

Studies on Heavy Metals in Fruits of Samta Village of Jessore in Bangladesh

by

Md. Abdur Rahim

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science in the Department of Chemistry



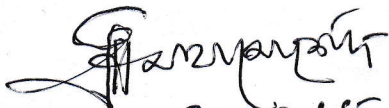
Khulna University of Engineering & Technology

Khulna-9203, Bangladesh

December, 2015

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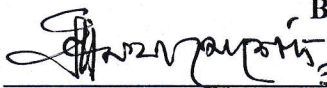


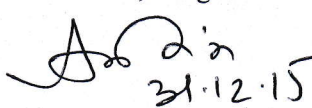
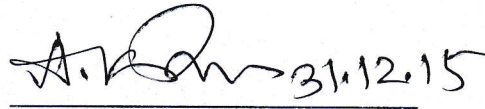
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Abstract

Various fruits such as Mango (*Mangifera indica* L.), Jackfruit (*Artocarpus heterophyllus* L.), Guava (*Psidium guajava* L.), Hog plum (*Spondias dulcis* L.), Carambola (*Averrhoa carambola* L.), Pomelo (*Citrus grandis* L.), Lemon (*Citrus limon*), Wax apple (*Syzygium samarangense*), Papaya (*Carica papaya* L.), Coconut (*Cocos nucifera* L.) and Sapodilla (*Manilkara zapota*) were collected from Samta village of Jessore district of Bangladesh and screened for arsenic, manganese, lead, cadmium and chromium by Atomic Absorption Spectrophotometer (AAS).

The average moisture contents in soil and fruits were found $11.90 \pm 0.19\%$ and $80.10 \pm 12.92\%$ respectively. The mean concentration of arsenic in irrigation water, soil and fruits were $0.51 \pm 0.17 \text{ mg/L}$, $8.40 \pm 1.73 \text{ mg/Kg}$ and $0.206 \pm 0.14 \text{ mg/Kg}$ respectively. Maximum concentration of arsenic in irrigation water, soil and fruits were monitored 0.78 mg/L , 11.31 mg/Kg and 0.53 mg/Kg respectively. Minimum concentration of arsenic in fruits was 0.10 mg/Kg . In case of irrigation water, arsenic concentration was higher than that of standard (0.100 mg/L) value of Bangladesh. The concentrations of arsenic in soil and fruits were observed somewhat less than that of standard value recommended by WHO.

The average concentrations of manganese in irrigation water, soil and fruits were found $0.10 \pm 0.03 \text{ mg/L}$, $269.14 \pm 20.71 \text{ mg/Kg}$ and 4.96 mg/Kg respectively. The maximum concentration of manganese in soil and fruits were 296.82 mg/Kg and 12.83 mg/Kg respectively which were lower than that of standard value recommended by WHO, EU and BADC. The presence of lead, cadmium and chromium was not found in water, soil and fruits in this study area.

In our research, 120 people were monitored for calculating the consuming of arsenic and manganese through daily intake of fruits and their health risk factor was analyzed. The average age, body weight and daily intake of fruits per person per day were 35.04 ± 14.55 year, $60.77 \pm 8.62 \text{ Kg}$ and 263.20 g respectively. Average 0.0018 mg of arsenic and 0.055 mg of manganese were consumed in each person (61 Kg body weight) per day which are lower than WHO standard for arsenic (0.002 mg/Kg body weight) and manganese (0.033 mg/Kg body weight) intake for human body.

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CHAPTER I

Introduction

CHAPTER I

Introduction

1.1 Overview

Fruits are specially valued in human diet as these contain micronutrients, fiber, potassium, vitamins, which work as antioxidants within the body as well as bio-functional components. 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, chromium, manganese, mercury and copper [1]. There are about 70 types of fruits are grown in Bangladesh. The most widely cultivated fruits are mango, jackfruit, black berry, jujube, pineapple, litchi, guava, papaya, coconut, custard apple, wood apple, elephant apple, Indian blackberry, tamarind, cashew nut, pomegranate, palmyra palm, rose apple, and Indian olive. There are many minor edible fruits too, which are locally available such as Burmese grape (latkan), monkey jack, rattan, river ebony, velvet apple, cowa, wild date palm etc [2, 3]. Consumption of fruits is essential for a diversified and nutritious diet. Sufficient consumption of fruit significantly reduce the incidence of chronic diseases, such as cancer, cardiovascular diseases and other aging-related pathologies [4]. Fruits offer protection against free radicals that damage lipids, proteins and nucleic acids. Polyphenols, carotenoids (pro-vitamin A), vitamins C and E present in fruits have antioxidant and free radical scavenging activities and play a significant role in the prevention of many diseases [4].

Groundwater contamination by arsenic has caused adverse health effects in Bangladesh [5]. In 1970s, a huge number of tubewells have been installed in the rural areas in order to provide microbiologically safe drinking water to the people in this country. That time it was not known that the tubewell water may contain a high level of toxic heavy metals like arsenic. By now the tubewell water has affected many people with the symptoms of arsenicosis. For this reason, arsenic entering the human body through drinking water has been a great focus of investigation in arsenic-related studies. Nevertheless, food could be another way of arsenic entry into human body through water-soil-plant transfer [6-8]. Arsenic-contaminated water used in irrigation contaminates soils and then uptake by plants causes arsenic contamination of the edible portions of plants, such as vegetables and rice grains. Arsenic in these contaminated foods is then consumed by humans.

Sources of food contamination include environmental and industrial pollution, agricultural practices, food processing and packaging. 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 [9]. Preliminary studies in different parts of Bangladesh indicate that the food chain is exposed to contamination by heavy metals and trace elements [10]. It is found that industrial sludge, often used as a soil conditioner or fertilizer has high concentrations of heavy metals. Similarly, high levels of heavy metals were found in soils in the Sundarban [11]. When these metals are absorbed by crops and animals they enter the food chain and constitute a serious health hazard. An analysis of heavy metal concentrations in vegetables in Jessore shows that all of the vegetables commonly consumed in diets contain dangerously high concentrations of heavy metals [12].

Soil is a complex amalgam and it is a non-renewable natural resource because it cannot be re-created except within the context of geological timescales. It can be defined as the unconsolidated mineral or organic material on the immediate surface of the Earth that serves as a natural medium for the growth of land plants [13]. Other definitions state it to be a reactor, transformer and integrator of material and energy from other natural resources (e.g. solar radiation, waters, biological resources) a medium for biomass production, storage of water, nutrients and heat, natural filter and a medium of past and present human actions [14-16]. It is a basic component of ecosystems and is one of the most vulnerable to contamination and degradation through accidental or deliberate mismanagement. According to the European Commission [17] in their soil protection strategy, the other functions are identified as biodiversity pool such as habitats, species and genes, source of raw materials, acting as carbon pool and archive of geological and archaeological heritage. But anthropogenic activities essentially inadequate agricultural and forestry practices, tourism, urban and industrial sprawl are responsible as the main impacting factors. These factors prevent the soil from performing to its full capacity leading to soil degradation. Soil degradation can also cause lower water retention capacity, drop in soil fertility, carbon and biodiversity; interrupt gas and nutrient cycles and reduce degradation of contaminants particularly metals [15].

The formation of soils of Bangladesh is dominated by different kinds of parent materials occurring in various topographic and drainage condition. There are considered into three major physiographic units: (i) Pleistocene terraces of Madhupur and Barind tracts, covering 8% of the total area, (ii) Recent floodplains, mainly comprising alluvial sediments of the Ganges, Brahmaputra and Meghna river systems, and occupying 80% of the country

and the rest covering 12% of the total area - northern and eastern hills of tertiary formations [18]. Genesis and properties of soils relating to fertility vary with physiography.

Bangladesh is an agricultural country with a per capita land of 0.06 hectare. About 85% of the total population in the country depends on agriculture directly or indirectly for their livelihood [19]. It possesses one of the lowest agriculture growth rates in the world [20]. The crop yield is lower than other countries due to a number of constraints of which soil is dominant. Using fertilizer is a major modern farming input, providing that about 50% of the world's crop production being attributed to fertilizer use [21]. It's true that modern farming depends on chemical fertilizer and pesticide application but it can be decreases our soil fertility and increases deficiencies of essential elements .

From early sixties, soils of Bangladesh have shown deficiencies of essential elements one after another. Organic matter content in the soils of Bangladesh is below 1% in about 60% of cultivable lands compared to an ideal minimum value of 3% [22]. Recently, deficiencies of micronutrients have been reported [23] but comprehensive studies are still lacking. Multiple micronutrient deficiencies (As, Pb, Zn, Mn, Cu, B, and Mo) occur in soils of the Indo Gangetic Plains (IGP) and are becoming prevalent as cropping intensity increases. Low organic matter levels, little retention of crop residues and limited application of animal manures to soils exacerbated these deficiencies. Along with macronutrients (e.g. NPK and S), deficiencies of some micronutrients (e.g. Zn, B and Mo) are also reported on some soils and crops [24 -26]. However there may be accumulated heavy metals in soils due to rapid advance in urbanization and industrialization.

At present, the consumption of various metals are increasing gradually, particularly among the urban community. A number of studies have shown heavy metals as important contaminants of the fruits and vegetables [27]. Fruits take up metals by through roots from contaminated soils, from deposits on different parts of the fruits exposed to pollution [28]. However, intake of heavy metal contaminated fruits may pose a risk to the human health. Prolonged human consumption of unsafe concentrations of heavy metals in food stuffs may lead to the disruption of many biological and biochemical processes in the human body [29].

Intake of fruits is an important path of heavy metal toxicity to human being. Dietary intake of heavy metals through contaminated fruits may lead to various chronic diseases. Heavy metals are not easily biodegradable and the accumulation of heavy metals in high rate cause unwanted health problems [30]. Heavy metals in fruits can affect our human health. Among the heavy metals when cadmium exerts effects on human health when it is present at higher concentration and causes severe diseases such as tubular growth, diarrhea, kidney

damage, cancer, gastrointestinal irritation, excessive salivation and vomiting [31]. Lead is sequestered in the bones and teeth, weakness in the wrist and figure, pancreases and gum, affect nervous bone, liver and also causes blood diseases [31]. Regular monitoring of these metals in fruits and in other food materials is essential for preventing excessive buildup of the metals in the food chain.

1.2 About heavy metals

There is no widely agreed criteria-based definition of a heavy metal. Criteria used to define heavy metals have included density, atomic weight, atomic number, aqueous chemistry or periodic table position [32]. Density criteria range from above 3.5 g/cm^3 to above 7 g/cm^3 . Atomic weight definitions start at greater than sodium (22.98) to greater than 40, or 200 or more [33]. Atomic numbers of heavy metals are generally given as greater than 20; sometimes this is capped at 92 (uranium). The United States Pharmacopeia includes a test for heavy metals, which is described as a test for "metallic impurities that are colored by sulfide ion" [34]. Hawkes, writing in 1997, and in the context of fifty years of experience with the term, said it referred to "metals with insoluble sulfides and hydroxides, whose salts produce colored solutions in water and whose complexes are usually colored." He suggested referring to heavy metals as "all the metals in Groups 3 to 16 that are in periods 4 and greater" or, in other words, the transition metals and post-transition metals, and commented that this definition "should serve the needs of most chemists and some others who use the term" [35, 36].

