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Studies on Ground Water Toxicants in Food Chain

Ali, Md. Rustom

University of Rajshahi

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Studies on Ground Water Toxicants in Food Chain



RAJSHAHI UNIVERSITY

**A THESIS
SUBMITTED TO THE UNIVERSITY OF RAJSHAHI
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY**

**SUBMITTED BY
Md. Rustom Ali
SESSION: JULY 2008**

**MOTIHAR GREEN
JUNE, 2014**

**PHYSICAL RESEARCH LABORATORY
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF RAJSHAHI, BANGLADESH**

STUDIES ON GROUND WATER TOXICANTS IN FOOD CHAIN



RAJSHAHI UNIVERSITY

**A THESIS
Submitted to the University of Rajshahi in Partial Fulfillment of
the Requirements for the Degree of**

*Doctor
of
Philosophy*

Submitted by

**Md. Rustom Ali
Session: July 2008**

Dr. M. Nazmul Islam
Associate Professor
Department of Chemistry
University of Rajshahi
Rajshahi, Bangladesh.

Dr. Entazul M. Huque
Professor
Department of Chemistry
University of Rajshahi
Rajshahi, Bangladesh.

**MOTIHAR GREEN
JUNE, 2014**

**PHYSICAL RESEARCH LABORATORY
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF RAJSHAHI, BANGLADESH**



DEDICATED

TO

MY PARENTS & ELDER BROTHERS

DECLARATION

I do hereby declare that the entire work as embodied in this dissertation towards the partial fulfillment of the Ph.D. degree is the result of my own investigation except where due acknowledgement has been given. It has not concurrently been submitted elsewhere for any other degree.

(MD. RUSTOM ALI)

CERTIFICATE

This is to certify that the thesis entitled “Studies on Ground Water Toxicants in Food Chain” submitted by Md Rustom Ali is the outcome of his own research work carried out at the Department of Chemistry, the University of Rajshahi, Bangladesh, under my supervision. Any part or whole of the dissertation has not been submitted elsewhere for any other degree.

Dr. M. Nazmul Islam
Associate Professor
Department of Chemistry
University of Rajshahi
Rajshahi, Bangladesh.

Dr. Entazul M. Huque
Professor
Department of Chemistry
University of Rajshahi
Rajshahi, Bangladesh.

ABSTRACT

Many of the metals are considered as essential nutrients for maintaining sound human health throughout life. But intake of heavy metal contaminated vegetables, rice, meat, fish, drinking water and dust may pose a risk to human health. Arsenic in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh. Lead and cadmium pollutions are also considered to be global issues. Considering these, two separate studies were carried out to find out the potential ways for remedy of arsenic, cadmium and lead toxicity in food grains as well as to assess human health risk due to arsenic, cadmium and lead exposures from dietary food products collected from two villages of Rajshahi City Corporation in Bangladesh.

In this investigation, six natural organic fertilizers that the Bangladeshi farmers use frequently were used to assess their potentials towards reduction of arsenic, cadmium and lead toxicity in corns. These were rotten cow-dung, rotten Dhunca, compost, drain mud, earthworm mud and water hyacinth. The selected corn plants grown in open field were paddy, sesame, maize and foxtail, and were irrigated with the contaminated water having concentrations of 4.8 mg L^{-1} of As, Pb and Cd simultaneously. The concentrations of arsenic, cadmium and lead in the environmental samples were determined by Graphite Furnace– Atomic Absorption Spectroscopy (GF-AAS) technique. To assess human health risk due to consumption of dietary products, drinking water and dust, US Environmental Protection Agency's (USEPA) guidelines were applied.

The overall efficiency of the studied organic fertilizers towards simultaneous reduction of arsenic, cadmium and lead toxicity in food grains was found as follows: CM (Compost) >> EW(Earthworm mud) \approx CD (Cow-dung) \approx DM (Drain mud) >> RD (Rotten Dhuncha) \approx WH (Water hyacinth).

Since compost, earthworm mud, cow-dung, drain mud and rotten Dhuncha were able to reduce the concentration of arsenic, cadmium and lead in the food grains simultaneously with respect to control, they could be recommended for remedy of arsenic, cadmium and lead toxicity in corns. The observed concentration range of arsenic, cadmium and lead in the studied food grains were: (0.329 - 2.105), (0.002 - 0.121) and (0.002 -1.495) mg kg⁻¹ on fresh weight basis. Based upon the accumulated concentrations of the concerned metals, the studied crops could be arranged in the follow the order:

Paddy > Sesame > Maize > Foxtail.

In the human health risk assessment investigation, arsenic, cadmium and lead concentration ranges in all the studied diet were found as dust (1.154-3.441 $\mu\text{g g}^{-1}$), rice (0.016-0.154 $\mu\text{g g}^{-1}$) and Fish (0.017-0.507 $\mu\text{g g}^{-1}$) respectively (ww). Generally, the concentrations of the concerned metals in the studied samples follow the order: Dust > Rice > Fish > Vegetables > Drinking water. It was found that 99.29% of meal exposure was due to ingestion, while only 0.71% due to inhalation. Sample wise contribution towards average total Hazard Quotient (HQ) values was found as follows:

For Arsenic : Dust > Rice > Fish > Vegetables > Drinking water

For Cadmium : Rice > Dust = Drinking water > Fish > Vegetables

For Lead : Dust > Rice > Fish > Vegetables > Drinking water

As, Cd and Pb contribute to 60.79%, 20.89%, 18.32% of exposures respectively for children. But for average person, As, Cd and Pb contributions

are 75.26 %, 24.48 % and 0.26 %. respectively. For senior person, the contributions are 70.15%, 17.50% and 12.38% respectively. In case of children population sub-group average HI value was 2.215. It reflects that all children are at risk due to consumption of the studied diet.

The HI values for Average Person and Senior population sub-group are 0.909 and 0.871 respectively. Hence both population sub-groups are in safe limit due to consumption of the same diet. Comparison among HI values suggests that the population sub-groups should be arranged in following order: Children > Average Person > Senior.

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The Author.

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ABBREVIATIONS AND SYMBOLS

A	Absorbance
ACS	American Chemical Society
Dapp	Applied Dose
AAS	Atomic Absorption Spectroscopy
\bar{C}	Average Concentration of Trace Element
ADD	Average Daily Dose
AT	Average Time
BW	Body Weight
DEFRA	Department for the Environment, Food and Rural Affairs(UK)
DPHE	Department of Public Health Engineering (Bangladesh)
DDW	Double Distilled Water
EDL	Electrodeless Discharge Lamp
E	Exposure
ED	Exposure Duration
FL	Flame
FAO	Food and Agriculture Organization
GI	Gastro-intestinal
HI	Hazard Index
HQ	Hazard Quotient
HE's	Highly Exposed Individuals
HCL	Hollow Cathode Lamp
HG	Hydride Generation
IR(t)	Ingestion or Inhalation Rate
IRIS	Integrated Risk Information System
Dint	Internal dose
IARC	International Agency for Research on Cancer

LOAEL	Lowest Observed Adverse Effect Level
MADL	Maximum Allowable Daily Level
MADL	Maximum Allowable Limit
MHS	Mercury Hydride System
MMA	Monomethylarsenic acid
NIST	National Institute of Standards and Technology (USA)
NOAEL	No Observed Adverse Effect Level
n	Number of Observation
ppm	Parts per Million
ppb	Parts per Billion
Dpot	Potential dose
QA	Quality Assurance
QC	Quality Control
QTA	Quartz Tube Atomizer
RfC	Reference Concentration
RfD	Reference Dose
SRM	Standard Reference Material
A _{ST}	Total Arsenic Concentration
TSP	Triple Superphosphate
UV-VIS	Ultraviolet and Visible
USEPA	United State Environmental Protection Agency
λ_{\max}	Wavelength of maximum absorptivity
WHO	World Health Organization
CD	Cow-dung
CM	Compost
DM	Drain mud
EW	Earthworm mud
RD	Rotten Dhuncha
WH	Water hyacinth

CHAPTER ONE

REVIEW OF LITERATURE

Introduction

Review of Literature

Chemical Properties of Arsenic, Lead and Cadmium

Solution Chemistry of Arsenic, Lead and Cadmium

Sources of arsenic, lead and cadmium

Worldwide Scenario of Groundwater Contamination

Characterization of Irrigation Water

Geological source of arsenic

Transport of arsenic within the aquifers

Arsenic, Lead and Cadmium in Soil

Statistical Analyses of Concentrations of Arsenic, Lead and Cadmium in the Corns

Rationale of the study

Conclusions

References

Chapter 1

Introduction

1.1 Review of Literature

Arsenic is an element (highly toxic metalloid) that raises much concern from the both environmental and human health standpoints. Humans may encounter arsenic in water from wells drilled into arsenic-rich ground state or in water contaminated by industrial or agrochemical waste, other than naturally contaminated groundwater [1]. They may come in contact with arsenic in contaminated dusts, fumes, or mists. They may eat food contaminated with arsenical pesticides or grown with arsenic-contaminated irrigation water or in arsenic-rich soil. For the food grown in arsenic affected areas, arsenic is not only found inside the food like cereals, pulses, fruits, but also may be found in external layer of food or fruits due to spreneld of arsenicated water.

Some recent studies have shown that a few of our foodstuffs such as vegetables, meat, fish, corn, cereals, poultry etc. might be contaminated with arsenic [2-4]. This is due to the presence of high concentrations of soluble arsenic in the soil where the foodstuffs are grown. The groundwater contamination by arsenic is already considered as a serious global environmental problem. It is one of the potential sources for intake of arsenic in the human body. Crops and vegetables grown on the arsenic-contaminated soils can also serve as a source of arsenic for human beings.

Williams et al. [5] and Huq and Naidu [6] reported that Arum, Amaranth and Ipomoea were good arsenic accumulators. They found arsenic levels in Arum and Potato up to 153 and 2.4 mg kg⁻¹ (dry wt.) respectively. They also reported arsenic concentration in irrigation water in affected areas of Bangladesh ranged from 0.136 to 0.555 mg L⁻¹. Williams et al. [5] from food market-basket survey showed that arsenic accumulation order was Arum stolon > Brinjal > Cucumber > Coriander > Potato > Long-yard Bean > Radish Leaf > Giant Taro (Mankochu) >

Vegetable Papaya. Out of 20 countries in different parts of the world, where groundwater arsenic contamination and human sufferings have been reported so far, the magnitude is considered to be the maximum in Bangladesh followed by West Bengal of India [7].

A study conducted by the British Geological Survey (BGS) showed that the groundwater from shallow tube-wells, a popular source of drinking water, in 61 out of 64 districts of Bangladesh was contaminated with arsenic [8]. An estimated 29 million people are directly exposed to this contamination and another 85 million are at risk [9]. Nearly 10,000 patients have been identified and a few deaths due to arsenic-related diseases have also been reported [9-12]. Clearly, Bangladesh is facing probably the largest mass poisoning in history.

About 33 percent of total land of Bangladesh is under irrigation facilities [13] and the lands are irrigated with groundwater from semi-deep or shallow aquifers through tube-wells as well as low-lift pumps. Most of the groundwater used for irrigation in Bangladesh are contaminated with arsenic [14]. The widespread uses of groundwater for irrigation suggested that ingestion of irrigated crops and food grains could be another major exposure route for arsenic [15, 16].

Bhattacharya et al. [17] carried out a study to assess the level of severity of arsenic contamination of the people of highly arsenic affected Nadia district of West Bengal, India. They investigated the concentrations of arsenic in irrigation water, soil, rice, wheat, common vegetables and pulses. Results revealed that the arsenic-contaminated irrigation water (0.318-0.643 mg L⁻¹) and soil (5.70-9.71 mg kg⁻¹, fresh wt.) considerably influenced the accumulation of arsenic in rice, pulse and vegetables in the area. Food and Agriculture Organization (FAO) permissible limit for irrigation water is 0.10 mg L⁻¹. But arsenic concentrations of the irrigation water samples were many fold higher than the WHO recommended permissible limit for drinking water (0.01 mg L⁻¹) [18] and Bangladesh recommended value for drinking water of 0.05 mg L⁻¹. However, the levels of arsenic in soil were lower than the reported global average of 10.0 mg kg⁻¹ and was much below the EU recommended maximum acceptable limit for agricultural soil (20.0 mg kg⁻¹) [19].

Arsenic causes serious health hazards to human beings through contamination of groundwater and drinking water. Among the inorganic species, As (III) is considered as the major As species present in natural water system and has higher toxicity than As(V), because it binds to particular chemical groups – sulfhydryl groups – found on proteins [20]. The epidemiological studies show that chronic As poisoning can cause serious health hazards including cancer, hyperkeratosis, restrictive lung disease, peripheral vascular disease, gangrene, diabetes mellitus, hypertension and ischemic heart disease [20, 21]. Arsenic seems to be a cancer promoter rather than a cancer initiator [22]. The World Health Organization (WHO) ranked this calamity as the largest poisoning of a population in history [23].

Uptake of arsenic by crop plants grown in soils contaminated with high concentrations of As and irrigated with As contaminated water has been reported by Abedin et al. [24]. Das et al. [25] reported that the concentrations of arsenic in some vegetables of Bangladesh like Kachu sak (*Volocasia antiquorum*), potato (*Solanum uberosum*), and Kalmi sak (*Ipomea reptans*) exceed the food safety limits of 1.0 mg kg⁻¹ (net wt.). In the study of arsenic accumulation in the agriculture plants of China and Nepal, Huang et al. [26] and Dahal et al. [27] have found that arsenic accumulated in the range of 0.003-0.116 and < 0.01-0.55 mg kg⁻¹ (dry weight) respectively. In a similar study, significantly lower amount of uptake and translocation of five toxic metals (Cd, Cr, Pb, As and Hg) in the rice grain compared with the uptake in the rice straw and root parts have been reported by Liu et al. [28]. Higher amount of arsenic was reported to accumulate in the root of the rice plants as compared with other parts [29, 30, 17]. Studies [31, 32] have shown that the contribution of arsenic pollution to human health through food chain is many times greater than that of drinking water in country. Presence of arsenic in vegetables and tubers crops and its translocation to the edible parts were observed to vary with crops [33] and even among the cultivars of the same crop [34]. Arsenic contamination in rainy season rice is not much of a problem due to its rainfed cultivation. But winter and summer crops are mainly cultivated through irrigation

using ground water by shallow tube-well which in turn creates lot of problems with regard to arsenic uptake. Lauren and Duxbury [35, 36] estimated of arsenic consumption from only rice and water indicating that arsenic from rice is an important source of exposure in the Bangladesh food system. They proposed that management strategies need to be developed to reduce arsenic uptake by rice. Despite their expectation that aerobic cultivation practices would reduce arsenic uptake by rice, results from experiments with permanent raised beds and System of Rice Intensification (SRI) have not shown differences in arsenic concentration (Fig 1.1).

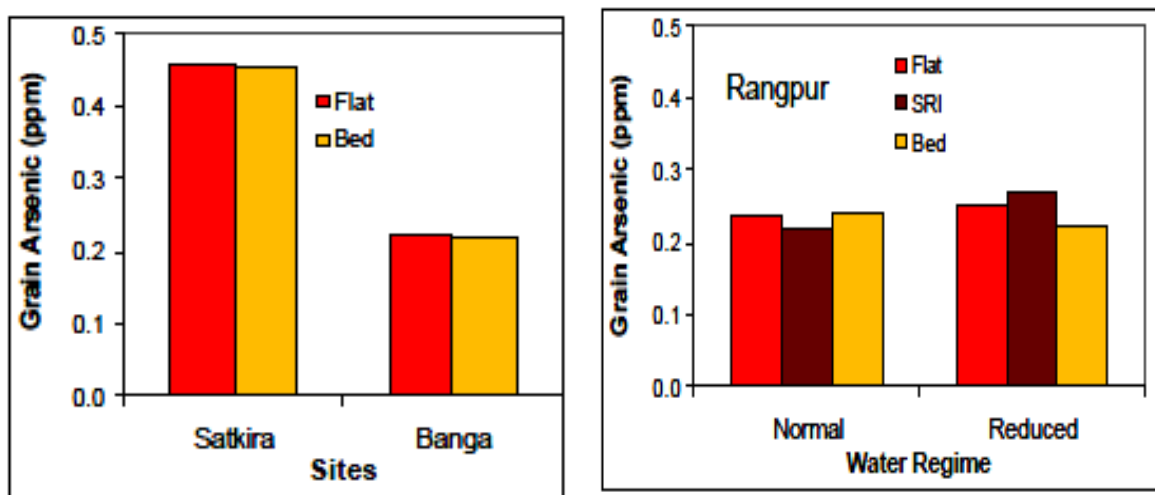


Figure 1.1 : Reduced arsenic uptake by rice in aerobic cultivation practice

Rose et al. [37] furnished an avoidance approach. They identified in their study that 24% of total irrigated boro rice in Bangladesh is grown in areas where groundwater arsenic is greater than the $50 \mu\text{g L}^{-1}$, Bangladeshi standard. Many of the areas with high groundwater arsenic ($> 200 \mu\text{g L}^{-1}$) are found in the central part of the country near the Padma and Meghna rivers with ample surface water. Development of more irrigation schemes with these surface water sources could provide a clean substitute for contaminated groundwater. Liu and colleagues [38] demonstrated that differences in arsenic uptake between rice varieties were influenced by iron plaque formation and regulated by plant phosphorus status.

In most parts of rural Cambodia, groundwater is used for bathing, cooking, washing and drinking and is used also for crops irrigation. It is the main source of

water among the rural population, after river (UNICEF 2007) [39]. The researches have shown that arsenic accumulation in plants depends on the plant species, soil composition, planting season, geographical location and growing method.

Davin et al. [40] investigated arsenic accumulation in crops (fruits and vegetables), particularly native species grown in arsenic-contaminated areas of Cambodia. The results of their study would be vital in deciding what crops can be grown in arsenic-contaminated areas, or what cultivation method is needed to reduce arsenic accumulation. During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of food stuffs contaminated by pesticides, heavy metals and/or toxins [41].

Heavy metals constitute a variety of groups that vary in their chemical properties and biological functions. Heavy metals are kept under environmental pollutant category due to their toxic effects in plants, human and food. Arsenic (As), Cadmium (Cd), Lead (Pb) and Mercury (Hg) is cumulative poisons. These heavy metals are persistence and not easily metabolized in other intermediate compounds and do not easily break down in environment. These metals are accumulating in food chain through uptake at primary producer level and then through consumption at consumer level. However, subsequent metal contamination discovered by testing water necessitated mitigation programs [42]. Like trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning [43]. Poisoning of heavy metal toxicity varies according to their oxidation state, solubility and many different inorganic and organic forms. The implication associated with heavy metal contamination is of great concern, particularly in agricultural production systems. These metals can pose a significant health risk to humans, particularly at elevated concentration above the very low body requirements [44]. Li and Tian [45] analyzed human health risk caused by heavy metals in a water source. They found the order of health risky gene toxic substances as $\text{Cr}^{6+} > \text{As} > \text{Cd}$ and that of body toxic substances as $\text{Pb} > \text{Cu} > \text{Hg}$.

Heavy metals are an important source of food contamination and health hazard. The main threats to human health are associated with exposure to arsenic, cadmium, lead, mercury and copper. Absorption of heavy metals through food has been shown to have serious consequences on health and thereby economic development associated with a decline in labor productivity as well as the direct cost of treating illnesses such as kidney disease, damage to the nervous system, diminished intellectual capacity, heart disease, gastrointestinal disease, bone fracture, cancer and death [46]. Trace elements are very harmful because of their non biodegradable nature, long biological half-lives, and their potential to accumulate in different body parts. High concentration of trace elements (Cu, Cd and Pb) in vegetables and fruits were related to prevalence of upper gastrointestinal cancer [47]. The International Agency for Research on Cancer (IARC) classified lead as a possible human carcinogen in 1987 [48]. Lead (Pb) is a physiologic and neurological toxin that can affect almost every organ or system in the human body. It can reduce cognitive development & intellectual performance in children and damage kidneys and the reproductive system [49]. Cadmium (Cd) accumulates in kidneys, where it damages filtering mechanisms. It also causes diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility, damage to the central nervous system, damage to the immune system, psychological disorders and possibly DNA damage.

Singh *et al.* in their study [50] for risk assessment of heavy metal toxicity found that waste water irrigation led to the accumulation of heavy metals in soil and consequently into the food grains. Heavy metal concentrations were varied among the test crops which reflected the difference in their uptake capabilities and their further translocation to edible portion of the crops. Consequently, concentrations of Cd, Pb and Ni had crossed the safe limits for human consumption in all the crops. Percent contribution of fruits, corns to daily human intake for Cu, Ni, Pb and Cr was higher than that of leafy plants. Target hazard quotient of heavy metals also suggested that the test crops had potential for human health risk due to consumption of plants grown in the area having long term use of treated and

untreated waste water for irrigation. Consumption of these food grains with elevated levels of heavy metals might lead to the high level of body accumulation leading to related health disorders.

Dietary exposure to heavy metals, namely Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu) has been identified as a risk to human health through the consumption of crops [51]. Heavy metals are given special attention throughout the globe due to their toxic and mutagenic effects even at very low concentration [52]. An exploratory study was carried out by Khan et al. [53] and they measured arsenic and cadmium in foods from Matlab, a rural area in Bangladesh, that is extensively affected by arsenic and the economy is agriculture-based. Results revealed that the concentration of arsenic of cooking rice is reduced than that of raw rice. In contrast, concentration of cadmium did not decrease in cooked rice after discarding water. Compared to raw vegetables (e.g. arum), concentration of arsenic increased significantly ($p=0.024$) when cooked with arsenic-contaminated water. They also showed in their study that arsenic and cadmium have entered the food-chain of Bangladesh, and the cooking practices influence the concentration of arsenic but not of cadmium in cooked food (Fig 1.2) [53].

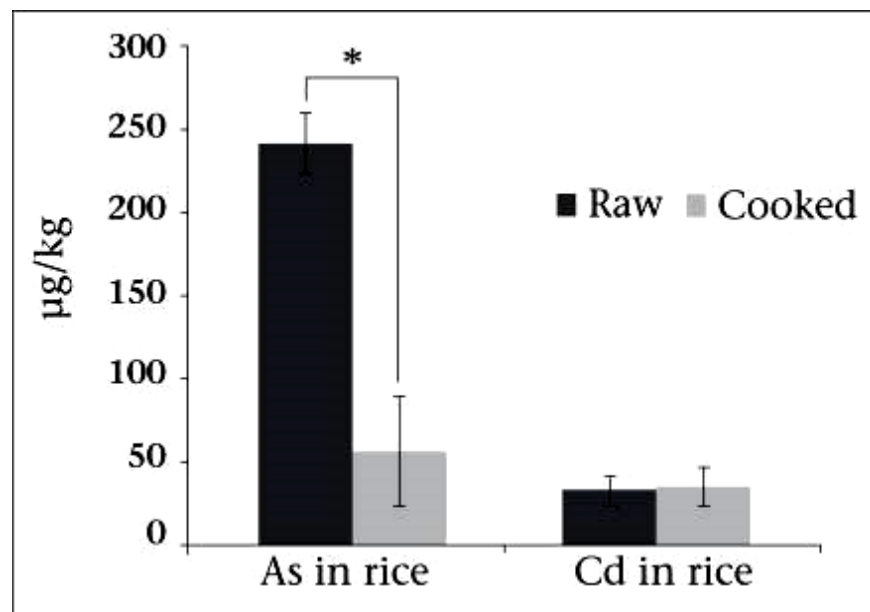


Figure 1.2 : Concentrations of arsenic and cadmium in raw and cooked rice

Dietary plants may contain hundreds of antioxidants. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance [54-56]. Saha and Zaman worked on concentration of selected toxic metals in groundwater and some cereals grown in Shibganj area of Chapai Nawabganj, Bangladesh [57]. This study assessed the extent of toxic metals, namely Pb, Cd, Cr, Mn and As in groundwater and some cereals collected from Shibganj area of Chapai Nawabganj, Bangladesh. They found that the mean concentrations of Pb, Cd and Mn in groundwater exceed the values of WHO, USEPA as well as Bangladesh Drinking Water Standards. However, arsenic content is within the permissible limit in terms of Bangladesh drinking water standards, but exceeds the WHO and USEPA values. Chromium is in negligible quantity in the examined groundwater samples. Results reveal wide variation in toxic metal content among the three cereal samples. In general, the mean toxic metal concentrations in cereals (rice, wheat and urid bean) are lower than the respective established safe limits for these elements, except for lead concentration in all samples.

Heavy metals are non biodegradable and persistent environmental contaminants, which may be deposited on surface soil and then absorbed into the tissues of food grains [58]. Plants may adsorb heavy metals from the deposits on the parts of the plants exposed to the polluted air and contaminated soils [51, 58 - 61]. Heavy metal contamination of vegetables may also occur due to irrigation with contaminated water [62, 63] and emission of heavy metals from the industries and vehicles during transport and marketing, the addition of fertilizers and metal based pesticides, the harvesting process, storage and/or at the point of sale [64].

To the best of our knowledge, most of the researches were done by collecting samples from sources like households, market-basket survey etc. Hence we have chosen land field in order to carry out research work under natural conditions by using model water, i.e., contaminated ground water and also by using natural organic fertilizers.

The present study was performed to evaluate the pattern of arsenic, lead and cadmium contamination in selective food grains (Sesame, Foxtail, Maize and Paddy) grown in preferred field in Puthia, Rajshahi, Bangladesh. This study also investigates the impacts of natural organic fertilizers towards reduction of As, Pb and Cd toxicity in food grains. That is finding out the potential ways for remedy of As, Pb and Cd toxicity in human food chain.

1.2 Overview of Arsenic, Lead and Cadmium

Arsenic is an element of group 15 and period 4 of the periodic table. Arsenic naturally occurs in many minerals, usually in conjunction with sulfur and metals, and also as a pure elemental crystal. Arsenic has some properties of metal such as it is electropositive, has high density and relatively low specific electrical resistivity, forms compounds with O, Cl and S, and also unstable hydride (AsH_3). Arsenic also resembles with non-metals in some properties like it is brittle, its oxides such as As_2O_3 and As_2O_5 are acidic, etc. Hence, it is classified chemically as a metalloid. Elemental arsenic is an α -crystalline metallic form. In compounds, arsenic typically exists in one of three oxidation states -3, 0, +3 and +5 [65].

Lead (Pb) is the heaviest member of the carbon family which remains in Group 14 and period 6 of the periodic table. But it behaves very differently from carbon. Lead is one of only a few elements known to ancient peoples, e.g., a small statue found in Egypt. Freshly cast lead is silvery in colour, but quickly turns dull grey to bluish grey, as its surface oxidizes in the presence of air. In compounds, lead typically exists in one of two oxidation states +2 and +4 [66].

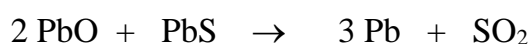
Cadmium (Cd) in its purest form, is a soft lustrous, silver-white, ductile, malleable metal. It is situated in groups 12 and period 5 in the periodic table. Cadmium and its congeners are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. Cadmium is much less abundant in the earth's crust. For its ductile and malleable properties, it is easily cut with a knife. It resembles with zinc in many of its physical properties. In compounds, cadmium typically exists in one of two oxidation states +1 and +2 [67].

Table 1.1 : Some notable properties of Arsenic, Lead and Cadmium

Property	Unit	Arsenic	Cadmium	Lead	Remark
Atomic number		33	48	82	
Atomic mass	g mol ⁻¹	74.922	112.411	207.200	
Electronic configuration		[Ar]3d ¹⁰ 4s ² 4p ³	[Kr]4d ¹⁰ 5s ²	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	Ground state
Oxidation state		-3,0, (+3),+5	0,+1,(+2)	0,(+2),+4	() represents Stable O.S.
Metallic radius	pm	139	151	154	
Ionic radius	pm	69 (+3)	109 (+2)	132(+2)	
Melting point	°C	816*	321	327.46	* (α form)
Boiling point	°C	615*	767	749	* (α form)
Latent heat of fusion	kJ K ⁻¹ mol ⁻¹	27.74	6.192	4.77	
Latent heat of sublimation	kJ K ⁻¹ mol ⁻¹	31.97		179.5	
Specific heat	J g ⁻¹ k ⁻¹	0.33	26.02	0.17	
Cristal shape		Rhombohedral	hcp	Cubic	
Density	g cm ⁻³	2.03	8.70	11.34 g cm ⁻³	At 20°C
Ionization enthalpy	KJ mol ⁻¹	947	866	715	1 st
Hardness		3.5	2.0	1.5	Mohs' scale

1.3 Chemical Properties of Arsenic, Lead and Cadmium

When arsenic is heated in air, it combines with oxygen to form arsenic trioxide [4As(s) + 3O₂ (g) → 2As₂O₃(s)]. Its oxides such as As₂O₃ and As₂O₅ are acidic. Arsenic does not dissolve in water or in most of cold acids. But it reacts with some hot acids to form arsenous acid (H₃AsO₃) or arsenic acid (H₃AsO₄). Like metal chloride, AsCl₃ undergoes hydrolysis reaction partially. Lead (Pb) is a moderately active metal in water and in most cold acids. It reacts more rapidly with hot acids. It does not react with oxygen in the air readily and does not burn. Various oxidized forms of lead are easily reduced to the metal, e. g.,



Lead is not attacked by sulfuric or hydrochloric acids. But it dissolves in nitric acid as follows:



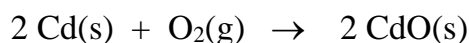
When Pb is heated with nitrates of alkali metals, metallic lead oxidizes to form PbO (also known as litharge), leaving the corresponding alkali nitrite. It is soluble

in nitric and acetic acids, from which solutions it is possible to precipitate halide, sulfate, chromate, carbonate (PbCO_3), and basic carbonate salts of lead [$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$]. Its sulfide can also be precipitated from acetate solutions. These salts are all poorly soluble in water. Lead dioxide (PbO_2), a powerful oxidizing agent, dissolves in alkali hydroxide solutions to form the corresponding plumbates [68].



Lead also has an oxide with mixed +2 and +4 oxidation states, red lead (Pb_3O_4), also known as minim. Lead readily forms an equi-molar $\text{Pb}(\text{OH})_2$ with sodium metal that reacts with alkyl halides to form organo-metallic compounds of lead such as tetraethyl lead.

Cadmium (Cd) reacts slowly with oxygen in moist air at room temperatures, forming cadmium oxide [69]. Although cadmium usually has an oxidation state of +2, it also exists in the +1 state. Cadmium is a moderately active metal in water and in most cold acids. It dissolves in slowly. It reacts more rapidly with hot acids. Cadmium burns in air to form brown amorphous cadmium (II) oxide (CdO); the crystalline form of this compound is a dark red which changes color when heated, similar to zinc oxide.



Hydrochloric acid, sulfuric acid and nitric acid dissolve cadmium by forming cadmium chloride (CdCl_2), cadmium sulfate (CdSO_4), or cadmium nitrate [$\text{Cd}(\text{NO}_3)_2$] respectively. The oxidation state +1 can be attained by dissolving cadmium in a mixture of cadmium chloride and aluminium chloride, forming the Cd_2^{2+} cation, which is similar to the Hg_2^{2+} cation in mercury (I) chloride [69].



It reacts with halides to form CdX_2 . But it does not react with water.

1.4 Principal Compounds of Arsenic, Lead and Cadmium and Their Uses

Arsenic has a fascinating history as a healer and killer. Early physicians, recommended arsenic for the treatment of some diseases, e.g., arsephenamine was used to treat syphilis. Arsenic in its inorganic form is used for the production of pressure-treated wood. Arsenic is also used in the leather tanning industry as a preservative. It is widely used as a weed killer and also used as an insecticide. Some binary compounds of arsenic are halides, oxides, hydrides, sulfides, telluride's and selenides. As_2O_3 is widely used laboratory reagent. All these arsenic compounds have been used in different sectors.

A relatively small amount of lead is used to make lead compounds. Although the amount of lead is small, the variety of uses for these compounds is large. For examples, some important lead compounds such as lead acetate ($Pb(C_2H_3O_2)_2$) and lead naphthenate ($Pb(C_7H_{11}O_2)_2$) are used as insecticides, waterproofing, varnishes, dyeing of cloth, production of gold, hair dye, wood preservative, paint and varnish drier. Lead antimonite ($Pb_3(SbO_4)_2$) is used as staining of glass, porcelain and other ceramics. Lead azide ($Pb(N_3)_2$) is used as a "primer" for high explosives. Lead chromate ("chrome yellow", $PbCrO_4$) as industrial paints (use restricted by law). Lead fluoride (PbF_2) is used to make lasers, specialized optical glasses. Lead iodide (PbI_2) is used in photography and cloud seeding to produce rain. Lead naphthenate ($Pb(C_7H_{12}O_2)$) is utilized for wood preservative, insecticide, additive for lubricating oil, paint and varnish drier. Lead phosphite ($2PbO.PbHPO_3$) is used to screen out ultraviolet radiation in plastics and paints. Lead stearate $Pb(C_{18}H_{35}O_2)_2$ is commonly used to make soaps, greases, waxes, paints, lubricant, drier for paints and varnishes. Lead telluride ($PbTe$) is used to make semiconductors, photoconductors, and other electronic equipment [70].

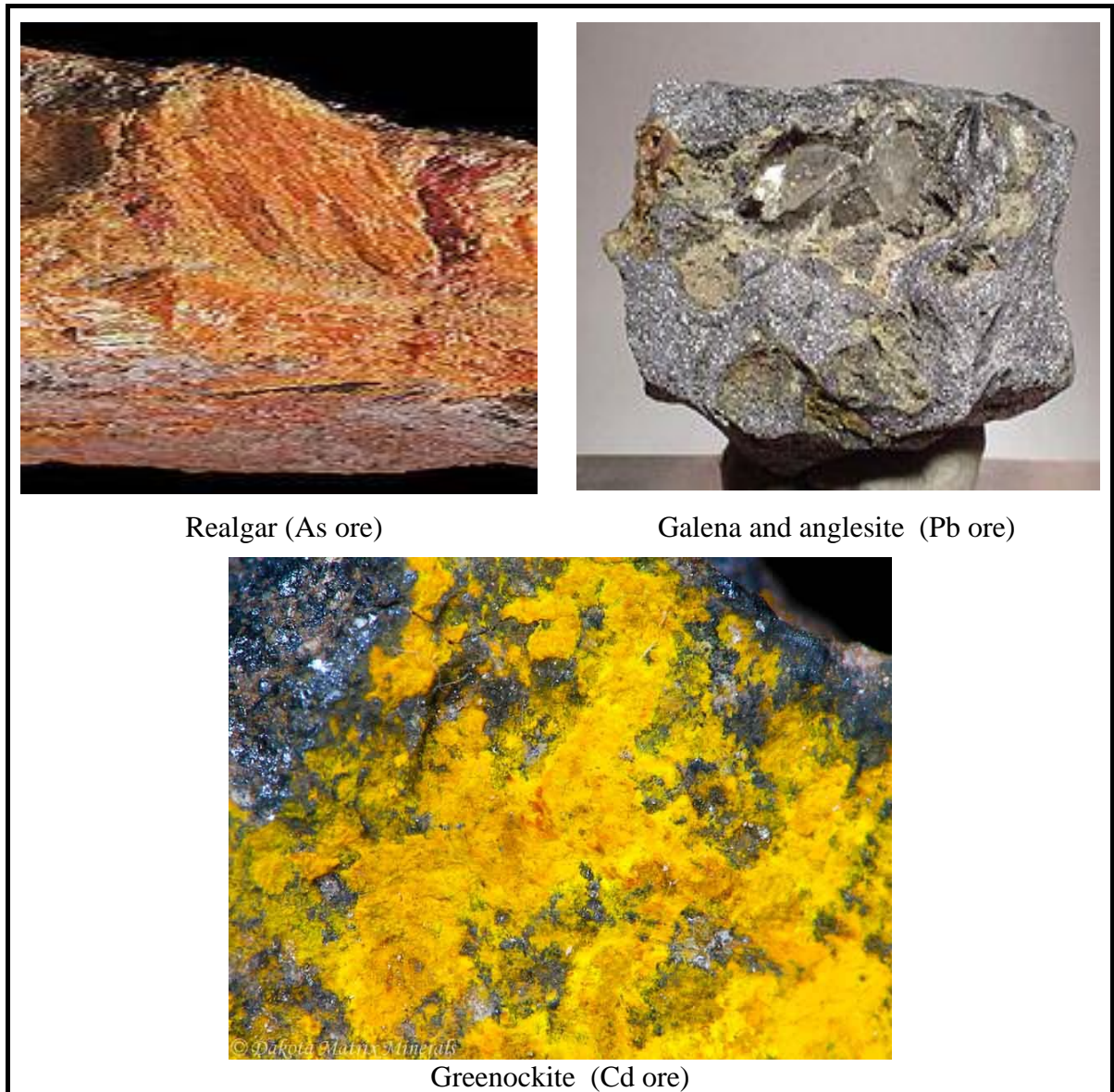


Figure 1.3 : Ores of arsenic, lead and cadmium

A popular use of cadmium compounds is as coloring agents. The two compounds most commonly used are cadmium sulfide (CdS) and cadmium selenide (CdSe). The sulfide is yellow, orange, or brown, while the selenide is red. These compounds are used to color paints and plastics. There is concern about possible environmental effects of using cadmium. However, no satisfactory substitutes have been found [70]. Cadmium salts of organic acids, generally cadmium laurate or cadmium stearate in combination with barium sulfate were widely used in the past as heat and light stabilizers for flexible polyvinyl.

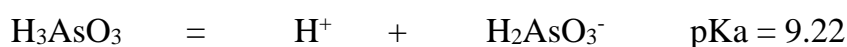
1.5 Solution Chemistry of Arsenic, Lead and Cadmium

Most of the chemical reactions take place in aqueous solution. The reacting substance should be dispersed condition in a suitable medium before appreciable interaction taking place. Arsenic chemistry in aqueous systems is quite complex because it can exist in four oxidation states. The valence and nature of its species depends on the oxidation-reduction conditions and pH of the water. The chemistry of arsenic with reference to acid-base, oxidation-reduction, adsorption-desorption and precipitation-dissolution are as follows:

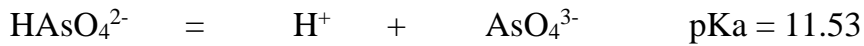
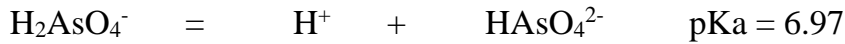
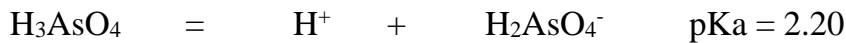
Acid-Base Chemistry: Arsenic is usually found as an anion with acid characteristics in the trivalent (+3) and pentavalent (+5) forms. The pentavalent (+5) arsenate species are H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} . The trivalent (+3) arsenite species include H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-} . The pentavalent arsenic species are predominant and thermodynamically stable in the oxygen-rich aerobic environments such as surface water, whereas trivalent arsenic species are predominant in moderately reducing anaerobic environments such as groundwater [71].

The oxides of both arsenic (III) and arsenic (V) are soluble in water. The dissolution implies direct reaction with water, hydration, where the oxides behave like non-metals and exhibit acidic character. Arsenic (III) forms arsenious acid (also called arsonic acid), while arsenic (V) forms arsenic acid (also called arsinic acid). The two acids dissociate to form respective arsenite and arsenate ions as shown in the following reactions[72-73]:

Dissociation of arsenious acid:



Dissociation of arsenic acid:



The predominance diagram of arsenic species as a function of pH is shown in Figure 1.4 [72].

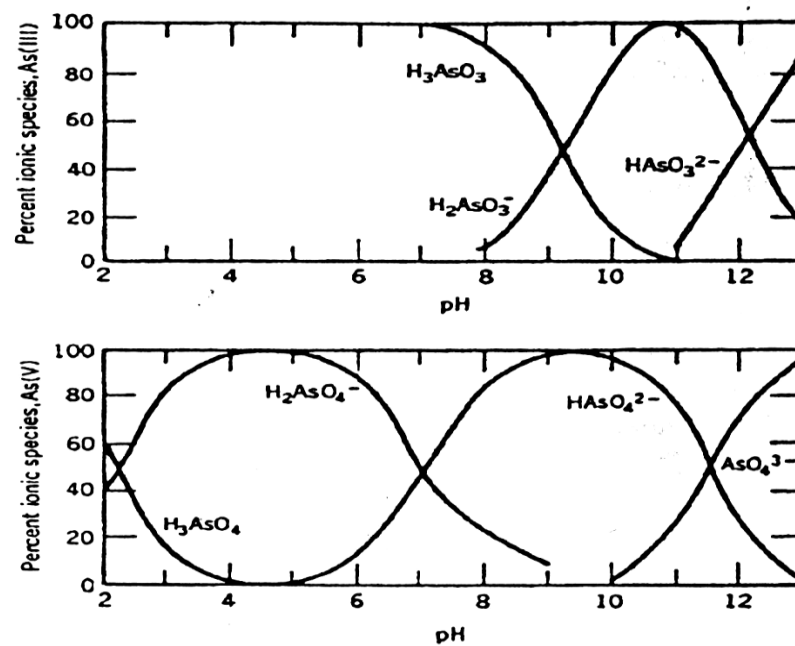


Figure 1.4 : Predominance diagram of As (III) and As(V) as a function of pH [72]

From the above figure it is evident that arsenic acid is stronger than arsenious acid. Within the pH range of natural water (particularly groundwater) (pH 6-9), the trivalent inorganic arsenic is found as non-dissociated arsenious acid (H_3AsO_3); while pentavalent arsenic is primarily found as the ionized dihydrogen arsenate (H_2AsO_4^-) and monohydrogen arsenate (HAsO_4^{2-}). The stability and the predominance of the arsenic species in the aquatic environment at different pH range [74] is shown in the following Table 1.2.

