes and acidified immediately by 5 mL concentrated hydrochloric acid. Some acid was added for preservation of the sample till analysis and to obtain total arsenic. Then the samples were transported from the field to the NAA laboratory. The samples were stored at low temperature (4^{0}C) and were irradiated in the reactor within 24 h. To assure the analytical accuracy and data intercomparison, standard reference materials (SRM) Arsenic 3103A and Trace Elements in Water 1643d from National Institute of Standard and Technology (NIST) were chosen. Water samples of 50 mL volume are dried in an oven at 45^{0}C and sample volumes of 10 mL were achieved A total of 200 μL of water from each sample was absorbed in two stages on the five folds of filter paper (Whatman No. 541, ≈ 1.0 cm diameter) using a micropipette and dried at the room temperature. Then the samples were put into ultra clean polyethylene bags and heat-sealed.

These bags were packed into polyethylene irradiation container and irradiated in the reactor (PARR-1). Polyethylene blank was also prepared and irradiated simultaneously to investigate contribution from polyethylene. Irradiation, decay and counting scheme for water measurement is shown in Figure 4.1. Irradiation, decay and counting times are selected to obtain good measurable gamma peak areas without any spectral interferences. Usually 10,000 counts are considered satisfactory in gamma spectrometric measurements. HPGe detector of 25% relative efficiency and 1.9 keV resolution at 1332.51 keV gamma line of ^{60}Co was used for gamma measurement. Peak areas were calculated using the software Silena-EMCAPLUS 3.00.0. Analysis was performed using the software developed locally.

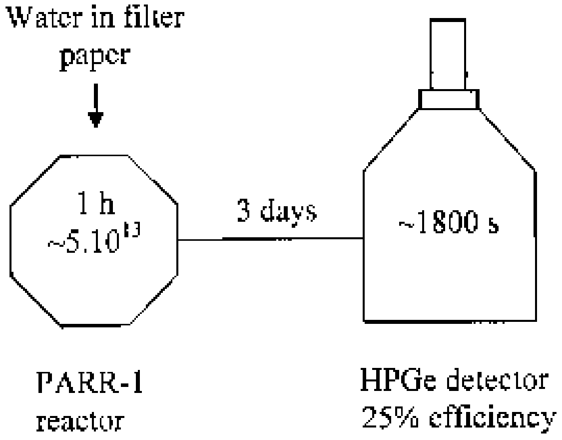

Figure 4.1 Irradiation, decay and counting scheme for the determination of arsenic in water (PINSTECH set-up).

4.1.2 *Measurement of arsenic concentrations in water using Hydride Generation-Atomic Absorption Spectrometry (HG-AAS)*

Eighteen water samples were analyzed for arsenic concentrations using Hydride Generation–Atomic Absorption Spectrometry method. It is not usually practiced to irradiate liquid sample inside the reactor core. Shimadzu AA6800 was used for this analysis. The samples were diluted 1+9 with deionized water on a gravimetric basis in order to ensure that the arsenic contents remain within the linear working range of the technique. All solutions contained 0.5 % v/v HNO_3 (Merck. suprapure). All volumetric plastic ware were acid washed prior to use. An aqueous single element standard 100 μg L^{-1} arsenic was prepared from a single element stock solution (1000±2 mg L^{-1}. Wako Pure Chemicals, Tokyo, Japan) in 0.5% nitric acid. The following concentrations of working standards were prepared by the variable by the variable micropipette (Eppendorf) by serial dilution: 0, 2, 4, 8 and 16 μg L^{-1} arsenic. Three measurements were performed on each calibration solution. Quantification was achieved against the aqueous calibration. The following parameters were used:

Analytical wavelength for arsenic: 193.7 nm
Slit width: 0.7 nm
Read time: 5.0 s

A quality contiol material (NIST 1643d; Trace elements in water) was analyzed in parallel with the test samples. To check the instrumental drift, an aqueous standard solution was measured after every 3 samples.

4.2 Analysis of soil samples

In order to monitor the arsenic load on soils from water, about 200 g of topsoils (0 - 15 cm) was collected from regions subjected to hand tubewell, shallow tubewell, deep tubewell and surface water irrigation.

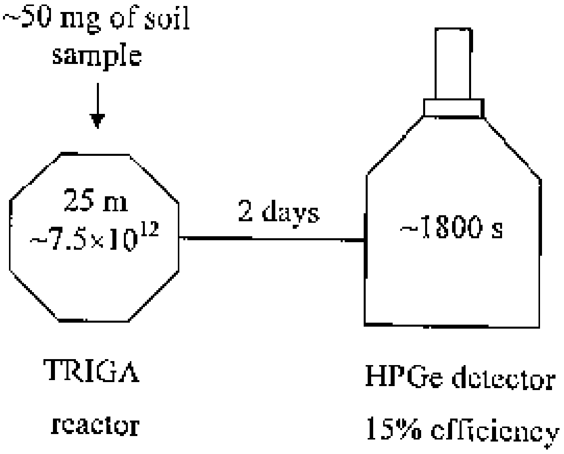

Figure 4.2 Irradiation, decay and counting scheme for the determination of arsenic in soil (INST set-up).

Soil samples were collected from Goainghat, Sylhet (unaffected area); Companiganj, Sylhet (moderately affected area); Faridganj, Chandpur and Lohajang, Munshiganj (highly affected areas). Iron as an element was also determined along with arsenic for correlation studies. Necessary samples were crushed in agate mortar, powdered and homogenized to uniform particle sizes. Soil was dried in an oven at 105°C till constant weight to remove moisture contents. Certified reference materials (CRMs) IAEA-Soil-7, IAEA-SL-1 and 1633b were used to determine arsenic and iron in soil. About 50 mg of each soil sample was irradiated in the reactor along with the CRMs (standard weight was in the range of 22 – 38 mg). Irradiation, decay and counting schemes for measurement of arsenic and iron in soil are shown in Figures 4.2 and 4.3, respectively.

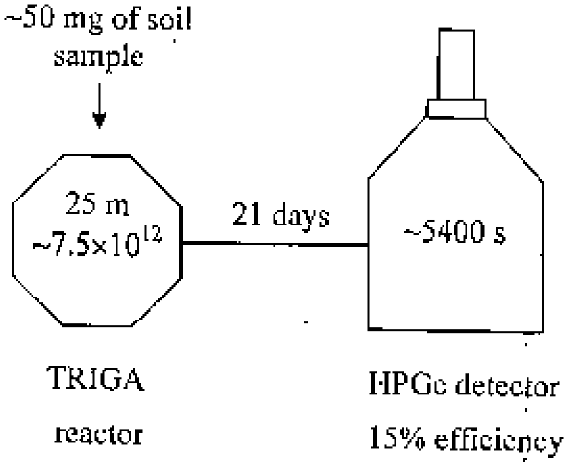

Figure 4.3. Irradiation, decay and counting scheme for the determination of iron in soil (INST set-up)

Gamma-ray acquisition was done using PC based System 100 MCA boards and software. Peak areas were determined and elemental analysis was done using the software PEAKGR 10.

4.3 Analysis of sediment samples

Undisturbed sediment samples were collected from two contrast sites: one is arsenic-free and another is highly affected area in the country. Seven sediment samples were collected from AERE, Savar campus (unaffected) and thirteen sediment samples were collected from the compound of Majumder's house, village: Sreerampur, P. S. Kachua, Dist: Chandpur under "The Deep Aquifer Characterization and Mapping Project" of Bangladesh Water Development Board (highly affected). Samples were collected from a depth of 5 to 350 feet. Samples were analyzed in Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan using PARR-2 research reactor. Initially the samples were oven-dried to constant weight at a temperature of 105°C, ground well for homogenization and approximately 50 mg of each sample was taken in paper envelope for irradiation. Irradiation time was 1 hour for arsenic and iron and 5 minutes for manganese. Neutron flux was 10^{12} n cm^{-2} s^{-1}.

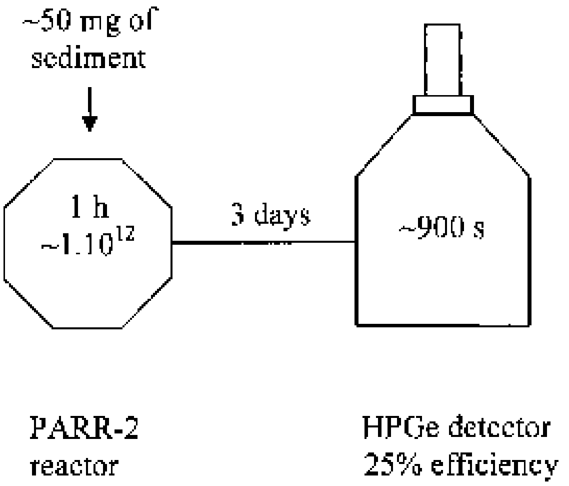

Figure 4.4 Irradiation, decay and counting scheme for the determination of arsenic in sediment (PINSTECH set-up).

After irradiation samples were transferred to pre-weighed polyethylene container for counting. Counting time was 900 sec for As, 300 sec for Mn and 5400 sec for Fe. Decay time was 3 days for As, 30 minutes for Mn and 3 weeks for Fe (Figures 4.4 to 4.6). IAEA standards SL-1 and Soil-7 were used for the relative determination of As, Mn and Fe.

4.4 Analysis of rice, husk and vegetable samples

Rice samples were collected from Goainghat, Sylhet (unaffected area); Companiganj, Sylhet (moderately affected area); Faridganj, Chandpur and Lohajang, Munshiganj (affected areas).

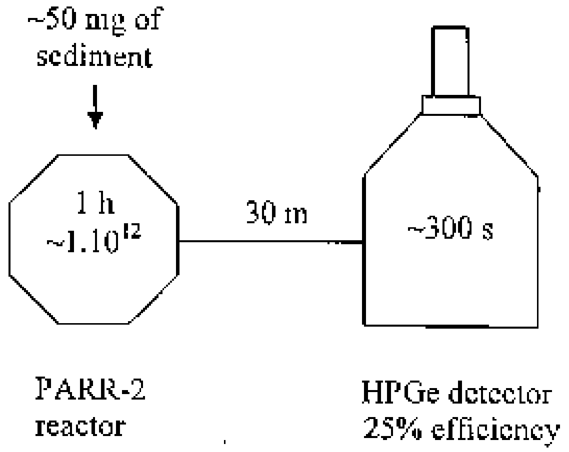

Figure 4.5 Irradiation, decay and counting scheme for the determination of manganese in sediment (PINSTECH set-up)

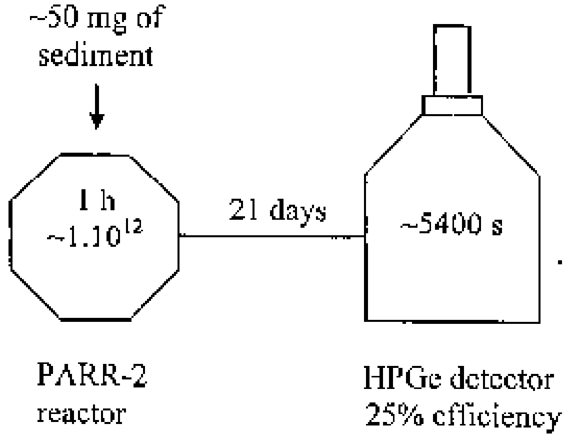

Figure 4.6 Irradiation, decay and counting scheme for the determination of iron in sediment (PINSTECH Set-up)

Vegetables were collected from Companiganj, Sylhet; Damurhuda, Chuadanga and Faridganj, Chandpur. For rice samples, husks were separated first, ground and oven dried at 70°C till constant weight. Approximately 150 mg of rice powder was taken in ultra clean polyethylene envelop for each sample. Citrus leaves and pepperbush were used as the quality control standard reference materials. Irradiation, decay and counting scheme is shown in Figure 4.7. Vegetable samples were washed with demineralized distilled water and chopped into small pieces and then dried in an oven at 70°C till constant weight. The samples (100 to 150 mg each) and blanks were irradiated in the TRIGA Mark-II research reactor at a neutron flux of ~1.5×10^{13} n cm^{-2} s^{-1} for 1 hour. Flux monitor foils were also irradiated simultaneously. Decay time was 2 days and counting time was 1800 sec per sample. For gamma-ray acquisition, DESPEC jr and MAESTRO-32 software were used. Peak areas were determined using the software Hypermat PC verson 5.1 Elemental analysis was done using the software PEAKGR 10 and MS-Excel.

A part of the rice samples was analyzed in PINSTECH, Islamabad. Facilities of PARR-I research reactor was used for the irradiation at a neutron flux level of ~5×10^{13} n cm^{-2} s^{-1} for 1 hour. Gamma counting was done using an HPGe detector with 25% relative efficiency, 1.9 keV resolution for 1332.5 keV gamma peak of ^{60}Co and peak-to-Compton ratio of 40:1. Peak areas were calculated using the software Silena-EMCAPLUS 3.00.0. Analysis was performed using the software developed locally.

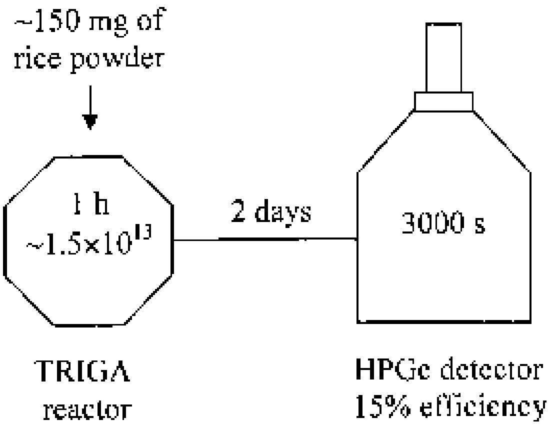

Figure 4.7 Irradiation, decay and counting scheme for measurement of arsenic in rice, husk and vegetables (JNST set-up)

4.5 Analysis of hair samples

Hair samples were collected from Goainghat, Sylhet (unaffected area); Companiganj, Sylhet (moderately affected area); Damurhuda, Chuadanga; Faridganj, Chandpur and Lohajang, Munshiganj (highly affected areas). Hair samples were washed with acetone at first, then three times by de-mineralized water and again by acetone. Samples were air-dried and cut into small pieces (~2 mm). Then the samples were put in polyethylene irradiation vials. Sample weights were in the range of 17.9 – 133.0 mg. Citrus leaves and pepperbush were used as the quality control standard reference materials. Irradiation, decay and counting scheme is shown in Figure 4.8.

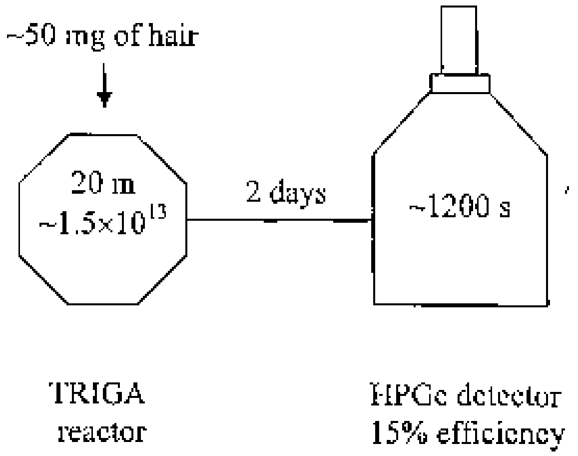

Figure 4.8 Irradiation, decay and counting scheme for arsenic measurement in hair (INST set-up)

A part of the hair samples of Damurhuda has been prepared and irradiated in the central thimble of the TRIGA Mark-II reactor at a thermal neutron flux of ~1.5×10^{13} n $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ for an irradiation time of 20 minutes. Gamma-ray counting of the irradiated samples was done in the gamma spectrometry lab after 2-day decay. Relative efficiency of the HPGe detector of the spectrometry system was 15%. Gamma-ray acquisition was done using DSPEC jr and MAESTRO-32 software. Peak areas were analyzed using the software Hypermat PC version 5.1. Elemental analysis for arsenic and iron was done using the software PEAKGR 10 and MS-Excel. Rest of the hair samples were analyzed in PINSTECH, Islamabad.

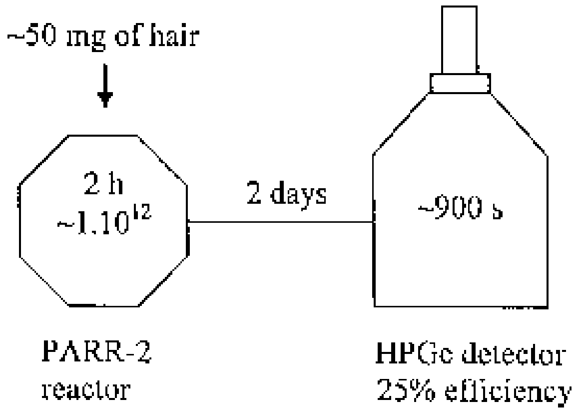

Figure 4.9 Irradiation, decay and counting scheme for arsenic measurement in hair (PINSTECH set-up)

In PINSTECH, the samples were irradiated in PARR-2 research reactor for 2 hrs at a thermal neutron flux of 1×10^{12} n cm^{-2} s^{-1}. Decay time was 2 days. Counting time for each sample was 900 sec as shown in Figure 4.9. Gamma counting was done using an HPGe detector with 25% relative efficiency, 1.9 keV resolution for 1332.5 keV gamma peak of ^{60}Co and peak-to-Compton ratio of 40:1. Peak areas were calculated using the software Silena-EMCAPLUS 3.00.0. Analysis was performed using the software developed locally. Gamma-ray spectra for irradiated soil, rice, husk, vegetables and human hair are presented in Figures 4.10 to 4.14, respectively.

4.6 Estimated uncertainties in NAA measurements

Any chemical measurement process consists of sampling and sample preparation, measurement of the test portion, evaluation of the measurement (data reduction), and reporting measurement results in terms of an estimate of the analyte amount (measurand) and its uncertainty (Currie, 1995). Uncertainty of measurement is defined (ISO, 1993; EURACHEM, 1995) as "a parameter associated with the results of the measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand". Table 4.1 shows estimated values of uncertainties in NAA (Kucera et al., 2000).

Table 4.1

Origin and typical magnitude of uncertainties in NAA

Uncertainty component	Origin	Typical uncertainty, %
u_1	Sample and comparator preparation	
u_{1a}	Mass determination of sample	0.05
u_{1b}	Mass determination of comparator	0.2
u_{1c}	Mass changes of sample due to moisture uptake during weighing	0.1
u_{1d}	Blank variation and the necessary correction (due to analyte content in irradiation vial)	0.5
u_2	Irradiation	
u_{2a}	Irradiation geometry difference	0.1
u_3	γ-ray spectrometry measurement	
u_{3a}	Counting statistics for sample and standard	Usually 0.2 to 30
u_{3b}	Counting geometry differences	3.0
u_{3c}	Pulse pileup losses (random coincidence)	0.5
u_{3d}	Blank correction'(due to counting room/shielding background)	0.3

Combined standard uncertainty $u_c(c_m)$ can be calculated according to the equation

$$u_c(c_m) = c_m\sqrt{(u_1^2 + u_2^2 + u_3^2)}$$

where

$$u_1 = \sqrt{(u_{1a}^2 + u_{1b}^2 + u_{1c}^2 + u_{1d}^2)}$$

$$u_2 = u_{2a}$$

$$u_3 = \sqrt{(u_{3a}^2 + u_{3b}^2 + u_{3c}^2 + u_{3d}^2)}$$

c_m stands for mass fraction.

4.7 Correction for flux gradient

In the relative method of NAA certified reference materials (CRMs) are irradiated simultaneously with the samples. During irradiation samples and standards occupy different positions. For this reason flux gradient correction is necessary. To determine flux gradient iron foils are placed in the top, middle and bottom of the irradiation container. Then flux gradient for each sample position is determined using decay corrected specific activities of the monitor foils.

4.8 Correction of reaction interferences

Arsenic is usually detected via the reaction $^{75}As(n,\gamma)^{76}As$ [$T_{1/2}$=26.3 h, E_γ=559.1 keV]. If bromine is present in the sample, ^{76}As may also be produced via the reaction $^{79}Br(n,\alpha)^{76}As$. In order to check the interference effect, about 20 mg of KBr was irradiated in the same irradiation location as the samples. No gamma peak was found at 559.1 keV energy. Fast neutron cross section of the reaction $^{79}Br(n,\alpha)^{76}As$ (16±6 mb) and fast neutron flux in sample irradiation location are very low. Therefore, there are insignificant reaction interferences in the detection of arsenic due to the presence of Br in the sample.

4.9 Decay data in arsenic determination

Decay data for arsenic measurement have been taken from literature and presented in Table 4.2.

TABLE 4.2

Decay data related in arsenic measurement (Erdtmann, 1976)

Target nucleus (% abundance)	Reaction	Radionuclide used	Half-life	Gamma-ray measured (% I_γ)
^{75}As (100)	(n,γ)	^{76}As	26.3 h	559.1 keV (44.6)

4.10 Quality control and quality assurance

Quality control and quality assurance in measurement were strictly maintained. Certified reference materials are irradiated simultaneously with the samples every time. Both the laboratories participate in inter-comparison runs in a regular basis.