A heavy metal is any of element possessing the properties of a metallic substance at room temperature, with the higher atomic weight. Heavy metals are a group of elements between copper and bismuth on the periodic table of the elements - having specific gravities greater than 4.0. In another way, it can be defined as it increases specificity to metal heavier than the rare earth metals, which are at the bottom of the periodic table [37]. Some general properties of heavy metals are described in table 1.

Table 1.1: General properties of some heavy metals [38]

Elements	Atomic No.	Atomic Weight (g/mol)	Density g/cm ³	Color
Arsenic	33	74.92	5.70	Silver gray
Cadmium	48	112.41	8.65	Silvery bluish-gray metallic
Manganese	25	54.94	7.43	Red-white
Chromium	24	51.99	7.19	Silvery metallic
Lead	82	207.19	11.34	Steel blue
Iron	26	55.85	7.86	Silver white
Nickel	28	58.71	8.90	Silver white
Copper	29	63.54	8.90	Pink
Zinc	30	65.39	7.11	Bluish white
Molybdenum	42	95.94	10.22	Silvery
Mercury	80	200.59	13.45	Silvery-metallic liquid

1.3 Heavy metals in environment

Heavy metals are found naturally in the earth, and become concentrated as a result of human caused activities. Common sources are from mining and industrial wastes, vehicle emissions, lead-acid batteries, fertilizers, paints, treated woods and aging water supply infrastructure [39]. Arsenic, cadmium and lead may be present in children's toys at levels that exceed regulatory standards. Lead can be used in toys as a stabilizer, color enhancer, or anti-corrosive agent. Cadmium is sometimes employed as a stabilizer, or to increase the mass and luster of toy jewelry. Arsenic is thought to be used in connection with coloring dyes [40].

Heavy metals are natural constituents of the earth's crust and are present in varying concentrations in all the components of ecosystems. But the anthropogenic activities have drastically changed the biogeochemical cycles and balance of some heavy metals in nature [37]. Heavy metals are stable and tenacious environmental contaminants because they cannot be degraded or destroyed. Therefore, they are prone to accumulate in the soils, seawater, freshwater, and sediments. Relatively volatile heavy metals and those that become attached to airborne particles can be widely dispersed on very large scales. Heavy metals conveyed in aqueous and sedimentary transport enter the normal coastal biogeochemical cycle and are largely retained within near-shore and shelf regions [37].

Lead is the most prevalent toxic heavy metal contaminant. As a component of tetraethyl lead, $(\text{CH}_3\text{CH}_2)_4\text{Pb}$, it was used extensively in gasoline during the 1930s–1970s [41]. Lead levels in the aquatic environments of industrialised societies have been estimated to be two to three times those of pre-industrial levels [42]. Although the use of leaded gasoline was largely phased out in North America by 1996, soils next to roads built before this time retain high lead concentrations. Lead (from lead azide or lead styphnate used in firearms) gradually accumulates at firearms training grounds, contaminating the local environment and exposing range employees to a risk of lead poisoning [43].

1.4 Common sources of heavy metals

There are two common sources of heavy metals e.g. natural and anthropogenic influences [44]. It is also concerned that higher levels of heavy metals are found in urban landscapes and industrial sites. Heavy metal pollutants can localize and lay dormant; unlike organic pollutants they do not decay posing a different approach for remediation. Plants exhibiting hyper accumulation can be used to remove metals through the process of concentrating them into their bio matter. An impending concern associated with the persistence of heavy metals is the potential for bioaccumulation and bio-magnification to become more prevalent to some organisms than would otherwise occur naturally [45].

Thornton [46] lists there to be seven principal categories for sources of metal contamination with almost all but one being anthropogenic in cause, they are as follows:

1. Natural sources, e.g. surface mineralization, volcanic out-gassings, spontaneous combustions of forest fires.
2. Application of metal containing agricultural ingredients
3. Waste disposal from mines or mills.
4. Industrial emissions from metal smelters and refineries.
5. Municipal incineration emissions from municipal incinerators.
6. Automobile emissions from moving sources
7. Other relatively minor sources of terrestrial contamination e.g. smaller scale industries that process metals.

Naturally, heavy metals occur in rocks and soil. Arsenic is commonly found in sulfide ores e.g. Arsenopyrite (Fe, As, S). Cadmium is linked with sphalerite. Lead is found in many ores and is also the natural byproduct of radioactive decay of uranium 206 and other elements [47].

All industrialized and non-industrialized countries have used and are deliberately using heavy metals for industrial, agricultural and domestic purposes without any consideration in advance of the treatment of the remnant metals. As a consequence, heavy metals are being deposited widespread in the environment [37]. Anthropogenic sources of heavy metal contaminants are more likely the cause of the higher more toxic concentrations in soil. Sources may include mining and smelting of ores, electroplating operations, fungicides and pesticides, sewage and sludge from treatment plants, and the burning of fossil fuels [48]. Other significant sources of pollution by metals in urban areas include metallic roofs, gutters and downspouts, metallic corrugated pipes, old lead pipes, storage areas, parking lots and automobile junk yards, landfills and other solid waste disposal sites [37].

1.5 Toxic effects of heavy metals

Heavy metals enter plant, animal and human tissues via air inhalation, diet and manual handling. Motor vehicle emissions are a major source of airborne contaminants including arsenic, cadmium, cobalt, nickel, lead, antimony, vanadium, zinc, platinum, palladium and rhodium [49]. Water sources (groundwater, lakes, streams and rivers) can be polluted by heavy metals leaching from industrial and consumer waste, acid rain can exacerbate this process by releasing heavy metals trapped in soils [50]. Plants are exposed to heavy metals through the uptake of water, animals eat these plants, ingestion of plant and animal-based foods are the largest sources of heavy metals in humans [51]. Absorption through skin contact, for example from contact with soil, is another potential source of heavy metal contamination [52]. Toxic heavy metals can bioaccumulate in organisms as they are hard to metabolize [53].

1.6 Picture about toxicity of Arsenic and other heavy metals

Toxic heavy metals "can bind to vital cellular components, such as structural proteins, enzymes, and nucleic acids, and interfere with their functioning" [54]. Symptoms and effects can vary according to the metal or metal compound, and the dose involved. Broadly, long-term exposure to toxic heavy metals can have carcinogenic, central and peripheral nervous system and circulatory effects. For humans, typical presentations associated with exposure to any of the classical toxic heavy metals, or chromium (another toxic heavy metal) or arsenic (a metalloid), are shown on the next page [55].



1



2



3



4



5



6

Figure 1.1: Some picture about toxic effects of arsenic [54]



7



8

Figure 1.2: Toxic effects of lead [54]

1.7 Aim of the present study

The objectives of the research work is to estimate the risks to health from certain elements in fruits. The specific aims are:

1. to analyze the concentration of As in fruits of Samta village
2. to search out the concentrations of heavy metals in fruits
3. to predict about the quality of fruits of Samta village.

1.8 Study area

Jessore district is situated in southern part of Bangladesh. Farmers and growers are cultivating various seasonal fruits. This research was conducted at Samta village under Sharsha upazila in Jessore district. Jessore district soil is fertile and climate is suitable for fruit growing. For fruits cultivation farmer are using chemical fertilizer, pesticide, herbicide, hormones and other chemical materials and which is possibility to reduce the soil fertility and chemical contamination. The study area was selected on the basis of irrigation water quality and arsenic contamination profile. Samta area was arsenic contaminated (Asia Arsenic Network) [56].

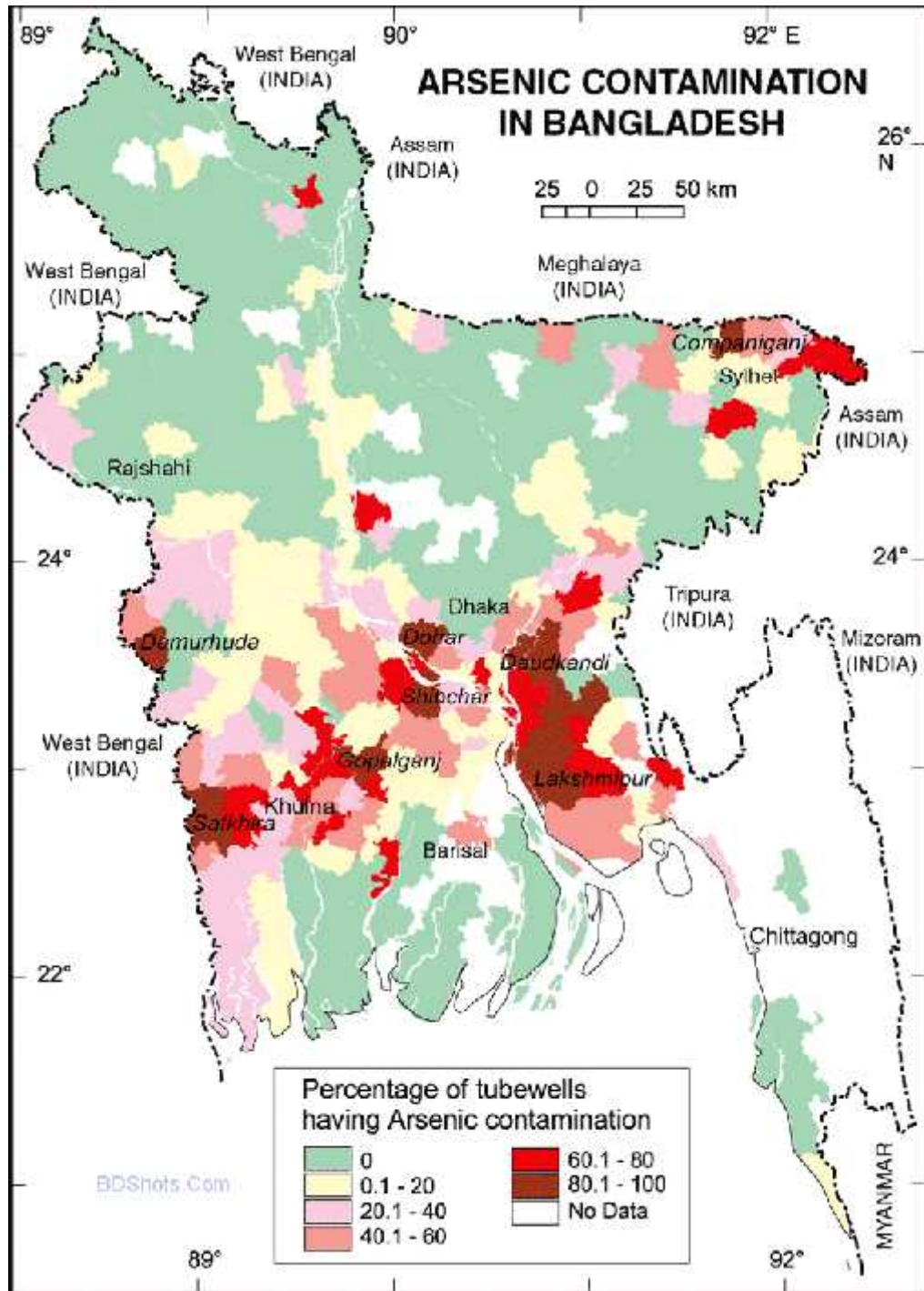


Figure 1.3: Arsenic contamination area of Bangladesh (Banglapedia 2011)[57]