Table 1.2 : Stability and predominance of arsenic species at different pH range

pH range	0 – 9	10 – 12	13	14
As (III)	H_3AsO_3	H_2AsO_3^-	HAsO_3^{2-}	AsO_3^{3-}
pH range	0 – 2	1 – 6	7 – 11	12 – 14
As (V)	H_3AsO_4	H_2AsO_4^-	HAsO_4^{2-}	AsO_4^{3-}

Lead has three oxidation states that should be considered when looking at aqueous reactions, IV, II and 0. Pb(IV) is so insoluble that the species it forms do not need to be considered in the aqueous phase. Pb (II) dissolves in the aqueous phase to form six compounds including Pb^{2+} , $\text{Pb}(\text{OH})_2$, PbCO_3 , $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and $\text{Pb}(\text{OH})_3^-$. Finally, Pb(0) as with Pb (IV) has a negligibly small dissolved concentration [75-81].

Solution chemistry of lead depends on its oxidation state, pH of the solution and the equilibrium solubility of the solution. The dissolution rates of both lead carbonate and lead phosphate increase with decreasing pH. Dissolution rates of lead carbonates and phosphates are comparable to those of calcium carbonates and phosphates. Dissolution rates are lower at lower temperatures.

In solution cadmium exists either dissolved or as part of insoluble complexes. Soluble cadmium is quite mobile in water and soil solution. Solubility is promoted by acidic condition (low pH value). Transformation processes for cadmium in soil solution is mediated by sorption form and desorption to water and include precipitation, dissolution, complexation and ion exchange. Low pH of soil solution tends to increase the availability of cadmium. Partitioning into the sediment is enhanced by precipitation and sorption to mineral surfaces and organic materials as well as by action of sediment bacteria. The levels in the sediment tend to be at least an order of magnitude higher than in the overlying water column. High levels of organic material in the water promote formation of organic complexes with cadmium which are poorly soluble. Also in reducing environment, cadmium may precipitate out as cadmium sulfide.

1.6 Sources of arsenic, lead and cadmium

The natural sources of arsenic, lead and cadmium include minerals, rocks, sediments, soils and the atmosphere. A number of sources have been observed as a major constituent in minerals, including elemental arsenic, lead, cadmium and their sulphides and oxides. A list of some of the most common arsenic, lead and cadmium minerals [77] are given in Table 1.3. Most are ore minerals.

Table 1.3 : Major arsenic, lead and cadmium minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal vein
Nicolite	NiAs	Vein deposits norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs Secondary mineral formed by oxidation of arsenopyrite,
Arsenolite	As ₂ O ₃	Native arsenic and other As As minerals
Orpiment	As ₂ S ₃	Hydrothermal veins, hot springs, volcanic sublimation product
Arsenopyrite	FeAsS	The abundant As mineral, dominantly
Scorodite	FeAsO ₄ .2H ₂ O	
Native lead	Pb	Secondary mineral, smelter wastes ;
Galena	PbS	Native born, brass, Galilean;
Anglesite	PbSO ₄	Mineral galena; Mineral anglesite, Quartz, Djurleite, Covellite, including a bladed microscopic lead sulfate silicate;
Cerussite	PbCO ₃	General mineral, silica and quartz;
Minim	Pb ₃ O ₄	
Chrome yellow	PbCrO ₄	
Mimetite	PbCl ₂ Pb ₃ (AsO ₄) ₂	
Native Cadmium	Cd	
Cadmium sulphide	CdS	
Sphalerite	ZnS with Cd	

1.7 Worldwide Scenario of Groundwater Contamination

As far as 70 countries are globally affected directly or indirectly with arsenic contamination in drinking water and 38 countries are affected more severely at present. The major affected countries of arsenic poisoning include Argentina, Chile, Mexico, Taiwan, and some parts of the United States. At the last quarter of 20th century three Asian countries (Bangladesh, China, and India) come to lime light due to their suffering from groundwater arsenic contamination. The major source of arsenic contamination was contaminated hand tube-wells. As of 2010 September, 13 Asian countries are arsenic affected and the level of arsenic contamination in Asian countries is more severe than the rest of the world. In India,

flood plains of all the states in Ganga and Brahmaputra rivers are arsenic affected. Access to safe water supply is one of the most important factors of health and socio-economic development [82]. More than 150 million people are affected worldwide by arsenic contamination in 70 countries, out of which 30 million people in India are at risk [80]. Arsenic contaminations in groundwater depend on the type of environments and sources under which they are developed. Arsenic is toxic in nature and the excess quantity of its use in drinking water leads to several health hazards.

Drinking water can also have dangerously high levels of lead. As many as one of five Americans are exposed to dangerously high levels of lead in water. Lead rarely found in water at its source. The water becomes contaminated as it moves through the water distribution system. The lead can come from lead pipes or connectors, lead solder used to connect pipes and fumes, brass fixtures, and lead lined tanks in water coolers. The most serious problems come when the water is acidic. The acidic water will greatly increase the amount of lead that will leech from lead plumbing. In 1986, the Federal Government has made it illegal to use lead solder (greater than 2% lead in solder) or nine (9%) in waterlines [83]. Newer pipes may pose more of a hazard than older pipes. In older pipes, a mineral scale develops on the interior of the pipe, preventing the lead from leaching into the water. Newer pipes do not have this scale.

Components causing lead contamination include lead pipes, lead-based copper piping solders and brass fixtures. Lead pipes for conveying drinking. Water has been used for centuries because of its flexibility, durability and long life. Lead pipes are used in the United States however, lead concentrations exceeding the regulation levels owing to lead pipe were reported in a number of cities. Levels of lead contamination found in natural raw waters, treatment plants or in distribution mains are typically low and rarely exceed drinking water regulations. However, high lead levels are usually found at consumers taps. Contamination of lead in groundwater origin from the dissolution of lead from soil and earth crust. Lead particulate from the combustion of leaded gasoline, fossil and ore smelting can

contaminate local surface water by surface runoff. Lead itself is a minor component in the earth crust. A wide distribution of lead in sedimentary rock and soils are reported. An average lead content of 10 ppm is usually found in upper ground soil and 7 to 12.5 ppm in sedimentary rock [83]. This means that lead generally present in a form of carbonates and hydroxide complex in soil. The solubility of lead controls the lead dissolution into surrounding water. Strongly absorption by soil and complexion by humus can further limit the lead concentrations in surface waters and groundwater. Children are more affected by the same amount of lead from these and other sources than adults. Foods such as baby formula may pose a significant lead poisoning hazard if lead contaminated water is used in its preparation. As many as 5% of children have high enough lead intake through water and foods to cause health risks [84, 85].

Waters sources near cadmium emitting industries, both with historic and current operations have shown a marked elevation of cadmium in water sediments and aquatic organisms [86, 87]. In surface water and ground water, cadmium can exist as the hydrated ion or as ionic complexes with other inorganic or organic substances.

Cadmium in soluble complex forms may migrate in water. On the other hand, cadmium is relatively nonmobile in insoluble complexes or adsorbed to sediments. Cadmium is taken up and retained by aquatic and terrestrial plants and is concentrated in the liver and kidney of animals that eat the plants [86-88]. Cadmium exposure through drinking water supply is a minor concern for the U.S. population. In supply water the cadmium concentration limit is to $<5\mu\text{g/L}$ [89]. Cadmium may be released to water by natural weathering process, by discharge from industrial facilities or sewage treatment plants, atmospheric deposition, by leaching from landfills or soils or phosphate fertilizers [89, 90]. Cadmium may also leach into drinking water supplies from pipes in the distribution system [89]. The average level of cadmium in ocean water has been reported between $<5\text{ mg/L}$ and 10 mg/L higher level of cadmium is reported in water near coastal areas and in marine phosphates and phosphorities [91].

1.8 Occurrence of Arsenic, Lead and Cadmium in Groundwater of Bangladesh

Groundwater arsenic problem in Bangladesh is explained by a number of hypotheses. The most widely accepted hypothesis is “Oxy-hydroxide Reduction” and it was supported by extensive modeling and in consistence with the findings of many workers, e.g., BGS/DPHE [77].

A nationwide survey [77] jointly conducted in Bangladesh in 1999 by the British Geological Survey (BGS) Team, UK and Department of Public Health Engineering (DPHE), Bangladesh suggests that the groundwater arsenic problem in Bangladesh arises on account of an unfortunate combination of three factors. These are geological source of arsenic (As is present in the aquifer sediments), mobilization of arsenic (As) is released from the sediments to the groundwater and transport of arsenic (As) is flashed away in the natural groundwater circulation.

Geological source of arsenic: A number of anthropogenic explanations had been given for the occurrence of arsenic in groundwater. While it is possible that some may explain isolated cases of arsenic contamination, none of the anthropogenic explanations can account for the regional extent of groundwater contamination in Bangladesh and West Bengal. There is no doubt that the source of arsenic is of geological. There have been insufficient analyses of the alluvial sediments to provide a regional picture but current data suggest that arsenic is usually in the range 2-20 mg/kg; only slightly greater than typical sediments (2-6 mg/kg). However, it appears that an unusually large proportion of the arsenic is present in a potentially soluble form. The high groundwater arsenic concentrations are associated with the grey sands rather than the brown sands. There is a good correlation between extractable iron and arsenic in the sediments and a relatively large proportion (often half or more) of the arsenic can be dissolved by acid ammonium oxalate, an extract that selectively dissolves hydrous ferric oxide and other poorly ordered oxides. It therefore appears likely that a high proportion of the arsenic in the sediments is present as adsorbed arsenic.

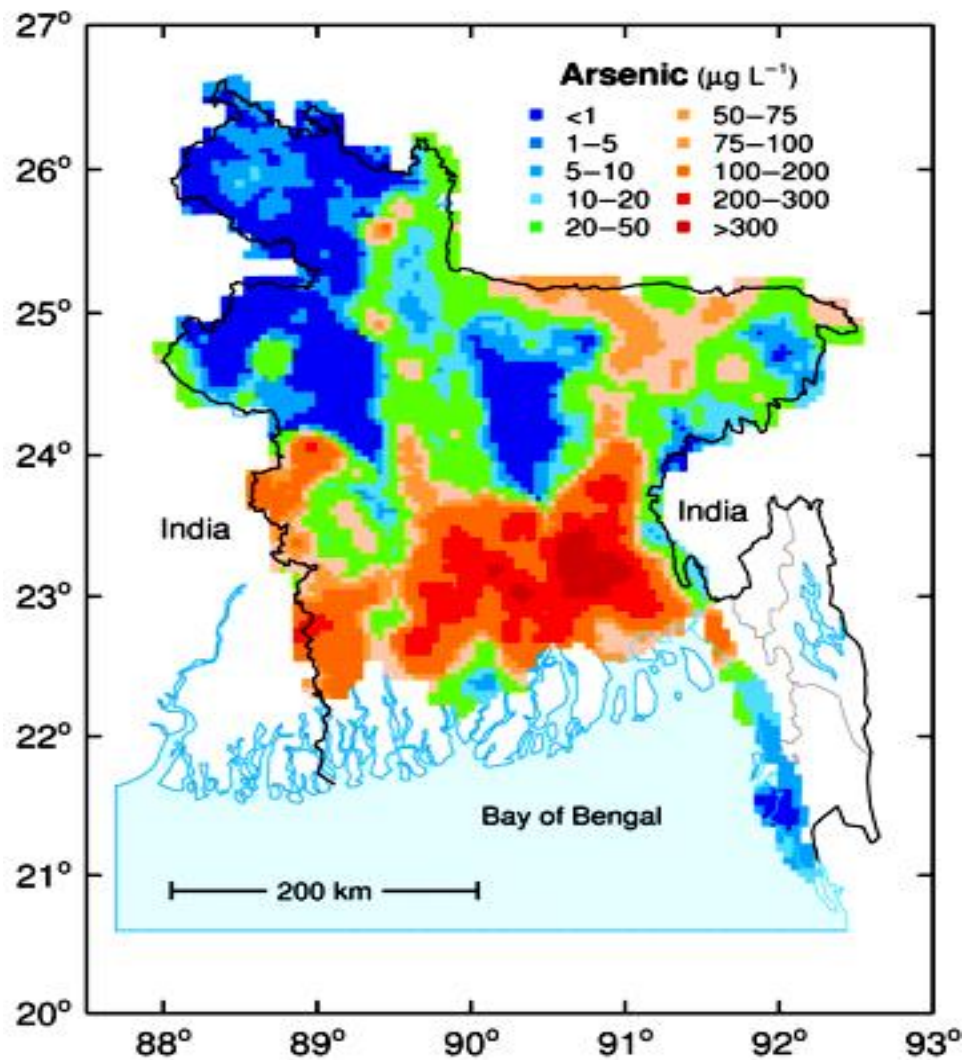


Figure 1.5 : Groundwater As Contamination Scenario in Bangladesh

The greatest arsenic concentrations are mainly found in the fine-grained sediments especially the grey clays. A large number of other elements are also enriched in the clays including iron, phosphorus and sulphur. In Nawabganj, the clays near the surface are not enriched with arsenic to any greater extent than the clays below 150 m. It is likely that the original sources of arsenic existed as both sulphide and oxide minerals. Oxidation of pyrite in the source areas and during sediment transport would have released soluble arsenic and sulphate. The sulphate would have been lost to the sea but the arsenic, as As(V), would subsequently have been sorbed by the secondary iron oxides formed. These oxides are present as colloidal-sized particles and tend to accumulate in the lower parts of the delta. The

finer-grained sediments tend to be concentrated in the lower energy parts of the delta. This is likely to be responsible for the greater contamination in the south and east of Bangladesh.

The map of arsenic contaminated groundwater shows that highly contaminated areas are found in the catchments of the Ganges, Brahmaputra and Meghna rivers strongly suggesting that there were multiple source areas for the As.

Mobilisation of the arsenic – redox processes: Microbial oxidation of the organic carbon has depleted the dissolved oxygen in the groundwater. This is reflected by the high bicarbonate concentrations found in groundwater in recent sediments. There is a relationship between the degree of reduction of the groundwaters and the arsenic concentration – the more reducing, the greater the arsenic concentration.

Transport of arsenic within the aquifers: Present groundwater movement is very slow because of the extremely low hydraulic gradients found in the delta region. Except where modified by pumping, groundwater circulation is largely confined to the shallow layers affected by local topographic features and the presence of rivers. Close to rivers, the enhanced groundwater flow may lead to a greater dispersion of arsenic along river banks. Annual fluctuations of the water table, typically about 5 m, will affect groundwater and arsenic movement in the shallow layers. There may have been some flushing of arsenic from the shallowest layers.

At greater depths, groundwater moves slowly in response to the low regional gradients. This is consistent with the old age of the waters. The lateral and vertical spread of contaminants is slow even without considering the retardation due to sorption. Modeling suggests that even in the most permeable layers, arsenic movement is likely to be limited to a few meters a year.

1.9 Scale and Magnitude of Groundwater Contamination in Bangladesh

The worst arsenic affected Bangladesh is one of the countries of the world, as its 61 out of 64 districts have arsenic contaminated groundwater above World Health Organization (WHO) level of 10 mg/L. Arsenic contamination in groundwater from the Padma-Meghna plain was first reported in 1995 [92, 93]. During 1998, 41 of the 64 districts in Bangladesh were identified as having concentrations of arsenic in groundwater exceeding 50 µg/L [94]. In a preliminary study, workers analyzed 52,000 tube well-water samples from Bangladesh and found that 2,000 and 2,450 villages, had arsenic levels of >50 µg/L and 10 µg/L respectively [95]. The survey revealed that 43.0% of the water samples exceeded 10 µg/L, and 31.0% exceeded 50 µg/L. They identified arsenic in hand-tubewell water samples >50 µg/L (permissible limit of arsenic in drinking-water in India and Bangladesh) in 50 of the 64 districts. The populations directly and indirectly at risk were 52 and 32 million respectively. [96, 97].

The area and population of 50 arsenic-affected districts in Bangladesh are 118,849 sq km and 105 million respectively compared to the total area and population of the country—148,393 sq km and 120 million respectively [97]. This does not mean that all the affected people are drinking arsenic-contaminated water and suffering from arsenic-related diseases, but no doubt they are at risk. The highest conc. of arsenic in groundwater of Bangladesh was found as 3,200 µg/L [98, 99]. The groundwater of Bangladesh is moderately contaminated with lead (Pb) and least contaminated with cadmium (Cd) [94].

Table 1.4 : Groundwater As, Pb and Cd Contamination the highest concentration.

Metals	WHO recom. value / µg L ⁻¹	Highest Conc. in Bangladesh / µg L ⁻¹	Highest Conc. in World / µg L ⁻¹
Arsenic (As)	10	2,500	11,500 (Argentina)
Lead (Pb)	10	28.60	7,400 (Florida, USA)
Cadmium (Cd)	3	0.66	4,000 (WHO)

1.10 Arsenic, Lead and Cadmium in Soil

Several field studies conducted in Bangladesh showed that irrigation with As-rich groundwater resulted in elevated topsoil As concentrations of up to $\sim 80 \text{ mg kg}^{-1}$ in the upper paddy soil layers, whereas background soil As contents were typically $< 10 \text{ mg kg}^{-1}$ [94, 96-98]. While increasing irrigation, As concentrations in topsoil of paddy fields were reported to decrease significantly during the monsoon season in regions with pronounced monsoon flooding [94]. In regions with less intense flooding during the monsoon season nearly all As added through irrigation was retained in the soil [98]. Several field studies reported relations between As in soil/irrigation water and rice plants [95, 97-101]. Pot experiments with natural or spiked soil/irrigation water As concentrations [95, 99-102] revealed similar trends and yield reduction was observed to occur at high As concentrations [102,103]. Panaullah et al. [98] reported approximately 80% grain yield decrease from ~ 9 to $\sim 2 \text{ t ha}^{-1}$ (i.e. by a factor of 4.5) across a soil As gradient of ~ 80 to $\sim 10 \text{ mg As kg}^{-1}$. Khan et al. [104] supported these findings in a field trial and reported yield reductions of boro and aman rice of up to 80% . A global “normal” range of 0.08 - 0.20 mg kg^{-1} for As in rice grain was recently derived by Zavala and Duxbury [105]. Approximately half of the samples from Bangladesh considered in their study contained more than the upper limit of this range. Meharg and Rahman reported grain As values up to 1.84 mg kg^{-1} from southwestern Bangladeshi districts, showing the highest soil As concentrations within the country. Recently it was found that in addition to causing elevated grain As levels, increasing soil As concentrations may also affect human nutrition by decreasing the content of important nutrients such as Se, Ni and Zn in rice grain grown in the field. Williams et al. [95] showed that rice plants physiologically control As transfer from straw into grain, resulting in exponentially decreasing transfer factors with increasing straw As content. Adomako et al. [100] recently confirmed this trend for data from Bangladesh. They further showed that straw and grain As are correlated with soil As and that As was more efficiently transferred to grain in the Bangladeshi plants compared to the European and US grown plants. According to the authors, this

difference in the grain to straw transfer is probably due to differing climatic conditions, i.e., temperate versus subtropical, or inherent cultivar differences [101].

The concentrations of lead in soil are typically in the range of 5-100 mg/kg [106], whereas lead from anthropogenic sources may result in concentrations exceeding 10,000 mg/kg. In particular, soil in or adjacent to lead smelters, lead mines, houses painted with lead paint, orchards treated with lead arsenate, and urban areas where there has been heavy automobile traffic is likely to contain high concentrations of lead. Ingestion of soil may therefore result in exposure to lead. This may occur by direct ingestion, deposition of soil on the hands, contamination of food, or by inhalation. The relationship between soil and lead varies greatly by soil type [106], perhaps due to behavioural differences among individuals and differences in the rates of absorption of lead from different sources.

The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm, but much higher and much lower values have also been cited depending on a large number of factors. Igneous and metamorphic rocks tend to show lower values, from 0.02 to 0.2 ppm whereas sedimentary rocks have much higher values, from 0.1 to 25 ppm. Naturally, zinc, lead and copper ores, which are mainly sulphides and oxides, contain even higher levels, 200 to 14,000 ppm for zinc ores and around 500 ppm for typical lead and copper ores. The raw materials for iron and steel production contain approximately 0.1 to 5.0 ppm, while those for cement production contain about 2 ppm. Fossil fuels contain 0.5 to 1.5 ppm cadmium, but phosphate fertilizers contain from 10 to 200 ppm cadmium [107].

Cadmium in soils must be distinctly classified in three separate areas with regard to their relative effects on human health and the environment. These three areas are agricultural soils, non-agricultural soils, and controlled landfills. Cadmium in controlled landfills is virtually immobile, and is unlikely to have any effect on human health or the environment simply because it is so well contained [108]. Cadmium in non-agricultural soil will generally not affect human health

because it does not enter the food chain readily. Cadmium in agricultural soils is likewise relatively immobile under normal conditions, but could become more mobile under certain conditions such as increased soil acidity and usage of phosphate fertilizers, manure or sewage sludge.

Since cadmium is a naturally occurring component of all soils, all food stuffs will contain some cadmium and therefore all humans are exposed to natural levels of cadmium. Although much attention has been focused upon the cadmium content of agricultural soils, it is important to recognize that the cadmium content of food items varies more as a function of the nature of the crop grown and the agricultural practices followed. Except in cases of extreme contamination, the concentration of cadmium in soils is not the primary determinant of cadmium in the human diet. For example, leafy vegetables and potato tubers naturally accumulate higher levels of cadmium than do fruits and cereals [103]. Moreover, tillage and crop rotation practices similarly have a greater impact upon the cadmium content of food than does the concentration of cadmium in soils [109]. Cadmium absorption may also depend on other factors.

1.11 Biotransformation

Ordinarily, the removal of electrons from or addition of electrons to the atom influences the chemical activity and therefore the ability of metallic elements to interact with tissue targets (ligands). Examples of charge relevance in crossing lipid barriers are represented by $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Hg^+/Hg^0 passages. Among the other metabolic transformations, the most important is bioalkylation, where mercury, tin, and lead undergo in microorganisms, whereas arsenic and selenium are additionally bioalkylated as part of their metabolic pathways in higher organisms. Alkylation reactions produce more hydrophobic species, leading to an increased bioavailability, penetration to cells and through the blood–brain barrier, as well as accumulation in fatty tissues. Biotransformation of arsenic involves methylation, leading to the formation and excretion of monomethylated and dimethylated compounds (Fig. 1.6). In most mammals, only trivalent arsenic species are

methylated i.e. in the metabolism, reduction and methylation alternate. Possibly, As (III) is bound to a dithiol, a carrier protein, before the methyl groups are attached. S-Adenosyl methionine is the main methyl donor in arsenic methylation.

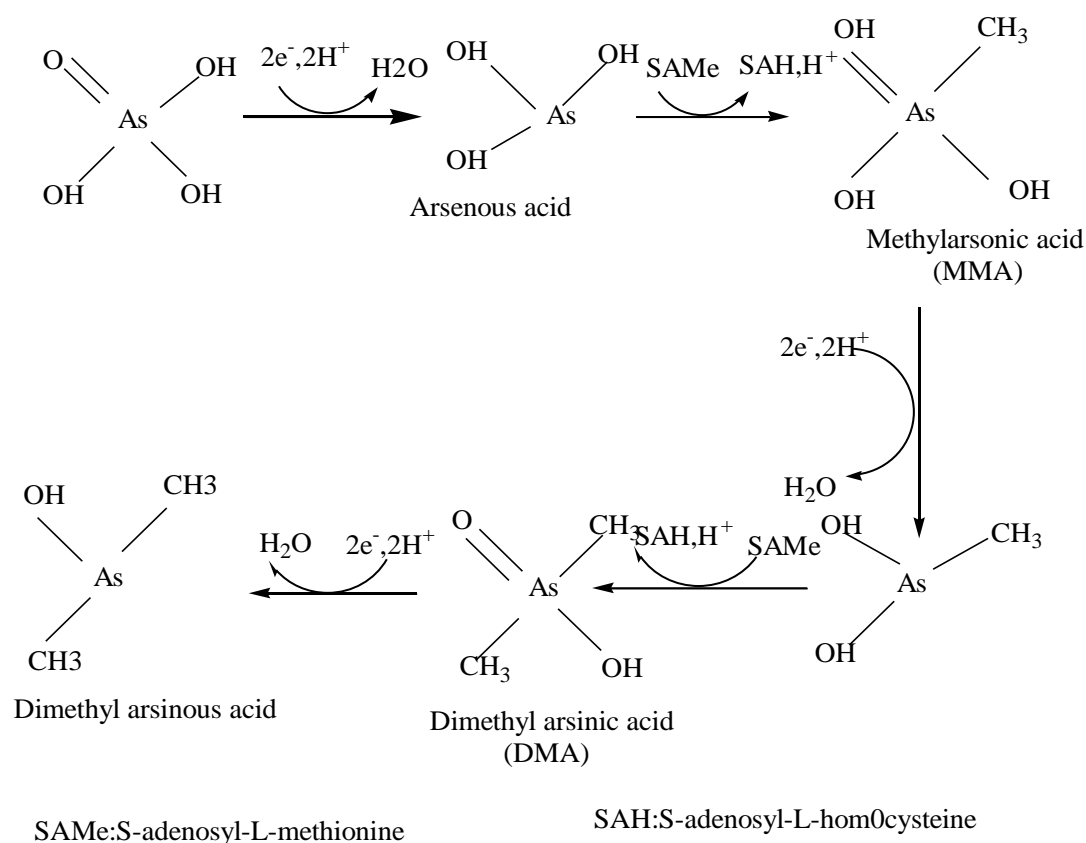


Figure 1.6 : Arsenic Biotransformation

The liver is an important site of arsenic methylation, especially following ingestion, when the absorbed arsenic initially passes the liver. This is supported by studies showing a marked improvement in the methylation of arsenic in patients with end-stage liver disease following liver transplantation. [110]

The rate of absorption of lead after ingestion can range from 3 to 80%. It is heavily influenced by food intake, much higher rates of absorption occurring after fasting than when lead is ingested with a meal. This effect may be due mainly to competition from other ions, particularly iron and calcium, for intestinal transport pathways. Absorption is also affected by age, the typical absorption rates in adults and infants being 10% and 50%, respectively [111, 112].

Several pharmacokinetic models have been developed in an attempt to relate exposure to lead concentrations in blood and other tissues. A model developed by the United States Environmental Protection Agency (1994) of lead in air, diet, dust, paint, soil, and drinking-water allows modeling of distribution in a 10-compartment model that includes plasma, erythrocytes, trabecular bone, and cortical bone. The parameters in the model were chosen to represent children, and the model presumes that exposure and pharmaco-kinetics are in a steady state. Population distributions are derived by using the model output to estimate the population geometric mean and a fixed geometric standard deviation. The concentration of lead in blood is the most widely used biomarker of exposure, largely because it is the measure that is the easiest to obtain. Blood lead concentration is typically reported in micrograms per deciliter. Because blood concentrations are strongly influenced by recent exposure, they may not reflect long-term exposure, particularly to intermittent or infrequent, high levels. A marker that was widely used before techniques for measuring blood lead became widely available is plasma delta-aminolaevulinic acid dehydratase activity, which correlates strongly with blood lead concentration [111]. Related markers that have sometimes been used are the urinary and blood concentrations of delta-amino-laevulinic acid and plasma d-aminolaevulinic acid synthetase. Both of these markers correlate positively with exposure to lead.

O'Flaherty [113] developed another pharmacokinetic model which represents the temporal relationships in the transfer of lead between blood, bone, and other tissues. Lead that is deposited in physiologically inactive cortical bone may persist for decades without substantially influencing the concentrations of lead in blood and other tissues [113], lead that is deposited in physiologically active trabecular bone is in equilibrium with blood. The accumulation of high concentrations in blood when exposure is reduced may be due to the ability of bone to store and release lead. Dietary lead that is not absorbed in the gastrointestinal tract is excreted in the faeces. Lead that is not distributed to other tissues is excreted through the kidney and to a lesser extent by biliary clearance [112].

In human body, Cd is basically taken up by the liver. In the liver, Cd can bind with glutathione (GSH) and be excreted into bile. Moreover, Cd can bind to metallothionein (MT) and be stored. Some Cd bound to MT leaks into the plasma and then is taken up by the kidney. The balance between CdMT and nonbound Cd in renal tissue may be responsible for the degree of Cd nephrotoxicity [114,115]. Therefore, susceptibility to Cd toxicity among individual may probably be related to genetic variations of Cd-metabolizing enzymes. Glutathione S-transferase (GST) gene is one of the potential candidate susceptibility genes-because it plays a significant role in Cd biotransformation and detoxification [116].

Lately, the possibilities of applying molecular techniques to toxicogenetics are considerably focused, especially for medical investigations and determinations of factors influencing chemical poisonings. These include biochemical and genetic determinants related to acute and chronic effects. To our knowledge, there are limited data on genetic predisposition influence on cadmium detoxification in the human body. Therefore, this study investigated the association of glutathione S-transferase genes (GSTT1, GSTM1, and GSTP1) polymorphisms and blood cadmium concentration in a nonoccupationally exposed population.

1.12 Toxicity of Arsenic, Lead and Cadmium

The relative toxicity of different As species to plants depends on a range of factors including experimental conditions and plant species and examined plant parameters [117]. Therefore, one should be cautious about using a generalized classification of As species according to toxicity. Taking that into account, inorganic As is generally regarded as being more toxic than organic As, with As (III) being the more toxic form [118]. Most toxicity experiments have been carried out with plants grown in water only (hydroponics). Such a design can be useful to study, for example, uptake mechanisms, internal transport, metabolism, and toxic effects. The design is however not suitable to generate toxicity data to evaluate concentrations in the environment because all interactions with the soil matrix influencing bioavailability are neglected. Exposure to arsenic is mainly via intake of food and drinking water,

food being the most important source in most populations. Long-term exposure to arsenic in drinking-water is mainly related to increased risks of skin cancer, but also some other cancers, as well as other skin lesions such as hyperkeratosis and pigmentation changes. Occupational exposure to arsenic, primarily by inhalation, is causally associated with lung cancer. Clear exposure-response relationships and high risks have been observed.

Toxicity experiments are also carried out with plants grown in soil to which a certain amount of As is added (spiked soil) shortly before the experiment. This setup has various limitations as well. Adding As to reach a certain soil concentration suggests that the results are representative of the field. However, in the field As is added over a number of years. The prolonged contact time between As and the soil in the field can result in a lower solubility of As and therefore lower uptake by plants in the field. Therefore, experiments with spiked soils often result in an overestimation of the adverse effects compared to the actual field situation [119].

In other studies, As has been added via irrigation water to the soil during the experiments. This is more in agreement with the field situation in Bangladesh compared to hydroponics and spiked soils. However, this experimental setup neglects that As levels in irrigation water in the field are relatively constant and that As is slowly added to the soils over a period of many years. Ideally, experiments should be performed with naturally contaminated soils and constant As concentrations in irrigation water.

To date, toxic effects have only been related to the irrigation water concentration and the total soil concentration. The As concentration in soil water (pore water) will surely deviate from the irrigation water because of interactions with the soil matrix. Total As in the soil is also unlikely to be a good predictor of As uptake and toxicity for different soil types as only part of the As in the soil is likely to be potentially available to the plants. Dose-response relationships based on irrigation water concentrations or total soil concentrations are only valid for the experiment from which they were derived and cannot be extrapolated to any other

system. With all these limitations in mind, various studies of the above mentioned types will be summarized and discussed. Soil micro-organisms may also be affected by As toxicity [70]. Effects of As and on the soil microbial community can be expected with As(III) being more toxic than As(V). Microbes can adapt to As contamination, but this can be accompanied by a change in density and structure of the community. Ghosh et al. [120] reported that microbial biomass and activity were negatively correlated with total and bioavailable As in soil samples from West Bengal. However, the description of the used soils was limited, making it difficult to assess if there were any other reasons like different soil types and land use that could explain the results.

As human activities increases, especially with the application of modern technologies, pollution, and contamination of the human food chain has become inevitable. Heavy metals uptake by plants grown in polluted soils has been studied to a considerable extent [121]. Heavy metal contamination in vegetables cannot be underestimated as these food stuffs are important components of human diet. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance [122,123].

The symptom picture of arsenic toxicity is characterized by dermal lesions, anemia, and an increased risk for cardiovascular disease, diabetes, and liver damage. Cadmium has a significant effect on renal function, and as a result alters bone metabolism, leading to osteoporosis and osteomalacia. Cadmium-induced genotoxicity also increases risk for several cancers. The mechanisms of arsenic- and cadmium-induced damage include the production of free radicals that alter mitochondrial activity and genetic information. The metabolism and excretion of these heavy metals depend on the presence of antioxidants and thiols that aid arsenic methylation and both arsenic and cadmium metallothionein-binding [124].

Both arsenic and cadmium are easily available in the environment, and the exposure via food, water, and other occupational sources can contribute to a spectrum of diseases. Cd exposure may pose adverse health effects, including kidney

dysfunction, and skeletal disorders, and may also affect bones and result in fractures [120]. Long-term exposure to Pb may cause neurological disorders such as memory deterioration, prolonged reaction times, and reduced cognitive ability [125].

The general population is exposed to lead from air and food in roughly equal proportions. During the last century, lead emissions to ambient air have caused considerable pollution, mainly due to lead emissions from petrol. Children are particularly susceptible to lead exposure due to high gastrointestinal uptake and the permeable blood-brain barrier. Blood levels in children should be reduced below the levels so far considered acceptable, recent data indicating that there may be neurotoxic effects of lead at lower levels of exposure than previously anticipated. Although lead in petrol has dramatically decreased over the last decades, thereby reducing environmental exposure, phasing out any remaining uses of lead additives in motor fuels should be encouraged. The use of lead-based paints should be abandoned, and lead should not be used in food containers. In particular, the public should be aware of glazed food containers, which may leach lead into food grains.

1.13 Clinical Manifestation and Treatment of Arsenic, Lead and Cadmium

Arsenic may be absorbed by ingestion, inhalation, and permeation of skin or mucous membranes and may cause adverse health effects.

(a) Non-Cancer: By ingestion, as little as 20 milligrams of arsenic may be life-threatening to man. Acute airborne exposure to high concentrations of arsenic (III) trioxide in occupational settings causes irritation of the eyes, nasal mucosa, and bronchi. Non-carcinogenic effects associated with chronic occupational exposure to high concentrations of airborne arsenic include nasal septum ulceration and perforation, respiratory tract irritation and peripheral neuropathy. The most sensitive non carcinogenic endpoints are vascular disorders (hemolysis), neurological disturbances, and adverse reproductive effects. Other reported effects from acute inhalation exposure include gastrointestinal effects (nausea, diarrhea, and abdominal pain). Chronic inhalation exposure to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes, while chronic oral

exposure has resulted in gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, and liver or kidney damage [126].



Figure 1.7 : Clinical manifestation of chronic arsenic toxicity

The United States Environmental Protection Agency has not established an RfD for arsine [123]. The most prominent chronic manifestations involve the skin, lungs, liver and blood systems. This was first diagnosed in West Bengal and Bangladesh patient of Khulna in December, 1984 [127,128] and by Prof. K. C. Saha in July 1982 at School of Tropical Medicine, Calcutta, India [129].

(b) Short-Term Effects: Ingestion of large doses of arsenic usually results in symptoms within 30 to 60 minutes, but may be delayed when taken with food. Acute arsenic poisoning usually starts with a metallic or garlic-like taste, burning lips and dysphasia. These gastrointestinal symptoms are the result of intestinal injury caused by dilatation of splanchnic vessels leading to mucosal vesiculation. These vesicles rupture causing bleeding, diarrhea and protein wasting. Gastrointestinal symptoms often result in dehydration and electrolyte imbalance, and may lead to the development of hypotension and hypoxia [130]. Fatal arsenic poisonings have been reported after oral exposure to estimated single doses of 2 g [131], 8 g [132] and 21 g [133]. Non-fatal outcomes (usually following treatment)

have been documented after oral single doses of 1-4 g [134]. Cullen et al. [135] found a serious acute effects in children after exposure to as little as 0.7 mg of As_2O_3 . Incidents in which continuous or repeated exposure to high levels of arsenic over a short period of time have also been described. Following consumption of water containing 108 mg As/L for one week, two of nine persons died, four developed encephalopathy and eight showed gastrointestinal symptoms.

(c) Chronic Arsenic Exposure: Chronic exposure to lower levels of arsenic has long since been linked to adverse health effects in human populations. The earliest reports date back to the latter part of the 19th century when the onset of skin (including pigmentation changes, hyperkeratosis and skin cancers) were linked to the consumption of arsenic in medicines and drinking water [136]. In the early 1900s, numerous reports of skin disorders in Argentina, Chile, Mexico and Taiwan, were attributed to arsenic exposure via drinking water, were published [137].

(d) Diabetes Mellitus: Diabetes mellitus has also been linked with drinking water arsenic exposure. Lai et al. [138] assessed the relationship between ingested inorganic arsenic and prevalence of diabetes mellitus in 891 adults residing in southern Taiwan. Their study found that residents in the BFD-endemic areas had a two-fold increase in the prevalence of diabetes mellitus (after adjustment for age and sex) when compared to residents in Taipei and the entire Taiwan population. The authors also described a dose-response relationship between the level of arsenic in water and the prevalence of diabetes after adjusting for age, sex, body mass index and activity level. Positive associations were also demonstrated in two further studies from Taiwan. An excess mortality from diabetes among the arsenic exposed population in four townships, relative to local and national rates, has been reported by Tsai et al. [139]. The incidence of diabetes mellitus in a cohort of inhabitants of the Taiwan BFD area was related to the cumulative exposure to arsenic in drinking water [140]. A positive association with diabetes has also been found in Bangladesh [141] used the presence of keratosis as an indicator of arsenic exposure and showed elevated risks for diabetes in those exposed to arsenic in their drinking water (prevalence ratio= 5.9). On the other hand, in the Utah mortality study, Lewis et al.[142] failed to find a significant excess

in the number of deaths from diabetes in males and females exposed to elevated levels of arsenic in drinking water. However, in the US diabetes is a condition with a low-case fatality rate, so an association with diabetes mellitus may not be observed. More work is needed prior to deciding whether there is an association in the US between diabetes and drinking water arsenic. Two occupational studies have found an association between arsenic exposure and diabetes mellitus. In both cases, however, the results were of borderline significance. Based on a case-referent analysis involving glass workers found a slightly elevated risk for diabetes among those glasswork employees considered to be exposed to inhaled forms of arsenic. In a smaller (12 exposed cases) case-referent study in the Rönnskär cohort [143], a slightly elevated risk of diabetes mellitus associated with arsenic exposure was also observed.

(e) Neurological Effects: It is generally accepted that acute arsenic poisoning causes neurological effects in humans, especially in the peripheral nervous system. To date, however, little work has been done on the possibility that lower-level, long-term exposure to arsenic may also lead to neurological effects. Of the limited number of available studies on this topic, several have described the onset of various neurological symptoms in subjects exposed to arsenic [144].

Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer, and lymphatic cancer. A very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions, and brain damage with men and women. Finally, inorganic arsenic can damage DNA. A lethal dose of arsenic oxide is generally regarded as 100 mg organic arsenic can cause neither cancer, nor DNA damage. But exposure to high doses may cause certain effects to human health, such as nerve injury and stomach aches [145,146].

Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food, water and air. The health effects of lead have become much better understood since the middle of the 20th century. At one time, the metal was regarded as quite safe to use for most applications. Now lead is known to cause both immediate and long-term health problems, especially with children. It is toxic when swallowed, eaten, or inhaled. Exposure to lead is typically greater in children, who are also more susceptible to the effects of lead than adults. Children are particularly at risk for the subtle adverse effects of chronic low-dose lead exposure, as are pregnant women/fetuses.

Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children [147]. Children absorb about 50% of ingested lead [148]. They have an abnormal desire to eat materials like dirt, paper, and chalk. Some symptoms of lead poisoning include nausea, vomiting, extreme tiredness, high blood pressure, and convulsions (spasms). Over a long period of time, these children often suffer brain damage. They lose the ability to carry out normal mental functions. Other forms of lead poisoning can also occur. For example, Lead poisoning through inhalation can lead to nerve damage and problems with the gastrointestinal system (stomach and intestines). Today, there is an effort to reduce the use of lead in consumer products. For instance, older homes are often tested for lead paint before they are resold. Lead paint has also been removed from older school buildings [149]. Lead exerts adverse effects on numerous organs and systems including the central nervous system (CNS), the kidneys and on the hematopoietic (blood forming) system. The identification of causal relationships between exposure and effects is complicated by the delay between the time of lead exposure and the onset of effects [150].

Dermal absorption of inorganic lead has been demonstrated in animals and human subjects, however, few studies have provided quantitative estimates of dermal absorption and the contribution of the dermal intake to lead body burden [151]. Absorption of lead through the skin has only been measured accurately for organic lead compounds. Exposure to lead from cosmetics

previously occurred from use of progressive hair dye preparations containing lead acetate [152], however, lead acetate is now prohibited for such use in Canada. The Drinking Water Guidelines in Canada limit the lead content to a Maximum Acceptable Concentration (MAC) of 0.010 milligrams per litre (0.010 ppm) of water [153]. Acceptable oral intake of lead impurities includes 0.1 ppm (US FDA for candy) to 10 ppm (USP for nutritional supplements). The World Health Organization (WHO) has established 25 micrograms of lead per kilogram of body weight per week as a provisional tolerable weekly intake (PTWI) for children. Health Canada's Natural Health Products Directorate (NHPD) limits lead in products applied to the skin to 10 ppm (NHPD Compendium of Monographs).

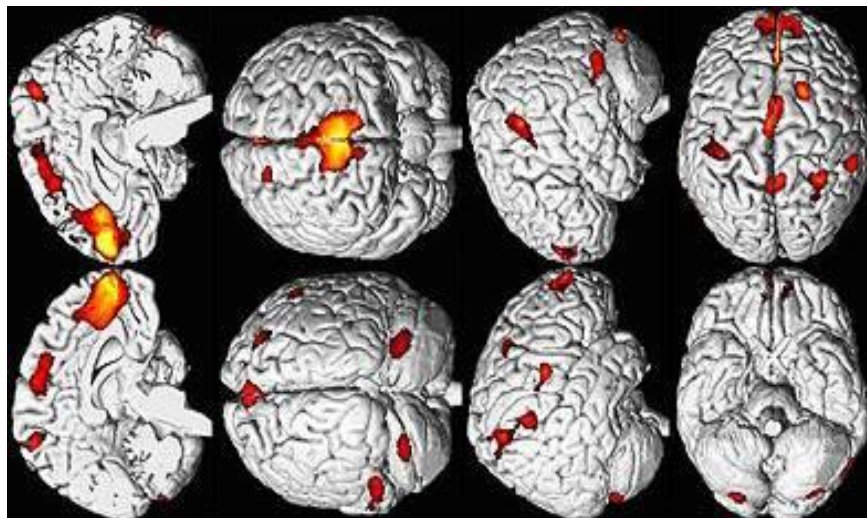


Figure 1.8 : The brains of adults who were exposed to lead as children show decreased volume, especially in the prefrontal cortex, on MRI. Areas of volume loss are shown in color over a template of a normal brain [154]

In general, the amount of cadmium that will cause health problems will vary depending on: (1) the type of exposure (eating or breathing), (2) the duration of the exposure (short-or long-term), and (3) the form of cadmium (pure cadmium or some combination). Studies show that humans can experience lung irritation after breathing as little as 1.0 milligrams per cubic meter of air (mg/m^3) of cadmium-contaminated air for a short period of time (less than or equal to 14 days). Breathing $0.01 \text{ mg}/\text{m}^3$ of cadmium- contaminated air over the long-term (greater

than 14 days) has resulted in chronic lung disease and kidney disease in humans. Human uptake of cadmium takes place mainly through food and water. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder, and dried seaweed. The major sources of cadmium in humans are cigarette smoking, certain foods (such as shellfish, liver, and kidney meats), coal burning, and contaminated water. Those most at risk for high intake of cadmium are people who work directly with the metal. Manufacturing plants where batteries are made use cadmium as a fine powder where it can easily be inhaled. Workers must be careful in handling cadmium. There is growing concern about the dangers of cadmium in the environment. Rechargeable batteries are made with cadmium and nickel. Cadmium can escape from landfills (where trash is buried) and get into the ground and ground water. From there, it can become part of the food and water those humans and animals ingest. Low levels of cadmium cause nausea, vomiting, and diarrhea. Inhaled, cadmium dust causes dryness of the throat, choking, headache, and pneumonia-like symptoms [155].

Cadmium is first transported to the liver through the blood. There, it is bound to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body [156]. Other health effects that can be caused by cadmium are [156]:

- Diarrhea, stomach pains, and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders
- Possibly DNA damage or cancer development

The effects of extensive cadmium exposure is not known, but are thought to include heart and kidney disease, high blood pressure, and cancer. A cadmium poisoning disease called Itai-Itai, Japanese for “Ouch-Ouch,” causes aches and pains in the bones and joints. In the 1970s, a number of cases of Itai-Itai were reported in Japan when waste from a zinc refinery got into the public water supply. Those wastes contained cadmium compounds [155].



Figure 1.9 : Bone fracture due to cadmium exposure.

1.14 Rationale of the study:

Arsenic, lead and cadmium are the most abundant toxic elements in the earth's crust that occur naturally in all environment media and may pollute air, soil, sediments and water causing serious health hazards to both human and animals. Recently arsenic in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh. BGS/DPHE nationwide survey [157,158] shows that in 61 out of 64 districts of Bangladesh, the groundwater is contaminated with arsenic. An estimated 29 million people are directly exposed to the arsenic problem [159] and 85 million are at the risk of arsenic contamination [160]. It has been reported [161] that about 10,000 patients are suffering from arsenicosis. SOES and DCH [163] reported a few death due to arsenic poisoning in

Bangladesh and West Bengal of India. In this point of view, Bangladesh is facing probably the largest mass poisoning in history.

Lead can end up in water through corrosion of leaded pipelines in a water transporting systems. Lead accumulates in the bodies of water organisms. Lead is a particularly dangerous chemical as it can accumulate in individual organisms as well as in entire food chains. Hence it can enter the human body through uptakes of food, water, and air. These might cause deleterious health effects to human beings. Hence, lead pollution is considered to be a worldwide issue.

Cadmium is emitted to the environment as a result of both natural and anthropogenic activities. Cadmium is released to the aquatic environment from a range of anthropogenic sources, including non-ferrous metal mining and smelting (from mine drainage water, waste water, tailing pond over flow, rainwater run off from mine areas), plating operations, phosphate fertilizers, sewage-treatment plants, land fills and hazardous waste site [162]. Cadmium ends up in surface waters when waste from fertilizer production is dumped by production companies. Cadmium can be transported over great distances when it is absorbed by sludge. This cadmium rich sludge can pollute surface water as well as soils. Cadmium accumulates in both human and animal body that causes serious diseases like lung cancer, kidney damage, diarrhea, bone fracture, damage to the central nervous system and damage to the immune system.

Soil is important natural resources for mankind but it also serve as a medium for the accumulation, transformation and migration of toxicants like arsenic, lead and cadmium. For example arsenic, lead and cadmium may accumulate in soil though the use of arsenical pesticides, lead pesticides, cadmium rich sludge, irrigation and disposal of industrial and animal wastes. The wide spread use of ground water and pesticides of arsenic, lead and cadmium for irrigation and cultivation suggests that ingestion of the irrigated crops could be another major exposure route of arsenic, lead and cadmium.

Since the arsenic, lead and cadmium problem in Bangladesh is terrible at present, it will be invaluable to understand the entrance of arsenic, lead and cadmium into human food chain from sources other than contaminated drinking water. Arsenic, lead and cadmium concentration in edible parts of plants due to irrigation by arsenic, lead and cadmium contaminated water – its extent and solution is still remains unfocused. No significant research is carried out yet for remedy of arsenic, lead and cadmium poisoning in plants or food grains. Especially, detoxification of contaminated soil by using natural organic fertilizers is not yet well-studied. Besides these, human health risk should be assessed to understand the threat. The above serious issues need to be addressed for ensuring safety of human health leads us to conduct this investigation.

1.15 Objectives of the study

The general objectives of the study is to find out the potential ways for remedy of arsenic, lead and cadmium toxicity in corn plants irrigated with contaminated water by using natural organic fertilizers and to assess human health risks due to arsenic, lead and cadmium exposures from dietary food products.

The specific objectives of the study include the followings:

- To characterize the studied six natural organic fertilizers.
- To investigate the pattern of arsenic, lead and cadmium accumulation in the corns after irrigation with contaminated water.
- To understand the impact of the fertilizers towards plant health and percent yield.
- To evaluate the potentiality of the fertilizers as measures against arsenic, lead and cadmium toxicity in food grains due to irrigation with contaminated water.
- To recommend particular fertilizers for ensuring food safety.
- To compare the heavy metal status in vegetables, fish, rice, dust and drinking water consumed by selected inhabitants of Rajshahi City Corporation (RCC) area.

- To assess overall potential risk due to arsenic, lead and cadmium exposure from die dietary consumption for children, adults and seniors population sub-group of RCC area.

1.16 Scope of the study

Arsenic, lead and cadmium are dietary toxic constituents and are present in many foods such as meat, fish, poultry, vegetables, grains, cereals, seafood, soft drinks, etc. Arsenic, lead and cadmium contents in the agricultural foodstuffs might increase many folds, when successive irrigations are made with arsenic, lead and cadmium contaminated water. This investigation has been conducted to the commonly grown plants, cereals and grains.

The precise dimension of the arsenic, lead and cadmium problems in the field of agriculture is not yet known in Bangladesh. The reasons include fluctuation in concentrations of arsenic, lead and cadmium load in different soils and variation in up taking rate of heavy metal pollutants from the soils by specific plants. Considering these facts, we have carried out our studies in fresh soil, irrigated with both natural underground and model water. This not only removes the possibility of introducing previous contaminations, but also facilitates to find out the actual several relationships amongst arsenic, lead and cadmium concentrations of water, soil and plant tissues.

We followed natural procedures of cultivation that the farmers of Bangladesh as well as many countries practiced traditionally. That's why, we utilized six natural organic fertilizers namely, Cow-dung, Water hyacinth, Compost, Drain mud, Rotten Dhuncha and Earthworm fertilizer. We ignored inorganic fertilizers as they do not improve soil organic matter (SOM), soil texture and overall fertility. Our irrigation pattern was also the same as the farmers practiced. We have sown the seed of Sesame, Foxtail Millet, Paddy and Maize.

Since the studied samples were acid-digested, GF-AAS allows us to estimate the concentrations of arsenic, lead and cadmium accurately. But we could not proceed to the metal speciation due to lack of instruments like HPLC-MS.

Based upon statistical regression analyses of the data obtained, the concentrations of arsenic, lead and cadmium in edible plant tissues could be correlated with those of irrigation water and soil, and we establishment several mathematical models. For human health risk assessment, we adapted US Environmental Protection Agency (USEPA) suggested Risk Assessment Model. We also utilized the data of Exposure Factor Handbook, Bangladesh Bureau of Statistics (BBS) and our found data from household survey. This leads to precise assessment of the human health risk from consumption of commonly food products.

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CHAPTER TWO

THEORETICAL BACKGROUND

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References

Chapter 2

Theoretical Background

2.1 Experiments

Experiment comprises the following features sequentially:

- The materials and reagents used in this investigation
- Instrumentation that comprises system description and operating conditions of the principal instruments involved
- Theories related to the measurement of the parameters involved
- The methodologies of water, plant tissue, fish, dust and soil sampling and analysis
- The adapted techniques for analysis of samples for physical, chemical and biological parameters
- Quality control (QC) or quality assurance steps taken
- The statistical analyses of the data obtained

2.1.1 Materials

All chemicals and reagents used in this investigation were of high purity analytical grade. Distilled deionized water (DDW) was used throughout. Several standard solutions, reducing solutions, buffer solutions, ternary acid mixture and other solutions were prepared according to the standard procedures [1, 2, 3, 4, 5]. All chemicals or reagents were used in this investigation without further purification.

2.1.2 Standard Stock Solutions

i) Arsenic (As^{3+}) [1000 ppm]: 1.320 g of As_2O_3 (Fluka, Switzerland) was dissolved in 20 mL of DDW containing 4 g of NaOH (Merck, Germany). After dissolution, it was diluted to 200 mL followed by adjustment of pH to 5.5 with 2M HCl (Merck, Germany) and finally diluted with DDW to 1000 mL.

ii) Lead (Pb) [1000 ppm]: 1.599 g of $\text{Pb}(\text{NO}_3)_2$ was dissolved in about 150 mL of distilled de-ionized water. 10 mL of concentrated HNO_3 was added to it and diluted up to 1000 mL with DDW.

iii) Cadmium (Cd) [1000 ppm]: 2.036 g of CdCl_2 was dissolved in 250 mL of distilled de-ionized water. After dissolution, it was diluted up to 1000 mL.

iv) Iron (Fe^{3+}) [200 mg L⁻¹]: 20 mL of 98% H_2SO_4 (Aldrich, USA) was added slowly to 50 ml of DDW and 1.404 g of ferrous ammonium sulfate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] (BDH, England) was dissolved in it. Then 0.1 N KMnO_4 (Merck, Germany) solution was added drop wise until a faint pink color persisted. This was diluted with DDW to 1000 mL. Freshly prepared standard iron solution was used for calibration purpose.

v) Calcium (Ca^{2+}) [500 mg L⁻¹]: To 1.249 g of CaCO_3 (Merck, Germany), previously dried at 180 °C for 1 h, 50 mL of DDW was added. The suspension was dissolved by adding 10.0 mL of concentrated HCl drop wise and diluted to 1000 mL with the water.

vi) Magnesium (Mg^{2+}) [1000 mg L⁻¹]: 1.658 g of MgO (Aldrich, USA) was dissolved in a minimum amount of 1:1 HNO_3 . 10.0 L of concentrated HNO_3 was added to it and diluted to 1000 mL with DDW.

vii) Manganese (Mn^{2+}) [1112.4 mg L⁻¹]: In a 1 L beaker, 3.20 g of KMnO_4 (Merck, Germany) was taken. It was dissolved with 1 L of distilled water and heated the solution at 90-95°C for several hours. After cooling and filtering to 1 L measuring flask, it was then diluted up to mark with DDW.

viii) Sodium (Na^+) [1000 mg L⁻¹]: 2.542 g of NaCl (Fluka, Switzerland), previously dried at 140°C for 4 g, was dissolved in DDW and diluted to 1000 mL.

ix) Potassium (K^+) [1000 mg L⁻¹]: 1.907 g of KCl (Merck, Germany), previously dried at 110 °C for 4 h, was dissolved in DDW and diluted to 1000 mL.

x) Chloride (Cl^-) [500 mg L⁻¹]: In a 500 mL measuring flask, 0.412 g of NaCl (Fluka, Switzerland) that was dried previously at 140°C was taken. It was then dissolved with DDW and diluted up to the mark.

xi) Fluoride (F⁻) [100 mg L⁻¹]: In a 500 mL measuring flask, 0.221 g of anhydrous NaF (Merck, Germany) was taken. It was then dissolved with DDW and diluted up to the mark.

xii) Sulfate (SO₄²⁻) [100 mg L⁻¹]: In a 1 L measuring flask, 0.1479 g of anhydrous Na₂SO₄ (BDH, England) was taken. It was then dissolved with DDW and diluted up to the mark.

The stock solutions were further diluted with appropriate amount of distilled deionized water (DDW) to prepare standard solutions of the desired concentrations.

2.1.3 Ternary Acid Mixture

In order to prepare ‘ternary acid mixture’ three concentrated acids, namely, 69% HNO₃, 98% H₂SO₄ and 60% HClO₄ were mixed together in the volume ratio of 10:1:4.

2.1.4 Other Solutions

i) HCl solution: 2M HCl solution was made by taking 82.5 mL of 37 % HCl in a 500 mL measuring flask and filling up to the mark with DDW. 5M HCl solution was also prepared similarly. 1.5% (v/v) HCl solution was also prepared by adding 15 mL of conc. HCl to DDW and made up to 1000 mL.

ii) NaOH solution: 1%(w/v) NaOH solution was prepared by dissolving 10 g of NaOH pellets in DDW and made up to 1000 mL.

iii) Model Water: Shallow tube-well water supplemented with appropriate amounts of the standard arsenic, lead and cadmium solutions was used as model water for irrigation purposes.

Besides these, a few special solutions, prepared according to standard procedure, were utilized.

2.1.5 Other Materials

The seeds of the corns were bought from regional office of BARC (Bangladesh Agricultural Research Council). The natural organic fertilizers were collected from the local farmers.

The commercial gases (99.99% pure nitrogen and acetylene) used were collected from BOC, Bangladesh and 99.999% pure argon gas from Singapore. Cultural media (OXOID, UK) was used for counting Fecal Coliform bacteria. Some reagents of HACH, USA were also used.

2.1.6 Standard Reference Materials

Two standard reference materials (SRM) were used to check the accuracy of the methods. Tomato Leaves (SRM 1573a) were from the U.S. National Institute of Standards and Technology (Gaithersburg, MD) and Pond Sediment (NIES 2) from the National Institute for Environmental Studies (Japan).

2.2 Instrumentation

2.2.1 Graphite Furnace – Atomic Absorption Spectroscopy (GF-AAS)

a. System Description: Total arsenic, lead and cadmium concentrations of water as well as plant tissues and soil digestates were analyzed by GF-AAS, using a Shimadzu AA-6800 (Kyoto, Japan) atomic absorption spectrometer. It is a double beam AA spectrometer and capable of performing automated single element analysis. The system is equipped with a computer with Microsoft® Windows CE® compatible “WinLab32™” software and a Canon BJC-2100SP printer. It is also coupled with an auto-sampler, ASC-6100 (Shimadzu, Japan).

The basic features of Shimadzu AA-6800 spectrometer system include: i) Light sources, ii) Graphite Furnace Atomizer, iii) Monochromator, iv) Detector and v) Display system. One type of line radiation source (lamp) was used in the instrument – Lumina™ Hollow Cathode Lamp (HCL). The furnace atomizer or burner system is of laminar or premix type and comprises the following components: i) Air-cooled premix type Burner, ii) Burner head, iii) Nebulizer, iv)

Chamber (Pyrolytic graphite tube), v) a detector (generally a photomultiplier tube) and vi) Gas control system (incorporated in the spectrometer).

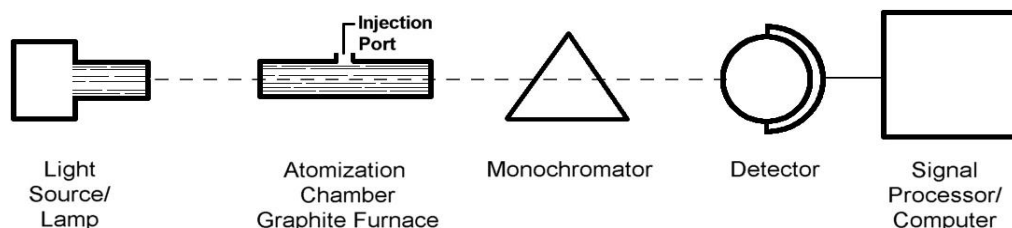


Figure 2.1 : Diagram of the basic components of a Graphite Furnace Atomic Absorption Spectrometer

Graphite furnace atomic absorption spectrometry (GF-AAS) has become a popular analytical technique in recent years, mainly because of its enhanced sensitivity that allows measurement in the picogram (10^{-12} g) range.

GF-AAS operates in the wavelength range from 190 to 900 nm and includes a Littrow configuration grating monochromator. The monochromator offers a choice of six spectral slit widths (0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 nm). It provides excellent detection limits for concentrations of metals in aqueous and solid samples. As a direct result of the high sensitivity, another practical problem that must be faced is the control of external contamination. Contamination can be introduced to standards and samples alike and come from a variety of sources, including reagents (such as matrix modifier), solvents (used in dissolution procedures), the laboratory atmosphere and contaminated glassware. Taken together these problems can give the impression that GF-AAS is a technique that many complex and poorly understood steps to be made before an analytical method can be successfully developed and proved.

Table 2.2 : Temperature program for GF-AAS

Element	Step	Temperature (°C)	Time (sec)	Heating mode	Flow rate (L min ⁻¹)
As	1	150	20	RAMP	0.10
	2	250	10	RAMP	0.10
	3	600	10	RAMP	1.00
	4	600	10	STEP	1.00
	5	600	3	STEP	0.00
	6	2200	2	STEP	0.00
	7	2500	2	STEP	1.00
Cd	1	150	20	RAMP	0.10
	2	250	10	RAMP	0.10
	3	500	10	RAMP	1.00
	4	500	10	STEP	1.00
	5	500	3	STEP	0.00
	6	2200	2	STEP	0.00
	7	2400	2	STEP	1.00
Pb	1	150	20	RAMP	0.10
	2	250	10	RAMP	0.10
	3	800	10	RAMP	1.00
	4	800	10	STEP	1.00
	5	800	3	STEP	0.00
	6	2400	2	STEP	0.00
	7	2500	2	STEP	1.00

2.2.2 Atomic Absorption Spectrometry

The atomic absorption spectrometry uses absorption of light of intrinsic wavelengths by atoms. All atoms are classified into those having low energies and those having high energies. The state having low energies is called the ground state and the state having high energies is called the excited state. The atom in the ground state absorbs external energies and is put in the excited state. For example, sodium is mainly in two excited states, having higher energies by 2.2eV and 3.6eV respectively than in the ground state, as shown in Fig. 2.1 When 2.2eV energy is given to the sodium atom in the ground state, it moves up to the excited state (I) and when 3.6eV energy is given, it moves up to the excited state (II). Energy is given as light, and 2.2eV and 3.6eV respectively correspond to energy of light at 589.9nm and 330.3nm wavelength. In the case of sodium in the ground state, only light of these wavelengths are absorbed and no other wavelength light is absorbed at all [7]

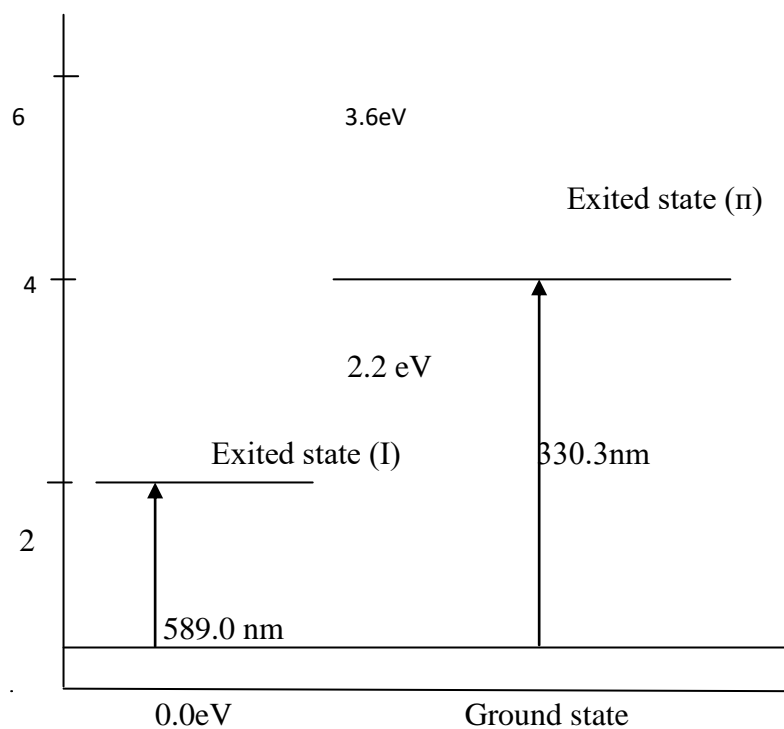


Figure 2.3 : Sodium energy states

The difference between energies in the ground state, and in the excited state is fixed by the element and wavelength of light to be absorbed. Atomic absorption spectrometry uses the hollow cathode lamp (HCL). The HCL gives off light characteristic to the elemental wavelength being measured. Thus, the light absorbed measures the atomic density [7].

Graphite furnace AAS has been used for the off-line measurement of elements in the elution fractions of LC, although insufficient detection limits proved to be a serious drawback in the case of many clinical applications, where the concentrations of the elemental species in the biological fluids and tissues are very low. When species can be converted to hydrides, such as is routinely done for mercury, selenium, arsenic, and antimony, then hydride generation AAS is a very interesting and cheap detection technique. An on-line method was developed for the speciation of arsenic in human serum, including MMA, DMA, arsenobetaine and arsenocholine. It has been applied for the speciation of arsenic in persons with abnormally high arsenic concentrations in serum, such as dialysis patients. The

method is based on cation exchange LC separation, UV photo-oxidation for sample digestion, and continuous hydride generation AAS for the measurement of arsenic in the LC eluent. By developing the technique of argon segmented flow in the post-column eluent, a substantial improvement in chromatographic resolution for the separation of these four arsenic species was obtained. The LC separation, photo oxidation, hydride generation, and AAS measurement could be completed on-line within 10 min. The response is different for the different species. The detection limits (as arsenic) were 1.0, 1.3, 1.4, and 1.5 $\mu\text{g/l}$ for MMA, DMA, arsenobetaine, and arsenocholine, respectively, in serum. The concentration of the four species was determined in serum samples of six patients with chronic renal insufficiency. Only arsenobetaine and DMA were significantly detected by this method. The main part of arsenic in human serum is arsenobetaine. No MMA, arsenocholine, or inorganic arsenic were detected in these six samples. AAS with a quartz tube atomizer is a very sensitive, specific, rugged, and comparatively inexpensive detector for GC. GC coupled with AAS has been described as a sensitive instrumentation for mercury speciation (Emteborg et al., 1996). On-line solid-phase extraction coupled to graphite furnace AAS has also been explored. Cold vapors AAS is the most widely used technique for measuring mercury. Direct coupling of solid-phase micro extraction and quartz tube AAS has been used for selective and sensitive determination of methyl mercury in seafood [8].

2.2.3 Principle of Atomic Absorption Spectroscopy

Atomic Absorption deals with the excitement of atoms. An atom absorbs light at discrete wavelengths. In order to measure this narrow light absorption with maximum sensitivity it is necessary to use a line source which emits the specific wavelengths that can be absorbed by the atom. The two most common line sources are the “hollow cathode lamp (HCL)” and the “electrode less discharge lamp (EDL)”. In HCL, when an electrical potential is applied between the anode and cathode, some of the fill gas atoms become positively charge and accelerated through the electrical field to collide with the negatively charge cathode and dislodge individual metal atoms in a process called “sputtering” (Figure 2.1).

Sputtered metal atoms are then excited to an emission state through a kinetic energy transfer by impact with fill gas ions [9]. The excited metal atom emits radiation at a wavelength characteristic for the sputtered metal. An EDL consists of a quartz bulb containing the analyte element, or a salt of the analyte element, in an inert gas atmosphere. When a radio frequency (RF) field is applied to the bulb, the inert gas will be ionized and the coupled energy will vaporize and excite the element specific atoms inside the bulb, causing them to emit their characteristic spectrum. This emission spectra are typically much more intense than those from HCLs.

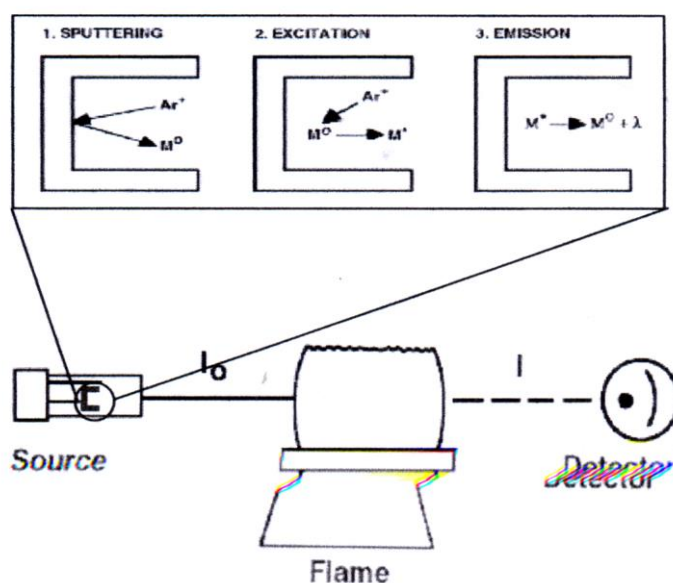


Figure 2.4 : Atomic absorption process

In order to get the atomic absorption process to occur, individual atoms from the sample (Which starts out as a solution of ions) must be produced. First, by the process of nebulization, the sample is aspirate into the burner chamber by the Ventura action caused by the flow of oxidant gas around the capillary tip, where it mixes as a fine aerosol with the fuel and oxidant gases. At this point, the metals are still in solution in the fine aerosol droplets. As these tiny droplets pass into the heat of the flame, the process of evaporation desolution removes the solvent and leaves tiny solid particles of sample material. As more heat is applied, liquefaction will take place, and additional heat will vaporize the sample (Figure 2.4). At this point

the metal of interest, called analyte, is still bound up with some anion to form a molecule which does not exhibit the atomic absorption phenomenon. By applying still more heat energy, this molecule is dissociated into the individual atoms which make it up. Since the thermal energy from the flame is responsible for producing the absorbing species, flame temperature is an important parameter governing the flame process. Several energy levels are possible, but usually only the first excited level (E_1) is of concern, since a very few electrons are excited beyond E_1 . The number of ground state metal atoms formed in step 5 of the flame process (Figure 2.5) will determine the amount of light absorbed.

	$M^+ + A^-$	(Solution)
1) Nebulization	$M^+ + A^-$	(Aerosol)
2) Desolation	MA	(Solid)
3) Liquefaction	MA	(Liquid)
4) Vaporization	MA	(Gas)
5) Atomization	$M^0 + A^0$	(Gas)
6) Excitation	M^*	(Gas)
7) Ionization	$M^+ + e^-$	(Gas)

Figure 2.5 : The flame process. “ M^+ ” is metal cation and “ A^- ” is the associated anion

The radiation beam intensity is attenuated by an amount that is proportional to the concentration of the element under consideration in the atomizer. Hence, Beer’s law is employed for quantitative determination of the analyte:

$$A = \epsilon bc$$

Where, A is Absorbance, ϵ molar extinction coefficient and b the thickness of the absorbing medium (i. e., the length of the light path intercepted by the absorption species in absorption cell) and c is the concentration of absorbing species.

When a molecule absorbs ultraviolet or visible light, its electrons get normally promoted to the excited state. In most of the cases, several electronic transitions like $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, occur resulting in the formation of several bands [10, 11].

For determination of the concentration of the analyte, wavelength of maximum absorptivity or minimum transmittance (λ_{\max}) of the analyte is evaluated by scanning the solution containing the analyte within the wavelength ranges. The wavelength corresponding to the maximum absorbance in the curve of absorbance versus wavelength gives the value. Then a series absorbencies are recorded by a UV-VIS spectrophotometer for a series of prepared standard solutions of the compound concerned at the λ_{\max} . A calibration curve is obtained by plotting absorbencies versus concentrations. The calibration curve should be straight line passing through the origin if Beer's law ($A=\epsilon bc$, where A is the absorbencies, c is concentration of the analyte, b path length and ϵ molar extinction coefficient) is obeyed [12]. Measuring the absorbance of the solution containing the analyte at the λ_{\max} , the corresponding concentration is determined from the calibration curve.

Absorbance of analyte was determined from UV-VIS spectrophotometer and slope from calibration curve (absorbance vs. conc. in $\mu\text{g/L}$). Then total arsenic concentration was estimated as follows:

$$\text{Conc. of As (mg/L)} = \frac{\frac{\text{Absorbance} = \mu\text{g As}}{\text{Slope}}}{\text{Total vol. of sample in generator flask (=70mL)}} \times \text{Dilution factor}$$

2.2.4 UV-VIS Spectroscopy

a. System Description: The UV-VIS spectrophotometer used in our colorimetric analysis was DR/4000 U (HACH Company, Colorado, USA). The DR/4000 U is a microprocessor controlled, single-beam spectrophotometer. The followings are the essential components of the system: i) Light sources, ii) Monochromator, iii) Detector and iv) Display system.

Two types of continuous light sources were used in DR/4000 U spectrophotometer: tungsten/halogen lamp and deuterium lamp [13]. The tungsten/halogen lamp is useful for the wavelength region between 240 and 2500

nm and deuterium lamp between 160 and 380 nm. In our investigation, the tungsten/halogen lamp was used.

The optical system is composed of a split-beam diffraction grating Seya-Namoika monochromator. The monochromator employs entrance and exit slits, rotating concave holographic grating, order sorting filter, fused silica beam splitter and convex fused silica lens (Figure 2.6). It provides a full 190 to 1100 nm wavelength range with a nominal bandwidth of 4 nm, wavelength accuracy ± 1 nm and resolution ± 0.1 nm [13].

The detector system comprises a photomultiplier tube (PMT) and an electrical signal processor. The DR/4000 U is a spectrophotometer with backlit, graphic LCD. With a measurement range of 190 to 1100 nm, it provides results in operator-selectable readout modes of Absorbance (ABS), Percent Transmittance (%T) or Concentration. Its dynamic range is -3.0 to 3.0 A with photometric linearity of ± 0.002 A [13].

A read-only memory (ROM) is provided with preprogrammed calibration data for over 130 test procedures to provide direct readout in concentration mode. DR/4000 U features a Standard Addition Option to improve the accuracy and precision of analyses and reports the percent of standard recovery. The instrument also provides for storage of up to 200 user-generated calibrations. Data can be transferred from DR/4000 U to computer using HachLink™ software as Excel spreadsheet. It also accommodates various sample cells of different sizes, but stray light is <1%.

b. Optical System: The optical system of DR/4000 U single-beam spectrophotometer is composed of a split-beam diffraction grating Seya-Namoika monochromator, tungsten/halogen and deuterium light sources and a PMT detector (Figure 2.6).

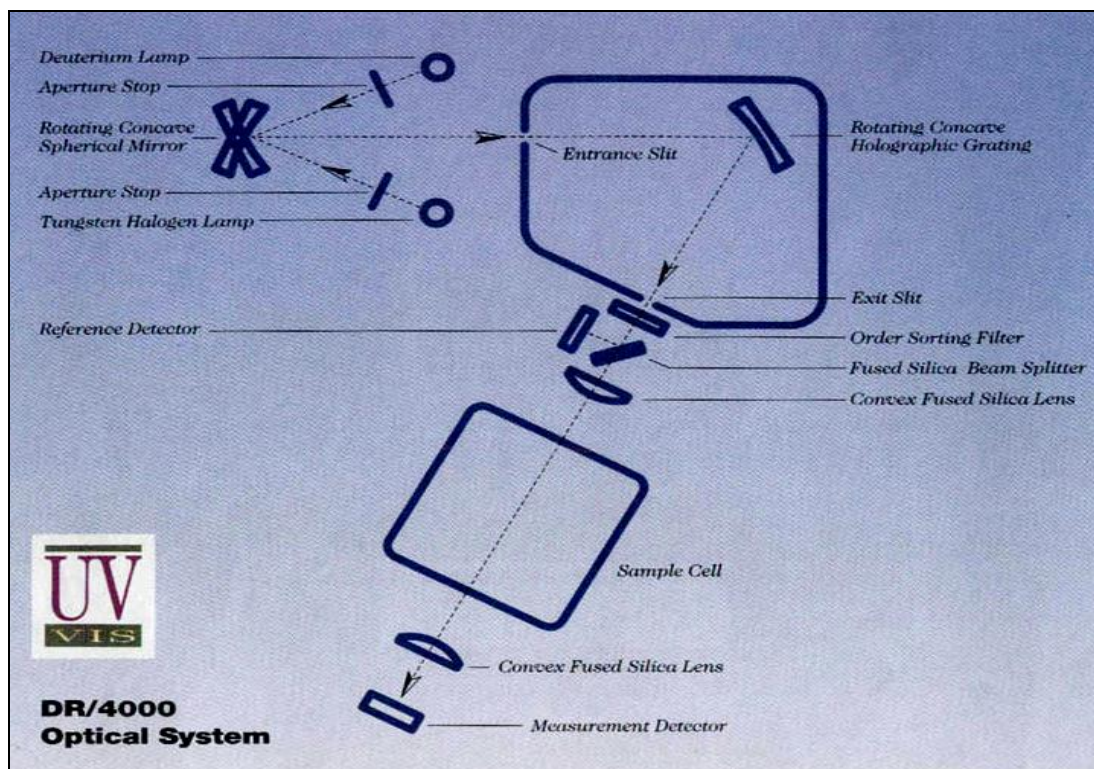


Figure 2.6 : Optical system of DR/4000 U UV-VIS spectrophotometer [13].

The primary source of light (tungsten/halogen or deuterium lamp) is dispersed into component wavelengths with the help of a rotating concave dispersion grating. The monochromatic light of desired wavelength, obtained through exit slit adjustment, is passed through the reference solvent and the sample solution and is focused on the detector. When the sample absorbs light, its intensity is lowered. Thus the detector receives an intense beam from reference cell and a weak beam from sample cell. This results in the generation of pulsating or alternating currents which flow from photomultiplier tube to signal processor. The signal for the absorption of the contents of the reference cell is automatically subtracted from those of the sample cell by signal processor, giving a net signal corresponding to the absorption for the analyte. The microprocessor controlled DR/4000 U featuring a reference detector automatically correct for the “dark current” of the photocell, i.e., the small current which passes even when the cell is not exposed to radiation.

2.2.5 Theory of Arsenic, Lead and Cadmium determination in supplied samples following spectrophotometry

The basis of the spectrophotometric analysis is the color of a solution varies with the concentration of components. The color of a solution is the indication of complex formation between the reagent added and the components. The spectrophotometry deals with the monochromatic light source. The chief advantage of spectrophotometric method is that it provides a simple means for determining minute quantities of substances. The technique is based on the theory given by Lambert and Beer. For valid application of Beer- Lambert law, the following conditions should be fulfilled.

- a) The sample solution should not be highly concentrated.
- b) The used light should be monochromatic.
- c) The incident radiation should not be reflect or scattered before absorption.
- d) Molecules or ions in solution should not remain associated, dissociated, hydrated or it's forming complex.
- e) The solute should not remain in equilibrium with other solutes in solution.
- f) The pH value of the solution should not be changed in any way.
- g) The environmental parameters e.g. temperature & pressure should not be fluctuated largely.

In order to apply the Beer-Lambert's law, the solution must be very dilute, because- Firstly, the absorptivity of a solution depends on the refractive index. In case of highly concentrated solution, association among the solutes may occur. Thus refractive index varies with concentration but it is approximately constant in case of dilute solution.

Secondly, in case of highly concentrated solution, the concentration of the solution slightly changes due to the association through hydrogen bonding in solutes, ion pair formation, solvation or any other chemical process. But in dilute solution all these process are negligible. So, in order to determine the concentration

of solution, the concentration of experimental solution must be a definite limit. But the different solution has different limits. So before determining the concentration of the unknown solution, its limit must be determined.

If the law is valid, a plot between absorbance and concentration is a straight line passing through origin. But when the solution is highly concentrated, the curve deviates from the straight line. These deviations may be positive or negative but in most cases the deviation becomes negative which is shown by the dotted lines in figure 2.7.

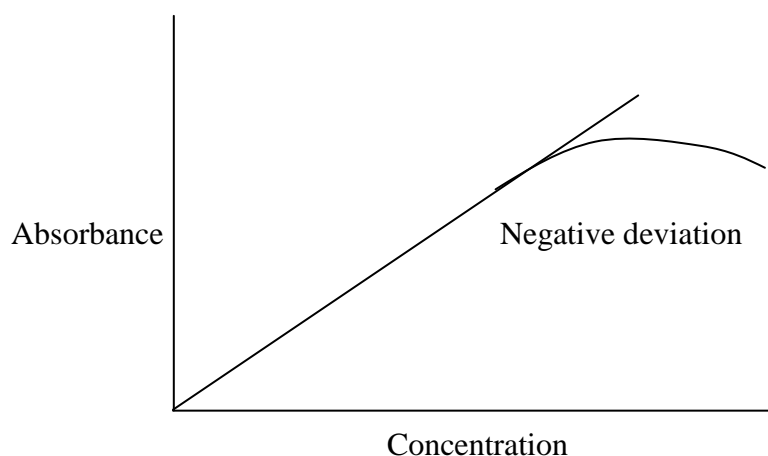


Figure 2.7 : Calibration line of absorbance versus concentration of solution

Solid environmental samples such as soils, biological samples, etc contain a large amount of organic arsenic, both in +3 and +5 oxidation state. In liquid environmental samples like geothermal water, inorganic arsenic predominates. The environmental samples, when subjected to pretreatment with a mixed acid such as nitric-sulfuric-perchloric, gives mainly inorganic arsenic (v) along with a small quantity of inorganic arsenic (III) [14].