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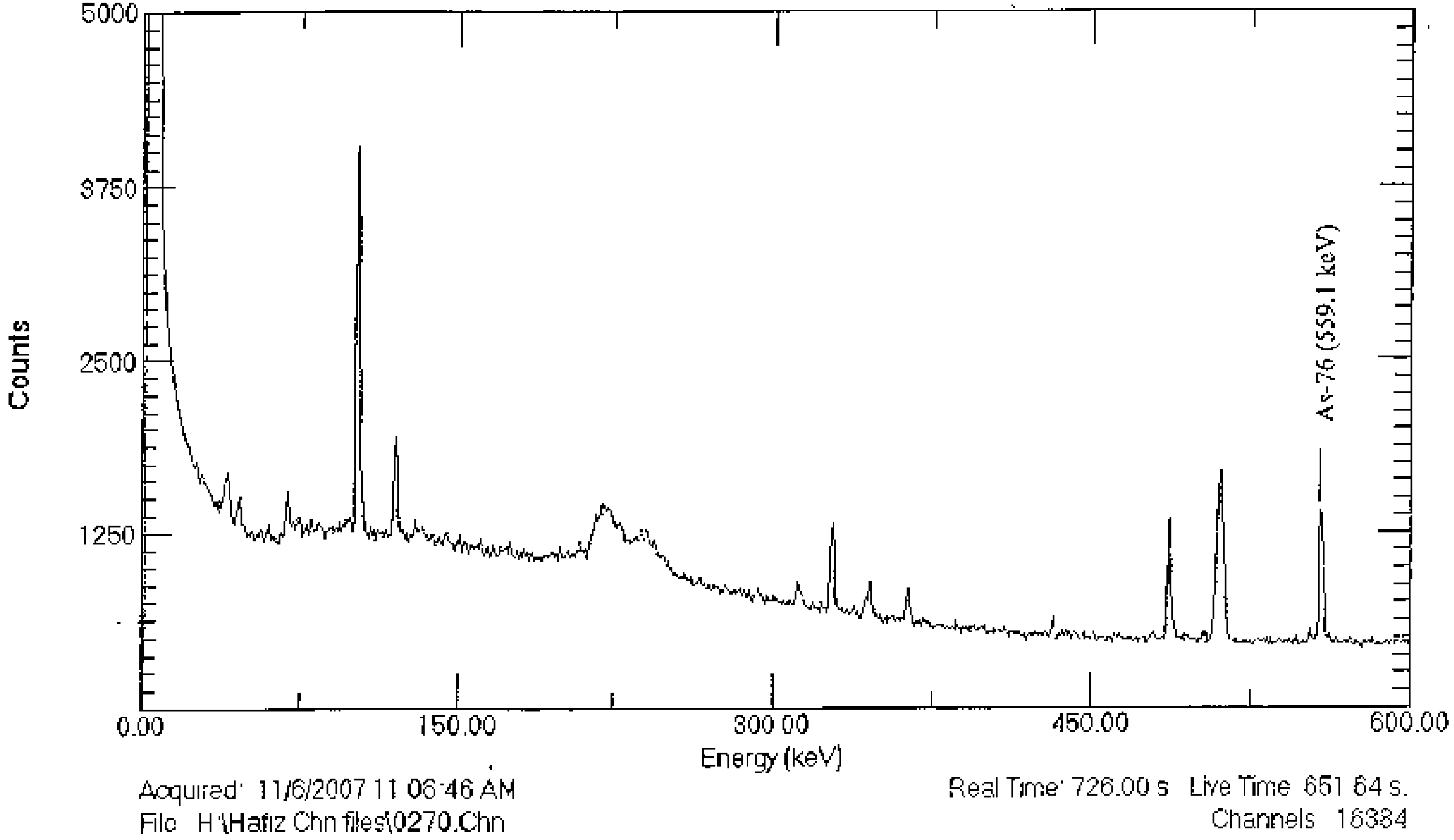

Figure 4.10 Gamma-ray spectrum of irradiated soil

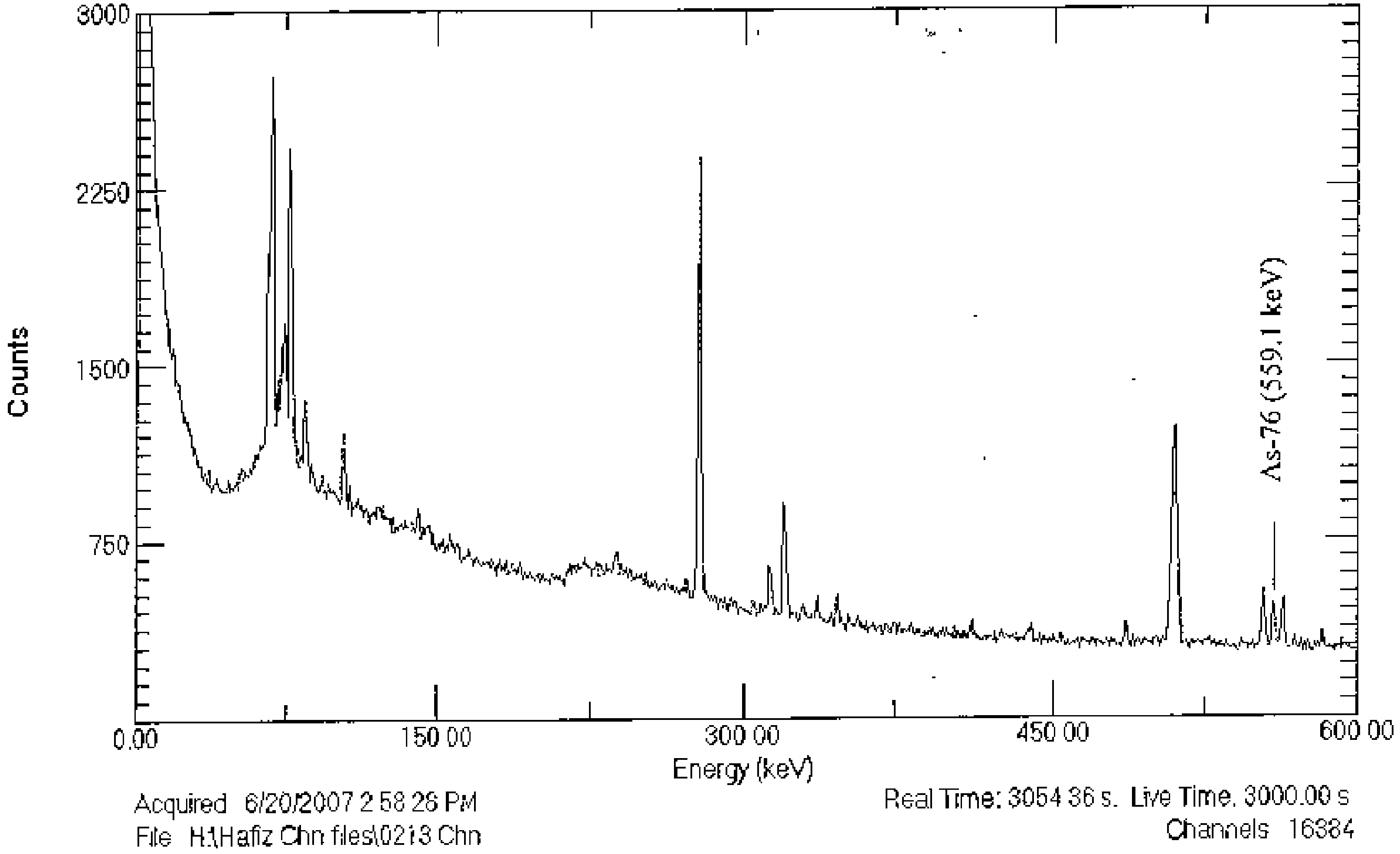

Figure 4.11 Gamma-ray spectrum of irradiated rice

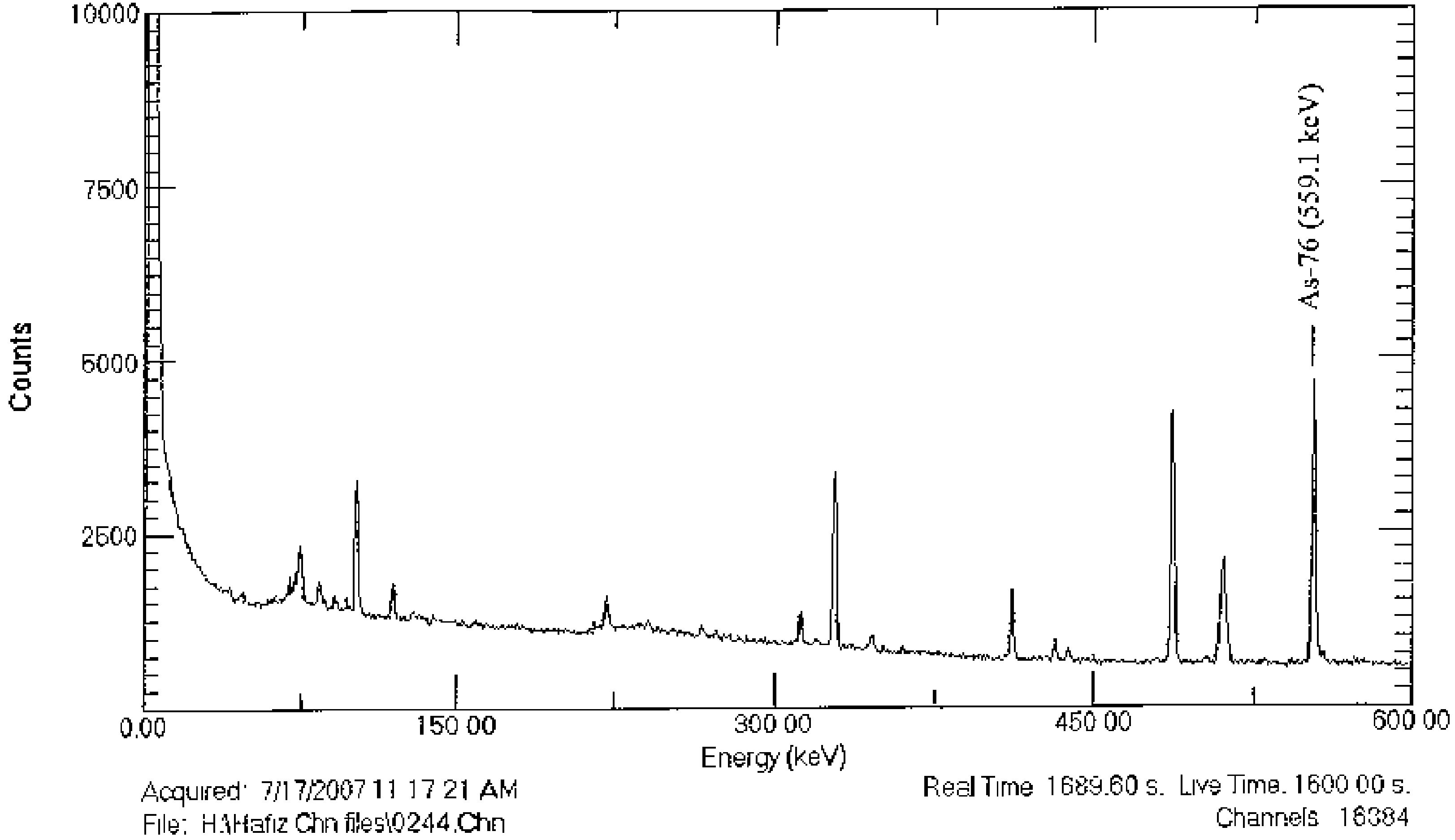

Figure 4.12 Gamma-ray spectrum of irradiated husk

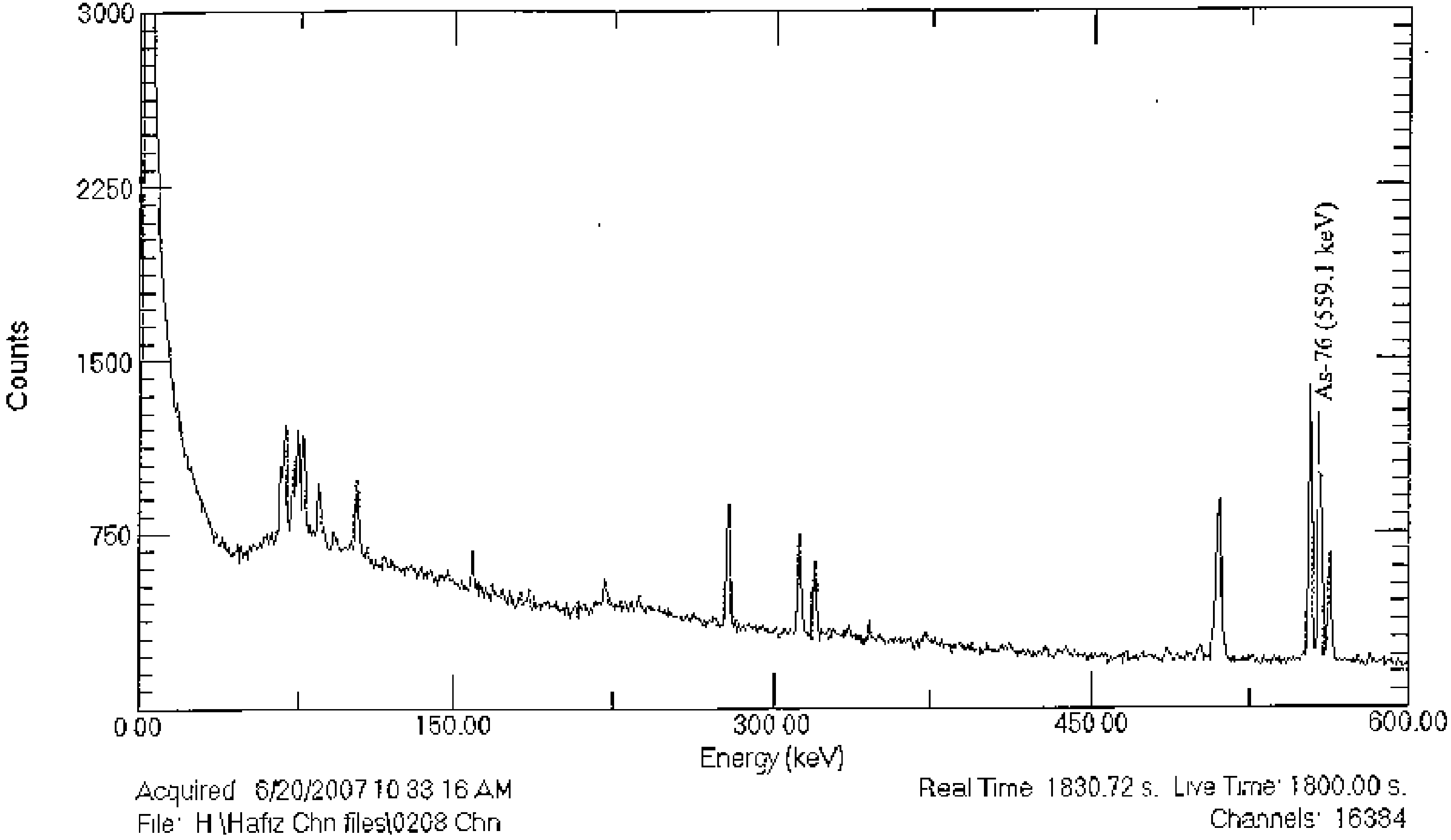

Figure 4.13 Gamma-ray spectrum of irradiated vegetables

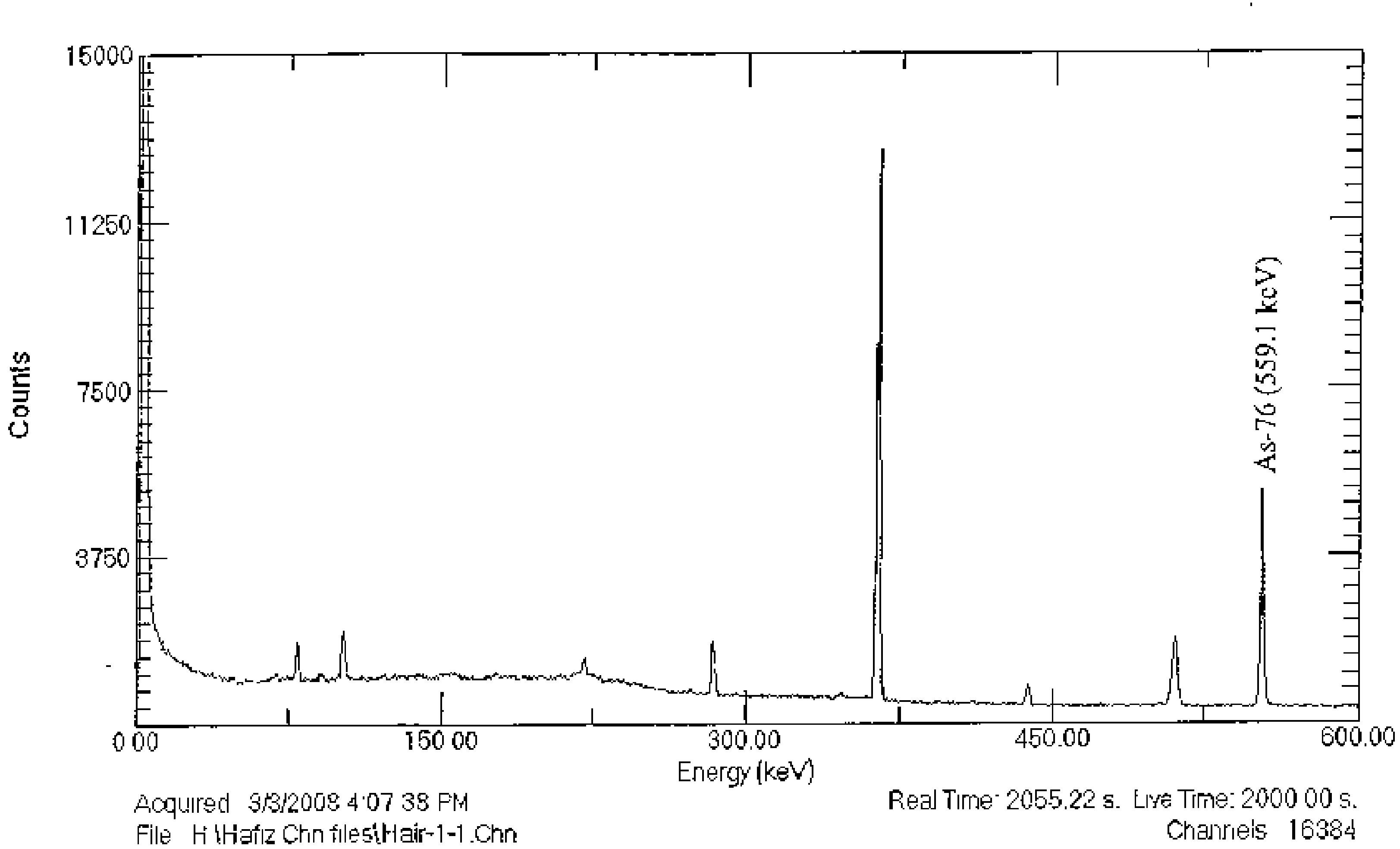

Figure 4.14 Gamma-ray spectrum of irradiated hair

CHAPTER V

RESULTS AND DISCUSSION

CHAPTER V

RESULTS AND DISCUSSION

For the present work the necessary samples, e.g., soil, sediment, rice, husk, vegetables, human hair and some water samples were collected from different areas of Bangladesh and each type of the samples was analyzed as described in Chapter IV. In the present chapter, results of the analysis and discussion on the results are given.

5.1 Unaffected areas

5.1.1 Water samples of Goainghat upazila, Sylhet

Two shallow tubewell water samples were analyzed to find the level of arsenic pollution of the area. Concentrations of arsenic in the water samples of Goainghat upazila, Sylhet are presented in Table 5.1., and quality control data of the measurement are shown in Table 5.2. Both the samples belong to Nandirgaon Union Parishad (UP) under Goainghat upazila. The distance between the two places is about 2 kilometers. Arsenic levels are found to be much less than the Bangladesh standard for arsenic in drinking water of 50 µg/L. Upazila average of arsenic concentrations in tubewell water of Goainghat in BGS-DPHE (2001) measurement was 21.03 µg/L. It indicates that the As contamination level in this area is below permissible level. Location map of Goainghat and Sylhet sadar is presented in Figure 5.1.

TABLE 5.1

Results of arsenic measurement in water samples of Goainghat, Sylhet

Sl. No.	Tubewell owner's name and address	Depth of the tubewell (ft)	Years of operation	No. of users	As concentration, (µg/L)
1	Abdul Matin Village: Bahar	140	4	10	10.70±0.45
2	Abdul Hannan Village: Angarjur	160	8	13	17.48±0.73

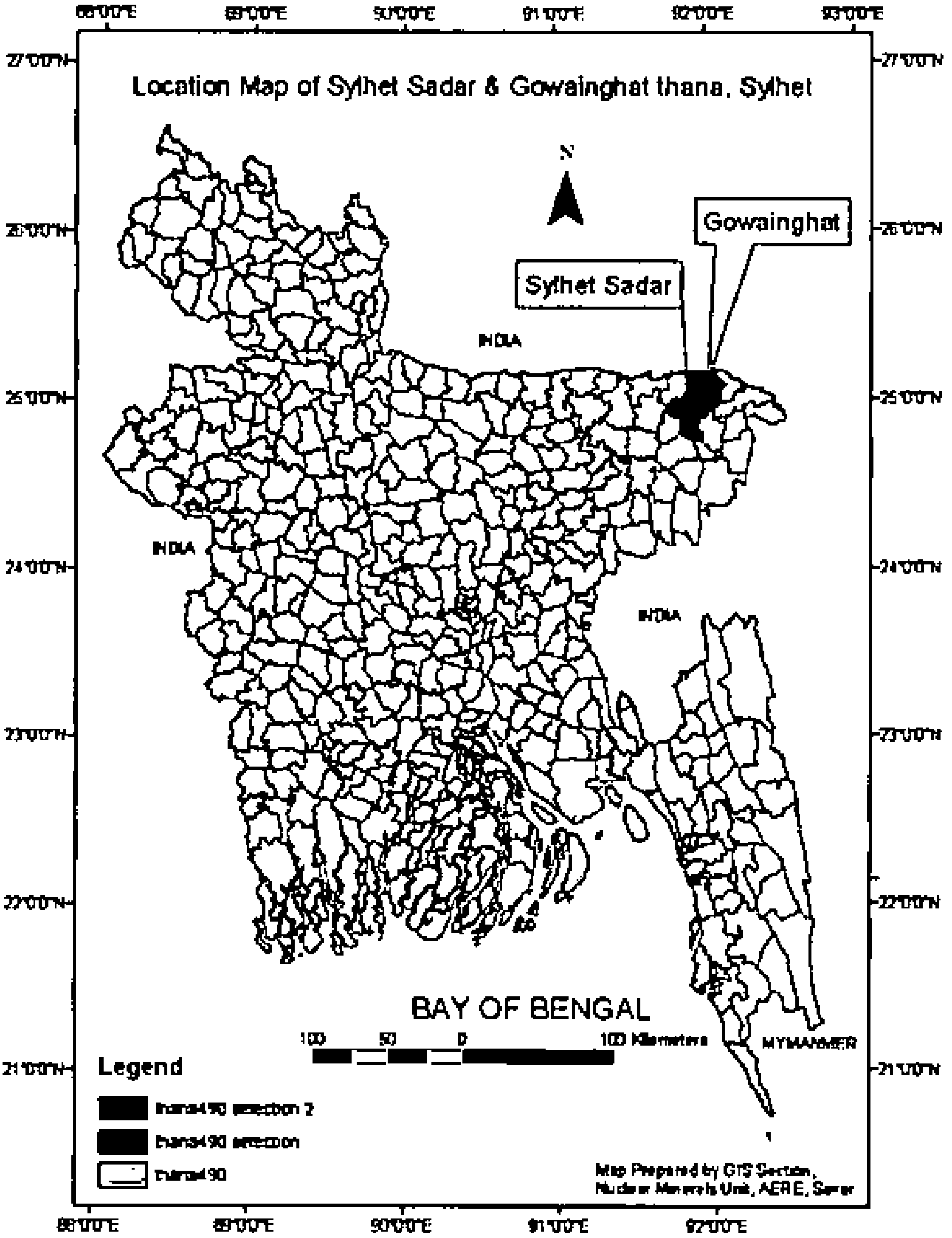

Figure 5.1 Unaffected sites of Sylhet sadar and Goainghat thana

TABLE 5.2

Quality control data of arsenic measurement in Goainghat water samples

Sl. No.	Standard value (mean), mg/L	Measured value (mean), mg/L	% Deviation
1	50	47.12	-5.76

5.1.2 Soil samples of unaffected areas of Goainghat and Companiganj upazilas, Sylhet

Concentrations of arsenic and iron in topsoils of unaffected areas of Goainghat and Companiganj upazilas are presented in Table 5.3 and quality control data of the measurement are shown in Table 5.4. Arsenic versus iron concentration in unaffected soil is presented in Figure 5.2 and strong correlation of R= 0.6869 was found.

TABLE 5.3

Results of arsenic and iron measurement in topsoil of unaffected areas of Sylhet

Soil code	Kind of soil	Owner of the land	Village	Thana	As. Concentration, ppm	Fe concentration, %
1	Silty clay	Abdul Matin	Bahar	Goainghat	2.43±0.27	3.39±0.21
2	Silty clay	Abdul Matin	Bahar	Goainghat	2.61±0.36	2.91±0.14
3	Clay with silt	Abdul Matin	Bahar	Goainghat	4.24±0.37	4.07±0.26
4	Silty clay	Abdul Matin	Bahar	Goainghat	2.46±0.26	3.75±0.22
5	Silty clay	Piar Uddin	Bahar	Goainghat	1.17±0.18	1.99±0.17
6	Silty clay	Piar Uddin	Bahar	Goainghat	1.53±0.23	1.59±0.11
7	Clay with silt	Mr. Mamun	Angarjur	Goainghat	3.49±0.39	3.00±0.19
8	Silty clay	Mamun	Angarjur	Goainghat	1.35±0.20	1.82±0.14
9	Clay	Chand Mian	Angarjur	Goainghat	2.34±0.24	2.01±0.12

Soil code	Kind of soil	Owner of the land	Village	Thana	As. Concentration, ppm	Fe concentration, %
10	Silty clay	Adu Mian	Angarjur	Goainghat	2.07±0.31	1.86±0.17
11	Silty clay	Sirajul Islam	Angarjur	Goainghat	1.24±0.25	1.54±0.17
12	Claye silt	Akbar Ali	Angarjur	Goainghat	3.22±0.48	1.27±0.14
13	Silty clay	Amir Uddin	Angarjur	Goainghat	1.71±0.26	1.52±0..18
14	Silty clay	Mr Tazi	Purna-chhagam	Companiganj	4.07±0.54	3.20±0.21
15	Silty clay	Mr. Tazi	Purna-chhagam	Companiganj	3.39±0.39	2.35±0.18
16	Silty clay	Zahir Uddin	Purna-chhagam	Companiganj	1.61±0.24	1.43±0.16
17	Silty clay	M. Rahman	Purna Chhagum	Companiganj	2.05±0.30	1.39±0.12
18	Silty clay	Mahmud Ali	Bahar	Goainghat	3.46±0.13	2.51±0.03
19	Silty Clay	Abdul Aziz	Bahar	Goainghat	5.73±0.46	3.46±0.07
20	Silty clay	Abdul Karim	Purna-chhagam	Companiganj	4.24±0.34	1.55±0.03
Average values					2.72	2.33

TABLE 5.4

Quality control data of arsenic and iron measurement in topsoils of unaffected areas of Sylhet

Name of the CRM	Elements	Certified value	Measured value	% Deviation
IAEA-Soil-1	Arsenic	13.4±0.1 ppm	13.31±0.54 ppm	-0.7
	Iron	2.57± 0.04 %	2.48±0.13%	-3.5

In the present measurement, maximum and minimum arsenic concentrations in the topsoil (0 – 15 cm) of unaffected areas of Sylhet are found to be 5.73±0.46 and 1.17±0.18 ppm, respectively. This range can be accepted as the background level of arsenic in paddy field soils in Bangladesh. Paddy fields of these areas are irrigated by canal and river water. Other researchers found this range as 4 to 8 ppm (Alam et al., 2000; Ullah, 1998) using different methods. Huq et al. (2003) investigated soils of 15 upazilas of depth 0- 150 mm and 150 -300 mm. With one or two exceptions the topsoil 0 – 150 mm contains more arsenic than the bottom-soil 150 – 300 mm. The average arsenic content in soil of Bangladesh is less than 10 ppm. In general concentrations of arsenic in the majority of soils are low with only a few high values: this suggests that the concentration in surface soils is largely unaffected by human activities meaning irrigation. In another study arsenic in soil of Comilla area was found to vary in the range 2.01 to 12.0 ppm (Alam et al., 2003). Dinajpur is also known as an unaffected area. Ali et al. (2003) observed arsenic concentrations in the topsoil layer to vary from 0.10 to 2.75 ppm in Dinajpur.