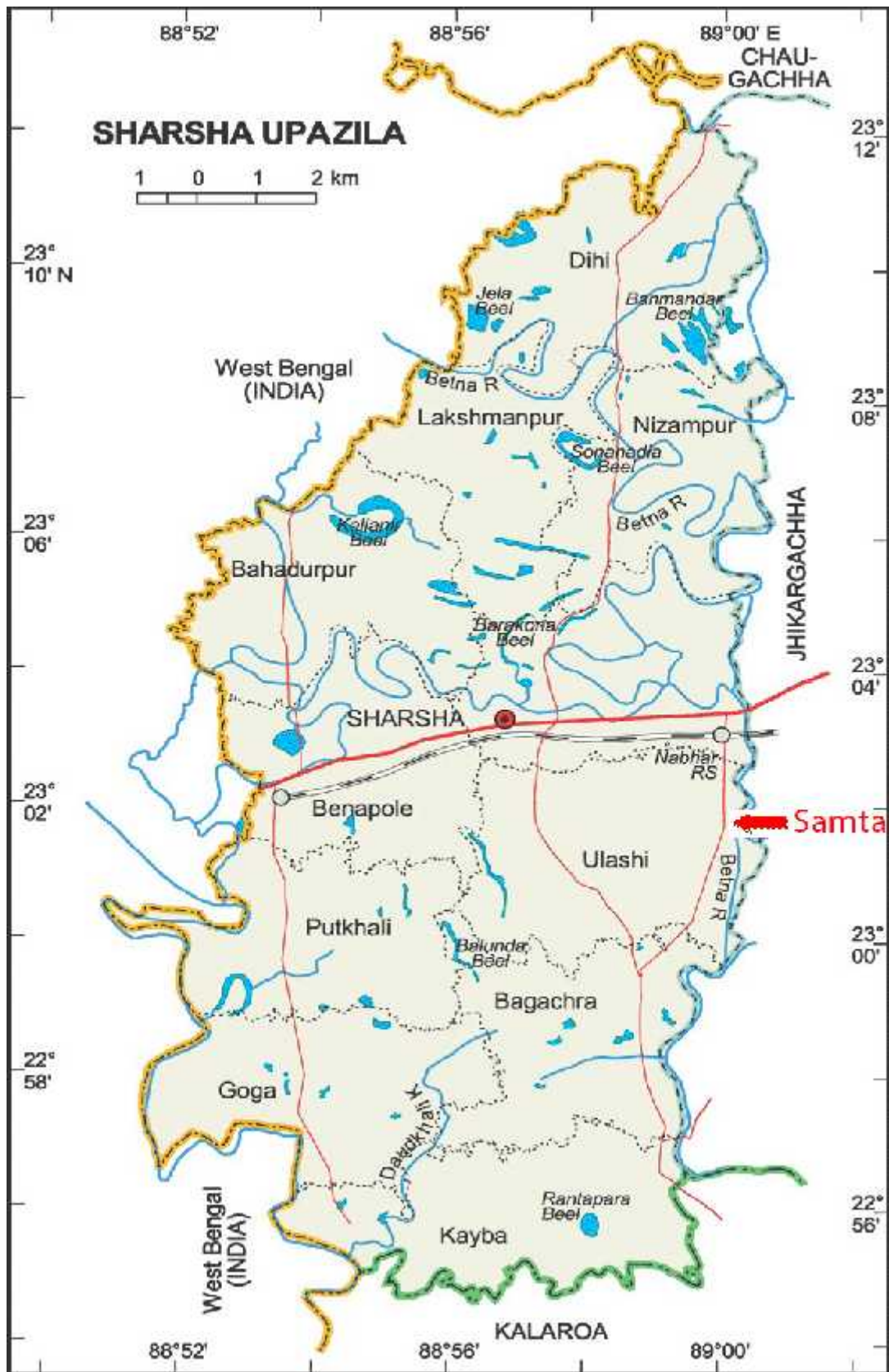


Figure 1.4: Map of the study area (Banglapedia 2011)[57]

CHAPTER II

Literature Review

CHAPTER II

Literature Review

2.1 Heavy metals in environment

2.1.1 Heavy metals in soil

In soils, metals are part of soil minerals or exist mostly as particulate complexes of different forms. Consequently, natural mineral weathering is responsible for the distribution of metals in all the components of ecosystem e.g. terrestrial, aquatic and atmospheric systems. Although heavy elements are minor components of the solid soil phase, they play an important role in soil fertility. The “normal concentrations” of trace elements in soils are of great interest as background values needed for any assessment of the degree of soil contamination [37]. The natural balance of the biogeochemical cycles has been considerably changed by the human activity causing enhanced mobilization of chemical elements into the environment as compared to the natural processes. Therefore, the essential processes under natural conditions may become harmful. The soil is able to store and accumulate trace metal to some extent due to its adsorption capacity [37].

2.1.2 Heavy metals in water

Natural water contains a large number of metal coming from various sources given below:

Table 2.1: Important trace elements in natural waters [37]

Element	Source	Effects and significance
Arsenic	Mining byproduct, chemical waste	Toxic, possibly carcinogenic
Chromium	Metal plating,	Essential as Cr(), toxic
Copper	Metal plating, mining to industrial wastes	Essential trace elements, toxic plants and algae at higher levels.
Iron	Industrial wastes, corrosion, Acid mine water, microbial action	Essential nutrient, damages fixtures by staining.
Lead	Industrial wastes, mining, Fuels	Toxic, harmful to wildlife damages fixtures by staining.
Manganese	Industrial wastes, acid mine water, microbial action	Toxic to plants, damages fixtures by staining.

2.2 Effect of heavy metals on plants

Heavy metal pollutants entering plant tissues are native in metabolic processes, but also can be stored as inactive compounds in cells and on the membranes, in each case; they may affect the chemical composition of plants without causing easily visible injury (Karim, 2007) [37]. The most common symptoms of phyto-toxicity of several heavy elements are described in table 2.2.

Table 2.2: Effects of heavy metals on plants [37]

Element	Symptoms
Ni	Gray-green leaves, brown and stunted roots and plant growth.
As	Red-brown necrotic spots, yellowing or browning of roots
Zn	Chlorotic and necrotic leaf tips, retarded growth, injured roots.
Cd	Brown margin of leaves, chlorosis, reddish veins and petioles
Cr	Chlorosis, necrotic spots and purpling tissues, injured root growth.
Cu	Dark green leaves, thick, short, or barbed-wire roots
Pb	Dark green leaves, wilting, stunted foliage, and brown short roots

2.3 Heavy metals in food chain

Heavy metals are non-biodegradable and persistent environmental contaminants which may be deposited on the surface and then absorbed into the fruits. They might accumulate in the food chain with risks to the health of animals and humans which are less sensitive to metal toxicity compared to plants but are capable of concentrating heavy metals. Wastewater irrigation is known to contribute significantly to the heavy metal contents of soils [27]. Problems occur in waterways when pollutants are leached out of the soil. If the plants die and decay, heavy metals taken into the plants are redistributed, so the soil is enriched with the pollutants. Uptake and accumulation of elements by plants may follow two different paths i.e., through the roots and foliar surface [58]. The uptake of metals from the soil depends on different factors such as their solubility, soil pH, plant growth stages, fertilizer and soil [59]. Plant species have various ways of removing and accumulating heavy metals, hence there are reports indicating that some species may accumulate specific heavy metals, causing a serious risk to human health when plant-based food stuff are consumed [60]. Disposal of sewage water and industrial wastes is a great problem. Often it is drained to the agricultural lands where it is used for growing crops including fruits. These sewage effluents are considered not

only a rich source of organic matter and other nutrients but also they elevate the level of heavy metals like Fe, Mn, Cu, Zn, Pb, Cr, Ni, Cd and Co in receiving soils [61].

2.4 Heavy metal and human health

At present, the toxicity of ingested heavy metals has been an important human health issue. Due to the prevalence of contamination from both natural and anthropogenic sources, the concern about the health effects of chronic low-level exposures has increased. There are found many researches on accumulating heavy metals in human health from fruits. Certain *Brassica species* (cabbage) are hyper accumulators of heavy metals into the edible tissues of the plant [62]. This is an important exposure pathway for people who consume fruits grown in heavy metal contaminated soil.

Certain plants can accumulate heavy metals in their tissues. Uptake is generally increased in plants that are grown in areas with increased soil concentration. Many people could be at risk of adverse health effects from consuming common fruits cultivated in contaminated soil. Often the condition of cultivated land soil is unknown or undocumented; therefore, exposure to toxic levels can occur. Xu and Thornton [63] suggest that there are health risks from consuming fruits with elevated heavy metal concentrations. The populations most affected by heavy metal toxicity are pregnant women or very young children [64]. Neurological disorders, CNS destruction, and cancers of various body organs are some of the reported effects of heavy metal poisoning [65]. Low birth weight and severe mental retardation of new born children have been reported in some cases where the pregnant mother ingested toxic amounts of a heavy metal [66].

2.5 Some study on heavy metals on land, water and fruits

The research on heavy metal accumulation in soil, water and fruits and other food grains is growing increasingly all over the world. Akan [67] analyzed the concentrations of some heavy metals and anions in vegetable samples spinach (*Amaranth caudatus*), lettuce (*lactuca sativa*), cabbage (*Brassica olemcea*) and onion (*Allium cepa*) which were freshly harvested within four agricultural locations (Mirnga, Zira, Wangaga and Malang) in Biu Local Government Area, Borno State, Nigeria. The results for vegetable samples showed that leaves contained much higher concentrations of heavy metals and anions than roots and stems. The concentrations of Cr detected in the vegetable samples ranged from 0.23 to 3.22mg/kg; 0.23 to 3.43mg/kg Mn; 0.23 to 3.45mg/kg Fe; 0.21 to 3.54mg/kg Ni; 0.25 to 4.56mg/kg Pb; 0.87 to 8.34mg/kg Zn; 0.34 to 5.44mg/kg Cd and 0.21 to 3.22mg/kg Cu.

These values were higher than those recommended by Food and Agricultural Organization (FAO) and the WHO/EU joint limits [67]. In Nigeria, Sobukola [28] studied heavy metal levels in sixteen different fruits and leafy vegetables. The results showed that the levels of Lead, Cadmium, Copper, Zinc, Cobalt and Nickel for the leafy vegetables ranged from 0.09 ± 0.01 to 0.21 ± 0.06 ; 0.03 ± 0.01 to 0.09 ± 0.00 ; 0.02 ± 0.00 to 0.07 ± 0.00 ; 0.01 ± 0.00 to 0.10 ± 0.00 ; 0.02 ± 0.00 to 0.36 ± 0.00 and 0.05 ± 0.04 to 0.24 ± 0.01 mg/kg [28]. On the other hand, Igwegbe [68] found in Nigeria, that the concentration of copper was negligible in all the crops; the highest concentrations of the metals were observed in spinach, these were 0.2250 ppm and 0.0325 ppm of lead and cadmium, respectively.