Total arsenic concentrations (A_{ST}) of the decomposed sample aliquots can be determined either by GF-AAS technique. In GF-AAS [2, 4, 14, 15], the sample is first treated chemically so that the analyte is present in ionic form in acidic solution. For hydride generation arsenic must be present in +3 oxidation state. To

attain the condition, potassium iodide (KI) solution, which is dispensed into the acidic sample solution, converts inorganic arsenic (III) to its hydride, arsine (AsH_3). The in the volatile metal hydride (AsH_3) is driven from solution by a stream of carrier gas Ar and transported to the heated QTA. The hydride decomposes in the QTA, the analyte is atomized and its atomic (As) absorption is measured,

2.3 Experimental Procedures

2.3.1 Materials

All analytical reagents and chemicals used in this experiment were of high purity analytical grade. Deionized double distilled water was used throughout the experimental work. Laboratory glassware was kept overnight in 10% (v/v) nitric acid. Before use, the glassware were rinsed with deionized water and dried in a dust free environment. All the apparatus like conical flask, burette, pipette and screw capped polyethylene bottle used in this work were washed with detergent solution and then rinsed with tap water and finally with distilled water. Several standard solutions, ternary acid mixture and other solutions were prepared according to the following procedure [1, 2, 3, 4, 5].

2.3.2 Standard Stock Solutions Preparation

2.3.2.1 Stock Standard

The standard samples used for atomic absorption metals or salts dissolved in acid. When it is stored for a long period it is precipitated, or absorbed by the container wall due to hydroxide and carbonate produced, and its concentration changes. The standard solutions available on the market are supplied in accordance with the standard solution examination system. It is based on the national standard, and is acid or alkaline. The guarantee period of one to two years is shown and it must be used within this period. The stock solution prepared by the standard solution method is a highly concentrated solution that is acidic or alkaline with a metal concentration of 1mg/ml . However, one year or longer use is not recommended. In storing any standard solution, avoid direct sunlight and store it in a cool place.

2.3.2.2 Other Solutions

i) HCl solution: 2M HCl solution was made by taking 82.5 mL of 37% HCl in a 500 mL measuring flask and filling up to the mark with DDW. 5M HCl solution was also prepared similarly. 1.5% (v/v) HCl solution was also prepared by adding 15 mL of conc. HCl to DDW and made up to 1L.

ii) NaOH solution: 1% (w/v) NaOH solution was prepared by dissolving 10g of NaOH pellets in DDW and made up to 1000 mL.

Tap water supplemented with appropriate amounts of the standard arsenic (III) solution was used as model water and natural arsenic contaminated groundwater of tube-wells as natural water for irrigation purposes.

The commercial gases (99.99% pure nitrogen and acetylene) used were collected from BOC, Bangladesh and argon gas from Singapore. Some reagents of HACH, were also used. Standard Reference Materials: Two external standard reference materials (SRM) were used to check the accuracy of the methods. Tomato Leaves (SRM1573a) were obtained from the U.S. National Institute of standards and Technology (Gaithersburg, MF) and Pond Sediment (NIES 2) from the National Institute for Environmental Studies (Japan). Internal reference material of water was prepared very cautiously from ACS- certified Arsenic Reference standard solution of HACH, USA (Cat.No. 14571-42) through successive dilution with distilled deionized water (DDW).

2.4 Methodology

A. Soil Preparation and Irrigation

A land was divided into 6 × 4 beds, each of area 1.5 ft × 1.5 ft. 2 additional beds were prepared for control and 1 for blank purposes. With fresh soil, NPK fertilizers and insecticide were mixed well (except blank). Among 6 natural organic fertilizers (Cow-dung, Water hyacinth, Compost, Drain mud, Rotten Dhuncha and Earthworm fertilizer), each was added as 10, 50, 100 and 200 g / kg of soil. After 120 hours, seeds of Sesame, Foxtail, Rice (Paddy) and Maize were sown.

Control-1		Blank		Control-2	
CD-10	WH-10	CM-10	DM-10	RD-10	EW-10
CD-50	WH-50	CM-50	DM-50	RD-50	EW-50
CD-100	WH-100	CM-100	DM-100	RD-100	EW-100
CD-200	WH-200	CM-200	DM-200	RD-200	EW-200

Figure 2.8 : Schematic diagram of prepared bed

After seeding, tube-well water amended with As, Pb and Cd solutions (each having conc. of 5 mg L^{-1}) was used for irrigation purpose. A total of 8 times of water were applied within the duration of 70-80 days as $3.0 \text{ L / bed / irrigation}$. The average interval of irrigation was 7 days.



Cow-dung



Compost



Earthworm



Drain mud



Water hyacinth



Rotten Dhuncha

Figure 2.9 : Natural organic fertilizers



Sesame

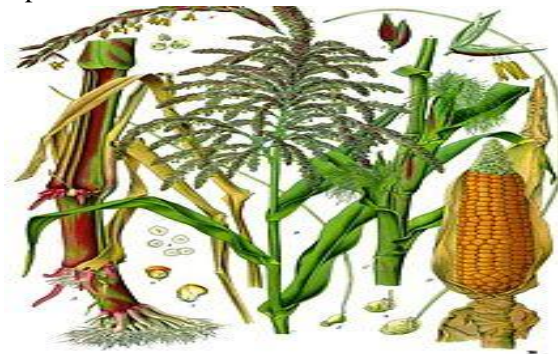
Scientific classification

Kingdom:	Plantae
(unranked):	Angiosperms
(unranked):	Eudicots
(unranked):	Asterids
Order:	Lamiales
Family:	Pedaliaceae
Genus:	<i>Sesamum</i>
Species:	<i>S. indicum</i>



Foxtail Millet

Kingdom:	Plantae
(unranked):	Angiosperms
(unranked):	Monocots
(unranked):	Commelinids
Order:	Poales
Family:	Poaceae
Subfamily:	Panicoideae
Genus:	<i>Setaria</i>
Species:	<i>S. italica</i>



Maize

Scientific classification

Kingdom:	Plantae
(unranked):	Angiosperms
(unranked):	Monocots
(unranked):	Commelinids
Order:	Poales
Family:	Poaceae
Subfamily:	Panicoideae
Tribe:	Andropogoneae
Genus:	<i>Zea</i>
Species:	<i>Z. mays</i>
Subspecies:	<i>Z. mays</i> subsp. <i>mays</i>

Trinomial name

Zea mays subsp. *mays*
L.



Rice (paddy)

Kingdom:	Plantae
Division:	Magnoliophyta
Class:	Liliopsida
Order:	Poales
Family:	Poaceae
Genus:	<i>Oryza</i>
Species:	<i>O. sativa</i>

Figure 2.10 : Cultivated Crops

B. Water Sampling and Analysis

1. Sample collection and preservation: Before to analysis, the tube wells were flushed with 2-3 tube-well volumes of groundwater, (e.g. 70L for tube well having depth of 20 m and i. d. of 4 cm) [16, 17]. the crystal clear water samples were collected in 500 mL acid washed polyethylene bottles, acidified with 10.0 mL of conc. HNO_3 to keep the pH below 2 and stored in refrigerator at 4°C [5].

2. Measurement of Physical Parameters: pH and dissolved oxygen (DO) of aquifer water were measured on-site with a microprocessor-based $\text{p}^{\text{H}}/\text{mV}/^\circ\text{C}$ meter p^{H} 211 (HANNA, Italy) and a DO-meter sensionTM 6 (HACH, USA). Before analysis, the pH-meter was with calibrated with buffer solutions (at pH 7.01 and 10.01) and DO-meter with electrolyte filling solution. Redox potential (E_{h}) was also measured on-site with the same $\text{pH}/\text{mV}/^\circ\text{C}$ meter. Electrical conductivity (EC) was measured on-site with a digital conductivity meter EC 214 (HANNA, Italy) after calibrating with conductivity solution (HI 7030). All the instruments have manual temperature compensation mode.

3. Pretreatment of Water Samples: Before to analysis of water samples for total iron and manganese, the water samples were subjected to mild digestion with HNO_3 (method 3030 E) [5]. 100 mL of well-mixed, acid- preserved water sample was taken in an Erlenmeyer flask (125 mL). 5mL of 68% HNO_3 was added to it and the flask was placed on a hot plate to evaporate (without boiling) to 15-20 mL. Additional conc. HNO_3 was added and heating was continued until digestion was complete as shown by a light-colored, clear solution. It was transferred to a 100 mL volumetric flask with two rinsing. The pH of the solution was adjusted to 4.0 with 1.0 M NaOH solutions followed by dilution with distilled, deionized water up to the mark.

For analyzing total arsenic (As_{T}) Lead and Cadmium and Chromium, the water samples were subjected to vigorous digestion with nitric acid- sulfuric acid method (method 3030 G) [5].

C. Plant Tissues Sampling and Analysis

1. Sample Preparation: Fresh corns tissue (food grains) samples were rinsed several times with distilled water, cut into pieces and dried in oven at 80°C for 48 hours. Drying of food grains materials was performed as quickly as possible to avoid the growth of molds and microorganism or contained respiration and to minimize loss of weight by enzymatic action in the tissues [2, 3]. The dried food grains materials were subjected to grinding with ceramic mortar and pestle followed by sieving with 0.5 mm screen.

2. Digestion of Biological Samplings: Oxidation of organic matter of food grains tissue and release of the elements such as arsenic was carried out through Wet Oxidation by means of oxidizing acids such as the HNO₃-H₂SO₄-HClO₄ ternary mixture [2, 3, 4, 18,]. All biotic samples (dried and powdered) were accurately weighed (1.0 ± 0.005 g) and taken in a 500 mL Erlenmeyer flask. After adding 10 mL of 69% HNO₃, the flask was swirled to moisten the entire mass of the tissue and was placed on a steam plate for 30 minutes. It was then placed on the electric plate at 180 °C. The suspension was boiled nearly to dryness. This pre-digestion with HNO₃ required about 45 minutes.

The digestion flask and contents were cooled slightly. Then 10 mL of the ternary acid mixture (prepared by mixing 69% HNO₃, 98% H₂SO₄ and 60% HClO₄ in the volume ratio of 10:1:4) was added. The digestion was carried out on the electric hot plate at 220°C until dense white fumes of H₂SO₄ and HClO₄ were vigorously evolved. The digestion was stopped when the residues in the flask were clear and white and only slightly moist with H₂SO₄. The HClO₄, at that point, had been largely removed. This digestion with ternary acid mixture require about 2 hours.

3. Preparation Stock Solution: The digestion flask containing the residue from the wet oxidation of corns tissue was cooled and 10 mL of 82% HCl was added. The flask was swirled and polished and then the solution was poured into a 100 mL measuring flask. Two additional rinsing of the digestion flask were given with

small portion of 6N HCl. The digestion flask was washed twice with distilled deionized water and dilute to make a final volume of 100 mL.

4. Analysis of Samples for total arsenic, Lead and Cadmium: After filtration and subsequent dilution, the aliquot was subjected to hydride generation reactions to determine the concentration of total As, Pb and Cd by both GF-AAS and UV-VIS Spectroscopy. The procedure was the same as that for measuring total As, Pb and Cd in water. Blanks were made under similar experimental and reagent conditions. Other parameters were also measured using standard procedures.

D. Soil Sampling and Analysis

1. Sample preparation: The composition of soil near the roots of the plants may differ from other areas due to absorption by plants. Hence the soils were collected from 3-6 cm beneath the surface layer and most distant from the root and were taken in labeled polyethylene bags. The soils were then dried in an electric oven at 105°C for about 24 hours. The dried mass was cooled and ground with ceramic mortar and pestle to make finer particles followed by sieving with 0.5 mm screen.

2. Digestion of soil samples: Digestion of soil samples were carried out by *modified method of Small and Mc Cants* with the oxidizing acids mixture such as H₂SO₄-HClO₄ acid mixture [4, 19]. Accurately 0.5 ± 0.005 g of the soil sample was heated in a 250-mL Erlenmeyer flask until fuming with 2 mL of 98% H₂SO₄. When the organic matter had been destroyed and the soil assumed a gray color, the flask was cooled and 3 mL of 70% HClO₄ were added with a few boiling chips. The mixture was boiled on an electric hot plate at 220°C for about 2 hours. Heating was discontinued when the soil was near to dryness.

3. Preparation of stock solution of samples: The digestion flask and the contents cooled and 10 mL of 82% HCl was added. The flask was swirled and polished and then the solution was poured into a 100mL measuring flask. Two additional rinsing of the digestion flask were given with small portions of 6N HCl. The digestion

flask was also washed twice with distilled, deionized water and diluted to make a final volume of 100 mL.

4. Analysis of samples for total Arsenic, Lead and Cadmium: After filtration and subsequent dilution, the aliquot was subjected to hydride generation reactions to determine the concentration of total As, Pb and Cd by GF-AAS and UV-VIS Spectroscopy. The procedure was the same as that for measuring total As, Pb and Cd in water. Blanks were made under similar experimental and reagent conditions. Other parameters were also measured using standard procedures.

E. Fish Sampling, Digestion and Analysis

1. Sample Preparation: The fresh fish purchased by the household owner was immediately kept in a refrigerator at -20°C without any processing. When frozen it was preserved in an ice-box for transport to the laboratory. The skin of the sample was then removed, washed with distilled deionized water and cut as small “fillets”, comprised of muscle tissue [20, 21]. It was then dried at 80°C in an oven for 48 hours. All the processes were performed as soon as possible to avoid the growth molds and microorganism and to minimize loss of weight by enzymatic action in the tissues [2, 3]. The dried fish materials were grinded with ceramic mortar and pestle followed by sieving with a screen.

2. Digestion, Preparation of Stock Solution and Analysis: The dried and ground fish samples were digested with ternary acid mixture following the same procedure as described details in case of corns’ tissues. Preparation of stock solution and analysis for total arsenic, cadmium and lead of the digested fish samples were also the same. This is referred to section 2.4 C.

F. Dust Sampling, Digestion and Analysis

In our investigation, the dust samples were collected from inside of the studied households. The samples were dried in an oven at 105°C, sieved with a 0.5 mm screen and digested with H₂SO₄-HClO₄ acid mixture [3]. Preparation of stock solution and analysis for total arsenic, cadmium and lead of the digested dust

samples were also the same as those of soil. This is discussed in section 2.4 D in detail.

G. Estimation of Arsenic, Lead and Cadmium Concentrations in Air

The concentration of inhaled arsenic in indoor air was estimated from existing indoor dust using the following equation [22, 23]:

$$[\text{As}]_{\text{air}} = D \times M_{\text{PM}} \times F_{\text{PM}} \times F_{\text{cont}}$$

Where, D is the concentration of dust in the air (assumed $70.0 \mu\text{g}/\text{m}^3$ which is the annual mean dust concentration for many countries like the United States). M_{PM} is the arsenic concentration on airborne particulate matter (assumed equal to $[\text{As}]_{\text{dust}}$ where dust is derived from the soil), F_{PM} is the proportion of particulate matter that is respirable [assumed $\text{PM}_{10} \sim 73\%$ as 27% of airborne particles are generally found to be $> 10 \mu\text{m}$ in equivalent diameter] and F_{cont} is the fraction of dust that is derived from the contaminated source. For time spent outdoors, F_{cont} was assumed to be equal to $[M_{\text{soil}}]$; when indoors, $F_{\text{cont}} = 0.445[M_{\text{soil}}]$ because 44.5% of indoor dust is considered to be derived from outdoor soil. Therefore,

$$\begin{aligned} [\text{As}]_{\text{air}} &= (70.0 \mu\text{g}/\text{m}^3) \times [\text{As}]_{\text{dust}} \times 0.27 \times 0.445 \\ &= 0.070 \times [\text{As}]_{\text{dust}} \times 0.27 \times 0.445 \mu\text{g}/\text{m}^3 \end{aligned}$$

Similar calculations were made for estimating concentration of inhaled lead and cadmium in indoor air.

2.5 Quality Control

To ensure quality of the measurements, analysis of reagent blanks, and analysis of duplicates, recovery of known additions and analysis of standard reference materials (SRM) were made.

1) Cleaning of glassware: All glassware were sunk into dilute HNO_3 solution about 24 h and then washed through double distilled water. After cleaning, put

them in a electric oven under 100 °C till complete dry. Beside the clean glassware, other equipment were handled with clean, accuracy and sincerity.

2) Analysis of Reagent Blanks: Replicate analyses of reagents blanks were common for each set of experiment. These were performed for estimation of As, Cd and Pb content in rice, vegetables, fish, water and dust.

3) Crosschecking of concentration: For assurance of getting result we have taken some pre-ready sample solution to Borendro laboratory and DPHE laboratory, Rajshahi. Borendro lab used kids' method and DPHE used HG-AAS system to analyze sample. DPHE is a renowned government institution which is performing large research and survey type work. Borendro lab has performed specially arsenic contamination based research. Results have matched to previous result without little deviation. After justifying, all calculations were performed and were finalized data.

4) Duplicate and Triplicate Analysis: At least 5% of total samples were analyzed in duplicates and when the agreement is not good enough those were measured in triplicates to assess precision.

Each duplicates result was analyzed for Relative Percent Difference (%RPD) by the following equation:

$$\% \text{ RPD} = [(DW_1 - DW_2) / [(DW_1 + DW_2) / 2]] \times 100$$

The acceptable %RPD for duplicates of digestion method is not specified by United States Environmental Protection Agency SW846 or by other standard methods. The Contract Laboratory Program (CLP) inorganic statement of work (Method 200 series CLP-M) lists a %RPD control limit of 20% [24, 25]. If any result of a specific sample is not comparable to the other two results, the deviated result was discarded while calculating the average.

5. Recovery of Known Additions: This method is also known as “Method of Standard Additions” which allows to verify the presence or absence of matrix interference. By taking known amounts of the samples (table 2.10), nothing was added

to the first sample, a measured amount of standard that approximates analyte concentration was added to the second and twice the first volume was added to the third. The samples were digested following the same procedure and were diluted to the same volume so that the final concentrations of the original sample constituents are the same in case. Only the amount of added analyte differs by a known amount. Four replicate experiments were performed separately. Recovery for the environmental samples (edible corns' tissues, soils and groundwater) were then analyzed.

6. Analysis of Standard Reference Materials: Two external standard reference materials (SRM) were used to check the accuracy of the accuracy of the methods. Tomato Leaves (SRM 1573a) were obtained from the U. S. National Institute of Standards and Technology (Gaithersburg, MD) and Pond Sediment (NIES 2) from the National Institute for Environmental Studies (Japan). Internal reference material of water was prepared very cautiously from ACS-certified Arsenic Reference Standard Solutions of HACH, USA (Cat.No.14571-42) through successive dilution with distilled deionized water (DDW). Recoveries in the samples were in the range of 91-140% for As_T , Pb_T and Cd_T .

2.6 Statistical Analysis

Statistical analyses have conducted on our getting data. It is a very good process to justify of data accuracy. Over all accuracy of data were performed through statistical analysis. To do this, have used two reliable software. The name of the softwares are excel and SPSS (version 11.5) [26]. Using this software have been calculated range of concentration, arithmetic mean, standard deviation, geometric mean, median and variance.

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CHAPTER THREE

Use of Natural Organic Fertilizers to Reduce of As, Pb and Cd Poisoning in corns

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Chapter 3

Use of Natural Organic Fertilizers

3.1 Introduction

Many crops act as very good accumulators of arsenic, lead, cadmium, etc. The extent of arsenic, cadmium and lead accumulation differs greatly from corns to corns as well as from organs to organs. Zhang et al [1] conducted a pot experiment to investigate the growth and arsenic (As) uptake of pakchoi cabbage and tomatos grown in a grey Fluvo-aquic soil. They observed that arsenic (As) accumulations in pakchoi cabbage were significantly greater than those of shoots of tomato. They also found that the accumulation of arsenic, cadmium and lead by plants is influenced by a number of factors such as the As, Cd and Pb concentration in soil, As, Cd and Pb availability and redox potential of As, Cd and Pb. According to A.J.M. Baker [2] plants can be divided into three groups depending on the response to the concentration of an element in soil. These are accumulators, indicators and excluders. The accumulators concentrate the element in the aboveground parts of the plants. The indicators reflects the external concentrations of the elements and the excluders prevents element uptake until the soil concentration is too high [2].

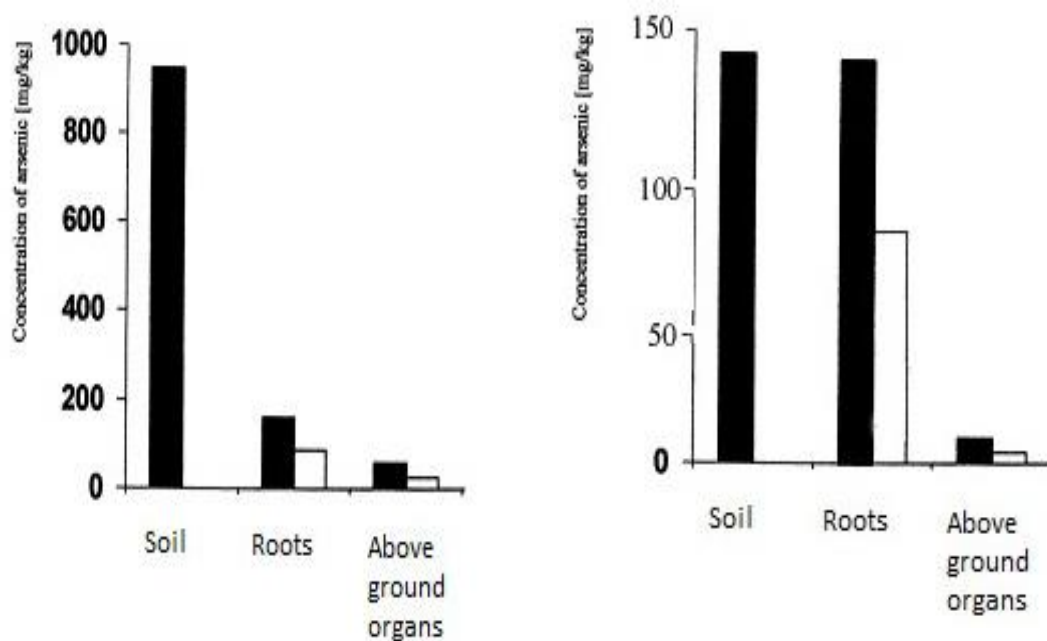
De Temmerman et al. [3] showed that the accumulation of As in terrestrial and emergent plants generally occurs via the roots and shoots in areas with atmospheric depositions of arsenic. Azizur Rahman et al. [4] studied and showed that aquatic macrophytes accumulate As from the water column as well as from the sediment. For uptake via roots, plants are able to modify the rhizosphere by the exudation of organic acids to render elements available. Marschner [5] showed that the organic acid has a major effect on the mobilization of elements bound to ion exchange sites in the rhizosphere. Moreno –Jimenez et al. [6] found that the action of organic acids originating from plant roots may also increase As availability in soil leading to an increased plant As uptake. Silva Gonzaga et al [7] showed a correlation between the As concentration in the plant and the As concentration in the soil for the action of organic acids on As availability in soil. Ghosh et al. [8]

showed that the bacteria in the rhizosphere may also help to increase the As availability, probably by the solubilizing arsenates from insoluble FeAsO_4 and AlAsO_4 in the soil, resulting in a higher plant As uptake.

Di Lonardo et al.[9] and Afrous et al.[10] showed that the terrestrial and emergent plants such as *Populus alba* and *Typha latifolia* primarily and most commonly accumulate As in the roots and low concentration in the shoot. Ma et al. [11] and Smith et al. [12] showed that the distribution of arsenic may be higher to the shoots compared with the roots in some plant species like hyperaccumulating fern *Pteris Vittata*. (*Raphanus sativus*) and in some non-hyperaccumulating plants like radish. Bergqvist and Greger [13] found that the As concentration in the shoots of submerged plants may be higher than the As concentration in the root due to the As accumulation by the shoots from the surrounding water column. Zhao et al. [14] found that arsenic accumulation occurs through silicon aquaglyceroporins and Azizur Rahman et al. [15] showed that it also facilitates the transport of MMA and DMA. Moreno – Jimenez et al. [16] showed that the only known paths for arsenate accumulation in plants are through phosphate transporters.

Anastasia and Kender [17] found that most of the arsenic was concentrated in the root tissues of blueberry, from where the accumulated arsenic was transferred to stem and leaves. Lue et al [18] found the descending order of arsenic concentration in plants as root to stem, stem to leaves and to edible plant tissues. Pitten at al [19] studied uptake of arsenic by terrestrial plants and concluded that the above-ground organs contained less arsenic than the roots. Their findings were represented in the following Histograms showing the concentration of arsenic in soil adhering to the roots, the roots and the above-ground organs of *Holcus lanatus*. and above-ground organs of *H. Lanatus* [19] (Fig 3.1).

Concentration of arsenic in soil adhering to the roots, the roots Black bars indicate samples that were analyzed immediately after the harvest, clear bars identify samples that were washed prior to the arsenic analysis to clean the plant of adhering soil and dust particles.



(a) For highly contaminated sites.

(b) For average contaminated sites.

Figure 3.1 : Concentration of arsenic in soil adhering to the roots, the roots and above-ground organs of *H. Lanatus*

Some authors observed that high levels of arsenic in soil were not reflected in plants, while the other authors observed the reverse cases. For instances, Pitten et al [19] found that in spite of the considerable high arsenic contamination of the soil (mean value 923 mg kg^{-1}), the terrestrial plant arsenic contamination remained comparatively low (mean value 4.1 mg kg^{-1} , dry wt.) They established the phenomenon that plants took up the organoarsenic compounds triphenylarsine and methyl diphenylarsine, not diphenylchloroarsine, diphenylcyanoarsine or phenyldichloroarsine from soil. Milton and Johnson [20] found high levels of arsenic in metalliferous mine (UK) tailings ($630 \pm 34 \text{ mg kg}^{-1}$) that were not reflected in live vegetation ($0.5 - 1.1 \text{ mg kg}^{-1}$) due to physico-chemical nature of the tailings which mitigate against plant uptake. Williams and Whetstone [21] found 14 ppm of arsenic in alpha alpha grass against soil arsenic content of 60 ppm. The transfer of arsenic from soil to vegetation would be evident from soil/plant ratios of arsenic concentration. It is practically notable that there is a large variation in the soil/vegetation ratios for arsenic elsewhere. It illustrates the important interactions between arsenic speciation and environmental impact, and the difficulty of assessing environmental risk from substrate concentrations of total arsenic alone.

Huq and Naidu [22] found that the relationship between soil arsenic and the corresponding arsenic in plant was negative, while the relationship between water arsenic and plant arsenic was positively correlated with $R^2=0.55$ with a multiple R-value of 0.7416. Liu and Gao [23] established that the soil arsenic and sweet potato arsenic were positively related. Ali et al. [24] studied on rice plants in Bangladesh and observed no strong correlation ($R^2=0.21$) between the presence of arsenic in soil and rice plant root. The same authors [24] had shown the correlations between arsenic in grains and arsenic in other parts of rice plants (BR-29 variety) collected from Srinagar and Sonargaon of Bangladesh. CAL Limei et al. [25] studied the spatial distribution, sources, accumulation characteristics and potential risk of heavy metals in the agricultural soils and vegetables. The results show that there are higher accumulation of heavy metals in agricultural soils such as Cu, Zn, Ni, Pb, Cd and Hg. They found the ratios of vegetables samples in which Ni, Pb and As concentrations higher than the Maximum Levels of Contaminants in Foods and the bio-concentration factors (BCF) of heavy metals in vegetables is in the order of Cd > Zn > Cu > As > Ni > Hg > Cr > Pb. They focused on potential risk of heavy metals for food safety and human's health from agricultural soils and vegetables in Dongguan city, Guangdong Province, China.

Soil is a natural body consisting of layers that are primarily composed of four constituents viz., minerals, organic matter, water and air. Soil is the end product of the influence of the climate, relief, biotic activities and parent materials acting over a period of time [26]. The uptake of arsenic, cadmium and lead by plants are dependent upon soil properties and plant physiological factors. Soils have physical and chemical characteristics. The physical characteristics of soil are texture, structure, bulk density, porosity, permeability, shear strength, soil profile and color. The chemical characteristics of soil are acidity, nutrient content and cation exchange capacity. These properties will determine the success or failure of any crop or pasture grown in the soil. The soil texture is simply determined by the relative proportions of sand, silt and clay in the soil. Soil texture is a function of sand, silt and clay particle sizes is shown in Figure 3.2.

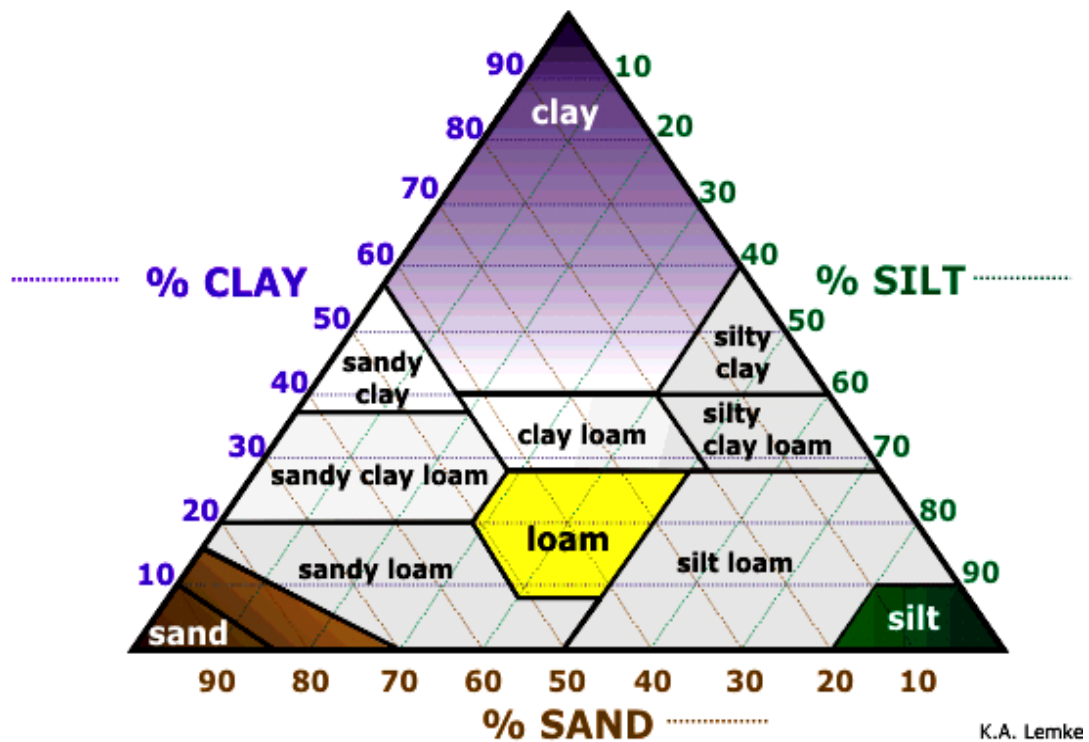


Figure 3.2 : Texture triangle of soil

Of all the factors influencing the evolution of soil, water is the most powerful factor due to its involvement in the solution, erosion, transportation, and deposition of the materials of soil. The amount of water available for plant uptake is determined by a number of factors including soil water potentials (matric and osmotic), soil depth and soil layering [27]. The mixture of water and dissolved and suspended materials is called the soil solution. Water is central to the solution, precipitation and leaching of minerals from the soil profile. Finally, water affects the type of vegetation that grows in a soil, which in turn affects the development of the soil profile.

The most influential factor in stabilizing soil fertility are the soil colloidal particles, clay and humus, which behave as repositories of nutrients and moisture and so act to buffer the variations of soil solution ions and moisture. Their contributions to soil nutrition are out of proportion to their part of the soil. Colloids act to store nutrients that might otherwise be leached from the soil or to release those ions in response to changes of soil pH [28].

Cation exchange capacity (CEC) of a soil is the measure of the capacity of the soil to hold positively charged ions (cations). With a decrease in CEC the elements' availability in the soil is known to increase due to the presence of fewer binding sites. In the heavy metal-contaminated soil the CEC change marginally.

The pH indicates the acidity or alkalinity (basic) of the soil. Different plants have differing optimum soil pH requirements. The majority of plants prefer a pH of around 6 to 7, which is very slightly acid. The soil pH is important in determining the availability of soil minerals. At extremes pH some minerals are “locked up” and cannot be used by the plants, whilst other minerals may become toxic. Aluminium, iron, zinc, copper, manganese and boron become more soluble under acidic conditions and can reach toxic levels.

The greatest influence on plant nutrition is soil pH, which is a measure of the hydrogen ion (acid-forming) soil reactivity, and is in turn a function of the soil materials, precipitation level, and plant root behavior. Soil pH strongly affects the availability of nutrients. Plants require a number of essential nutrients for growth and development. Both the soil and the atmosphere can provide these nutrients. Some of these minerals are needed in large amounts (major elements or macronutrients) and others are needed in smaller amounts (trace elements or micronutrients).

The organic material of the soil has a powerful effect on its development, fertility, and available moisture. Following water and soil colloids, organic material is next in importance to soil's formation and fertility. The importance of soil organic matter in supplying nutrients, contributing to cation exchange capacity and improving soil structure is well recognized [29]. With a decrease in soil organic matter there is an increase in the availability of heavy metals to plants due to fewer binding sites being present in the soil. The organic materials of the soil, mixing with natural organic fertilizers leaching the trace metals into the roots of corns or food grains.

3.2 Experimental Procedures

3.2.1 Materials

The materials employed for the investigation is described in section 2.1. The only additional material is Lauryl Sulfate broth, a cultural media for Fecal Coliform bacteria counting. Sterilized distilled deionized water (DDW) was used for the process involved in counting Fecal Coliform.

Lauryl Sulfate broth: A quantity of 38.10 g of the powdered cultural media (OXOID, UK) (comprised 20.0, 5.0, 2.75, 2.75, 5.0 and 0.1 g of Tryptose, Lactose, K_2HPO_4 , KH_2PO_4 , NaCl and Sodium lauryl sulfate, respectively) was taken in a beaker and 500 mL of sterilized DDW was added to it and heated gently (not evaporated) until completely dissolved. The deep red colored broth was then sterilized in an autoclave by maintaining a temperature and pressure of $121^{\circ}C$ and 0.106 MPa respectively for about 10 minutes [18]. After attaining at room temp., it was stored in refrigerator. Caution was exercised for having no bubble in the broth.

3.2.2 Methods

The methods of fertilizers and soil preparation, and irrigation [20] were the same as mentioned in chapter 2. Water, food grains and soil sampling and analysis procedures [21-24] are discussed elaborately in the previous chapter, and hence not mentioned here. Only the method of microbiological examination is described here.

Microbiological examination

Membrane Filter (MF) method was used to count total and Fecal Coliform bacteria. A volume of 100 ml water was filtered through gridded nontoxic Nitrocellulose membrane filter (Millipore, USA), 47 mm in diameter having pore size of $0.45\ \mu m$, under manual vacuum condition. It was placed in a glass Petri dish, with support of absorbing pad, containing 4 ml of the specific cultural media and incubated in a B-28 incubator (Binder, Germany) for 24 h at $35^{\circ}C$ for total coliform and $44.5^{\circ}C$ for Fecal Coliform. Finally the produced colonies were counted with aid of a microscope.

3.3 Results and Discussion

3.3.1 Characterization of Cultivated Soil

The soils that were cultivated for the study were characterized by measuring physical, chemical and biological parameters. The physical parameters include pH, redox potential (E_h), moisture content, organic matter (OM), sand and clay/silt content. The chemical parameters include total concentrations of arsenic, lead, cadmium, nitrogen and sulfur. Besides these, water soluble arsenic, exchangeable phosphorus and reactive calcium and iron were measured. The only microbiological parameter was counting of Fecal Coliform bacteria. These are represented in Table 3.1. All the parameters were measured using standard procedures and properly calibrated instruments.

Table 3.1 : Selected physical, chemical and microbiological parameters of the studied soil

Parameter	Unit	Cultivated soil		
		Blank [†]	Control	Fertilizer amended [‡]
Physical:				
pH	unit less	6.92	6.41	6.15
Redox Potential (E_h)	mV	35	44	64
Moisture Content	%	8.82	11.97	13.85
Organic Matter (OM)	%	0.67	0.79	1.16
Sand	%	20.99	21.81	21.13
Clay	%	16.98	18.90	18.88
Silt	%	62.03	59.29	59.99
Chemical:				
Exchangeable P	mg L ⁻¹	155	106	111.4
Total N	mg L ⁻¹	0.03	0.07	0.06
Total S	mg L ⁻¹	20.4	29.0	31.7
Reactive Ca	mg L ⁻¹	0.413	0.101	0.149
Reactive Fe	mg L ⁻¹	0.400	0.115	0.121
Total As	mg L ⁻¹	1.565	4.027	2.518
Water soluble As	mg L ⁻¹	0.7931	0.6941	1.117
Total Pb	mg L ⁻¹	0.046	0.192	0.174
Total Cd	mg L ⁻¹	0.011	0.038	0.042
Microbiological:				
<i>Fecal Coliform</i>	CFU/100 g	1.2×10^4	5.7×10^5	2.4×10^8

[†] in blank soil no water was applied.

[‡] averaged values are considered.

Table 3.3.1 reflects that the studied soil is slightly acidic in nature and the acidity is increased slightly after being amended with the fertilizer. This might be due to increase in sulphure content and coliform beateria in amended soil. However, at extreme pH some minerals are “locked up” and cannot be used by the plants, whilst other minerals may become toxic. Aluminium, iron, zinc, copper, manganese and boron become more soluble under acidic conditions. It is to be noted that the majority of corns plants prefers a soil pH of around 6 to 7 (characteristic soil of moist climate) [30], and our studied soil was within the range.

The soil contains very low fraction of organic matter (OM), although it is improved after mixing the fertilizer. Consequently, moisture content is increased from control to fertilizer amended soil. Analysis of sand, clay and silt shows that the soil is of silt loam type. Calculation of hydraulic properties [31] reflects that the soil has the saturation of $0.474 \text{ m}^3 \text{ water} / \text{m}^3 \text{ soil}$ and the available water is $0.175 \text{ m}^3 \text{ water} / \text{m}^3 \text{ soil}$. Microbiological examination shows that amongst the bacteria, only *Fecal Coliform* is increased to about 10^4 fold when fertilizers are added.

The organic matter of the soil in Bangladesh is from $< 1.0\%$ to 3.5% and the pH range from 5.25 to 6.50 [32]. In this point of view, the soil of our study field is similar to barind tracts of Rajshahi in Bangladesh.

3.3.2 Characterization of Irrigation Water

The tube-well water of shallow aquifer of depth 78 ft was used as control irrigation water. For preparation of model water calculated amounts of As_2O_3 , $\text{Pb}(\text{NO}_3)_2$ and CdCl_2 were mixed with the water to achieve the desired concentration of 5 ppm each. The waters were characterized by measuring physical, chemical and biological parameters. The physical parameters include pH, redox potential (E_h) and electrical conductivity (EC). The studied chemical parameters include total concentrations of As, Pb, Cd and Fe as well as available concentrations of Ca, Mg, Mn, Cl and F. The only microbiological parameter was counting of Fecal Coliform bacteria. These are represented in Table 3.2. All the parameters were measured using standard procedures with properly calibrated instruments.

Table 3.2 Selected physical, chemical and microbiological parameters of the irrigation water

Parameter	Unit	Irrigation water	
		Tube-well	Solution amended (Model water)
<i>Physical:</i>			
Temperature	°C	29.4	29.6
pH	unit less	6.83	7.01
Redox Potential (E _h)	mV	30	33
Electrical Conductivity (EC)	µS cm ⁻¹	564	518
<i>Chemical:</i>			
Total As	mg L ⁻¹	0.018	4.875
Total Pb	mg L ⁻¹	0.263	4.819
Total Cd	mg L ⁻¹	0.045	4.801
Total Fe	mg L ⁻¹	0.42	0.30
Ca	mg L ⁻¹	352.7	168.3
Mg	mg L ⁻¹	111.8	72.9
Mn	mg L ⁻¹	0.68	0.32
Cl ⁻	mg L ⁻¹	188.9	395.6
F ⁻	mg L ⁻¹	1.97	0.48
<i>Microbiological:</i>			
Fecal Coliform	CFU/100 g	0	0

From the above table it is clear that the tube-well water is nearly neutral in nature. The higher value of electrical conductivity indicates the presence of more ions in water. The concentrations of calcium and magnesium indicate the tube-well water is hard. The water also contains considerable amounts of chloride and fluoride. It is also free from Fecal Coliform bacteria.

