STUDIES ON BIOACCUMULATION AND MOBILIZATION OF HEAVY METALS IN CROPS AND VEGETABLES GROWN AROUND INDUSTRIAL ENVIRONMENTS

By

Lokman Hosen

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE

REQUIREMENT FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMISTRY

April 2021

Supervisor:

Dr. Md. Abdul Goni

Department of Chemistry

BANGLADESH UNIVERSITY OF ENGINEERING AND THECHNOLOGY (BUET), DHAKA -1000

CANDIDATE'S DECLARATION

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

Lokman Hosen

Signature of the candidate

BANGLADESH UNIVERSITY OF ENGINEERING AND THECHNOLOGY

(BUET), DHAKA -1000

Department of chemistry

Certification of Thesis

A Thesis on

STUDIES ON BIOACCUMULATION AND MOBILIZATION OF HEAVY METALS IN CROPS AND VEGETABLES GROWN AROUND INDUSTRIAL ENVIRONMENTS

By

Lokman Hosen

Roll No: 1018032715, Session: October-2018 has been accepted as satisfactory in partial fulfillment of the requirements for the degree of Master of Science (M.Sc.) in chemistry and certifies that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on April 11, 2021.

Board of Examiners

1. **Dr. Md. Abdul Goni**
   Assistant Professor
   Department of chemistry
   BUET, Dhaka-1000
   11-4-2021
   Supervisor and Chairman
2. **Dr. Md. Shakhawat Hossain Firoz**
   Head and Professor
   Department of chemistry
   BUET, Dhaka-1000
   ....
   Head/Director
3. **Dr. Md. Nazrul Islam**
   Professor
   Department of chemistry
   BUET, Dhaka-1000
   ....
   Member
4. **Dr. Ummey Rayhan**
   Professor
   Department of Chemistry
   Dhaka University of Engineering and Technology (DUET), Gazipur
   .... 11'04'2021
   Member (External)

DEDICATED

TO

MY BELOVED

PARENTS

Acknowledgements

First of all, I am very much grateful to Almighty Allah and all the glorification to Him who is constantly guiding me in the darkness, difficulties, and for giving me physical and mental ability, patience, strength and courage in enabling the author of this thesis to complete the research work and to prepare this manuscript for the fulfilment of the degree of Master of Science in department of Chemistry at Bangladesh University of Engineering and technology (BUET), Dhaka Bangladesh.

I would like to express sincere appreciation and deepest sense of gratitude to my full-fledge respected supervisor, **Dr. Md. Abdul Goni**, Assistant Professor, Department of Chemistry, Bangladesh University of Engineering and Technology(BUET) for his supervision, highly valued guidance, relentless inspiration, enlightened suggestions, limitless patience, and constant monitoring throughout the research work and in the preparation of this manuscript. Without his generous help, this dissertation would be nearly impossible.

I would also like to show my gratitude to our respected teacher Professor **Dr. Md. Shakhawat Hossain Firoz**, honorable Head of the Department of Chemistry, BUET for giving me his wonderful support and encouragement to move through the academic processes during this M.Sc Program.

I would like to covey my deepest gratitude to all teachers including Professor **Dr. Nazrul Islam, Dr. Al-Nakib Chowdhury and Dr. Md. Abdur Rashid,** Associate professor **Dr. Abu Bin Imran**, Assistant professor **Dr. Chanchal Kumar Roy, Dr. Sharmin Nishat and Dr. Ayesha Sharmin,** Department of Chemistry, BUET, for their valuable suggestions, appreciated comments, guidance and encouragement during my research work

I also feel great pleasure to convey profound veneration and deep appreciation to my all respected teachers of the department for their cordial help during my study period. I would also like to thank all of the officers and staffs of the Department of Chemistry, BUET for their continuous help during my study period.

I like to express my deepest sense of gratitude and indebtedness to **Abu Shamim Khan**, Chemist, Asia Arsenic Network, Jessore for his excellent guidance, crucial support and inspiration of this thesis work.

I am grateful to the "Department of Chemistry in BUET" for the laboratory support to complete this research. I would also like to express sincere thanks to the "Asian Arsenic Network" laboratory of Jessore for their generous cooperation in analyzing samples for trace metals by AAS.

I am highly obliged to all members of the board of examiners for their valuable suggestions and appreciate comments.

My heart full of thanks to all of my friends specially **Md. Abdullah-Al-Mamun, Md Alamgir Hossen, Mst. Sathi Khatun, Sharmin Sultana** and all others friends for their co-operation, fruitful discussion and for their cordial help during my study period and all sorts of encouragement throughout my University life.

I am very much thankful to the CASR, BUET for providing financial support to complete this research work.

Finally, I would like to express my deep appreciation and heartfelt indebtedness gratitude to my beloved father, mother and all of my family members for their endless encouragement, understanding and sacrifice. Without their careful assistance, it would not possible to complete my Master's study. I would like to delicate this thesis to my family.

…………………………………

April 11, 2021 **(Lokman Hosen)**

Abstract

Crops and vegetables provide essential nutrients to human diet. Plants import chemical elements and nutrients directly from the soil or water by root absorption, resulting in accumulation within different tissues. The most common route for metals to enter into the food chain and human body is the cultivation of crops and vegetables in industrially contaminated soil. Heavy and toxic metals concentrations in contaminated water, soil, crops, and vegetables from two different study areas are investigated in this study. One of the study areas was selected and recognized as highly contaminated area (Savar, Dhaka) and another area was identified as long range contaminated area (Kalihati, Tangail). The samples were collected directly from the study areas following the standard procedures and protocols. Different soil, crops, and vegetables were digested using a mixture of HNO_3, H_2SO_4, $HClO_4$ in a ratio of 5:1:1, and the resulting mixtures were analyzed for heavy and toxic metals using the Flame AAS method. A total of seven metals (Cu, Pb, Fe, Ni, Mn, Cd, and As) have been analyzed in crops, vegetables, arable soil, and irrigation water and the results were compared with the permissible values reported by FAO, WHO, USEPA, EU, and others. All the studied samples collected from Savar area showed heavy and toxic metal concentrations relatively higher than the tolerable limits. However, most of the environmental samples obtained from Kalihati Upazila contained different metal concentrations which were lower than the safety levels of FAO, WHO, and USEPA. Heavy metal concentrations in different parts of crops and vegetables plants were also investigated in the present study to understand the mobilization and transportation trend of these metals from roots to shoots. Pollution Load Index (PLI) was calculated for better understanding of pollution levels in irrigation water, contaminated soil, crops and vegetables. Bioconcentration factor (BCF) of metals was evaluated to visualize the transfer rate of heavy metals from soil to food plant bodies. Health risks due to the consumption of contaminated food items were investigated for both adult and children in terms of non-carcinogenic risk and carcinogenic risk. Almost all the studied crops and vegetables showed higher non-carcinogenic risk for both adult and children. Non-carcinogenic risks associated with samples collected from Savar area were observed to be higher than those obtained from Kalihati Upazila. Considerable carcinogenic risks were realized in all the studied samples for both adult and children. In addition, carcinogenic risks were higher in crops and vegetables samples collected from Savar area than those grown in the long range contaminated site, Kalihati Upazila. The risks assessment data suggested that children are of at a higher risk than adult in terms of both carcinogenic and non-carcinogenic risks. Metal Pollution Index (MPI) was determined in each of the crops and vegetables samples and the order of MPI values was: Green spinach > Water spinach > Spinach > Red spinach > Rice > Lady's finger > Brinjal grown in Savar area whereas the MPI trend in crops and vegetables collected from Kalihati, Tangail area was: Spinach > Water spinach > Rice > Lady's finger > Red spinach > Brinjal > Green spinach. These MPI data indicated that the crops and vegetables grown in the Savar area are highly contaminated than those obtained from the Kalihati Upazila. The present research findings has revealed that long time consumption of metal contaminated crops and vegetables grown in and around the industrial polluted areas could cause a severe health risks to the local people who are directly consume them.

Keywords: Waste water irrigation, Heavy metals, Soil pollution, Crops and Vegetables, Transfer factor, Health risk, Metal pollution.

CONTENTS

Chapter One - Introduction

Chapter Two - Study Area

Chapter Three - Materials, Sampling, and Methodology

Chapter Four - Results and Discussions

Chapter Five - Conclusions and Recommendations

List of Figures

List of Tables

List of Abbreviations of Technical Symbols and Terms

1. Atomic Absorption Spectrometer (AAS)
2. Hydride Generator (HG)
3. Arsenic (As)
4. Cadmium (Cd)
5. Copper (Cu)
6. Nickel (Ni)
7. Lead (Pb)
8. Manganese (Mn)
9. Iron (Fe)
10. Food and Agricultural Organization (FAO)
11. World Health Organization (WHO)
12. Joint FAO/WHO Expert Committee on Food Additives (JECFA)
13. Maximum Allowable Concentration (MAC)
14. European Union (EU)
15. Department of Environment (DoE)
16. United States Environmental Protection Agency (USEPA)
17. Highly Contaminated Sites (HCS)
18. Long Range Contaminated Sites (LCS)
19. Bank Town (BT)
20. Dhaka Export Processing Zone (DEPZ)

CHAPTER-1

INTRODUCTION

1 Introduction

1.1 General considerations

Heavy and toxic metals contamination in soil, water, crops, and vegetables have drawn a significant attention in recent years because of toxicity, abundance, persistence, and subsequent excessive accumulation property [1]. Some heavy metals are considered as essential elements for human body and some are not. Essential metals play a vital role in different biological functions, but they can also cause toxic effects when present in higher concentrations by affecting metabolic processes [2, 3]. On the other hand non-essential metals pose carcinogenic risks when present even in the trace amounts [4]. Vegetables provide essential nutrients (vitamins, proteins, carbohydrates, minerals, and fibers) along with other essential micronutrients and trace metals to human diet and so are important parts of it [5]. Consumption of a variety of fruits and vegetables is recommended by "Guidelines for Americans 2015–2020" for entire lifespan even in the time of pregnancy [6].

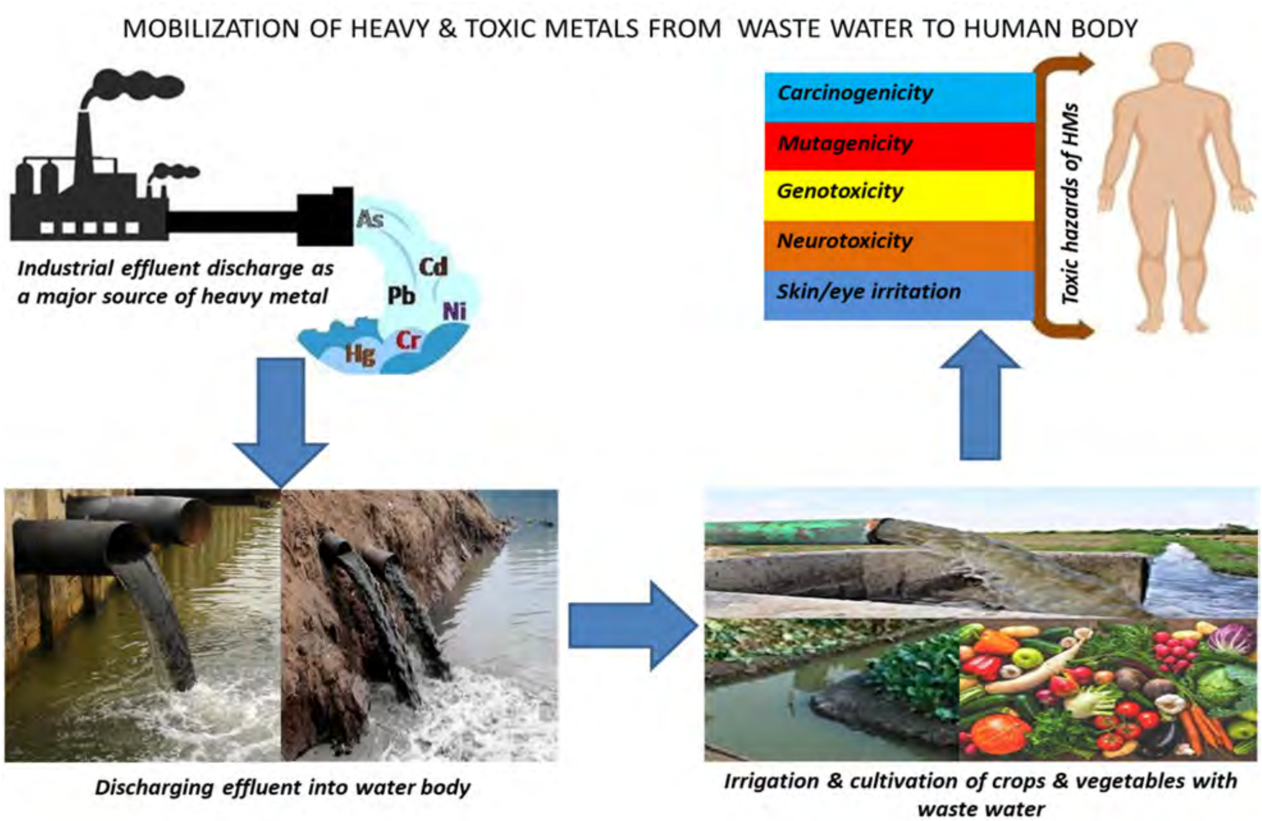


Figure 1.1: Mobilization of heavy and toxic metals to the human body

Heavy metal-induced stress in vegetation due to adverse effect on photosynthetic process is caused by exposure to unusual levels of heavy metals [7]. Plants import chemical elements and nutrients directly from the soil or water by root absorption, resulting in accumulation within different tissues [8]. Soluble metal ions present in excessive concentrations in the soil can be easily absorbed by plants together with essential nutrients [9]. Depending on chemical form and biochemical interactions, chemical compounds retained in different tissues during bioaccumulation processes [10]. According to the studies which have been done on urban environments, due to its detrimental effect, heavy metal pollution has become one of the most controversial issues especially when standard pollution levels exceeded [11]. However, concentration of chemical contaminants in vegetables cultivated in peri-urban areas is higher than those grown in rural areas which have been highlighted in various recent studies [12]. Cultivation of crops, vegetables, and medicinal plants on contaminated soil near industrial establishments and highways is a very common route for metals to enter into the food chain and human body [13].

1.2 Environment and it’s contamination

Environment is referred to as someone’s surroundings that consist of atmosphere, hydrosphere, and lithosphere, having resources for life sustenance [14]. Environmental quality and sustainability are the two major indicators of sustaining the healthy human life in the planet that we live in. An environment can be ideal and highly sustainable for the survival of human beings or can be polluted or contaminated. Environmental pollution is the undesirable and unwanted change of our surroundings caused totally or largely by human activities. Direct or indirect effects of the changes in energy pattern, radiation levels, chemical and physical constitution and abundance of organisms are the main cause for environmental pollution. Due to having severe long-term consequences, environmental pollution has now become a global problem including both developed as well as developing countries, and so is drawing a significant attention in recent years [15]. Environmental pollution can be caused by the foreign substances or even by its own component when present above the natural background level [16]. The substance in this case that causes contamination is called contaminant or pollutant.

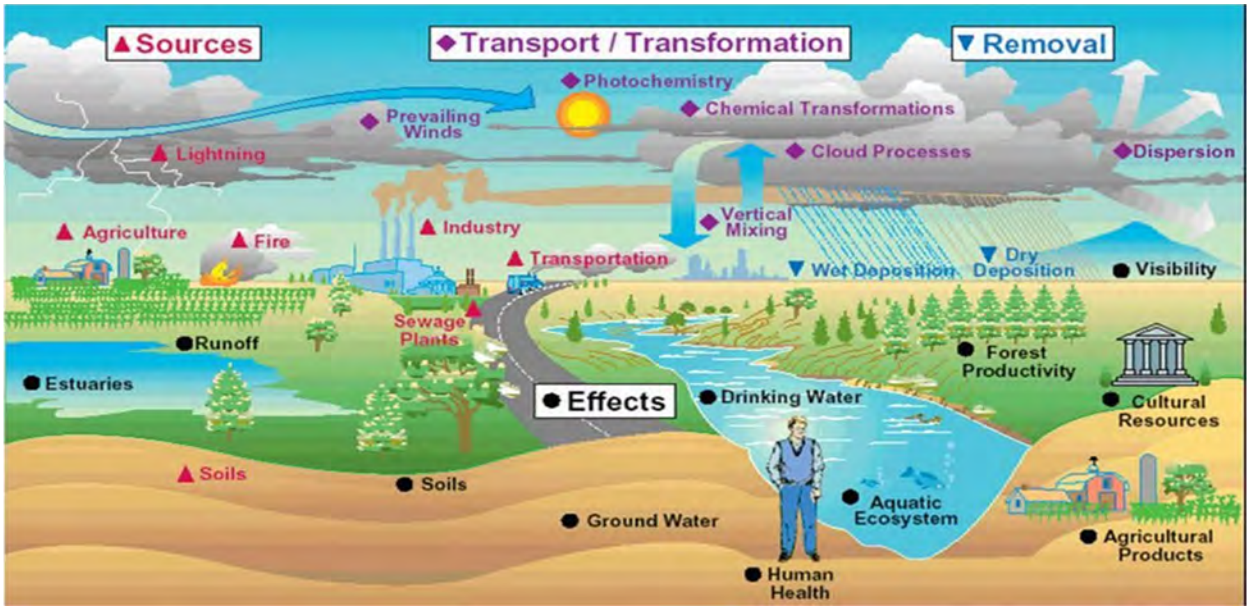


Figure 1.2: Environmental pollution (sources, transportation, transformation, removal, and effects)

1.2.1 Contamination of atmosphere (air pollution)

The release of various gases, finely divided solids, or finely dispersed liquid (aerosols) into the atmosphere at a rate responsible for exceeding the natural capacity of the environment to dissipate and dilute or absorb them is referred to as air pollution. Such a high concentrations of these substances may cause undesirable health, economic, or aesthetic effects. Major Air Pollutants are classified into different categories: **Criteria Pollutants**, **Fine Particulates,** and **Air Toxics**. The criteria pollutants are the substances whose concentrations in the atmosphere indicate overall air quality. According to U.S. Environmental Protection Agency (USEPA) there are six major air pollutants that have been considered as criteria pollutants which are carbon monoxide (CO), nitrogen oxides (NO and NO_2), sulfur dioxide (SO_2), ozone (O_3), particulate matter and lead (Pb). Fine particulates generally refer to very small fragments of solid materials or liquid droplets suspended in air. Rather than by chemical composition, they are usually characterized on the basis of their sizes and phases (solid or liquid) except for airborne lead, as it is treated as a separate category. For example, solid particulates between roughly 1 and 100 μm in diameter are called dust particles, whereas airborne solids less than 1 μm in diameter are called fumes. Air toxics are substances which are hazardous even when present in trace amounts in the air. Some of them cause different health problems, such as adverse effects on brain tissue or fetal development while many of them cause genetic mutations or cancer.

Although, the air toxics are comparable to the criteria pollutants, these pollutants can pose an immediate health risk to exposed individuals and can cause other environmental problems. Major air toxics are organic chemicals, carbon containing molecules, hydrogen, and other atoms. Volatile organic compounds (VOCs) are another major source of air toxics. VOCs include pure hydrocarbons, partially oxidized hydrocarbons, and organic compounds containing chlorine, sulfur, or nitrogen. Some examples of air toxics are arsenic, asbestos, benzene, chlorine, coke oven emissions, cyanide compounds, mercury compounds, radionuclides (radon, radium, uranium), selenium compounds, vinyl chloride etc [17].

1.2.2 Contamination of hydrosphere (water pollution)

Water pollution is the release of substances (that interferes with beneficial use of the water or with the natural functioning of ecosystems) into subsurface groundwater or into lakes, streams, rivers, and oceans. In addition water pollution may also be caused by the release of energy, in the form of radioactivity or heat, into bodies of water. A wide variety of substances can cause pollution to water bodies, such as pathogenic microorganisms, putrescible organic waste, plant nutrients, toxic chemicals, sediments, heat, petroleum (oil), and radioactive substances. Different types of water pollutants generated by human activities are Domestic sewage, Toxic waste, Sediment, Thermal pollution and Petroleum (oil) pollution. Domestic sewage is the primary source of pathogens (disease-causing microorganisms) and putrescible organic substances. Pathogens exert a direct threat to public health and putrescible organic matters present a different sort of threat to water quality. Decomposition of theses organics include consumption of dissolved oxygen and this content of the water is depleted which endangers the fish and other aquatic organisms as high levels of oxygen are required for their subsistence. When the waste is poisonous, radioactive, explosive, carcinogenic, mutagenic, teratogenic (causing birth defects), or bioaccumulative, then it is considered as a toxic waste. Discharging of industrial effluents without proper treatment and surface runoff containing pesticides used on agricultural areas are the main sources of toxic wastes. Suspended sediments interfere with the penetration of sunlight into different layers of water and interrupt the ecological balance of water body. Sediment resulting from soil erosion can be carried into water bodies by surface runoff. Heat decreases the capacity of water to hold dissolved oxygen in solution, and it increases the rate of metabolism of fish that’s why, heat is considered to be a water pollutant.

Discharging of cooling water from power plants into rivers is a major source of thermal pollution. Accidental oil spills and surface runoff from roads and parking lots into water bodies are the major sources of Petroleum (oil) pollution [18].

1.2.3 Contamination of lithosphere (soil pollution)

Soil is the thin layer of organic and inorganic materials that covers the Earth's rocky surface. The organic portion (derived from the decayed remains of plants and animal) is concentrated in the dark uppermost topsoil and inorganic portion (made up of rock fragments) was formed over thousands of years by physical and chemical weathering of bedrock. Consistence of toxic compounds, chemicals, salts, radioactive materials, or disease causing agents (having adverse effects on plant growth and animal health) in the soil is defined as Soil pollution. Petroleum hydrocarbons, heavy metals, pesticides, solvents are the most common soil polluting chemicals. Different ways for soil pollution are seepage from a landfill, discharge of industrial waste into the soil, penetration of contaminated water into the soil, rupture of underground storage tanks, excess application of pesticides, herbicides, fertilizer and solid waste seepage [19].

1.3 Types of pollutants

Environmental pollution become most alarming global concern in recent years and is one of the great challenges faced by the global community. We encounter a variety of pollutants in our daily life which can be classified into different categories, namely biological, organic and inorganic. Regardless of different categories, all the pollutants receive considerable attention as they possess adversary impacts. The relationship between environmental pollution and world population has become an inarguable directly proportional relationship as it is being observed that the amount of potentially toxic substances released into the environment is continuously increasing with the dramatic rise of global population [20]. As we are much concern about water and soil pollution in this case due to their direct contribution in this research so, will discuss water and soil pollutants more specifically.

1.3.1 Biological pollutants

Biological pollutants are described as contaminants which exist as a result of human activities and which pose negative impacts on the quality of aquatic and terrestrial environment. This type of pollutants include bacteria, viruses, parasites, molds, mildew, animal dander and cat saliva, house dust, mites, cockroaches and pollens [21]. Studies have reported different sources of these types of pollutants, including pollens originating from plants; viruses that are being transmitted by people and animals; bacteria which are carried out by people, animals, soil and plant debris.