In Tanzania, Mwegoha and Kihampa, (2010)[69] found that the concentration of chromium in water ranged from (1.414 ± 0.922) to 0.01 mg/L. Maximum and minimum lead concentrations of 0.113 and 0.083 mg/L were detected. The concentration of copper was generally low at all sites, ranging from (0.013 ± 0.005) to (0.016 ± 0.005) mg/L. Cadmium concentrations at all sampling points were lower than the permissible concentration of 100 mg/kg in soils [70].

In Pakistan, Mahmood and Malik, [71] studied to the human health risks associated via food chain contamination of heavy metals routing from irrigation of urban and industrial wastewater. The present study revealed that wastewater irrigated soil wastewater and food crops grown at WWZ were enriched with Cr^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Mn^{2+} , and Zn^{2+} . They also revealed that the leafy vegetables have a higher capability to accumulate the heavy metals from soil compared with the others (tuber/bulbs, etc.) [71]. In Australia, Kachenko and Sing [72] revealed the potential accumulation of heavy metals, particularly Cd and Pb, in vegetables grown in the vicinity of smelters. Vegetables from Boolaroo contained the highest levels of Cd ($0.079\text{--}2.22$ mg kg⁻¹ FW) and Pb ($0.693\text{--}57$ mg kg⁻¹ FW), and samples from Port Kembla had the highest mean levels of Cu in all vegetable types.

In Bangladesh, Sajib studied that the daily intake of arsenic, cadmium, lead, mercury and chromium through fresh fruits may not constitute a health hazard for consumers because the values were below the recommended daily intake of these metals. However, these amounts can be hazardous if the fruits are taken in large quantities [73].

2.6 Heavy metal contamination of Bangladesh

In Bangladesh, there have contaminated some sort of research on heavy metals on soil, land, water vegetables and fruits. Naser [74] found that the levels of lead (Pb), cadmium (Cd), and nickel (Ni) in spinach (*Spinacia oleracea*), tomato (*Lycopersicon esculentum*) and cauliflower (*Brassica oleracea*) and in the rizosphere soils of the industrially polluted (Konabari, Gazipur; Keranigonj, Dhaka), and non-polluted (Bangladesh Agricultural Research Institute-BARI, Gazipur) areas. Lead concentration was higher in tomato, followed by spinach and the least in cauliflower irrespective of the location. Cadmium and Nickel concentration were found in the order of spinach>tomato>cauliflower, especially in the industrially polluted areas [74]. Akter [75], conducted a study to evaluate the status of organic matter, mineral nutrients and heavy metals content in seven different soils from fourteen selected regions of Bangladesh. This study showed that the organic matter of these soils very low to very high (0.65% in Madhupur to 28.24% in Dumuria) and the total N content of soil followed the same trend of organic matter ranging 0.056 to 1.638% in Modhupur and Dumuria region respectively [75]. The available P and S in the top of soils ranged from 3.77 $\mu\text{g g}^{-1}$ in Moheskhali to 17.28 $\mu\text{g g}^{-1}$ in BAU farm and 13.40 $\mu\text{g g}^{-1}$ in Madhupur to 420.32 $\mu\text{g g}^{-1}$ in Moheskhali, respectively [75]. Possible contamination of the studied soils by heavy metals was not significantly observed.

2.7 Features of the soil sample

2.7.1 Soil moisture

The moisture content varies considerably with 2% to 22%. It is noted that the moisture content rate are averagely high in Samta. The range also varies with cultivated vegetables [76].

2.7.2 pH in soil

pH is the most important factor in agriculture soil for nutrients availability and specific crops cultivation. Soil pH significantly influences heavy metal concentrations in both soil and plant tissues. The pH value indicates whether or not the soil is acid or alkaline and to what degree. A value between 6.5 and 7.5 is considered neutral, whereas values below 6.5 are acidic and values above 7.5 are alkaline. Acidic soil will increase metal availability in soil. Soil pH should be maintained within neutral range. In the study area, soil pH is found in the range of 5.58 to 8.04 [76].

2.7.3 Organic matter in soil

Organic matter is essential in agriculture soil for nutrients availability crops growth. Soil organic matter should be maintaining at least 5% for soil fertility. It is found that the soil organic matter concentration ranges 2.23 % to 2.99 % [76]. All of soil Organic matter concentration is lower than 5%. Soil fertility and crops production capacity are decreasing due to lack of organic matter in soil. For increasing soil fertility and sustainable crops production farmers should be used organic fertilizer for crop production [76].

2.7.4 Metal contents in soil

Some metals are available in soil but heavy metal contamination can possibility to health risk through vegetables. Arsenic contamination in ground water is major problem in our food chain. In dried soil sample iron, copper, zinc, lead, cadmium, nickel & molybdenum concentration ranges are 9200.97 mg/Kg to 17361.11 mg/Kg, 9.69 mg/Kg to 20.39 mg/Kg, 45.25 mg/Kg to 140.40 mg/Kg, 3.55 mg/Kg to 7.71 mg/Kg, 0.00 mg/Kg to 0.77 mg/Kg, 15.76 mg/Kg to 23.63 mg/Kg and 0.00 mg/Kg respectively. Micronutrient is the most essentials for soil. But micronutrient (molybdenum) is not detected in any soil sample [76].

CHAPTER III

Experimental Method

CHAPTER III

Experimental Method

3.1 Study area

Sharsha is an upazila of Jessore district in the division of Khulna, Bangladesh. The study was conducted in Samta village of Jessore district, approximately 12 km from the border with West Bengal, India. The total area of the village is 3.2 km², with 3606 people living in residential Samta village (1.5 km²), with the remaining area being cultivated land. Eighty nine percent of the population were Muslim and rest Hindu. The average annual income of the villagers is Taka 32 000 (US\$667). A small river called the Betna bounds the village on the east, but the main source of water for the village are 284, mainly shallow, wells and tubewells. There are also six deep tubewells that are used mainly for irrigation purposes. The average dissolved As concentration of the contaminated water in Samta village was 0.24 mg L⁻¹ and the highest As concentration detected was 1.80 mg L⁻¹ (Banglapedia 2011) [57].

3.2 Sample collection

3.2.1 Soil sampling

Soil from cultivar land was collected by digging a monolith of 10-10·15 inch size by using a plastic scooper. Non-soil particles e.g. stones, wooden pieces, rocks, gravels, organic debris were removed from soil. Soil was oven dried and this dried soil was sieved through a 2 mm sieve and stored in the labeled polythene sampling bags [77]. The soil samples were taken from up to 10 cm deep and put into plastic container. Soil samples were collected randomly in the vicinity of the surface water sampling sites.

3.2.2 Water sampling

The water sample was collected on tube-well in the study area. First we kept the water in a 100 ml bottle and then we mixed 2 ml HNO₃ for preserved the water.

3.2.3 Fruits sampling:

The 11 samples of fruits (Mango, Jackfruit, Guava, Hog plum, Carambola, Pomelo, Lemon, wax apple, Papaya, Coconut and Sapodilla) were collected during May to November 2015 in the study area at Samta village in Jessore district.



Figure 3.1: Collection of fruit.



Figure 3.2: Collection of soil and water.



Figure 3.3: Packaging and numbering.



a



b



c



d

21

Figure 3.4: Collected samples: (a) papaya (b) carambola (c) guava (d) lemon.

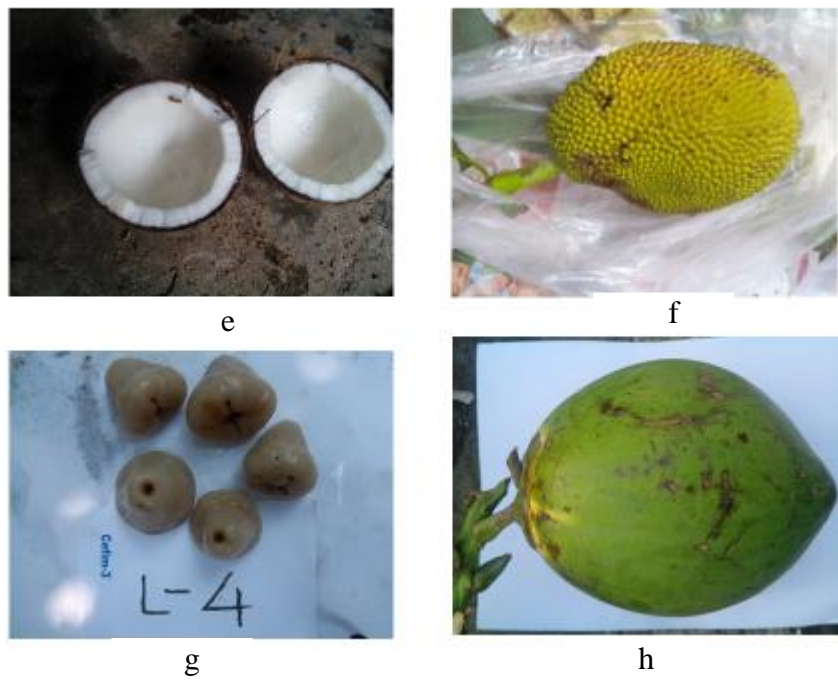


Figure 3.5: Collected samples: (e) coconut (f) jackfruit (g) wax apple (h) green coconut.



Figure 3.6: Collected samples: (i) pomelo (j) hog plum (k) mango (l) sapodilla.



Figure 3.7: Cutting and packaging sample.

WORKING METHOD

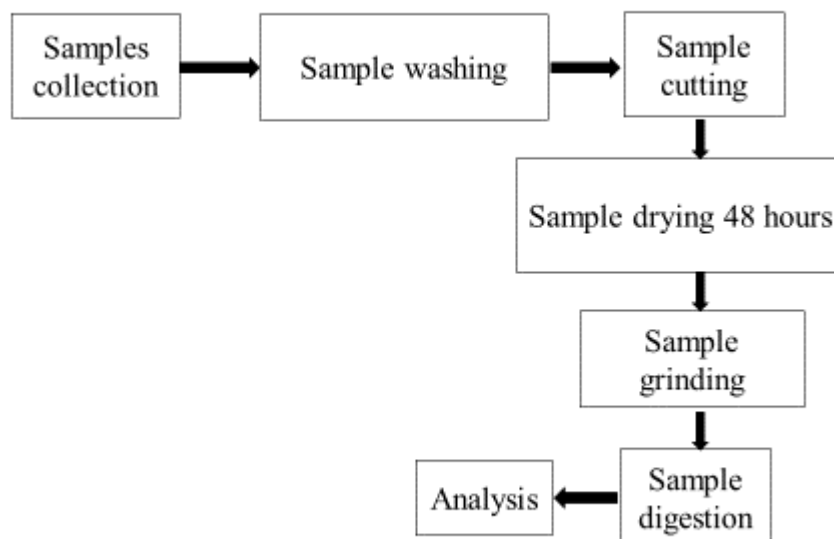


Figure 3.8: Working method.