It is interesting to note that the metal ion concentrations except added As, Pb and Cd in model water are less than those in tube-well water. Hence the hardness of the model water is less than the tube-well water. This is probably due to formation of complexes that reduces the free ions concerned. This is reflected in electrical conductivity measurement.

3.3.3 Characterization of Natural Organic Fertilizers

The studied six natural organic fertilizers are rotten cow-dung, rotten dhuncha tree (*Eschynomene Cannabina*), compost, drains mud, dried water hyacinth and earthworm fertilizers. These six fertilizers are frequently used by Bangladeshi farmers traditionally.

These fertilizers were characterized by measuring physical, chemical and biological parameters. The physical parameters include moisture content, pH and redox potential (E_h). The chemical parameters include total concentrations of N, P and S as well as water soluble concentration of As, Pb and Cd. The only microbiological parameter was counting of Fecal Coliform bacteria. These are shown in Table 3.3. All the parameters were measured using standard procedures and properly calibrated instruments.

It is reflected from Table 3.3 that moisture content is the maximum in water hyacinth (11.45%) and minimum in drain mud (2.45%) with the average of 6.71%. All the fertilizers except water hyacinth and rotten Dhuncha are alkaline in nature and ranges from 7.27 to 7.73. The fertilizers are in reduced condition. The N, P and S contents in the fertilizers are characteristics of Bangladeshi soil. They also contain a significant fraction of As, Pb and Cd which is water soluble. The fertilizers also contain a huge amount of bacteria, e.g., only Fecal Coliform bacteria of order of 10^7 - 10^8 per 100 g of fertilizer.

Table 3.3 : Selected physical, chemical and microbiological parameters of the studied natural organic fertilizers

Fertilizer	Moisture Content (%)	pH	E _h (mV)	Organic Matter (%)	Organic C (%)	Total N (%)	Total P (as P ₂ O ₅) (%)	Total S (as SO ₄) (%)	Water Soluble As (mg kg ⁻¹)	Water Soluble Cd (mg kg ⁻¹)	Water Soluble Pb (mg kg ⁻¹)	Fecal Coliform (CFU/100g)
Cow-dung	8.15	7.72	- 89	50.72	30.32	1.13	0.62	0.47	0.187	0.133	3.783	1.3 × 10 ⁷
Drain Mud	2.45	7.41	- 47	35.33	30.09	0.27	0.33	0.07	0.169	0.119	2.834	1.5 × 10 ⁷
Compost	4.65	7.27	- 63	65.17	15.32	0.29	0.83	0.12	0.204	0.135	4.044	1.6 × 10 ⁸
Earthworm Mud	3.19	7.62	- 84	30.72	17.74	0.18	0.51	0.19	0.191	0.128	3.362	8.8 × 10 ⁶
Water Hyacinth	11.45	6.60	23	32.94	19.10	0.52	0.86	0.12	0.174	0.130	3.711	3.7 × 10 ⁶
Rotten Dhuncha	10.36	6.35	- 8	18.12	10.51	1.68	1.02	1.25	0.143	0.123	3.448	1.4 × 10 ⁷
Average	6.71	7.16	- 45	38.83	20.51	0.68	0.70	0.37	0.178	0.128	3.530	3.6 × 10⁷

3.3.4 Plant Height and Yield

It was generally observed that as the amount of applied natural organic fertilizers was increased, the height of the corn's plants was also increased. The effect of studied six natural organic fertilizers for the height of studied four corn's plants is represented in Figure. 3.3.

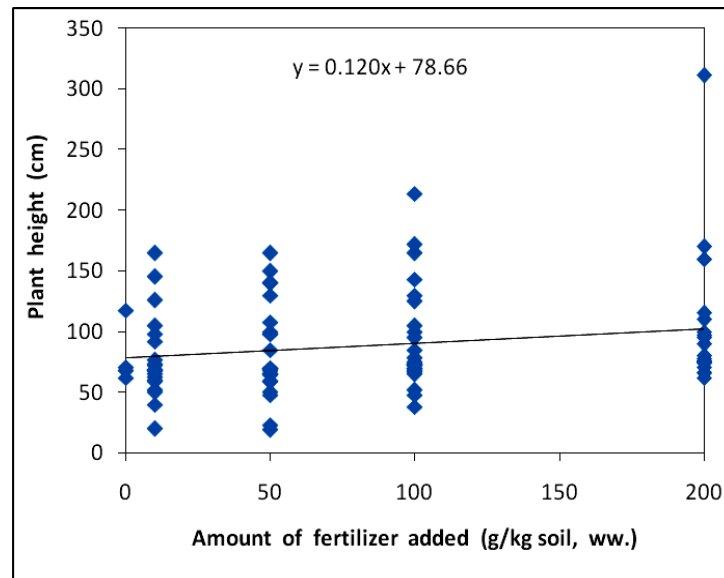


Figure 3.3 : Plant height as a function of organic fertilizer added

The above trend is valid for each of the fertilizers involved. One, namely, the fertilizer Earthworm mud, is shown below as an example.

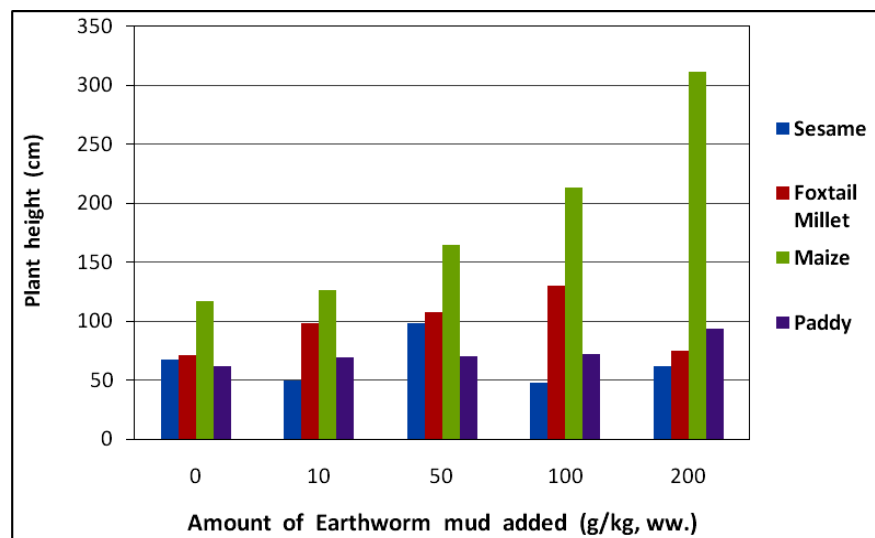


Figure 3.4 : Plant height as a function of Earthworm mud fertilizer added

It was generally noticed that as the amount of the natural organic fertilizers were increased, the yield, that is, the amount of corns obtained was increased. This is depicted in the following figures, where fresh weight of corns is considered. The increment roughly follows a linear pattern Figure 3.5.

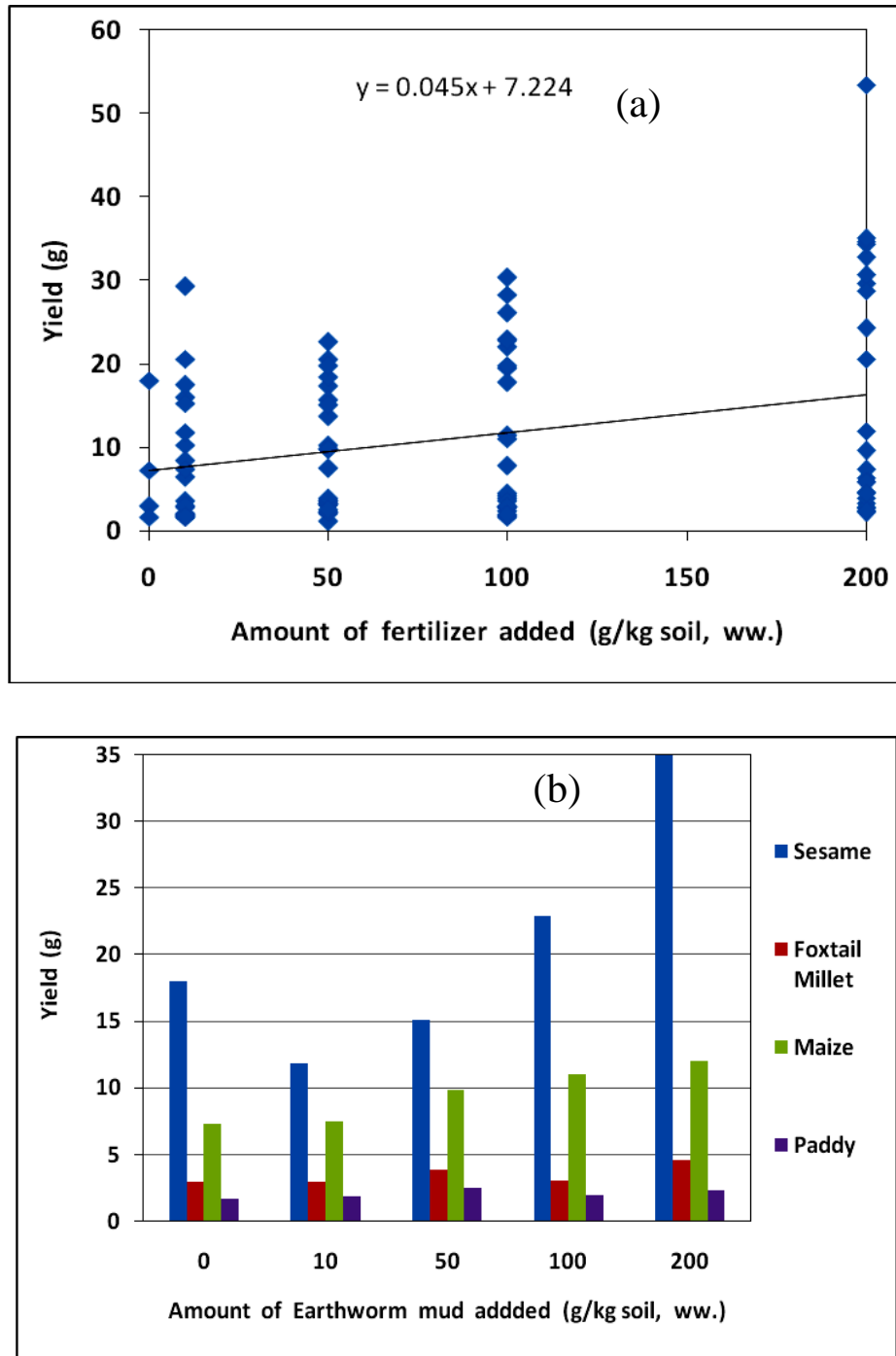


Figure 3.5 Corn yields as a function of Earthworm mud fertilizer added [a] for all fertilizers, b) for Earthworm mud alone]

From the above discussion it obvious that as the amount of natural organic fertilizers was increased in soil, both plant height and corns yield were increased. This means that plant health was improved when more organic fertilizers was added to soil. This is probably due to the following two reasons. Firstly, when natural organic fertilizer was added, the soil becomes enriched in organic matter (OM), which is supported in our data (Table 3.3.31st). The OM, being most part of cellulose, has a tendency to adsorb the toxic ions of As, Pb and Cd. Thus the bioavailability of As, Pb and Cd for the corn plants is decreased. Secondly, the natural organic fertilizers being enriched in micro-organism such as bacteria (Table 3.3.33), the microbial activities are increased when they are added to soil. As a result of these, reduction, bio-methylation, etc. occur that may generate some volatile gases that reduce As, Pb and Cd content in soil. Such process for arsenic is shown in the Figure 3.6. Both factors contribute to detoxification of As, Pb and Cd poisoning in plants.

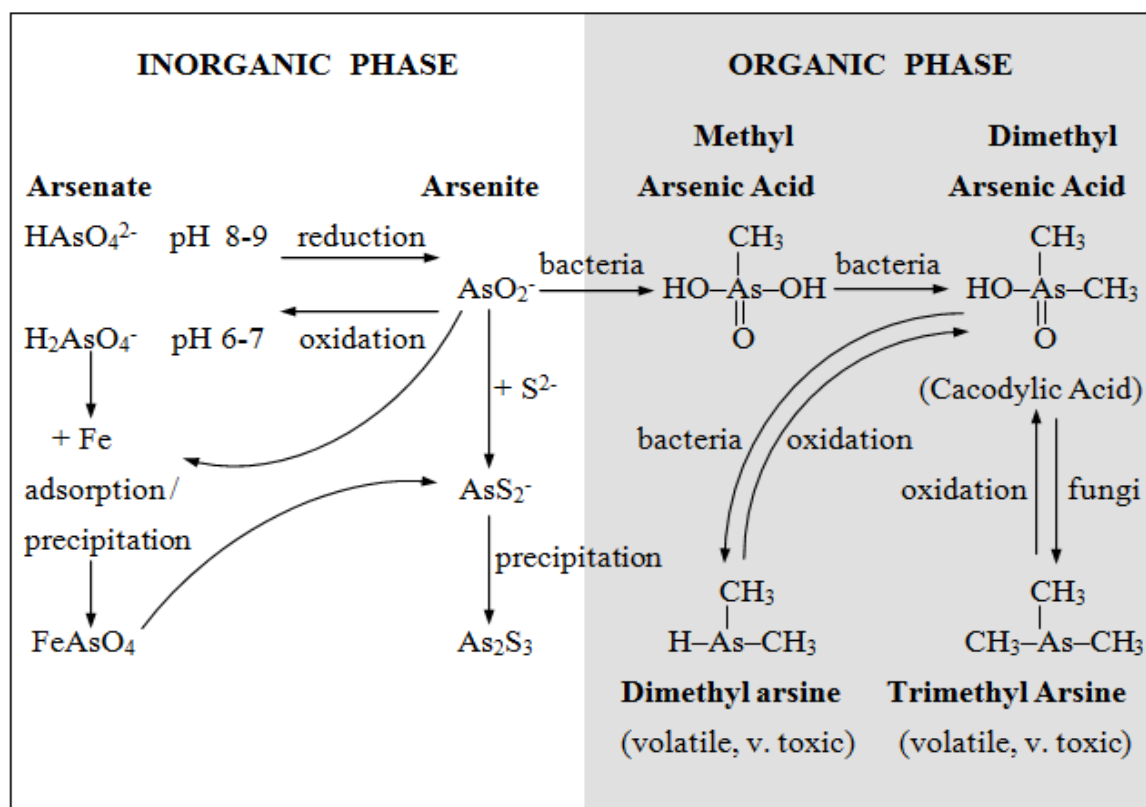


Figure 3.6 : Chemical forms of arsenic and their transformations in soil [28]

3.3.5 Probable Mechanism for Reduction of Arsenic, Cadmium and Lead Load in The Corns Due to Application of The Fertilizers:

Several mechanisms might be employed for reduction of arsenic, cadmium and lead load in crops (corn plants) due to application of natural organic fertilizers. Among these two mechanisms are suggested by our investigations. These include – 1) adsorption of heavy metals and metalloids on soil organic matter contents and 2) bio-methylation and other reactions of heavy metals and metalloids induced by soil microorganisms to generate volatile gases. These are also supported with our data (Table-3.4).

Table 3.4 : Organic matter and Fecal Coliform status of the fertilizer amended soils

Type of bed	Organic Matter (%)	Fecal Coliform (CFU/100g soil)
Control-1	0.76	1.20×10^4
Control-2	1.03	1.12×10^5
CD-10	0.96	2.10×10^6
CD-50	1.34	7.40×10^5
CD-100	1.43	2.50×10^7
CD-200	1.43	3.00×10^6
CM-10	0.83	4.08×10^6
CM-50	1.43	5.30×10^7
CM-100	0.90	1.96×10^8
CM-200	1.43	7.36×10^8
WH-10	0.93	4.00×10^6
WH-50	1.43	5.40×10^7
WH-100	1.58	2.10×10^8
WH-200	1.93	7.80×10^8
DM-10	0.93	3.80×10^6
DM-50	1.03	5.20×10^7
DM-100	1.00	2.00×10^8
DM-200	0.97	7.30×10^8
RD-10	1.00	5.30×10^6
RD-50	1.29	6.80×10^7
RD-100	1.43	2.30×10^8
RD-200	1.29	8.60×10^8
EW-10	1.09	1.40×10^6
EW-50	0.93	4.80×10^7
EW-100	1.03	3.20×10^8
EW-200	1.26	8.80×10^8

The findings are represented in Figure. 3.7 [where organic matter (OM) is expressed in % and Fecal Coliform (FC) bacteria in CFU/100 g soil]. Obviously, as the studied natural organic fertilizers are applied, both of soil organic matter and Fecal Coli form bacteria increases. The increment is less for OM and more for FC.

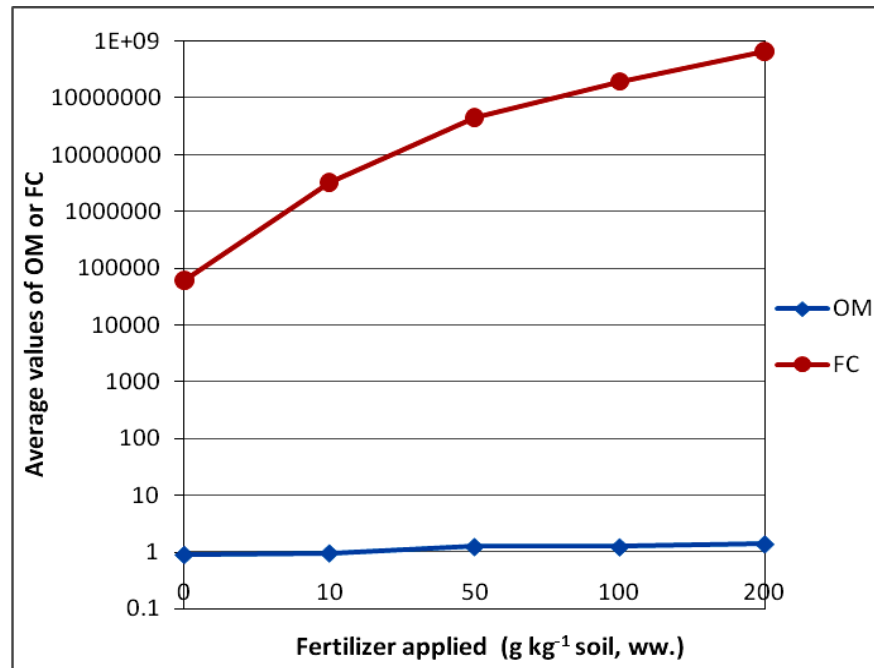


Figure 3.7 : Average values of organic matter and Fecal Coliform of the fertilizer amended soils [the zero value stands for control

Soil organic matter (SOM) plays an important role in the maintenance and improvement of soil properties. It is a dynamic material and is one of the major sources of nutrient elements for plants. SOM is derived to a large extent from plant residues together with the small quantities of animal remains, excreta and microbial tissues. SOM is made up of a large number of substances of widely different chemical composition and the amount of each substance varies with the type, nature and age of plants. All the organic compounds constituting SOM can be summarized in the following Table-3.5.

Table 3.5 : Organic substances of undecomposed soil organic matter [33, 34].

Category	Type	Examples
Nitrogenous	Water soluble	Nitrates, ammonical compounds, amides, amino acids, etc.
	Water insoluble	Proteins, nucleoproteins, peptides, alkaloids purines, pyridines, chitin, etc.
Non-nitrogenous	Carbohydrates	Sugars, starch, hemicellulose, gums, mucilage, pectins, etc.
	Miscellaneous	Lignin, tannins, organic acids, etc.
	Ether soluble	Fats, oils, wax, etc.

Since pH of our studied soil was slightly acidic (average value of 6.15), the trivalent inorganic arsenic should be found as non-dissociated arsenious acid (H_3AsO_3); while pentavalent arsenic as dihydrogen arsenate ion (H_2AsO_4^-) and monohydrogen arsenate (HAsO_4^{2-}). Since As (III) sorption is practically independent at pH of 6-9, but As (V) is much more strongly bound at low pH [35], it is reasonable that the adsorbing material for arsenic is H_2AsO_4^- and HAsO_4^{2-} .

The oxide surfaces, notably iron, manganese, and aluminum oxides, carbonate surfaces, and insoluble organic matter can generate a significant number of positive charges as the pH decreases. The edges of clay minerals also carry pH dependent charge. These edge sites may be important sites of retention of anions at pH below the point of zero charge (PZC) [36].

Cellulose used as an adsorbent. In some studies carried out previously, chemical modification of cellulosic materials significantly enhanced their ion-binding properties, providing greater flexibility in their application to a wide range of heavy metals adsorption [37, 38, 39]. The entire modified agricultural wastes contain cellulose that possesses some ion-exchange properties due the presence of small number of carboxyl, hydroxyl, sulphur, cyano and amino group in their structure. The chemical modification is expected to improve metal ion binding capacity of materials. Bead cellulose loaded with iron oxyhydroxide (BCF) [40] and Starch and Carboxymethyl cellulose (CMC) stabilized with synthetic nanoscale zerovalent iron (NZVI) [41] were applied for the adsorption and removal of arsenate and arsenite from aqueous systems. Cellulose beads are considered to be a

promising adsorbent due to their special properties like hydrophilic, porous, high surface area. Studies on applying cellulose beads as carriers for arsenic removal are still scarce. Cellulose beads and cellulose derivative beads are widely used as ion exchangers, packing materials for chromatography, adsorbents for heavy metal ions and metalloids, proteins, cosmetic additives and carriers for immobilization of biocatalysts [42, 43, 44]. Results revealed that starch stabilized particles (S-nZVI) presented an outstanding ability to remove both arsenate and arsenite. In all cases, the adsorption capacity for arsenite and arsenate was pH dependent. The maximum removal efficiency of both arsenic species was obtained at $\text{pH} = 5 \pm 0.1$ and starched nanoparticles was effective in slightly acidic and neutral pH values. In general, the removal rate of arsenate decreased with increasing pH [41].

It has been observed that Pb forms strong complexes with SOM, and that it can compete with most other metals for adsorption sites on SOM [45- 48]. Lead has a strong affinity for organic ligands. The Pb sorption capacity of the SOM is estimated to be at least 810 mmol kg^{-1} [49]. Manceau et al. [50] used x-ray absorption fine structure (XAFS) spectroscopy to predict that the speciation of Pb in a contaminated soil was 60% Pb-salicylate complexes and 40% Pb-catechol complexes.

These complexes involve the formation of a five-membered chelate complex between the phenol functional groups of the catechol, and a six membered chelate complex formed between the phenol and carboxyl functional groups of the salicylate. Our findings reveal that as SOM is increased; lead bioavailability is decreased causing decreases in lead load in food grains. This is in accordance with the findings of the others.

Organic matter is able to bind heavy metals and metalloids. The soil content of high organic matter could reduce the content of bioavailable metal species as a result of complexation of heavy metal ions. This process could be used for remediation to protect plants against metal pollution.

A brown coal preparation was used as an amendment of soils artificially contaminated with Cd, Pb and Zn. The content of bioavailable zinc, lead and cadmium in soil decreased along with an increase in the amendment dosage of a brown coal preparation [51]. Elevated levels of heavy metals in soils depend on soil pH value, organic matter and clay contents and the fertilization [52]. The fluctuation of mentioned parameters can significantly affect their bioavailability [53, 54]. In recent studies, organic matter has been implicated for alleviating bioavailability of heavy metals in soils. Some researches showed that amendment of contaminated soils with organic matter reduced bioavailability of heavy metals [55].

Cadmium may be absorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Evidence suggests that adsorption mechanisms may be the primary source of Cd removal from soils [56, 57]. The chemistry of Cd in the soil environment is controlled by pH. Under acidic conditions Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6, cadmium is absorbed by the soil solid phase or may be precipitated, and the solution concentrations of cadmium are greatly reduced. Cadmium forms soluble complexes with inorganic and organic ligands. The formation of these complexes decreased the bioavailability of cadmium as well as cadmium load in food grains.

Soil organisms decompose plant and animal residues yielding carbon dioxide and water or synthesized into compounds that comprise humus. It is estimated that 60-80% of the total soil metabolism is due to the microflora. The relative number of soil flora and fauna commonly found in surface soil [34] is presented in **Table-3.6**.

Table 3.6 : Relative number of soil flora and fauna found in surface soil^a

Organism	Number	
	per square meter	per gram
Microflora:		
Bacteria	$10^{13} - 10^{14}$	$10^8 - 10^9$
Actinomycetes	$10^{12} - 10^{13}$	$10^7 - 10^8$
Fungi	$10^{10} - 10^{11}$	$10^5 - 10^6$
Algae	$10^9 - 10^{10}$	$10^4 - 10^5$
Microfauna:		
Protozoa	$10^9 - 10^{10}$	$10^4 - 10^5$
Nematoda	$10^6 - 10^7$	$10 - 10^2$
Other fauna	$10^3 - 10^5$	
Earthworms	30 - 300	

^a generally considered 15 cm (6 in.) deep except for earthworms.

Due to presence of huge amount microorganisms in surface soil biotransformation of metal and metalloid take place. Microbial transformations of metals occur through redox conversions of inorganic forms and conversions from inorganic to organic form and vice versa, typically methylation and demethylation. Microbial methylation plays an important role in the biogeochemical cycle of metals, because methylated compounds are often volatile.

Formation of As (III) also may lead to the volatilization of arsine (AsH_3) and methylarsines from soils. Under soil conditions of high organic matter, warm temperatures, adequate moisture, and other conditions conducive to microbial activity, the reaction sequence is driven towards methylation and volatilization [58]. The loss of organic arsenical compounds from the soil was far greater than for the inorganic source of arsenic. Due to microbial methylation lead and cadmium also converted into volatile dimethylated lead and cadmium [59]. The content of organic matter and fecal coli form bacteria increase in soil along with an increase in the amendment dosages of studied natural organic fertilizers. As a result of bioavailability of As, Cd and Pb in soil as well as in the corn plants decreased. The overall results of the studied six natural organic fertilizers represent in the Figurre-3.7–3.10.

3.3.6 Concentration of Arsenic, Lead and Cadmium in corns

It was generally observed that as the amount of natural organic fertilizers was increased, the concentration of the accumulated arsenic, cadmium and lead was also decreased in most cases. The probable reasons are mentioned in section 3.4. However, the concentrations of arsenic, cadmium and lead in the studied crops as a function of the fertilizer applied are tabulated in Tables-3.7, 3.8, 3.9, 3.10, 3.11 and 3.12 the variations are represented in Figures 3.8, 3.9 and 3.10. It is to be noted here that the concentrations in dry weight are represented in parentheses.

Table 3.7 : Concentration of arsenic in corns (mg kg⁻¹) on fresh weight basis

Type of bed	Concentration of As in corns (mg kg ⁻¹ , ww.)			
	Sesame	Foxtail Millet	Maize	Paddy
Control	0.565	0.841	0.793	0.979
CD-10	0.924	0.917	1.655	0.862
CD-50	0.853	0.810	0.666	0.728
CD-100	0.759	0.662	6.045	0.750
CD-200	0.625	0.526	4.389	0.794
CM-10	0.677	0.131	0.907	0.877
CM-50	0.855	0.339	1.489	0.961
CM-100	0.463	0.757	0.998	0.751
CM-200	0.944	0.982	2.123	1.495
WH-10	0.505	0.836	1.684	0.627
WH-50	0.824	0.521	2.160	1.586
WH-100	0.984	0.491	1.197	1.493
WH-200	0.712	0.711	1.211	0.613
DM-10	0.894	0.500	1.285	0.927
DM-50	0.679	0.237	1.377	1.244
DM-100	0.743	0.289	1.561	1.952
DM-200	0.824	0.594	0.893	0.945
RD-10	0.775	0.576	1.445	0.928
RD-50	0.715	0.548	0.748	0.928
RD-100	0.594	0.444	0.718	0.864
RD-200	0.329	0.860	1.231	0.821
EW-10	0.747	0.869	1.463	1.325
EW-50	0.652	0.931	1.755	0.848
EW-100	0.599	0.547	2.337	0.920
EW-200	0.924	0.917	1.655	0.862

CD = Cow-dung, CM = Compost, WH = Water-hyacinth, DM = Drain mud, RD = Rotten Dhuncha, EW = Earthworm mud

Table 3.8 : Concentration of arsenic in corns (mg kg⁻¹) on dry weight basis

Type of bed	Concentration of As in corns (mg kg ⁻¹ , dw.)			
	Sesame	Foxtail Millet	Maize	Paddy
Control	1.686	2.588	1.773	1.044
CD-10	2.165	2.194	3.302	1.226
CD-50	2.153	2.260	1.622	1.150
CD-100	2.184	2.463	7.055	1.150
CD-200	1.798	1.652	7.923	1.241
CM-10	1.833	0.437	2.941	1.616
CM-50	2.510	0.875	2.455	2.144
CM-100	1.839	1.751	2.337	1.571
CM-200	2.471	2.199	3.252	2.184
WH-10	1.363	1.893	2.657	1.510
WH-50	1.650	2.204	3.206	2.088
WH-100	2.056	1.355	1.890	1.846
WH-200	3.097	1.966	1.703	1.682
DM-10	2.452	1.383	2.059	1.672
DM-50	1.673	0.655	2.503	2.073
DM-100	1.900	0.801	3.391	3.100
DM-200	2.203	1.905	1.992	1.629
RD-10	1.992	1.693	1.753	1.652
RD-50	1.870	2.488	2.024	1.652
RD-100	1.500	1.416	2.005	1.738
RD-200	1.178	2.149	2.414	1.191
EW-10	2.401	2.314	2.163	2.027
EW-50	1.737	2.564	1.850	1.523
EW-100	2.120	2.630	1.223	1.485
EW-200	2.165	2.194	3.302	1.226

CD = Cow-dung, CM = Compost, WH = Water-hyacinth, DM = Drain mud, RD = Rotten Dhuncha, EW = Earthworm mud

Table 3.9: Concentration of cadmium in corns (mg kg⁻¹) on fresh weight basis.

Type of bed	Concentration of Cd in corns (mg kg ⁻¹ , ww.)			
	Sesame	Foxtail Millet	Maize	Paddy
Control	0.082	0.005	0.031	0.008
CD-10	0.106	0.003	0.004	0.005
CD-50	0.096	0.002	0.005	0.005
CD-100	0.081	0.003	0.009	0.006
CD-200	0.087	0.002	0.005	0.007
CM-10	0.093	0.004	0.004	0.004
CM-50	0.085	0.004	0.014	0.006
CM-100	0.060	0.005	0.011	0.004
CM-200	0.075	0.008	0.013	0.012
WH-10	0.077	0.007	0.014	0.006
WH-50	0.049	0.004	0.011	0.006
WH-100	0.121	0.008	0.012	0.124
WH-200	0.038	0.006	0.018	0.004
DM-10	0.067	0.006	0.017	0.007
DM-50	0.102	0.010	0.014	0.013
DM-100	0.098	0.014	0.011	0.007
DM-200	0.061	0.005	0.012	0.005
RD-10	0.060	0.008	0.032	0.006
RD-50	0.059	0.009	0.057	0.008
RD-100	0.058	0.014	0.107	0.008
RD-200	0.027	0.009	0.009	0.008
EW-10	0.037	0.009	0.027	0.008
EW-50	0.093	0.009	0.051	0.008
EW-100	0.052	0.013	0.097	0.004
EW-200	0.106	0.003	0.004	0.005

CD = Cow-dung, CM = Compost, WH = Water-hyacinth, DM = Drain mud, RD = Rotten Dhuncha, EW = Earthworm mud

Table 3.10 : Concentration of cadmium in corns (mg kg⁻¹) on dry weight basis

Type of bed	Concentration of Cd in corns (mg kg ⁻¹ , dw.)			
	Sesame	Foxtail Millet	Maize	Paddy
Control	0.246	0.016	0.090	0.009
CD-10	0.250	0.007	0.009	0.008
CD-50	0.244	0.009	0.013	0.010
CD-100	0.235	0.015	0.011	0.011
CD-200	0.250	0.008	0.010	0.012
CM-10	0.251	0.009	0.015	0.009
CM-50	0.251	0.007	0.023	0.011
CM-100	0.242	0.012	0.027	0.008
CM-200	0.198	0.018	0.020	0.018
WH-10	0.208	0.017	0.022	0.015
WH-50	0.223	0.017	0.017	0.009
WH-100	0.253	0.022	0.019	0.007
WH-200	0.166	0.018	0.028	0.013
DM-10	0.184	0.018	0.028	0.013
DM-50	0.254	0.032	0.027	0.022
DM-100	0.251	0.047	0.025	0.011
DM-200	0.165	0.018	0.027	0.013
RD-10	0.162	0.024	0.039	0.012
RD-50	0.159	0.031	0.054	0.017
RD-100	0.154	0.047	0.084	0.017
RD-200	0.097	0.023	0.019	0.019
EW-10	0.121	0.026	0.019	0.012
EW-50	0.247	0.026	0.174	0.014
EW-100	0.184	0.065	0.346	0.007
EW-200	0.250	0.007	0.009	0.008

CD = Cow-dung, CM = Compost, WH = Water-hyacinth, DM = Drain mud, RD = Rotten Dhuncha, EW = Earthworm mud

Table 3.11 : Concentration of lead in corns (mg kg⁻¹) on fresh weight basis

Type of bed	Concentration of Pb in corns (mg kg ⁻¹ , ww.)			
	Sesame	Foxtail Millet	Maize	Paddy
Control	1.040	0.057	0.385	0.059
CD-10	1.450	0.048	0.070	0.029
CD-50	1.126	0.039	0.049	0.393
CD-100	0.554	0.026	0.112	0.023
CD-200	1.107	0.025	0.054	0.049
CM-10	0.716	0.258	0.037	0.023
CM-50	0.338	0.186	0.070	0.015
CM-100	0.429	0.044	0.066	0.001
CM-200	0.673	0.042	0.080	0.026
WH-10	0.899	0.037	0.062	0.020
WH-50	1.104	0.016	0.104	0.032
WH-100	1.558	0.025	0.067	0.036
WH-200	0.507	0.033	0.063	0.018
DM-10	0.649	0.190	0.056	0.035
DM-50	1.049	0.388	0.073	0.042
DM-100	1.157	0.782	0.058	0.002
DM-200	0.884	0.051	0.073	0.004
RD-10	0.873	0.036	0.110	0.005
RD-50	0.834	0.057	0.156	0.008
RD-100	0.834	0.079	0.248	0.008
RD-200	0.398	0.053	0.064	0.041
EW-10	0.555	0.051	0.163	0.016
EW-50	0.782	0.041	0.288	0.043
EW-100	0.443	0.098	0.536	0.026
EW-200	1.450	0.048	0.070	0.029

CD = Cow-dung, CM = Compost, WH = Water-hyacinth, DM = Drain mud, RD = Rotten Dhuncha, EW = Earthworm mud

Table 3.12 : Concentration of lead in corns (mg kg⁻¹) on dry weight basis

Type of bed	Concentration of Pb in corns (mg kg ⁻¹ , dw.)			
	Sesame	Foxtail Millet	Maize	Paddy
Control	3.120	0.176	1.119	0.063
CD-10	3.396	0.116	0.141	0.042
CD-50	2.768	0.108	0.120	0.042
CD-100	1.596	0.099	0.130	0.035
CD-200	3.186	0.081	0.099	0.077
CM-10	1.938	0.700	0.120	0.042
CM-50	0.994	0.500	0.116	0.035
CM-100	1.707	0.102	0.155	0.021
CM-200	1.763	0.095	0.123	0.038
WH-10	2.425	0.084	0.099	0.049
WH-50	2.577	0.070	0.155	0.042
WH-100	3.256	0.070	0.106	0.048
WH-200	2.206	0.092	0.097	0.049
DM-10	1.781	0.464	0.092	0.063
DM-50	2.584	0.929	0.134	0.070
DM-100	2.957	1.859	0.127	0.003
DM-200	2.355	0.166	0.162	0.008
RD-10	2.326	0.106	0.134	0.010
RD-50	2.291	0.182	0.099	0.017
RD-100	2.221	0.251	0.029	0.017
RD-200	1.425	0.134	0.127	0.063
EW-10	1.784	0.142	0.407	0.024
EW-50	2.083	0.113	0.757	0.077
EW-100	1.567	0.471	1.457	0.042
EW-200	3.396	0.116	0.141	0.042

CD = Cow-dung, CM = Compost, WH = Water-hyacinth, DM = Drain mud, RD = Rotten Dhuncha, EW = Earthworm mud

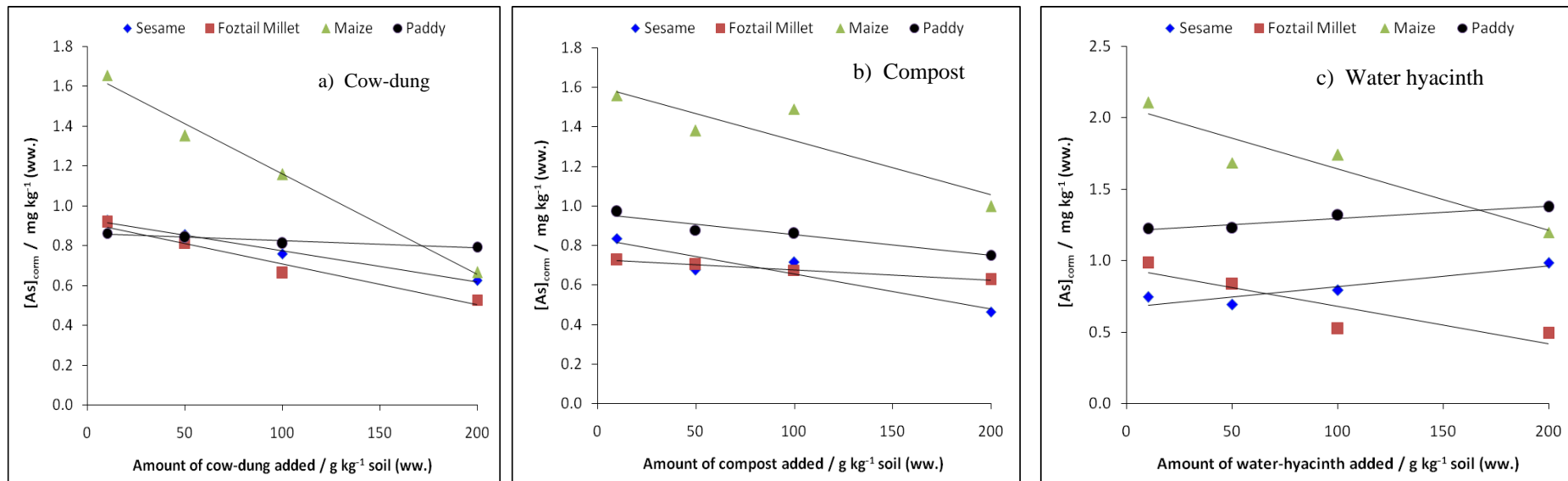


Figure 3.8(a): Effect of the six fertilizers on accumulation of arsenic in corns

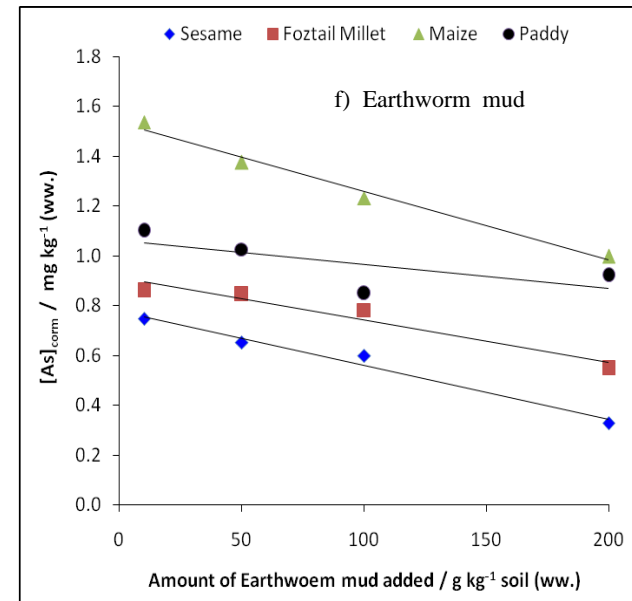
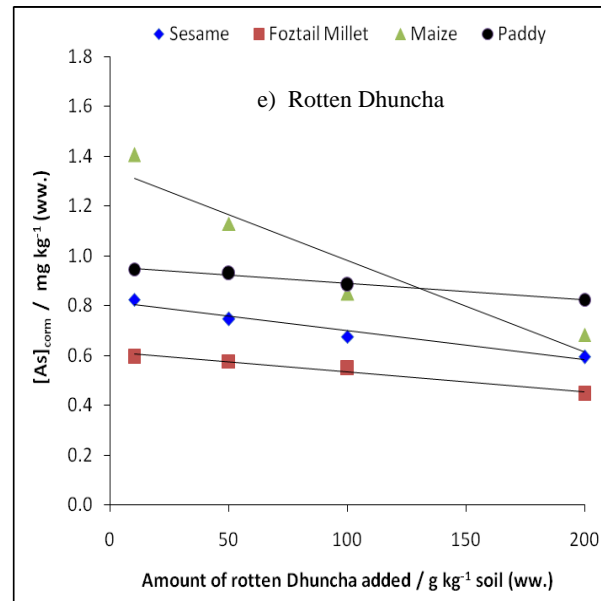
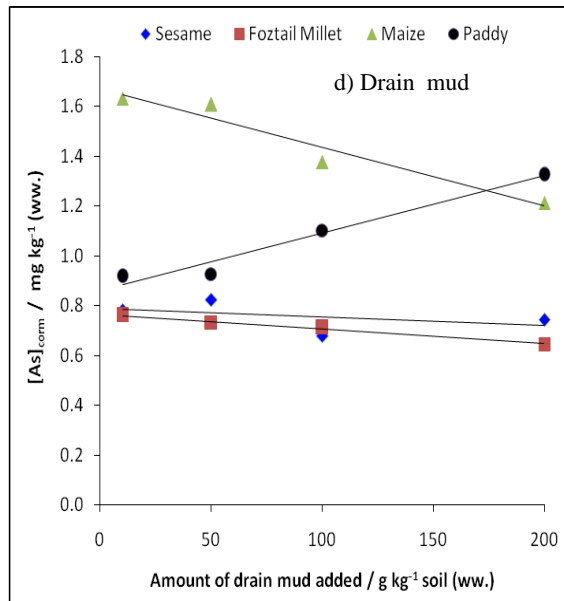