1.3.2 Organic pollutants

Organic pollutants can be briefly defined as biodegradable contaminants in an environment [22]. Many insecticides and herbicides that that are generally used in pest control and agriculture respectively are included into organic pollutants. Dichlorodiphenyltrichloroethane (DDT) is a pesticide, highly effective in controlling mosquitos, which was banned in the USA in 1972 due to having toxic effect. Although the common sources of organic pollutant are natural (caused by the environment), but to fulfill the human needs anthropogenic activities also have contribution to production of organic pollutants. Some of the common organic pollutants which have been noted to be of special concern are human waste, food waste, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), pesticides, petroleum and organochlorine pesticides (OCPs). Organic pollutants have drawn considerable attention in recent years because of having their pernicious effects on the environment. Properties of organic pollutants may include high lipid solubility, stability, lipophilicity and hydrophobicity which have recently made organic pollutants to be recognized as persistent pollutants [23, 24]. These properties provide organic pollutants the ability to easily bioaccumulate in the different spheres of the environment, thus causing toxicological effects.

1.3.3 Inorganic pollutants

Inorganic pollutants are usually substances of mineral origin, with metals, and salts. In addition inorganic pollutants are one of the major classes of pollutants discharged by chemical and allied industries such as refineries, fertilizers, and pharmaceuticals. Trace elements, mineral acids, metals, metal compounds, inorganic salts, metals with organic compounds are the common inorganic pollutants.

Inorganic pollutants may be non-biodegradable and they persist in the surrounding environment. Many inorganic pollutants have disruptive effect on public health. Inorganic pollutants enter into the environment through different anthropogenic activities such as sewerage drainage, mine drainage, smelting, metallurgical and chemical processes, as well as natural processes [25, 26]. As this study is based on the heavy metal concentration, we should have a clear idea about this pollutant and so, we will discuss little more about heavy metal.

1.4 Heavy metals

Any criterion-based definition of a heavy metal is not widely agreed. For different context the term can reflect different meanings. We can define metal on the basis of chemical behavior as a chemist would likely be more concerned with chemical behavior. Density criteria ranges from above 3.5 g/cm^3 to above 7 g/cm^3 and weight ranges from greater than sodium (atomic weight 22.98); greater than 40 (excluding s- and f-block metals, hence starting with scandium); or more than 200(from mercury onwards) [27]. The term "heavy metals" is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. Very recently, a broader definition for the term have been proposed, and heavy metals have been defined as "naturally occurring metals having atomic number greater than 20 and an elemental density greater than $5\,g{\cdot}cm^{-3}$ [28]. Among environmental pollutants heavy metals are the most investigated one. Regarding the roles of heavy metals in biological systems, they can be classified as essential and nonessential. Essential heavy metals are important for living organisms while nonessential heavy metals have no known biological role in living organisms. Examples of essential heavy metals are Mn, Fe, Cu, and Zn, while the heavy metals Cd, Pb, and Hg are toxic and are regarded as biologically nonessential [29]. The heavy metals Mn, Fe, Co, Ni, Cu, Zn, and Mo are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites [30]. Either deficiency or excess of an essential heavy metal leads to diseases or abnormal conditions. However, the lists of essential heavy metals may be different for different groups of organisms such as plants, animals, and microorganisms. It means a heavy metal may be essential for a given group of organisms but nonessential for another one. The interactions of heavy metals with different organism groups are much complex [31].

Almost every heavy metal and metalloid may be potentially toxic to biota depending upon the dose and duration of exposure. Many elements are classified into the category of heavy metals, but some are relevant in the environmental context. List of the environmentally relevant most toxic heavy metals and metalloids contains Cr, Ni, Cu, Zn, Cd, Pb, Hg, and As [32]. Heavy metal pollutants most common in the environment are Cr, Mn, Ni, Cu, Zn, Cd, and Pb [33]. Some other heavy metals are also hazardous to living organisms depending upon dose and duration of exposure. For example, Mansouri *et al.* have found Ag as more toxic than Hg to a freshwater fish [34].

1.4.1 Sources of heavy metals in the environment

Sources of heavy metals in the environment can be both natural/geogenic/lithogenic and anthropogenic. The natural or geological sources of heavy metals in the environment include weathering of metal-bearing rocks and volcanic eruptions. The global trends of industrialization and urbanization on earth have led to an increase in the anthropogenic share of heavy metals in the environment [35].

1.4.1.1 Anthropogenic sources

The anthropogenic sources of heavy metals in the environment include mining, industrial and agricultural activities. These metals (heavy metals) are released during the mining and extraction of different elements from their respective ores. Heavy metals released into the atmosphere during mining, smelting, and other industrial processes can readily return to the land through dry and wet deposition. Discharge of wastewaters such as industrial effluents and domestic sewage add heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic input of heavy metals in the environment. Regarding contents of heavy metals in commercial chemical fertilizers, phosphate fertilizers are particularly important. In general, phosphate fertilizers are produced from phosphate rock (PR) by acidulation. In the acidulation of single superphosphate (SSP), sulfuric acid is used, while in acidulation of triple superphosphate (TSP), phosphoric acid is used. The final product contains all of the heavy metals present as constituents in the phosphate rock. Commercial inorganic fertilizers, particularly phosphate fertilizers, can potentially contribute to the global transport of heavy metals.

Heavy metals added to agricultural soils through inorganic fertilizers may leach into groundwater and contaminate it [29]. The anthropogenic sources of Cr include electroplating industries, leather tanneries, textile industries, and steel industries [36]. Globally, about 50,000 t/year of Cr may be emitted from coal combustion, wood burning, and refuse incineration [37].

Figure 1.3: Anthropogenic sources of heavy metals

1.4.1.2 Natural sources

The presence of heavy metals in the environment leads to a number of adverse impacts. Such impacts affect all spheres of the environment, that is, hydrosphere, lithosphere, biosphere and atmosphere. Until the impacts are dealt with, health and mortality problems break out, as well as the disturbance of food chains. Many studies have documented different natural sources of heavy metals. Under different and certain environmental conditions, natural emissions of heavy metals occur. Such emissions include volcanic eruptions, sea-salt sprays, forest fires, rock weathering, biogenic sources and wind-borne soil particles.

Natural weathering processes can lead to the release of metals from their endemic spheres to different environmental compartments. Heavy metals can be found in the form of hydroxides, oxides, sulphides, sulphates, phosphates, silicates, and organic compounds. The most common heavy metals are lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), zinc (Zn), and copper (Cu). Although the aforementioned heavy metals can be found in traces, they still cause serious health problems to human and other mammals.

Figure 1.4: Natural sources of heavy metals

1.4.2 Effects of heavy metal contamination

Heavy and toxic metals contamination has already become a serious issue of concern around the world as it has gained momentum due to the increase in the use and processing of heavy metals during various activities to meet the needs of the rapidly growing population. Soil, water and air are the major environmental compartments which are affected by heavy metal pollution [38].

1.4.2.1 Effects of heavy metals on soil

Most of the heavy metals do not undergo microbial or chemical degradation because they are non-degradable, and consequently their total concentrations last for a long time after being released into the environment [39]. The accumulation and deposition of heavy metals in soils is a serious issue due to their mobilization and transportation into the food chains which severely impact the entire ecosystem. As much as organic pollutants can be biodegradable, their biodegradation rate, however, is decreased by the presence of heavy and toxic metals in the environment, and this in turn doubles the environmental pollution with the aspects of the presence of both organic pollutants and heavy metals. There are various ways through which heavy metals pose risks to humans, animals, plants, and ecosystems as a whole. Such ways include direct ingestion, accumulation by plants, food chains, consumption of contaminated water and alteration of soil pH, porosity, color, and its natural chemistry which in turn impact on the soil quality [40].

1.4.2.2 Effects of heavy metals on water

Heavy metals can be found in traces amount in water sources and still be very toxic and impose serious health problems to humans and other ecosystems. This is because the toxicity level of a metal depends on factors such as the organisms which are exposed to it, its nature, its biological role and the period at which the organisms are exposed to the metals. Food chains and food webs symbolize the relationships among the organisms. Therefore, the contamination of water by heavy and toxic metals actually affects all organisms. Humans, an example of organism feeding at the highest level, are more prone to serious health problems because the extents of heavy and toxic metals have dramatically increase in the food chain in recent years [41].

1.4.2.3 Effects of heavy metals on air

Increase in industrialization and urbanization due to the rapid growth of world population have recently caused the air pollution as a major environmental problem around the world. Air pollution has been accelerated by the presence of dust and particulate matters (PMs) in the environment particularly fine particles such as $PM^{2.5}$ and PM^{10} which are being released through natural and anthropogenic processes.

Natural processes which release particulate matters into air include dust storms, soil erosion, volcanic eruptions and rock weathering, while anthropogenic activities are more industrial and transportation related [42]. Particulate matters are important and require special attention as they can lead to serious health problems such as skin and eyes irritation, respiratory infections, premature mortality and cardiovascular diseases. These pollutants also cause deterioration of infrastructures, corrosion, formation of acid rain, eutrophication and haze [43]. Amongst others, heavy metals such as group 1 metals (Cu, Cd, Pb), group 2 metals (Cr, Mn, Ni, V and Zn) and group 3 metals (Na, K, Ca, Ti, Al, Mg, Fe) originate from industrial areas, traffic and natural sources, respectively [42,44].

1.5 Sources of heavy metal exposure to human

Heavy and toxic metals exposure to humans may occur in a variety of ways. During the mining activities, heavy metals are being released from the ores and scattered in the open environment; deposited in the soil, transported by air and water to other areas. Moreover, when these heavy metals are used in the industries for various industrial purposes, some of these elements are released into the air during combustion or into the soil or water bodies as effluents. In addition, different industrial products such as paints, cosmetics, pesticides, and herbicides also serve as sources of heavy and toxic metals. Heavy metals could also be transported through erosion, run-off or acid rain to different locations in soils and water bodies. This type of pollution can be recognized as long range contamination. The heavy metals most commonly associated with poisoning of humans are lead, mercury, arsenic and cadmium. The exposures of heavy and toxic metals are varied depending on their sources which are described below:

1.5.1 Sources of iron exposure

Iron is an attractive transition metal for various biological redox processes due to its inter-conversion between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions. The sources of iron in surface water are anthropogenic and are related to different mining activities. The production of sulfuric acid as well as the discharge of ferrous ion (Fe^{2+}) takes place due to the oxidation of iron pyrites (FeS_2) that are commonly found in coal seams [45].

1.5.2 Sources of nickel exposure

Nickel, a known heavy metal is found at very low levels in the environment. Nickel is available in all soil types and meteorites and also erupts from volcanic emissions. In the environment, nickel is principally bound with oxygen or sulfur and forms oxides or sulfides in earth crust. The vast industrial use of nickel during its production, recycling and disposal has led to widespread environmental pollution. Nickel is discharged into the atmosphere either from nickel mining or by various industrial processes, such as power plants or incinerators, rubber and plastic industries, nickel-cadmium battery industries, nickel-plated jewelry industries, steel manufacturing industries, and electroplating industries. The extensive use of nickel in various industries or its occupational exposure is definitely a matter of serious threat on human health [46].

1.5.3 Sources of manganese exposure

There are many environmental sources of Mn, which include eroded rocks, soils, and decomposed plants. Ocean spray, forest fires, vegetation, and volcanic activities are other major natural atmospheric sources of manganese. The major anthropogenic sources of environmental manganese include emission from manganese ore mining, manganese alloy production, welding, coke ovens, dry alkaline battery manufacturing, and manganese salt production. Its widespread applications in ceramics production and in the manufacture of glass, aluminum cans, and electronic components must also be noticeable. Some additional sources of Mn, included the fungicides, maneb and mancozeb, medical imaging contrasting agents, and water purification agents. Additionally, several countries including the USA, Canada, Argentina, Australia, Bulgaria, France, Russia, New Zealand, China, and the European Union have approved use of the fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT). Combustion of gasoline containing MMT releases Mn phosphates, sulfates, and oxides into the air, especially where there is high traffic density releasing particles within the respirable size range. Mn-containing emissions contaminate soil, dust, and plants near roadways, which introduces additional Mn to the environment [47, 48].

1.5.4 Sources of lead exposure

Lead is a slightly bluish, bright silvery metal. Natural lead pollution occurs from volcanic explosions and forest fires [49]. The main sources of lead exposure include drinking water, food, cigarette, industrial processes and domestic sources. The industrial sources of lead pollution include gasoline combustion, house painting and plumbing of lead pipes, uses of lead bullets, lead storage batteries, pewter pitchers, toys and faucets. Lead is released into the atmosphere from industrial processes as well as from vehicle exhausts [50]. Human exposure to lead and its compounds occurs mostly in lead related occupations with various sources like leaded gasoline, industrial processes such as smelting of lead and its combustion, pottery, boat building, lead based painting, lead containing pipes, battery recycling, grids, arm industry, pigments, printing of books, etc [51].

1.5.5 Sources of copper exposure

Heavy metal, Copper is used in the industries to produce copper pipes, cables, wires, copper cook wares, plating, rayon, electrical and electronic tools, pesticides, paints, and pigments. Copper is also used in textile industries. Copper contents in foodstuff vary according to the local conditions. Copper concentration in soil, slurry/manure spreading, use of copper compounds as bactericides or fungicides on many crops and copper emissions from melting and casting industries may affect the copper contents in cereals, fruits, and vegetables and to a lesser extent in meat and animal products [52].

1.5.6 Sources of cadmium exposure

Cadmium is regularly found in ores together with zinc, copper and lead. Therefore volcanic activity is one of the natural sources for having a temporary increase in environmental cadmium concentrations. Cadmium is widely used in different industrial processes, e.g.: as an anticorrosive agent, as a stabilizer in PVC products, as a color pigment, a neutron-absorber in nuclear power plants, and in the fabrication of nickel-cadmium batteries. Phosphate fertilizers also contribute to have higher cadmium load in agricultural soil. Although some cadmium-containing products can be recycled, a large percentage of the general cadmium pollution is caused by dumping and incinerating cadmium-contaminated wastes [53].

Cadmium is emitted from various industrial processes and from cadmium smelters into sewage sludge, fertilizers, and groundwater which could remain in soils and sediments for several decades and consequently taken up by plants [29]. The possible pathway of human exposure to Cd is through the food chain. Cd is a common contaminant found in most of the human foodstuffs due to the high metal transfer properties of the respective plants. The bioaccumulation of Cd from soil to the foodstuffs makes diet a primary source of Cd exposure among non-smoking, non-occupationally exposed populations. Certain foods such as shellfish, kidney, liver, mushrooms and root crops contain high levels of cadmium [54].

1.5.7 Sources of arsenic exposure

Arsenic associated with arsenide of copper, lead, gold, iron hydroxides and sulfides, is stored in geological bedrocks (sedimentary rocks) or in the arsenic-rich aquifer matrices in many regions of the world such as Bangladesh, Australia, Canada, India, Vietnam, and Latin America [55]. The inorganic forms of arsenic such as arsenite and arsenate compounds are lethal to humans and other organisms in the environment. Humans get in contact with arsenic through several means which include industrial sources such as smelting and microelectronic industries, Phosphate fertilizers, Paints materials, Textile and Pharmaceutical products, Pesticides, Smelting of gold, lead, copper, nickel and others [56].

1.6 Effects of heavy and toxic metals on the human health

The heavy and toxic metals such as Cd, Pb, Hg, and As deplete the major antioxidants of cells, particularly antioxidants and enzymes having the thiol group (—SH). Such metals may increase the generation of reactive oxygen species (ROS) like hydroxyl radical ($HO^{\cdot}$), superoxide radical ($O_2^{\cdot}-$), and hydrogen peroxide (H_2O_2). Increased generation of ROS can devastate the inherent antioxidant defenses of cells and lead to a condition called “oxidative stress” [57]. Heavy metals, including Cd, Pb, and Hg, are nephrotoxic, especially in the renal cortex [58]. The chemical form of the heavy metals is important in their toxicity. Mercury toxicity largely depends on Hg speciation [59]. Relatively higher concentrations of toxic heavy metals, i.e., Cr, Cd, and Pb, and comparatively lower concentrations of the antioxidant element Se have been found in the patients suffering from cancer and diabetes in the Lahore city, Pakistan [60].

More specifically, heavy metals could also cause several serious health problems in humans, affecting the nervous system, kidney, liver, and respiratory functions. Most trace metal elements (MTEs) are strongly carcinogenic. MTEs could also cause the delays in the human growth and development, and disruption of bioregulatory systems responsible for functional or psychosomatic disorders, like chronic fatigue syndrome, and neurodegenerative pathologies, such as the Parkinson's and Alzheimer's diseases. Intoxication by some heavy metals, such as mercury and lead, could also lead to autoimmunity phenomena, in which the immune system of the patient attacks his own cells. This could cause the development of joint diseases, such as rheumatoid arthritis, and kidney, circulatory, or nervous problems in the human bodies. **Figure 1.6** shows the development of different diseases in human bodies for the long time exposure of heavy and toxic metals to humans from various sources [61].

Acute poisoning: This happens if someone get a high dose at one time and the symptoms usually appear on quickly.

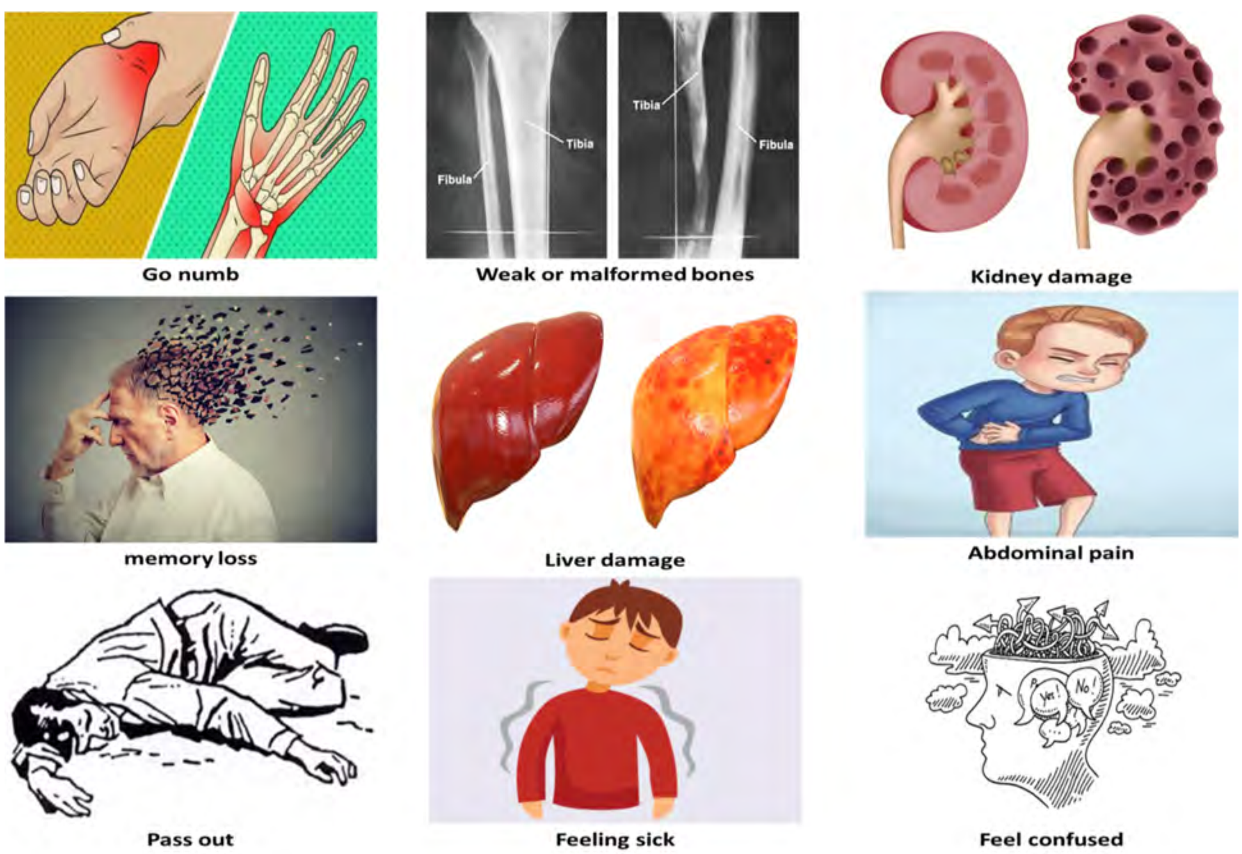


Figure 1.5: Some acute poisoning of heavy metals

Chronic poisoning: Results are observed after contact with a low dose over a long time and the symptoms come on slowly.

Figure 1.6: Some chronic poisoning of heavy metals

1.6.1 Effects of iron on human health

Iron toxicity is classified as corrosive or cellular. Ingested iron could cause direct caustic injury to the gastrointestinal mucosa, resulting in nausea, vomiting, abdominal pain, and diarrhea. Significant fluid and blood loss can lead to hypovolemia. Hemorrhagic necrosis of gastrointestinal mucosa can lead to hematemesis, perforation, and peritonitis. At the cellular level, iron impairs cellular metabolism in the heart, liver, and central nervous system. Free iron enters into the cells and concentrates in the mitochondria. This disrupts oxidative phosphorylation, catalyzes lipid peroxidation, forms free radicals, and ultimately leads to cell death [62].

1.6.2 Effects of nickel on human health

Acute toxicity of Nickel in human occurred from the absorption through the gastrointestinal tract or by inhalation through lungs. Nickel carbonyl inhalation causes two kinds of acute toxic effects: instant and delayed. The symptoms of acute toxicities include nausea, vomiting, vertigo, irritation, etc. These symptoms last for a few hours to a couple of days. Instant symptoms are followed by delayed symptoms like stiffness of the chest, constant cough, dyspnea, cyanosis, tachycardia, palpitations, sweating, visual disturbances and weakness etc. Death due to cardiac arrest has been reported in a 2 ½ year old girl, who consumed nickel sulfate accidentally [46].

Figure 1.7: Effects of nickel poisoning

Chronic inhalation and exposure to nickel dusts and aerosols contribute to all the types of respiratory disorders, including asthma, bronchitis, etc. Another study reported that nickel refinery workers were displaying higher incidences of pulmonary and nasal cancer [46].

1.6.3 Effects of manganese on human health

In a human study utilizing magnetic resonance imaging and spectroscopy (MRI/S) to investigate changes in neurochemistry of smelting workers, increases in GABA and decreases in myo-inositol were seen in the thalamus. Changes in thalamic GABA were associated with reduced fine motor performance [63]. Mn exposure alters neurotransmitter and metabolite levels [64].