Figure 3.9: Sample digestion and preparation for analysis.



Figure 3.10: Sample analysis at JUST laboratory.



Figure 3.11: Analyzing sample

3.3 Sample preparation

3.3.1 Washing of samples

The collected fruit samples were washed with distilled water to remove dust particles. The samples were then cut to separate the roots, stems and leaves using a knife.

3.3.2 Drying of samples

Soil sample was dried by air for nitrate, pH and organic matter analysis. On the other hand fruits sample were dried in an electric oven at 105°C for 24 to 48 hours and then cooled in a desiccator.

3.3.3 Grinding of samples

Dried soil and fruits samples were ground into a fine powder (80 mesh) using a commercial blender (TSK- West Point, France) and stored in polyethylene bags, until used for acid digestion.

3.3.4 Sample digestion

Soil, water and fruits samples were digested separately by using USEPA method (3050B). About 0.50g to 5.00g of soil and fruits sample was taken in to clean and dried 100 ml borosilicate glass beaker and 15ml of concentrated nitric acid (HNO_3 , Analytical grade, Sigma Aldrich) was added to it. The beaker was covered by watch glass and the mixture was preserved through overnight under fume hood. The beakers were placed on hot plate and heated the acid mixed sample at $95 \pm 5^\circ\text{C}$ for 2-4 hours under fume hood. The acid digestion was repeated for completed the reaction (addition of 5 ml of conc. HNO_3) until no brown fumes given off by the sample. The beakers were cooled at room temperature, and then 2ml of di-ionized water and 3 ml of 30% hydrogen peroxide (H_2O_2 , Analytical grade, Sigma Aldrich) was added and covered the beaker with a watch glass. Heated the beaker at $95 \pm 5^\circ\text{C}$ on hot plate to start the peroxide reaction until the effervescence subsided and allowed the beaker to be cooled. After cooling the beaker was rinsed by 5 ml of 1+5 hydrochloric acid (HCl , Analytical grade, Sigma Aldrich) and di-ionized water and filtered through Whatman-41 filter paper. The filtered sample was transferred into 100ml of volumetric flask and diluted to 100ml by adding di-ionized water. Finally the digested sample was stored in polyethylene

bottles and kept at 4⁰C in refrigerator. Acid digested sample metal analysis was conducted by HG-AAS method [77].

3.3.5 Sampling protocol

The standard protocol for sampling was followed during the sampling period. The important steps are included:

- Location of the sampling point and identified it on the location map.
- Numbering of the liquid samples
- Temperature of the samples at degree Celsius
- Time and date of sample collection
- The sampling point was marked on the locations map on the containers by a permanent marker pen.
- The collected samples were stored at 4°C in the freeze for analysis

3.3.6 Sample information and coding

Table 3.1: Soil and water sampling and coding

Sample ID	Local name	English name	Collection location
S-4A	Mati	Soil	South para
S-4B	Mati	Soil	South para
S-4C	Mati	Soil	South para
S-5A	Mati	Soil	West para
S-5B	Mati	Soil	West para
S-5C	Mati	Soil	West para
S-6A	Pani	Water	South para
S-6B	Pani	Water	South para
S-6C	Pani	Water	South para
S-7A	Pani	Water	West para
S-7B	Pani	Water	West para
S-7C	Pani	Water	West para

Table 3.2: Coconut water and green coconut water sampling

Sample ID	Local name	English name	Collection location
S-8A	Daber pani	Green Coconut water	South para
S-8B	Daber pani	Green Coconut water	South para
S-9A	Daber pani	Green Coconut water	West para
S-9B	Daber pani	Green Coconut water	West para
S-10A	Narkeler pani	Coconut water	South para
S-10B	Narkeler pani	Coconut water	South para
S-11A	Narkeler pani	Coconut water	West para
S-11B	Narkeler pani	Coconut water	West para

Table 3.3 : Fruits sampling and coding

Sample ID	Local name	Fruit sample name	Scientific name	Collection location
S-1A	Kagji lebu	Lemon	<i>Citrus limon</i>	South para
S-1B	Amra	Hog plum	<i>Spondias dulcis</i> L.	South para
S-1C	Kamranga	Carambola	<i>Averrhoa carambola</i> L.	South para
S-1D	Peyara	Guava	<i>Psidium guajava</i> L.	South para
S-1E	Pepe	Papaya	<i>Carica papaya</i> L.	South para
S-2A	Aam	Mango	<i>Mangifera indica</i> L.	West para
S-2B	Kathal	Jackfruit	<i>Artocarpus heterophyllus</i> L.	West para
S-2C	Batabi lebu	Pomelo	<i>Citrus grandis</i> L.	West para
S-2D	Jamrul	Wax apple	<i>Syzygium samarangense</i>	West para
S-3A	Sofeda	Sapodilla	<i>Manilkara zapota</i>	West para
S-3B	Narkel	Coconut	<i>Cocos nucifera</i> L.	West para

3.4 Sample analysis

3.4.1 Moisture contents analysis

Soil and fruits sample moisture determination is a major significance for sample preparation, digestion and analysis. Soil moisture influences crop growth not only by affecting nutrient availability, but also nutrients transformation and biological behavior. All analyses in the laboratory were related to an oven-dry basis, and therefore must consider the actual soil moisture content [78].

Apparatus:

1. Electric Oven
2. Desiccator
3. Glass Petridis
4. Electronic Balance

Procedure: Glass Petri dishes were cleaned by 10% nitric acid and dried in electric oven at 120 °C. After drying then Petridis was kept in desiccator for cooling. After cooling then dried empty Petri dish weight was taken and data was recorded. 100g of Soil and fruits sample was taken in Petridis and it was dried in electric oven for 24 hours at 105°C until constant weight was obtained on cooling in a desiccator. The weight of raw sample with empty Petri dishes and dried sample with Petri dishes data was taken and recorded in table [78]. Calculated the percentage of moisture content in soil and fruits samples by using the following equation:

$$(W1-W2) \times 100 / W1$$

Where,

W1=Weight of raw sample in gm

W2=Weight of dried sample in g (oven dry that 105°C)

3.4.2 Heavy metal analysis in soil, water and fruits

Atomic absorption (AA) spectroscopy can be used to analyze the concentration of over 62 different metals in a solution. It is based on the absorption of radiation by free atoms. Each chemical element in the atomic states absorbs only radiation of well-defined wavelengths characteristics of the particular element involved. Atomic absorption takes place when unexcited atoms absorb energy and become excited atoms. Electrons can exist in one of two states: [79].

Ground State: In this state, the electron contains the least energy possible, orbiting as close as it can to the nucleus. Excited State: In this state, the electron contains more energy than in its ground state, orbiting further from the nucleus of the atom. Absorption therefore is carried out by unexcited atoms, whereas emission arises from excited atoms.

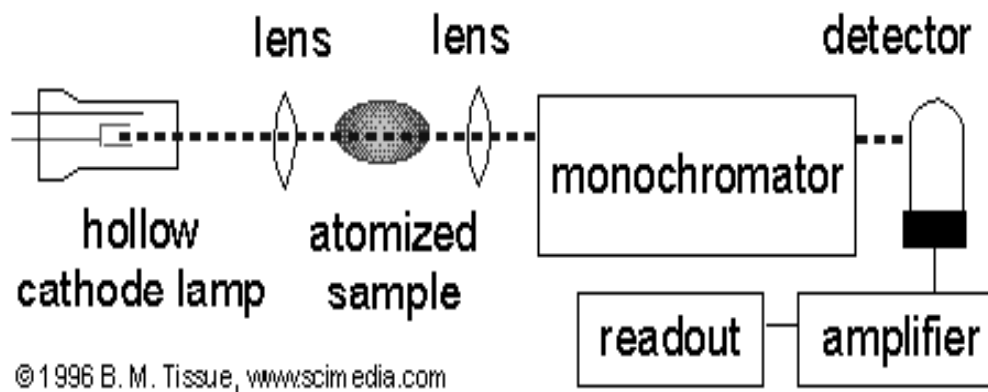


Figure 3.12: Equipment used in AAS.

The equipment used in AAS is basically the same as for other spectroscopic absorption methods. It consists of;

Radiation source

The light source is usually a hollow-cathode lamp of the element that is being measured. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow atomic absorption and atomic fluorescence measurements in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time [79].

Monochromator

The function of the monochromator is to select radiation of the correct wavelength and eliminate other radiation from the light path. For many elements such as sodium, potassium, and copper the spectrum is simple and only low resolution monochromator is required. However, for certain other elements, particularly the transition elements, high resolution is necessary to prevent unabsorbable emission lines.

Detectors

Photomultipliers are used exclusively on commercial equipment. In practice, it is the function of the detector to measure the intensity of radiation before and after absorption by the sample. From this one can calculate how much radiation has been absorbed from the intense beam [79].

Optical slit system

Two slits are included in the optical system, an entrance slit and an exit slit. The entrance slit serves to obtain a narrow, parallel beam of light from the source. The exit slit is used to select radiation of the correct wavelength after it emerges from the monochromator.

Atomizer

The function of the atomizer is to convert the combined atoms of the liquid sample into free atoms. The most common atomizer is the flame. In practice the liquid sample is introduced into the flame in the form of a droplet. The droplets evaporate and leave a solid residue. The residue, which contains the same atoms, is decomposed by the flame and free atoms are liberated. These free atoms absorb the radiation which is measured in this procedure [79]. The metal concentrations (Cu, Zn, Fe, Pb, Cd, Mo and Ni) are determined by atomic absorption spectrometry using a Shimadzu model AA7000 (Japan) Atomic Absorption Spectrophotometer (AAS). During analysis the instrument are calibrated by using reference standard solution for each metal concentration analysis. Calibration curve relation coefficients are 0.995 to 0.999 and laboratory control standard recovery are 99 % to 105%. According to blank sample analysis data this instrument detection level are 0.002 mg/L.

3.4.3 Transfer factor (TF)

Soil to plant metal transfer was computed as transfer factor (TF), which was calculated by using the equation

$$TF = C_{\text{Fruit}}/C_{\text{Soil}}$$

where, C_{Fruit} is the concentration of heavy metals in fruits and C_{Soil} is the concentration of heavy metals in soil.

3.4.4. Daily intake of metals (DIM)

Daily intake of fruits in adult was calculated by data obtained during the survey though a questionnaire. DIM was calculated by the following equation

$$DIM = C_{\text{metal}} \times C_{\text{factor}} \times D_{\text{food intake}} / B_{\text{average weight}} [80].$$

where, C_{metal} represents the heavy metal concentrations in fruits (mg kg^{-1}), C_{factor} indicates conversion factor (0.085), $D_{\text{food intake}}$ represents daily intake of fruits and $B_{\text{average weight}}$ represents average body weight, respectively. The average fruits intake was calculated by conducting a survey where about 120 people (18+ ages males and females) having an average body weight of 60 kg were asked for their daily intake of particular fruits from sampling sites.