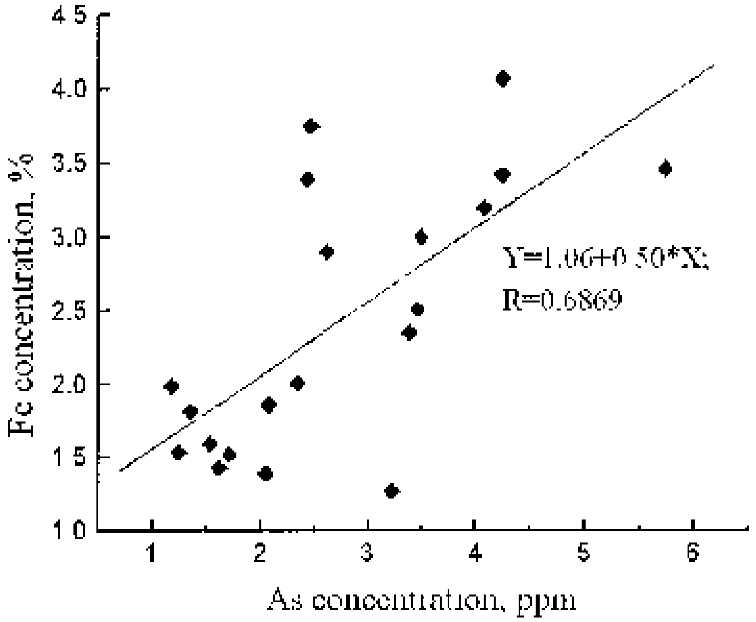

Figure 5.2 Arsenic versus iron concentrations in Sylhet unaffected soil

5.1.3 Sediments of Atomic Energy Research Establishment (AERE) campus, Savar, Dhaka

Results of arsenic measurement in sediments of Atomic Energy Research Establishment (AERE) campus, Savar, Dhaka along with lithological description of the samples are presented in Table 5.5. Quality control data of the measurement are shown in Table 5.6. Location of the AERE campus has been shown in Figure 5.14.

Savar is an arsenic–free area. Upazila average of arsenic concentrations in tubewell water of Savar as per British Geological Survey (BGS)-Department of Public health Engineering (DPHE, 2001) measurement was only 0.343 μg/L. Ranges of arsenic, iron and manganese in AERE sediments were found to be 0.72±0.03 to 6.82±0.26 ppm, 1.36±0.02 to 3.38±0.07 % and 257±14 to 2194±116 ppm, respectively.

TABLE 5.5
As, Fe and Mn concentrations in sediment samples of AERE campus, Savar, Dhaka

Sl No.	Depth, ft (1ft=0.3048m)	Lithological description	As concentration ppm	Fe concentration %	Mn concentration ppm×100
1	5 - 25	Brick red mottled clay	6.82±0.26	3.38±0.07	8.38±0.44
2	25 - 30	Yellowish brown very fine sand	2.2±0.08	1.52±0.03	3.13±0.01
3	30 - 55	Light yellow very fine sand	2.12±0.17	1.93±0.04	3.66±0.01
4	55 - 65	Grey very fine sand, little fine sand, trace silt, mica, black minerals	1.43±0.05	2.05±0.02	21.94±1.16
5	125-130	Light yellow fine to very fine sand	1.54±0.06	2.01±0.02	3.75±0.20
6	130-150	Grey brown fine to very fine sand with significant amount of mica	0.73±0.03	1.81±0.02	15.77±0.83
7	150-160	Grey brown fine sand	0.72±0.03	1.36±0.02	2.57±0.14

TABLE 5.6
Quality control data of arsenic, iron and manganese measurements in AERE sediment

Name of CRM	Element	Certified value	Measured value	%Deviation
IAEA-SL-1	Arsenic	27.6±0.3 ppm	26.15±1 ppm	-5.23
	Manganese	3460±13.7 ppm	3445±69 ppm	-0.43
	Iron	6.74±0.01%	6.63±0.13%	-1.63

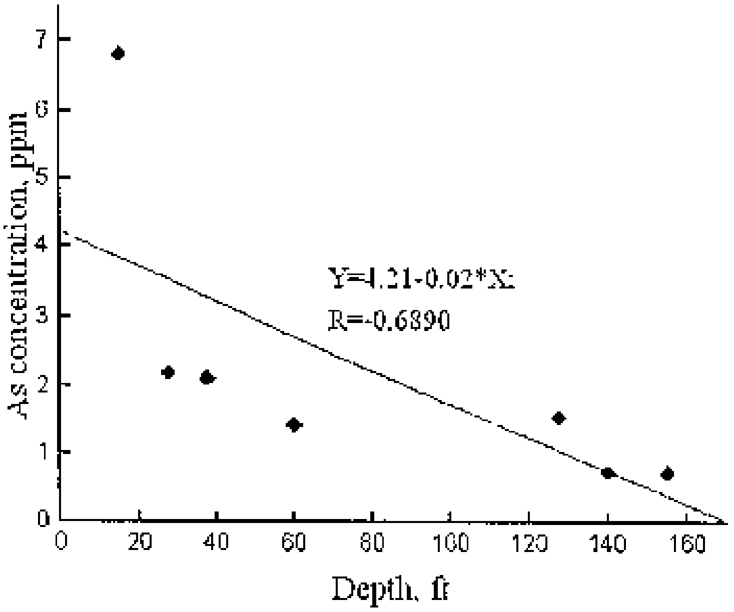

Figure 5.3 Arsenic concentration versus depth in AERE sediments

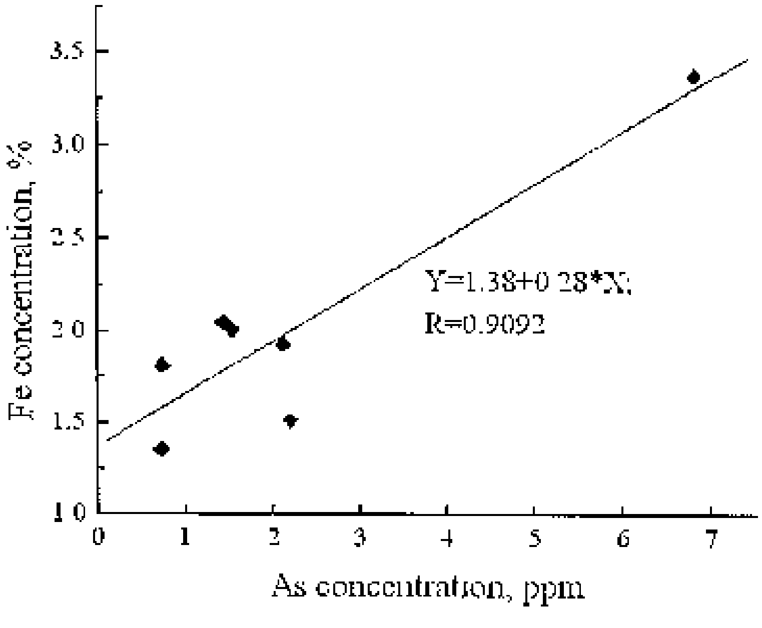

Figure 5.4 Arsenic versus iron concentrations in AERE sediment

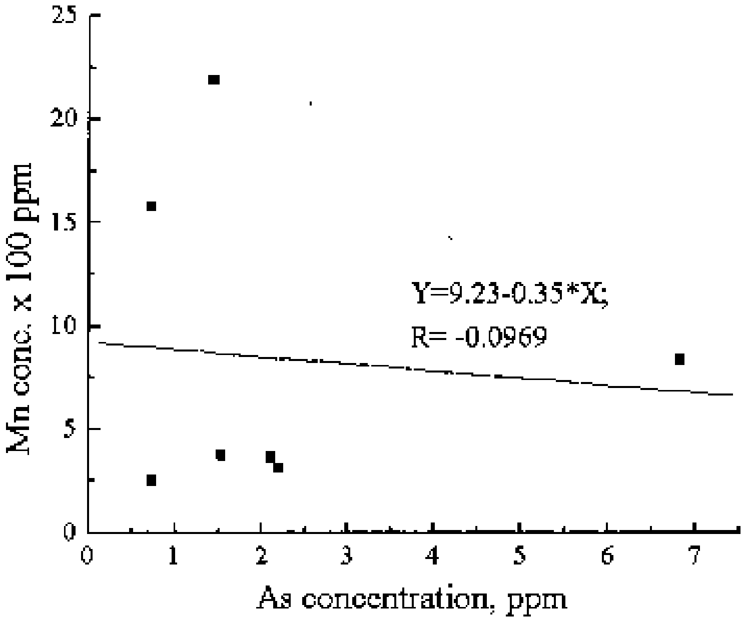

Figure 5.5 Arsenic versus manganese concentrations in AERE sediment

Arsenic concentration decreases with depth. Coefficient of correlation was -0.6890 (Figure 5.3). Figure representing arsenic versus iron concentrations shows a strong correlation (R= 0.9092) between these two elements (Figure 5.4). However, no correlation was found between arsenic and manganese (Figure 5.5).

5.1.4 Rice samples analyzed in PINSTECH, Islamabad

Results of arsenic measurement in rice samples of Goainghat upazila measured in PINSTECH, Islamabad and quality control data of the measurement are shown in Tables 5.7 and 5.8, respectively. Arsenic values vary from 0.03±0.001 to 0.12±0.005 ppm which is far below the permissible limit (1.00 ppm) set by the Food Standards Agency (2002). All values indicate concentrations in dry weight basis. Moisture contents in the rice samples were 7.57-31.73%. These values of arsenic concentrations in rice samples can be taken as the normal background values of arsenic in rice of Bangladesh. Arsenic concentrations in rice of other areas of Bangladesh are found to lie in the range 0.103±0.021 to 0.717±0.192 ppm (Table 5.33).

TABLE 5.7
Results of arsenic measurement in Sylhet rice samples measured in PINSTECH, Islamabad

Location of the paddy fields: Villages- Bahar (Sl. No. 1-3) and Angarjur (Sl. No. 4-6), Nandirgaon Union Parishad, Upazila-Goainghat, zila, Sylhet

Sl. No.	Farmers Name	Rice species	Harvesting time	Arsenic in rice grain, ppm (Dry wt. basis)	Arsenic in husk, ppm (Dry wt. basis)
1	Mahmud Ali	*Lanjoir (Aman)*	Nov/Dec	0.07±0.003	0.10±0.004
2	Mahmud Ali	*Moina Shail*	Nov/Dec	0.03±0.001	0.07±.0.003
3	Abdul Aziz	*Maloti (IRRI)*	Nov/Dec	0.12±0.005	2.00±0.08
4	Abdul Karim	*Boro*	April	0.05±0.002	<0.07±0.003
5	Abdul Karim	*Meghraj*	Dec/Jan	0.12±0.005	0.14±0.006
6	Babul Chaudhury	*Meghraj*	Dec/Jan	0.06±0.002	0.09±0.004
Average values				0.075	0.412

TABLE 5.8
Quality control data of arsenic measurement in rice samples

Sl. No.	Element	Certified value (mean), ppm	Measured value (mean), ppm	% Deviation
1	Arsenic	50	47.1	-5.8

Therefore, it may safely be concluded that according to Food Standards Agency (2002) the analyzed rice samples are free from arsenic pollution. Arsenic in husk was found to be about 5.5 times higher than the arsenic in grain.

5.1.5 Rice samples analyzed in INST, Savar, Dhaka

Concentrations of arsenic in rice samples of unaffected areas of Goainghat and Companiganj upazilas, Sylhet are presented in Table 5.9 and quality control data of the measurement are shown in Table 5.10. Samples no. 1-6 belong to the village Bahar, sample no. 7-13 belong to the village Angarjur of Nandirgaon UP under Goainghat upazila and sample no. 14-16 belong to village Purnachhagam of Daxin Ranikhai UP under Companiganj upazila. Moisture content in the rice samples was 10.95 to 15.92%. Maximum, minimum and average values of arsenic concentrations are found to be 0.112±0.011, 0.038±0.004 and 0.055 ppm, respectively. Detection limit of arsenic in the present experiment was 0.038±0.004. A great portion of Bangladesh is already affected by arsenic pollution and new areas are being affected in the course of time. In this context determination of normal background value of arsenic in rice of control area is of much importance. Present experimental values can be accepted as the base line values for arsenic concentrations in rice of Bangladesh.

Alam et al. (2003) found arsenic content in different rice grains of Comilla district to lie in the range 0 to 0.094 ppm. Hironaka et al. (2003) found the concentration in rice of Rajshahi area to lie in the range 0.03 to 0.34 ppm. The authors also reported that arsenic concentrations of market rice from Rajshahi and Dhaka lie in the range 0.03 to 0.28 ppm. These values are consistent with the present results. Arsenic concentration in rice versus soil has been presented in Figure 5.6 having correlation coefficient of R=0.3162.

TABLE 5.9
Results of arsenic measurement in Sylhet rice samples measured in INST, Dhaka

Sl. No.	Farmer's name	Village	Rice species	As concentration in rice grain, ppm (Dry wt. basis)	As concentration in husk, ppm (Dry wt. basis)
1	Abdul Matin	Bahar	*Meghraj*	0.069±0.006	<0.194±0.015
2	Abdul Matin	Bahar	*Maloti*	<0.038±0.004	<0.194±0.015
3	Abdul Matin	Bahar	*Beruin*	0.089±0.009	0.714±0.034
4	Abdul Matin	Bahar	*BR-29*	0.038±0.004	0.614±0.031
5	Piar Uddin	Bahar	*Chinigura*	0.042±0.004	<0.194±0.015
6	Piar Uddin	Bahar	*Maloti*	0.042±0.004	<0.194±0.015
7	Mamun	Angarjur	*Mukta*	<0.038±0.004	0.571±0.030
8	Mamun	Angarjur	*Hati*	0.052±0.005	0.337±0.005
9	Chand Mia	Angarjur	*Chinigura*	0.045±0.004	<0.194±0.015
10	Apu Mia	Angarjur	*Maloti*	0.054±0.005	0.492±0.034
11	Sirajul Islam	Angarjur	*Hati*	0.066±0.006	<0.194±0.015
12	Akbar Ali	Angarjur	*Biruin*	0.112±0.011	0.529±0.028
13	Amir Ali	Angarjur	*Mati*	0.066±0.006	0.249±0.017
14	Mujibur Rahman	Purnachhagam	*Biruin*	0.072±0.008	0.505±0.028
15	Zahir Uddin	Purnachhagam	*Meghraj*	0.038±0.004	<0.194±0.015
16	Mujibur Rahman	Purnachhagam	*Meghraj*	0.054±0.006	0.273±0.016
Average value				0.055	0.310

TABLE 5.10

Quality control data of arsenic measurement in rice samples

Name of CRM	Element	Certified value, ppm	Measured value, ppm	% Deviation
Citrus leaves	Arsenic	3.1±0.3	3.22±0.32	+3.87

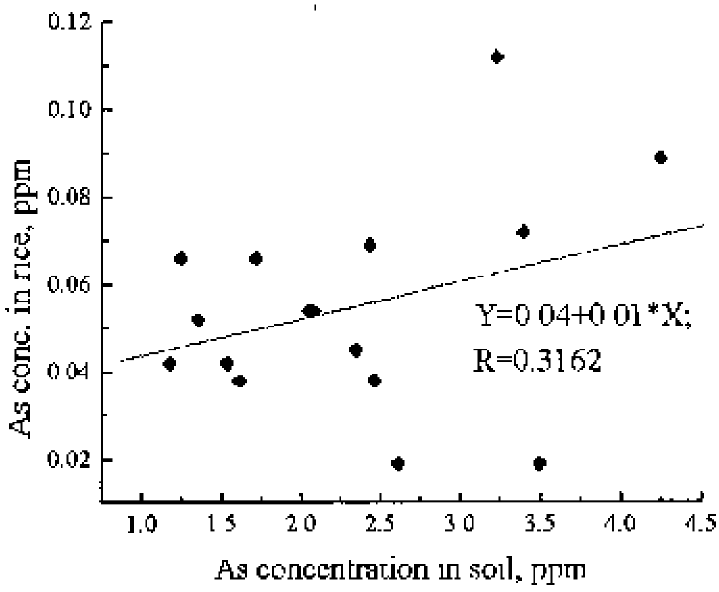

Figure 5.6 Arsenic concentration in soil versus arsenic concentration in rice of unaffected areas

5.1.6 Hair samples of Sylhet area

Results of arsenic measurement in human hair samples of Sylhet area are shown in Table 5.11 and quality control data of the measurement are shown in Table 5.12. It was found that arsenic concentration values lie in the range <0.20 to 0.84±0.04 ppm. In contrast, arsenic concentrations in Chuadanga hair samples were in the range 1.04±0.06 to 48.66±1.32 ppm (Table 5.37). Normal level of arsenic in human hair is less than 1.00 ppm (Arnold et al, 1990). Two persons of Sylhet area having arsenic concentrations of 0.84 and 0.75 ppm in hair seem interesting and they may be monitored closely in the follow-up studies because they are at the risk of arsenic toxicity.

TABLE 5.11

Arsenic concentrations in Sylhet hair samples

Sampling locations:
Bahar (Sl. No. 1-4); Angarjur (Sl. No. 5, 6), Nandirgaon UP, Goainghat thana,
Pir Mahalla (Sl. No. 7, 8, 11); Subid Bazar (Sl. No. 9, 10); Housing Estate
(Sl. No. 12), Sylhet Sadar thana

Sl. No.	Person code	Age, years	Distance of hair from scalp, inch	As concentration in hair, ppm
1	Female-1	48	11	0.75±0.04
2	Female-2	25	8	0.22±0.01
3	Female-3	48	6	0.22±0.01
4	Female-4	45	4	<0.20
5	Female-5	40	6	0.55±0.03
6	Female-6	60	9	0.51±0.03
7	Female-7	16	3	0.58±0.03
8	Female-8	44	3	0.53±0.03
9	Male-1	49	1	0.20±0.04
10	Female-9	43	18	0.23±0.04
11	Female-10	46	28	0.84±0.04
12	Female-11	61	6	0.50±0.03

TABLE 5.12

Quality control data of arsenic measurement in Sylhet hair samples

Name of CRM	Element	Certified value, ppm	Measured value, ppm	% Deviation
IAEA-Soil-7	Arsenic	13.4±0.1	13.7±0.55	+2.24

The regions under study are at present arsenic-free. Upazila averages of arsenic concentrations in tubewell water in BGS-DPHE (2001) measurement of upazilas Goainghat, Companiganj and Sylhet sadar are only 21.03, 40.28 and 6.71 μg/L, respectively. Arsenic content in tubewell water of the region should be monitored once in every year. Arsenic concentrations in hair versus age of the persons are shown in Figure 5.7 which indicates that the relationship is not significant. However, the Figure indicates that the age group of 40 to 48 years contains more arsenic in hair than in the hair of persons of other age groups.

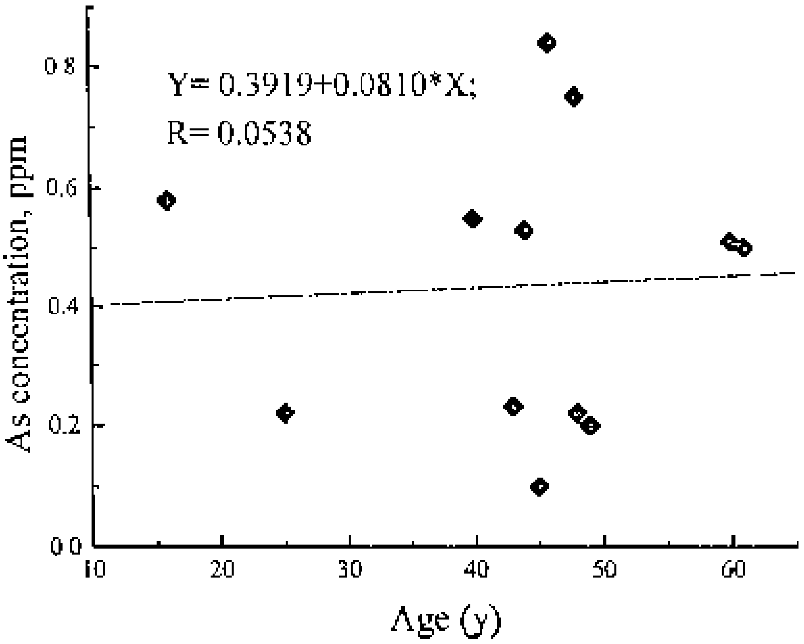

Figure 5.7. Arsenic concentration in hair versus age of the individuals of unaffected areas of Sylhet

5.2 Moderately affected areas

5.2.1 Water samples of Companiganj upazila, Sylhet

Eighteen water samples were analyzed to find the level of arsenic pollution of the Companiganj area. Results and quality control data of water samples analyses are presented in Tables 5.13 and 5.14, respectively. Location map of Companiganj, Sylhet is presented in Figure 5.8. Arsenic versus iron and arsenic versus manganese in water are presented in Figures 5.9 and 5.11, respectively. The range of arsenic concentrations in water was found to be 6.90±0.51 to 87.23±0.75 µg/L which indicates that the area is moderately affected. Upazila average of arsenic concentration in groundwater according to BGS-DPHE measurement (2001) was 40.3 µg/L. Acceptable level of arsenic in drinking water in Bangladesh is 50 µg/L. In the present study 14 out of 18 water samples fail to be acceptable as safe drinking water. Although the arsenic concentration values are less than double the acceptable value, this is a warning signal for the region. In this experiment one surface water sample from a *beel* was analyzed and the value of arsenic concentration was found to be 9.96 µg/L. In Bangladesh surface water is arsenic free is supported by this observation. The water looks transparent. It can probably be used for drinking purpose after sufficient boiling.

Iron concentrations in water lie in the range of 0.46 to 37.30 mg/L whereas Bangladesh standard for iron in drinking water is 2.0 mg/L and WHO guideline value for iron in high quality water is 0.3 mg/L. Iron concentration values as high as 41.7 mg/L has been reported by BGS and DPHE (1999) in a water sample from the same region. All the samples exceeded WHO limit and 16 out of 18 samples exceeded Bangladesh limit. High iron content is a general feature of the region. Iron does not itself represent a health problem but acceptability may be restricted because of tangible taste, smell and discoloration problems in waters with concentrations above around 1 mg/L.