Mn exposure inhibits myocardial contraction, dilates blood vessels, and induces hypotension, suggesting that Mn exposure has a significant effect on cardiac function. Mn has a direct effect on mitochondrial function resulting in a reduced myocardial contraction, and causes vasodilation, leading to a decreased blood pressure following acute exposure. Gender may also be a contributing factor to developing cardiovascular toxicity after Mn exposure. In a study on male and female smelters exposed to Mn, female smelters had significantly shorter P–R intervals compared to controls, and there was no difference in males. QRS and T waves were also significantly different for female smelters [65]. An increase in the mortality of infants born in Bangladesh was observed in their first year of life who are being exposed to Mn concentrations at or above the WHO's standard of 400 µg Mn/L compared to the unexposed infants [66].

1.6.4 Effects of lead on human health

Lead exposure occurs through various ways like inhalation, ingestion or skin contact. Direct contact of lead or lead-based compounds occurs through the mouth, nose, eyes, and through the cracking of the skin may also increase lead levels. Lead disrupts the maintenance of the cell membrane, red blood cells with a damaged membrane become more fragile, which results in anemia. Lead is also speculated to alter the permeability of blood vessels and collagen synthesis. Lead could damage the activity of cells of the immune system, such as polymorphonuclear leukocytes, resulted in decreasing the immune activity. Chronic lead nephropathy occurred due to years of lead exposure manifested in kidney biopsy by moderate focal atrophy, loss of proximal tubules and interstitial fibrosis. Low level environmental lead exposure may accelerate renal insufficiency in patients without diabetes who have chronic renal disease. The previous studies also showed that repeated chelation therapy may improve renal function and slow down the progression of renal insufficiency [51]. The reproductive systems of both males and females are affected by lead poisoning. In males sperm count is reduced and other changes occur in the volume of sperm when blood lead levels exceed 40 µg/dL. Activities like motility and the general morphology of sperm are also affected at this level. The problems with the reproductivity of females due to lead exposure are more severe. Toxic levels of Pb can lead to miscarriages, prematurity, low birth weight, and problems with development during childhood. The brain is the most sensitive organ to lead exposure. In a child's developing brain, synapse formation is greatly affected in the cerebral cortex by lead pollution.

Lead also interferes with the development of neurochemicals, including neurotransmitters, and organizing of ion channels. Lead poisoning also causes the loss of neuron myelin sheath, reduction in the number of neurons. It interferes with neurotransmission and decreases neuronal growth. The brain of adults exposed to increased lead levels during their childhood also shows a decreased volume, especially in the prefrontal cortex [51].

1.6.5 Effects of copper on human health

Acute and chronic exposures to excess copper could cause some sever health effects on humans bodies. The emphasis is placed on acute exposure effects of copper on the gastrointestinal (GI) system. The effects include GI mucosal ulcerations and bleeding, acute hemolysis and hemoglobinuria, hepatic necrosis with jaundice, nephropathy with azotemia and oliguria, cardiotoxicity with hypotension, tachyeardia and tachypnea, and central-nervous-system (CNS) manifestations, including dizziness, headache, convulsions, lethargy, stupor, and coma. A major target of chronic copper toxicity is the liver. Liver toxicity is usually seen in specific populations, such as individuals with Wilson disease and children with various cirrhosis syndromes. Hemolytic anemia due to high concentrations of circulating copper could also occur. Small amounts of copper from intrauterine devices can prevent embryogenesis by blocking implantation and blastocyst development. Genotoxicity, mutagenicity, and carcinogenicity of copper are also documented [67].

1.6.6 Effects of cadmium on human health

Generally there are three possible ways of cadmium resorption: Gastrointestinal, pulmonary and dermal. The respiratory system is severely affected by the inhalation of cadmium-contaminated air. Shortness of breathing, lung edema and destruction of mucous membranes are the parts of cadmium-induced pneumonitis. Cadmium-contaminated foods cause acute gastrointestinal effects, such as vomiting and diarrhea. Kidney damage has long since been described to be the main problem for patients chronically exposed to cadmium. Cadmium could find its way to the kidney in the form of cadmium-metallothionein (Cd-MT). Cd-MT is being filtrated in the glomerulus, and subsequently reabsorbed in the proximal tubulus. It is then remained in the tubulus cells and makes up the major part of the cadmium enriched body.

The amount of cadmium in the kidney tubulus cells can increase during the life span of every person. Effects of cadmium are also observed in the reproductive biology. The most harmful effects are realized in the productions of progesterone and testosterone. Cadmium intoxication is also highly connected to the bone damage, e.g. in workers exposed to cadmium-polluted fume and dust [68]. Cadmium associated renal cancer in humans was confirmed by clinical studies [69].

1.6.7 Effects of arsenic on human health

Integumentary system is the largest organ of the body which can easily be affected by arsenic poisoning. Skin abnormalities hold the hallmark of chronic arsenic exposure in adults. Moreover, men are likely to develop arsenic induced skin disorders compared to women. Arsenic attacks dermal system (skin lesions), cardiovascular system (black foot disease), renal system (proximal tubul degeneration, papillary and cortical necrosis), nervous system (peripheral neuropathy, encephalopathy), hepatic system (hepatomegaly, cirrhosis, altered hemi metabolism), endocrine system (diabetes), and hematological system (bone marrow depression) etc. [70]

Figure 1.8: Effects of arsenic poisoning

Objectives with specific aims:

The main purpose of this work is to examine the bioaccumulation and mobilization trend of heavy and toxic metals from industrial waste water to crops and vegetables through contaminated soil. The main objectives of the present research are:

1) To investigate heavy and toxic metals contamination in industrially contaminated water.
2) To find out heavy and toxic metals concentrations in soil irrigated with industrially contaminated water.
3) To determine heavy and toxic metals concentrations in crops and vegetables grown in and around industrial areas.
4) To evaluate the heavy metal pollution load indexes in contaminated water, soil, crops, and vegetables.
5) To find out the mobilization trend of heavy and toxic metals from waste water to soil, crops, and vegetables.
6) To estimate daily intake of different heavy metals by consumption of contaminated food items.
7) To evaluate potential non-carcinogenic risks associated with consumption of metal contaminated food items for both adults and children.
8) To assess potential carcinogenic risks of metals in crops and vegetables plants for both adults and children.

References

1. Z. Zhang, Y. Lu, H. Li, Y. Tu, B. Liu, Z. Yang, “Assessment of heavy metal contamination, distribution and source identification in the sediments from the Zijiang River, China”, Science of the Total Environment, vol. 645 pp. 235–243 (2018).
2. Y.F. Song, Z. Luo, C. Huang, X. Liu, Y.X. Pan, Q.L. Chen, “Effects of calcium and copper exposure on lipogenic metabolism, metal element compositions and histology in Synechogobius hasta”, *Fish Physiology and Biochemistry,* Vol. 39, pp. 1641–1656(2013).
3. I. Santos, M.S. Diniz, M.L. Carvalho, J.P. Santos, “Assessment of essential elements and heavy metals content on Mytilus galloprovincialis from River Tagus estuary”, *Biological Trace Element Research,* Vol. 159, pp. 233–240(2014).
4. S. V. Copaja, C. A. Pérez, C. Vega-Retter, D. Véliz, “Heavy Metal Content in Chilean Fish Related to Habitat Use Tissue Type and River of Origin”, *Bulletin of Environmental Contamination and Toxicology*, Vol. 99:6, pp. 695-700(2017).
5. M. Alam, M. Khan, A. Khan, S. Zeb, M. A. Khan, N. U. Amin, M. Sajid, A. M. Khattak, “Concentrations, dietary exposure, and human health risk assessment of heavy metals in market vegetables of Peshawar, Pakistan”, Environ Monit Assess, vol. 190: 505, pp.1-15 (2018).
6. Y.-H. Chiua, P. L. Williams, M. W. Gillman, R. Hauser, S. L. Rifas-Shiman, A. Bellavia, A. F. Fleisch, E. Oken, J. E. Chavarro, “Maternal intake of pesticide residues from fruits and vegetables in relation to fetal growth”, Environment International, vol. 119, pp. 421–428 (2018).
7. B. P. Banerjee, S. Raval, H. Zhai, P. J. Cullen, “Health condition assessment for vegetation exposed to heavy metal pollution through airborne hyperspectral data”, Environ Monit Assess, vol. 189: 604, pp. 1-11 (2017).
8. T.M. Galal, “Health hazards and heavy metals accumulation by summer squash (Cucurbita pepo L.) cultivated in contaminated soils”, *Environmental Monitoring and Assessment*, Vol. 188(7), (2016).

9. L. V. Antisari, F. Orsini, L. Marchetti, G. Vianello, & G. Gianquinto, “Heavy metal accumulation in vegetables grown in urban gardens”, *Agronomy for Sustainable Development*, Vol. 35(3), pp. 1139–1147(2015).
10. G. D. Pecoraro, M. A. Hortellani, Y. S. Hagiwara, E. S. Braga, J. E. Sarkis, J. S. Azevedo, “Bioaccumulation of Total Mercury (THg) in Catfish (Siluriformes, Ariidae) with Different Sexual Maturity from Cananéia-Iguape Estuary, SP, Brazil”, Bulletin of Environmental Contamination and Toxicology, vol. 102(2), pp. 175-179 (2019).
11. R. Sawut, N. Kasima, B.i Maihemuti, L. Hue, A. Abliz, A. Abdujappar, M. Kurban, “Pollution characteristics and health risk assessment of heavy metals in the vegetable bases of northwest China”, Science of the Total Environment, vol. 642, pp. 864–878 (2018).
12. A. Margenat, V. Matamoros, S. Díez , N. Cañameras, J. Comas , J. M. Bayona, “Occurrence and human health implications of chemical contaminants in vegetables grown in peri-urban agriculture”, *Environment International*, vol. 124, pp. 49–57 (2019).
13. S. Pajevic, D. Arsenov, N. Nikolic, M. Borisev, D. Orcic, M.Zupunski, N. Mimica-Dukić, “Heavy metal accumulation in vegetable species and health risk assessment in Serbia”, *Environmental Monitoring and Assessment*, vol.190: 459, pp.1-14(2018).
14. N.R. Prasad, J.M. Patil, “A study of physico-chemical parameters of Krishna river water particularly in western Maharashtra”, *Rasayan Journal of Chemistry*, Vol. 1:4, pp. 943-958(2008).
15. K. Nahar, M. Chowdhury, M.Chowdhury, A. Rahman, K.M. Mohiuddin, “Heavy metals in handloom-dyeing effluents and their biosorption by agricultural byproducts”, *Environmental Science and Pollution Research*, Vol. 25:8, pp. 7954-7967(2018).
16. M. Mahurpawar, “Effect of Heavy Metals on Human Health”, *International Journal of Research-Granthaalayah*, Vol. 31, pp. 1-7(2015).
17. A. J. Nathanson, “Air pollution”, *Encyclopedia Britannica*, 19 Oct. 2020.
18. A. J. Nathanson, “Water pollution”. *Encyclopedia Britannica*, 22 Dec. 2020.
19. M. A. Ashraf, M. J. Maah, I. Yusoff, “Soil Contamination, Risk Assessment and Remediation”, *Environmental Risk Assessment of Soil Contamination*, pp. 3-56(2014).

20. V. C. Pandey, V.Singh, "Exploring the Potential and Opportunities of Current Tools for Removal of Hazardous Materials from Environments", *Phytomanagement of Polluted Sites*, pp. 501-516(2019).
21. M. Elliott, "Biological pollutants and biological pollution- an increasing causes for concern", *Marine pollution Bulletin*, Vol. 46, pp. 275-280(2003).
22. W. Salomons, U. Forstner, P. Mader, the book of heavy metals: problems and solutions, Springers- Verlag. Berlin, Germany((1995).
23. M. S. El-Shahawi, A. Hamza, A. S. Bashammakh, W. T. Saggaf Al-,"An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants", *Talanta*, Vol. 80(5), pp. 1587-1597. 2010.
24. L. M. Schell, K. L. Knutson, S. Bailey, "Environmental Effects on Growth", *Human Growth and Development,* pp. 245–286(2012).
25. M. Gavrilescu, K. Demnerová, J. Aamand, S. Agathos, F. Fava,"Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation", *New Biotechnology*, Vol. 32(1), 2015.
26. K. L. Wasewar, S. Singh, S. K. Kansal, "Process intensification of treatment of inorganic water pollutants", *Inorganic Pollutants in Water*, pp. 245–271(2020).
27. S.A. Muhammad, S.I. Abubakar, H. Babashani, A.E. Asagbra, A.J. Alhassan, "Assessment Of Heavy Metals Concentration In Crude Oil Contaminated Water Samples Of Three Communities Of Ikpokpo, Atanba, And Okpele-Ama Of Gbaramatu Kingdom, Along The Escravos River In Warri South West Local Government Area Of Delta State, Nigeria", *International Journal of Environment and Pollution Research*, Vol.8:3, pp.41-59(2020).
28. H. Ali, E. Khan, "What are heavy metals? Long-standing controversy over the scientific use of the term' heavy metals'-proposal of a comprehensive definition", *Toxicological & Environmental Chemistry*, vol. 100:1, pp. 6–19(2018).
29. H. Ali, E. Khan, I. Ilahi, "Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation", *Journal of Chemistry*, vol. 2019: 6730305, pp. 1-14(2019).
30. K.-J. Appenroth, "What are 'heavy metals' in Plant Sciences?", *Acta Physiologiae Plantarum*, vol. 32: 4, pp. 615–619(2010).

31. O. Chalkiadaki, M. Dassenakis, and N. Lydakis-Simantiris, “Bioconcentration of Cd and Ni in various tissues of two marine bivalves living in different habitats and exposed to heavily polluted seawater”, *Chemistry and Ecology*, vol. 30: 8, pp. 726–742(2014).
32. M. A. Barakat, “New trends in removing heavy metals from industrial wastewater”, *Arabian Journal of Chemistry*, vol. 4:4, pp. 361–377(2011).
33. T. Khan, S. Muhammad, B. Khan, and H. Khan, “Investigating the levels of selected heavy metals in surface water of shah alam river (a tributary of River Kabul, Khyber Pakhtunkhwa),” *Journal of Himalayan Earth Sciences*, vol. 44: 2, pp. 71–79(2011).
34. B. Mansouri, R. Baramaki, and M. Ebrahimpour, “Acute toxicity bioassay of mercury and silver on Capoeta fusca (black fish)”, *Toxicology and Industrial Health*, vol. 28:5, pp. 393–398(2012).
35. P. C. Nagajyoti, K. D. Lee, and T. V. M. Sreekanth, “Heavy metals, occurrence and toxicity for plants: a review”, *Environmental Chemistry Letters*, vol. 8:3, pp. 199–216(2010).
36. P. R. Palaniappan, S. Karthikeyan, “Bioaccumulation and depuration of chromium in the selected organs and whole body tissues of freshwater fish Cirrhinus mrigala individually and in binary solutions with nickel”, *Journal of Environmental Sciences*, vol. 21: 2, pp. 229–236(2009).
37. E. Merian, “Introduction on environmental chemistry and global cycles of chromium, nickel, cobalt beryllium, arsenic, cadmium and selenium, and their derivatives”, *Toxicological & Environmental Chemistry*, vol. 8: 1, pp. 9–38(1984).
38. V. Masindi, K. L. Muedi,“Environmental Contamination by Heavy Metals”, *Heavy Metals,* Chapter 7, pp 1-20(2018).
39. M. Athar, S.B. Vohora,“Heavy Metals and Environment,New Delhi”, *New Age International (P) Limited,* (2001).
40. J. Musilova, J. Arvay, A. Vollmannova, T. Toth, J.Tomas, “Environmental contamination by heavy metals in region with previous mining activity”, *Bulletin of Environmental Contamination and Toxicology*, Vol. 97, pp. 569-575(2016).
41. G. Lee, J.M. Bigham, G. Faure, “Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee”, *Applied Geochemistry*, Vol. 17:5 pp. 569-581(2002).

42. M. Soleimani, N. Amini, B. Sadeghian, D. Wang, L. Fang, "Heavy metals and their source identification in particulate matter (PM2.5) in Isfahan City, Iran", *Journal of Environmental Sciences*, In press, 2018.
43. N. Herawati, S. Suzuki, K. Hayashi, I.F. Rivai, H. Koyoma, "Cadmium, copper and zinc levels in rice and soil of Japan, Indonesia and China by soil type", *Bulletin of Environmental Contamination and Toxicology*, Vol. 64, pp. 33-39(2000).
44. L.M.B. Ventura, V.L. Mateus, A.C.S.L. de Almeida, K.B. Wanderley, F.T. Taira, T.D. Saint'Pierre, A. Gioda, "Chemical composition of fine particles (PM2.5): Water-soluble organic fraction and trace metals", *Air Quality, Atmosphere and Health*, Vol. 10, pp. 845-852(2017).
45. M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew, K. N. Beeregowda, "Toxicity, mechanism and health effects of some heavy metals", *Interdisciplinary Toxicology*, Vol. 7:2, pp. 60–72(2014).
46. K.K. Das, R.C. Reddy, I.B. Bagoji, S. Das, S. Bagali, L. Mullur, J.P. Khodnapur, M.S. Biradar, "Primary concept of nickel toxicity–an overview" *Journal of basic and clinical physiology and pharmacology*, Vol. 30:2, pp.141-152(2019).
47. H. B. Röllin, C. M. C. A. Nogueira,"Manganese: Environmental Pollution and Health Effects", *Encyclopedia of Environmental Health*, pp.617-629(2011).
48. S. L. O'Neal, W. Zheng, "Manganese Toxicity Upon Overexposure: a Decade in Review", *Current environmental health reports*, Vol. 2:3, pp. 315–328((2015).
49. A. L. Wani, A. Ara, J. A. Usmani, "Lead toxicity: A review", *Interdisciplinary Toxicology*, Vol. 8:2, pp. 55-64(2015).
50. R. Zhang, V. L. Wilson, A. Hou, G. Meng, "Source of lead pollution, its influence on public health and the countermeasures", *Health, Animal science and Food safety*, Vol. 2:1, pp. 18 – 31(2015).
51. A. L. Wani, A. Ara, J. A. Usmani, "Lead toxicity: a review", *Interdisciplinary toxicology*, Vol. 8:2, pp. 55–64(2015).
52. M. Bost, S. Houdart, M. Oberli, E. Kalonji, J.-F. Huneau, I. Margaritis, "Dietary copper and human health: Current evidence and unresolved issues", *Journal of Trace Elements in Medicine and Biology*, Vol. 35, pp. 107–115(2016).

53. L. Jarup, "Hazards of heavy metal contamination", *Br Med Bull*, Vol. 68, pp. 167–182(2003).
54. R. Chunhabundit, "Cadmium Exposure and Potential Health Risk from Foods in Contaminated Area, Thailand", *Toxicological Research*, Vol. 32:1, pp. 65–72(2016).
55. Y. –C. Janga, Y. Somannaa, H. Kim, "Source, Distribution, Toxicity and Remediation of Arsenic in the Environment – A review", *International Journal of Applied Environmental Sciences*, Vol. 11:2, pp. 559-581(2016).
56. J.-Y. Chung, S.-D. Yu, Y.-S. Hong, "Environmental Source of Arsenic Exposure", *Journal of Preventive Medicine and Public Health*, Vol. 47:5, pp.253–257(2015).
57. N. Ercal, H. Gurer-Orhan, and N. Aykin-Burns, "Toxic metals and oxidative stress Part I: mechanisms involved in metal-induced oxidative damage," *Current Topics in Medicinal Chemistry*, vol. 1: 6, pp. 529–539(2001).
58. A. Wilk, E. Kalisińska, D. I. Kosik-Bogacka et al., "Cadmium, lead and mercury concentrations in pathologically altered human kidneys," *Environmental Geochemistry and Health*, vol. 39: 4, pp. 889–899(2017).
59. M. Ebrahimpour, M. Mosavisefat, and R. Mohabbati, "Acute toxicity bioassay of mercuric chloride: an alien fish from a river," *Toxicological & Environmental Chemistry*, vol. 92: 1, pp. 169–173(2010).
60. M. Salman, R. Rehman, T. Mahmud et al., "Assessment of concentration of lead, cadmium, chromium and selenium in blood serum of cancer and diabetic patients of Pakistan," *Journal of the Chemical Society of Pakistan*, vol. 33:6, pp. 869–873(2011).
61. M. L. Sall, A. K. D. Diaw, D. Gningue-Sall, S. E. Aaron, J. J. Aaron, "Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review", *Environmental Science and Pollution Research*, Vol. 27, pp. 29927–29942(2020).
62. H. W. Yuen, W. Becker, Iron toxicity, *StatPearls [Internet]*, (2020).
63. Z. Long, X.R. Li, J. Xu, R.A. Edden, W.P. Qin, L.L. Long, J.B. Murdoch, W. Zheng, Y.M. Jiang, U. Dydak, "Thalamic GABA predicts fine motor performance in manganese-exposed smelter workers", *PLoS One*, Vol. 9:2, pp. e88220(2014).

64. B.A. Racette, M. Aschner, T.R. Guilarte, U. Dydak, S.R. Criswell, W. Zheng, "Pathophysiology of manganese-associated neurotoxicity", *NeuroToxicology,* Vol. 33 pp. 881–886(2012).
65. Y. Jiang, W. Zheng, "Cardiovascular toxicities upon manganese exposure", *Cardiovasc Toxicol*, Vol. 5, pp. 345–354(2005).
66. D. Hafeman, P. Factor-Litvak, Z. Cheng, A. Van Geen, H. Ahsan, "Association between manganese exposure through drinking water and infant mortality in Bangladesh" *Environ Health Perspect*, Vol. 115:7, pp. 1107-1112(2007).
67. National Research Council (US) Committee on Copper in Drinking Water. Health Effects of Excess Copper; In "Copper in Drinking Water", *National Academies Press, Washington (DC)*, Chapter 5. pp. 78-113(2000).
68. J. Godt, F. Scheidig, C. Grosse-Siestrup, V. Esche, P. Brandenburg, A. Reich, D. A. Groneberg, "The toxicity of cadmium and resulting hazards for human health", *Journal of occupational medicine and toxicology*, Vol. 1, pp. 22((2006).
69. D. S. G. G. Il'yasova, "Cadmium and renal cancer" *Toxicol Appl Pharmacol*, Vol. 207, pp. 179–186(2005).
70. K. S. M. Abdul, S. S. Jayasinghe, E. P. S. Chandana, C. Jayasumana, P. M. C. S. De Silva, "Arsenic and human health effects: A review", *Environmental Toxicology and Pharmacology*, Vol. 40:3, pp. 828–846(2015).