3.4.5. Health risk index (HRI)

To assess the human health risk of heavy metals, it is necessary to calculate the level of human exposure to that metal by tracing the route of exposure of pollutant to human body. There subsist many exposures routes for heavy metals that depend upon a contaminated media of soil and fruits on the recipients. Receptor population use the fruits enriched with higher concentration of heavy metals which enters the human body leading to health risks [81]. In the present research work, fruits were collected from the study area and their metal concentration was used to calculate the health risk index (HRI). The health risk index of the present research work was compared with the one reported by Khan et al. [81] and Jan et al. [82]. Results of HRI were found to be lower than those of Khan et al.[81] and Jan et al. [82]. Value of HRI depends upon the daily intake of metals (DIM) and oral reference dose (R_{fD}). R_{fD} is an estimated per day exposure of metal to the human body that has no hazardous effect during life time [83]. The health risk index for As, Cr, Pb, Cd and Mn by consumption of contaminated fruits was calculated by following equation

$$\text{HRI} = \text{DIM} / R_{fd} \text{ [82].}$$

where DIM represents the daily intake of metals and R_{fd} represents reference oral dose. R_{fd} value for As, Cr, Pb, Cd and Mn is 1.0, 1.5, 0.004, 0.001 and 0.033 (mg/kg bw/day) respectively [83].

CHAPTER IV

Results and Discussion

CHAPTER IV

Results and Discussion

Fruits are the essential for recovery of vitamins and minerals in human body. Fruits sample moisture contents was higher than solid contents. Fruits quality and safety depends on irrigation water and soil quality. Arsenic contaminated areas irrigation water and soil arsenic contamination can make a fruits safety. This study was analyzed 5 water, 5 soil and 11 fruits sample arsenic, manganese, lead, cadmium and chromium by atomic absorption spectrophotometric method.

4.1 Features of the sample fruits, soil and water

4.1.1 Moisture contents in fruits sample

Moisture content is the most important factor for fruits sample quality analysis. Moisture contents in fruits was showed in figure 4.1 and table 4.1. Average moisture and solid contents in fruits sample was $80.10 \pm 12.92\%$ & $19.90 \pm 12.92\%$ respectively. Maximum moisture contents was showed 92.24% in papaya sample and minimum moisture contents was 48.12% in coconut (cornel) sample. On the other hand a maximum solid content was found 51.88% in coconut sample and minimum solid contents was showed 7.76% in papaya sample.

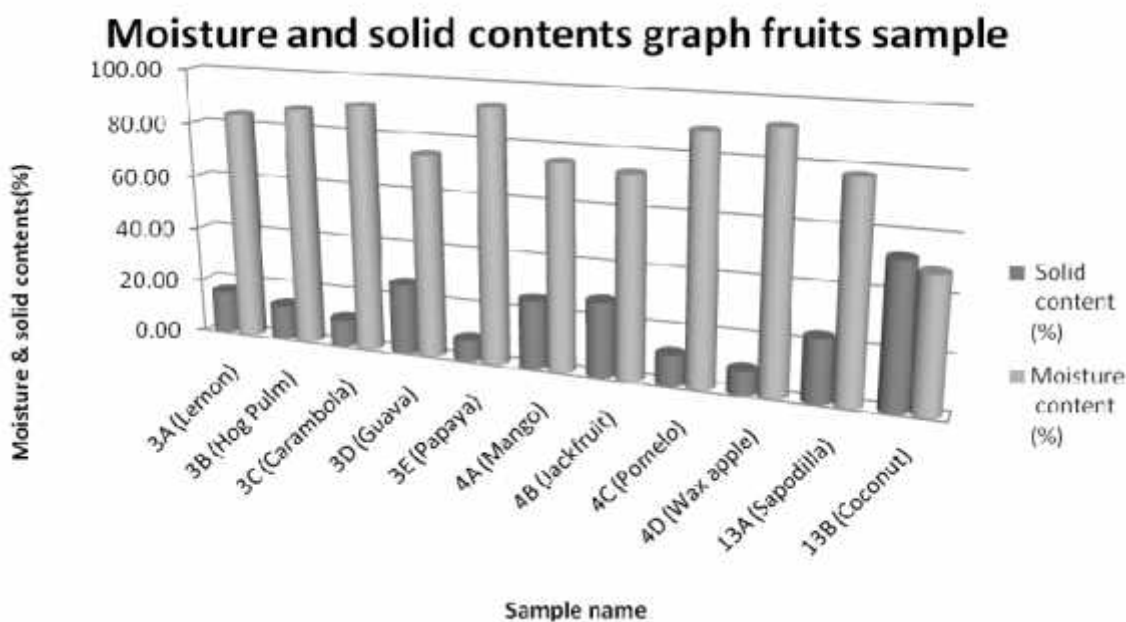


Figure 4.1: Moisture contents in various fruits and soil samples

Table 4.1: Moisture contents in various fruits sample

Sample ID	Local name	Fruit sample name	Solid Sample (%)	Moisture content (%)
S-3A	Kagji lebu	Lemon	15.79	84.21
S-3B	Amra	Hog plum	12.77	87.23
S-3C	Kamranga	Carambola	10.00	90.00
S-3D	Peyara	Guava	25.97	74.03
S-3E	Pepe	Papaya	7.76	92.24
S-4A	Aam	Mango	25.21	74.79
S-4B	Kathal	Jackfruit	27.20	72.80
S-4C	Batabi lebu	Pomelo	11.11	88.89
S-4D	Jamrul	Wax apple	8.47	91.53
S-13A	Sofeda	Sapodilla	22.71	77.29
S-13B	Narkel	Coconut	51.88	48.12
Maximum			51.88	92.24
Minimum			7.76	48.12
Average			19.90	80.10
STD. deviation			12.92	12.92

4.1.2 Moisture contents in soil sample

Moisture content in soil sample was showed in figure 4.2 and table 4.2. Average moisture and solid contents in soil sample were $11.90 \pm 0.19\%$ & $88.10 \pm 0.19\%$ respectively.

Table 4.2: Moisture contents in soil samples

Sample ID	Soil collection Location Name	Solid Sample (%)	Moisture content (%)
S-14A	South para	12.101	87.899
S-14B	South para	12.015	87.985
S-14C	South para	11.961	88.039
S-15A	West para	11.626	88.374
S-15B	West para	11.965	88.035
S-15C	West para	11.716	88.284
	Maximum	12.101	88.374
	Minimum	11.626	87.899
	Average	11.897	88.103
	STD. deviation	0.185	0.185

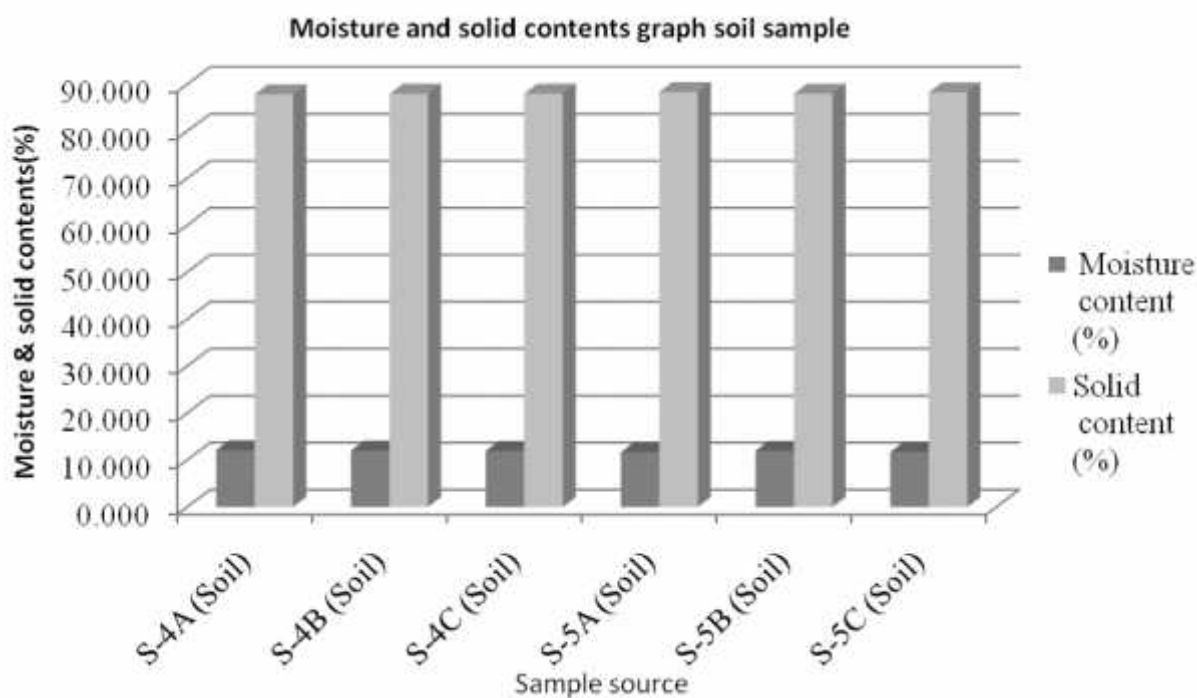


Figure 4.2: Moisture contents in various soil samples

4.1.3 Metal concentrations in fruits pulp, soil and water

4.1.3.1 Arsenic concentrations in fruits pulp, soil and water

Trace level of arsenic in food is threat for human health. This study was detected arsenic in irrigation water, soil and fruits sample by using HG-AAS method. Arsenic detection level was 0.001mg/L and calibration curve relation coefficients was >0.995 which was calibrated by using 1ppb,5ppb,10ppb,20ppb,40ppb arsenic standard solution.

Average concentration of arsenic in irrigation water was 0.51 ± 0.17 mg/L. Maximum concentration of arsenic in irrigation water was 0.78 mg/L in S-6C(water) sample and minimum concentration of arsenic was 0.39 mg/L detected in S-6A(water) sample. It was showed that all of irrigation tube wells water arsenic concentration was exceed than DoE drinking water and BADC irrigation water standard [84, 85].

In soil sample average concentration of arsenic was 8.40 ± 1.73 mg/kg. Maximum concentration of arsenic in soil sample was 11.31 mg/kg in S-5C(soil) sample. On the other hand minimum concentration of arsenic was found 6.5 mg/kg in S-4B(soil) sample. Average concentration of arsenic was bellow than the agriculture soil standard 20.00mg/kg which was recommended by Bangladesh ministry of agriculture and WHO [84].

In coconut water and green coconut water sample, average concentration of arsenic was 0.0059 ± 0.0023 mg/L.

In fruits sample average concentration of arsenic was 0.206 ± 0.14 mg/kg. Maximum concentration of arsenic in fruits sample was 0.533mg/kg in papaya sample. On the other hand minimum concentration of arsenic was found 0.10mg/kg in guava sample. Average concentration of arsenic was bellow than the EU and WHO standard 1.00mg/kg which was recommended by Bangladesh ministry of agriculture and WHO [84].