Table 5.13
Description of Companiganj water samples and analyses results

Sample collection location - Union Parishad: Islampur West. Upazila: Companiganj, District: Sylhet

Sample ID	Owner's name	Village	Depth of tube well (ft)	Years of operation	No. of users	As patients	As, µg/L	Fe, ppm	Mn, ppm
W1	Hazi Sikandar Ali	Parua	35	44	10	None	14.52±1.72	1.15±0.02	1.14±0.02
W2	Hazi Hormuz Ali	Rajarkhal	200	25	150	None	69.42±3.14	5.33±0.03	0.18±0.01
W3	Masjid	,,	200	5	350	None	61.94±2.70	5.17±0.08	0.23±0.03
W4	Mohd. Ali	Lamba-khandi	250	6	50	None	81.55±2.98	5.83±0.02	0.12±0.09
W5	Jenu Mia	,,	240	9	40	12	74.50±1.29	3.70±0.05	0.30±0.05
W6	Md. Zainal	,,	220	7	35	4	65.93±2.75	4.52±0.14	0.44±0.07
W7	Maznu Mia	,,	150	10	40	1	81.49±0.07	5.96±0.12	0.50±0.01
W8	Sattar Mia	,,	220	2	20	None	81.03±0.22	4.54±0.06	0.71±0.06
W9	M. Hussain Khan	,,	210	6	25	None	87.23±0.75	7.93±0.06	0.38±0.07
W10	Osman Mia	,,	220	3	12	None	83.06±3.32	7.20±0.18	0.30±0.02
W11	Madham Para Zame Masjid	,,	210	20	400	None	62.91±2.98	7.48±0.02	0.32±0.12
W12	Md Roju Mia	,,	190	15	300	None	68.70±4.24	7.30±0.17	0.24±0.03
*W13	Taju mia	Kathalbari	50	5	---	--	40.62±5.45	37 30±0.15	0.77±0.10
**W14	Delai Dharam Haor	Tola khal		--	--	--	9.96±0.48	3.04±0.08	0.21±0.01
W15	Hanif Mia	Kathalbari	320	15	50	2	66.38±0.18	5.52±0.05	0.36±0.01
W16	Humayun Mia	,,	215	4	25	3	81.16±2.81	5.74±0.02	0.19±0.03
W17	Shiraj Mia	,,	160	2	200	None	6.90±0.51	0.46±0.02	0.23±0.03
W18	Mahmud Ali	Rajarkhal	205	6	12	12	66.51±3.33	5.87±0.06	0.27±0.05

* Irrigation well; ** Surface water

Table 5.14
Quality control data of arsenic measurement in Companiganj water

Reference ID	Certified value, ppb	Measured value, ppb
NIST-1643d	56.02±0.73	57.47±1.30
USGS-SR-T 165	25.90±2.07	25.72±0.99

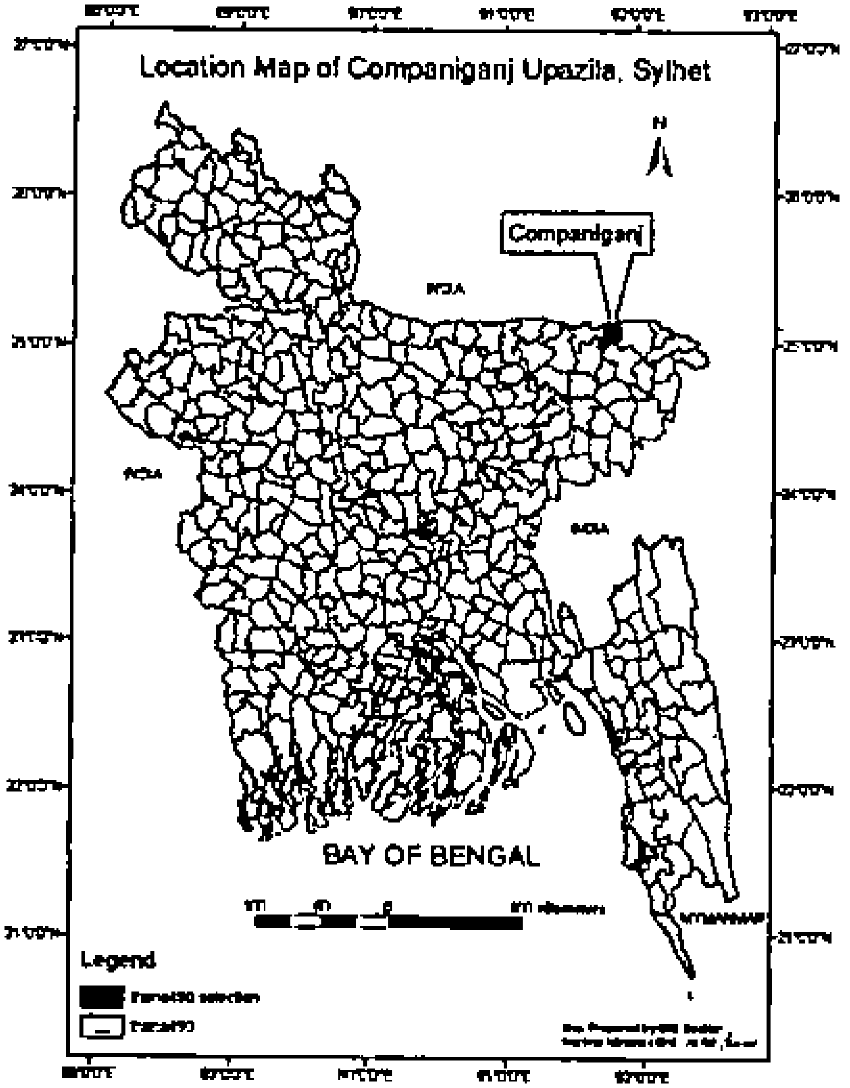

Figure 5.8 Location map of Companiganj upazila, Sylhet

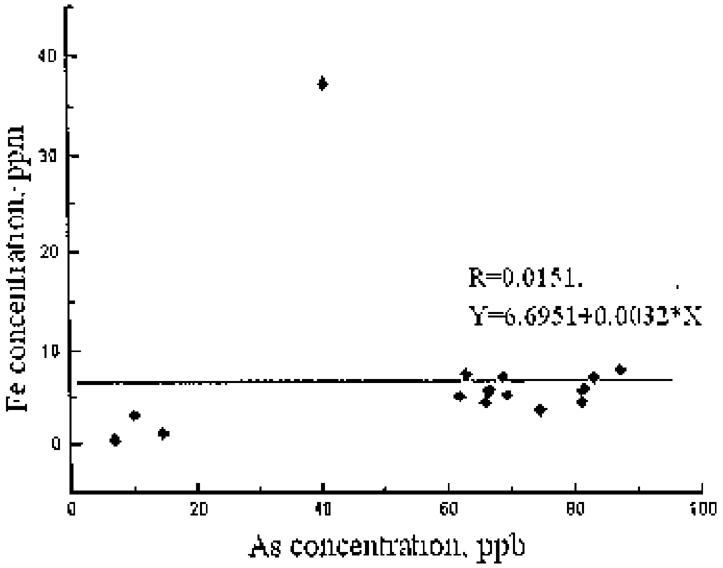

Figure 5.9 Arsenic versus iron concentrations in Companiganj water

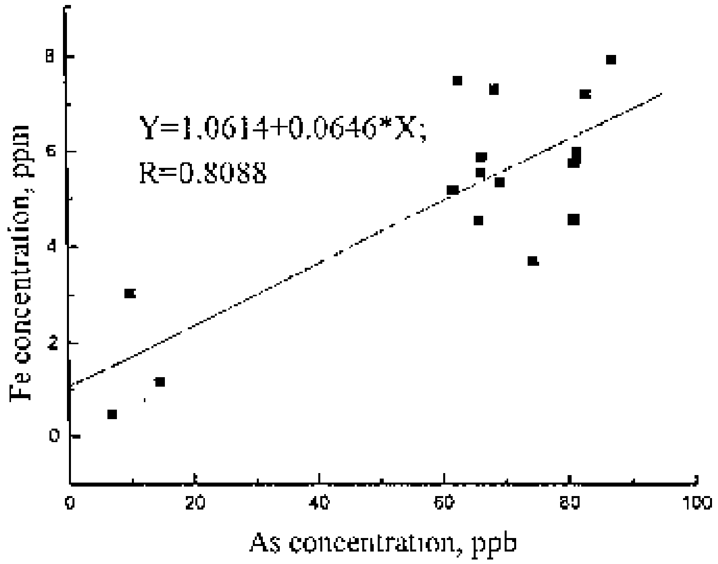

Figure 5.10 As versus Fe concentration in Companiganj water ignoring the datum for As=40.62 ppb and Fe= 37.30 ppm in regression analysis

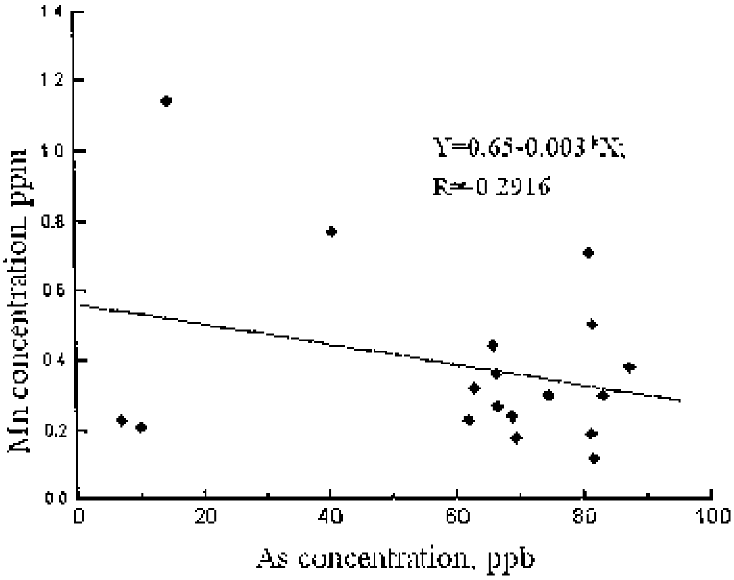

Figure 5.11 Arsenic versus manganese concentrations in Companiganj water

In the present study As versus Fe in Companiganj water exhibits almost no correlation (Figure 5.9). This situation is exceptional for this location. In many other measured data a strong correlation between As and Fe in water has been found. If groundwater contains arsenic as well as iron it is advantageous for the point of mitigation purpose. The datum representing As =40.62 ppb and Fe = 37.30 ppm seems not reliable. If this point is ignored Figure 5.10 is obtained. In Figure 5.10 strong correlation (R=0.8088) between arsenic and iron in water is observed as generally expected.

Manganese concentrations lie in the range of 0.18 to 1.14 mg/L. The WHO recommended limit for manganese in drinking water is 0.5 mg/L (BGS and DPHE, 2001) and only 3 out of 18 samples in the present measurement exceeded the WHO value. So, manganese is not a problem for this region.

5.2.2 Soil samples of Companiganj upazila, Sylhet

Eight soil samples mostly silty clay of Companiganj upazila were analyzed for arsenic and iron using NAA method. Results of the arsenic and iron measurements and quality control data are shown in Tables 5.15 and 5.16, respectively. Ranges of arsenic and iron concentrations were found to lie between 3.60±0.14 to 7.95±0.29 ppm and 4.48±0.27 to 6.05±0.25%, respectively. Average values of arsenic and iron concentrations were 5.35 ppm and 5.52 %, respectively. These values are about double the values found for unaffected areas of Sylhet. Arsenic versus iron concentrations in soil are shown in Figure 5.12. Here the data points are found to be scattered. More data points are required to explain the iron versus arsenic relationship in Companiganj soil.

TABLE 5.15

Results of arsenic and iron measurement in topsoil of Companiganj upazila, Sylhet

Sl. No.	Kind of soil	Owner of the land	Village	Thana	As. Concentration, ppm	Fe concentration, %
1	Silty clay	Hazi Hormuj Ali	Rajarkhal	Companiganj	3.60±0.14	5.75±0.24
2	Silty clay	Mohammad Ali	Lambakhandi	Companiganj	5.98±0.23	6.03±0.25
3	Clay with silt	Jenu Mia	Lambakhandi	Companiganj	3.79±0.15	5.82±0.24
4	Silty clay	Mojnu Mia	Lambakhandi	Companiganj	5.19±0.20	6.05±0.25
5	Silty clay	Roju Mia	Lambakhandi	Companiganj	5.16±.20	4.48±0.27
6	Silty clay	Tajul Islam	Kathal Bari	Companiganj	6.39±0.24	4.77±0.22
7	Clay with silt	Humayun Miah	Kathal Bari	Companiganj	7.95±0.29	5.36±0.22
8	Silty clay	Mahmud Ali	Rajar Khal	Companiganj	4.75±0.19	4.97±0.19
Average values					5.35	5.52

TABLE 5.16

QC of arsenic and iron measurement in topsoil of Companiganj area

Name of the CRM	Elements	Certified value	Measured value	% Deviation
IAEA-Soil-1	Arsenic	13.4±0.1 ppm	13.23±0.39 ppm	-1.26
IAEA-SL-1	Iron	6.74±0.01 %	6.25±0..24%	-7.24

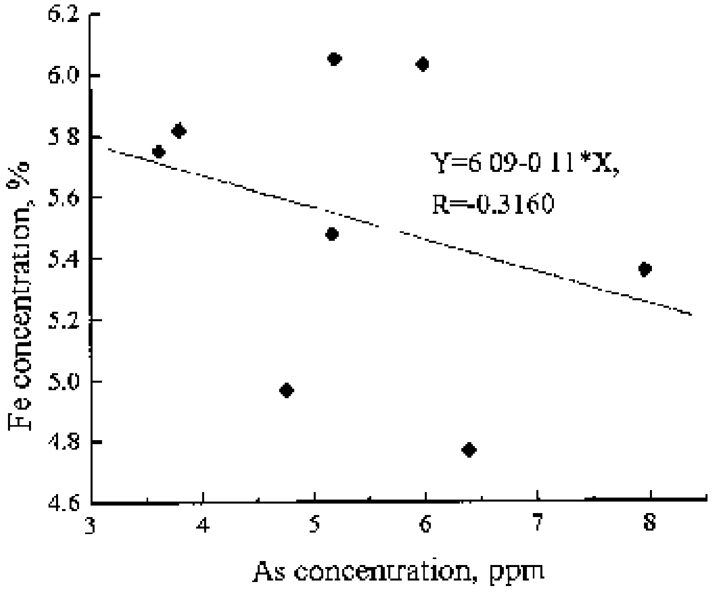

Figure 5.12 Arsenic versus iron concentrations in Companiganj soil

5.2.3 Rice samples of Companiganj, Sylhet

Five rice and five husk samples of Companiganj upazila were collected and arsenic concentrations were measured. The results of the analysis and quality control data are presented in Tables 5.17 and 5.28, respectively. Moisture contents in these rice samples were 10.95 – 15.92 %. Ranges of arsenic concentrations in rice and husk samples were found to be <0.038±0.004 to 0.108±0.010 and <0.194±0.015 to 0.566±0.028 ppm, respectively. Arsenic content is found to be much less than the permissible limit of 1 ppm in rice and other food items.

TABLE 5.17

Arsenic concentrations in rice grain and husk samples of Islampur West, Companiganj, Sylhet area. Rice harvesting time is November/December

Sl. No.	Farmer's name	Farmer's address	Rice species	As concentration in grain, ppm (Dry wt. basis)	As concentration in husk, ppm (Dry wt. basis)
1	Hazi Sikandar Ali	Village-Parua	Aman	<0.038±0.004	<0.194±0.015
2	Hazi Harmuj Ali	Village-Rajarkhal	Maloti	0.076±0.008	<0.194±0.015
3	Mohammad Ali	Village-Lambakandi	Beruin	0.045±0.004	<0.194±0.015
4	Mr. Humayun	Village-Lambakandi	BR-29	0.108±0.010	0.566±0.028
5	Mahmud Ali	Village-Rajarkhal	Kalizira	0.062±0.006	<0.194±0.015
Average values				0.062	0.501

5.2.4 Companiganj vegetable samples

Five vegetable samples were collected from Islampur West Union Parishad (UP) of Companiganj upazila and analyzed for arsenic concentration. The vegetables were beans, coriander leaf, onion, water gourd leaf and betel nut. Arsenic concentration values in vegetables and the quality control data of these samples are presented in Tables 5.18 and 5.19, respectively. Arsenic concentration in water gourd leaf was 0.110±0.016 ppm and for the rest of the vegetables it was less than 0.110 ppm. It thus indicates that arsenic content in vegetables of Companiganj area is safe for food.

TABLE 5.18

Arsenic concentrations in vegetable samples of Companiganj, Sylhet

Sl. No.	Vegetable name	Collected from	Arsenic concentration (dry weight basis), ppm
1	Beans	Lambakhandi, Companiganj	<0.110±0.016
2	Coriander leaf	Lambakhandi, Companiganj	<0.110±0.016
3	Onion	Lambakhandi, Companiganj	<0.110±0.016
4	Water gourd leaf	Lambakhandi, Companiganj	0.110±0.016
5	Betel nut	Parua Bazar, Companiganj	< 0.110±0.016

TABLE 5.19

QC of arsenic measurement in vegetable samples

Name of CRM	Element	Certified value, ppm	Measured value, ppm	% Deviation
Oyster tissue	As	7.65±0.65	5.67±0.91	-25.83

5.2.5 Companiganj hair samples

Arsenic concentrations in human hair samples of Companiganj upazila are presented in Table 5.20 and quality control data of the measurement are shown in Table 5.21. The range of arsenic concentrations was found to be <0.32±0.01 to 2.28±0.09 ppm. Normal level of arsenic in human hair is less than 1 ppm. Only four hair samples out of fourteen exceeded the normal level. Correlation between hair arsenic and related drinking water was investigated in Figure 5.13 which depicts that there is no well-marked correlation (R=0.1312) between water and hair arsenic. Arsenic in hair is a complex function of the biology of the concerned person. It depends on the body resistance, biological half-life of arsenic for the person and his level of nutrition etc.

TABLE 5.20

Arsenic concentrations in Companiganj hair samples

Sl. No. 1-3 address: Village- Rajarkhal, Sl No. 4-14 address: Village- Lambakandi, Union-Islampur West, Upazila-Companiganj, District-Sylhet

Sl. No.	Person code	Age (y)	Distance of hair from scalp. cm	As concentration in hair, ppm
1	Male-1	16	2.5	0.51±0.02
2	Male-2	45	2.5	<0.32±0.01
3	Female-1	10	1	<0.32±0.01
4	Female-2	8	30	<0.32±0.01
5	Male-3	23	1	<0.32±0.01
6	Female-3	6	15	<0.32±0.01
7	Female-4	26	45	<0.32±0.01
8	Female-5	25	1	0.32±0.01
9	Female-6	5	10	<0.32±0.01
10	Male-4	40	2.5	<0.32±0.01
11	Female-7	30	1	1.66±0.07
12	Female-8	32	2.5	1.06±0.04
13	Female-9	15	10	2.28±0.09
14	Female-10	12	5	1.10±0.04

TABLE 5.21

Quality control data of arsenic measurement in Companiganj hair samples

Name of CRM	Element	Certified value, ppm	Measured value	% Deviation
IAEA-SL-1	Arsenic	27.6±0.3	29.08±1.16	-5.36

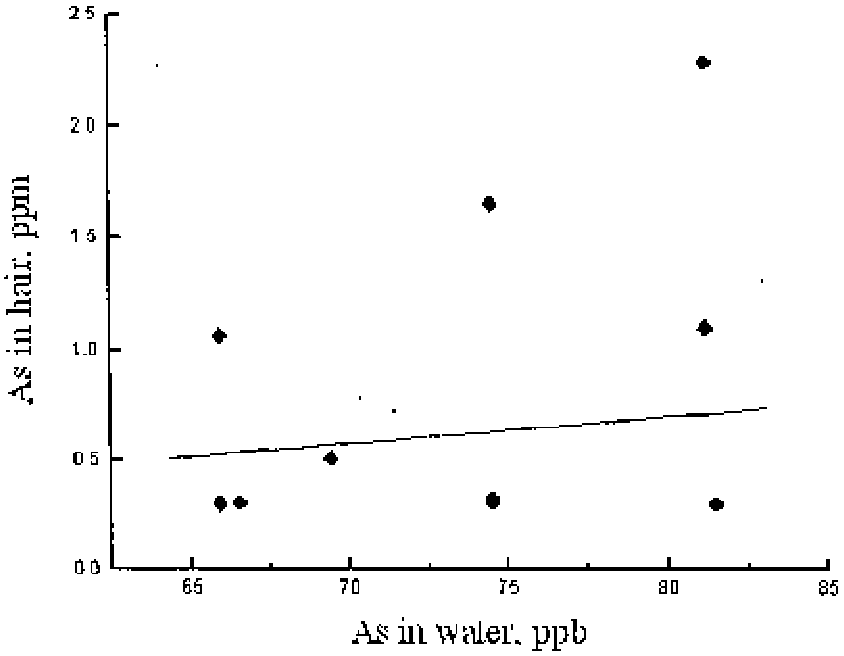

Figure 5.13 Arsenic in water versus arsenic in hair of Companiganj upazila

Figure 5.13 indicates that hair arsenic does not correlate with water arsenic. Well arsenic data set and hair-arsenic data set are not linked together.

5.3 Affected areas

5.3.1 Sediments of Kachua, Chandpur

Arsenic, iron and manganese concentrations were determined in undisturbed sediment samples collected from Majumder's house compound, Sreerampur, Kachua, Chandpur. Location map of Sreerampur is shown in Figure 5.14. Upazila average of arsenic concentrations in tubewell water of Kachua in BGS-DPHE measurement (2001) was found to be 292.9 μg/L. It indicates that the area is highly arsenic affected. Results of the measurement are presented in Table 5.22. Quality control data of this measurement are given in Table 5.23. A comparison of arsenic concentrations in some randomly selected sediment samples measured both in PINSTECH, Islamabad and INST, Dhaka is presented in Table 5.24.

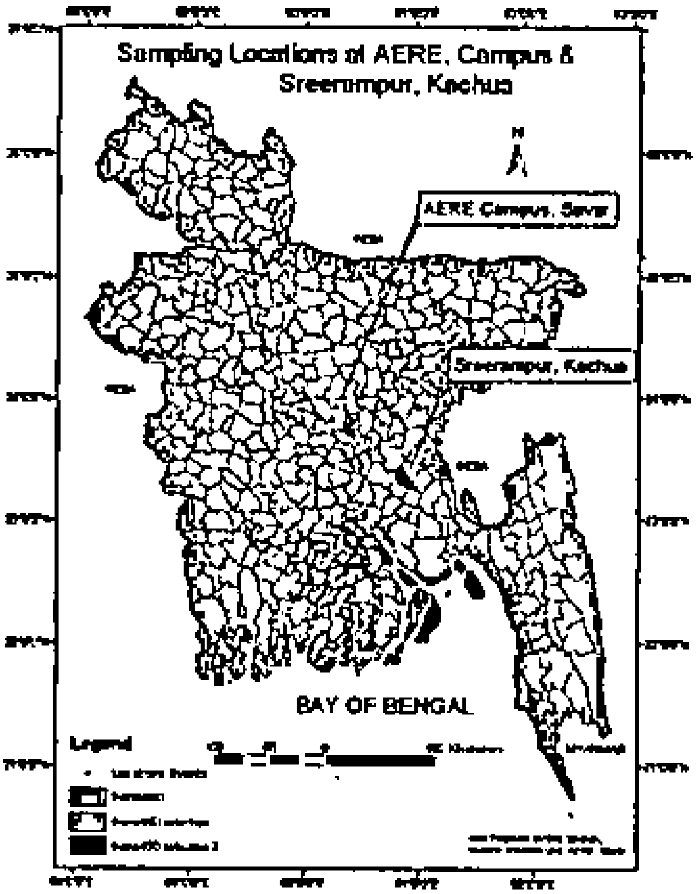

Figure 5.14 Location map of Sreerampur, Kachua and AERE, Savar

TABLE 5.22

Results of As, Fe and Mn measurements in Kachua sediment

Sl. No.	Depth	Lithological description	As concentration, ppm	Fe concentration, %	Mn concentration, ppm×100
1	30′ + 5″	Grey very fine sand, little silt, trace mica, dark materials	0.66±0.03	2.39±0.05	5.86±0.12
2	50′ + 3″	Grey very fine sand, little silt, trace mica, dark materials	1.45±0.12	2.86±0.06	10.04±0.11
3	80′ + 10.5″	Silt and very fine sand, trace mica, black minerals	9.02±0.34	4.39±0.05	9.83±0.20
4	100′ + 11″	Grey very fine sand, little fine sand, trace silt, mica, black minerals	0.97±0.08	2.23±0.05	4.99±0.06
5	130′ + 9″	Grey very fine sand, little fine sand, trace silt, mica, black minerals	9.15±0.35	4.56±0.05	10.09±0.11
6	160/ + 8″	Light bluish clay	8.06±0.31	4.04±0.05	5.09±0.10
7	250′ + 9″	Grey fine sand	1.41±0.11	1.18±0.02	4.02±0.08
8	270′ + 8.5″	Grey clay, trace silt	6.72±0.26	4.12±0.08	4.48±0.05
9	300′ + 11″	Grey fine sand, little medium sand, trace silt, mica, dark materials	1.51±0.12	0.86±0.01	3.38±0.04
10	330′ +11″	Grey fine sand. little medium sand, trace silt, mica, dark materials	1.11±0.04	1.34±0.02	4.89±0.05
11	350′ + 8″	Grey fine sand, trace silt, mica, dark materials	0.67±0.05	1.27±0.03	1.78±0.04

Sl. No.	Depth	Lithological description	As concentration, ppm	Fe concentration, %	Mn concentration, ppm×100
12	370′ +11″	Grey fine sand, little medium sand, trace silt, mica, dark materials	0.94±0.07	1.49±0.03	16.46±0.33
13	390′ + 11″	Grey fine sand, trace medium sand, trace mica, black minerals	0.65±0.05	0.86±0.01	9.99±0.53

TABLE 5.23

Quality control data of arsenic, iron and manganese measurements in sediment

Name of CRM	Element	Certified value	Measured value	% Deviation
IAEA-SL-1	Arsenic	27.6±0.3 ppm	26.15±1 ppm	-5.23
	Manganese	3460±13.7 ppm	3445±69 ppm	-0.43
	Iron	6.74±0.01%	6.63±0.13%	-1.63

TABLE 5.24

Comparison of arsenic concentrations in some randomly selected sediment samples analyzed both in INST, Savar and PINSTECH, Islamabad

SL. NO.	Sample ID	Description	PINSTECH* value	INST** Value	% Deviation
1	Sed-1	Affected	0.66±0.03	0.59±0.04	10.60
2	Sed-4	Affected	0.97±0.08	1.00±0.07	3.09
3	Sed-8	Affected	6.72±0.26	6.90±0.51	2.68
4	Sed-1	Unaffected	6.82±0.26	6.54±0.48	4.11
5	Sed-2	Unaffected	2.20±0.08	2 05±0.15	6.82

*Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

** Institute of Nuclear Science and Technology, Savar, Dhaka, Bangladesh

5.3.2 Arsenic versus iron

Arsenics versus iron concentration values in sediments of affected areas are shown in Figure 5.15. From the Figure it is evident that there is a strong positive correlation (R=0.9042) between arsenic and iron concentrations in sediments.