CHAPTER-2

STUDY AREA

2. General information

Bangladesh is an agricultural as well as a developing country. The economy of this country is growing fast because of the dramatic rapid increase in industrialization and urbanization in recent years. However, the industrialization is occurring without any proper plans and guidelines. Most of the industrial establishments occur in and around agricultural lands. Most of the industries are emitting their toxic effluents without any prior treatment into nearby surrounding environments and thus contaminating air, water, soil, crops, vegetables and other environmental components. We have selected two different areas to perform environmental pollution studies. Savar upazila in Dhaka district was selected as highly contaminated area as a large number of industries are located in this area. Dhaka is the capital of Bangladesh and a great variety of industries found their location around the Dhaka city. These industries are continuously discharging their toxic effluents to the surrounding environments and consequently polluting surface water, soil, crops and vegetables grown in and around industrial zones. **Table 2.1** highlights the different types industries located in Savar area and possible sources of various metals from them. Kalihati Upazila in Tangail district was selected as long range contaminated site since the area is about 60 k.m. away from the nearest industrial zone. Crops and vegetables are cultivated in both study areas to satisfy local needs and sometimes transported to other areas of the country. The detailed information on the two study areas are given below:

2.1 Geographical locations of the study area-1 (highly contaminated area)

2.1.1 Geography

Our study area covers the area from 23.81650° N to 23.94880° N latitude and from 90.24390° E to 90.26870°E longitude of Savar, Dhaka (**Table 2.2)**. Two industrial areas of Savar (Dhaka export processing zone and Bank Town industrial establishment) were selected for sampling (**Figure 2.1**). Paddy and a large variety of vegetables are being cultivated in the Savar area which latter on transported to Dhaka city. Major portion of vegetables consumed by Dhaka city people is being supplied from Savar area. It is matter of sever concern that in this area, all of the vegetables are continuously cultivating in industrially contaminated soil and are irrigated with industrially contaminated waste water of Ashulia lake and Bangshi river.

Table 2.1: List of the industries located in Savar area and possible sources of metals from them

Metals	Sources
Arsenic	Phosphate fertilizer, paint, textile, pharmaceutical, pesticide, metal hardening and other industries.
Cadmium	Fertilizer, electronics, paint, battery, PVC and other industries.
Iron	Iron and steel, sulfuric acid industry and other industries.
Chromium	Metal plating, rubber, photography, tanning, leather industry, textile industry, paints and other industries.
Nickel	Electroplating, semiconductor goods, iron and steel, battery and other industries.
Manganese	Dry-cell, fertilizer, brick, and other industries.
Lead	Gasoline (refinery), paint, plumbing pipe, lead bullet, battery, toy and other industries.
Copper	Plating, Rayon, electronics, Pesticide, Paints and pigment industry, Textile industry and other industries.

Table 2.2: Location of different sampling points of the study area-1

Sample ID	Location of sample	North	East
S-1	Vagolpur	23.83000°	90.24880°
S-2	Muradjang Road	23.82000°	90.25380°
S-3	Bannk Town Bridge	23.81930°	90.25700°
S-4	Unnamed Road	23.81650°	90.26870°
S-5	Baipayl A.H. Road	23.90200°	90.26230°
S-6	Kaichabari	23.94600°	90.25900°
S-7	Dagortoly	23.94240°	90.24440°
S-8	Maijhail	23.94840°	90.24390°
S-9	Zele Para	23.94880°	90.24670°

The total area of Savar is 280.13 square kilometers (108.16 sq. mi.) and it has 66,956 units of household. It is bounded by Kaliakair and Gazipur Sadar upazilas on the north, Keraniganj upazila on the south, Mirpur, Mohammadpur, Pallabi and Uttara thanas of Dhaka City on the east, and Dhamrai and Singair upazilas on the west. The study area directly links to Dhaka city with comparatively higher traffic density and has significant industrial influences [1]. The length of the land gradually increases from the east to the west. The southern part of the Upazila is composed of the alluvium soil of the Bangshi and Dhalashwari rivers.

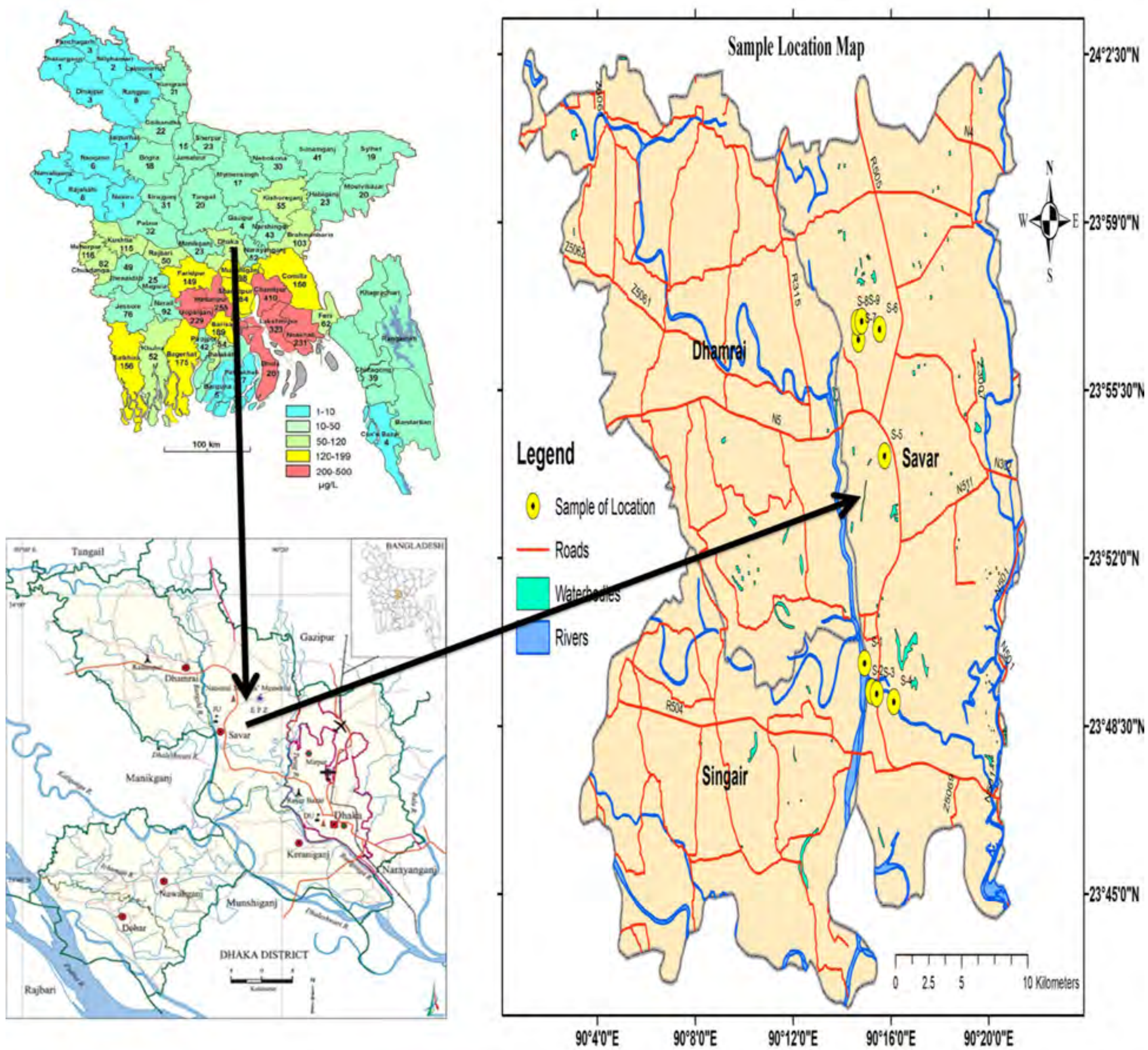


Figure 2.1: Map of the study area-1

Bangshi River has consequential significance in agricultural activities because of its area and location. The river is about 238 k.m. long and it was originated in Jamalpur and passed through Tangail, Ghazipur and Savar areas before flowing into Dhaleshwari River.

In Savar area, the river flows through densely populated town and agricultural fields in which water from the river is being used for cultivation of vegetables and crops. At present the river is used as a convenient means for the continuous disposal of untreated liquid wastes from Dhaka Export Processing Zone (DEPZ) and other industrial establishments located in the Savar area [2].

2.1.2 Industries and economy

Agricultural activities and industrial manufacturing are the two major economic sectors in Savar area. The major crop grown in this area is Paddy and common vegetables are ladies finger, garlic, chili, spinach, and other vegetables. The extinct or nearly extinct crops in the region are Aous paddy, Asha Kumari paddy, Linseed, Kali mator, Randhuni saj, Mitha saj, Kaun and Mas kalai (local names of the crops). There are 181 combined fisheries, dairies, and poultries dairy, 5 hatcheries, 209 poultries, and 1319 fisheries establishment are currently available in this area. The manufacturing facilities include ceramic industry, beverage industry, press and publications industry, garments industry, foot ware, jute mills, textile mills, printing and dying factory, transformer industry, automobile industry, biscuit and bread factory, pharmaceutical industry, soap factory, brick field, welding etc. [3, 4]. The following chart shows the contributions of different sectors in the total economy of the study area [3, 4].

Agriculture %	Industry %	Service %
23.6	59.6	16.8

2.1.3 Temperature

The hot season lasts for 3.5 months, from March 12 to June 26, with an average daily high temperature above 89°F in the study area. The hottest day of the year is April 15, with an average high temperature of 93°F and low temperature of 77°F. The cool season lasts for 1.5 months from December 13 to January 31, with an average daily high temperature below 78°F. The coldest day of the year is January 12, with an average low temperature of 57°F and high temperature of 75°F.

2.1.4 Rainfall

The long-term trend of annual rainfall in Dhaka shows no significant change, however, the trend in the seasonal rainfall appears to be erratic and variable. To show the variation within the months and not just the monthly totals, we show the rainfall accumulated over a sliding 31-day period centered on each day of the year. The capital city Dhaka and its surrounding areas such as Savar experiences extreme seasonal variation in monthly rainfall [5].

Figure 2.2: Discharging of industrial effluents into the nearby water body of Savar area (study area-1)

The rainy season of a year lasts for 9.5 months from February 13 to November 29 with a sliding 31-day rainfall of at least 0.5 inches. The most rain falls observed during the 31 days periods on July 3, with an average total accumulation of 9.9 inches. The rainless period of a year lasts for 2.5 months, from November 29 to February 13. The least rain falls is being realized around January 8 with an average total accumulation of 0.2 inches.

2.2 Geographical locations of the study area-2 (long range contaminated area)

2.2.1 Geography

In this case, the present study covers the area from 24.321331° N to 24.369617° N latitude and from 89.906387° E to 89.978952° E longitude of Kalihati, Tangail (**Table 2.3)**. Map of the study area-2 is illustrated in the **Figure 2.3**.

Kalihati Upazila was selected as long range contaminated site because this area is about 60k.m. away from the nearest industrial establishments and different crops and vegetables are cultivated there to meet the demands of the local needs. In this area all crops and vegetables are cultivated using the surface water from river, lake and bill. Long range contamination is quite possible in this case because the area is directly connected to the industrial area through the rivers. There is no industrial establishment available in this particular study area. Kalihati Upazilla is highly rural area located at 24.3833°N 90.0083°E and far away from Tangail city. It has 65035 households and total area is of 295.6 km^2 [6]. The Upazila is surrounded by Bhuapur and Ghatail Upazila on the north, Basail Upazila on the south, Sakhipur Upazila on the east, and the Jamuna River on the west.

Table 2.3: Location of the sampling points on the study area-2

Sample ID	Location of sample	North	East
S-1	Bolikhondo	24.340042°	89.978952°
S-2	Pouzan	24.322842°	89.959213°
S-3	Baniafoyr	24.321331°	89.961849°
S-4	Elenga	24.321888°	89.931539°
S-5	Fultola	24.362094°	89.920855°
S-6	Bangra	24.369617°	89.964387°
S-7	Babla	24.361871°	89.906387°

Kalihati Upazilla is divided into 2 municipalities and 13 union parishads: Balla, Bangra, Bir-Bashinda, Dashkia, Durgapur, Gohaliabari, KokDohora, Nagbari Union, Narandia, Paikara, Parkhi, Salla and Shahadebpur. There are about 1200 industries located in and around Tangail city area which include textile and garments industries, dyeing industries, battery manufacturing industries, packaging industry, glass industries, tanneries, metal workshops, pesticide and fertilizer industries, and food processing industries which collectively produce large volumes of effluents containing different toxic metals [7]. These industries discharge their untreated effluents randomly into the surrounding environment.

Though the Kalihati Upazilla is far away from the industrial establishments located in and around Tangail city area and free from direct contact of industrial activities with point source pollution, during the rainy season with heavy rainfall, frequent occurrence of flood, and constant flow of the contaminated river water can potentially carry out, transport, and mobilize heavy and toxic metals from industrial contaminated areas to rural non-contaminated regions and thus may contaminate the water bodies, soil, food chain, and aquatic organisms of the respective safe areas.

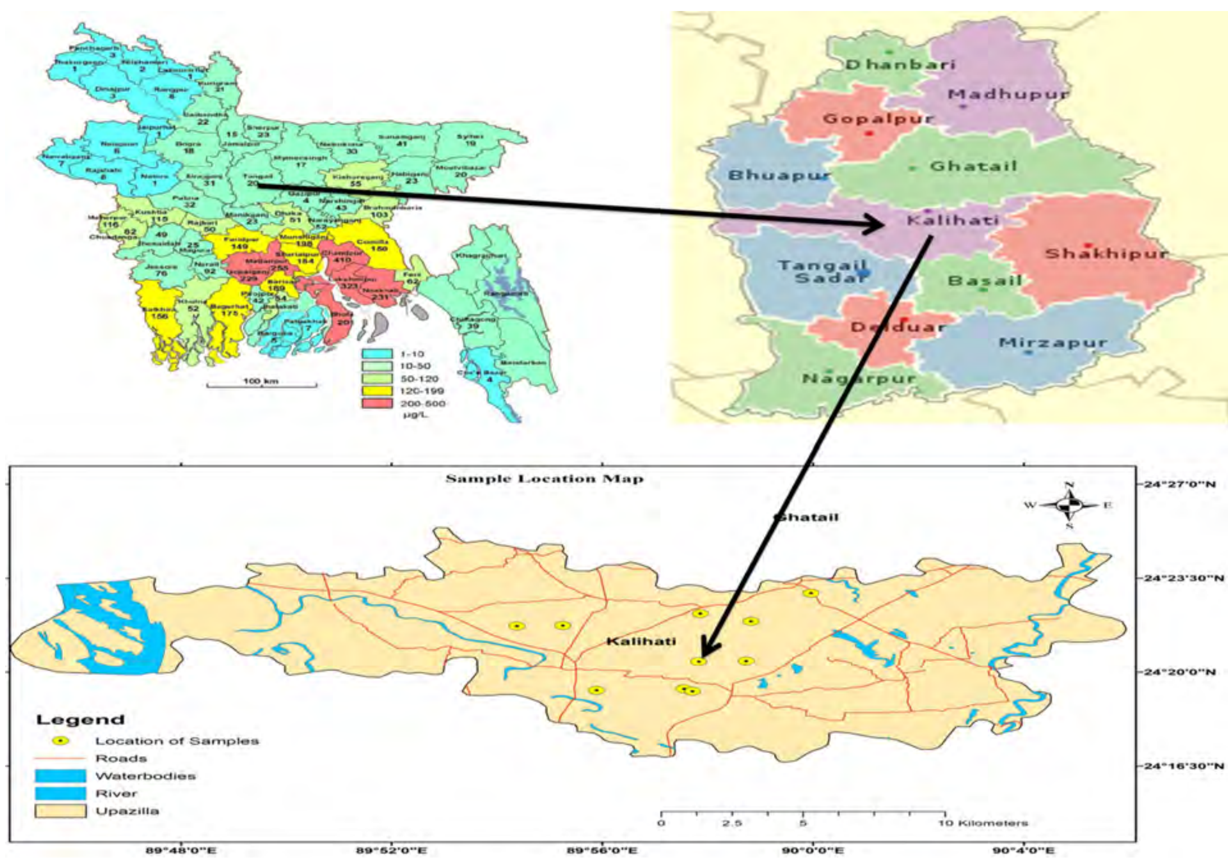


Figure 2.3: Map of the study area-2

However, it may take longer time to realize and observe the real consequences of this long range pollution in different components of the corresponding environments and the respective impacts on the people who like to live in a clean and safe zone totally free from hazardous industrial pollution.

The long range pollution is a potential threat in our country because Bangladesh is a land of river with considerable rainfall in most of the time in a year which causes the frequent occurrence of flood in various regions of the country that eventually poses potential risks of having long range contamination from highly industrial polluted areas. Long term effects of long range industrial pollution may result the distribution and spreading out of environmental contaminants in all over areas of Bangladesh.

2.2.2 Economy

Main sources of income of people in Khalihati Upazilla, Tangail is agriculture which is about 46.75%, non-agricultural activity 3.73%, industry 2.21%, commerce 15.53%, transportation and communication 3.53%, service 6.20%, construction 1.24%, religious service 0.20%, rent and remittance 2.90% and others 17.71% [8]. In the present study we recognized the local area of Kalihati Upazila at Tangail District as a lower contamination site from where water, soil, crops, and vegetables samples were collected for analysis.

2.2.3 Temperature and rainfall

Tangail has a tropical climate. In winter, there is much less rainfall than in summer. According to Köppen and Geiger, this climate is classified as Aw, (tropical savanna climate with dry winter characteristics). The temperature here averages 25.5°C. About 1872 mm of precipitation falls annually [9].

References

1. F. Ahmed, A. N. M. Fakhruddin, M. T. Imam, N. Khan, A. T. M. Abdullah, T. A. Khan, M. M. Rhaman, M. N. Uddin, "Assessment of roadside surface water quality of Savar, Dhaka, Bangladesh using GIS and multivariate statistical techniques", *Applied Water Science*, Vol. 7:7, pp. 3511–3525(2017).
2. M. S. Rahman, N.Saha, A. H. Molla, " Potential ecological risk assessment of heavy metal contamination in sediment and water body around Dhaka export processing zone, Bangladesh", *Environmental Earth Sciences*, Vol.71:5, pp. 2293–2308(2013).
3. M. L. Rahman, M. M. Isla, M. L. Mamun, "Commuter's Modal Choice: A Case Study of Savar Pourashava", *Journal of Bangladesh Institute of Planners*, Vol. 2, pp. 78-97(2009).
4. M, Aktaruzzaman, A. N. Fakhruddin, M. A. Chowdhury, Z. Fardous, M. K. Alam, "Accumulation of heavy metals in soil and their transfer to leafy vegetables in the region of Dhaka Aricha Highway, Savar, Bangladesh", *Pakistan Journal of Biological Sciences*, Vol. 16:7, pp. 332-8(2013).
5. M. Alam, M. D. G. Rabbani, "Vulnerabilities and responses to climate change for Dhaka", *Environment and Urbanization*, Vol. 19:1, pp. 81–97(2007).
6. C. N. Shymal, Banglapedia: National Encyclopedia of Bangladesh, Asiatic Society of Bangladesh, Bangladesh (2012).
7. T. Kormoker, R. Proshad, M. S. Islam, T. R. Tusher, M. Uddin, S. Khadka, A. Sayeed, "Presence of toxic metals in rice with human health hazards in Tangail district of Bangladesh", *International Journal of Environmental Health Research*, pp. 1–21(2020).
8. "Population Census Wing, BBS". Archived from the original on 2005-03-27,(2006). https://en.wikipedia.org/wiki/Kalihati_Upazila.
9. "Climate: Tangail". climate-data.org. https://en.climate-data.org/asia/bangladesh/dhaka-division/tangail-59250.

CHAPTER-3

SAMPLING, MATERIALS, AND METHODOLOGY

3.1 Chemicals and reagents

The chemicals and reagents used in this research were analytical grade and used without further purification. Stock solutions of 1000 mgL^{-1} were arranged from their corresponding salts for the selected heavy metals (Cu, Cr, Fe, Mn, Ni, Pb, AS, and Cd). Double distilled and deionized water was used in all solution preparation and dilution purposes throughout the experimental procedures. The list of chemicals and reagents are given below:

Chemicals	Sources	Purity (W/W basis)
Sulfuric Acid	Aldrich	69%
Nitric Acid	Aldrich	98%
Hydrogen peroxide	Aldrich	30%
Per chloric Acid	BDH	70%
Hydrochloric Acid	Merck Germany	37%
Ethyl alcohol	Merck India	99.5%
Potassium Iodide	Merck Germany	Pure
Sodium Borohydride	BDH	pure

3.2 Instruments

Analysis of the samples was performed using the following instruments:

1. Oven (Lab Tech, LDO-030E)
2. Digital Balance (AB 265/S/SACT METTLER, Toleto, Switzerland)
3. Hot plate (RC- 1887/166, Velp Scientific, Italy)
4. Atomic Absorption Spectroscopy (SHIMADZU AA-7000)

3.3 Sampling design and sampling technique

Samples (**Table 3.1)** were collected directly from the sampling sites, obviously maintaining the standard procedure reported by Tran *et al.* and Islam *et al.* [1, 2]. Random sampling procedures were used for sampling and three replicates were taken (at least 5 meters away from each other) for each sample. Water samples were collected from the middle layer into HDPE bottle (previously acid cleaned) and carried out to the laboratory, filtered, acidified with HNO_3 ($pH < 2$) and preserved into refrigerator (4°C) for further analysis. Crops and vegetable samples were taken from the inner part of the land to eliminate edge effect. Edible part and root of each crop and vegetable sample were collected in different zipped plastic bag and the samples were taken to the laboratory, washed by tap water followed by distilled and deionized water.

Table 3.1: Samples with their scientific name

Samples	Scientific name
Rice	*Oryza sativa*
Brinjal	*Solanum melongena*
Lady's finger	*Abelmoschus esculentus*
Water spinach	*Ipomoea aquatic*
Red spinach	*Amaranthus dubius*
Green spinach	*Spinacia oleracea*

Each of the crop and vegetable samples was dried in air in the presence of sunlight for 2 days and then oven dried at 70-80°C until a constant weight was achieved. The dried samples were then grinded by an electrical grinder (made of stainless steel) and passed through a 2 mm sieve and finally the powdered samples were transferred into polythene zip-bags and were preserved into refrigerator (4°C) for analysis. Soil samples were collected from just under the root of crop and vegetables plants. The samples were collected from 15 cm depth in each case and put in pre-cleaned zipped plastic bag. Finally the soil samples were transported to the laboratory, air dried at room temperature followed by oven drying at 105°C for 4 h to remove all of the moisture content. The soil samples were then grinded by stainless steel made electrical grinder, sieved through a 2 mm nylon mesh to remove large debris, stones, and pebbles and preserved in polythene zip-bags as described before for further analysis.

All types of samples were transported to the laboratory using ice box at a temperature of 4°C within 8 hours. The respective samples bottles or plastic bags were labeled on by the permanent marker and the information (name, source, GPS data etc) associated with each sample ID was noted into a note book.