Figure 3.8 (b): Effect of the six fertilizers on accumulation of arsenic in corns

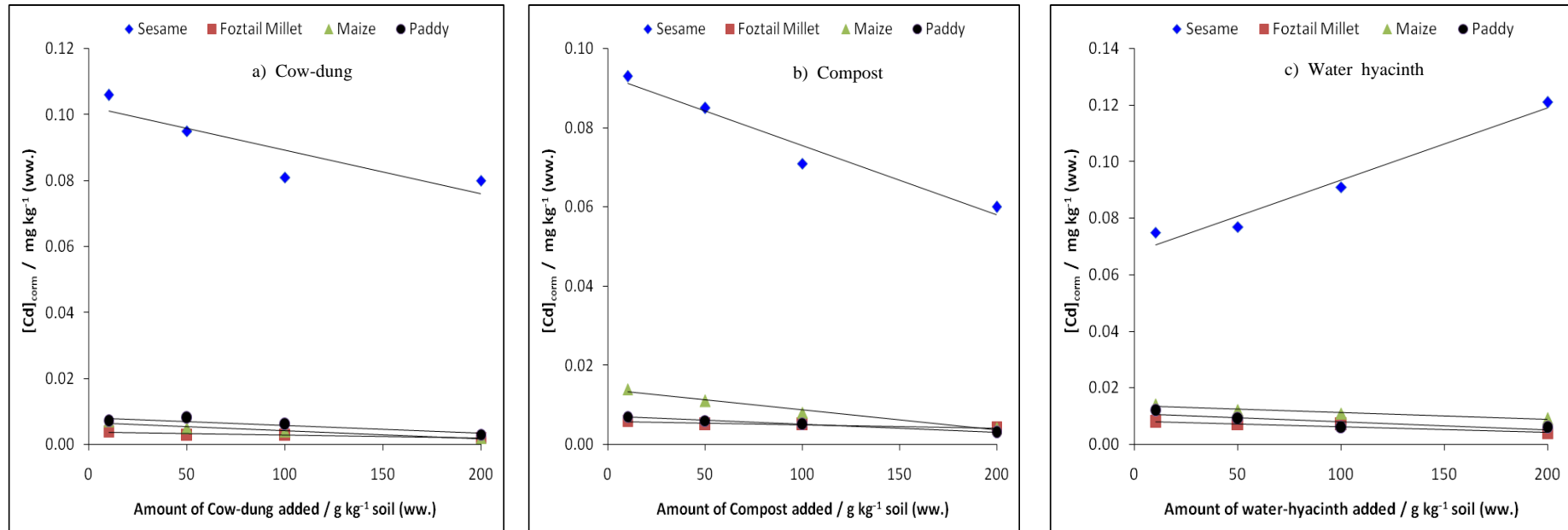


Figure 3.9 (a): Effects of the six fertilizers on accumulation of cadmium in corns

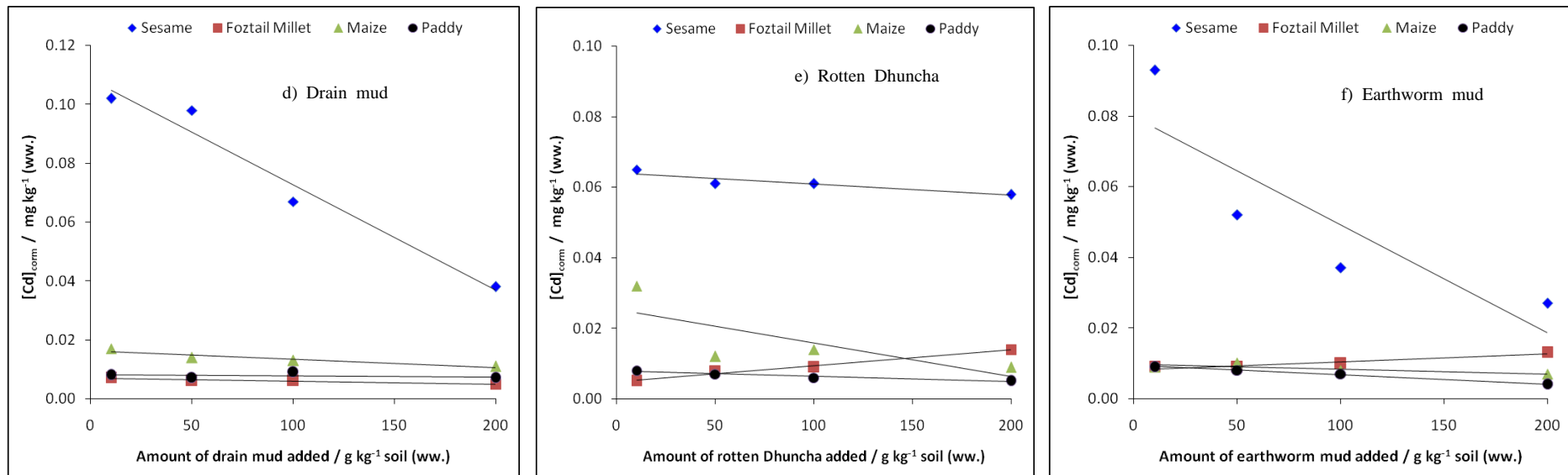


Figure 3.9 (b): Effects of the six fertilizers on accumulation of cadmium in corns

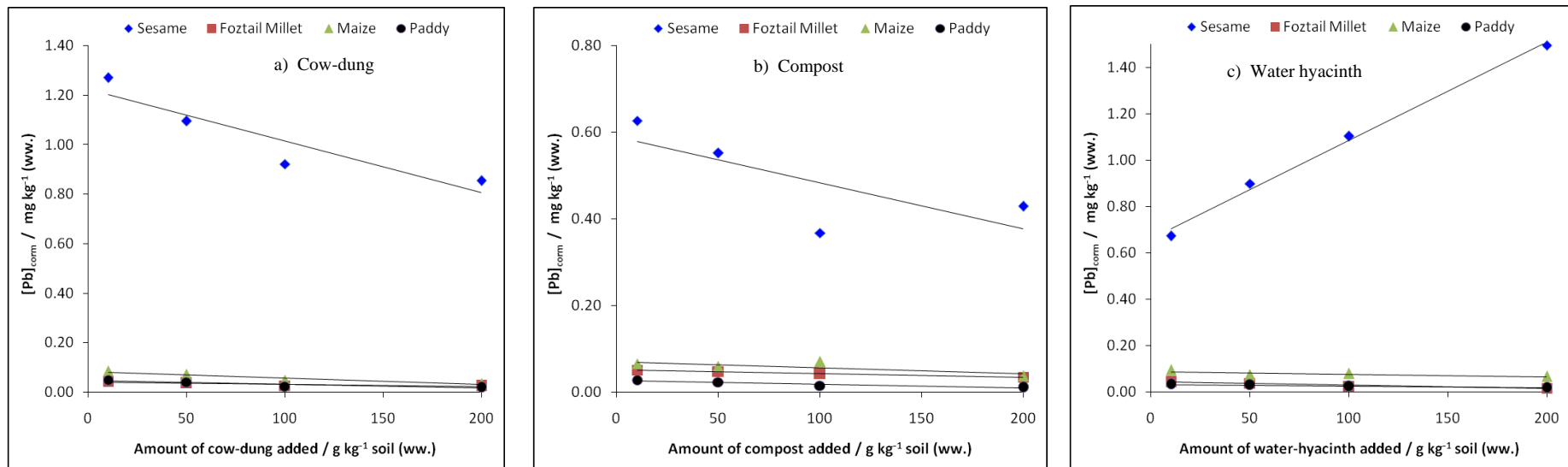


Figure 3.10(a) : Effect of the six fertilizers on accumulation of lead in corns

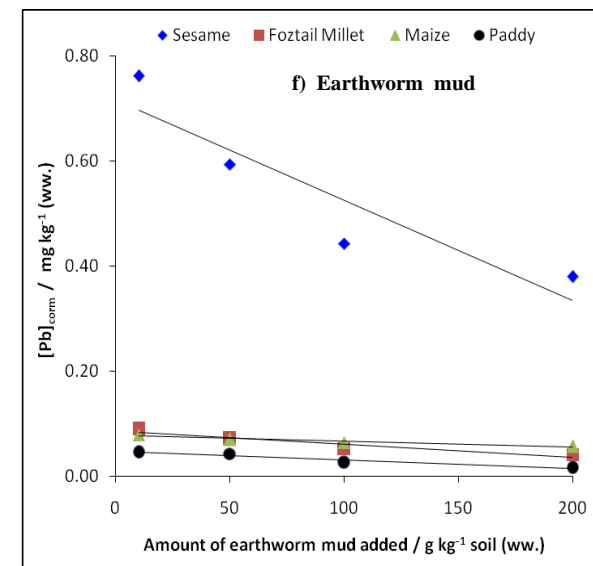
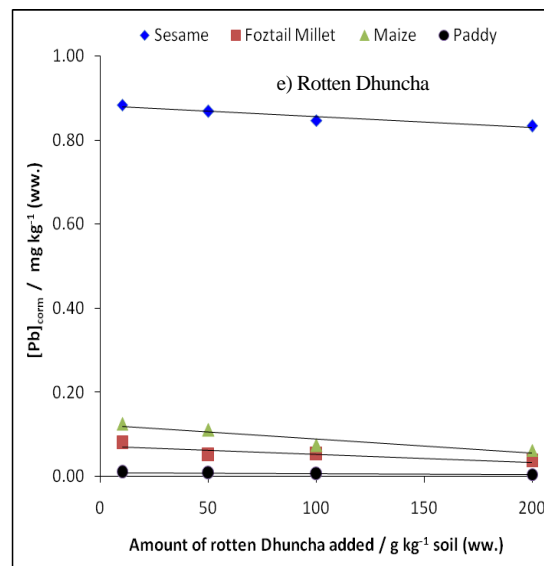
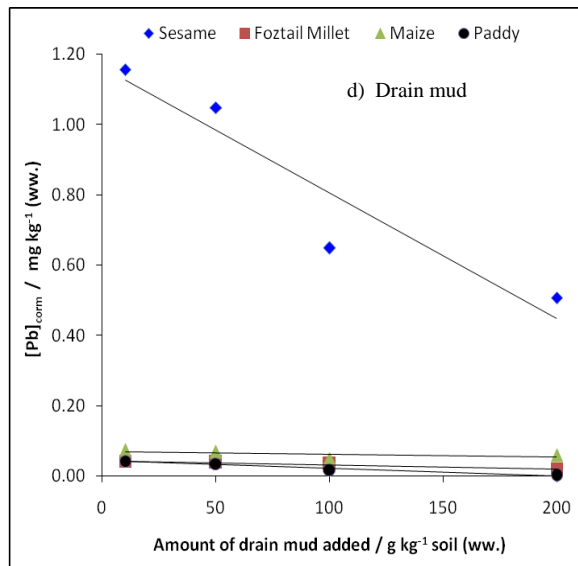


Figure 3.10 (b): Effect of the six fertilizers on accumulation of lead in corns

3.3.7 Statistical Analyses of Concentrations of Arsenic, Lead and Cadmium in The corns

The central tendency indicating the location of the distribution were measured by mean and median, while dispersion showing the dissimilarity of the values by range, standard deviation and variance. These were analyzed for each group of the corns for arsenic, lead and cadmium using SPSS. The analysis results are represented in Table- 3.13

Table 3.13 : Statistical analyses of arsenic, cadmium and lead data sets of the corns

Studied Corns	Range (Min - Max)	Mean \pm SE	Geometric Mean	Median	Standard Deviation	Variance	Skewness
Arsenic (As):							
Sesame	0.329 – 0.984 (1.178 – 3.097)	0.027 \pm 0.712 (2.001 \pm 0.084)	0.697 (1.959)	0.743 (1.946)	0.139 (0.414)	0.020 (0.172)	-0.695 (0.444)
Foxtail	0.444 – 0.982 (0.437 – 2.630)	0.694 \pm 0.028 (1.812 \pm 0.128)	0.680 (1.664)	0.702 (1.935)	0.142 (0.628)	0.020 (0.395)	0.120 (-0.799)
Maize	0.666 – 2.105 (1.223 – 7.923)	1.312 \pm 0.070 (2.729 \pm 0.323)	1.262 (2.457)	1.375 (2.250)	0.353 (1.582)	0.125 (2.504)	-0.078 (2.527)
Paddy	0.791 – 1.373 (1.150 – 3.100)	0.984 \pm 0.035 (1.681 \pm 0.090)	0.970 (1.632)	0.927 (1.640)	0.179 (0.441)	0.032 (0.195)	0.954 (1.391)
Cadmium (Cd):							
Sesame	0.027 – 0.121 (0.097 – 0.254)	0.075 \pm 0.004 (0.205 \pm 0.009)	0.071 (0.199)	0.077 (0.215)	0.022 (0.046)	0.001 (0.002)	-0.229 (-0.682)
Foxtail	0.002 – 0.014 (0.007 – 0.047)	0.022 \pm 0.002 (0.043 \pm 0.003)	0.006 (0.018)	0.006 (0.018)	0.002 (0.014)	0.000 (0.000)	0.833 (1.577)
Maize	0.002 – 0.032 (0.009 – 0.346)	0.011 \pm 0.001 (0.047 \pm 0.014)	0.009 (0.028)	0.011 (0.024)	0.005 (0.072)	0.000 (0.005)	1.753 (3.475)
Paddy	0.003 – 0.012 (0.007 – 0.045)	0.006 \pm .000 (0.014 \pm .001)	0.006 (0.012)	0.007 (0.012)	0.001 (0.007)	0.000 (0.000)	0.137 (3.094)
Lead (Pb):							
Sesame	0.368 - 1.495 (0.994- 3.396)	0.812 \pm 0.058 2.234 \pm 0.124	0.759 (2.149)	0.847 (2.256)	0.292 (0.608)	0.086 (0.370)	0.335 (0.142)
Foxtail	0.016 - 0.090 (0.070- 1.859)	0.043 \pm 0.003 (0.294 \pm 0.081)	0.040 (0.178)	0.042 (0.123)	0.017 (0.401)	0.000 (0.161)	0.970 (2.977)
Maize	0.034 - 0.127 (0.029-1.457)	0.071 \pm 0.004 (0.244 \pm 0.067)	0.068 (0.156)	0.070 (0.127)	0.022 (0.328)	0.001 (0.108)	0.955 (2.834)
Paddy	0.002 - 0.059 (0.003 - 0.077)	0.024 \pm 0.003 0.040 \pm 0.004	0.019 (0.032)	0.023 (0.042)	0.015 (0.020)	0.000 (0.000)	0.437 (0.029)

3.3.8 Efficiency of the Fertilizers

To understand the efficiency of the studied organic fertilizers towards remedial measure of arsenic, cadmium and lead poisoning in food grains, a comparison was made with respect to the control. For this, the average concentrations of arsenic, cadmium and lead found in the studied four crops as a function of the applied fertilizers were first tabulated. These are represented in the following three tables.

Table 3.14 : The average concentration of arsenic in the fresh corns grown in fertilizers used bed

	Average concentration of arsenic (mg kg ⁻¹ , ww.)			
	Sesame	Foxtail	Maize	Paddy
Control	0.723	0.841	1.882	0.979
Cow-dung	0.790	0.729	1.208	0.827
Compost	0.673	0.701	1.357	0.865
Water hyacinth	0.803	0.780	1.682	1.284
Drain mud	0.757	0.712	1.457	1.068
Rotten Dhuncha	0.710	0.573	1.016	0.895
Earth worm mud	0.582	0.758	1.201	0.974

Table 3.15 : The average concentration of cadmium in the fresh corns grown in fertilizers used bed

	Average concentration of cadmium (mg kg ⁻¹ , ww.)			
	Sesame	Foxtail	Maize	Paddy
Control	0.082	0.007	0.018	0.008
Cow-dung	0.091	0.003	0.006	0.006
Compost	0.077	0.005	0.009	0.005
Water hyacinth	0.091	0.007	0.012	0.008
Drain mud	0.076	0.006	0.014	0.008
Rotten Dhuncha	0.060	0.009	0.017	0.007
Earth worm mud	0.052	0.010	0.009	0.007

Table 3.16: The average concentration of lead in the fresh corns grown in fertilizers used bed.

	Average concentration of lead (mg kg ⁻¹ , ww.)			
	Sesame	Foxtail	Maize	Paddy
Control	1.040	0.057	0.127	0.059
Cow-dung	1.036	0.033	0.060	0.033
Compost	0.494	0.044	0.058	0.019
Water hyacinth	1.043	0.030	0.078	0.026
Drain mud	0.841	0.033	0.062	0.024
Rotten Dhuncha	0.859	0.055	0.092	0.007
Earth worm mud	0.545	0.064	0.064	0.033

The change in concentration of arsenic, cadmium and lead accumulated in the studied crops with respect to the control values were calculated. In the change, increase is indicated by (+) signs and decrease by (-) sign. The results are summarized in metal wise as in Table 3.17, 3.18 and 3.19.

Table 3.17 : Percent change in concentration of arsenic with respect to control

	Change in concentration of arsenic with respect to control (%)			
	Sesame	Foxtail	Maize	Paddy
Cow-dung	(+) 9.27	(-)13.32	(-)35.81	(-)15.53
Compost	(-) 6.92	(-)16.65	(-)27.90	(-)11.64
Water hyacinth	(+)11.07	(-)7.25	(-)10.63	(+)31.15
Drain mud	(+)4.70	(-)15.34	(-)22.58	(+)9.09
Rotten Dhuncha	(-)1.80	(-)31.87	(-)46.01	(-)8.58
Earth worm mud	(-)19.50	(-)9.87	(-)36.18	(-)0.51

Table 3.18 : Percent change in concentration of cadmium with respect to control

	Change in concentration of cadmium with respect to control (%)			
	Sesame	Foxtail	Maize	Paddy
Cow-dung	(+)10.98	(-)57.14	(-)66.67	(-)25.00
Compost	(-)6.10	(-)28.57	(-)50.00	(-)37.50
Water hyacinth	(+)10.98	0.00	(-)33.33	0.00
Drain mud	(-)7.32	(-)14.29	(-)22.22	0.00
Rotten Dhuncha	(-)26.83	(+)28.57	(-)5.56	(-)12.50
Earth worm mud	(-)36.59	(+)42.86	(-)50.00	(-)12.50

Table 3.19 : Percent change in concentration of lead with respect to control

	Change in concentration of lead with respect to control (%)			
	Sesame	Foxtail	Maize	Paddy
Cow-dung	(-)0.38	(-)42.11	(-)52.76	(-)44.07
Compost	(-)52.50	(-)22.81	(-)54.33	(-)67.80
Water hyacinth	(+)0.29	(-)47.37	(-)38.58	(-)55.93
Drain mud	(-)19.13	(-)42.11	(-)51.18	(-)59.32
Rotten Dhuncha	(-)17.40	(-)3.51	(-)27.56	(-)88.14
Earth worm mud	(-)47.60	(+)12.28	(-)49.61	(-)44.07

The overall change for arsenic, cadmium and lead is shown in Table 3.20.

Table 3.20 : Percent change in concentration of arsenic, cadmium and lead with respect to control.

Overall change (%)			
	As	Cd	Pb
Cow-dung	(-) 13.85	(-)34.46	(-)34.83
Compost	(-)15.78	(-)30.54	(-)49.36
Water hyacinth	(+) 6.08	(-)5.59	(-)35.40
Drain mud	(-)6.03	(-)10.96	(-)42.94
Rotten Dhuncha	(-)22.06	(-)4.08	(-)34.15
Earthworm mud	(-)16.52	(-)14.06	(-)32.25

The findings can be represented in the following Figure. 3.11.

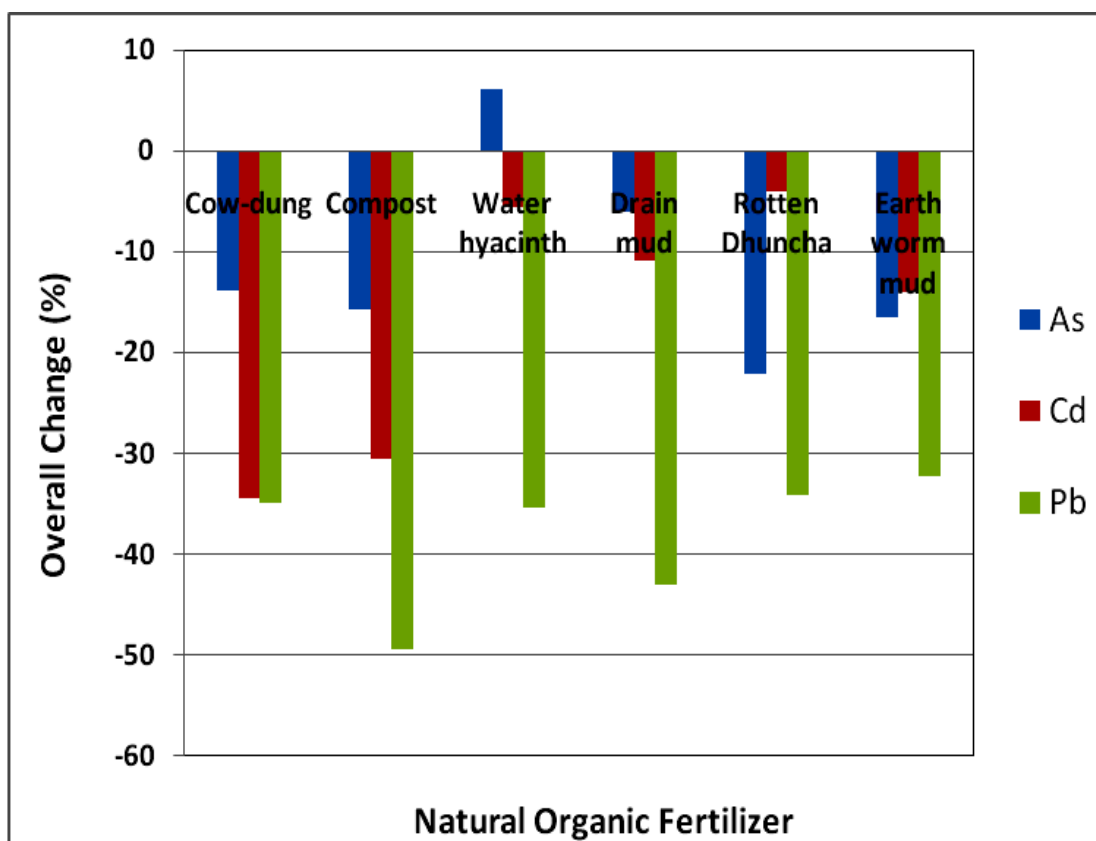


Figure 3.11 : Efficiency of the studied six natural organic fertilizers to reduce toxic ions

The above Table and Figure show that the studied six natural organic fertilizers can be arranged in the following order in terms of their efficiencies to reduce the toxic ions.

For Arsenic: Rotten Dhuncha > Earthworm mud > Compost > Cow-dung > Drain mud > Water hyacinth

For Cadmium: Cow-dung > Compost > Earthworm mud > Drain mud > Water hyacinth > Rotten Dhuncha

For Lead: Compost > Drain mud > Water hyacinth > Cow-dung > Rotten Dhuncha > Earthworm mud

Therefore, the overall order for all the fertilizers are for Simultaneous Reduction of Arsenic, Cadmium and Lead are as follows

Compost >> Earthworm mud \approx Cow-dung \approx Drain mud >> Rotten Dhuncha \approx Water hyacinth.

The above findings suggest that the first five natural organic fertilizers of overall order, namely, Compost, Earthworm mud, Cow-dung, Drain mud and Rotten Dhuncha can be utilized in the agricultural soil for simultaneous reduction of arsenic, cadmium and lead toxicity of corn's plants. Fortunately, in Bangladesh the usual practice of the farmers is to use the mentioned five fertilizers. They sometimes replace drain mud by pond mud or ditch mud. However, earthworm mud and water hyacinth are not frequently used due to their relatively low availability.

Inspection of the carbon to nitrogen ratio (C: N) of the studied fertilizers (Table 3.3.3) show that the overall average C: N ratio of the fertilizers is 55.44 (C as 20.51% and N as 0.68%). The overall average organic matter (OM) of the fertilizers is 38.83%, a moderate level. Both of these reveal that the fertilizers are good for use in agricultural purpose. It is also reported that the studied fertilizers are very good in restoring soil texture, good soil condition for bacterial growth and many other properties. This is supported in our data.

3.4 Conclusions

Analyses of irrigation water, cultivated soils, the natural organic fertilizers (rotten cow-dung, rotten Dhuncha tree, compost, drain mud, dried water hyacinth and earthworm mud) and edible plant tissues of the food grains (Sesame, Foxtail, Maize, Paddy) lead to the following conclusions:

1. When the studied natural organic fertilizer is mixed with soil, its Organic Matter content is increased to 57%. Fecal Coliform bacteria is also increased to 1000 fold. That is, soil condition is improved.
2. After harvesting with contaminated water, total As, Pb and Cd content in soil is decreased with respect to control in most cases, although 120 mg of each of As, Pb and Cd is added in 2.25 sq. ft area through irrigation and the fertilizers themselves contain considerable amount of As, Pb and Cd.
3. Generally, as the amount of applied natural organic fertilizers were increased, the plant height as well as percent yield were both increased. The increment roughly follows a linear pattern. This is due to improvement in plant health as more fertilizers are added. This may be caused by increment in organic matter (OM) of soil that has a tendency to adsorb the toxic ions of As, Pb and Cd, and enrichment in bacteria which facilitate reduction, bio-methylation, etc. of ions of As, Pb and Cd to generate their volatile gases.
4. The studied fertilizers themselves contain considerable amount of As, Pb and Cd. For example, the average values of water soluble part of As, Pb and Cd in the studied fertilizers were 0.178, 3.530 and 0.128 mg kg⁻¹ respectively.
5. Generally, the studied fertilizers reduce As, Pb and Cd toxicity in corns simultaneously. Compost is the best fertilizer in this regard.
6. The efficiency of the studied fertilizers in simultaneous reduction of metal toxicity are as follows: (Compost) >> (Earthworm mud) ≈ (Cow-dung) ≈ (Drain mud) >> (Rotten Dhuncha) ≈ (Water hyacinth).

7. The reduction of metal toxicity in corn plants is attributed to two reasons – a) adsorption of metal by organic matter and b) bi-methylation to volatile gases caused by bacteria.
8. It is interesting to note that Sesame contains more As, Cd and Pb than any other corn. This might be due to fair solubility of As, Cd and Pb in oil.

So, the first five fertilizers could be recommended for remedy of As, Pb and Cd toxicity in corns.

The concluding remarks refer that the first five fertilizers, namely, Compost, Earthworm mud, Cow-dung and Drain mud, could be recommended for remedy of arsenic, cadmium and lead toxicity in food grains. Fortunately, in Bangladesh and in many Asian countries, the usual practice of the farmers is to use the mentioned five fertilizers.

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CHAPTER FOUR

RISK ASSESSMENT TO ARSENIC, CADMIUM AND LEAD EXPOSURE

Introduction

Experimental

Materials

Methods

Results And Discussion

Concentrations of Arsenic, Lead and Cadmium in Environmental Samples:

Statistical analyses of Arsenic, Lead and Cadmium in Environmental Samples:

Individual Contribution from As, Cd and Pb Exposure

Risk assessment

Comparison

Conclusion

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Chapter 4

Risk Assessment

4.1 Introduction

Risk assessment has been defined as “the characterization of the potential adverse health effects of human exposures to environmental hazards” [1]. In a risk assessment, the extent to which a group of people has been or may be exposed to a certain chemical is determined, and the extent of exposure is then considered in relation to the kind and degree of hazard posed by the chemical, thereby permitting an estimate of the present or potential health risk to the group of people involved. Risk assessment typically involves four steps: exposure assessment, toxicity assessment, risk characterization, and uncertainty analysis. The first step is to determine the potential health effects of toxic endpoints that may result from excess exposure to a metal. This is followed by dose-response studies, either conducted through large scale human epidemiologic studies on human populations with a broad range of human exposures or based on animal studies [2]. Human health risk assessment is also defined as the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future, by the United States Environmental Protection Agency (USEPA). Health risk assessment sprang up during the 1980s. It involves identifying the potential of a risk source to introduce risk agents into the environment, estimating the amount of risk agents that come into contact with the human-environment boundaries and quantifying the health consequence of exposure. Since the birth of health risk assessment, it has drawn a lot of attention from many scientists across the world and many assessments relating to drinking purpose and human health have been reported. Alam et al. carried out a study of the water quality conditions of Sylhet city of Bangladesh and its restaurants and assessed the risks to human health. At the same time in China, massive studies have been done on health risk assessment.

Li and Tian analyzed health risk caused by heavy metals in a water source and found the health risk comparisons caused by gene toxic substances was $\text{Cr}^{6+} > \text{As} > \text{Cd}$ and risk comparisons caused by body toxic substances was $\text{Pb} > \text{Cu} > \text{Hg}$ [3]. Heavy metals are an important source of food contamination and health hazard. The main threats to human health are associated with exposure to arsenic, cadmium, lead and mercury and copper. Absorption of heavy metals through food has been shown to have serious consequences on health and thereby economic development associated with a decline in labour productivity as well as the direct costs of treating illnesses such as kidney disease, damage to the nervous system, diminished intellectual capacity, heart disease, gastrointestinal diseases, bone fracture, cancer and death [4]. Trace elements are very harmful because of their non biodegradable nature, long biological half-lives, and their potential to accumulate in different body parts. High concentrations of trace elements (Cu, Cd, and Pb) in vegetables and fruits were related to prevalence of upper gastrointestinal cancer high [5]. Millions of people worldwide consume arsenic-contaminated rice; however, little is known about the uptake and bioavailability of arsenic species after arsenic-contaminated rice ingestion [6]. Environmental risk factors include unsafe water, sanitation and hygiene, indoor and outdoor air pollution, chemicals, wastes, recreational environment, water resources management, land use, noise, radiation, occupation, climate change, and others.

Water-pollutants are a major source of morbidity and mortality in developing countries [7]. Heavy metals constitute a very heterogeneous of elements widely group varied in their chemical properties and biological functions. Heavy metals are kept under environmental pollutant category due to their toxic effects in plants, human and food. Arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) are cumulative poison. These heavy metals are persistence, accumulate and not metabolized in other intermediate compounds and do not easily break down in environment. These metals are accumulating in food chain through uptake at primary producer level and then through consumption at consumer level. However, subsequent metal contamination discovered by testing water necessitated mitigation

programmes [8]. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning [9]. The International Agency for Research on Cancer (IARC) classified lead as a possible human carcinogen in 1987 [10]. Causes of arsenic toxicity include ingestion of arsenic (found in insect poisons), skin contact (e.g. some linseed oils) and even drinking water. Arsenic is typically considered a heavy metal and shares many toxic characteristics with the other heavy metals (eg, lead, mercury) [11]. Humans may come in contact with arsenic in contaminated dusts, fumes, or mists. They may eat food contaminated with arsenical pesticides or grown with arsenic-contaminated water or in arsenic-rich soil [12]. Initially arsenic enters into the human body through ingestion, inhalation, or skin absorption. After entering into the body it is distributed in a large number of organs including the lungs, liver, kidney and skin [13]. The body has need for approximately 70 friendly trace element heavy metals, but there are another 12 poisonous heavy metals, such as Lead, Mercury, Aluminum, Arsenic, Cadmium, Nickel, etc., that act as poisonous interference to the enzyme systems and metabolism of the body. No matter how many good health supplements or procedures one takes, heavy metal overload will be a detriment to the natural healing functions of the body. Some metals are naturally found in the body and are essential to human health. Iron, for example, prevents anemia, and zinc is a cofactor in over 100 enzyme reactions. Magnesium and copper are other familiar metals that, in minute amounts, are necessary for proper metabolism to occur. Toxic heavy metals have no function in the body and can be highly toxic. Heavy metals are taken into the body via inhalation, ingestion, and skin absorption. If heavy metals enter and accumulate in body tissue faster than the body's detoxification pathways can dispose of them, a gradual buildup of these toxins will occur. Metals are particularly toxic to the sensitive, rapidly developing systems of fetuses, infants, and young children. Some metals, such as lead and mercury, easily cross the placenta and damage the fetal brain. Childhood exposure to some metals can result in learning difficulties, memory impairment, damage to the nervous system, and behavioral problems such as aggressiveness and hyperactivity. At

higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults [14].

Currently, millions of people living in and around Bangladesh are at risk for organ dysfunction and cancer from chronic arsenic poisoning from the water supply [15]. There are some heavy metals that are necessary to support life in very small doses, but in large amounts are toxic and can present a health hazard if they build up in the system. Zinc is important to the body, as is cobalt atoms found in vitamin B-12. Iron is another good heavy metal, and so is copper, manganese, chromium and selenium. On the other hand lead, mercury and cadmium are heavy metals that are very toxic to humans, and have no known benefit to the body. Lead, mercury, cadmium, and arsenic are the most common examples of toxic metal exposure [16]. Toxicity is of the utmost concern in dealing with hazardous substances. This includes both long term chronic effect from continual or periodic exposure to low levels of toxicants and acute effects from a single large exposure [17]. Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. The major route of exposure to cadmium for the non-smoking general population is via food; the contribution from other pathways to total uptake is small. A major part of cadmium in the human diet comes from agricultural products.

The pathway of human exposure from agricultural crops is susceptible to increases in soil cadmium. Cadmium accumulates in the human body and especially in the kidneys. The accumulation of cadmium in the kidney (in the renal cortex) leads to dysfunction of the kidney with impaired reabsorption of proteins, glucose, and amino acids [18]. In the general non-smoking adult population, the major exposure pathway of lead is from food and water. Airborne lead may contribute significantly to occupational exposure and exposure of smokers. For infants and young children lead in dust and soil often constitutes a major exposure pathway and this exposure has been one of the main concerns as to the exposure of the general population. The intake of lead will be influenced by the age and behavioral characteristics of the child and the bioavailability of lead in the source

material. In adult humans approximately 10% of the dietary lead is absorbed. However, in infants and young children as much as 50% of dietary lead is absorbed. Depending upon the type of lead compounds, particle size, and solubility in body fluids, up to 50% of inhaled lead compounds may be absorbed.

Current studies indicate that even minute levels of toxic elements have negative health consequences; however, these vary from person to person. Nutritional status, metabolic rate, the integrity of detoxification pathways (ability to detoxify toxic substances), and the mode and degree of heavy metal exposure all affect how an individual responds. Children and the elderly, whose immune systems are either underdeveloped or age-compromised, are more vulnerable to toxicity [19]. Although some investigators prefer to determine lead and cadmium etc in the liver of fish, an investigation was carried out in the edible tissue only as the dietary habit of the people of Bangladesh excludes liver of fishes. The levels of Pb vary between $0.29 \mu\text{g g}^{-1}$ in *Mystus vittatus* and $10.055 \mu\text{g g}^{-1}$, *Sicamugil cascasisa* (Kachki) and those of Cd, between $0.03 \mu\text{g g}^{-1}$, *Mastacembelus armatus* and $0.16 \mu\text{g g}^{-1}$, *Ompok pabda* (Pabda). These variations are likely to be due to the living nature and dietary habits of the different species of fish. Shorputi is the bottom living fish. *Tenualosa ilisha* (Ilish) is a fish of migrating nature. This fish is largely available in the river, the Meghna at the mouth of the Bay of Bengal. The levels of Pb and Cd in this fish are 1.64 and $0.10 \mu\text{g g}^{-1}$. In two medium size popular fish species, *Labeo rohita* (rui) and *Pangasius pangasius* (Pangas), Pb levels range between 1.25 and $3.09 \mu\text{g g}^{-1}$ and those of Cd, 0.09 and $0.13 \mu\text{g g}^{-1}$. Due to dietary difference between these fish species and the other fish samples is unlikely to be the source of higher metal [20]. Concern has been raised by Bangladeshi and international scientists about elevated levels of arsenic in Bengali food, particularly in rice grain. That was the first inclusive food market-basket survey from Bangladesh, which addresses the speciation and concentration of arsenic in rice, vegetables, pulses, and spices. Three hundred thirty Aman and Boro rice, 94 vegetables, and 50 pulse and spice samples were analyzed for total arsenic, using inductivity coupled plasma mass spectrometry (ICP-MS). The districts with

the highest mean arsenic rice grain levels were all from southwestern Bangladesh: Faridpur (boro) 0.51 > Satkhira (boro) 0.38 > Satkhira (aman) 0.36 > Chuadanga (boro) 0.32 > Meherpur (boro) 0.29 $\mu\text{g As g}^{-1}$. The vast majority of food ingested arsenic in Bangladesh diets was found to be inorganic; with the predominant species detected in Bangladesh rice being arsenite (As^{III}) or arsenate (As^{V}) with dimethyl arsenic acid (DMA^{V}) being a minor component. Vegetables, pulses, and spices are less important to total arsenic intake than water and rice. Predicted inorganic arsenic intake from rice is modeled with the equivalent intake from drinking water for a typical Bangladesh diet. Daily consumption of rice with a total arsenic level of 0.08 $\mu\text{g As g}^{-1}$ would be equivalent to a drinking water arsenic level of 10 $\mu\text{g L}^{-1}$ [21]. Environment is defined as the totality of circumstances surrounding an organism or group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of organisms. It consists of the flora, fauna and the biotic, and includes the aquatic, terrestrial and atmospheric habitats.

The environment is considered in terms of the most tangible aspects like air, water and food, and the less tangible, though no less important, the communities we live in. A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance has to be present in the environment beyond a set or tolerance limit, which could be either a desirable or acceptable limit. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment [22]. Heavy metal may enter the body through inhalation of dust, direct ingestion of soil, and consumption of food plants grown in metal contaminated soil [23].