5.3.3 Arsenic versus manganese

As versus Mn concentration values in sediments of affected areas are shown in Figure 5.16 which shows no significant correlation (R=0.111) between arsenic and manganese concentrations in sediments. However some of the data indicate a negative correlation between these two elements.

5.3.4 Arsenic versus depth

Arsenic concentrations decrease with depth. Figure 5.17 shows a negative coefficient of correlation of – 0.3549 between arsenic concentration and depth.

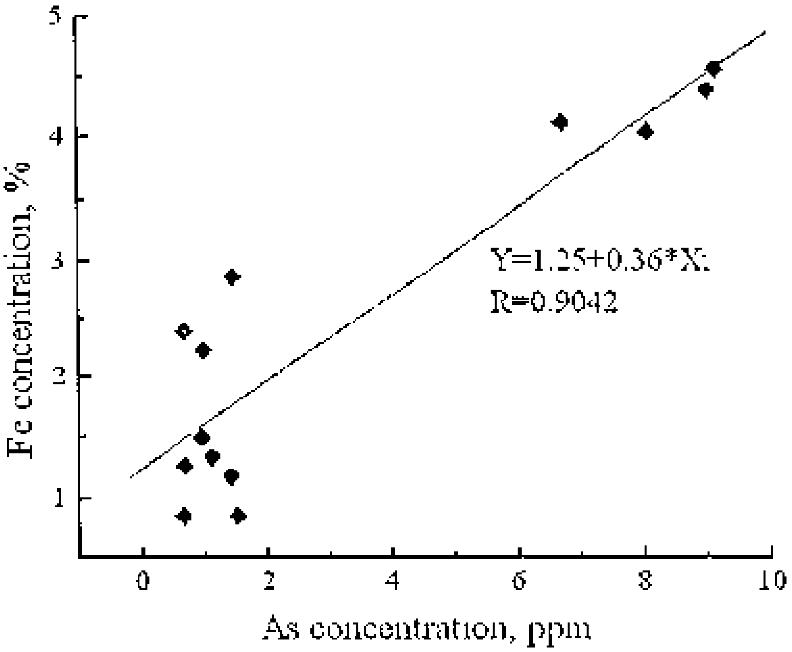

Figure 5.15 Arsenic versus iron concentrations in Kachua sediment

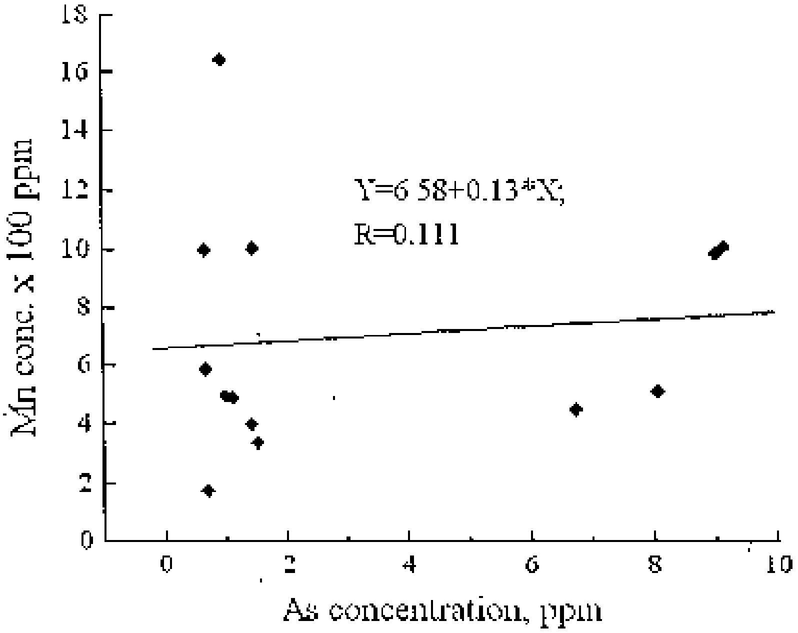

Figure 5.16 Arsenic versus manganese concentrations in Kachua sediment

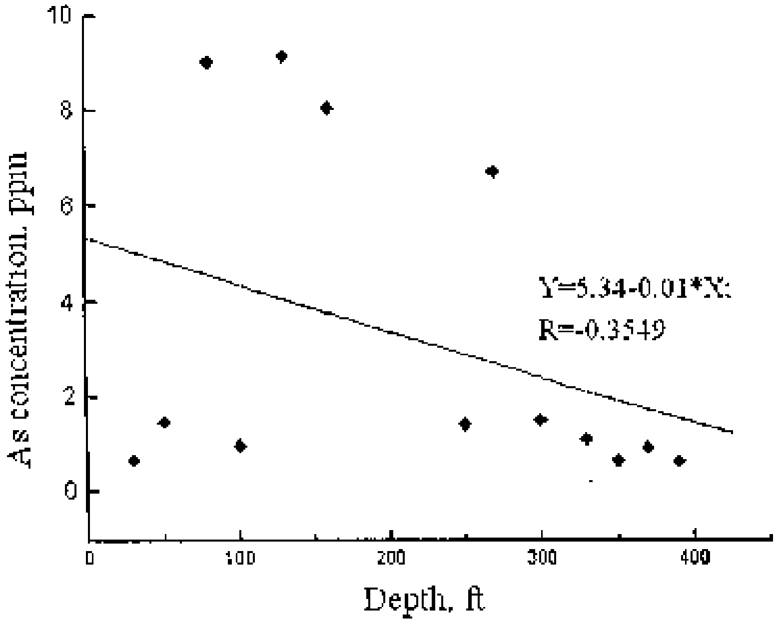

Figure 5.17 Arsenic concentrations as a function of depth in Kachua sediment

5.3.5 Soil samples of Faridganj, Chandpur

Fourteen soil samples of Faridganj upazila, Chandpur were analyzed. Results of the analysis and quality control data of the measurement are shown in Tables 5.25 and 5.26, respectively. Upazila average of arsenic concentrations in tubewell water of Faridganj in BGS-DPHE (2001) measurement was found to be 395 μg/L. It indicates that the area is highly arsenic affected.

TABLE 5.25
Concentrations of arsenic and iron in topsoils of Faridganj, Chandpur

Sl. No.	Kind of soil	Owner of the land	Village	Union	As. Concentration, ppm	Fe concentration, %
1	Sticky soil	Miah Raja Patwary	Srikalia	Gupty	4.77±0.17	3.61±0.15
2	Sticky soil	Saleh Uddin Ahmed	Srikalia	Gupty	3.22±0.12	3.37±0.14
3	Sticky soil	Abul Kalam Patwary	Narikeltola	Gupty	3.44±0.13	3.70±0.16
4	Sticky soil	Harun-ur-Rashid	Digdair	Gupty	5.12±0.18	3.38±0.14
5	Sticky soil	Sukumar Das	Digdair	Gupty	4.56±0.17	4.52±0.19
6	Sticky soil	Abdul Latif	Tora	Munshir-hat	6.31±0.22	4.40±0.18
7	Sticky soil	Mojammel Hoque	Narikeltola	Gupty	4.48±0.16	3.70±0.16
8	Sticky soil	Abdur Rab	Mulpara	Balithuba	5.51±0.19	4.62±0.20
9	Sticky soil	Sridam Das	Rupsha	Rupsha	5.77±0.21	4.51±0.20
10	Sticky soil	Bokul Sardar	Laxmipur	Ghonia	5.65±0.20	4.21±0.18
11	Sticky soil	Joynal Abedin	Boichatory	East Gupty	7.38±0.26	5.46±0.22
12	Sticky soil	Abdul Mannan	Boichatory	East Gupty	6.58±0.23	4.92±0.20
13	Sticky soil	Abu Sufian Manik	Boichatory	East Gupty	5.83±0.20	4.77±0.20
14	Sticky soil	Abdul Mannan	Boichatory	East Gupty	5.77±0.20	4.37±0.18
Average values					5.31	4.25

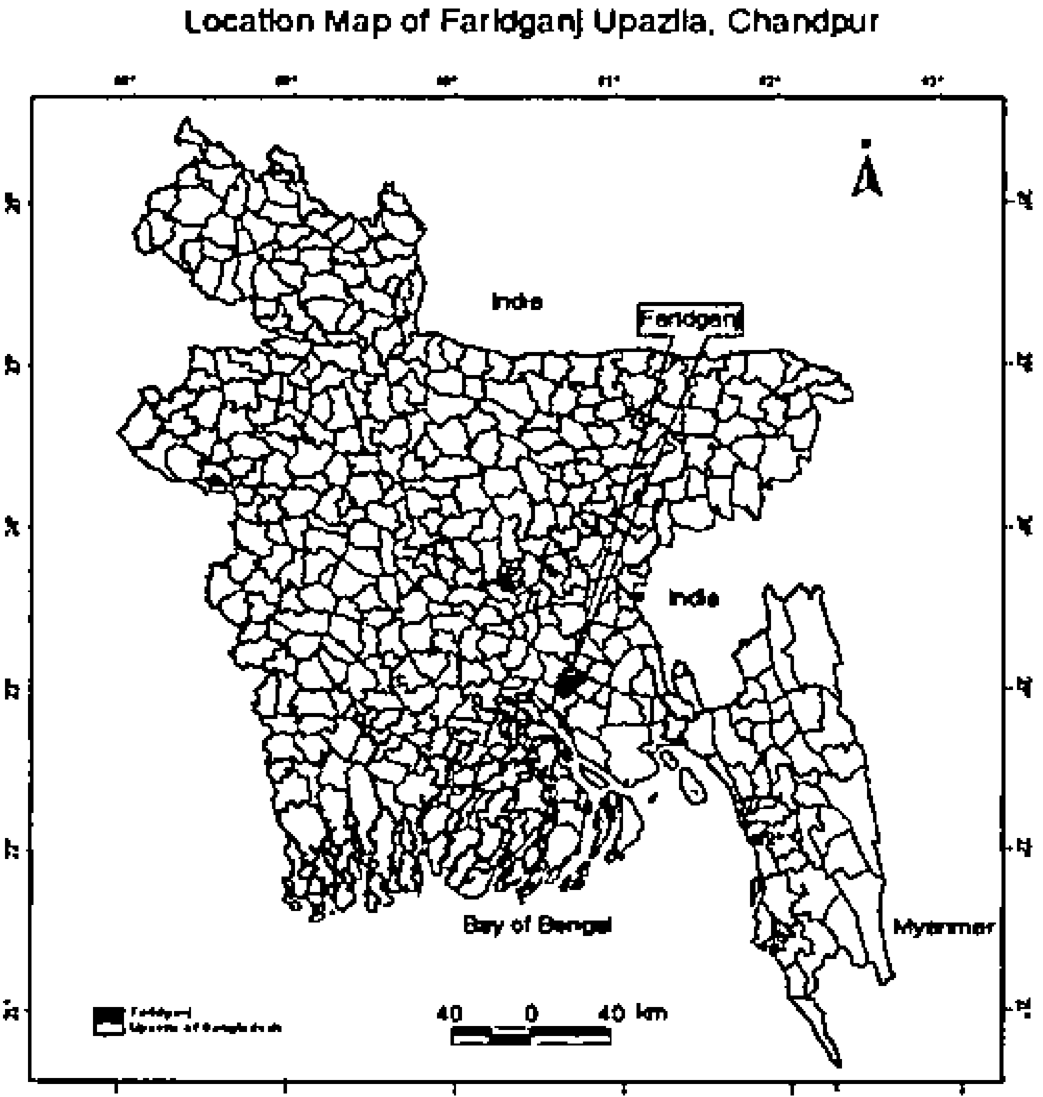

Figure 5.18 Location map of Faridganj upazila, Chandpur

TABLE 5.26

Quality control data of arsenic and iron measurement in topsoil of Faridganj, Chandpur

Name of CRM	Element	Certified value	Measured value	% Deviation
IAEA-Soil-7	Arsenic	13.4±0.1 ppm	13.23±0.47 ppm	-1.24
IAEA-SL-1	Iron	6.74± 0.01 %	6.25±0.24%	-7.27

The location map of Faridganj is presented in Figure 5.18. Although Faridganj is a highly affected area, in the present experiment we found relatively low concentrations of arsenic in soil. The paddy field soil was irrigated with arsenic-free surface water of canals and water of deep tubewell. As the highly polluted shallow ground water was not used for irrigation, it could not contaminate the irrigated soil. It is notable that average concentrations of arsenic and iron in Faridganj soil are 5.31 ppm and 4.25%, respectively. These two values for Sylhet unaffected soil were 2.72 ppm and 2.33%, respectively. Therefore, although Faridganj soil contains relatively low amount of arsenic, it is still higher than arsenic contents of unaffected areas of Sylhet.

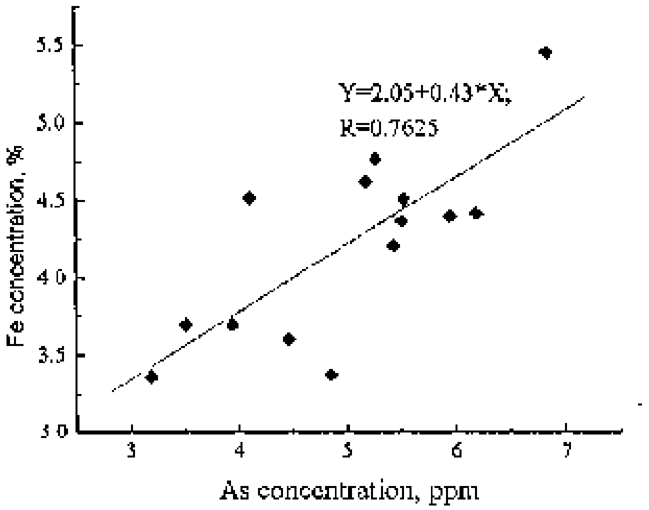

Figure 5.19 Arsenic versus iron concentrations in Faridganj soil

There is strong correlation between arsenic and iron in Faridganj soil. In Figure 5.19 coefficient of correlation is found to be 0.7625.

5.3.6 Rice samples of Faridganj, Chandpur

Fourteen rice samples of Faridganj, Chandpur were analyzed for arsenic concentration. Arsenic concentrations and quality control data of the area are presented in Table 5.27 and 5.28, respectively.

TABLE 5.27

Concentrations of arsenic in rice samples of Faridganj, Chandpur

Sl. No.	Kind of rice	Farmer's name	Village	Union	As concentration in rice grain (dry wt. basis) ppm	As concentration in rice husk (dry wt. basis) ppm
1	BR-29	Miah Raja Patwary	Srikalia	Gupty	0.29±0.02	0.23±0.01
2	BR-29	Salah Uddin Ahmed	Srikalia	Gupty	0.27±0.02	0.22±0.01
3	BR-29	Abul Kalam Patwary	Narikeltola	Gupty	0.15±0.01	0.20±0.01
4	BR-29	Harun-ur Rashid	Digdair	Gupty	0.23±0.02	0.24±.0.01
5	HEERA	Sukumar Das	Digdair	Gupty	0.22±0.02	0.25±0.01
6	BR-29	Abdul Latif	Tora	Munshir-hut	0.27±0.02	0.29±0.01
7	BR-29	Mojammel Hoque	Narikeltola	Gupty	0.24±0.02	0.36±0.01
8	BR-29	Abdur Rab	Mulpara	Balithuba	0.15±0.02	0.22±0.01
9	BR-29	Sridam Das	Rupsha	Rupsha	0.18±0.01	0.33±0.01
10	BR-29	Bokul Sardar	Laxmipur	Ghonia	0.25±0.02	0.28±0.01
11	BR-29	Joynal Abedin	Boichatory	East Gupty	0.25±0.01	0.33±0.01
12	BR-29	Abdul Mannan	Boichatory	East Gupty	0.17±0.01	0.23±0.01
13	BR-29	Abu Sufian Manik	Boichatory	East Gupty	0.22±0.01	0.37±0.02
14	BR-29	Abdul Mannan	Boichatory	East Gupty	0.32±0.01	0.19±0.01

TABLE 5.28

Quality control data of arsenic measurements in rice samples of Faridganj, Chandpur, and Companiganj, Sylhet

Name of CRM	Element	Certified value	Measured value	% Deviation
Citrus leaves	Arsenic	3.1±0.3	2.87±0.10	-7.42

In the present experiment range of arsenic concentration in rice grain is found to be 0.150±0.021 to 0.324±0.014 ppm. Average values of arsenic concentrations in rice grain and husk are found to be 0.229 and 0.267 ppm, respectively. Ali et al. (2003) reported that arsenic concentrations in roots of rice plant samples collected from the Srinagar site varied from 2.81 to 16.8 ppm,. (with a mean of 8.9 ppm), while that in the rice grain varied from <0.05 ppm to 1.52 (with a mean of 0.48 ppm). The authors, however, used a different method (AAS). For the samples collected from the Sonargoan site, arsenic in root varied from 2.88 to 26.1 ppm (with a mean of 11.9 ppm), while that in the rice grain varied from <0.05 ppm to 1.23 ppm (with a mean of 0.46 ppm). Two grain samples (out of nine) from Srinagar exceeded the Australian food hygiene limit of 1.0 ppm. Hironaka et al. (2003) found arsenic concentrations in rice at Samta village in Jessore in the range of 0.11 to 0.94 ppm.

No correlation exists between arsenic concentration in soil and arsenic concentration in rice grain (Figure 5.20). Thus it appears that arsenic present in soil is not translocated to rice grain. Similarly no correlation was found between arsenic in rice grain and arsenic in husk (Figure 5.21).

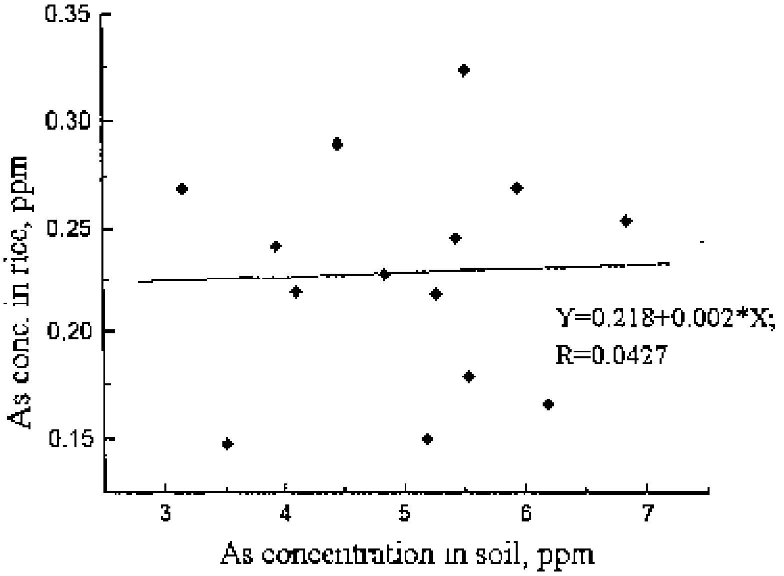

Figure 5.20 Arsenic concentrations in soil versus arsenic concentrations in rice grain of Faridganj, Chandpur

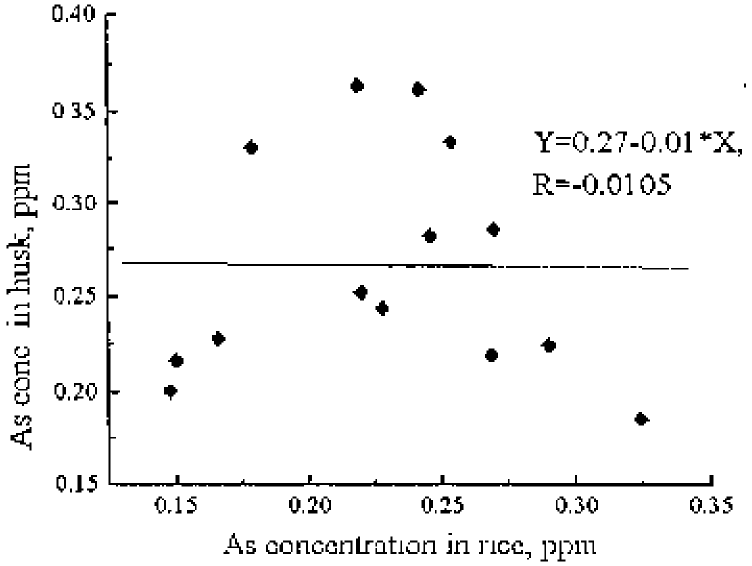

Figure 5.21 Arsenic concentrations in rice versus arsenic concentrations in husk of Faridganj

5.3.7 Vegetable samples of Faridganj, Chandpur

Arsenic concentrations in seven vegetable samples of Faridganj, Chandpur were measured. Tables 5.29 and 5.30 give the measured concentrations and quality control data, respectively. However all the vegetable samples contain arsenic below detection limit of 0.110 ppm.

TABLE 5.29

Arsenic concentrations in vegetable samples of Faridganj, Chandpur

Sl. No.	Vegetable name	Collected from	Arsenic concentration, ppm (dry weight basis)
1	Red amaranth	Abdulla-al-Mamun, Boichatory, East Gupty	<0.110±0.004
2	Papaya	Abdulla-al-Mamun, Boichatory, East Gupty	<0.110±0.004
3	Snake gourd	Village market, Boichatory, East Gupty	<0.110±0.004
4	Ribbed gourd	Abdulla-al-Mamun, Boichatory, East Gupty	<0.110±0.004
5	Chillies	Joynal Abedin, Boichatory, East Gupty	<0.110±0.004
6	Chillies	Abu Sufian, Boichatory, East Gupty	<0.110±0.004
7	Chillies	Abdul Mannan, Boichatory, East Gupty	<0.110±0.004

TABLE 5.30

Quality control data of arsenic measurement in vegetable samples

Name of CRM	Element	Certified value, ppm	Measured value, ppm	% Deviation
Oyster tissue	As	7.65±0.65	5.67±0.91	-25.83

5.3.8 Human hair samples of Faridganj, Chandpur

Arsenic concentrations in 20 human hair samples of Faridganj, Chandpur were measured. Tables 5.31 and 5.32 give the measured concentrations and quality control data, respectively.