3.4 Digestion procedures for water, soil, crop, and vegetable samples

Water samples were digested by conventional digestion method i.e. 100 mL preserved water was taken to a conical flask and 10 mL conc. HNO_3 was added. 0.5 mL H_2SO_4 was also added and heated until the volume of the mixture was reduced to about 5 mL. The sample was then cooled and filtered (using Whatman-42-filter paper) to a high density polyethene (HDPE) bottle and diluted to 100 mL with deionized water and preserved for metal analysis. All of the soil, crop, and vegetable samples were wet digested. 0.5 gm of each soil, crop, and vegetable samples was digested with 14 mL of an acid mixture of HNO_3, H_2SO_4, and $HClO_4$ following a ratio of 5:1:1 [3, 4]. During the digestion process, the sample and acid mixtures were heated at about 90ºC using a hot plate until the volume of the resulting mixture was reduced to about 3-5 mL. The mixture was then cooled to room temperature and filtered using Whatman No.42 filter paper, to HDPE bottle, diluted with 100 mL deionized water, sealed, and preserved for the metal analysis using AAS. Blank digestion was also performed using the same water used for the dilution following the same procedure.

3.5 Quality assurance and quality control

All the apparatus, reagents, and chemicals used in this study were of analytical grade. Glass wares were made of high quality quartz glass and steel apparatus were made of stainless steel.

Table 3.2: Analytical parameters for the AAS to investigate the heavy metals

Elements	Wavelength (nm)	Slit (nm)	Lamp Current (mA)	Mode	Calibration Range (mg/ L)	Detection limit (mg/ L)
As	193.70	0.7	12.0	HG-AAS	0.001-0.010	0.001
Ni	232.00	0.2	12.0	Flame-AAS	0.50-10.00	0.080
Cd	228.80	0.7	8.0	Flame-AAS	0.05-1.00	0.004
Cu	324.80	0.7	6.0	Flame-AAS	0.50-4.00	0.026
Fe	248.30	0.2	10.0	Flame-AAS	0.50-6.00	0.060
Pb	217.00	0.7	10.0	Flame-AAS	0.50-10.00	0.035
Mn	279.50	0.5	8.0	Flame-AAS	0.00-2.00	0.020

Chemicals and reagents were purchased from Merck Millipore and Sigma-Aldrich in most cases. HDPE bottles were used to collect and preserve the water and digested samples. High quality polythene zip-bags were used for transportation and primary preservation of the soil, crops, and vegetables samples.

Table 3.3: Metal concentrations found in certified reference materials (CRM) by AAS

Elements	Certified value	Measured value	Deviation (%)	Recovery (%)
As(μg/L)	10.00± 0.02	9.95±0.05	1.55	99.50
Ni(mg/L)	2.00±0.05	1.96±0.04	0.53	98.00
Cd(mg/L)	0.20±0.02	0.19±0.02	0.75	95.00
Cu(mg/L)	2.00±0.02	2.00±0.07	1.20	100.00
Fe(mg/L)	1.00±0.10	0.93±0.06	0.96	93.00
Pb(mg/L)	4.00±0.05	3.98±0.01	1.77	99.50
Mn(mg/L)	1.00±0.01	0.98±0.02	1.23	97.00

Different factors (midpoint standard checks, blanks, calibration curve and spiked sample) were inspected to ensure quality control, quality assurance and calibration curve construction. All of the calibration procedures were evaluated based on their corresponding correlation coefficients (R2) of the calibration curves. The respective calibration curve was made precisely with the correlation coefficient (R2), where, Cu-9996, Pb-0.9992, Mn-0.9997, Fe-0.9988 and Ni-0.9994. 0.25 to 5.5% was found as the result of mid-point checks for the metals. A range of 96.54 to 98.85% was found in Spike recovery [5].

3.6 Heavy and toxic metal analysis

Preserved digested samples were transported to the metal analysis lab for the investigating of heavy and toxic metals in the samples. An Atomic Absorption Spectrophotometer (Shimadzu-6800) was used to investigate the concentration of heavy metals in the samples. A total of seven heavy and toxic metals were investigated in water, soil, crops, and vegetables samples, six of them were analyzed by flame AAS method and one (As) was determined by hydrate generated AAS method. The operating conditions of instrument and different related parameters were maintained appropriately. Arsenic concentrations in the samples were analyzed by Hydride generation techniques using AAS. The technique provides a means of introducing samples containing arsenic into an atomizer in the gas phase.

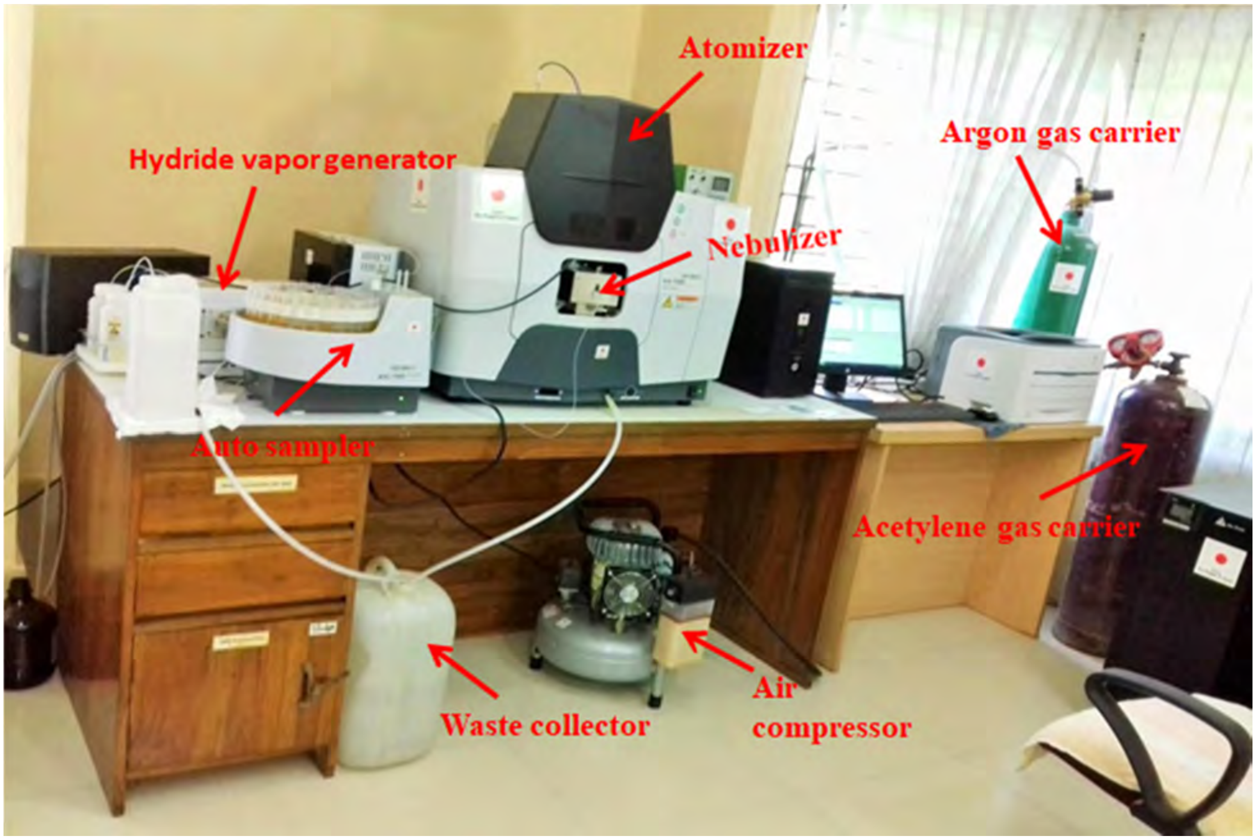
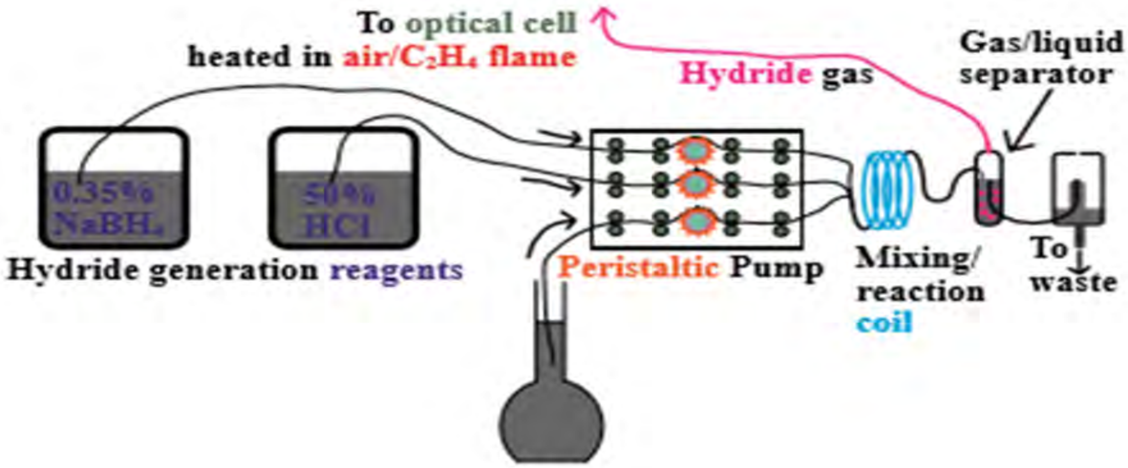


Figure 3.1: Atomic absorption spectrophotometer

Hydride generation occurs by adding an acidified aqueous solution of the sample to a 0.35% aqueous solution of sodium borohydride, all of them are placed in a glass vessel. The volatile hydride generated from the reaction that occurs and is being swept into the atomization chamber by an inert gas, where it undergoes decomposition. This process forms an atomized form of the analyte, which can then be measured by atomic absorption spectrometry.

3.7 Statistical analysis

Different reliable statistical software were used to analyze the concentrations of heavy and toxic metals in the water, soil, crops, and vegetables samples of the study area. Microsoft excel-2013 was used to calculate the mean, standard deviation, and other health related parameters. Pearson's correlation package SPSS (version 16.0) was also used for source analysis of heavy metals found in the samples studied.



$$AsCl_3 + HCl + NaBH_4 \longrightarrow AsH_3 + NaCl + BH_3$$

Figure 3.2: Working principle of hydride generator in AAS

3.7.1 Bioconcentration factor (BCF)

Bioconcentration factor (BCF) sometimes called Transfer Factor (TF) is a meaningful factor that describe the quantity of heavy metals that are transferred from soil to crops and vegetables.

$$BCF_{soil\ to\ plant} = {C_{plant}}/{C_{soil}}$$

It is usually the ratio of metal concentration in the plants and that in soil when the transfer of metals from soil to plants is being considered. The transfer factor can be calculated for each crop and vegetable item at each site separately. Transfer factor can also be used to evaluate the potential capability of plants to transfer metals from soil to roots and edible tissues [6-8].

3.7.2 Pollution load index (PLI)

Pollution Load Index (PLI) is a parameter that is used to demonstrate the pollution level or degree of contamination in the soil. It provides us significant information about the extent of pollution that is occurring in a contaminated area and the types of necessary measures that should be adopted to minimize the pollution patterns.

Generally, the PLI is determined by using the following equation

$$PLI = {C_i}/{C_r}$$

Where, C_i and C_r are concentrations of heavy and toxic metals in the soil sample and the reference concentrations of heavy and toxic metals in the soil respectively [9-11].

3.7.3 Methods for risk assessment

Health risk assessment is an effective and meaningful way to evaluate the human health risk caused by the direct and indirect ingestion of metals contaminated specific food items [12]. Different health risk assessment parameters such as THQ, HI, and TCR were calculated in the present study to investigate the human health risks associate with the consumption of contaminated vegetables and crops.

3.7.3.1 Estimated daily intake (EDI)

EDI is the amount of heavy metal taken by a person daily due to the consumption of metal polluted food items. It is calculated by using the formula given bellow,

$$EDI = \frac{C \times FIR \times EF \times ED}{BW \times AT}$$

Here, C: metal concentration; EF: exposure frequency (365 d y^{-1}); ED: exposure duration (30 y for adults and 15 y for children) [13]; BW: average body weight (adult = 60 kg and children = 16 kg) [14]; AT: average time (ED×EF); FIR is the food ingestion rate of the food items. A survey was conducted on 27 families (3 families from each sampling site) to find the FIR values for different samples [15, 16].

3.7.3.2 Target hazard quotient (THQ)

Target hazard quotient sometimes called hazard quotient (HQ) is the non-carcinogenic risk caused by any individual metal due to the consumption of any specific food item. The following formula is used to calculate the THQ [17].

$$THQ = \frac{C \times FIR \times EF \times ED}{BW \times AT \times RfD} \times 10^{-3}$$

Here, RfD is the oral reference dose for metals. THQ value less than 1 (THQ<1) indicates the absence of non-carcinogenic risk for human health, THQ equal to 1 (THQ=1) means that it is within the boundary position and THQ becomes severe matter of concern and alarming issue when its values become higher than 1 (THQ>1). In that case, heavy and toxic metals show higher carcinogenic risk [18, 19].

3.7.3.3 Hazard index (HI)

Hazard index (HI) demonstrates the health risk posed by a mixture of metals. If the HI values are found less than 1, then there is least probability of having non-carcinogenic risk. However, the extents of HI greater than 1 provide a significant health risks associated with metal contaminated foods.

$$HI = \sum TTHQ$$

$$= TTHQ_1 + TTHQ_2 + TTHQ_3 + \cdots + TTHQ_n$$

The above formula usually used to determine the HI value, where prefixes indicate different food items. TTHQ is given by:

$$TTHQ = \sum THQ$$

$$= THQ_1 + THQ_2 + THQ_3 + \cdots + THQ_n$$

Here the prefixes indicate different heavy metals. TTHQ is the sum of THQ values for different metals in the individual environmental sample and HI is the sum of TTHQ values for all studied samples [20-22].

3.7.3.4 Target carcinogenic risk (TCR)

Target carcinogenic risk (TCR) sometimes called lifetime cancer risk is the cancer forming risk caused by individual metal throughout the whole life due to the consumption of contaminated food items.

In the present study, the TCR values were calculated based on the carcinogenic slop factor (CFSo) and the equation obtained from the USEPA Region III Risk-Based Concentration data Table (USEPA 2006). Higher the TCR values signify the greater potential risk of having the cancer [23-25]. The equation used to determine the TCR values is given as follows:

$$\boldsymbol{TCR = \frac{C \times FIR \times EF \times ED \times CFSo}{BW \times AT} \times 10^{-3}}$$

3.7.4 Metal pollution index (MPI)

MPI represents the total metal content in any specific environmental sample. It (Metal pollution index) is the combined effects in any specific sample exerted by all the studied metals. It is calculated by using the following formula:

$$\boldsymbol{MPI = (C_1 + C_2 + C_3 + \cdots C_n)^{1/n}}$$

Where, C_1, C_2, C_3……C_n are the concentrations of different metals in a specific sample [26, 27]. The higher MPI values correspond to the presence of greater quantity of the heavy metals in any specific food item and thus pose the stronger health risks due to the consumption of that contaminated food item.

References

1. T.H.M. Tran K.G. Nguyen, “Metal and metalloid concentrations in soil, surface water, and vegetables and the potential ecological and human health risks in the northeastern area of Hanoi, Vietnam”, *Environmental Monitoring and Assessment*, 190: 624(2018).
2. M.S. Islam M.F. Hoque, “Concentrations of heavy metals in vegetables around the industrial area of Dhaka city, Bangladesh and health risk assessment” *International Food Research Journal*, Vol. 21:6, pp. 2121-2126(2014).
3. M.A. Goni, J.U. Ahmad, M.A. Halim, M.A. Mottali, D.A. Chowdhury, “Uptake and translocation of metals in different parts of crop plants irrigated with contaminated water from DEPZ area of Bangladesh”, *Bulletin of Environmental Contamination and Toxicology*, Vol. 92, pp. 726–732(2014).
4. M. Rahman, M.A. Islam, “Concentrations and health risk assessment of trace elements in cereals, fruits, and vegetables of Bangladesh” *Biological Trace Element Research*, (2019).
5. P.K. Maurya, D.S. Malik, K.K. Yadav, A. Kumar, S. Kumar, H. Kamyab, “Bioaccumulation and potential sources of heavy metal contamination in fish species in River Ganga basin: Possible human health risks evaluation”, *Toxicology Reports*, Vol. 6, pp. 472–481(2019).
6. T. Sarwar, M. Shahid, Natasha, S. Khalid, “Quantification and risk assessment of heavy metal build-up in soil–plant system after irrigation with untreated city wastewater in Vehari, Pakistan”, *Environmental Geochemistry and Health*, (2019).
7. F.T. Gemeda, D.D. Guta, F.S. Wakjira, G. Gebresenbet, “Occurrence of heavy metal in water, soil, and plants in fields irrigated with industrial wastewater in Sabata town, Ethiopia” *Environmental Science and Pollution Research*, (2020).
8. 24. C.-W. Liu, Y.-Y. Chen, Y.-H. Kao, S.-K. Maji, “Bioaccumulation and translocation of arsenic in the ecosystem of the Guandu Wetland, Taiwan”, *Wetlands*, Vol. 34, pp. 129–140(2014).
9. P. F. Ávila, E. F. Silva, C. Candeias, “Health risk assessment through consumption of vegetables rich in heavy metals: the case study of the surrounding villages from Panasqueira mine, Central Portugal”, *Environmental Geochemistry and Health*, Vol. 39:3, pp. 565–589 (2016).

10. L. Chen, S. Zhou, Y. Shi, C. Wang, B. Li, Y. Li, S. Wu, "Heavy metals in food crops, soil, and water in the Lihe River Watershed of the Taihu Region and their potential health risks when ingested", *Science of The Total Environment*, Vol. 615, pp. 141–149(2018).
11. Z. I. Khan, I. Ugulu, S. Sahira, K. Ahmad, A. Ashfaq, N. Mehmood, Y. Dogan, "Determination of Toxic Metals in Fruits of Abelmoschus esculentus Grown in Contaminated Soils with Different Irrigation Sources by Spectroscopic Method", *International Journal of Environmental Research*, Vol. 12:4, pp. 503–511(2018).
12. S. A. Doabi, M. Karami, M. Afyuni, M. Yeganeh, "Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran", *Ecotoxicology and Environmental Safety*, Vol. 163, pp. 153–164(2018).
13. Y. Li, S. Wang, Z. Nan, F. Zang, H. Sun, Q. Zhang, W. Huang, L. Bao, "Accumulation, fractionation and health risk assessment of fluoride and heavy metals in soil-crop systems in northwest China", *Science of The Total* Environment, Vol. 663, pp. 307–314(2019).
14. M. Rahman, M. A. Islam, "Concentrations and Health Risk Assessment of Trace Elements in Cereals, Fruits, and Vegetables of Bangladesh", *Biological Trace Element Research*, (2019).
15. T. Zhong, D. Xue, L. Zhao, X. Zhang, "Concentration of heavy metals in vegetables and potential health risk assessment in China", *Environmental Geochemistry and Health*, Vol. 40:1, pp. 313–322(2017).
16. F. Sanaei, M.M. Amin, Z.P. Alavijeh, R.A. Esfahani, M. Sadeghi, N.S. Bandarrig, A. Fatehizadeh, E. Taheri, M. Rezakazemi, "Health risk assessment of potentially toxic elements intake via food crops consumption: Monte Carlo simulation-based probabilistic and heavy metal pollution index", *Environ Sci Pollut Res*, (2020).
17. S. Kladsomboon, C. Jaiyen, C. Choprathumma, T. Tusai, A. Apilux, "Heavy metals contamination in soil, surface water, crops, and resident blood in Uthai District, Phra Nakhon Si Ayutthaya, Thailand", *Environmental Geochemistry and Health*, (2019).
18. A. Margenat, V. Matamoros, S. Díez, N. Cañameras, J. Comas, J.M. Bayona, "Occurrence and human health implications of chemical contaminants in vegetables grown in peri-urban agriculture", *Environment International*, Vol. 124, pp. 49–57(2019).

19. L. Yang, L. Di, F. Sun, W. Tian, B. Huang, G. Fan, "Bioaccessibility and health risk assessment of trace metals in soils of greenhouse vegetable production near the industrial areas of the Yangtze River Delta, China", *Environmental Science and Pollution Research*, (2020).
20. M.I. Hussain, A.S. Qureshi, "Health risks of heavy metal exposure and microbial contamination through consumption of vegetables irrigated with treated wastewater at Dubai, UAE", *Environmental Science and Pollution Research*, (2020).
21. J.N. Ihedioha, P.O. Ukoha, N.R. Ekere, "Ecological and human health risk assessment of heavy metal contamination in soil of a municipal solid waste dump in Uyo, Nigeria", *Environmental Geochemistry and Health*, (2016).
22. T. Kormoker, R. Proshad, M.S. Islam, T.R. Tusher, M. Uddin, S. Khadka, K. Chandra, A. Sayeed, "Presence of toxic metals in rice with human health hazards in Tangail district of Bangladesh", *International Journal of Environmental Health Research*, (2020).
23. A. Sardar, M. Shahid, Natasha, S. Khalid, H. Anwar, M. Tahir, G.M. Shah, M. Mubeen, "Risk assessment of heavy metal(loid)s via Spinacia oleracea ingestion after sewage water irrigation practices in Vehari District", *Environmental Science and Pollution Research*, (2020).
24. M.A. Islam, D. Romic, M.A. Akber, M. Romic, "Trace metals accumulation in soil irrigated with polluted water and assessment of human health risk from vegetable consumption in Bangladesh", *Environmental Geochemistry and Health*, (2017).
25. R. Proshad, T. Kormoker, M.S. Islam, K. Chandra, "Potential health risk of heavy metals via consumption of rice and vegetables grown in the industrial areas of Bangladesh", *Human and Ecological Risk Assessment*, (2019).
26. T. Eliku, S. Leta, "Heavy metals bioconcentration from soil to vegetables and appraisal of health risk in Koka and Wonji farms, Ethiopia", *Environmental Science and Pollution Research*, Vol. 24:12, pp. 11807–11815(2017).
27. S. Pajević, D. Arsenov, N. Nikolić, M. Borišev, D. Orčić, M. Župunski, N. Mimica-Dukić, "Heavy metal accumulation in vegetable species and health risk assessment in Serbia", *Environmental Monitoring and Assessment*, Vol. 190:8, (2018).

CHAPTER-4

RESULTS AND DISCUSSIONS

4. General information

In the present study water, soil, different crops and vegetables samples were collected from two study areas i.e. Savar Upazila, Dhaka district and Kalihati Upazila, Tangail district. Savar area has been highly recognized for agricultural activities for long time even before having any industrial establishment in this region. Various types of vegetables and crops have been grown in and around of Savar Upazila, for years. However, rapid industrialization and growing urbanization in the Savar region have greatly affected the agricultural activities in this area in recent years. A large variety of industries have been established in Savar area which are continuously discharging almost untreated toxic industrial effluents into surrounding environment and thus constantly contaminating water bodies, sediments, lakes, canals, rivers, and agricultural lands in the respective areas with different types of toxic metallic, non-metallic, and organic substances. The present research works have concentrated on the determination and evaluation of heavy and toxic metals pollution in water bodies, arable soil, as well as crops and vegetables cultivated in the Savar area. The study has also determined the potential ecological impacts and subsequent health risks of people who are highly exposed to industrial contaminated water bodies, crops and vegetables. The present investigation has also included Kalihati Upazila at Tangail districts as a long range contaminated site and collected similar environmental samples such as water, soil, and crops and vegetables. Thus the heavy and toxic metals pollution status in the respective area was also evaluated.