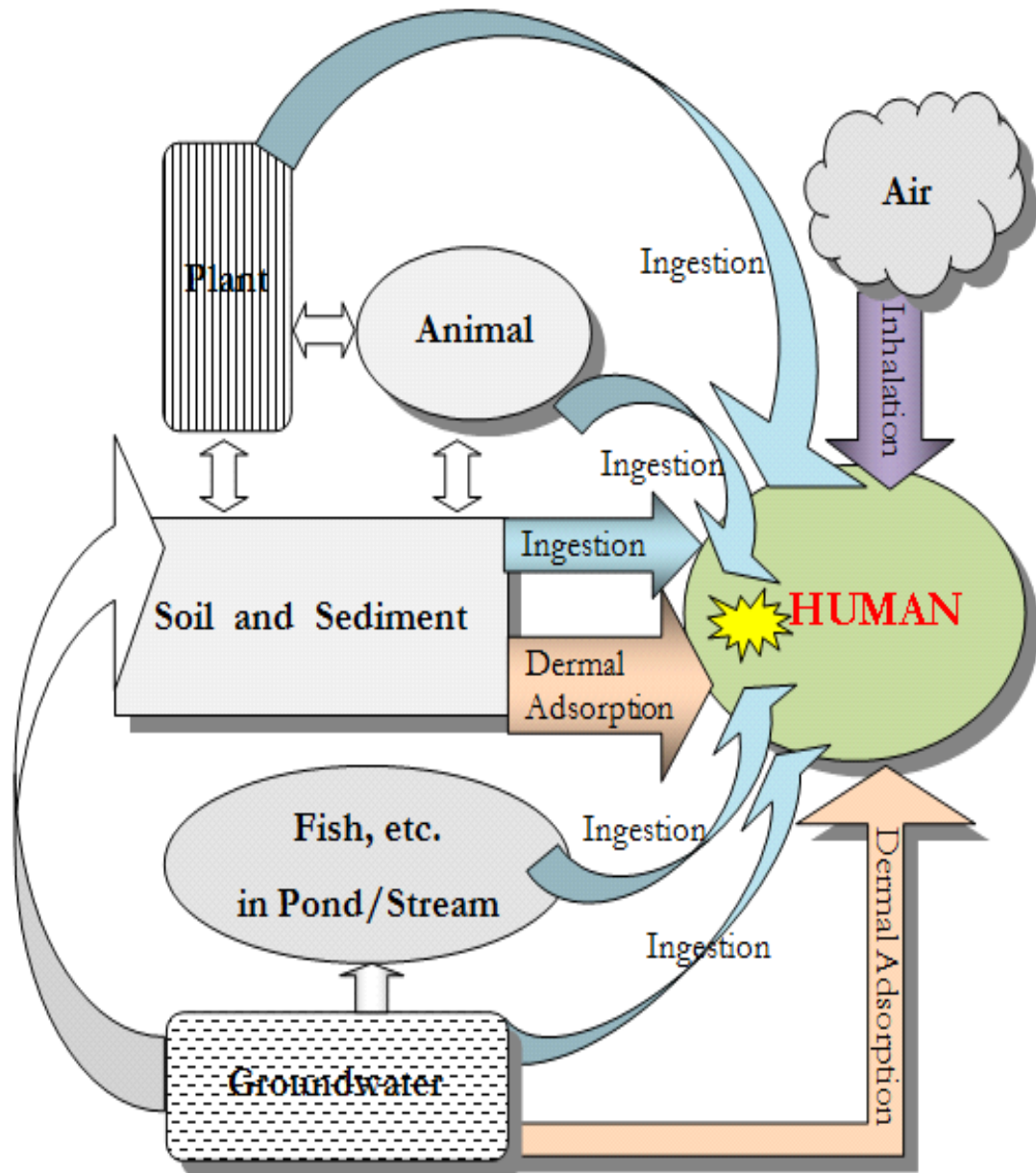


Figure 4.1 : Exposure pathways of heavy metal to human beings in nature

So it is important to determine the human health risk assessment in Rajshahi City Corporation. For this purpose a risk assessment of metal exposure to population subgroups living on, and growing food on, urban site was performed. Uptake of Arsenic, Lead, and Cadmium was modeled for a selection of commonly available food in Rajshahi City Corporation Population subgroups were including Children, Average Persons and Senior.

4.2 Experimental Procedures

4.2.1 Materials

The materials employed for the investigation is described in section 2.3.

4.2.2 Methods

The methods of analyses of drinking water, vegetables [20] were the same as mentioned in chapter 2. Dust and rice analyzed as same procedures soil and edible plants tissue. These are discussed elaborately in the previous chapter 2 [21-24]. For fish samples analyses first the sample were preserved ice/ refrigerator and removed scale and cut into pieces and dried in an oven at 105⁰c for 24 h. After the samples were digested with HNO₃-HClO₄-H₂SO₄ ternary acid mixture, dilute with HCl and analyzed with GF- ASS.

4.3 Results and Discussion

4.3.1 Profile of the Concerned Households

The environment is considered in terms of the most tangible aspects like air, water and food, and the less tangible, though no less important, the communities we live in. A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance has to be present in the environment beyond a set or tolerance limit, which could be either a desirable or acceptable limit. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment [22]. Trace elements are very harmful because of their no biodegradable nature, long biological half-lives, and their potential to accumulate in different body parts. High concentrations of trace elements (Cu, Cd, and Pb) in vegetables and fruits were related to prevalence of upper gastrointestinal cancer high [5]. Cadmium may promote skeletal demineralization and increase bone fragility and fracture risk.

In Rani Bazar and Shaheb Bazar moholla (Town) of Rajshahi City Corporation, all the people are educated and well established. Few houses were very old and others are new or built before ten years ago. The house owner's

someone employer, someone businessman and others are unemployed. Maximum house have 5-6 members. All house member use tube-well water for drink and tap water for cook their food. They collect their daily foods from nearer market. Each house owner's monthly income is minimum Tk. 13,000.00 and maximum Tk. 25,000.00. Some house has tube-well inside in and others are collecting their water from far away tube-well. Some house has children of 6-7 years old. Some people in each house are between 35 to 40 years old. Two houses have ½ member are between 55 to 60 years old. The entire houses are made with bricks, sand and cement. All the houses have colored by limbo. The roads of these places are always busy with many types of vehicles like rickshaws, auto-rickshaws, buses. Besides these moholla there are some shops. There are no ponds or canals near these places only the river Padma beside Rani Bazar and Shaheb Bazar. The houses are very nearest to each other. All house member use gas/kerosene to cook their food. All house owners have capacity to buy meat/fish in a week. The samples were collected from their rice, fish vegetable, water and dust. Dusts were collected from the floor of each house. The study area located roughly between 24°22' N to 24°21' N and 88°35' E. The studied households are marked in Table 4.1.

Table 4.1 : Profile of studied household owners

Ward No	Village	Owner's Name	GPS	Sample Code
12	Rani Bazar	Omoresh Roy	24°22'04.26"N; 88°36'05.99"E	R-BF12-01
		Zahurul Islam	24°22'04.63"N; 88°36'06.26"E	V-BF12-02
		Bithil Pal	24°22'04.14"N; 88°36'06.27"E	F-BF12-03
		Bahrullah Bhuia	24°22'02.39"N; 88°36'02.95"E	W-BF12-04
		Azizul Haque	24°22'01.91"N; 88°36'03.60"E	D-BF12-05
	Shaheb Bazar	Abdul Hamid	24°21'48.91"N; 88°35'55.35"E	R-BR12-01
		Abdur Sobur	24°21'51.34"N; 88°35'49.63"E	V-BR12-02
		Nsasiruddin	24°21'51.23"N; 88°35'53.52"E	F-BR12-03
		Asikuddin	24°21'50.38"N; 88°35'51.74"E	W-BR12-04
		Omor Ali	24°21'46.06"N; 88°35'49.44"E	D-BR12-05

4.3.2 Risk assessment Model

For estimating the exposure of arsenic, cadmium and lead for consumers of studied sample, we first calculated Average Daily Dose (ADD) using equation (1.1) as suggested by U.S.EPA Guidelines for Exposure As

$$ADD = \frac{\bar{C}_{veg} \cdot IR \cdot ED}{BW \cdot AT} \dots\dots\dots (1.1)$$

Where \bar{C}_{veg} the average concentration of arsenic in vegetables, IR is ingestion rate for vegetables, ED is exposure duration, BW is the body weight and AT is averaging time.

Similar ADD would be obtained from Rice, Fish, Water and dust. Dust Inhalation would be calculated using the equation:

$$ADD = \left(\frac{M_{soil} R_{in}}{B} \right) F_{ex} \dots\dots\dots (1.2)$$

$$ADD_{As} = ADD_{Rice} + ADD_{Veg} + ADD_{Fish/Meat} + ADD_{Dust} + ADD_{Water} \dots\dots (1.3)$$

$$HQ_{As} = \frac{ADD_{As}}{RfD} \dots\dots\dots (1.4)$$

Similar, HQ_{Pb} and HQ_{Cd} would be calculated.

Finally, HI would be estimated using

$$HI = HQ_{As} + HQ_{Pb} + HQ_{Cd} \dots\dots\dots (1.5)$$

Risk may be characterized using a hazard quotient (HQ). This is the ratio of the average daily dose (ADD; milligrams per kilogram per day) of a chemical to a reference dose (RfD, milligrams per kilogram per day) defined as the maximum tolerable daily intake of a specific metal that does not result in any deleterious health effects.

If $HQ > 1.00$, then the ADD of a particular metal exceeds the RfD, indicating that there is a potential risk associated with that metal. In the United Kingdom, DEFRA and the Environment Agency have published reference doses for Cd and Ni (DEFRA and Environment Agency 2002d, 2002e). Reference doses for Cu, Pb, and Zn were derived using the framework recommended for U.K. risk assessments. Index doses (to assess cancer risk) for Cd and Ni were not employed because they are set at a level similar to background concentrations and because they were derived for compounds of Cd and Ni, which are rarely present in a non occupational environment and are difficult to assess from measures of total metal concentration. The RfDs used in this study are given in Table no.1. The RfDs may be derived from a no observed adverse effect level (NOAEL) or a lowest observed adverse effects level (LOAEL) which could lead to inconsistencies in the final RfD estimation. Essential elements (Cu and Zn in this study) have greater RfD values because of their lower toxicity.

Table 4.2 : Parameters involved in the risk assessment model

Factors	Unit	Population sub-group		
		Children (0-6 yr)	Average Person	Senior
Age	yr	6	39.5	60.3
Body weight (BW)	kg	18.6	80.8	82.6
Rice ingestion rate	g (ww.) d ⁻¹	100	344	300
Vegetable ingestion rate	g (ww.) d ⁻¹	60	155	120
Fish ingestion rate	g (ww.) d ⁻¹	40	60	60
Water ingestion rate	L d ⁻¹	1.4	2.5	2
Soil & dust ingestion rate	mg (ww.) d ⁻¹	100	50	50
Dust inhalation rate	m ³ d ⁻¹	10.1	16	15.7
Exposure frequency (EF)	d yr ⁻¹	350	350	350
Year	d	365.25	365.25	365.25
Averaging time (AT)	yr	6	30	50
Exposure duration (ED)	yr	6	30	50
RBAF [‡] of As	(unit less)	0.4		
RBAF of Pb	(unit less)	0.6		
RBAF of Cd	(unit less)	0.6		
As reference dose (^{As} RfD)	mg kg ⁻¹ d ⁻¹	0.0003	0.0003	0.0003
Pb reference dose (^{Pb} RfD)	mg kg ⁻¹ d ⁻¹	0.0005	0.05	0.001
Cd reference dose (^{Cd} RfD)	mg kg ⁻¹ d ⁻¹	0.0005	0.0005	0.0005

[‡] RBAF stands for relative bio-availability factor.

4.3.3 Concentration of Arsenic, Cadmium and Lead in Dietary Products, Drinking Water and Dust

The concentrations of arsenic, cadmium and lead in the studied dietary products, drinking water and dust are enlisted in table 4.3, 4.4 and 4.5. Each data corresponds to mean of triplicate measurement.

Table 4.3 : Concentrations of arsenic in dietary products, drinking water and dust

Village	Owner's name	Concentration of As ($\mu\text{g g}^{-1}$) [†]					
		Rice	Vegetable	Fish	Dust	Air ^{§,‡}	Water [‡]
Rani Bazar	Omoresh Roy	0.090(0.101)	0.017(0.189)	0.109(0.507)	2.741(2.812)	2.31E-05	0.003
	Zahurul Islam	0.061(0.070)	0.059(0.590)	0.187(0.581)	1.359(1.366)	1.14E-05	0.002
	Bithil Pal	0.276(0.311)	0.119(0.628)	0.158(0.553)	1.329(1.349)	1.12E-05	0.002
	Bahrullah Bhuia	0.063(0.069)	0.048(0.488)	0.179(0.657)	1.751(1.756)	1.47E-05	0.001
	Azizul Haque	0.069(0.074)	0.010(0.116)	0.124(0.506)	1.677(1.699)	1.41E-05	0.003
Shaheb Bazar	Abdul Hamid	0.067(0.072)	0.034(0.309)	0.118(0.431)	2.396(2.409)	2.02E-05	0.002
	Abdur Sobur	0.078(0.084)	0.063(0.809)	0.130(0.469)	2.723(2.872)	2.29E-05	0.002
	Nasiruddin	0.069(0.077)	0.024(0.139)	0.150(0.486)	1.154(1.175)	9.71E-06	0.002
	Asikuddin	0.061(0.066)	0.035(0.327)	0.044(0.273)	3.441(3.640)	2.89E-05	0.002
	Omor Ali	0.081(0.088)	0.037(0.151)	0.083(0.492)	2.009(2.052)	1.69E-05	0.002

[†] the values in parentheses represent dry weight based concentration.

[§] the values are estimated based on the mentioned model.

[‡] the concentrations of air and water are expressed in $\mu\text{g m}^{-3}$ and mg L^{-1} respectively.

Table 4.4 : Concentrations of Cadmium in dietary products, drinking water and dust

Village	Owner's name	Concentration of Cd ($\mu\text{g g}^{-1}$) [†]					
		Rice	Vegetable	Fish	Dust	Air ^{§,‡}	Water [‡]
Rani Bazar	Omoresh Roy	0.098(0.110)	0.011(0.119)	0.020(0.092)	0.132(0.135)	1.40E-07	0.003
	Zahurul Islam	0.056(0.064)	0.009(0.092)	0.059(0.182)	0.017(0.017)	3.20E-07	0.004
	Bithil Pal	0.130(0.147)	0.028(0.146)	0.031(0.011)	0.028(0.028)	2.82E-07	0.004
	Bahrullah Bhuia	0.143(0.156)	0.010(0.103)	0.034(0.123)	0.025(0.025)	3.20E-07	0.004
	Azizul Haque	0.083(0.090)	0.007(0.083)	0.033(0.136)	0.038(0.039)	3.35E-06	0.004
Shaheb Bazar	Abdul Hamid	0.154(0.166)	0.006(0.056)	0.025(0.009)	0.048(0.048)	4.04E-08	0.005
	Abdur Sobur	0.019(0.021)	0.004(0.049)	0.039(0.142)	0.074(0.078)	6.22E-08	0.006
	Nasiruddin	0.016(0.018)	0.013(0.078)	0.066(0.214)	0.060(0.061)	5.05E-08	0.005
	Asikuddin	0.097(0.105)	0.012(0.011)	0.017(0.103)	0.046(0.049)	3.87E-08	0.005
	Omor Ali	0.053(0.058)	0.028(0.116)	0.019(0.112)	0.057(0.058)	4.79E-08	0.007

[†] the values in parentheses represent dry weight based concentration.

[§] the values are estimated based on the mentioned model.

[‡] the concentrations of air and water are expressed in $\mu\text{g m}^{-3}$ and mg L^{-1} respectively.

Table 4.5 : Concentrations of lead in dietary products, drinking water and dust

Village	Owner's name	Concentration of Pb ($\mu\text{g g}^{-1}$) [†]					
		Rice	Vegetables	Fish	Dust	Air ^{§, ‡}	Water [‡]
Rani Bazar	Omoresh Roy	0.060(0.068)	0.030(0.333)	0.013(0.061)	0.017(0.017)	1.11E-07	0.001
	Zahurul Islam	0.052(0.059)	0.003(0.034)	0.015(0.047)	0.038(0.038)	1.43E-08	0.002
	Bithil Pal	0.049(0.055)	0.008(0.040)	0.002(0.006)	0.034(0.034)	2.35E-08	0.000
	Bahrullah Bhuia	0.051(0.055)	0.002(0.023)	0.032(0.119)	0.038(0.038)	2.10E-08	0.003
	Azizul Haque	0.043(0.047)	0.003(0.038)	0.014(0.055)	0.398(0.404)	3.20E-08	0.001
Shaheb Bazar	Abdul Hamid	0.036(0.038)	0.003(0.030)	0.015(0.056)	0.023(0.023)	1.40E-06	0.002
	Abdus Sobur	0.024(0.026)	0.002(0.026)	0.014(0.051)	0.028(0.029)	1.69E-06	0.001
	Nasiruddin	0.019(0.021)	0.006(0.032)	0.041(0.132)	0.029(0.030)	1.75E-06	0.004
	Asikuddin	0.027(0.030)	0.003(0.032)	0.009(0.056)	0.020(0.021)	1.20E-06	0.001
	Omor Ali	0.020(0.021)	0.005(0.021)	0.009(0.051)	0.029(0.030)	1.75E-06	0.001

[†] the values in parentheses represent dry weight based concentration.

[§] the values are estimated based on the mentioned model.

[‡] the concentrations of air and water are expressed in $\mu\text{g m}^{-3}$ and mg L^{-1} respectively.

In the studied samples arsenic concentrations in rice, vegetables, fish, drinking water and dust ranged from 0.061-0.276, 0.010-0.119, 0.044-0.187, 0.001-0.003 and 1.154-3.441 $\mu\text{g g}^{-1}$ respectively on fresh weight basis. Obviously arsenic concentration was highest in dust (3.441 $\mu\text{g g}^{-1}$, ww) and lowest in drinking water (0.010 $\mu\text{g L}^{-1}$). Cadmium concentrations in rice, vegetables, fish, drinking water and dust ranged from 0.016-0.154, 0.004-0.028, 0.017-0.066, 0.003-0.007 and 0.017-0.132 $\mu\text{g g}^{-1}$ (ww) respectively. It is clear that cadmium concentration was highest in rice (0.154 $\mu\text{g g}^{-1}$, ww) and lowest in drinking water (0.003 $\mu\text{g g}^{-1}$, ww) respectively. It was also found that lead concentration in rice, vegetables, fish, drinking water and dust ranged from 0.019-0.060, 0.002-0.032, 0.002-0.041, 0.000-0.004 and 0.017-0.398 $\mu\text{g g}^{-1}$ respectively. This reflects that lead concentration was highest in dust (0.398 $\mu\text{g g}^{-1}$, ww) and lowest in drinking water (0.000 $\mu\text{g L}^{-1}$).

In the investigation, the concentrations of heavy metals in the studied samples follow the following order:

As: Dust > Fish > Rice > Vegetables > Drinking water

Pb: Dust > Rice > Fish > Vegetables > Drinking water

Cd: Rice > Dust = Drinking water > Fish > Vegetables

Generally, the concentrations of the concerned metals in the studied samples follow the order: Dust > Rice > Fish > Vegetables > Drinking water.

Williams et al. [24] found that the mean arsenic level of Bangladesh rice was 0.13 (range 0.03-0.30) mg/kg which is in good agreement with our findings. A survey of the levels of cadmium, lead and arsenic in different types of rice available on the Swedish retail market was carried out in 001-03[25]. The types of rice included long and short grain, brown, white, and parboiled white rice. The mean levels found were as follows: total As: 0.20 mg kg⁻¹, (inorganic As: 0.11 mg kg⁻¹); Cd: 0.024 mg kg⁻¹; and Pb: 0.004 mg kg⁻¹. Our studied values for As in rice ranged from 0.045 to 0.276 µg g⁻¹, values for Cd in rice ranged from 0.0003 to 0.0143 µg g⁻¹ and values for Pb in rice ranged from 0.018-0.063 µg g⁻¹. Afshar et al [26] determined Cd content in Amol rice (a variety of Iranian rice) found that the mean Cd concentration in Amol rice was 0.09 µg g⁻¹.

But in highly contaminated areas the levels of As, Pb and Cd are considerably higher. For example, in Samota village, Jessore, Bangladesh (a highly arsenic contaminated village) the arsenic concentration in snake gourd vegetables was 0.401 (range 0.306-0.489) µg g⁻¹[27]. In highly contaminated areas from Copsa Mica, Zlatna and Baia Mare of Romania [28] the cadmium concentration ranged 0.10-0.27 µg g⁻¹ and lead concentration ranged 1.0-5.50 µg g⁻¹ (fresh matters) in root vegetables grown.

Air lead levels were recorded as being very high in Dhaka, Bangladesh between 1997-2000 [6]. In a cross-sectional study of 49 children from three areas in Dhaka, the mean ± SD of blood lead levels was 17.6 ± 4.9 µg/dL[7].

4.3.4 Statistical analysis of arsenic, cadmium and lead in Environmental samples

Statistical analysis show that average value of arithmetic and geometric mean of the studied samples are 0.278 µg g⁻¹ and 0.261 µg g⁻¹ for As, 0.003 µg g⁻¹ and 2.06×10⁻⁰³ µg g⁻¹ Cd, 0.022 µg g⁻¹ and 1.49×10⁻⁰² µg g⁻¹ for Pb. Standard deviation and variance for As, Cd and Pb are also include in table 4.6, 4.7 and 4.8 respectively.

Table 4.6 : Statistical analyses of arsenic data sets[§] of the studied samples

Sample	Concentration mg/kg						
	Range (Min -Max)	Mean \pm SE	Geometric	Median	Standard Deviation	Variance	Skewness
Rice	0.060-0.276 (0.066-0.311)	0.091 \pm 0.020 (0.102 \pm 0.023)	0.080 (0.090)	0.068 (0.075)	0.065 (0.074)	0.004 (0.006)	2.987 (3.000)
Vegetable	0.010-0.119 (0.116-0.809)	0.042 \pm 0.010 (0.378 \pm 0.075)	0.033 (0.311)	0.034 (0.318)	0.032 (0.238)	0.001 (0.057)	1.577 (0.621)
Fish	0.044-0.187 (0.273-0.657)	0.130 \pm 0.010 (0.497 \pm 0.031)	0.122 (0.486)	0.127 (0.506)	0.041 (0.100)	0.002 (0.010)	-0.715 (-0.905)
Drinking water	0.002-0.003	0.002 \pm 0.0001	0.002	0.002	0.0004	0.000	-0.467
Dust	1.154-3.441 (1.175-3.640)	2.131 \pm 0.245 (2.189 \pm 0.263)	2.001 (2.046)	2.073 (2.082)	0.776 (0.832)	2.603 (0.693)	0.258 (0.356)

[§] the values in parentheses represent dry weight

Table 4.7 : Statistical analyses of cadmium data sets[§] of the studied samples

Sample	Concentration mg/kg						
	Range (Min - Max)	Mean \pm SE	Geometric Mean	Median	Standard Deviation	Variance	Skewness
Rice	0.016-0.154 (0.018-0.166)	0.084 \pm 0.015 (0.093 \pm 0.016)	0.067 (0.074)	0.090 (0.097)	0.048 (0.053)	0.002 (0.003)	-0.057 (-0.090)
Vegetable	0.004-0.028 (0.011-0.146)	0.012 \pm 0.002 (0.085 \pm 0.012)	0.010 (0.071)	0.010 (0.087)	0.008 (0.039)	0.000 (0.002)	1.314 (-0.429)
Fish	0.017-0.507 (0.009-0.214)	0.083 \pm 0.047 (0.112 \pm 0.020)	0.043 (0.079)	0.033 (0.117)	0.149 (0.065)	0.022 (0.004)	3.098 (-0.367)
Drinking water	0.004-0.007	0.005 \pm 0.0002	0.005	0.005	0.0009	0.000	0.426
Dust	0.017-0.135 (0.017-0.135)	0.052 \pm 0.010 (0.053 \pm 0.010)	0.044 (0.045)	0.047 (0.048)	0.032 (0.033)	0.001 (0.001)	1.672 (1.617)

[§] the values in parentheses represent dry weight

Table 4.8 : Statistical analyses of lead data sets[§] of the studied samples

Sample	Concentration mg/kg						
	Range (Min - Max)	Mean \pm SE	Geometric Mean	Median	Standard Deviation	Variance	Skewness
Rice	0.019-0.060 (0.021-0.068)	0.038 \pm 0.004 (0.042 \pm 0.005)	0.035 (0.038)	0.039 (0.042)	0.014 (0.017)	0.000 (0.000)	-0.014 (3.142)
Vegetable	0.002-0.030 (0.021-0.333)	0.006 \pm 0.002 (0.060 \pm 0.030)	0.004 (0.038)	0.003 (0.032)	0.008 (0.095)	0.000 (0.009)	2.880 (3.139)
Fish	0.002-0.041 (0.006-0.132)	0.016 \pm 0.003 (0.063 \pm 0.011)	0.012 (0.051)	0.014 (0.055)	0.011 (0.036)	0.000 (0.001)	1.349 (0.860)
Drinking water	0.000-0.004	0.001 \pm 0.0003	0.000	0.001	0.001	0.000	0.989
Dust	0.017-0.398 (0.017-0.404)	0.065 \pm 0.037 (0.066 \pm 0.037)	0.035 (0.036)	0.029 (0.030)	0.017 (0.118)	0.014 (0.014)	3.141 (3.142)

[§] the values in parentheses represent dry weight

The maximum permissible limits (MPL) of arsenic, cadmium and lead concentrations in drinking water were suggested by World Health Organization, WHO [8] as 0.01, 0.003 and 0.01 mgL⁻¹ respectively. In Bangladesh MPL of As, Pb and Cd concentration in drinking water was suggested by Department of Environment of Govt. of Bangladesh as 0.05, 0.005 and 0.05 mgL⁻¹ respectively. Obviously the MPLs of Bangladesh is roughly 5 times higher than those of international standard.

The Joint FAO/WHO Expert Committee on Food Additives (JCEFA) has proposed a maximum level of 0.2 µg g⁻¹ Cd in rice but the community warned that people who eat a of rice from regions containing the higher levels of cadmium could be significantly exposed. And also JCEFA has set the Provisional Tolerable Weekly Intake (PTWI) for the cadmium and lead equal to 7 and 25 µg g⁻¹of body weight, respectively [42].

Permissible limits of Copper, Lead, Cadmium and Chromium in vegetables as recommended by WHO/FAO are 40, 0.3, 0.2, 2.3 mg kg⁻¹ respectively [43]. Levels of cadmium and lead Concentration in fishes are 0.030 mg kg⁻¹ and 0.050 mg/kg as reported in WHO [44]

4.3.5 Individual Contribution from As, Cd and Pb Exposure

For estimating the exposure of arsenic, lead and cadmium for consumers of the studied samples, we first calculated Average Daily Dose (ADD) using equation (1.1) as suggested by U.S.EPA in Guidelines for Exposure Assessment [30].

$$ADD = \frac{\bar{C}_{veg} \cdot IR \cdot ED}{BW \cdot AT} \dots\dots\dots 1.1$$

Where \bar{C} the average concentration of As, Cd or Pb in the sample, IR is ingestion rate, ED is the exposure duration, BW is the body weight and AT is averaging time. The details of ADD calculation are described in Method section. It is to be noted that some data were adapted from the standard exposure factors [34-35] and data of Bangladesh survey and standards [25-27].

The Average Daily Dose (ADD) were estimated for three population subgroups: ‘*Children*’, ‘*Average Person*’ and ‘*Senior*’. The children of age 0-6 years are referred to as ‘*High Exposed Individuals (HEIs)*’. The average persons and seniors are considered as of 39.5 and 60.3 years. The details are represented in **Table 4.2**. The ADD for arsenic, cadmium and lead for the three population subgroups are shown in the following nine Tables.

The calculation of Average Daily Dose (ADD) for children (6 yr) of As from rice ingestion is shown in the following box.

For Children (6 yr): ADD of As from Rice Ingestion

$$\text{Conc. of Arsenic in Rice, } {}^{\text{As}}C_{\text{rice}} = 0.090 \text{ mg kg}^{-1} \text{ (ww.)}$$

$$\text{Ingestion Rate of Rice, IR} = 0.1 \text{ kg}$$

$$\text{Relative Bioavailability Factor, RBAF} = 0.4$$

$$\text{Exposure Duration, ED} = 350 \text{ yr}^{-1} \text{ 6 yr}$$

$$\text{Body Weight, BW} = 18.6 \text{ kg}$$

$$\text{Averaging Time, AT} = 365.25 \text{ d yr}^{-1} \text{ 6 yr}$$

$$\begin{aligned} {}^{\text{As}}\text{ADD}_{\text{rice}} &= \frac{0.090 \times 0.1 \times 0.4 \times 350 \times 6}{18.6 \times 365.25 \times 6} \\ &= 1.85 \times 10^{-4} \text{ mg kg}^{-1}\text{d}^{-1} \end{aligned}$$

$${}^{\text{As}}\text{ADD}_{\text{rice}} = \frac{C_{\text{rice}} \cdot \text{IR} \cdot \text{RBAF} \cdot \text{ED}}{\text{BW} \cdot \text{AT}} \quad \text{Insertion of the values to equation (1.1)}$$

yields

Table 4.9 : Average daily dose (ADD) of arsenic for children population sub-group

Village	Owner's name	Average Daily Dose (ADD) of As / mg kg ⁻¹ d ⁻¹						
		AsADD _{rice}	AsADD _{veg}	AsADD _{fish}	AsADD _{water}	AsADD _{dust}	AsADD _{Air}	AsADD _{total}
Rani Bazar	Omoresh Roy	1.85E-04	7.30E-05	8.98E-05	9.23E-05	5.65E-06	4.80E-06	4.51E-04
	Zahurul Islam	1.26E-04	1.47E-04	1.54E-04	6.35E-05	2.80E-06	2.38E-06	4.96E-04
	Bithil Pal	5.69E-04	5.93E-05	1.30E-04	7.79E-05	2.74E-06	2.33E-06	8.41E-04
	Bahrullah Bhuia	1.30E-04	1.24E-05	1.48E-04	5.48E-05	3.61E-06	3.07E-06	3.51E-04
	Azizul Haque	1.42E-04	4.20E-05	1.02E-04	9.52E-05	3.45E-06	2.94E-06	3.88E-04
Shaheb Bazar	Abdul Hamid	1.38E-04	4.20E-05	9.72E-05	7.80E-05	4.80E-06	4.20E-05	4.02E-04
	Abdus Sobur	1.61E-04	7.80E-05	1.07E-04	6.93E-05	5.70E-06	4.77E-05	4.68E-04
	Nasiruddin	1.42E-04	2.97E-05	1.24E-04	8.37E-05	2.40E-06	2.01E-05	3.83E-04
	Asikuddin	1.26E-04	4.32E-05	3.63E-05	8.07E-05	7.20E-06	6.03E-05	3.53E-04
	Omor Ali	1.67E-04	4.56E-05	6.84E-05	8.07E-05	4.20E-06	3.51E-05	4.01E-04

Table 4.10 : Average daily dose (ADD) of Cadmium for children population sub-group

Village	Owner's name	Average Daily Dose (ADD) of Cd/ mg kg ⁻¹ d ⁻¹						
		CdADD _{rice}	CdADD _{veg}	CdADD _{fish}	CdADD _{water}	CdADD _{dust}	CdADD _{Air}	CdADD _{total}
Rani Bazar	Omoresh Roy	1.85E-04	7.30E-05	8.98E-05	9.23E-05	5.65E-06	4.80E-06	4.51E-04
	Zahurul Islam	1.26E-04	1.47E-04	1.54E-04	6.35E-05	2.80E-06	2.38E-06	4.96E-04
	Bithil Pal	5.69E-04	5.93E-05	1.30E-04	7.79E-05	2.74E-06	2.33E-06	8.41E-04
	Bahrullah Bhuia	1.30E-04	1.24E-05	1.48E-04	5.48E-05	3.61E-06	3.07E-06	3.51E-04
	Azizul Haque	1.42E-04	4.20E-05	1.02E-04	9.52E-05	3.45E-06	2.94E-06	3.88E-04
Shaheb Bazar	Abdul Hamid	4.76E-05	1.10E-06	3.10E-06	2.37E-04	1.53E-08	1.30E-08	2.88E-04
	Abdus Sobur	5.85E-06	7.50E-07	4.80E-06	2.61E-04	2.36E-08	2.01E-08	2.72E-04
	Nasiruddin	4.95E-06	2.40E-06	8.15E-06	2.36E-04	1.92E-08	1.63E-08	2.51E-04
	Asikuddin	3.00E-05	2.25E-06	2.10E-06	2.37E-04	1.47E-08	1.25E-08	2.71E-04
	Omor Ali	1.64E-05	5.20E-06	2.35E-06	3.03E-04	1.82E-08	1.55E-08	3.26E-04

Table 4.11 : Average daily dose (ADD) of Lead for children population sub-group

Village	Owner's name	Average Daily Dose (ADD) of Pb / mg kg ⁻¹ d ⁻¹						
		PbADD _{rice}	PbADD _{veg}	PbADD _{fish}	PbADD _{water}	PbADD _{dust}	PbADD _{Air}	PbADD _{total}
Rani Bazar	Omoresh Roy	1.10E-04	6.12E-06	1.87E-05	6.53E-05	6.99E-10	6.12E-08	3.15E-04
	Zahurul Islam	7.30E-05	3.71E-06	1.74E-05	6.10E-05	8.46E-10	7.40E-08	2.49E-04
	Bithil Pal	5.93E-05	1.02E-05	5.03E-05	1.76E-04	8.76E-10	7.67E-08	1.75E-04
	Bahrullah Bhuia	8.47E-05	6.31E-06	1.10E-05	3.85E-05	6.00E-10	5.25E-08	3.41E-04
	Azizul Haque	6.03E-05	9.64E-06	1.06E-05	3.72E-05	8.73E-10	7.64E-08	2.16E-04
Shaheb Bazar	Abdul Hamid	1.10E-04	6.00E-06	1.85E-05	6.55E-05	7.00E-10	5.00E-08	2.00E-04
	Abdus Sobur	7.30E-05	3.50E-06	1.75E-05	6.10E-05	8.45E-10	5.00E-08	1.55E-04
	Nasiruddin	5.95E-05	1.00E-05	5.0E-05	1.76E-04	8.75E-10	1.00E-07	2.95E-04
	Asikuddin	8.45E-05	6.50E-06	1.10E-05	3.85E-05	6.00E-10	5.00E-08	1.41E-04
	Omor Ali	6.05E-05	9.50E-06	1.05E-05	3.70E-05	8.75E-10	1.00E-07	0.08E-04

Table 4.12 : Average daily dose (ADD) of arsenic for Average population sub-group

Village	Owner's name	Average Daily Dose (ADD) of As / mg kg ⁻¹ d ⁻¹						
		AsADD _{rice}	AsADD _{veg}	AsADD _{fish}	AsADD _{water}	AsADD _{dust}	AsADD _{Air}	AsADD _{total}
Rani Bazar	Omoresh Roy	1.47E-04	1.25E-05	3.10E-05	3.80E-05	6.58E-07	1.75E-06	2.31E-04
	Zahurul Islam	9.95E-05	4.34E-05	5.32E-05	2.61E-05	3.26E-07	8.68E-07	2.23E-04
	Bithil Pal	4.50E-04	8.75E-05	4.50E-05	3.20E-05	3.19E-07	8.48E-07	6.16E-04
	Bahrullah Bhuia	1.03E-04	3.53E-05	5.09E-05	2.25E-05	4.20E-07	1.12E-06	2.13E-04
	Azizul Haque	1.13E-04	7.35E-06	3.53E-05	3.91E-05	4.02E-07	1.07E-06	1.96E-04
Shaheb Bazar	Abdul Hamid	1.09E-04	2.49E-05	3.36E-05	3.21E-05	6.00E-07	1.53E-05	2.15E-04
	Abdus Sobur	1.27E-04	4.62E-05	3.69E-05	2.85E-05	6.00E-07	1.74E-05	2.56E-04
	Nasiruddin	1.13E-04	1.77E-05	4.26E-05	3.45E-05	3.00E-07	7.50E-06	2.34E-04
	Asikuddin	9.96E-05	2.58E-05	1.26E-05	3.33E-05	9.00E-07	2.19E-05	0.22E-04
	Omor Ali	1.32E-04	2.73E-05	2.37E-05	3.33E-05	6.00E-07	1.29E-05	2.29E-04

Table 4.13 : Average daily dose (ADD) of Cadmium for Average population sub-group.

Village	Owner's name	Average Daily Dose (ADD) of Cd/ mg kg ⁻¹ d ⁻¹						
		CdADD _{rice}	CdADD _{veg}	CdADD _{fish}	CdADD _{water}	CdADD _{dust}	CdADD _{Air}	CdADD _{total}
Rani Bazar	Omoresh Roy	2.40E-05	1.21E-06	8.54E-07	6.59E-05	4.75E-09	1.26E-08	9.20E-05
	Zahurul Islam	1.37E-05	9.93E-07	2.52E-06	7.73E-05	6.12E-10	1.63E-09	9.45E-05
	Bithil Pal	3.18E-05	3.09E-06	1.32E-06	8.86E-05	1.01E-09	2.68E-09	1.25E-04
	Bahrullah Bhuia	3.50E-05	1.10E-06	1.45E-06	8.28E-05	9.00E-10	2.39E-09	1.20E-04
	Azizul Haque	2.03E-05	7.72E-07	1.41E-06	8.57E-05	1.37E-09	3.64E-09	1.08E-04
Shaheb Bazar	Abdul Hamid	3.77E-05	6.50E-07	1.05E-06	9.85E-05	1.73E-09	4.60E-09	1.27E-04
	Abdus Sobur	4.65E-06	4.50E-07	1.65E-06	1.08E-04	2.67E-09	7.10E-09	1.14E-04
	Nasiruddin	3.90E-06	1.45E-06	2.80E-06	9.79E-05	2.16E-09	5.75E-09	1.06E-04
	Asikuddin	2.38E-05	1.30E-06	7.50E-07	9.85E-05	1.66E-09	4.41E-09	1.24E-04
	Omor Ali	1.30E-05	3.10E-06	8.00E-07	1.26E-04	2.05E-09	5.45E-09	1.42E-04

Table 4.14 : Average daily dose (ADD) of Lead for Average population sub-group

Village	Owner's name	Average Daily Dose (ADD) of Pb / mg kg ⁻¹ d ⁻¹						
		PbADD _{rice}	PbADD _{veg}	PbADD _{fish}	PbADD _{water}	PbADD _{dust}	PbADD _{Air}	PbADD _{total}
Rani Bazar	Omoresh Roy	1.48E-04	3.30E-05	5.64E-06	2.37E-05	5.98E-09	1.59E-08	2.10E-04
	Zahurul Islam	1.26E-04	3.75E-06	6.40E-06	2.70E-05	1.37E-08	3.64E-08	1.63E-04
	Bithil Pal	1.20E-04	8.38E-06	7.26E-07	3.05E-06	1.21E-08	3.21E-08	1.32E-04
	Bahrullah Bhuia	1.24E-04	2.54E-06	1.38E-05	5.82E-05	1.37E-08	3.65E-08	1.98E-04
	Azizul Haque	1.06E-04	3.64E-06	5.76E-06	2.43E-05	1.43E-07	3.81E-07	1.40E-04
Shaheb Bazar	Abdul Hamid	1.00E-06	5.00E-08	5.00E-08	2.50E-07	8.40E-11	2.23E-10	1.00E-06
	Abdus Sobur	5.00E-07	2.21E-08	5.00E-08	2.50E-07	1.02E-10	2.70E-10	8.20E-07
	Nasiruddin	5.00E-07	5.00E-08	1.50E-07	7.50E-07	1.0E-10	2.80E-10	1.40E-06
	Asikuddin	5.00E-07	5.00E-08	5.00E-08	1.50E-07	7.20E-11	1.92E-10	7.50E-04
	Omor Ali	5.00E-07	5.00E-08	5.00E-08	1.50E-07	1.05E-10	2.79E-10	7.50E-07

Table 4.15 : Average daily dose (ADD) of arsenic for senior population sub-group

Village	Owner's name	Average Daily Dose (ADD) of As / mg kg ⁻¹ d ⁻¹						
		AsADD _{rice}	AsADD _{veg}	AsADD _{fish}	AsADD _{water}	AsADD _{dust}	AsADD _{Air}	AsADD _{total}
Rani Bazar	Omoresh Roy	1.25E-04	9.47E-06	3.03E-05	2.97E-05	6.30E-07	1.68E-06	1.97E-04
	Zahurul Islam	8.49E-05	3.29E-05	5.21E-05	2.04E-05	3.13E-07	8.33E-07	1.91E-04
	Bithil Pal	3.84E-04	6.63E-05	4.40E-05	2.51E-05	3.06E-07	8.14E-07	5.21E-04
	Bahrullah Bhuia	8.77E-05	2.67E-05	4.98E-05	1.76E-05	4.03E-07	1.07E-06	1.83E-04
	Azizul Haque	9.61E-05	5.57E-06	3.45E-05	3.06E-05	3.86E-07	1.03E-06	1.68E-04
Shaheb Bazar	Abdul Hamid	9.33E-05	1.89E-05	3.30E-05	2.52E-05	6.00E-07	1.47E-05	2.04E-04
	Abdus Sobur	1.09E-04	3.51E-05	3.63E-05	2.22E-05	6.00E-07	1.68E-05	2.36E-04
	Nasiruddin	9.60E-05	1.35E-05	4.17E-05	2.70E-05	3.00E-07	7.20E-06	15.22E-04
	Asikuddin	8.49E-05	1.95E-05	1.23E-05	2.61E-05	9.00E-07	2.10E-05	1.64E-04
	Omor Ali	1.13E-04	2.07E-05	2.31E-05	2.61E-05	6.00E-07	1.23E-05	1.95E-04

Table 4.16 : Average daily dose (ADD) of Cadmium for senior population sub-group

Village	Owner's name	Average Daily Dose (ADD) of Cd/ mg kg ⁻¹ d ⁻¹						
		CdADD _{rice}	CdADD _{veg}	CdADD _{fish}	CdADD _{water}	CdADD _{dust}	CdADD _{Air}	CdADD _{total}
Rani Bazar	Omoresh Roy	2.05E-05	9.19E-07	8.35E-07	5.11E-05	4.62E-09	1.21E-08	7.33E-05
	Zahurul Islam	1.17E-05	7.52E-07	2.46E-06	5.99E-05	5.95E-10	1.56E-09	7.48E-05
	Bithil Pal	2.71E-05	2.34E-06	1.29E-06	6.86E-05	9.80E-10	2.57E-09	9.94E-05
	Bahrullah Bhuia	2.99E-05	8.35E-07	1.42E-06	6.42E-05	8.75E-10	2.30E-09	9.63E-05
	Azizul Haque	1.73E-05	5.85E-07	1.38E-06	6.64E-05	1.33E-09	3.49E-09	8.57E-05
Shaheb Bazar	Abdul Hamid	3.22E-05	5.00E-07	1.05E-06	7.63E-05	1.68E-09	4.41E-09	8.10E-05
	Abdus Sobur	3.95E-06	3.50E-07	1.65E-06	8.38E-05	2.59E-09	6.80E-09	8.90E-05
	Nasiruddin	3.35E-06	1.10E-06	2.75E-06	7.59E-05	2.10E-09	5.50E-09	8.30E-05
	Asikuddin	2.03E-05	1.00E-06	7.00E-07	7.63E-05	1.61E-09	4.23E-09	9.82E-05
	Omor Ali	1.11E-05	2.35E-06	8.00E-07	9.73E-05	2.00E-09	5.25E-09	1.11E-05

Table 4.17 : Average daily dose (ADD) of Lead for senior population sub-group

Village	Owner's name	Average Daily Dose (ADD) of Pb / mg kg ⁻¹ d ⁻¹						
		PbADD _{rice}	PbADD _{veg}	PbADD _{fish}	PbADD _{water}	PbADD _{dust}	PbADD _{Air}	PbADD _{total}
Rani Bazar	Omoresh Roy	0.000125918	1.24874E-05	5.51285E-06	1.83761E-05	5.81E-09	1.52573E-08	1.62E-04
	Zahurul Islam	0.000107542	1.41998E-06	6.2646E-06	2.08819E-05	1.33E-08	3.49264E-08	1.36E-04
	Bithil Pal	0.000102112	3.17406E-06	7.09988E-07	2.36662E-06	1.1725E-08	3.07904E-08	1.08E-04
	Bahrullah Bhuia	0.000105454	9.60572E-07	1.35315E-05	4.51049E-05	1.3335E-08	3.50183E-08	1.65E-04
	AzizulHaque	9.0418E-05	1.37821E-06	5.63814E-06	1.87937E-05	1.39405E-07	3.66084E-07	1.17E-04
Shaheb Bazar	AbdulHamid	3.70E-05	7.00E-07	3.15E-06	1.05E-05	4.08E-09	1.07E-08	0.51E-04
	Abdus Sobur	2.46E-05	4.00E-07	2.90E-06	9.80E-06	4.93E-09	1.29E-08	0.37E-04
	Nsahiruddin	2.01E-05	1.15E-06	8.50E-06	2.83E-05	5.10E-09	1.34E-08	0.58E-04
	Asikuddin	2.86E-05	7.00E-07	1.85E-06	6.20E-06	3.50E-09	9.20E-09	1.06E-04
	Omor Ali	2.05E-05	1.10E-06	1.80E-06	6.00E-06	5.10E-09	1.32E-08	0.29E-04

Amongst the ingestion and inhalation processes, dust driven air includes in inhalation and the others are in ingestion processes. Studied metal exposure contribution for the three population sub-groups are shown in table 4.18. It is clear that ingestion processes cover more contribution than inhalation process towards metal exposure. On an average, 98.63% exposure is contributed from ingestion processes, while the rest (1.37 %) from inhalation process.