TABLE 5.31

Arsenic concentrations in Faridganj hair

Sl. No.	Person code (age)	Village	Union	Distance of hair from scalp, cm	Source and duration of drinking water	Concentration of arsenic in hair, ppm
1	M-1 (38)	Gupty	East Gupty	1	DTW, 2y	0.46±0.09
2	F-1(4)	Srikalia	East Gupty	2.5	DTW, 2y	0.58±0.08
3	F-2 (30)	Boicha-tory	East Gupty	30	DTW, 2y	0.69±0.09
4	F-3 (18)	Mulpara	Balithuba	25	DTW, 1y	<0.35±0.07
5	M-2 (8)	Srikalia	East Gupty	2.5	DTW, 2y	<0.35±0.07
6	M-3 (18)	Srikalia	East Gupty	2.5	DTW, 6m	2.09±0.13
7	M-4 (52)	Srikalia	East Gupty	2.5	DTW, 1y	0.83±0.10
8	M-5 (20)	Boicha-tory	East Gupty	5	DTW, 2y	<0.35±0.07
9	F-4 (4)	Boicha-tory	East Gupty	2.5	DTW, 2y	0.39±0.08
10	F-5 (6)	Boicha-tory	East Gupty	15	DTW, 2y	0.67±0.11
11	F-6 (30)	Srikalia	East Gupty	35	DTW, 2y	3.45±0.19
12	M-6 (22)	West Gupty	East Gupty	2.5	DTW, 1y	<0.35±0.07
13	M-7 (33)	West Gupty	East Gupty	2.5	DTW, 1y	0.58±0.12
14	M-8 (15)	Narikel-tola	East Gupty	2.5	DTW, 1y	0.44±0.11
15	M-9 (15)	Srikalia	East Gupty	2.5	DTW, 1y	1.40±0.10
16	M-10 (27)	Gupty	East Gupty	2.5	DTW, 1y	1.18±0.10
17	M-11 (40)	Gupty	East Gupty	2.5	DTW, 1y	<0.35±0.07
18	M-12 (55)	Gupty	East Gupty	2.5	DTW, 1y	0.58±0.08
19	F-7 (23)	Gupty	East Gupty	30	DTW, 2y	2.36±0.13
20	F-8 (12)	Srikalia	East Gupty	25	DTW, 2y	0.41±0.08

TABLE 5.32

Quality control data of arsenic measurement in Faridganj hair samples

Name of CRM	Element	Certified value. Ppm	Measured value, ppm	% Deviation
IAEA-SL-1	As	27.6±0.3	27.31±1.02	-1.04

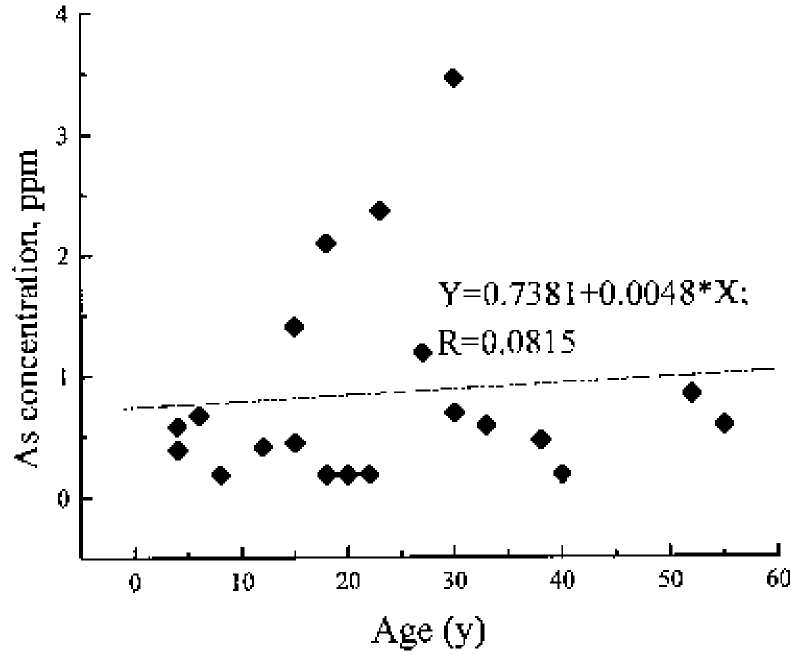

Figure 5.22 Age versus arsenic concentrations in hair samples of Faridganj, Chandpur

Figure 5.22 shows that the age group of 15-30 years has more arsenic in their hair than persons of other ages. The reason is that persons of age group 15-30 years take more food and water, which contribute more arsenic in their bodies.

Because shallow tubewells are producing arsenic contaminated water, people of Faridganj are now using deep tubewell for drinking purpose. Deep tubewell water is arsenic-free. In Figure 5.23 positive correlation between arsenic concentration in hair and distance of hair from the scalp (R^2=0.2268) indicates that long distant hair carried arsenic in the past when the people took shallow tubewell water for drinking purpose.

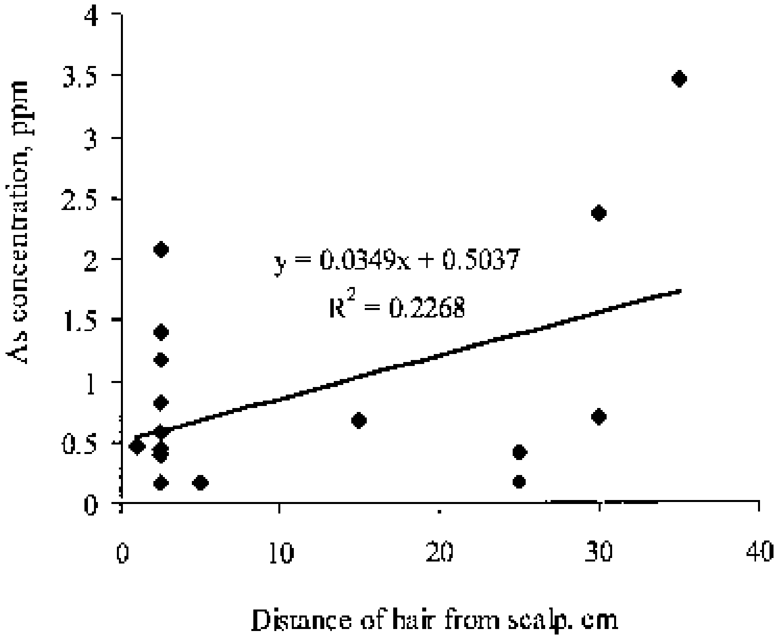

Figure 5.23 Arsenic concentrations versus distance of hair from scalp

5.3.9 Rice samples supplied by Ministry of Food

Sixteen rice samples of different districts supplied by Ministry of Food were analyzed in the work for arsenic and results of the analysis are presented in Table 5.33. Quality control data of the measurement are shown in Table 5.34. In the present work highest arsenic concentration in rice grain was found to be 0.717±0.192 ppm, which is still less than 1 ppm - the Australian food hygiene limit. It may be noted that only limited standards are available on safe limits on arsenic in food. In another study (Duxbury et al., 2002), concentrations of total arsenic in 150 samples of paddy grains collected from Barisal, Comilla, Dinajpur, Rajshahi and Rangpur districts of Bangladesh were found to range from 0.010 to 0.415 ppm dry weight. Rice is a staple food in Bangladesh. It is fortunate that most of the rice produced in Bangladesh is found to be safe as indicated in the present study.

TABLE 5.33

Arsenic concentration in rice samples supplied by Ministry of Food

Sl. No.	Address of farmer/species of rice	As concentration, ppm (Dry wt. basis)
1	Md. Johre Ali, Gobindapur, Burichong, Comilla	0.33±0.05
2	Md. Johre Ali, Gobindapur, Burichong, Comilla	0.40±0.06
3	Shouvo Rice Mill, C/O Md.Matlubar Rahman, Uttam Hazir Hatt, Rangpur	0.44±0.06
4	Kofil Rice Mill, Pucha Para, Nawhata, Pacha, Rajshahi	0.26±0.03
5	Gias Rice Mill,Mahananda Khali, Soyhata,Noyhata, Pacha, Rajshahi	0.27±0.02
6	Md. Rashedul Rice Mill, C/O Md. Abdul Hai, Munshi para, Pirgang, Rangpur	0.15±0.02
7	Irri,Boro Rice Sample, Container No. 3. Nababgang, Dinajpur	0.53±0.05
8	BR-29, Ashutosh Bishwash, C/O Prokash Chandra Bishwash Tiakhali, Barisal Sadar, Barisal	0.10±0.02
9	BR-29, Ashutosh Bishwash. C/O Prokash Chandra Bishwash Tiakhali, Barisal	0.66±0.06
10	Monirul Islam Chowdhury, C/O Mojammel Haque Chowdhury Chowara, Comilla Sadar. Comilla	0.72±0.19
11	Md. Alal Uddin, Mahanandra Khali, Noyhata, Pacha, Rajshahi	0.68±0.11
12	Siddique Ali, Bhugrail, Pacha. Rajshahi	0.14±0.05
13	Md. Alamgir Khan, Faridabad, Baidhanathpur Taragang, Rangpur	0.26±0.10
14	Irri Boro Paddy sample, Container no.-2, Nababganj, Dinajpur	0.16±0.06
15	B.R.-29 Paddy, Bikash Chandra Bishwash Tiakhali. Barisal Sadar. Barisal	0.36±0.08
16	B.R.-29 Paddy, Bikash Chandra Bishwash Tiakhali, Barisal Sadar, Barisal	0.29±0.10

TABLE 5.34

Quality control data of arsenic measurement in rice samples of different districts

Name of CRM	Element	Certified value, Ppm	Measured value, ppm	% Deviation
IAEA-SL-1	As	27.6±0.3	25.12±1.02	-8.99

5.3.10 Vegetable samples of Damurhuda, Chuadanga

Nine vegetable samples were collected from Damurhuda upazila and analyzed for arsenic concentration. Concentration values and quality control data are presented in Tables 5.35 and 5.36, respectively. The maximum value of arsenic concentration was found to be 7.22 ± 0.43 ppm in an arum root sample. Arsenic was detected only in arum samples.

TABLE 5.35

Arsenic in Chuadanga vegetable samples

Sl. No.	Sample code	Description	As concentration, ppm
1	V-1	Turmeric (root)	<0.12
2	V-4	Turmeric (root)	<0.12.
3	V-5	Arum (root)	0.89 ± 0.19
4	V-6	Arum (root)	2.32 ± 0.50
5	V-8	Sweet potato	<0.12
6	V-10	Arum (root)	0.67 ± 0.13
7	V-11	Arum (root)	5.23 ± 0.42
8	V-12	Arum (root)	7.22 ± 0.43
9	V-13	Arum (stem)	3.68 ± 0.21

TABLE 5.36

Quality control data of arsenic measurement in Chuadanga vegetable samples

Name of CRM	Element	Certified value, Ppm	Measured value, ppm	% Deviation
IAEA-SL-1	Arsenic	27.6±0.3	30.65±1.84	+11.05

Ali et al. (2003) reported arsenic concentration in some vegetables of Sonargaon site. Arsenic concentration in edible parts of *lalshak* was found to be <0.39 to 0.96 ppm;

for *datashak* it ranged from 0.56 to 1.06 ppm, for cabbage 0.38 to 1.6 ppm and for cauliflower 0.35 ppm. Arsenic concentration in the five tomato samples ranged from 0.18 to 1.33 ppm, as Ali et al. reported.

5.3.11 Hair samples of Damurhuda, Chuadanga

Results and quality control data of arsenic measurement in Chuadanga hair samples are presented in Tables 5.37 and 5.38, respectively. All Chuadanga hair samples were collected from the persons having various symptoms of arsenicosis on there skins. Location map of Damurhuda has been presented in Figure 5.24.

TABLE 5.37
Arsenic concentrations in Chuadanga hair samples

Sampling location: Village - Boro Dudpalila, Upazila-Damurhuda, District-Chuadanga, Bangladesh

Sl. No.	Person code	Age, years	Affected from, years	As concentration in hair, ppm
1	Female-1	45	10	48.52±2.21
2	Female-2	38	3	12.12±0.18
3	Female-3	24	4	10.04±0.14
4	Male-1	16	7	17.42±0.85
5	Male-2	53	23	17.89±1.00
6	Male-3	22	5	12.94±0.63
7	Male-4	23	13	4.80±0.27
8	Male-5	20	13	2.78±0.16
9	Female-4	36	13	2.65±0.14
10	Female-5	20	13	3.36±0.19
11	Female-6	35	2	3.01±0.04
12	Female-7	35	6	13.03±0.73
13	Male-6	14	6	5.70±0.34
14	Male-7	40	6	21.06±1.00
15	Female-8	33	6	6.79±0.39

Sl. No.	Person code	Age, years	Affected from, years	As concentration in hair, ppm
16	Female-9	50	6	2.16±0.03
17	Female-10	11	6	1.61±0.09
18	Female-11	34	6	10.96±0.58
19	Female-12	68	3	1.04±0.06
20	Male-8	43	6	2.28±0.13
21	Male-9	28	8	8.16±0.47
22	Male-10	30	15	21.95±1.09
23	Male-11	22	5	6.45±0.36
24	Female-13	42	4	48.66±1.32
25	Male-12	22	4	6.71±0.38
26	Female-14	50	4	3.32±0.05
27	Male-13	19	4	20.82±0.94
28	Male-14	50	10	6.03±0.32
29	Female-15	45	10	2.51±0.15

TABLE 5.38

Quality control data of arsenic measurement in Chuadanga hair samples

Name of CRM	Element	Experimental facility	Certified value, ppm	Measured value, ppm	% Deviation
IAEA-SL-1	Arsenic	INST	27.6±0.3	28.38±1.28	+2.83
		PINSTECH	27.6±0.3	29.10±1.30	+5.43