4.1 Heavy and toxic metals pollution in water, soil, crops, and vegetables grown in Savar area (highly contaminated site (HCS): study area–1)

4.1.1 Contamination of irrigation water

The results of heavy and toxic metal analysis in irrigation water samples are presented in the **Table 4.1**. The highest concentration of metal in irrigation water was observed for Fe which was 2.9468 mg/L used in the of Brinjal and the minimum concentration was 0.0022 mg/L found in water used in the rice field (**Table 4.1)** The extent of different metal concentrations was in the order of: Fe>Mn>Ni>Cu>Pb>Cd>As.

Table 4.1: Heavy metal concentrations (mg L^{-1}) in effluent-contaminated water used for irrigation in Savar area: Mean ± SD and (range)

Sample type	Fe	Ni	Mn	Pb	Cu	Cd	As
Water (used in rice(DEPZ) field)	1.6544±0.0034 (1.6513-1.6580)	0.0720±0.0019 (0.0702-0.0739)	0.2654±0.0028 (0.2627-0.2683)	0.0440±0.0030 (0.0413-0.0472)	0.8317±0.0006 (0.8310-0.8321)	0.0713±0.0071 (0.065-0.079)	0.0024±0.0005 (0.002-0.0029)
Water (used in rice(BT) field)	0.8678±0.0049 (0.8628-0.8725)	0.0845±0.0038 (0.0808-0.0883)	1.0697±0.0039 (1.0658-1.0736)	0.0442±0.0037 (0.0409-0.0482)	0.1141±0.0042 (0.1103-0.1186)	0.0352±0.0051 (0.0300-0.0402)	0.0022±0.0005 (0.0019-0.0028)
Water (used in brinjal (DEPZ) field)	2.9468±0.0030 (2.9438-2.9498)	0.3847±0.0042 (0.3805-0.3889)	0.49739±0.0041 (0.49703-4.9783)	0.1423±0.0062 (0.1359-0.1482)	0.1186±0.0049 (0.1136-0.1234)	0.0090±0.0007 (0.0083-0.0096)	0.0042±0.0005 (0.0038-0.0047)
Water (used in lady's finger (DEPZ) field)	0.8858±0.0414 (0.8520-0.9320)	0.9651±0.0047 (0.9603-0.9697)	0.3649±0.0043 (0.3608-0.3694)	0.1757±0.0039 (0.1719-0.1796)	0.1462±0.0035 (0.1427-0.1497)	0.0543±0.0053 (0.0500-0.0602)	0.0026±0.0006 (0.0020-0.0032)
Water (used in water spinach (DEPZ) field)	1.9469±0.0030 (1.9438-1.9498)	0.0843±0.0043 (0.0804-0.0889)	0.1761±0.0034 (0.1728-0.1796)	0.1438±0.0033 (0.1412-0.1475)	0.0839±0.0041 (0.0803-0.0884)	0.0233±0.0031 (0.0200-0.0260)	0.0032±0.0004 (0.0029-0.0036)
Water (used in red spinach (BT) field)	1.0989±0.0040 (1.0948-1.1028)	0.0523±0.0033 (0.0492-0.0558)	0.8366±0.0031 (0.8332-0.8391)	0.1674±0.0029 (0.1641-0.1698)	0.1545±0.0040 (0.1503-0.1583)	0.0083±0.0011 (0.0074-0.0095)	0.0030±0.0008 (0.0023-0.0038)
Water (used in green spinach (DEPZ) field)	1.8265±0.0034 (1.8229-1.8297)	0.2553±0.0034 (0.2518-0.2585)	0.3832±0.0036 (0.3802-0.3871)	0.1742±0.0040 (0.1704-0.1783)	0.1099±0.0035 (0.1068-0.1137)	0.0603±0.0068 (0.0537-0.0673)	0.0029±0.0009 (0.0020-0.0038)
Water (used in green spinach (BT) field)	2.9353±0.0039 (2.9317-2.9395)	0.7490±0.0038 (0.7452-0.7528)	0.9362±0.0035 (0.9327-0.9397)	0.1244±0.0046 (0.1204-0.1294)	0.1368±0.0030 (0.1337-0.1396)	0.0260±0.0052 (0.0200-0.0294)	0.0026±0.0006 (0.0020-0.0031)
Water (used in spinach (BT) field)	2.9364±0.0036 (2.9327-5.9399)	0.7934±0.0055 (0.7883-0.7993)	0.1932±0.0037 (0.1902-0.1973)	0.1362±0.0035 (0.1327-0.1396)	0.0757±0.0039 (0.0717-0.0795)	0.0908±0.0021 (0.0893-0.0932)	0.0036±0.0006 (0.0030-0.0041)
Safe limit[a]	5	0.2	0.2	5	0.2	0.01	0.1
Safe limit[b]	-	-	0.1	0.1	0.05	0.01	-
Safe limit[c]	-	1.5	-	2.5	30	1.5	-

[a]FAO standard (www.fao.org/3/t0234e/t0234e06.htm); [b] Indian Standard (Awashthi 2000); [c]USEPA standard (2010); DEPZ means Dhaka Export Processing Zone and BT means Bank Town area.

The range of different heavy metals concentration in water are: Fe (0.8678-2.9468 mg/L), Mn (0.1761-1.0697 mg/L), Ni(0.0523-0.9651 mg/L), Cu (0.0757-0.8317mg/L), Pb (0.0440-0.1757 mg/L), Cd (0.0083-0.0908 mg/L), and As (0.0022-0.0042 mg/L). Among all of the metals studied, the extent of arsenic was observed lowest in each of the water samples. Nowadays, the application treated waste water in irrigation and other agricultural activities has become a very common practice in most of the developing countries due to scarcity of enough fresh water. Small and progressive farmers often use the treated waste water in irrigation for the production of crops and vegetables all over the world [1, 2]. Metal concentrations observed in all water samples in the present study were compared with the permissible levels set by FAO, USEPA and other countries (**Table 4.1**). The data observed in water bodies for different heavy metals in the present study are highly comparable to the results reported previously by Ugulu *et al.* [3] and Sardar *et al.* [7]. Though Fe concentrations were recorded highest among all other metals examined, these concentrations were lower than the maximum allowable limit reported by FAO and USEPA. However, Ni concentrations in five water samples were found higher than the tolerable limit of FAO and USEPA. The extents of Mn and Pb in water were higher than Indian standard and USEPA standard except for Pb in two water samples in the corresponding metal quantities were lower than the permissible level of FAO (**Table 4.1**). Arsenic concentrations in all water samples were found lower than FAO standard. The result shows that Cd concentrations in irrigation water were observed to be higher than permissible levels of FAO and Indian standard. Appearance of relatively larger quantity of cadmium in water bodies may be due to direct discharge of cadmium contaminated industrial and municipal wastes [4, 5]. Most of the Cu concentrations were higher than Indian standard, however they were found to be lower than USEPA standard. Higher concentration of Cu in water might be attributed by the contamination of water bodies from the direct emission of liquid wastes from metal processing and tanning industries of the respective areas [6]. Water pollution load index caused by the presence of excessive level of metals in water bodies is displayed in the **Figure 4.1**. The diagram (**Figure 4.1**) above demonstrates that Nickel and lead pollution were relatively higher in most of the irrigation water samples. Similarly the pollution load index values for manganese, copper, and cadmium the contaminated water bodies were very much higher than the recommended safety limits.

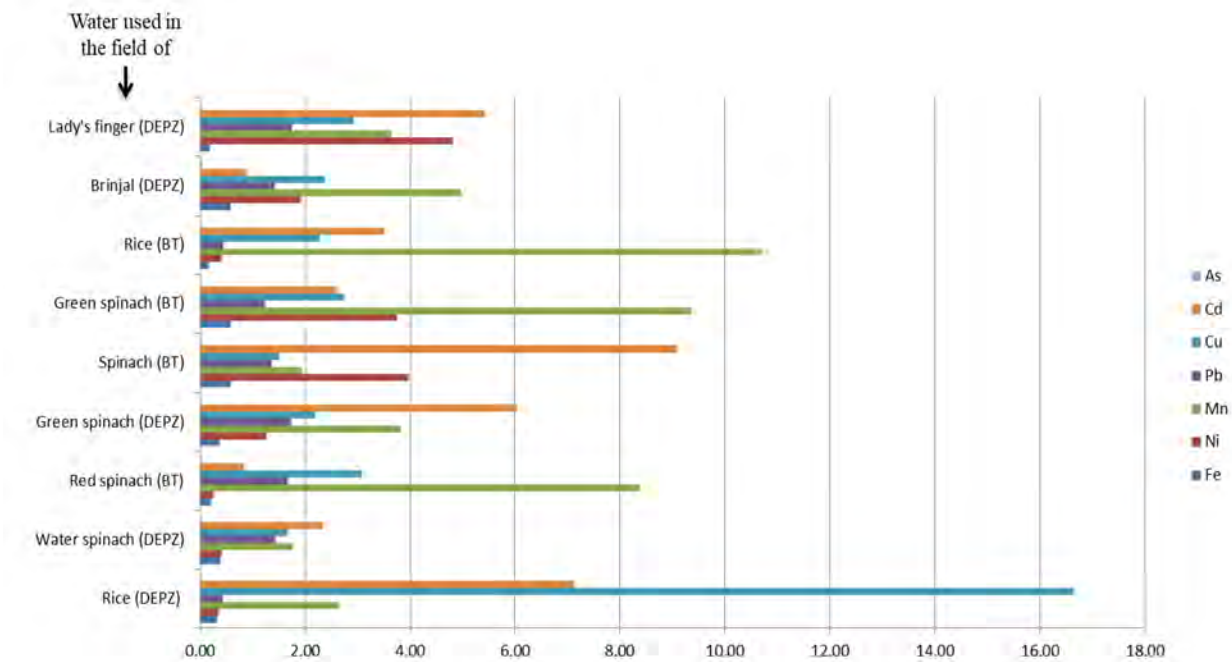


Figure 4.1: Water pollution load index

Based on FAO standard it has been realized that irrigation water is highly polluted with Mn and Cd and comparing with the USEPA and Indian permissible levels water is highly contaminated with Mn, Pb, Cu, and Cd.

4.1.2 Contamination of arable soil

The results of different metal concentrations found in agricultural soil have been displayed in the **Table 4.2**. Iron concentration was found highest and the minimum concentration was observed for cadmium in all soil samples. Soil from the paddy field accumulates highest amount of iron (54447.04 mg/kg) and nickel (85.47 mg/kg) as well as the highest amount of arsenic (16.70 mg/kg). Lowest concentration of iron was 11810.93 mg/kg found in soil of Lady's finger (DEPZ) field whereas the lowest concentration of arsenic (12.09 mg/kg) was observed in soil of Green spinach (BT) field which also contained the highest concentration of manganese (161.71 mg/kg). Soil of Red spinach (BT) field contained the lowest concentration of both manganese (54.33 mg/kg) and lead (8.62 mg/kg) whereas soil from Water spinach (DEPZ) field accumulates the maximum amount of lead (35.23 mg/kg), copper (89.56 mg/kg) and cadmium (9.69 mg/kg). Lowest amount of copper (12.55 mg/kg) and cadmium (6.60 mg/kg) were determined in soil of Brinjal (DEPZ) and Green spinach (DEPZ) fields respectively.

Table 4.2: Heavy metal concentrations (mg kg^{-1}) in soil contaminated by waste water in Savar area: Mean ± SD and (range)

Sample type	Fe	Ni	Mn	Pb	Cu	Cd	As
Soil (from rice (DEPZ) field)	54447.04±427.53 (54018.52-54873.58)	85.47±6.07 (79.21-91.34)	138.30±10.88 (127.27-149.03)	17.34±1.03 (16.18-18.14)	25.66±1.39 (24.19-26.96)	7.40±0.68 (6.73-8.09)	12.86±1.09 (11.79-13.96)
Soil (from rice (BT) field)	45159.42±373.60 (44781.25-45528.27)	13.44±1.05 (12.58-14.61)	149.42±11.02 (138.92-160.89)	23.50±1.53 (21.97-25.03)	40.39±3.05 (37.54-43.61)	9.64±0.81 (9.02-10.55)	16.70±1.09 (15.62-17.79)
Soil (from brinjal (DEPZ) field)	12252.32±167.30 (12069.18-12397.13)	31.48±2.06 (29.59-33.67)	123.48±11.04 (112.61-134.68)	17.05±1.32 (15.63-18.24)	12.55±1.05 (11.37-13.38)	6.94±0.74 (6.16-7.63)	12.84±0.92 (11.92-13.75)
Soil (from lady's finger (DEPZ) field)	11810.93±126.84 (11678.81-11931.72)	36.41±2.11 (36.18-37.38)	66.19±4.46 (61.74-70.66)	27.23±2.33 (24.98-29.63)	47.48±4.37 (43.19-51.92)	8.49±0.84 (7.96-9.46)	13.01±0.88 (12.18-13.93)
Soil (from water spinach (DEPZ) field	37288.57±403.57 (36884.98-37692.12)	61.26±3.47 (57.79-64.73)	82.45±6.03 (76.28-88.32)	35.23±2.30 (33.23-37.74)	89.56±6.95 (82.79-96.68)	9.69±0.86 (8.98-10.64)	15.00±0.79 (14.38-15.89)
Soil (from red spinach (BT) field)	43921.91±336.31 (43560.37-44225.46)	14.25±1.05 (13.19-15.28)	54.33±3.46 (50.91-57.82)	8.62±0.97 (7.92-9.73)	42.17±3.59 (38.29-45.37)	8.28±0.88 (7.28-8.94)	12.68±0.75 (12.02-13.49)
Soil (from green spinach (DEPZ) field	29613.35±159.33 (29429.66-29714.22)	34.54±2.49 (31.99-36.96)	60.54±4.58 (60.02-61.18)	9.06±0.89 (8.19-9.96)	19.58±1.06 (18.39-20.42)	6.60±0.89 (5.62-7.35)	14.01±0.91 (13.14-14.95)
Soil (from green spinach (BT) field)	19344.26±180.16 (19161.04-19521.19)	14.62±1.08 (13.76-15.83)	54.63±4.03 (50.79-58.82)	11.17±1.02 (10.02-11.98)	42.53±2.99 (39.39-45.35)	8.73±0.82 (8.06-9.65)	12.09±0.77 (11.29-12.82)
Soil (from spinach (BT) field	19104.51±154.76 (18944.71-19253.69)	65.43±4.11 (61.48-69.69)	161.71±11.97 (149.58-173.52)	12.66±0.97 (11.73-13.67)	16.24±1.00 (15.13-17.08)	7.77±0.84 (7.04-8.69)	12.08±0.81 (11.33-12.94)
Safe limit[a]	40000	50	1000	35	30	0.35	6
Safe limit[b]	-	60	-	250	100	0.6	40
Safe limit[c]	-	50	2000	100	100	3	-

[a]Coskun *et al.* (2006); [b]MAC National Environmental Protection Agency of China, GB 15618 (1995); [c]European Union Standards European Union (2006); DEPZ means Dhaka Export Processing Zone and BT means Bank Town area.

Appearance of highest concentration of Fe in soil might be due to the long-term use of Fe in the production of machine tools, pigments, paints, and alloying in various industries of the study area (Ahmad *et al.*) [8]. The arable soil may contain relatively lower Cd contents which might be supported by the results of previous studies conducted by Leblebici *et al.* [9]. The order of other metals contents in soil was found to be: Mn>Ni> Cu >Pb>As. Fe and Ni concentrations in all soil samples were found to be lower than the permissible levels recommended by Coskun *et al.* [10]. Mn, Pb, and Cu concentrations in most of the soil samples were observed to be lower that the permissible limits reported by EU, USEPA, China, India, and Coskun *et al.* (**Table 4.2**) [10]. Cd and As concentrations in all soil samples were found to be higher than tolerable levels reported by Coskun *et al.*[10]. However, in some cases, the metal concentration data were within the permissible levels of MAC National Environmental Protection Agency of China, GB 15618 (1995). Higher heavy metal concentrations demonstrate the contamination of arable soil which is also explained by soil pollution load index given in the **Figure 4.2**. Cd, Cu, As, and Ni showed relatively higher pollution load index values in most of the soil samples studied. Among the seven metals, the highest PLI in soil was observed for Cd and the minimum PLI was recorded for Mn. **Figure 4.2** shows a very large variation of pollution load index (PLI) as it ranges from 27.69 to 0.054. Among the seven metals, the highest PLI value was found for Cd in soil from water spinach field (DEPZ) and the minimum PLI was found for Mn in soil from Red spinach field (BT).

4.1.3 Heavy and toxic metal contamination in crops and vegetables

Heavy metal concentrations determined in various crops and vegetables samples in the present investigation has been presented in **Table 4.3**. The highest concentration of heavy metal was recorded for iron (510.31 mg/kg) in Green spinach (BT) whereas the lowest concentration was recorded for arsenic (0.78 mg/kg) in Rice (BT). In all crops and vegetable samples the maximum accumulation was realized with iron and lowest accumulation trend was noticed for arsenic with the exception of Red spinach (BT) in which the lowest uptake of metal by the plant was Cd. Average metal concentrations in different crops and vegetables samples was found in the order of Fe>Mn>Ni>Cu>Pb>Cd>As. Analysis of metals in different parts of plant bodies revealed that in most cases concentrations of heavy metals were observed much higher in roots in comparison to the upper parts of plant bodies.

However, in some cases, metal concentrations were found higher in the edible part than root. This might be due to the variation in the uptake of metals in different parts of the plant bodies. Highest concentration of Ni (49.00 mg/kg), Mn (174.23 mg/kg), Pb (8.75 mg/kg), Cu (19.73 mg/kg), Cd (3.05 mg/kg) and As (1.45 mg/kg) were found in Green spinach (DEPZ), Red spinach (BT), Water spinach (DEPZ), Rice (DEPZ), Brinjal (DEPZ) and Red spinach (BT) respectively. The lowest concentration of Fe (125.58 mg/kg), Ni (14.30 mg/kg), Mn (19.61 mg/kg), Pb (5.47 mg/kg), Cu (8.90 mg/kg) and Cd (1.00 mg/kg) were observed in Lady's finger (DEPZ), Rice (DEPZ), Rice (BT), Green spinach (DEPZ) and Red spinach (BT).

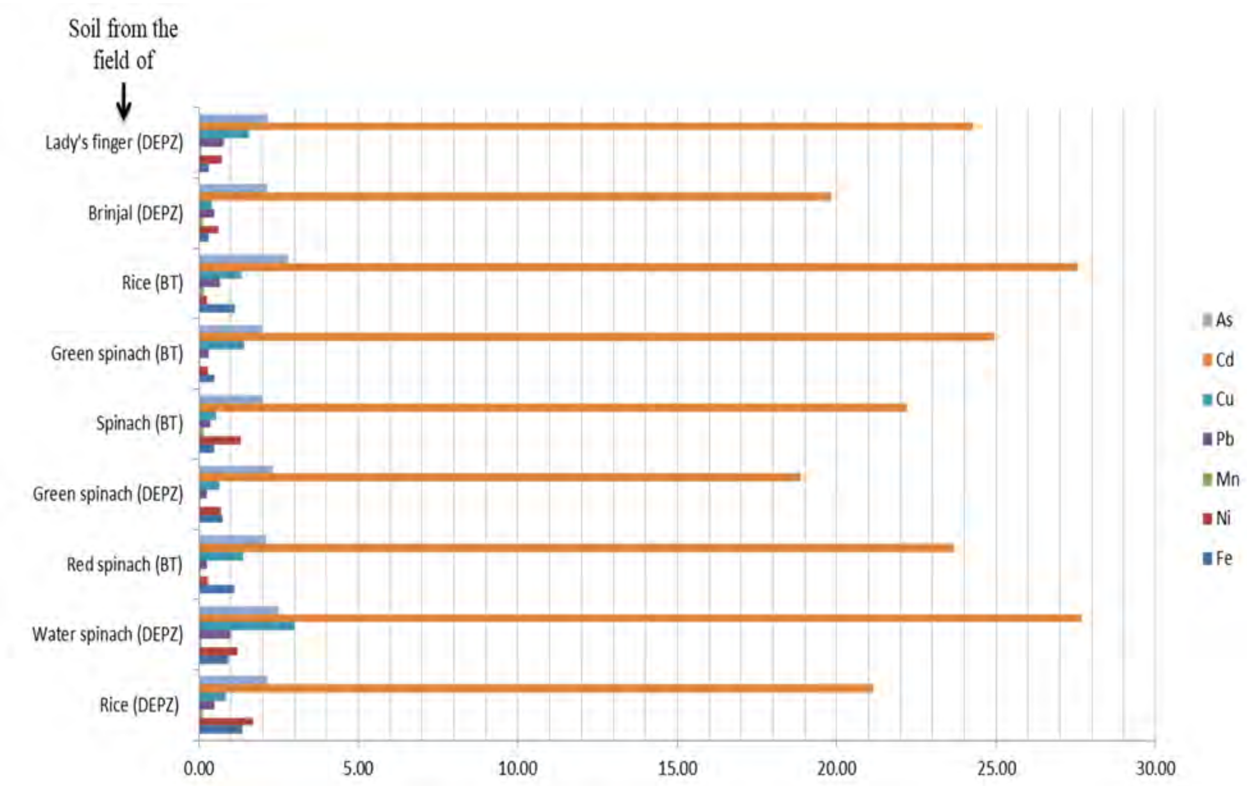


Figure 4.2: Soil pollution load index

All heavy metal concentrations determined in different crops and vegetables samples in the present study were compared with the permissible values of FAO/WHO, EU, USEPA, Indian standard and others (Gebeyehu *et al.*) [11]. Highest accumulation of Fe in edible part of all the crops and vegetable samples in the present study showed a good agreement with the results reported by Latif *et al.* for metal analysis in similar vegetables grown in the other country [12].