4.1.3.2 Manganese concentrations in fruits pulp, soil and water: Manganese concentration was measured in irrigation water, soil and fruits sample which was collected from study area. Average concentration of manganese in irrigation water was 0.10 ± 0.03 mg/L which was lower than Bangladesh drinking water standard (<0.01 mg/L) [84]. Concentration of manganese in coconut water was not detected.

Average concentration of manganese in soil sample was 269.14 ± 20.71 mg/kg which value was lower than European Union soil standard (<2000 mg/kg) [84]. Maximum concentration of manganese was detected 296.82 mg/kg in S-4C (soil) sample. Minimum concentration of manganese was detected 243.28 mg/kg in S-5C (soil) sample.

Average concentration of manganese was monitored 4.95 ± 4.28 mg/kg in fruits sample. Maximum concentration of manganese was monitored 12.83mg/kg in guava sample. Minimum concentration of manganese was detected 0.56mg/kg in sapodilla sample. This study was showed that concentration of manganese was lower than European Union food standard (<500 mg/kg) [84].

4.1.3.3 Lead, cadmium and chromium concentrations in fruits pulp, soil and water: Concentration of lead cadmium and chromium in water, soil and fruits sample was analyzed by Flame-AAS method. Concentration of lead cadmium and chromium was bellow than detection level in all of water, soil and fruits sample. It was indicated that water, soil and fruits was safe from lead, cadmium and chromium concentration in this study area.

Table 4.3 : Arsenic and heavy metal concentrations of soil sample.

Sample ID	Conc. Of arsenic (mg/kg)	Conc. Of manganese (mg/kg)	Conc. Of chromium (mg/kg)	Conc. Of lead (mg/kg)	Conc. Of cadmium (mg/kg)
S-4A (Soil)	7.05	250.17	<0.36*	<0.04*	<0.02*
S-4B (Soil)	6.5	262.23	<0.36	<0.04	<0.02
S-4C (Soil)	7.95	243.28	<0.36	<0.04	<0.02
S-5A (Soil)	9.35	278.62	<0.36	<0.04	<0.02
S-5B (Soil)	8.21	283.77	<0.36	<0.04	<0.02
S-5C (Soil)	11.31	296.82	<0.36	<0.04	<0.02
Maximum	11.31	296.82			
Minimum	6.5	243.28			
Average	8.39	269.14			
STD. deviation	1.73	20.71			

* Detection level.

Table 4.4: Arsenic concentrations of water sample.

Sample ID	Sample name	Sample collection location	Conc. Of arsenic (mg/L)
S-6A	Water	South para	0.39
S-6B	Water	South para	0.41
S-6C	Water	South para	0.45
S-7A	Water	West para	0.60
S-7B	Water	West para	0.71
S-7C	Water	West para	0.78
	Maximum		0.78
	Minimum		0.39
	Average		0.51
	STD. deviation		0.17

Table 4.5 : Arsenic concentrations of coconut water sample.

Sample ID	Sample name	Sample collection location	Conc. Of arsenic (mg/L)
S-8A	Green coconut water	South para	0.0036
S-8B	Green coconut water	South para	0.0042
S-9A	Green coconut water	West para	0.0039
S-9B	Green coconut water	West para	0.0031
S-10A	Coconut water	South para	0.0081
S-10B	Coconut water	South para	0.0078
S-11A	Coconut water	West para	0.0089
S-11B	Coconut water	West para	0.0075
Maximum			0.0089
Minimum			0.0031
Average			0.005888
STD. deviation			0.002391

Table 4.6 : Arsenic and heavy metal concentrations of various fresh fruits pulp.

Sample ID	Local name	Conc. of arsenic in fruits sample (mg/kg)	Conc. of manganese in fruits sample (mg/kg)	Conc. of chromium in fruits sample (mg/kg)	Conc. of lead in fruits sample (mg/kg)	Conc. of cadmium in fruits sample (mg/kg)
1A (Lemon)	Kagji lebu	0.118±0.00	4.007±0.048	<0.36*	<0.04*	<0.02*
1B (Hog Pulm)	Amra	0.097±0.00	4.961±0.014	<0.36	<0.04	<0.02
1C (Carambola)	Kamranga	0.213±0.00	6.336±0.007	<0.36	<0.04	<0.02
1D (Guava)	Peyara	0.097±0.001	12.834±0.015	<0.36	<0.04	<0.02
1E (Papaya)	Pepe	0.533±0.002	6.589±0.008	<0.36	<0.04	<0.02
2A (Mango)	Aam	0.399±0.001	0.89±0.001	<0.36	<0.04	<0.02
2B (Jackfruit)	Kathal	0.177±0.00	0.682±0.011	<0.36	<0.04	<0.02
2C (Pomelo)	Batabi lebu	0.151±0.001	1.077±0.013	<0.36	<0.04	<0.02
2D (Wax apple)	Jamrul	0.165±0.002	4.736±0.010	<0.36	<0.04	<0.02
3A (Sapodilla)	Sofeda	0.214±0.001	0.561±0.001	<0.36	<0.04	<0.02
3B (Coconut)	Narkel	0.1±0.00	11.756±0.015	<0.36	<0.04	<0.02
Maximum		0.533	12.834			
Minimum		0.097	0.561			
Average		0.206	4.948			
STD. deviation		0.139	4.278			

* Detection level.

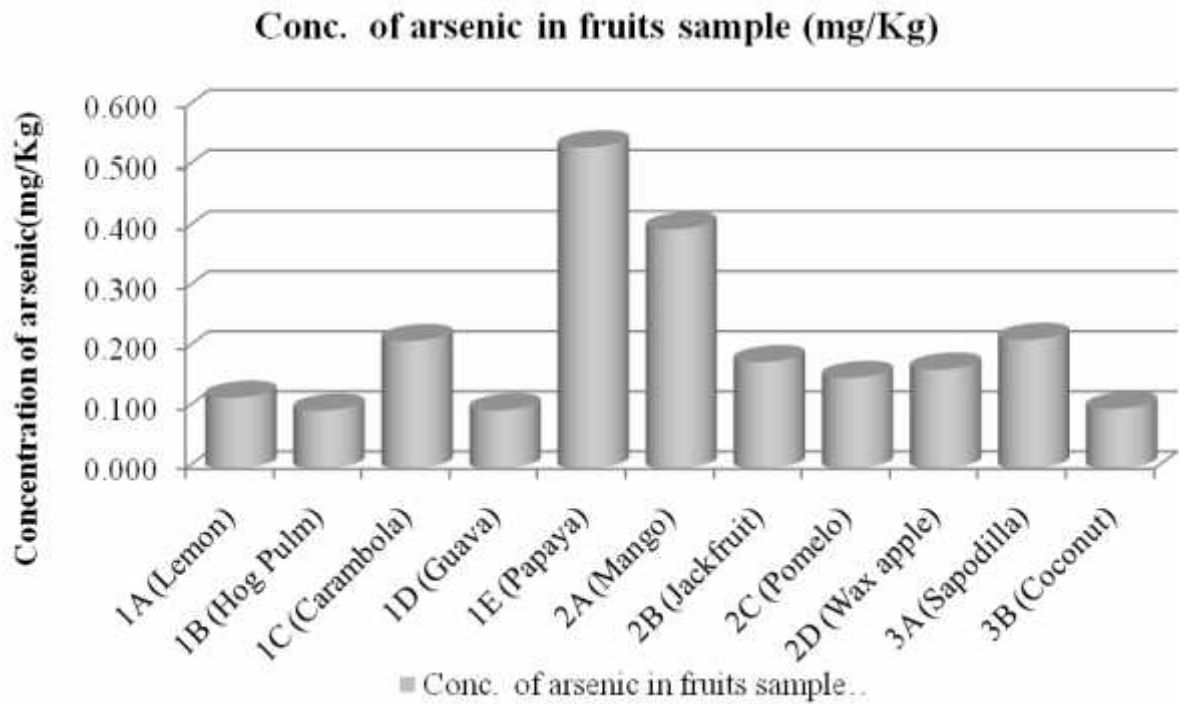


Figure 4.3: Concentration of arsenic in fruits sample

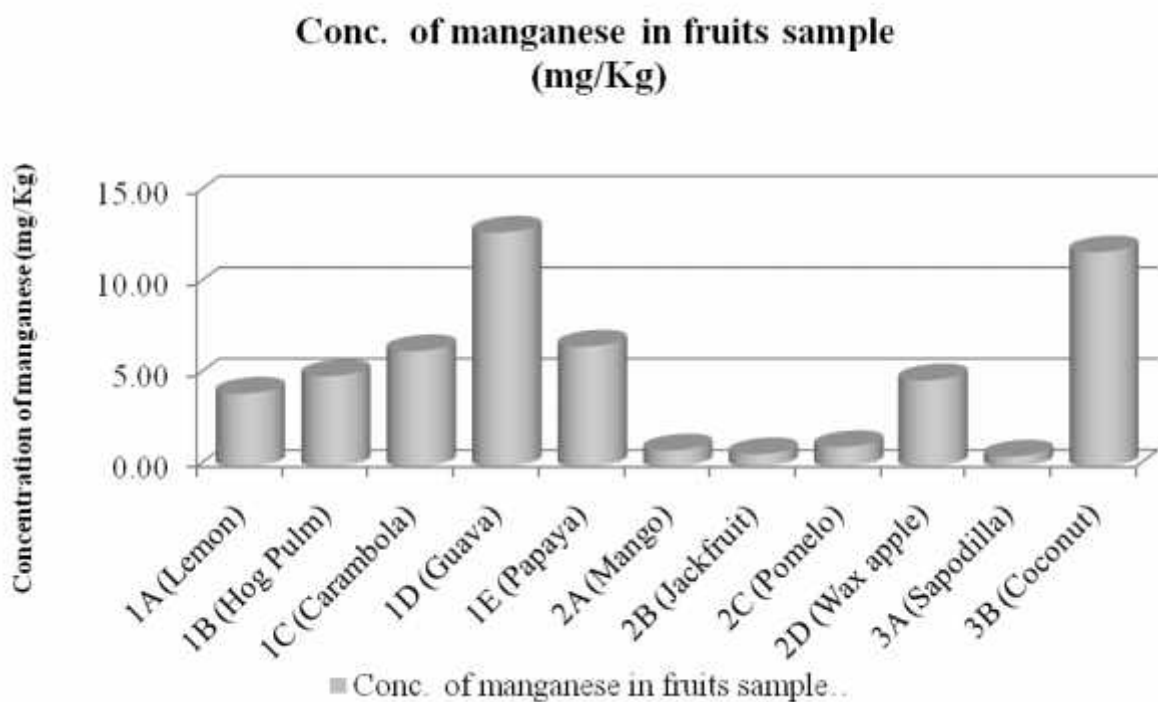


Figure 4.4: Concentration of manganese in fruits sample

4.2 Transfer factor of metals from soil to Fruits.

Metal transfer factor from soil to plants is a key module of human exposure to heavy metals via food chain. Transfer factor of metals is essential to investigate the human health risk index [86]. TF of metals varied significantly in different fruits. Among fruits, papaya (0.064) for As and guava (1.523) for Mn showed a higher metal transfer factor from soil to plants than other vegetables.