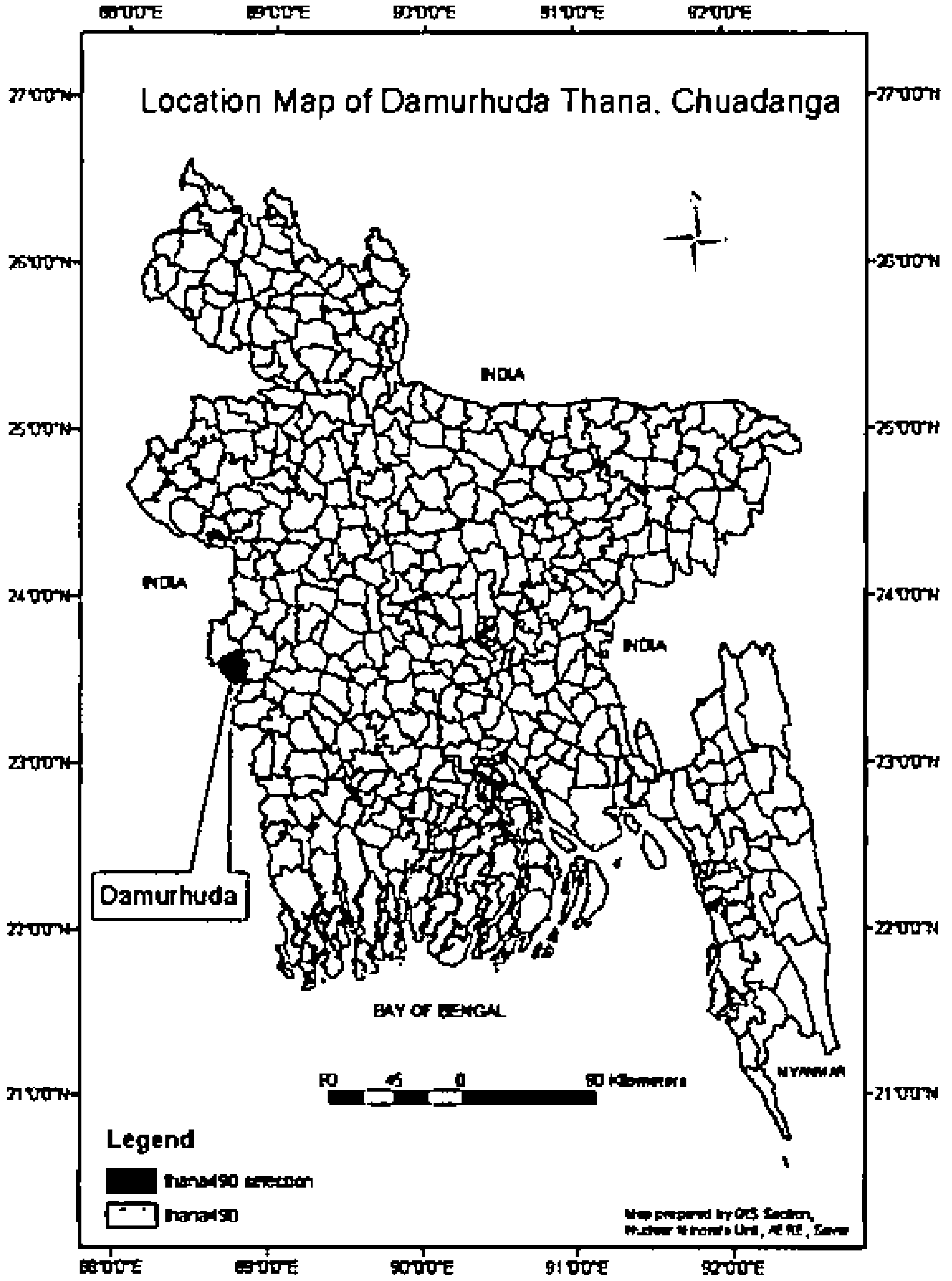

Figure 5.24 Location map of Damurhuda, Chuadanga

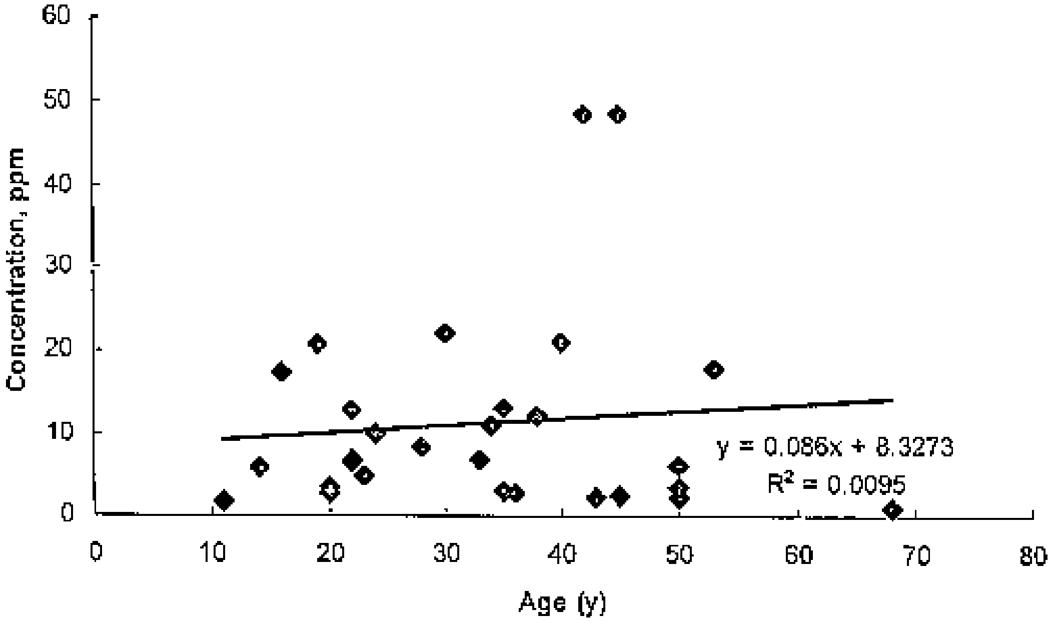

Figure 5.25 Age versus arsenic in hair samples of Damurhuda, Chuadanga

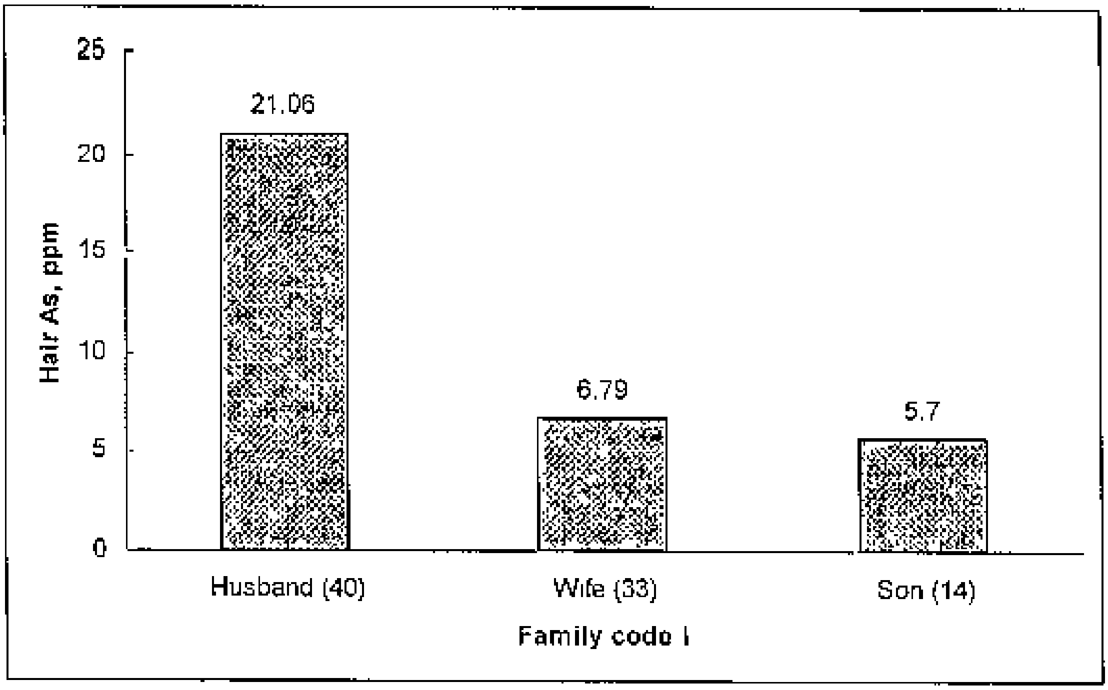

Figure 5.26 a

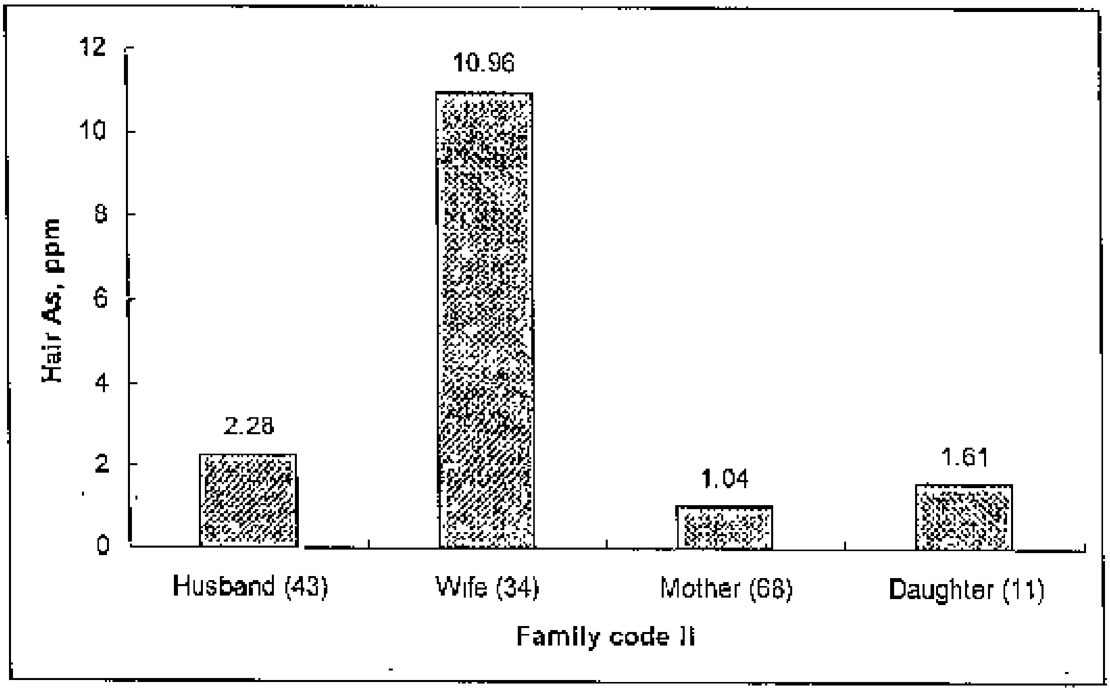

Figure 5.26 b

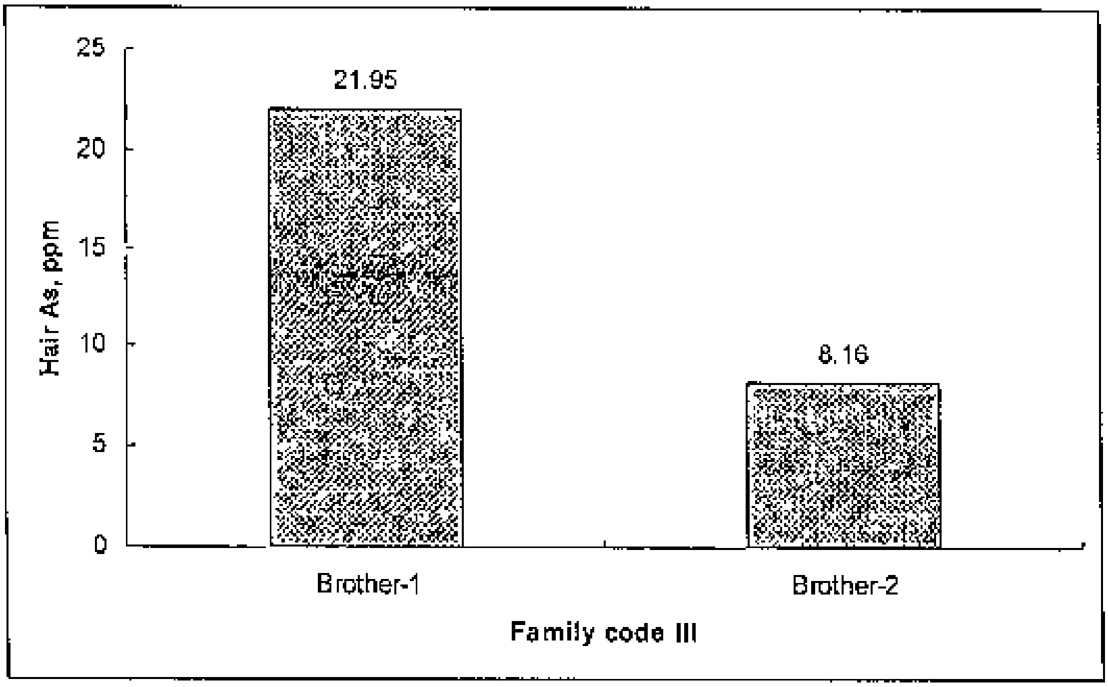

Figure 5.26 c

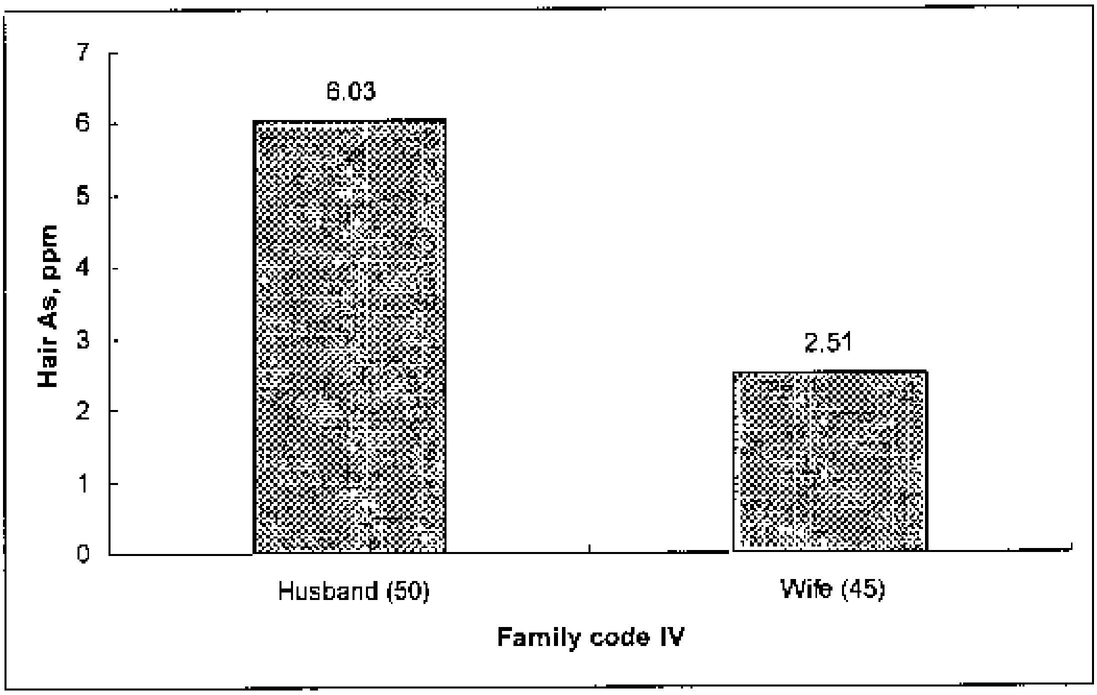

Figure 5.26 d

Figures 5.26 (a-d). Arsenic concentrations in the hair samples of the members of four families

Upazila average of arsenic concentrations in tubewell water of Damurhuda in BGS-DPHE (2001) measurement is 141.2 µg/L indicating that the area is highly arsenic affected. Arsenic concentrations in hair were found to lie in the range of 1.04±0.06 to 48.66±1.32 ppm whereas normal level of arsenic in human hair is less than 1 ppm (Arnold et al., 1990). In the affected site all the hair samples exceeded this limit. No correlation was, however, found (R^2=0.0095) between age of a patient and arsenic accumulated in his body (Figure 5.25). In a separate study age group 15-30 years showed to contain more arsenic in hair compared to other ages. Also, no correlation was found between length of time the individual suffered and the amount of arsenic contamination in his hair. Figures 5.26 (a-d) indicate that there are no consistencies in the arsenic level in hair of the members of the same family. It means that even though some individuals living in the same house and take same tubewell water, because of their varying body resistances, biological half-lives for arsenic and personal food habits the arsenic contaminations in their bodies are different. The same fact was previously observed in a study conducted in West Bengal, India

(Chowdhury et al. 1997). Generally males have more arsenic accumulated in the body than the females because males take more water and food than the females. In Figure 5.2b either the wife came from an arsenic affected area or the husband's working place is arsenic-free. This matter was not investigated during the sample collection. A comparison of arsenic concentrations in two randomly selected hair samples measured both in PINSTECH, Islamabad and INST, Dhaka is presented in Table 5.39.

TABLE 5.39

Comparison of arsenic concentrations in two randomly selected hair samples

SL. NO.	Sample ID	PINSTECH* value	INST** Value	% Deviation
1	Hair-6	12.94±0.63	12.24±0.17	5.41
3	Hair-17	1.61±0.09	1.69±0.02	4.97

*Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan

** Institute of Nuclear Science and Technology, Savar, Dhaka, Bangladesh

5.3.12 Hair samples of Dhaka Community Hospital

Eighteen hair samples collected from Dhaka Community Hospital (DCH) were analyzed for arsenic concentrations. The results of the measurement and quality control data are presented in Tables 5.40 and 5.41, respectively. In the present study arsenic concentration values lie in the range of 1.87±0.34 to 42.31±2.55 ppm. Normal value of arsenic concentration in human hair is less than 1 ppm (Arnold et al., 1990). All of the present samples are of arsenic affected patients, consequently arsenic concentrations in their hair are higher than 1 ppm. The patient with arsenic concentration in hair of 42.31 ppm (1^{st} sample) is extremely affected. Accuracy of the measurement is quite acceptable because the deviation is only –4.19 %. Detection limit of arsenic in the present measurement was 0.16 ppm. In a separate study, arsenic in human hair of upazilas Daudkandi and Begumganj were reported to lie in the range of 2.41 to 14.91 ppm (Das et al., 2003).

TABLE 5.40

Arsenic concentration in human hair samples of Dhaka Community Hospital

SL. NO.	Sample code	Concentration in ppm	Remarks
1	310	42.31±2.55	Highest
2	0001	12.48±1.34	
3	0014	5.82±0.65	
4	0015	10.22±1.24	
5	H-111	15.23±1.06	
6	H-117	7.50±0.52	
7	H-121	8.22±0.63	
8	H-123	15.87±1.26	
9	H-125	20.89±1.6	
10	H-129	2.42±0.35	
11	H-133	1.87±0.34	Lowest
12	H-135	4.62±0.47	
13	H-137	3.13±0.33	
14	H-139	7.09±0.75	
15	H-143	10.72±1.14	
16	H-149	8.1±0.87	
17	H-157	6.97±0.74	
18	H-163	6.09±0.65	

TABLE 5.41

QC of arsenic measurement in DCH human hair samples

Name of CRM	Element	Certified value, ppm	Measured value, ppm	% Deviation
Citrus Leaves	As	3.1±0.3	2.97±0.31	-4.19

5.3.13 Soil samples of Lohajang, Munshiganj

Results of arsenic measurements of Lohajang topsoils and quality control data are shown in Tables 5.42 and 5.43, respectively.

TABLE 5.42

Concentrations of arsenic and iron in topsoils of Lohajang, Munshiganj

Sl. No.	Kind of soil	Owner of the land	Village	Union	As. Concentration, ppm	Fe concentration, %
1	Dark clay	Abdul Aziz Shaikh	Shimulia	Haldia	10.95±0.40	4.72±0.19
2	Dark clay	Abdul Aziz Shaikh	Shimulia	Haldia	11.23±0.43	4.83±0.21
3	Yellowish clay	Mazid Hawladar	Kumarbhog	Kumar-bhog	7.46±0.28	4.70±0.19
4	Silty clay	Mazid Hawladar	Kumarbhog	Kumar-bhog	7.48±0.31	4.39±0.20
5	Dark clay	Solaiman Talukdar	Haldia	Haldia	16.04±0.58	4.59±0.19
6	Dark silty clay	Solaiman Talukdar	Haldia	Haldia	11.23±0.43	4.66±0.20
7	Clay with silt	Farid Ali	Pashchim Kumarbhog	Kumar-bhog	37.96±1.35	4.67±0.19
8	Dark silty clay	Farid Ali	Pashchim Kumarbhog	Kumar-bhog	30.19±1.07	4.43±0.19
9	Clay with some silt	Mujibur Khan	Pashchim Kumarbhog	Kumar-bhog	27.54±0.99	4.28±0.18
10	Dark clay	Mujibur Khan	Pashchim Kumarbhog	Kumar-bhog	23.80±0.85	4.34±0.22
11	Weathered clay	Jamal Bepari	South Medini-mondal	Medini-mondal	5.15±0.23	4.68±0.20
12	Silty clay	Jamal Bepari	South Medini-mondal	Medini mondal	9.54±0.37	5.02±0.21
13	Clay	Mofiz Miah	South Medini-mondal	Medini-mondal	5.77±0.25	4.39±0.20
14	Clay with silt and mica	Mofiz Miah	South Medini-Mondal	Medini-mondal	6.79±0.28	4.52±0.21
15	Dark clay	Raja Miah	North Medini-Mondal	Medini-mondal	6.29±0.26	4.25±0.19
16	Clay with some silt and mica	Raja Miah	North Medini-Mondal	Medini-mondal	6.88±0.27	4.81±0.22

Sl. No.	Kind of soil	Owner of the land	Village	Union	As. Concentration, ppm	Fe concentration, %
17	Yellowish weathered clay	Samad Bepari	Sitarampur	Medini-mondal	10.40±0.40	4.72±0.21
18	Yellowish silty clay	Samad Bepari	Sitarampur	Medini-mondal	9.98±0.32	5.32±0.22
19	Bluish grey soil	Abul Hossain	North Medini-mondal	Medini-mondal	28.06±1.01	4.36±0.21
20	Silty clay	Abul Hossain	North Medini-Mondal	Medini-mondal	16.42±0.59	4.93±0.22
Average values					14.46	4.66

The upazila average of arsenic concentrations in tubewell water of Lohajang in BGS-DPHE (2001) measurement is 221.6 μg/L. It indicates that the area is highly arsenic affected. The location map of Lohajang is presented in Figure 5.27. In the present measurement, maximum and minimum concentrations of arsenic in topsoils of Lohajong upazila were found to be 37.96±1.35 and 5.15±0.23 ppm, respectively. The allowed arsenic concentration level in agricultural field is 20 ppm. Therefore, highly contaminated areas of Lohajang need clean-up for cultivation. In a similar study of soil samples of depth 0.5 to 1.5 feet of areas Daudkhandi and Begumganj arsenic concentrations were found to lie in the range of 5.64 to 29.47 ppm (Das et al., 2003).

Ali et al. (2003) conducted some important experiments on plant-soil environment at Srinagar and Sonargaon. Some of their results are being mentioned here for comparison. Arsenic concentration in the topsoil layer varied from about 7 to 27.5 ppm at Srinagar. The mean arsenic concentration in the top layer was 14.5 ppm. At the Sonargaon site, arsenic concentration in the top layer varied from about 3.2 to 19 ppm. The mean arsenic concentration in the topsoil layer was 8.9 ppm.

The regulatory limit established for environmental health investigation levels in Australia is 20 ppm (NEPCACS, 1999). This suggests that in agricultural soils, arsenic concentrations exceeding 20 ppm will require clean-up. In contrast, the regulatory limit established by the UK is set at 10 ppm for domestic gardens, 40 ppm for parks, playing fields and open spaces (O'Neil, 1990).

In Lohajang soil samples arsenic concentration values vary from 5.15±0.23 to 37.96±1.35 ppm but the concentrations of iron remain very close to the mean value of 4.66 ppm, thus indicating that arsenic and iron concentrations are not correlated in Lohajang soil.

TABLE 5.43

Quality control data of arsenic and iron measurements in topsoils of Lohajang, Munshiganj

Name of CRM	Element	Certified value	Measured value	% Deviation
1633 b	Arsenic	136.2±1.7 ppm	131.77±6.58 ppm	-3.25
1633 b	Iron	7.78± 0.23 %	7.54±0.30 %	-3.34

5.3.14 Rice samples of Lohajang

Results of arsenic measurements of rice samples of Lohajang and its quality control data are presented in Tables 5.44 and 5.45, respectively.

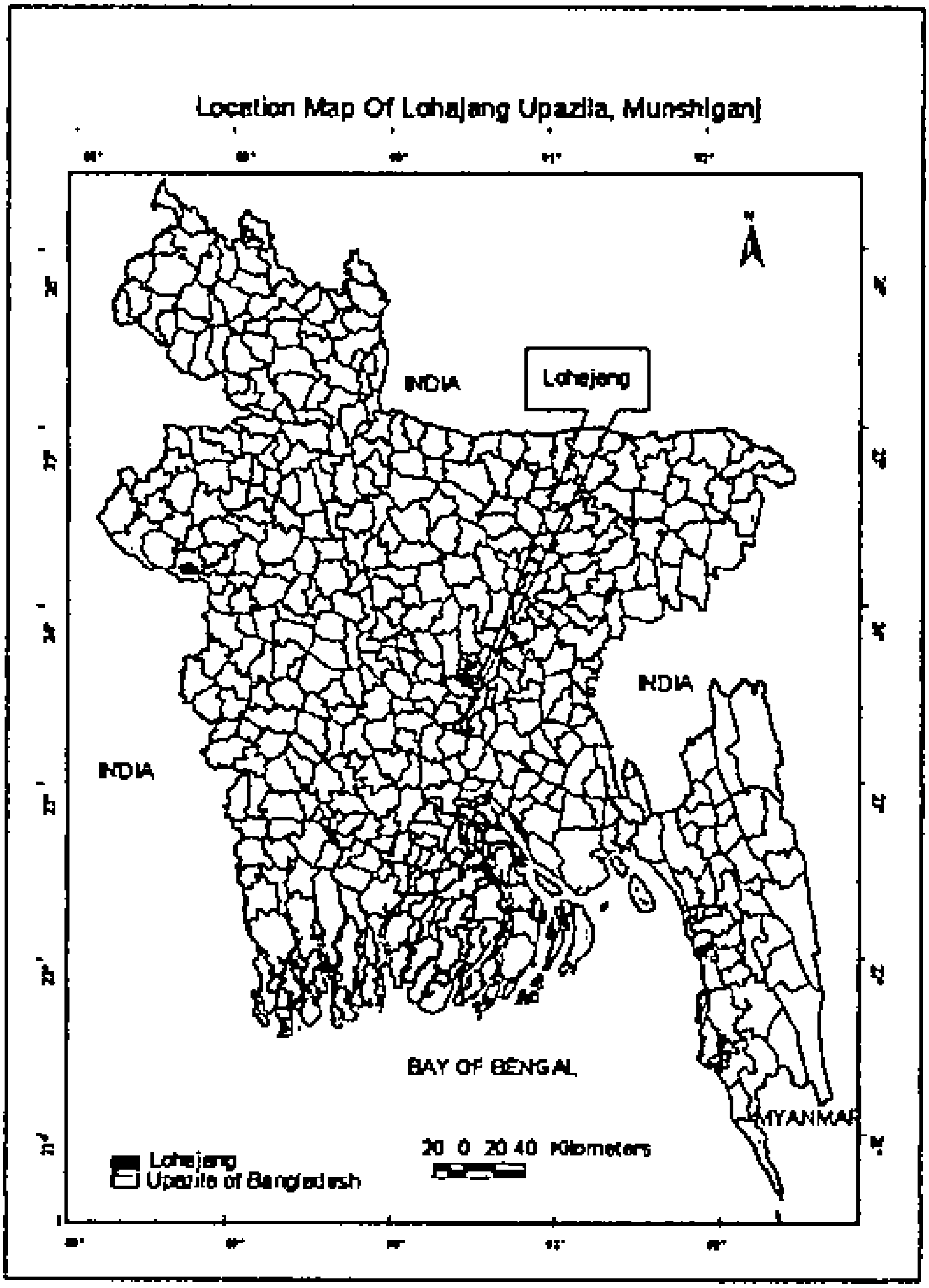

Figure 5.27 Location map of Lohajang, Munshiganj

TABLE 5.44

Concentrations of arsenic in rice samples of Lohajang, Munshiganj

Sl. No.	Kind of rice	Farmer's name	Village	Union	As concentration in rice grain (dry wt. basis) ppm
1	IRRI -29	Abdul Aziz Shaikh	Shimulia	Kumar bhog	0.15±0.01
2	IRRI-29	Majid Hawladar	Kumar Bhog	Kumar bhog	0.54±0.02
3	IRRI-29	S. Talukdar	Mouchha	Haldia	0.17±0.01
4	IRRI-29	Farid Dhali	Paschim Kumarbhog	Kumar bhog	0.88±0.04
5	Piar-29	Majibur Khan	Paschim Kumarbhog	Kumar bhog	0.26±0 01
6	IRRI-29	Jamal bepari	Dakhin Medini mandal	Medinimandal	<0.04
7	IRRI-29	Mofiz Mia	Dakhin Medini mandal	Medinimandal	0.26±0.01
8	IRRI-28	Raja Miah	Uttar Medini Mandal	Medinimandal	0.11±0.01
9	IRRI-29	Samad Bepari	Shitaram Pur	Medinimandal	<0.04
10	IRRI-29	Abul Hossain	Uttar Medini Mandal	Medini mondal	0.21±0.01

TABLE 5.45

Quality control data of arsenic measurement in rice samples of Lohajang, Munshiganj

Name of CRM	Element	Certified value	Measured value	% Deviation
Citrus leaves	Arsenic	3.1±0.3	2.87±0.10	-7.42

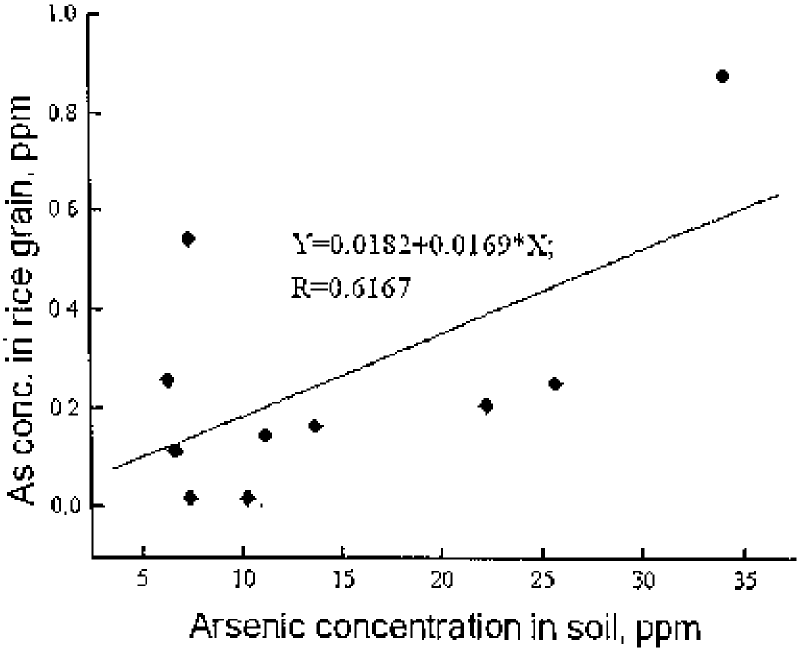

Figure 5.28 Correlation of arsenic concentrations in paddy field soil and rice grain of Lohajang

A good correlation coefficient amounting 0.6167 has been found between arsenic in rice grain and paddy soil of Lohajang (Figure 5.28). This is expected but has not been observed in many other cases.

5.3.15 Human hair samples of Lohajang

Arsenic concentrations in human hair samples of Lohajang and quality control data of the measurement are shown in Tables 5.46 and 5.47, respectively. Lohajang is a highly affected site. The population of the sampling area is using deep tubewell water for drinking and cooking purposes for the last several years. For this reason arsenic content in their hair is not too high at present. Here, the range of arsenic concentrations in hair is found to vary from <0.16 to 2.81±0.12 ppm. Most of the arsenic leave the body after a few days but a portion remains for several months and even longer.

TABLE 5.46

Arsenic concentrations in Lohajang hair

Sl. No.	Person code (age)	Village	Union	Distance of hair from scalp, inch	Source of drinking water and duration	Concentration of arsenic in hair, ppm
1	F-1 (60)	Bashirai	Kalma	4	DTW, 8y	0.53±0.03
2	F-2(35)	Bashirai	Kalma	5	DTW. 8y	0.44±0.02
3	M-1 (12)	Bashirai	Kalma	1	DTW, 8y	0.40±0.04
4	F-3 (60)	Bashirai	Kalma	10	DTW, 8y	0.82±0.05
5	M-3 (55)	Bashirai	Kalma	1	DTW, 8y	0.47±0.03
6	M-4 (80)	Bashirai	Kalma	1	DTW, 8y	<0.16
7	M-5 (8)	Bashirai	Kalma	2	DTW, 8y	0.79±0.05
8	M-6 (30)	Bashirai	Kalma	2	DTW, 8y	2.81±0.12
9	M-7 (60)	Paschim varakar	Kalma	1	DTW, 8y	<0.16
10	F-3 (40)	Paschim varakar	Kalma	6	DTW, 8y	0.18±0.02
11	F-4 (10)	Dohri	Dohri	7	DTW, 8y	1.34±0.06
12	F-5 (30)	Dohri	Dohri	6	DTW, 8y	0.46±0.03
13	F-6 (40)	Gorakanda	Kalma	5	DTW, 8y	0.57±0.0.03
14	M-7 (60)	North Medini-mondal	Medini-mondal	1	DTW. 8y	0.42±0.02

TABLE 5.47

Quality control data of arsenic measurement in Lohajang hair samples

Name of CRM	Element	Certified value, ppm	Measured value, ppm	% Deviation
IAEA-SL-1	As	27.6±0.3	26.93±1.10	-2.43

CHAPTER VI

SUMMARY AND CONCLUSIONS

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Arsenic contents in topsoils, food (rice and vegetables) and human hair samples collected from different regions of Bangladesh were studied in the present work using (NAA) technique. In addition, some water and sediment samples were also analyzed. The research work was carried out at the Institute of Nuclear Science and Technology (INST), Savar, Dhaka, Bangladesh and Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan. TRIGA Mark-II, PARR-I and PARR-II research reactors were utilized for the irradiation of the samples. Samples were collected from unaffected, moderately affected and highly affected areas of Bangladesh.