Table 4.3: Heavy metal concentrations (mg kg^{-1}) in crops and vegetables grown in Savar industrial area of Dhaka, Bangladesh: Mean ± SD and (range)

Sample source	Plant organs	Fe	Ni	Mn	Pb	Cu	Cd	As
Rice (DEPZ)	Root	2938.82±60.04 (2893.38-3006.89)	78.28±5.46 (72.27-82.93)	123.33±5.68 (117.96-129.28)	15.19±1.14 (13.92-16.13)	65.35±2.90 (62.27-68.02)	1.97±0.32 (1.68-2.31)	1.92±0.11 (1.81-2.02)
	Edible Part	345.47±18.73 (327.22-364.64)	14.30±1.04 (13.22-15.30)	26.24±1.10 (25.01-27.13)	5.47±0.94 (4.80-6.55)	19.73±1.08 (18.93-20.96)	1.57±0.30 (1.25-1.83)	0.86±0.13 (0.74-0.99)
Rice (BT)	Root	2467.59±71.89 (2395.21-2538.97)	103.33±6.89 (97.74-111.02)	126.51±8.65 (117.87-135.16)	14.36±0.62 (13.82-15.03)	32.56±1.39 (31.17-33.94)	3.66±0.36 (3.27-3.97)	1.13±0.10 (1.03-1.22)
	Edible Part	509.74±20.27 (489.12-529.63)	16.83±1.34 (15.55-18.23)	19.61±1.19 (18.30-20.62)	5.89±0.81 (5.30-6.82)	10.97±0.98 (9.86-11.69)	2.75±0.28 (2.43-2.97)	0.78±0.09 (0.68-0.84)
Brinjal (DEPZ)	Root	1137.41±68.76 (1083.45-1214.83)	28.43±2.47 (26.38-31.17)	55.93±3.99 (51.79-59.76)	5.28±0.83 (4.43-6.09)	27.07±1.08 (26.21-28.28)	1.86±0.26 (1.57-2.06)	0.68±0.06 (0.62-0.74)
	Edible Part	150.38±14.75 (138.07-166.73)	22.71±1.56 (21.18-24.29)	21.06±1.86 (19.03-22.67)	8.74±0.71 (7.99-9.39)	16.51±0.85 (15.83-17.46)	3.05±0.27 (2.78-3.31)	0.93±0.09 (0.82-0.99)
Lady's finger (DEPZ)	Root	1085.29±75.71 (997.86-1129.22)	21.84±1.75 (19.86-23.17)	50.09±3.91 (46.03-53.82)	5.53±0.64 (4.89-6.16)	21.86±1.28 (20.81-23.29)	3.42±0.38 (3.07-3.82)	0.75±0.06 (0.70-0.82)
	Edible Part	125.58±16.34 (109.88-142.50)	30.33±3.25 (26.92-33.39)	92.99±6.25 (86.59-99.07)	5.83±0.93 (5.10-6.88)	14.54±0.94 (13.47-15.23)	2.58±0.40 (2.15-2.93)	1.33±0.11 (1.26-1.46)
Water spinach (DEPZ)	Root	1072.10±42.92 (1023.87-1106.08)	36.27±2.86 (33.24-38.91)	35.92±2.22 (33.85-38.27)	6.35±0.67 (5.74-7.07)	24.81±1.12 (23.84-26.03)	2.39±0.32 (2.14-2.75)	1.03±0.13 (0.94-1.17)
	Edible Part	432.91±17.19 (414.98-449.26)	26.16±1.38 (24.78-27.53)	66.20±3.14 (62.93-69.19)	8.75±1.00 (8.02-9.89)	18.25±0.98 (17.14-19.02)	1.36±0.33 (1.02-1.68)	0.84±0.09 (0.74-0.92)
Red spinach (BT)	Root	1459.71±69.45 (1382.83-1517.93)	126.88±9.95 (117.89-137.57)	90.07±5.49 (84.96-95.88)	26.05±1.24 (24.89-27.36)	23.57±1.33 (22.26-24.92)	1.91±0.23 (1.74-2.17)	1.88±0.08 (1.82-1.97)
	Edible Part	246.23±19.17 (225.27-262.87)	20.23±2.49 (17.49-22.36)	374.23±7.29 (367.29-381.83)	7.28±0.96 (6.48-8.35)	15.43±1.06 (14.25-16.31)	1.00±0.35 (0.68-1.37)	1.45±0.16 (1.29-1.60)
Green spinach (DEPZ)	Root	1452.89±65.97 (1392.47-1523.28)	52.22±3.45 (48.49-55.31)	63.75±4.46 (59.27-68.18)	6.62±0.62 (5.97-7.20)	11.48±0.78 (10.83-12.34)	3.46±0.34 (3.07-3.72)	2.53±0.10 (2.42-2.59)
	Edible Part	305.52±24.58 (279.18-327.86)	49.00±2.03 (47.09-51.14)	425.99±16.38 (409.03-441.72)	6.18±0.77 (5.49-7.01)	9.54±0.94 (8.52-10.36)	2.76±0.29 (2.47-3.04)	1.18±0.11 (1.07-1.29)
Green spinach (BT)	Root	1906.71±46.41 (1867.63-1958.00)	44.77±2.66 (41.83-47.02)	52.42±4.11 (48.49-56.68)	15.48±1.04 (14.33-16.37)	16.43±0.84 (15.83-17.39)	2.59±0.34 (2.31-2.97)	1.51±0.09 (1.41-1.59)
	Edible Part	510.31±25.49 (486.66-537.30)	17.66±1.55 (16.12-19.22)	40.39±1.95 (38.62-42.48)	6.69±0.93 (5.83-7.67)	11.20±0.90 (10.18-11.89)	2.23±0.20 (2.02-2.41)	0.95±0.14 (0.81-1.09)
Safe limit[abcd]		425[a]	0.5[c]	500[b]	0.2[c]	20[d]	0.3[a]	0.1[c]
Safe limit[e]		-	10	500	0.1-0.3	10-40	0.05-0.2	0.1
Safe limit[f]		-	1.5	-	2.5	30	1.5	-

[a]FAO/WHO standard (Codex Alimentarious Commission 1984); [b]WHO/FAO (2007); [c](JECFA 2005); [c](FAO/WHO 2002b); [d]European Union Standards European Union (2006); [e]Gebeyehu *et al.*[11]; [f]Indian Standard (Awashthi 2000); DEPZ means Dhaka Export Processing Zone and BT means Bank Town area

The presence of higher concentration of Fe in crops and vegetables might be due to the long-term use of Fe in the production of machine tools, pigments, paints, and alloying in various industries of the study area. Lower accumulation of As in all crops and vegetable samples was highly related to the extent of As in the respective arable soil in which the As concentration was also observed in lesser quantity. The arsenic data obtained from the present study was more or less similar to the research findings of Margenat *et al.* which was conducted in the vegetables grown in Barcelona, Spain [13]. Arsenic concentrations in crops and vegetables from the present investigation were lower than those observed in the similar research conducted by *Gebeyehu et al.* in Mojo, Ethiopia [11]. However, the data were found higher than those obtained from another research work performed in agricultural plants cultivated in the industrial zone in Beijing, China (Bo *et al.*) [14]. All the samples showed Ni concentrations higher than the permissible level of JECFA and Indian standard. Ni contents determined in the present research was also significantly higher than the data reported from similar studies performed in different countries such as in Barcelona, Spain by Margenat *et al.* ; Beijing, China by Bo *et al.* and Lahore, Pakistan by Mahmood *et al.)* [13, 14, 15]. Appearance of such a high concentrations of nickel in crops and vegetables might be due to the discharging of effluents from battery industry, nickel-plated jewelry industry, machine parts industry, steel, wire and electrical parts manufacturing industries etc. in the respective areas. Mn contents observed in all crops and vegetables samples were significantly more than the safety limits of FAO, USEPA, and EU. Concentrations of Mn obtained from the present investigation were also found higher than the results of metal contamination study performed by Mahmood *et al.* [15] in Lahore, Pakistan but they were relatively lower than the Mn contents determined by Gebeyehu *et al.*[11] in similar vegetables grown in Mojo, Ethiopia. Contamination of food plants by manganese might be arised from the emission of manganese enriched effluents from manganese alloy production industry, ceramics production industry and glass manufacturing industry. Application of manganese-containing agrochemicals, aluminum cans production, and welding activities may also release Mn enrich effluents and thus can contaminate the surrounding agricultural areas. All the crops and vegetables showed Pb concentrations higher than the tolerable levels of FAO/WHO, USEPA, and other sources.

Pb contents determined in the present were also observed to be higher than those observed in the similar studies conducted in Mojo, Ethiopia (Gebeyehu *et al.*) [11] as well the data were highly comparable to the findings of other study performed in agricultural plants grown in the around the Tangail city, Bangladesh (Proshad *et al.*) [16]. The sources of the contamination of lead in agricultural plants may include painting of homes with lead containing products, plumbing with lead pipes, uses of lead bullets and lead storage batteries. Automobile emission may be another cause of higher Pb pollution in crops and vegetables as the study area is located adjacent to the major highways. In comparison to the EU standard and Indian standard, Cu concentrations in crops and vegetables were below the permissible values. However, the trend of copper accumulation in different food plants was highly comparable and showed a good agreement with the results of the similar metal contamination studies conducted previously in different countries around the world (Mojo, Ethiopia by Gebeyehu *et al.* [11]; Latif *et al.*[12] at Dera Ghazi Khan, Pakistan; Beijing, China Bo *et al.* [14]; Tamale Municipal, Ghana by Ametepey *et al.* [17]). The **Table 4.4** shows the comparison of the results of heavy and toxic metal analysis in crops and vegetables in the present investigation with other research works conducted previously in various industrially contaminated agricultural plants including crops and vegetables in different countries in the world. Elevated concentrations of Cd were realized in most of the crops and vegetables samples which were significantly more than the permissible limits of FAO/WHO, US-EPA, EU, China, and India (**Table 4.3**). Comparison of Cd contents measured in the food plants in the present investigation with other similar studies showed that the Cd levels in crops and vegetables were higher than those found in the vegetables grown in Tamale Municipal area, Ghana (Ametepey *et al.*) [17] and the data were lower than those observed in agricultural plants grown in Noakhali District, Bangladesh (Rahman *et al.*) [18]. Incorporation of copper and cadmium into the food chain might be due to the discharge of toxic effluents from copper pipe manufacturing industry, cables, wires, copper cookware, plating, rayon, pesticides, paints, pigments paints, pigments alloys, coatings, batteries as well as plastics manufacturing industries in the respective areas. Pollution load index values of crops and vegetables from the Savar area (study area-1) are illustrated in the **Figure 4.3**. The figure demonstrate that PLI values for lead and nickel were about 35 folds higher than the permissible levels for all the studied samples. The extents of cadmium and arsenic pollution in all crops and vegetables were also much above the tolerable limit (about 8 times higher than the safety level).

All other metals also showed PLI values higher than the permissible levels in most of the crops and vegetables samples. Appearance of higher PLI values for metals in most of the agricultural plants particularly in the edible parts were strongly correlated to the elevated concentration of those metals in the respective arable soil and irrigation water (Coskun *et al.*) [10].

4.1.4 Mobilization of heavy metals

Mobilization of any metal from water, soil to plant bodies can be evaluated using Bioconcentration Factor (BCF). BCF values for different metals in various environmental samples are presented in the **Figure 4.4**. In case of mobilization of metals from soil to food, the highest BCF value was recorded 3.207 for Mn in Red spinach (BT) and lowest value was 0.05 found for As in Rice (DEPZ). There were significant variations among the BCF values of different metals in various crops and vegetables. This might be due to the presence of different metal concentrations in arable soil of the corresponding crops and vegetables fields as well as the variation in the metals uptake capacities of different crops and vegetables (Cui *et al.*) [19]. According to WHO/FAO guidelines 2011, the heavy metal contamination may occur if the BCF value exceeds 0.2.

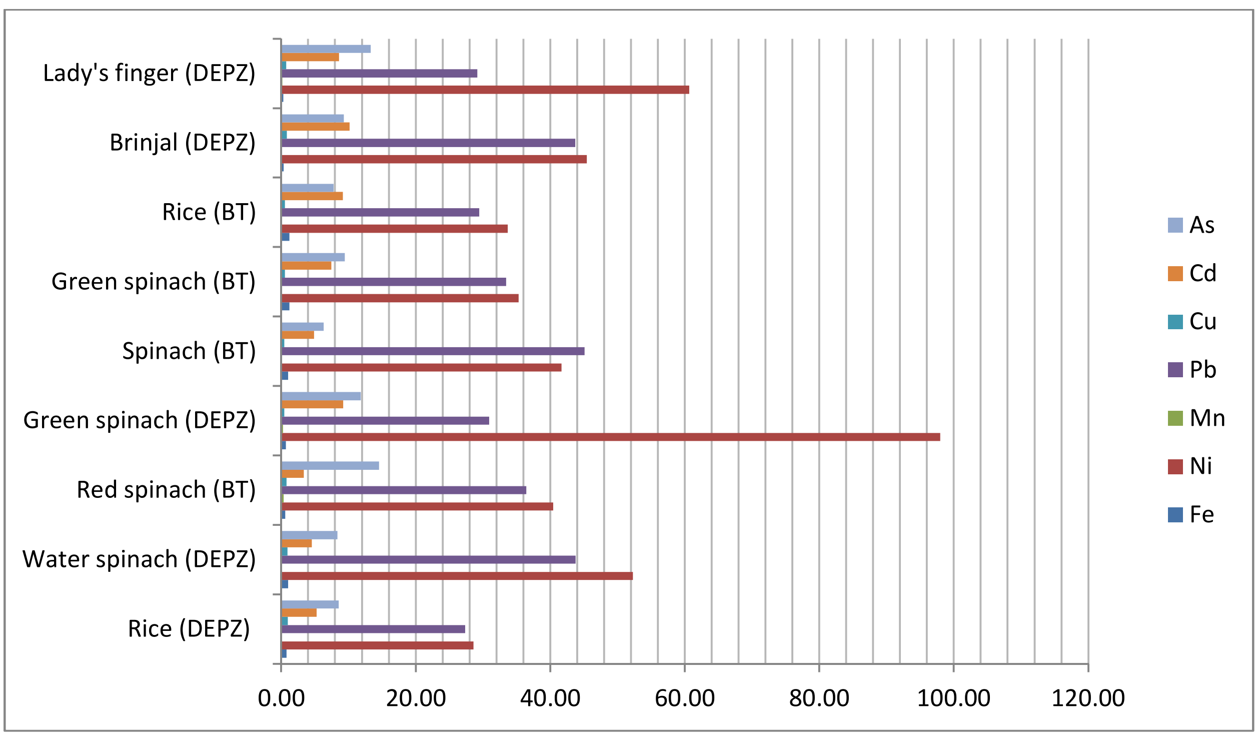


Figure 4.3: Pollution load index of crops and vegetables grown around industrial environment

Table 4.4: Comparison of the results of the present investigation with the research findings reported previously in the literatures

District (Country)	Fe	Ni	Mn	Pb	Cu	Cd	As	References
DEPZ Area (Bangladesh)	328.27 (125.58-510.31)	24.65 (14.30-49.00)	70.84 (19.61-174.23)	6.86 (5.47-8.75)	14.52 (9.54-19.73)	2.17 (1.00-3.05)	1.04 (0.78-1.45)	This study
Dera Ghazi Khan (Pakistan)	384.35 (129.00-968.25)	3.63 (1.8-5.05)	47.36 (18.67-137.30)	-	34.9 (22.25-65.24)	0.26 (0.04-0.39)	-	Latif *et al.* [12]
Beijing (China)	-	0.053 (0.001- 1.689)	-	0.046 (0.001- 0.655)	0.51 (0.024- 8.25)	0.010 (0.001- 0.101)	0.013 (0.001- 0.479)	Bo *et al.* [14]
Tamale Municipal (Ghana)	3.71 (3.04-4.47)	-	0.17 (0.06-0.95)	BDL (BDL-0.04)	0.07 (0.04-0.09)	0.05 (0.01-0.07)	-	Ametepey *et al.* [17]
Lahore (Pakistan)	-	5.75 (0.18-32.51)	29.28 (6.57-87.37)	1.65 (0.19-4.23)	4.93 (1.09-10.94)	0.51 (0.08-3.08)	-	Mahmood *et al.* [15]
Noakhali (Bangladesh)	-	2.1 (0.32–5.68)	124 (4–881)	3.1 (0.67–16.5)	18 (2–86)	134 (6–428)	113 (11–464)	Rahman *et al.* [18]
Mojo (Ethiopia)	287.78	2.995	164.715	5.595	12.845	1.06	3.83	Gebeyehu *et al.* [11]
Barcelona (Spain)	-	0.06	2.25	0.08	1.33	0.009	0.0003	Margenat *et al.* [13]

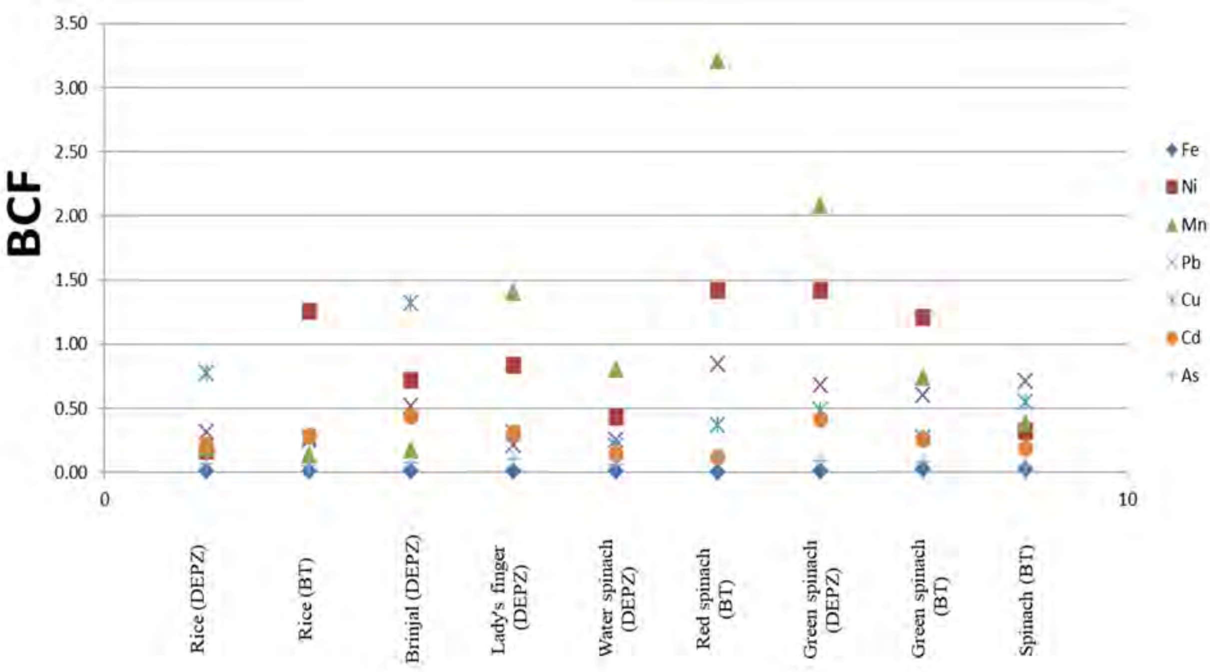


Figure 4.4: Bioconcentration factor (BCF) of heavy metals in different crops and vegetables of the study area

In rice collected from around DEPZ area, Savar, the highest and lowest BCF value was recorded for Cu and Fe respectively, which indicates that paddy plants accumulates Cu most and they have the lowest tendency to uptake Fe. The order of BCF values for other metals is observed to be: Pb>Cd>Mn>Ni>As. However, for the paddy plants collected from Bank Town area of Savar the order of BCF values was: Ni>Cd>Cu>Pb>Mn>As>Fe. BCF value of Ni was 1.25 which was much higher than the other metals indicating the very higher probability of occurring Ni pollution in rice as well as in other vegetables. The order of BCF values of seven metals in Brinjal (DEPZ) was: Cu>Ni> Pb> Cd> Mn>As>Fe; Lady's finger (DEPZ): Mn> Ni>Cu> Cd>Pb>As>Fe, Green spinach (BT): Ni>Mn> Pb> Cu> Cd>As>Fe. These results indicate that the affinity of different crops and vegetables to accumulate and uptake metals are varied significantly among the metals. Minimum metal pollution was realized for Fe as indicated by the lower BCF value which is also demonstrated in a previous study performed by Ahmed *et al.* [20]. Mn and Ni pollution in every crop and vegetable sample were relatively higher as reflected by their respective BCF values (**Figure 4.4**).

Higher metal BCF values in different crops and vegetables demonstrates the excessive uptake of various metals by the respective agricultural plants which may depend on the availability of metals in arable soil, irrigation water, speciation of metals, nature of plants, moisture content, and growth of the plants (Gemeda *et al.*, Sultana *et al.*) [21, 22].

4.1.5 Human health risks assessment

Human health risks assessments were determined by the evaluation of both carcinogenic and non-carcinogenic risks associated with direct or indirect consumption of metal contaminated crops and vegetables. Total target hazard quotient (TTHQ) expresses the total non-carcinogenic risk due to consumption of any contaminated crops or vegetables.

4.1.5.1 Estimated daily intake

Estimated daily intake expresses the amount of heavy metal taken by anybody due to consumption of food items. Generally EDI of individual metal for each food item was calculated. In the present study EDI for both adult and children were investigated and the corresponding data are presented in **Table 4.5**. The results show that calculated TEDI (Total Estimated Daily Intake) values were much higher than maximum tolerable daily intake for all the metals. EDI values of all seven metals for children were found to be higher than those obtained for adult. Highest TEDI value was 7460.84 recorded for Fe in children whereas the minimum value was 15.31 was found for As (**Table 4.5**). To determine the health risks associated with direct or indirect exposure of metals through the contaminated foods, it is highly necessary to determine their estimated daily intake (EDI) (Latif *et al.*)[12]. The calculated EDI data of different metals in the present study indicates that both adults and children are at a high risk of heavy and toxic metal pollution through the consumption crops and vegetables grown in and around industrial areas of Bangladesh. The results of EDI calculation clearly show that children are having a greater health risks compared to the adults since the TEDI values of each metal for children were found much higher than the adults. The TEDI calculation in crops and vegetables from a research work in Beijing, China by Bo *et al.*[14] also showed the similar results.

The TEDI values of different metals for adults were observed as Cu(47.03), Pb(440.85), Fe(342.51), Ni(485.07), Mn(215.31), Cd(16.31), As(116.40) which were sever folds higher than the MTDI values of metals such as 3.02% (Cu), 1.32% (Pb), 73.37% (Fe), 6.23% (Ni), 15.37% (Mn), 0.47% (Cd), 0.22% (As) of total heavy metal intake respectively. Similarly TEDI values of different metals for children were found as Cu(66.57), Pb(625.41), Fe(488.50), Ni(688.71), Mn(307.62), Cd(23.06), As(165.15) which were times more than the MTDI values of metals and the results are 3.00% (Cu), 1.32% (Pb), 73.39% (Fe), 6.21% (Ni), 15.41% (Mn), 0.46% (Cd), 0.22% (As) of total heavy metal intake respectively. These data also suggest that the percentages of total heavy metal intake for different metals are almost identical for both children and adults.