Table 4.7 summarizes the metal transfer factor in fruits from the study area. TF for fruits grown on study area ranges from 0.0004–0.064 and 0.00–1.523 for As^{3+} and Mn^{2+} respectively.

Table 4.7 : Transfer Factor (TF) of various fresh fruits.

Sample ID	TF of As	TF of Mn	TF of Cr	TF of Pb	TF of Cd
1A (Lemon)	0.0141	0.4773	<0.36*	<0.04*	<0.02*
1B (Hog Pulm)	0.0115	0.5910	<0.36	<0.04	<0.02
1C (Carambola)	0.0253	0.7547	<0.36	<0.04	<0.02
1D (Guava)	0.0115	1.5288	<0.36	<0.04	<0.02
1E (Papaya)	0.0635	0.7849	<0.36	<0.04	<0.02
2A (Mango)	0.0475	0.1061	<0.36	<0.04	<0.02
2B (Jackfruit)	0.0211	0.0812	<0.36	<0.04	<0.02
2C (Pomelo)	0.0180	0.1283	<0.36	<0.04	<0.02
2D (Wax apple)	0.0197	0.5641	<0.36	<0.04	<0.02
3A (Sapodilla)	0.0256	0.0668	<0.36	<0.04	<0.02
3B (Coconut)	0.0119	1.4003	<0.36	<0.04	<0.02
Green coconut water	0.0004	0.0000	<0.36	<0.04	<0.02
Coconut water	0.0010	0.0915	<0.36	<0.04	<0.02
Maximum	0.0635	1.5288			
Minimum	0.0004	0.0000			
Average	0.0208	0.5058			
STD. deviation	0.0182	0.5309			

* Detection level.

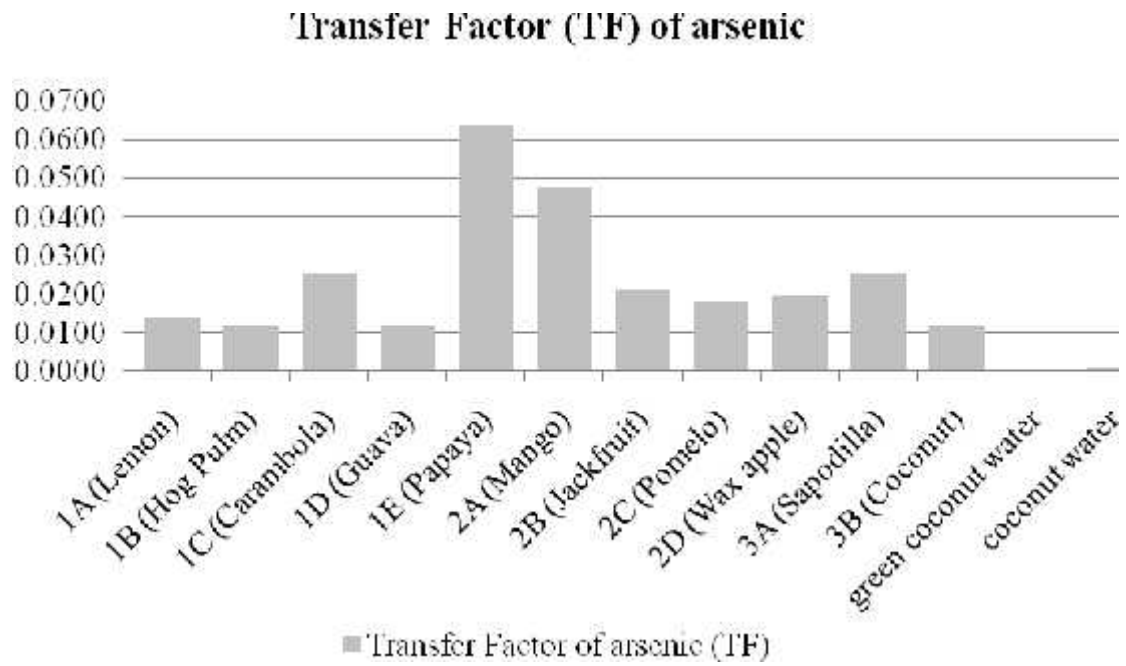


Figure 4.5: Transfer Factor (TF) of arsenic

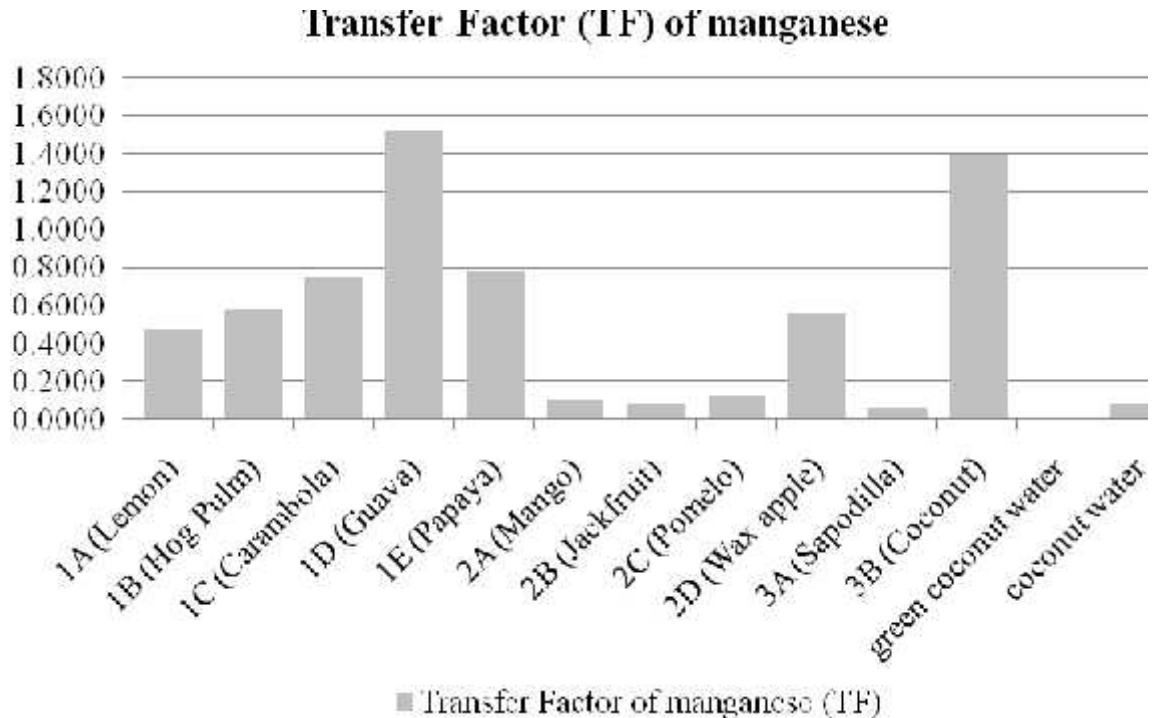


Figure 4.6: Transfer Factor (TF) of manganese

4.3 DIM and HRI of heavy metals in Fruits.

Values of DIM calculated for adults (average age 35 years), are presented in Table 4.8. Daily intake of metal for As^{3+} and Mn^{2+} ranged from 0.00001–0.00028 and 0.00002–0.0095 respectively.

The Health risk index for heavy metals by consumption of fruits grown on study area for adults was calculated and values are given in Table 4.9. The maximum HRI was found papaya grown at study area. All the fruits were totally free from any risk.

Table 4.8 : DIM of various fresh fruits.

Sample ID	DIM of arsenic (mg/person/day)	DIM of Manganese (mg/person/day)
1A (Lemon)	0.000001	0.00002
1B (Hog Pulm)	0.000015	0.00077
1C (Carambola)	0.000024	0.00071
1D (Guava)	0.000072	0.00950
1E (Papaya)	0.000274	0.00338
2A (Mango)	0.000277	0.00062
2B (Jackfruit)	0.000097	0.00037
2C (Pomelo)	0.000029	0.00020
2D (Wax apple)	0.000049	0.00140
3A (Sapodilla)	0.000064	0.00017
3B (Coconut)	0.000037	0.00437
Green coconut water	0.000002	0.00038
Coconut water	0.000001	0.00002
Maximum	0.000277	0.00950
Minimum	0.000001	0.00002
Average	0.000078	0.00182
STD. deviation	0.000098	0.00285

Table 4.9: HRI of various fresh fruits.

Sample ID	HRI of As (mg/kg/person/day)	HRI of Mn (mg/kg)
1A (Lemon)	0.00000	0.001
1B (Hog Pulm)	0.00001	0.023
1C (Carambola)	0.00002	0.022
1D (Guava)	0.00005	0.288
1E (Papaya)	0.00018	0.102
2A (Mango)	0.00018	0.019
2B (Jackfruit)	0.00006	0.011
2C (Pomelo)	0.00002	0.006
2D (Wax apple)	0.00003	0.042
3A (Sapodilla)	0.00004	0.005
3B (Coconut)	0.00002	0.133
Green coconut water	0.00000	0.012
Coconut water	0.00000	0.001
Maximum	0.00018	0.288
Minimum	0.00000	0.001
Average	0.00005	0.055
STD. deviation	0.00007	0.086

CHAPTER V

Conclusions and Recommendations

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Fruits are excellent source of human diet for vitamins and minerals. Contaminated irrigation water and soil can transfer arsenic and manganese from soil to fruits through irrigation water. This study was indicated that heavy metals level in different fruits varied significantly. Arsenic (As) and manganese (Mn) not only can contaminate water but also intoxicate soil, food grains and fruits. These are also consequently endanger human and animal health by various routes of ingestion. Some amount of arsenic and manganese were found in the fruits sample. The amount of the heavy metals cadmium (Cd), lead (Pb) and chromium (Cr) were not found in the fruits sample. But there are higher amount of arsenic and manganese in the soil of Samta village from selected study areas in this research. From this analysis, the obtained results can be presented as:

- i. New information about arsenic (As) and heavy metals (Pb, Cd, Cr and Mn) concentrations in fruits are found out.
- ii. Average, maximum and minimum concentration of arsenic in fruits sample was 0.206 ± 0.14 mg/kg, 0.533 mg/kg in papaya and 0.10 mg/kg in guava.
- iii. The concentration of arsenic in soil and water was found 8.40 ± 1.73 mg/kg and 0.51 ± 0.17 mg/L respectively in the study area.
- iv. All the fruits are hygienic according to WHO's suggestions (Arsenic for water 0.05 mg/L and for fruit 1.00 mg/kg).

The results of this study indicate that these amounts of arsenic may be hazardous if highly metal contaminated fruits are taken in large quantities. It is therefore suggested that the use of contaminated fruits must be strictly prohibited in order to prevent excessive build-up of these metals in the human food chain. Considering its hazardous aspects, the use of contamination must be strictly monitored and controlled. Further studies are needed in order to assess more closely the heavy metal intake as well as to identify sources of heavy metal intake in those populations.

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