Table 4.18 : Metal exposure contribution for three population sub groups

Population subgroups	Exposure Contribution (%)		
	Metal	Ingestion	Inhalation
Children	As	93.36	6.64
	Cd	99.99	0.01
	Pb	99.97	0.03
Average person	As	99.45	0.55
	Cd	99.99	0.01
	Pb	99.98	0.02
Senior	As	94.95	5.05
	Cd	99.99	0.01
	Pb	99.98	0.02
Overall Average	As	95.92	4.08
	Cd	99.99	0.01
	Pb	99.98	0.02

Average total HQ value ($^M\text{HQ}_{\text{Total}}$) of arsenic, cadmium and lead contents for children are 1.43, 0.49 and 0.45, respectively (**Table 4.19**). The table reflects that for the same diet and atmosphere, As, Cd and Pb contribute to 59.47%, 22.64% and 17.89% respectively for children.

But for average person, the As, Cd and Pb contributes is 75.26 %, 24.48 % and 0.26 %. For senior person, the As, Cd and contributes is 68.21 %, 20.34 % and 11.45 %. In total exposure the order is As > Cd > Pb for all population sub-groups.

Table 4.19 : Average HQ contribution in HI value

Population sub-group	Contribution of metal HQ in HI value (%)			
	$^{\text{As}}\text{HQ}_{\text{Total}}$	$^{\text{Cd}}\text{HQ}_{\text{Total}}$	$^{\text{Pb}}\text{HQ}_{\text{Total}}$	HI
Children	59.47	22.64	17.89	100.00
Adult	75.26	24.48	0.26	100.00
Senior	68.21	20.34	11.45	100.00
Average	67.65	22.49	9.87	100.00

For all population sub-groups metal contribution towards HQ values followed the order; for arsenic: rice (50.52) > fish (18.99) > drinking (14.25) > vegetable (11.32) > dust (4.61); for cadmium: drinking (86.26) > rice (10.61) > vegetable (1.61) > fish (1.53) > dust (0.002) and for lead: rice (68.55) > drinking (19.99) > vegetable (5.89) > fish (5.52) > dust (0.056) (Table 4.18). Table 4.19 and 4.20 summarize the HQ values for different population sub-groups that is shown in Tables 4.21-4.29.

Table 4.20 : Average contribution of HQ value in Average total HQ value (%)

Population Sub groups	Metal	Sample wise contribution in Average total HQ value (%)				
		Rice	Vegetable	Fish	Water	Dust
Children	As	39.76	11.35	24.60	17.81	5.82
	Cd	6.72	1.32	1.67	90.30	0.002
	Pb	58.34	7.50	7.58	26.52	0.075
Average person	As	55.98	12.00	15.10	13.02	3.78
	Cd	12.04	1.80	1.31	84.88	0.002
	Pb	71.83	6.93	4.07	17.12	0.042
Senior Person	As	55.82	10.62	17.26	11.91	4.23
	Cd	13.06	1.71	1.62	83.61	0.002
	Pb	75.47	3.24	4.90	16.33	0.050

Table 4.21 : Arsenic contributed hazard quotient (HQ) for children population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		^{As} HQ _{rice}	^{As} HQ _{veg}	^{As} HQ _{fish}	^{As} HQ _{water}	^{As} HQ _{soil}	^{As} HQ _{dust}	^{As} HQ _{total}
Rani Bazar	Omoresh Roy	0.618	0.070	0.299	0.308	0.019	0.160	1.474
	Zahurul Islam	0.419	0.243	0.514	0.212	0.009	0.079	1.476
	Bithil Pal	1.896	0.490	0.434	0.260	0.009	0.078	3.167
	Bahrullah Bhuia	0.433	0.198	0.492	0.183	0.012	0.102	1.419
	Azizul Haque	0.474	0.041	0.341	0.317	0.012	0.098	1.283
Shaheb Bazar	Abdul Hamid	0.460	0.140	0.324	0.260	0.016	0.140	1.341
	Abdus Sobur	0.536	0.260	0.357	0.231	0.019	0.159	1.561
	Nasiruddin	0.474	0.099	0.412	0.279	0.008	0.067	1.339
	Asikuddin	0.419	0.144	0.121	0.269	0.024	0.201	1.178
	Omor Ali	0.556	0.152	0.228	0.269	0.014	0.117	1.337

Table 4.22 : Cadmium contributed hazard quotient (HQ) for children population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		^{Cd} HQ _{rice}	^{Cd} HQ _{veg}	^{Cd} HQ _{fish}	^{Cd} HQ _{water}	^{Cd} HQ _{soil}	^{Cd} HQ _{dust}	^{Cd} HQ _{total}
Rani Bazar	Omoresh Roy	0.0606	0.0041	0.0049	0.3176	8.42E-05	7.16E-05	0.3874
	Zahurul Islam	0.0346	0.0033	0.0146	0.3722	1.08E-05	9.23E-06	0.4247
	Bithil Pal	0.0804	0.0104	0.0077	0.4267	1.79E-05	1.52E-05	0.5252
	Bahrullah Bhuia	0.0884	0.0037	0.0084	0.3990	1.60E-05	1.36E-05	0.4996
	Azizul Haque	0.0513	0.0026	0.0082	0.4129	2.42E-05	2.06E-05	0.4750
Shaheb Bazar	Abdul Hamid	0.0952	0.0022	0.0062	0.4743	3.06E-05	2.60E-05	0.5780
	Abdus Sobur	0.0117	0.0015	0.0096	0.5210	4.72E-05	4.02E-05	0.5440
	Nasiruddin	0.0099	0.0048	0.0163	0.4717	3.83E-05	3.26E-05	0.5028
	Asikuddin	0.0600	0.0045	0.0042	0.4743	2.93E-05	2.50E-05	0.5430
	Omor Ali	0.0328	0.0104	0.0047	0.6050	3.64E-05	3.09E-05	0.6529

Table 4.23 : Lead contributed hazard quotient (HQ) for children population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		PbHQ _{rice}	PbHQ _{veg}	PbHQ _{fish}	PbHQ _{water}	PbHQ _{soil}	PbHQ _{dust}	PbHQ _{total}
Rani Bazar	Omoresh Roy	0.0606	0.0041	0.0049	0.3176	8.42E-05	7.16E-05	0.3874
	Zahurul Islam	0.0346	0.0033	0.0146	0.3722	1.08E-05	9.23E-06	0.4247
	Bithil Pal	0.0804	0.0104	0.0077	0.4267	1.79E-05	1.52E-05	0.5252
	Bahrullah Bhuia	0.0884	0.0037	0.0084	0.3990	1.60E-05	1.36E-05	0.4996
	Azizul Haque	0.0513	0.0026	0.0082	0.4129	2.42E-05	2.06E-05	0.4750
Shaheb Bazar	Abdul Hamid	0.219	0.012	0.037	0.131	1.40E-06	0.0001	0.400
	Abdus Sobur	0.146	0.007	0.035	0.122	1.69E-06	0.0001	0.310
	Nasiruddin	0.119	0.020	0.101	0.352	1.75E-06	0.0002	0.592
	Asikuddin	0.169	0.013	0.022	0.077	1.20E-06	0.0001	0.281
	Omor Ali	0.121	0.019	0.021	0.074	1.75E-06	0.0002	0.236

Table 4.24 : Arsenic contributed hazard quotient (HQ) for adult population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		AsHQ _{rice}	AsHQ _{veg}	AsHQ _{fish}	AsHQ _{water}	AsHQ _{soil}	AsHQ _{dust}	AsHQ _{total}
Rani Bazar	Omoresh Roy	0.490	0.042	0.103	0.127	0.002	0.058	0.822
	Zahurul Islam	0.332	0.145	0.177	0.087	0.001	0.029	0.771
	Bithil Pal	1.501	0.292	0.150	0.107	0.001	0.028	2.079
	Bahrullah Bhuia	0.343	0.118	0.170	0.075	0.001	0.037	0.744
	Azizul Haque	0.375	0.025	0.118	0.130	0.001	0.036	0.685
Shaheb Bazar	Abdul Hamid	0.364	0.083	0.112	0.107	0.002	0.051	0.719
	Abdus Sobur	0.424	0.154	0.123	0.095	0.002	0.058	0.857
	Nasiruddin	0.375	0.059	0.142	0.115	0.001	0.025	0.717
	Asikuddin	0.332	0.086	0.042	0.111	0.003	0.073	0.646
	Omor Ali	0.441	0.091	0.079	0.111	0.002	0.043	0.765

Table 4.25 : Cadmium contributed hazard quotient (HQ) for adult population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		CdHQ _{rice}	CdHQ _{veg}	CdHQ _{fish}	CdHQ _{water}	CdHQ _{soil}	CdHQ _{dust}	CdHQ _{total}
Rani Bazar	Omoresh Roy	0.0480	0.0024	0.0017	0.1319	9.50E-06	2.53E-05	0.184
	Zahurul Islam	0.0274	0.0020	0.0050	0.1545	1.22E-06	3.26E-06	0.189
	Bithil Pal	0.0636	0.0062	0.0026	0.1772	2.02E-06	5.36E-06	0.250
	Bahrullah Bhuia	0.0700	0.0022	0.0029	0.1657	1.80E-06	4.79E-06	0.241
	Azizul Haque	0.0406	0.0015	0.0028	0.1714	2.74E-06	7.28E-06	0.216
Shaheb Bazar	Abdul Hamid	0.0754	0.0013	0.0021	0.1969	3.46E-06	9.19E-06	0.276
	Abdus Sobur	0.0093	0.0009	0.0033	0.2163	5.33E-06	1.42E-05	0.230
	Nasiruddin	0.0078	0.0029	0.0056	0.1958	4.32E-06	1.15E-05	0.212
	Asikuddin	0.0475	0.0026	0.0015	0.1969	3.31E-06	8.81E-06	0.249
	Omor Ali	0.0259	0.0062	0.0016	0.2512	4.10E-06	1.09E-05	0.285

Table 4.26 : Lead contributed hazard quotient (HQ) for adult population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		PbHQ _{rice}	PbHQ _{veg}	PbHQ _{fish}	PbHQ _{water}	PbHQ _{soil}	PbHQ _{dust}	PbHQ _{total}
Rani Bazar	Omoresh Roy	0.003	0.0007	0.0001	0.0005	1.20E-07	3.18E-07	0.004
	Zahurul Islam	0.003	0.0001	0.0001	0.0005	2.74E-07	7.28E-07	0.003
	Bithil Pal	0.002	0.0002	0.0000	0.0001	2.41E-07	6.42E-07	0.003
	Bahrullah Bhuia	0.002	0.0001	0.0003	0.0012	2.74E-07	7.30E-07	0.004
	Azizul Haque	0.002	0.0001	0.0001	0.0005	2.87E-06	7.63E-06	0.003
Shaheb Bazar	Abdul Hamid	0.002	0.0001	0.0001	0.0005	1.68E-07	4.46E-07	0.002
	Abdus Sobur	0.001	0.0000	0.0001	0.0005	2.03E-07	5.40E-07	0.002
	Nasiruddin	0.001	0.0001	0.0003	0.0015	2.10E-07	5.59E-07	0.003
	Asikuddin	0.001	0.0001	0.0001	0.0003	1.44E-07	3.83E-07	0.002
	Omor Ali	0.001	0.0001	0.0001	0.0003	2.10E-07	5.57E-07	0.001

Table 4.27 : Arsenic contributed hazard quotient (HQ) for senior population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		AsHQ _{rice}	AsHQ _{veg}	AsHQ _{fish}	AsHQ _{water}	AsHQ _{soil}	AsHQ _{dust}	AsHQ _{total}
Rani Bazar	Omoresh Roy	0.418	0.032	0.101	0.099	0.002	0.056	0.707
	Zahurul Islam	0.283	0.110	0.174	0.068	0.001	0.028	0.663
	Bithil Pal	1.281	0.221	0.147	0.084	0.001	0.027	1.760
	Bahrullah Bhuia	0.292	0.089	0.166	0.059	0.001	0.036	0.643
	Azizul Haque	0.320	0.019	0.115	0.102	0.001	0.034	0.591
Shaheb Bazar	Abdul Hamid	0.311	0.063	0.110	0.084	0.002	0.049	0.618
	Abdus Sobur	0.362	0.117	0.121	0.074	0.002	0.056	0.731
	Nasiruddin	0.320	0.045	0.139	0.090	0.001	0.024	0.618
	Asikuddin	0.283	0.065	0.041	0.087	0.003	0.070	0.548
	Omor Ali	0.376	0.069	0.077	0.087	0.002	0.041	0.651

Table 4.28 : Cadmium contributed hazard quotient (HQ) for senior population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		CdHQ _{rice}	CdHQ _{veg}	CdHQ _{fish}	CdHQ _{water}	CdHQ _{soil}	CdHQ _{dust}	CdHQ _{total}
Rani Bazar	Omoresh Roy	0.0409	0.0018	0.0017	0.1022	9.24E-06	2.43E-05	0.147
	Zahurul Islam	0.0234	0.0015	0.0049	0.1197	1.19E-06	3.12E-06	0.150
	Bithil Pal	0.0543	0.0047	0.0026	0.1373	1.96E-06	5.15E-06	0.199
	Bahrullah Bhuia	0.0597	0.0017	0.0028	0.1284	1.75E-06	4.60E-06	0.193
	Azizul Haque	0.0347	0.0012	0.0028	0.1328	2.66E-06	6.99E-06	0.171
Shaheb Bazar	Abdul Hamid	0.0643	0.0010	0.0021	0.1526	3.36E-06	8.82E-06	0.220
	Abdus Sobur	0.0079	0.0007	0.0033	0.1676	5.18E-06	1.36E-05	0.179
	Nasiruddin	0.0067	0.0022	0.0055	0.1517	4.20E-06	1.10E-05	0.166
	Asikuddin	0.0405	0.0020	0.0014	0.1526	3.22E-06	8.46E-06	0.197
	Omor Ali	0.0221	0.0047	0.0016	0.1946	3.99E-06	1.05E-05	0.223

Table 4.29 : Lead contributed hazard quotient (HQ) for senior population sub-group

Village	Owner's name	Hazard Quotient (HQ)						
		PbHQ _{rice}	PbHQ _{veg}	PbHQ _{fish}	PbHQ _{water}	PbHQ _{soil}	PbHQ _{dust}	PbHQ _{total}
Rani Bazar	Omoresh Roy	0.1259	0.0125	0.0055	0.0184	5.81E-06	1.53E-05	0.162
	Zahurul Islam	0.1075	0.0014	0.0063	0.0209	1.33E-05	3.49E-05	0.136
	Bithil Pal	0.1021	0.0032	0.0007	0.0024	1.17E-05	3.08E-05	0.108
	Bahrullah Bhuia	0.1055	0.0010	0.0135	0.0451	1.33E-05	3.50E-05	0.165
	Azizul Haque	0.0904	0.0014	0.0056	0.0188	1.39E-04	3.66E-04	0.117
Shaheb Bazar	Abdul Hamid	0.0741	0.0014	0.0063	0.0210	8.16E-06	2.14E-05	0.103
	Abdus Sobur	0.0493	0.0008	0.0059	0.0196	9.87E-06	2.59E-05	0.076
	Nasiruddin	0.0401	0.0023	0.0170	0.0567	1.02E-05	2.68E-05	0.116
	Asikuddin	0.0572	0.0014	0.0037	0.0124	7.00E-06	1.84E-05	0.075
	Omor Ali	0.0407	0.0022	0.0036	0.0120	1.02E-05	2.67E-05	0.058

4.4 Risk Assessment

Hazard Index (HI) was calculated to show the greatest potential risk it and was used to generate risk map. Standard risk assessment procedure involves summation of HQ for the individual metals to provide a hazard index (HI); (Hampshire Research Institute 1995). For our model: $HI = HQ_{As} + HQ_{Pb} + HQ_{Cd}$.

The generate HI indexed maps show clearly where the greatest potential risks were located. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. The hazard quotients in table are calculated for the most sensitive life stage.

Hazard Quotients is a complex parameter used for the estimation of potential health risks associated with long term exposure to chemical pollutants. The hazard index which is the sum of hazard quotients, is a screening risk assessment technique commonly used to judge whether there is concern for additive effects between chemicals. If the hazard index is less than unity (1.0) it indicates that even if all the metals acted on the same organ or interacted in some other way to cause health effects the risk of these effects would be low. The hazard quotients and hazard index were calculated to assess potential health risk to local populations through dietary product (rice, vegetable, fish) drinking water and dust consumption. Based on the HQ values in

this study, due to the HQ value ($HQ > 1$) for children of Rani Bazar and Shaheb Bazar have danger of As. But HQ value of Cd and Pb is safe.

Risk assessment strategies are often aimed at population subgroups. It is common practice to identify vulnerable people in society, such young children or elderly, and assess potential risk to the health of these population subgroups [Dhuka and Miller 1999; Government /Research councils Initiative on risk Assessment and Toxicology (GRCIRAT) 1999]. Ryan and Chaney (1995) considered young children to be highly exposed individuals (HEIs). Thus risk assessment can usually focus on highly exposed subpopulations on the basis that if the risk to the HEI is acceptable then most of the population is protected [12]. **Figure 4.2, 4.3 and 4.4** shows the HI maps for the children, average person and senior population subgroups for the studied area. The average HI value was 2.36 for children. The HI values for children population subgroups reflect that all children, since $HI > 1.00$ is in risk. For the population subgroup (Figure 4.1) 50% (5 out of 10) provides $HI > 2$ to 3; 40% (4 out of 10) provides $HI > 1$ to 2 and 10% (1 out of 10 provides $HI > 3$ to 4.

Table 4.30 : Hazard Index for Children population sub-groups

Village	Owner's name	Hazard Index (HI)			
		^{As} HQ _{total}	^{Pb} HQ _{total}	^{Cd} HQ _{total}	HI
Rani Bazar	Omoresh Roy	1.474	0.387	0.387	2.248
	Zahurul Islam	1.476	0.425	0.425	2.326
	Bithil Pal	3.167	0.525	0.525	4.217
	Bahrullah Bhuia	1.419	0.500	0.499	2.418
	Azizul Haque	1.283	0.475	0.475	2.233
Shaheb Bazar	Abdul Hamid	1.341	0.400	0.578	2.318
	Abdus Sobur	1.561	0.310	0.544	2.415
	Nasiruddin	1.339	0.592	0.503	2.434
	Asikuddin	1.178	0.281	0.543	2.002
	Omor Ali	1.337	0.236	0.653	2.226

Table 4.31 : Hazard Index for Average population sub-groups

Village	Owner's name	Hazard Index (HI)			
		^{As} HQ _{total}	^{Pb} HQ _{total}	^{Cd} HQ _{total}	HI
Rani Bazar	Omoresh Roy	0.822	0.184	0.004	1.010
	Zahurul Islam	0.771	0.189	0.003	0.963
	Bithil Pal	2.079	0.250	0.003	2.331
	Bahrullah Bhuia	0.744	0.241	0.004	0.989
	Azizul Haque	0.685	0.216	0.003	0.904
Shaheb Bazar	Abdul Hamid	0.719	0.002	0.276	0.998
	Abdus Sobur	0.857	0.002	0.230	1.089
	Nasiruddin	0.717	0.003	0.212	0.932
	Asikuddin	0.646	0.002	0.249	0.896
	Omor Ali	0.705	0.001	0.285	1.051

Table 4.32 : Hazard Index for Senior population sub-groups

Village	Owner's name	Hazard Index (HI)			
		^{As} HQ _{total}	^{Pb} HQ _{total}	^{Cd} HQ _{total}	HI
Rani Bazar	Omoresh Roy	0.707	0.162	0.147	1.016
	Zahurul Islam	0.663	0.136	0.150	0.949
	Bithil Pal	1.760	0.108	0.199	2.067
	Bahrullah Bhuia	0.643	0.165	0.190	0.998
	Azizul Haque	0.591	0.117	0.171	0.879
Shaheb Bazar	Abdul Hamid	0.618	0.103	0.220	0.941
	Abdus Sobur	0.731	0.076	0.179	0.987
	Nasiruddin	0.618	0.116	0.166	0.900
	Asikuddin	0.548	0.075	0.197	0.820
	Omor Ali	0.651	0.058	0.223	0.932

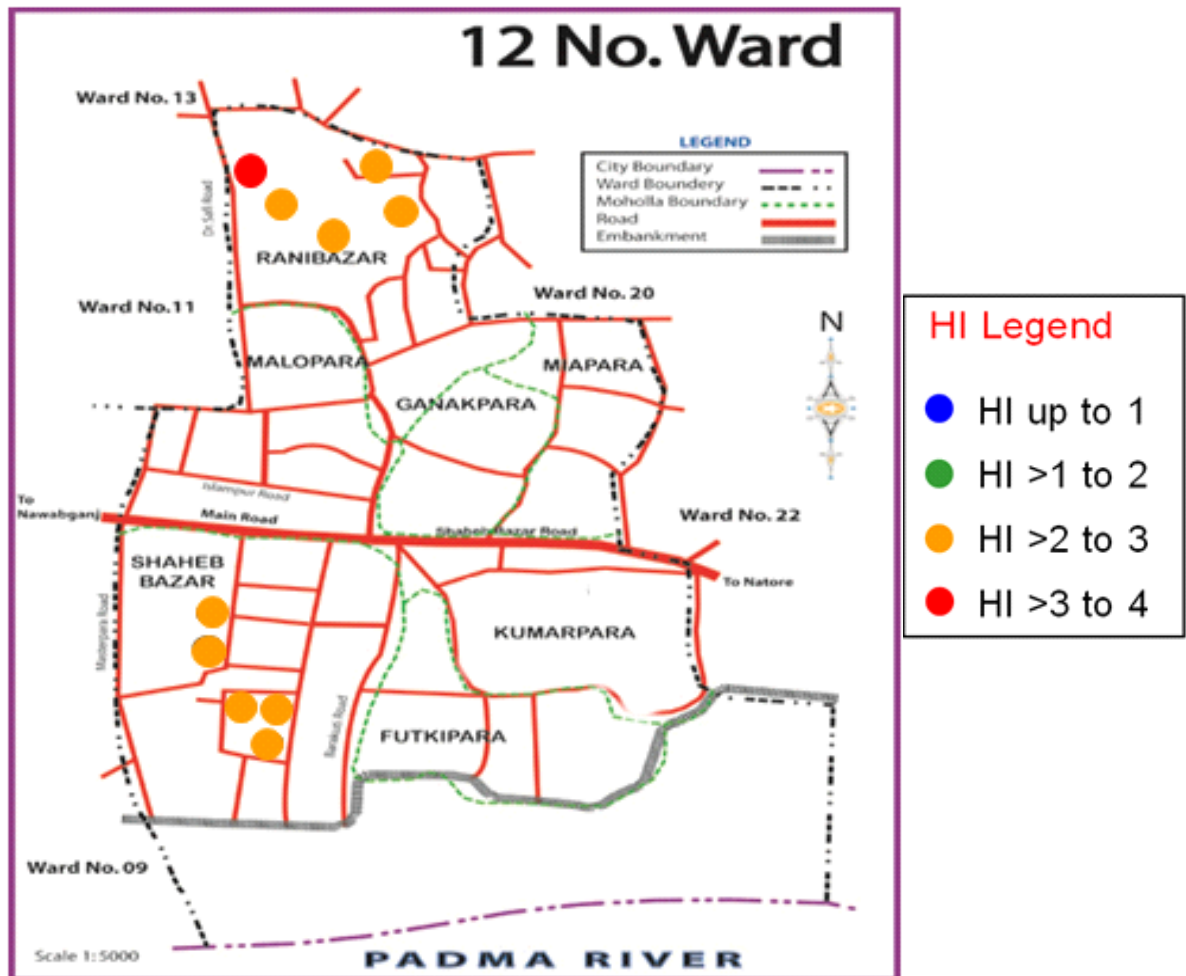


Figure 4.2 : Map of HI values for the children population sub-group of Rani Bazar and Shaheb Bazar

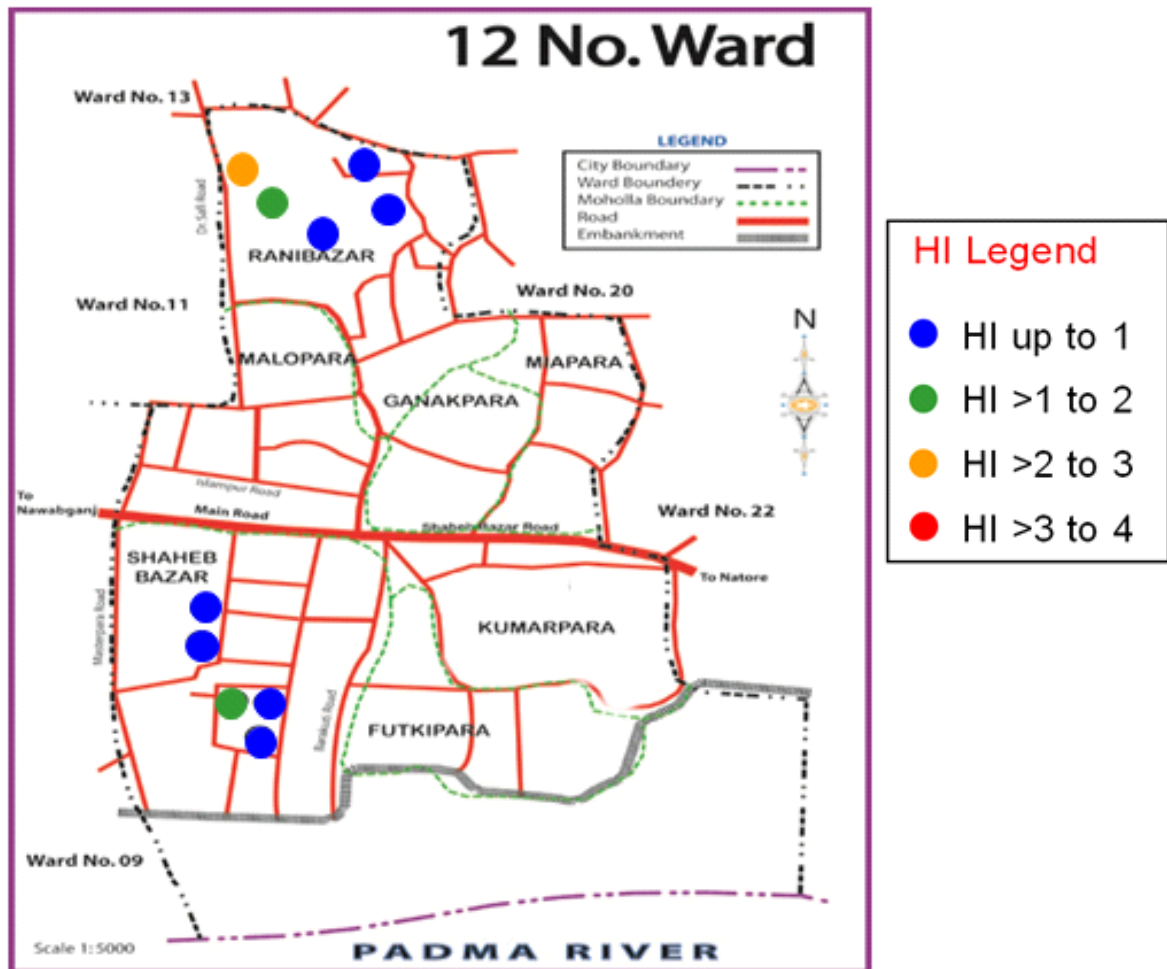


Figure 4.3 : Map of HI values for the average population sub-group of Rani Bazar and Shaheb Bazar

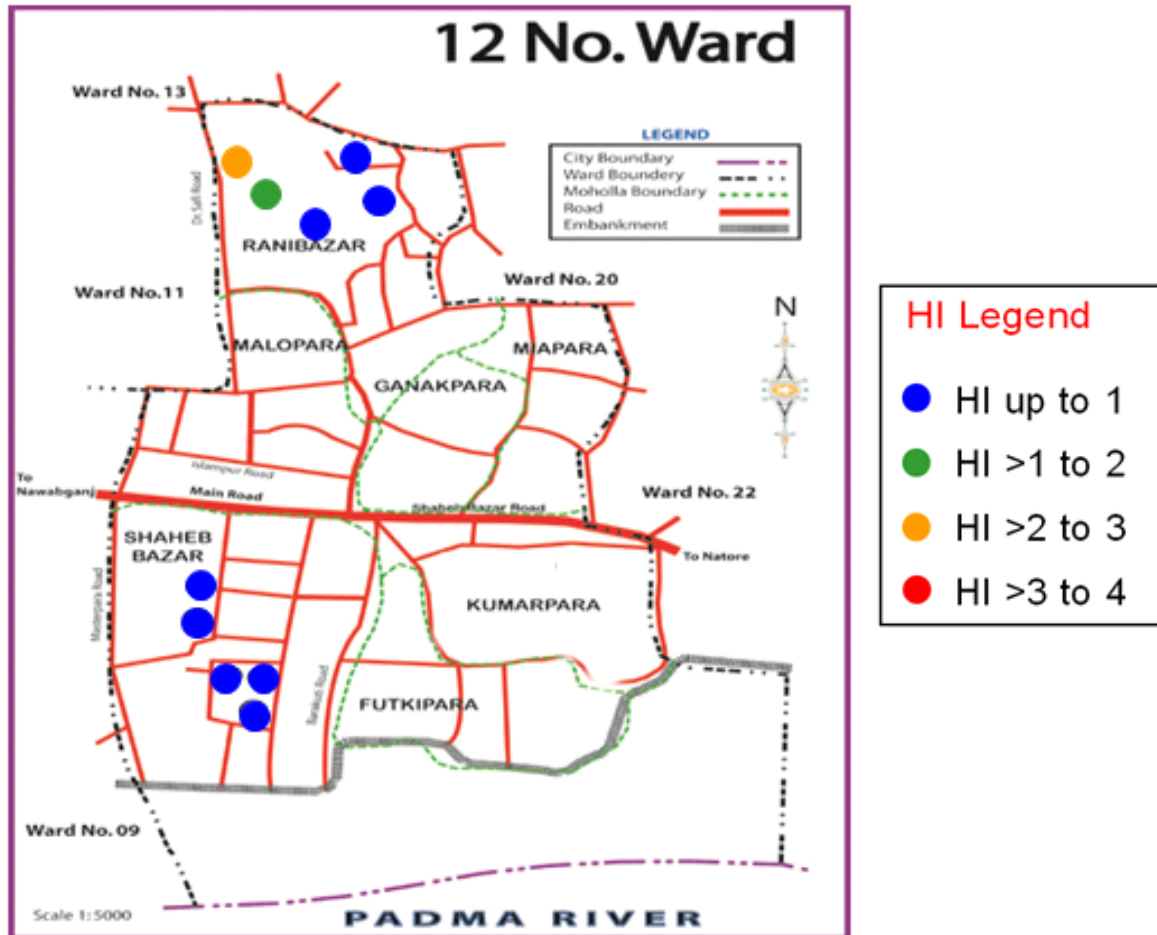


Figure 4.4 : Map of HI values for the senior population sub-group of Rani Bazar and Shaheb Bazar.

4.5 Conclusion

1. In the investigation, the concentrations of heavy metals in the studied samples follow the following order:
For Arsenic: Dust > Rice > Fish > Vegetables > Drinking water
For Cadmium: Rice > Dust > Fish > Vegetables > Drinking water
For Lead: Dust > Rice > Fish > Vegetables > Drinking water
2. Ingestion is the main route of metal exposure that accounts for 93.4 to 99.9% exposure. Almost all of Pb and Cd, and 96% of As are exposed through Ingestion.
3. The children population sub-group in the studied area are at health risk, since HI exceeds 1.000 in all cases. The average HI is 2.483.
4. 80% of seniors and 70% of adults (i.e., average persons) in the studied area are safe in consuming the foods. The average HI values for seniors and adults are 1.049 and 1.110 respectively.
5. Relative average high values of HI indicates that the safe persons are at borderline stages.
6. Senior persons are comparatively safer than average persons.
7. The contribution of the studied metals in total exposure is As (68%) > Cd (22%) > Pb (10%) for all population sub-groups.

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CHAPTER FIVE
RECOMMENDATIONS FOR FUTURE WORK

Chapter 5

Concluding Remarks

5.1 Remarks

Bangladesh is mainly an agricultural country. The total lands of her are used in various sectors of harvesting. The cultivated lands are irrigated with tube-wells [1]. Since groundwater arsenic contamination in shallow aquifer, from which water of the tube-wells are depended out, is a very common phenomenon in Bangladesh [2]. We made attempts to study the accumulation of arsenic (heavy metals) in food grains from irrigation, in general. For this, we studies on some common food grains that are produced commercially in Bangladesh.

Our findings reveal that the groundwater used for irrigation purpose are hard and contain various metals and arsenic at very high concentrations. The main value of arsenic concentration was found in high range. This observation is an agreement with those reported by authors [2, 3]. This is probably due to reducing conditions of aquifers which is supported by low value of red ox potential.

A very wide range of arsenic concentrations in food grains were reported by many investigators [4, 5]. The great fluctuations of arsenic content in food grains are probably due to the facts that uptake of metals by plants is dependents upon soil properties and plant physiological factors that varies greatly [6].

It is observed that the harvesting crops (food grains) become As, Pb and Cd poisoned [8, 9], when the crops are irrigated. The accumulation of arsenic, lead and cadmium are in the food grains decreased by using organic fertilizer.

The efficiency of the studied six organic fertilizers in simultaneous reduction of metal toxicity are as follows:

CM (Compost) >> EW(Earthworm Mud) \approx CD (Cow-dung) \approx DM (Drain Mud) >>
RD (Rotten Dhuncha) \approx WH (Water Hyacinth).

So, the first four organic fertilizers could be recommended for remedy of As, Pb and Cd toxicity in corns.

Generally, the studied fertilizers reduce As, Pb and Cd toxicity in corns simultaneously. Compost is the best fertilizer in this regard.

5.2 Recommendations for future study

Heavy metals such as arsenic, cadmium, lead, chromium and mercury are some of the important environmental pollutants. Their significant presence in the atmosphere, soil and water may cause serious problems to all organisms. Their bio-accumulation in the food chain can be treated as a potential threat to human health. So human health risk assessment involves a lot of variables. Besides these, there are some potential ways to take remedial measure against those. With regard to the considerations, the following studied could be carried out in future. Studies related to remedy of environmental pollution:

1. In this investigation, we were confined in four natural organic fertilizers that the farmers of Bangladesh use frequently. There are some other similar fertilizers, namely, rotten weeds, baggage (Obtained from crushing sugarcane), poultry stool, rotten used tea leaves, etc. that could be studied for remedial measure against significant bio-accumulation of toxic elements in food grains.
2. The mentioned study of remedial measure using natural organic fertilizers could also be applied to several types of corns like paddy, maize, wheat, pulse, etc.
3. It was observed that entrance of heavy metal pollutants in corns' plants affected adversely the yield of crops. The same adverse effect was reported for rice by arsenic. This is a national as well as a global threat towards food security. Therefore, this study should be extended to affected areas extensively. That is, more site-specific studies should be carried out.

4. Some cations and anions may affect the uptake of toxic elements in food grains. To understand this, more studies might be carried out that include the influence of foreign cations such as Na^+ , Ca^{2+} , Fe^{3+} , etc. and foreign anions such as NO_3^- , SO_4^{2-} , PO_4^{3-} , etc. The kinetic studies related to these are also important.

Studies related to human health risk assessment

1. The organic pesticides and insecticides like D.D.T., **Organophosphates, N-Methyl Carbamates, Organochlorines**, etc. are used to control pests and insects. These herbicides and fungicides enter into the human body through food chain. For prolonged exposure a considerable amount of the pesticides and insecticides retained in human body that might cause serious health hazards. For example, D.D.T. remains undegraded in human muscles for 40 years! With this regards the study may be extended.
2. British Geological survey in 2000 reports that toxic elements like fluoride, iodide, nickel, strontium, uranium, etc. are found in plenty in groundwater of Bangladesh. So Hazard Index (HI) for human health risk assessment should include those elements in addition.
3. In this investigation, two villages are considered for collection of some selected samples with the aim to assess the levels and determined hazard quotient and hazard index for human risk assessment of toxic elements (arsenic, cadmium and lead). Site-specific integrated risk assessment should be made covering all possible exposure pathways. This will provide the actual total risk due to exposure of the toxic elements.
4. More diet like soft drinks, beer, whisky, fast-foods, appetizers, etc. might contain toxic elements which may pose a risk to the human health. More study might be carried out with this regards.

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