6.1 Summary

Unaffected areas in the present study are the parts of Goainghat, Companiganj and Sylhet sadar upazilas of Sylhet district and Savar upazila, Dhaka. Arsenic concentration values in two water samples of Goainghat upazila were found to be 10.70±0.45 and 17.48±0.73 μg/L. Arsenic concentrations in the soils of Sylhet unaffected areas range from 1.17±0.18 to 5.73±0.46 ppm. Iron concentrations in the samples were 1.27±0.14 to 4.07±0.26%. Strong correlation (R=0.6869) exists between arsenic and iron concentrations. Arsenic, iron and manganese concentrations were measured in seven sediment samples of Savar area, Dhaka in the PINSTECH laboratory. The minimum and maximum values of arsenic concentrations were found to be 0.72±0.03 and 6.82±0.26 ppm, respectively. Iron and manganese concentration values lie in the range of 1.36±0.02 to 3.38±0.07 % and 257±14 to 2194±116 ppm, respectively. Coefficient of correlation between arsenic concentration and depth was -0.6894. Strong positive correlation was found between arsenic and iron concentrations (R=0.9092). No correlation exists between arsenic and manganese. In the PINSTECH lab, six rice and six husk samples of Goainghat area were analyzed. The minimum and maximum values of arsenic concentrations in the rice grain were found to be 0.03±0.001 and 0.12±0.005 ppm, respectively. Arsenic concentrations in the husk samples were found in the range of <0.07±0.003

to 2.00±0.08 ppm. In the INST lab, sixteen rice and sixteen husk samples of Sylhet unaffected areas were analyzed. The minimum and maximum values of arsenic concentrations in the rice grain were found to be <0.038±0.004 and 0.112±0.011 ppm, respectively. For husk, corresponding values are <0.194±0.015 and 0.714±0.034 ppm, respectively. Coefficient of correlation in soil arsenic versus arsenic in rice was 0.3162. In the PINSTECH lab twelve human hair samples of Sylhet unaffected areas were analyzed. The minimum and maximum values of arsenic concentrations in the hair samples were <0.20±0.01 and 0.84±0.04 ppm, respectively.

Atomic absorption spectrometry (AAS) method was used to analyze eighteen water samples of Companiganj upazila, Sylhet, which is supposed to be a moderately polluted area. The minimum and maximum values of arsenic concentrations in the water samples were found to be 6.90±0.51 and 87.23±0.75 μg/L, respectively. Iron and manganese concentrations were also determined. The corresponding values for iron were 0.46±0.02 and 37.30±0.15 ppm and those for manganese are 0.12±0.09 and 1.14±0.02 ppm. The minimum and maximum values of arsenic concentrations in the soil samples of this upazila were found to be 3.60±0.14 and 7.95±0.29 ppm, respectively. The corresponding values for iron were 4.48±0.27 and 6.03±0.25%, respectively. Five rice grain and five husk samples of this area were also analyzed. The minimum and maximum values of arsenic concentrations in the rice grain samples were found to be <0.038±0.004 and 0.108±0.010 ppm, respectively. The corresponding values for husk were <0.194±0.015 and 0.566±0.028 ppm, respectively. Arsenic concentration was detected only in one vegetable sample (0.110±0.016 ppm) of Companiganj area. The minimum and maximum values of arsenic concentrations in the hair samples of Companiganj area were found to be <0.32±0.01 and 2.28±0.09 ppm, respectively.

Kachua and Faridganj upazilas under Chandpur district; Damurhuda upazila under Chuadanga district and Lohajang upazila under Munshiganj district are known to be highly arsenic affected areas. Thirteen undisturbed sediment samples of Kachua upazila were analyzed for arsenic, iron and manganese concentrations. Depths of the sediments were from 30 to 390 feet. The minimum and maximum values of arsenic concentrations in the sediment samples were found to be 0.65±0.05 and 9.15±0.35 ppm, respectively. The corresponding values of iron were found to be 0.86±0.01 and 4.56±0.05%, respectively. For manganese, these two values were 178±4 and 1646±33 ppm. Strong positive correlation (R=0.9042) was found between arsenic and iron concentrations. No correlation (R=0.111) was found between arsenic and manganese concentrations. Coefficient of correlation between arsenic concentration and depth was found to be –0.3549. The minimum and maximum values of arsenic concentrations in Faridganj soil samples were found to be 3.22±0.12 and 7.38±0.26 ppm, respectively. The corresponding values of iron were 3.70±0.16 and 5.46±0.22 %, respectively. Strong correlation was found between arsenic and iron concentrations in soil (R=0.7625). The minimum and maximum values of arsenic concentrations in Faridganj rice grain were found to be 0.148±0.012 and 0.324±0.014 ppm, respectively. The corresponding values for husk were 0.186±0.008 and 0.369±0.015 ppm, respectively. No correlation was found between arsenic in soil and arsenic in rice grain. In addition, no correlation was found between arsenic in rice grain and arsenic in husk samples. Arsenic concentration values in Faridganj vegetables lie below the detection limit of 0.110 ±0.004 ppm. The range of arsenic concentrations in Faridganj hair samples was found to be <0.35±0.07 to 3.45±0.19 ppm. Age group 15-30 years possesses higher arsenic concentrations. Sixteen rice samples of Comilla, Rajshahi, Rangpur, Dinajpur and Barisal districts were analyzed. The minimum and maximum values of arsenic concentrations in rice grain of these areas were 0.103±0.021 and 0.717±0.192 ppm, respectively. The minimum and maximum values of arsenic concentrations in Damurhuda vegetable samples are found to be <0.12 and 7.22 ±0.43 ppm, respectively. The minimum and maximum values of arsenic concentrations in Damurhuda hair samples were found to be 1.04±0.06 and 48.66±1.32 ppm, respectively. Eighteen hair samples collected from Dhaka Community Hospital were also analyzed. The minimum and maximum values of arsenic concentrations in the DCH hair samples were found to be 1.87±0.34 to 42.31±2.55 ppm. The minimum and maximum values of arsenic concentrations in the Lohajang soil samples were found to be 5.15 ± 0.23 and 37.96 ± 1.35 ppm, respectively. Thus Lohajang soil exceeds the allowed limit of arsenic in paddy field soil of 20 ppm. The corresponding values for iron were found to be 4.25±0.19 and 5.32±0.22%, respectively. The minimum and maximum values of arsenic concentrations in the Lohajang rice samples were found to be <0.04 and 0.878±0.0.035 ppm, respectively. It may be mentioned that in the present investigations 0.878 ppm is the highest arsenic concentration value in rice grain. This value is close to 1 ppm - the safe limit of arsenic concentration in food items. The minimum and maximum values of arsenic concentrations in the Lohajang hair samples were found to be <0.16 and 2.81±0.12 ppm, respectively.

Arsenic concentrations in soil samples of different studied-areas are presented in Figure 6.1. The highest arsenic concentration in soil in the present study is 37.96 ppm in Lohajang.

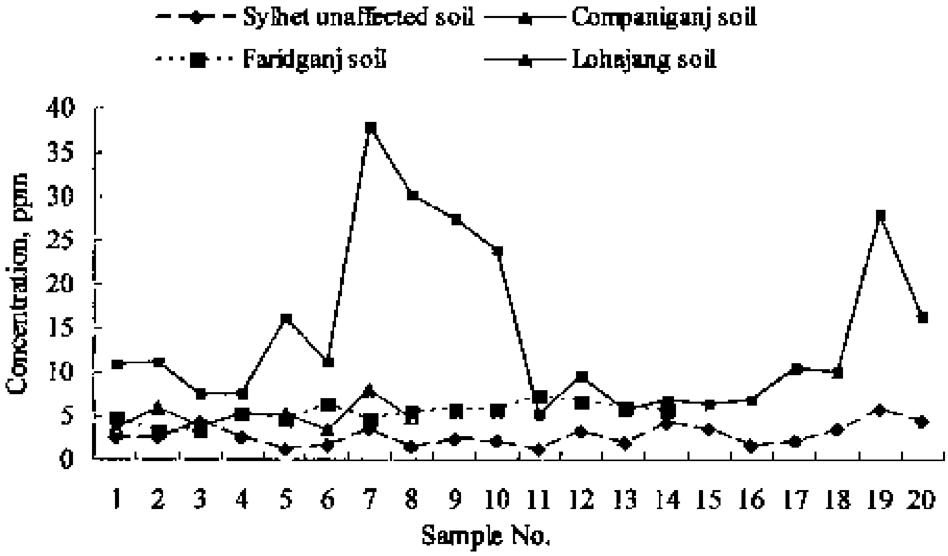

Figure 6.1 Arsenic concentrations in soils of different studied-areas

Arsenic concentrations in rice samples of different studied-areas are presented in Figure 6.2. From the Figure the highest arsenic concentration in rice in the present study is 0.878 ppm in Lohajang. This value does not exceed the permissible level of arsenic concentration of 1 ppm in rice.

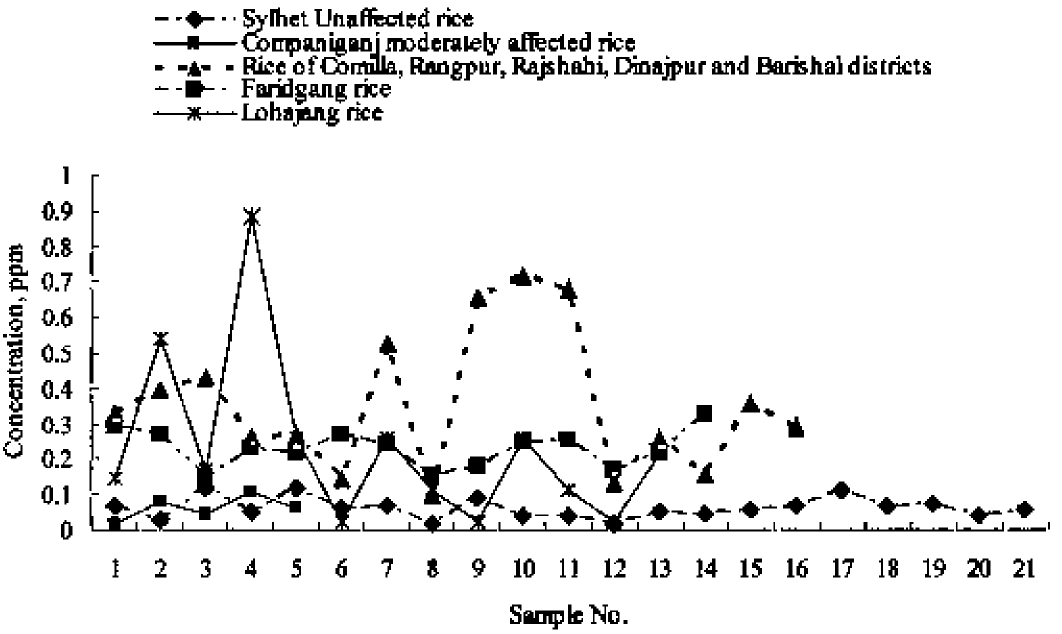

Figure 6.2 Arsenic concentrations in rice grain of different studied-areas

Arsenic concentrations in hair samples of different studied-areas are presented in Figure 6.3 from where one would find that the maximum arsenic concentration is close to 50 ppm in a Damurhuda hair sample. The second highest hair arsenic concentration is found in an arsenicosis patient of Dhaka Community Hospital (DCH).

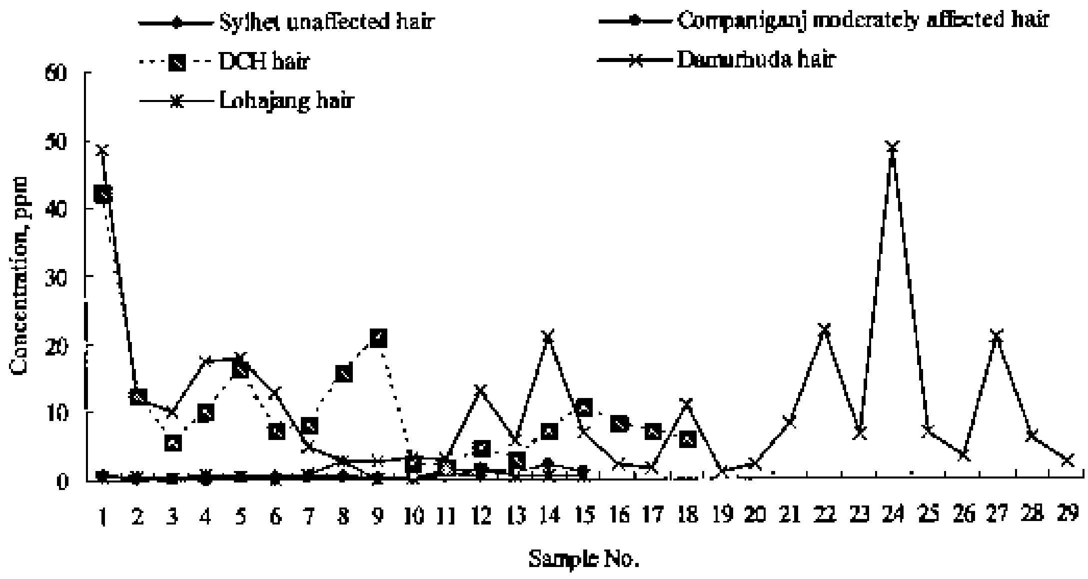

Figure 6.3 Arsenic concentrations in hair samples of different studied-areas

6.2 Conclusions

In the studied-areas soil arsenic is found to be much less than 20 ppm except at Lohajang. Soil arsenic exceeding 20 ppm may hamper crop production. Limited available data suggest significant variation of arsenic content among different varieties of crop/vegetables and also among different parts of the same plant.

In a recent study (Abedin et al., 2002), a rice variety was irrigated with water containing 0-8 mg/L of arsenate. It was found that increasing concentration of arsenate significantly decreased plant height, grain yield, the number of filled grains, grain weight and root biomass. For the highest dose of 8 mg/L arsenate, grain arsenic concentration reached a maximum of about 0.6 ppm. However at lower levels of exposure which are more relevant to Bangladesh situation, grain arsenic did not differ greatly from the zero exposure, which was about 0.2 mg/L (Meharg et al.,2001).

For the highest arsenic dose, concentration of arsenic in rice straw and root reached as high as 91.8 and 107.5 ppm, respectively (Abedin et al., 2002). Maximum arsenic concentration in rice grain found in the present study is 0.878 ppm, whicb is less than

1 ppm - the permissible level of arsenic in any food item. This suggests that arsenic can be easily translocated to paddy shoot but not in the grain.

Concentration of arsenic in arum has been found to be 7.22 ± 0.43 ppm in the present study. However, Huq et al. (2006) reported arsenic concentration in arum as high as 150 ppm. It should be noted that very little is known about the chemical forms of arsenic (e.g., inorganic and organic) in crop/vegetables, which in turn is needed for estimating its toxicity. Some recent studies (Chakroborti et al., 2001; Magara, 2002) suggest that a significant portion of arsenic in rice and vegetable exists as As (V). Chakroborti et al., (2001) reported 95% inorganic and 5% organic arsenic in rice and 96% inorganic and 4% organic arsenic in vegetables. Magara (2002) also found significant fraction of total arsenic as As (V) in rice grain. Speciation of arsenic in rice straw (Abedin et al., 2002) revealed that the predominant species present in straw was arsenate followed by arsenite and dimethylarsenicacid (DMA). Since inorganic arsenic is more toxic than organic arsenic, these results raise serious health concerns.

Smith et al. (2001) have shown that yield of both tomato and silverbeet, grown in soil containing 100-200 ppm arsenic, were significantly reduced (5 to 10% of the control yield). From present studies, it was found that all vegetables except arum contain arsenic below 1 ppm (maximum permissible limit). Thus these items may be safe for use as food.

There is considerable variation in arsenic contents in soil, grain and straw, but they are not correlated each other. This needs further investigations. Some researchers (Ali et al., 2003) found the straw arsenic concentration well above 1 ppm which needs investigation for its adverse effects when they are used as feed for cattle.

Arsenic concentrations in hair samples of unaffected areas are less than 1 ppm. Arsenic in Damurhuda hair was found to be extremely high (~50 ppm). The patient data set is not linked to the tubewell data set. In Damurhuda only 20% well is affected but highest prevalence of 2.6/1000 occurs (Rosenboom, 2004).

In INST measurement conditions, minimum detection limits of arsenic in soil, rice, vegetable and human hair samples were found to be 0.20, 0.04, 0.11 and 0.16 ppm, respectively. Detection limits of arsenic in soil, rice and human hair samples in PINSTECH measurement conditions were found to be 0.65, 0.03 and 0.20 ppm, respectively. The present experimental data may be accepted for reference values of arsenic contents in soil, food and biomatrix for their reliability and accuracy.

Arsenic contamination in ground water affects at least nine countries in South- and Southeast Asia. Bangladesh is the country having maximum experience in addressing this problem, certainly from a perspective of mass screening of tubewells and identifying patients. In many ways, other countries can be benefited from Bangladesh's experience.

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APPENDICES

APPENDIX I

ACTIVATION EQUATION

In a neutron induced reaction, the growth of the product is dependent on the size of the neutron flux. The larger the neutron flux, the greater the rate at which interaction occurs:

$$\text{Activation rate} \propto \text{neutron flux } (\phi)$$

Activation rate is also directly proportional to the number of target nuclei present:

$$\text{Activation rate} \propto \text{No. of target nuclei } (n)$$

The relationship between activation rate, the number of target nuclei and the neutron flux is expressed by the term "cross Section" (σ). The cross section is simply a physical constant:

$$\text{Activation rate} = \sigma\phi n$$

$$\text{Production rate} = \text{activation rate} - \text{decay rate}$$

$$\text{or, } \frac{dN^*}{dt} = n\sigma\phi - \lambda N^*$$

$$\text{or, } \frac{dN^*}{dt} + \lambda N^* = n\sigma\phi$$

(1)

Multiplying both sides of equation (1) by the integrating factor $e^{\int \lambda dt} = e^{\lambda t}$

$$e^{\lambda t}\frac{dN^*}{dt} + e^{\lambda t}\lambda N^* = n\sigma\phi e^{\lambda t}$$

$$\text{or, } \frac{d}{dt}(e^{\lambda t}N^*) = n\sigma\phi e^{\lambda t}$$

$$\text{or, } e^{\lambda t}N^* = n\sigma\phi\left(\frac{1}{\lambda}e^{\lambda t} + c_1\right)$$

At $t=0$, $N^*=0$, $c_1 = -\frac{1}{\lambda}n\sigma\phi$; substituting value of c_1 we have

$$\lambda N^{*} = n\sigma\phi(1 - e^{-\lambda t})$$

$$\text{or, } A = n\sigma\phi(1 - e^{-\lambda t})$$

$$\text{or, } dps = n\sigma\phi(1 - e^{-\lambda t})$$

Symbols have the following meanings

n = No. of target nuclei

= WN_AF/M

σ = reaction cross section, cm^2

ϕ = neutron flux, n cm^{-2} s^{-1}

λ = decay constant, s^{-1}

W = weight of element in the sample, g

N_A = Avogadro constant

F = isotopic abundance

M = atomic weight

dps = disintegrations s^{-1}.

APPENDIX II

CALCULATION OF ELEMENTAL CONCENTRATIONS

A. After the end of irradiation count rate decays exponentially as shown in the figure below.

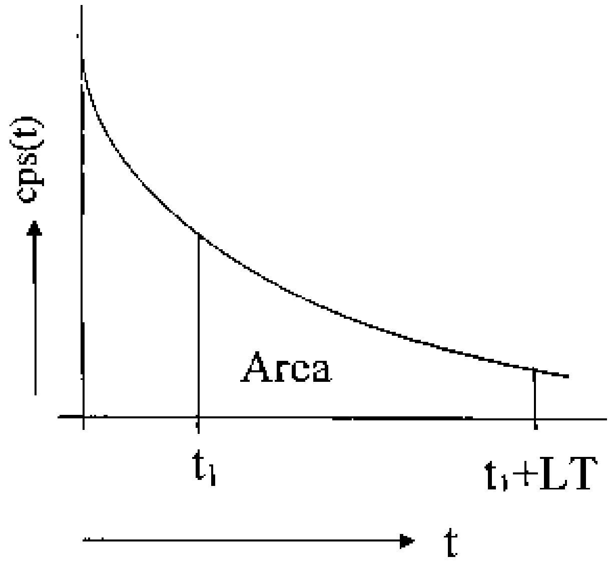

Figure A1: Decay of count rate with time.

Let t_1 be the decay time, LT be the live time, N be the net counts and cps(t) be the count rate at time t after the end of irradiation.

Then we have, N = $\int_{t_1}^{t_1+LT} cps(t)dt$

$$= \int_{t_1}^{t_1+LT} cps(0)e^{-\lambda t}dt$$

$$= \frac{cps(0)}{\lambda} e^{-\lambda t_1}\left[1 - e^{-\lambda LT}\right]$$

$$= \frac{cps(t_1)}{\lambda}\left[1 - e^{-\lambda LT}\right]$$

Then, $\mathrm{cps}(t_1) = \dfrac{N\lambda}{1-e^{-\lambda\, LT}}$

Decay corrected initial cps

$$= cps(t_1)e^{\lambda t_1}$$

$$= \frac{N\lambda}{1-e^{-\lambda\, LT}}e^{\lambda t_1}$$

$$\frac{\text{Amount of element in the sample}}{\text{Amount of element in the standard}} = \frac{\text{Decay corrected cps in the sample}}{\text{Decay corrected cps in the standard}}$$

$$\text{Elemental concentration} = \frac{\text{Amount of element in the sample}}{\text{Sample weight}} \times 10^6 \text{ ppm}$$

APPENDIX III

Water sampling instructions and protocol

Instructions:

Step–1: Press the tube well at least ten minutes before collecting water.
Step-2: Wash bottle at least 3 times before collecting sample.
Step-3: Add 25 ml of conc. hydrochloric acid (HCl) in 500-ml water and shake well.

Protocol:

Sample ID:

Date of Sampling (DD MM YYYY):

1. Owner of the tube well /community based:

   i. Name:...
   ii. Address: Vill. ....
   P.O. ....
   Union ....
   Thana ....
   Dist. ....

3. Depth of the tube well: ft Material:

4. Establishment date (DD MM YYYY):

5. Number of users:

6. Arsenic patient available: Yes /No If Yes, How many?

   Name & Age: (1)...
   (2)...
   (3)...

6. Arsenic concentration data from previous measurement conducted by NGO or Govt.

Organization: Date of measurement:

Concentration: ppb

Name & signature of sample collector ....

APPENDIX IV

Hair sampling instructions and protocol

Water sample ID: Hair Sample ID:

Date of sample collection:

1. Name: Sex:

2. Date of birth: Age:

3. Father's/Husband's Name:

4. Permanent address : Present address:

Vill./Town-	Vill./Town-
Ward -	Ward -
Union-	Union-
P.O-	P.O.-
P.S-	P.S-
District-	District-

5. No. of family members:

6. Present source of drinking water:

7. Whether the tube-well the person uses is marked: . Red . Green . None

8. Hair length from the scalp: inches/cm. Hair colour:

Segment: 1. 2. 3. 4. 5.

9. Arsenic affected symptom: Melanosis / Keratosis, others

10. Whether the person uses:

i) Shampoo	Yes/No. If yes, last time of use…… …	days ago
ii) Oil	Yes/No. If yes, last time of use………..	days ago
iii) Soap	Yes/No. If yes, last time of use………..	days ago
iv) Mehedi	Yes/No. If yes, last time of use………..	days ago
v) Hair cream	Yes/No. If yes, last time of use………..	days ago
vi) Hair dying	Yes/No. If yes, last time of use………..	days ago

11. Living history of last ten years:

Name & signature of the sample collector……………………………………………