4.1.5.2 Non carcinogenic risks

The parameter which is most commonly used to explain the non-carcinogenic risks associated with heavy and toxic metal intake is the target hazard quotient (THQ). THQ demonstrates the non-carcinogenic risks associated with individual metal for the consumption of each food item. Total target hazard quotient (TTHQ) represents the total non-carcinogenic risks exerted by all studied metals due to the consumption of any specific food item. Hazard index (HI) of metal was also investigated in the present study. The estimated THQ, TTHQ, and HI values of different metals are presented in the **Table 4.6**. In the present study, very large range of THQ values was obtained. Maximum THQ value was recorded for Fe (54.30) in children in Rice (DEPZ) whereas the lowest value was found for Mn (0.03) in adult for Water spinach (DEPZ) **Table 4.6**. Similarly, TTHQ values of metals in different crops and vegetables also displayed a large variation (3.49-148.47) **Figure 4.5**. The lowest TTHQ value was obtained for adult in Water spinach (DEPZ) while the maximum value was found for children in Rice (BT). Higher the hazard index (HI) greater the health risk. HI values of metals for children were also observed to be higher than those observed in adult. THQ values of Cu were found higher than the acceptable value 1 for both adult and children in all the studied crops and vegetables except in Rice (BT) associated with adult. The metal health risk data from the present investigation were significantly higher than the results reported previously by Li *et al.*; Margenat *et al.*)[24, 13].

Table 4.5: Estimated daily intake (EDI) of different metals from crops and vegetables

Sample	EDI													
	Cu		Pb		Fe		Ni		Mn		Cd		As	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Rice (DEPZ)	114.70	162.89	31.80	45.16	2008.00	2851.66	83.12	118.04	152.52	216.60	9.14	12.99	4.98	7.07
Rice (BT)	2.56	4.22	1.38	2.27	118.94	195.93	3.93	6.47	4.57	7.54	0.64	1.06	0.18	0.30
Brinjal (DEPZ)	7.28	7.68	3.85	4.06	66.27	69.93	10.01	10.56	9.28	9.79	1.35	1.42	0.41	0.43
Lady's finger (DEPZ)	4.24	6.40	1.70	2.57	36.59	55.25	8.84	13.34	27.09	40.91	0.75	1.14	0.39	0.59
Water spinach (DEPZ)	3.97	5.62	1.91	2.70	94.30	133.39	5.70	8.06	14.42	20.40	0.30	0.42	0.18	0.26
Red spinach (BT)	4.50	6.79	2.12	3.20	71.74	108.34	5.89	8.90	50.76	76.66	0.29	0.44	0.42	0.64
Green spinach (DEPZ)	55.46	78.76	35.94	51.04	1775.78	2521.87	284.81	404.47	732.31	1039.99	16.06	22.81	6.88	9.78
Green spinach (BT)	17.81	24.65	10.64	14.72	811.56	1123.31	28.08	38.87	64.24	88.92	3.55	4.92	1.51	2.08
TEDI	211.62	299.58	92.58	131.34	5137.58	7327.45	436.56	619.84	1076.53	1538.09	32.62	46.11	15.13	21.47
MTDI	**4.50[a]**		**0.21 [b]**		**15[b]**		**0.90[a]**		**5 [b]**		**2.00[a]**		**0.13[b]**	

[a]Islam *et. al.* [(FAO/WHO 2002) [23], (FAO/WHO 2004), (JECFA 2005)]; [b] Gebeyehu, *et al.* [11]

Pb shows THQ values higher than 1 in four crops and vegetables samples for adult and in five corresponding samples for children and the average value was much above than the findings of previous research works performed by Margenat *et al.*; Li *et al.*; Kladsomboon *et al.* for both adult and children [13. 24, 25]. Non carcinogenic risks associated with Fe and Ni exposures through the contaminated foods was found within the safety limits except for three crops and vegetables samples such as Rice (DEPZ), Green spinach (DEPZ), Green spinach (BT) for both adult and children (**Table 4.6**). It was noticeable that the THQ of Ni in Green spinach from DEPZ was found significantly more for both adult and children. THQ values of Mn were lower than 1 in most of the food items which were comparable with the results obtained for Mn from similar study conducted by Margenat *et al.*[13]. However some exceptions were observed in the case health risks data associated with both children and adult in the consumption of Rice and Green spinach collected from DEPZ area, Savar. Cd and As showed the non-carcinogenic risks for most of the crops and vegetables studied in the present study. The higher health risks associated with Cd and As exposure through food contamination are also reported previously from other research work (Kormoker *et al.*) [26]. Rice and Green spinach from DEPZ exert highest non carcinogenic risk for both adult and children among all the studied crops and vegetables (**Table 4.6**). The study conducted previously by Real *et al.* [27] also supported that rice and green spinach can pose significant non-carcinogenic threat to both adult and children. TTHQ and HI values of metals in crops and vegetables determined in the present study indicate higher non-carcinogenic risks for both adult and children due to consumption of then those contaminated food items (**Table 4.6**). TTHQ values of metals for in different samples also suggested that children are relatively at greater non-carcinogenic risks for the exposure of metal contaminated foods than adult.

4.1.5.3 Carcinogenic risks

Like non-carcinogenic risks, carcinogenic risks of metals were also analyzed for both adult and children. TCR associated with different metals and various crops and vegetables samples are presented in **Table 4.7**. The results showed a wide range of variation in the TCR values. The maximum value of TCR was recorded for children for Ni in Rice (BT) whereas the lowest value was found for adult for Lead in Green spinach (DEPZ) (**Table 4.7**).

Table 4.6: Non-carcinogenic risk assessments (THQ, TTHQ, and HI) for adult and children

Samples	Adult								Children							
	Cu	Pb	Fe	Ni	Mn	Cd	As	**TTHQ**	Cu	Pb	Fe	Ni	Mn	Cd	As	**TTHQ**
Rice (DEPZ)	38.23	7.95	2.87	4.16	1.09	18.29	16.59	**89.18**	54.30	11.29	4.07	5.90	1.55	25.97	23.56	**126.65**
Rice (BT)	0.85	0.34	0.17	0.20	0.03	1.28	0.61	**3.49**	1.41	0.57	0.28	0.32	0.05	2.11	1.00	**5.74**
Brinjal (DEPZ)	2.43	0.96	0.09	0.50	0.07	2.69	1.37	**8.11**	2.56	1.02	0.10	0.53	0.07	2.84	1.44	**8.56**
Lady's finger (DEPZ)	1.41	0.42	0.05	0.44	0.19	1.51	1.29	**5.32**	2.13	0.64	0.08	0.67	0.29	2.27	1.95	**8.04**
Water spinach (DEPZ)	1.32	0.48	0.13	0.28	0.10	0.59	0.61	**3.53**	1.87	0.67	0.19	0.40	0.15	0.84	0.86	**4.99**
Red spinach (BT)	1.50	0.53	0.10	0.29	0.36	0.58	1.41	**4.78**	2.26	0.80	0.15	0.44	0.55	0.88	2.13	**7.23**
Green spinach (DEPZ)	18.49	8.99	2.54	14.24	5.23	32.12	22.95	**104.55**	26.25	12.76	3.60	20.22	7.43	45.62	32.59	**148.47**
Green spinach (BT)	5.94	2.66	1.16	1.40	0.46	7.10	5.02	**23.74**	8.22	3.68	1.60	1.94	0.64	9.83	6.95	**32.86**
Spinach (BT)	1.69	1.29	0.36	0.59	0.26	1.67	1.20	**7.06**	2.73	2.08	0.57	0.96	0.41	2.69	1.94	**11.38**
HI								**249.75**	**HI**							**353.92**

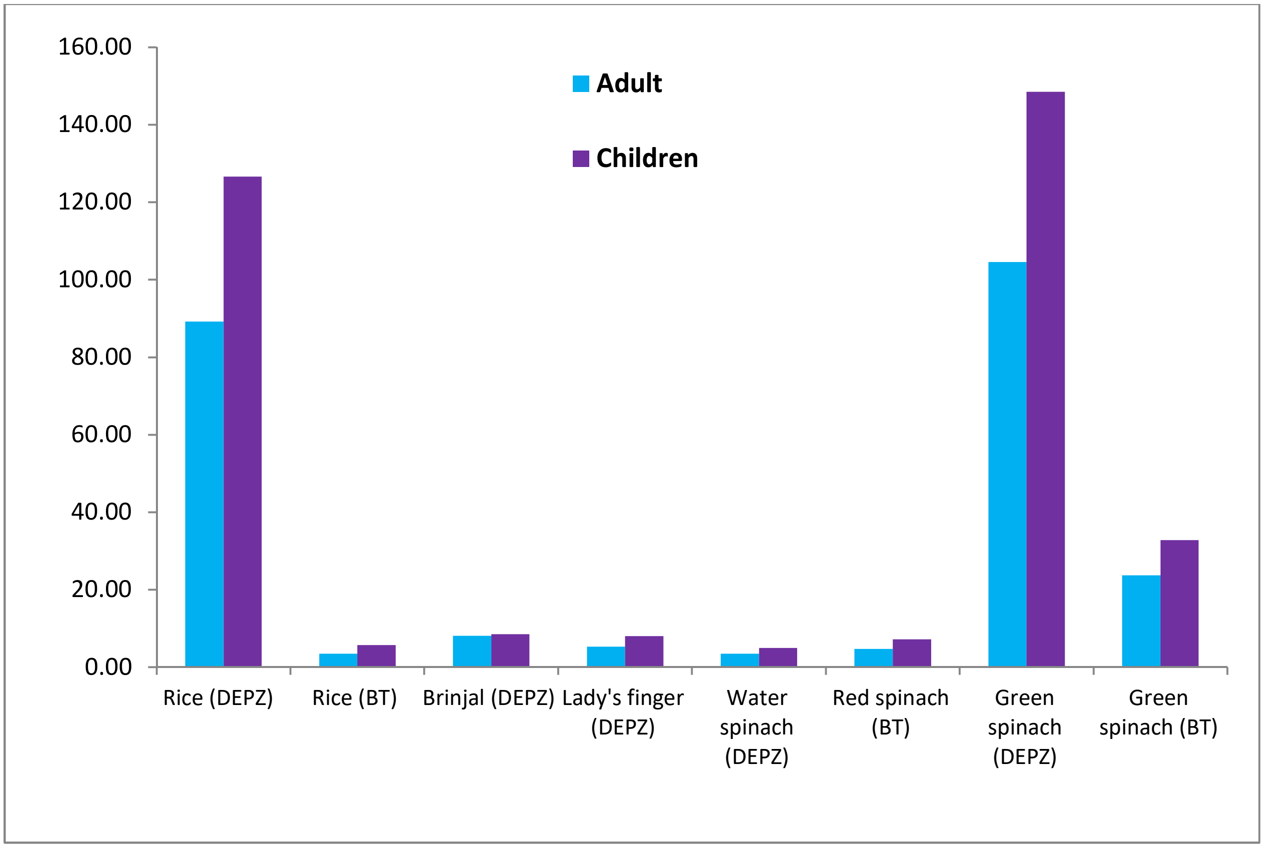


Figure 4.5: TTHQ values of metals for adult and children from the consumption of contaminated crops and vegetables

Total target carcinogenic risk (TTCR) values of all seven metals indicate that children are at higher risk of having cancer than the adult due to consumption of metal contaminated food items. All the target cancer risks (TCR) determined in the present study (**Table 4.7**) were found significantly higher than the results of previous research performed by Rahman *et al.* [28]. TCR values of different metals ranges from 0.000012 to 0.687595 (**Table 4.7**). The research findings from the present investigation demonstrated that children are more vulnerable to deadly carcinogenic risks than adult. The TCR data of different metals from the present study also showed a good agreement with the results of various research works conducted earlier by different authors (Rahman *et al.*; Islam *et al.*) [28, 29].

Table 4.7: Carcinogenic risk assessments (TCR, TTCR) for adult and children

Samples	Nickel		Lead		Cadmium		Arsenic	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Rice (DEPZ)	0.14130	0.20067	0.00027	0.00038	0.05578	0.07922	0.00747	0.01060
Rice (BT)	0.00668	0.01100	0.00001	0.00002	0.00391	0.00645	0.00027	0.00045
Brinjal (DEPZ)	0.01701	0.01795	0.00003	0.00003	0.00821	0.00866	0.00062	0.00065
Lady's finger (DEPZ)	0.01502	0.02268	0.00001	0.00002	0.00459	0.00693	0.00058	0.00088
Water spinach (DEPZ)	0.00969	0.01370	0.00002	0.00002	0.00181	0.00256	0.00027	0.00039
Red spinach (BT)	0.01002	0.01513	0.00002	0.00003	0.00178	0.00269	0.00064	0.00096
Green spinach (DEPZ)	0.48417	0.68760	0.00031	0.00043	0.09797	0.13914	0.01033	0.01466
Green spinach (BT)	0.04774	0.06607	0.00009	0.00013	0.02167	0.02999	0.00226	0.00313
Spinach (BT)	0.02022	0.03262	0.00004	0.00007	0.00509	0.00820	0.00054	0.00087
TTCR	**0.75184**	**1.06742**	**0.00080**	**0.00114**	**0.20082**	**0.28385**	**0.02297**	**0.03259**

The TTCR values of As, Pb, and Cd were much higher for both adult and children in comparison to those observed in the research findings of other authors (Rahman *et al.*; Miri *et al.*) [28, 30] whereas the TTCR values of Ni for adult and children also observed significantly more than those estimated in the research work of Mohammadi *et al.* [31].

4.1.6 Metal pollution index (MPI) in crops and vegetables

Metal pollution load index (MPI) combined all aspects of metal pollution in different crops and vegetables by adding the impact of pollution caused by each of the metals studied. The results of MPI analysis of seven metals in different crops and vegetables samples are presented in the **Figure 4.6.** Metal pollution index (MPI) values determined in various crops and vegetables samples ranged from from 2.17 (in Brinjal, DEPZ) to 2.49 (in Green spinach, BT). All crops and vegetables studied in the present investigation are more or less polluted with heavy and toxic metals as evidenced by the metal pollution index (MPI) values (**Figure 4.6**).

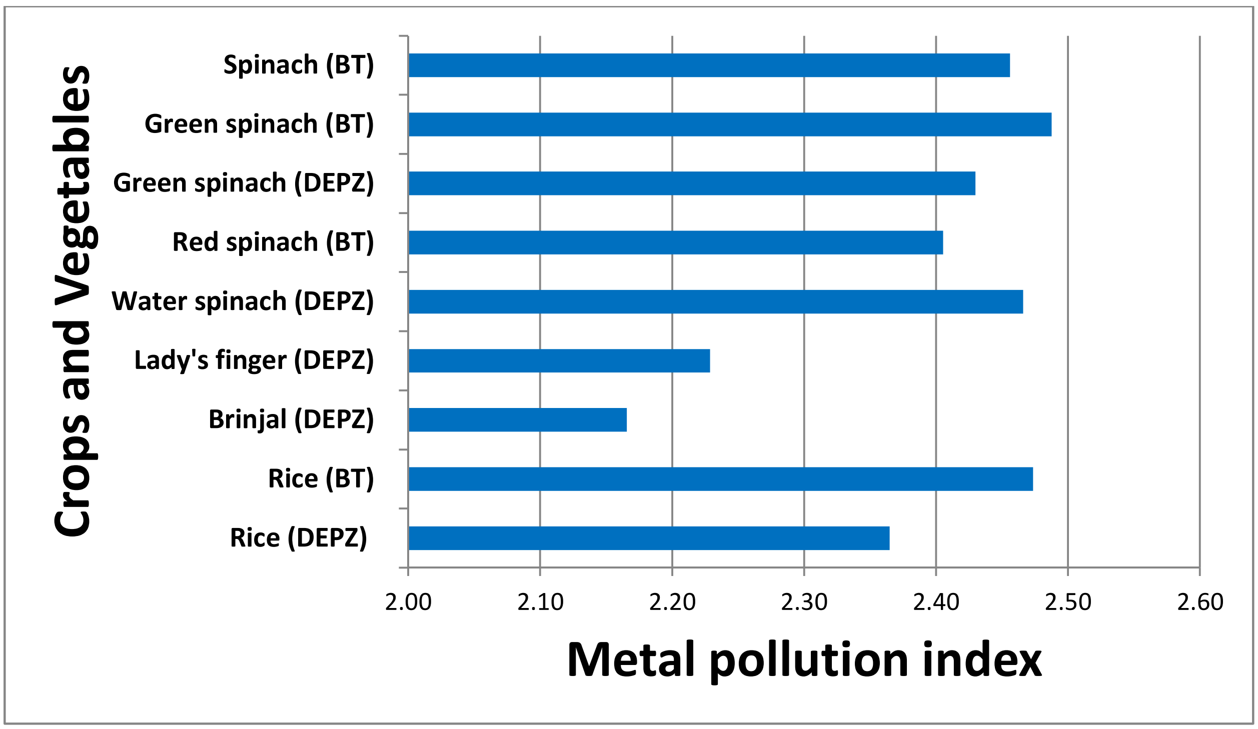


Figure 4.6: Metal pollution index (MPI) in different crops and vegetables grown in and around industrial establishments within Savar area, Dhaka.

4.1.7 Correlation analysis of heavy metals in crops and vegetables

A correlation analysis was performed to visualize the interrelationship among the heavy metals contents observed in different crops and vegetables. Correlation analysis provides us hypothetical information about the source and accumulation property of heavy metals (Kormoker *et al.*) [26]. The result of Pearson correlation analysis of metals is presented in the **Table 4.8**. The presence of significant correlation between heavy metal concentrations in different agricultural plants suggests that they have similar or almost identical accumulation properties. However, it also depends on the metal sources, speciation of metals and uptake properties of plants (Abbasi *et al.*; Ahmed *et al.*) [32, 33]. In the present study a negative correlation was showed between Fe and As which indicates that with increasing the concentration of Fe, As concentration will be decreased and vice versa. A very strong positive correlation was found between Mn and As which demonstrates that elevated concentration of Mn in agricultural plants would cause the excessive uptake of As in them. No signification correlation was noticed among other metals (**Table 4.8**).

Table 4.8: Correlation analysis among the heavy metals

Correlations	Fe	Ni	Mn	Pb	Cu	Cd	As
Fe	1						
Ni	-.335	1					
Mn	-.364	.497	1				
Pb	.017	-.078	-.031	1			
Cu	-.359	-.327	-.124	.011	1		
Cd	-.235	.360	-.378	-.272	-.306	1	
As	-.649*	.401	.790**	-.355	.124	-.003	1

*. Correlation is significant at the 0.05 level

**. Correlation is significant at the 0.01 level

4.2 Heavy and toxic metals contamination in in water, soil, crops, and vegetables grown in Kalihati upazila, Tangail [long range contaminated site (LCS): study area – 2]

4.2.1 Contamination of irrigation water

The results for heavy metal analysis in irrigation water from Kalihati Upazila, Tangail have been presented in the **Table 4.9**. Among the seven metals studied, the maximum concentration was 0.9747 mg/L recorded for Fe in irrigation water used in the Brinjal field and the lowest concentration was 0.0078 mg/L observed for As in water used in the Spinach field. The concentrations of Pb and Cd in all water samples were found below the detection limits. The order of average concentration for other five metals was: Fe>Cu>Ni>Mn >As. The ranges of different heavy metals were: Fe (0.9747-0.536 mg/L), Mn(0.389-0.0371 mg/L), Ni(0.381-0.0265 mg/L), Cu(0.389-0.0371 mg/L), and As(0.0295-0.0078 mg/L). The Arsenic concentrations in all water samples were relative lower in comparison to other metals. Metal concentrations determined in irrigation water samples collected from Kalihati Upazila also compared with the permissible levels reported by FAO/WHO, USEPA, EU, as well as China and India (**Table 4.9**). Fe concentrations in all water samples collected from long range contaminated site were relatively higher in comparison with other metals studied but they were found below the tolerable level of FAO/WHO. All metal concentrations measured in different water samples were observed to be lower than the safety limits FAO/WHO, USEPA and others with the of exception of Ni, Mn, and Cu concentrations in water (used in paddy field) as well as Fe and As in water (used in Brinjal field) respectively which were found higher than the tolerable level. The results of the metal analysis in water bodies from longe range contaminated site were observed to be highly comparable with the studies performed previously by others (Ugulu *et al.*; Sardar *et al.*)[3, 7]. Since almost all the data of metal analysis in different water samples were found below the permissible limits, the calculation of pollution load index (PLI) was not significant and meaningful in this case.

Table 4.9: Heavy metal concentrations (mg L^{-1}) in effluent-contaminated water used for irrigation in the long range contaminated site (LCS): Mean ± SD and (range)

Sample type	Cu	Pb	Fe	Ni	Mn	As	Cd
Water (used in rice field)	0.3890±0.0066 0.3826-0.3958	BDL	0.8441±0.0049 0.8397-0.8494	0.3810±0.0079 0.3738-0.3895	0.1677±0.0065 0.1610-0.1739	0.0198±0.0017 0.0183-0.0217	BDL
Water (used in brinjal field)	0.0629±0.0042 0.0589-0.0672	BDL	0.9747±0.0046 0.9702-0.9793	0.0265±0.0048 0.0217-0.0312	0.0820±0.0028 0.0803-0.0852	0.0295±0.0009 0.0284-0.0302	BDL
Water (used in lady's finger field)	0.0754±0.0048 0.0703-0.0799	BDL	0.6334±0.0060 0.6272-0.6392	0.0331±0.0044 0.0292-0.0379	0.0473±0.0053 0.0426-0.0531	0.0110±0.0021 0.0098-0.0134	BDL
Water (used in water spinach field)	0.0432±0.0061 0.0379-0.0498	BDL	0.7381±0.0067 0.7318-0.7452	0.0404±0.0065 0.0342-0.0472	0.0645±0.0046 0.0602-0.0693	0.0078±0.0006 0.0072-0.0084	BDL
Water (used in red spinach field)	0.0619±0.0057 0.0573-0.0683	BDL	0.5367±0.0038 0.5326-0.5402	0.0348±0.0047 0.0302-0.0396	0.0680±0.0056 0.0629-0.0739	0.0156±0.0048 0.0103-0.0198	BDL
Water (used in green spinach field)	0.0371±0.0044 0.0327-0.0415	BDL	0.5360±0.0055 0.5304-0.5413	0.0434±0.0048 0.0384-0.0479	0.0340±0.0043 0.0299-0.0385	0.0135±0.0042 0.0096-0.018	BDL
Water (used in spinach field)	0.0549±0.0047 0.0503-0.0597	BDL	0.6449±0.0046 0.6401-0.6492	0.0374±0.0061 0.0316-0.0437	0.0786±0.0052 0.0736-0.0839	0.0260±0.0027 0.0231-0.0284	BDL
Safe limit[a]	0.2	5	5	0.2	0.2	0.1	0.01
Safe limit[b]	0.05	0.1	-	-	0.1	-	0.01
Safe limit[c]		-	-	0.05	0.015	1.0	0.005

[a]FAO standard (www.fao.org/3/t0234e/t0234e06.htm); [b] Indian Standard (Awashthi 2000); [c]USEPA standard (2010).

4.2.2 Contamination of arable soil

Heavy metal concentrations in different soil samples showed a large variation (**Table 4.10**). Iron concentration was found highest in comparison to all other metals whereas the minimum concentration was displayed by cadmium (**Table 4.10**). Metal concentrations in different soil samples collected from various agricultural fields of the long range contaminated site were found below the maximum tolerable limits of FAO/WHO, USEPA China and India. However, two exceptions were noticed where copper concentrations in soil collected from Brinjal field and soil samples from Red spinach field were exceeded the permissible levels. Relatively higher concentrations of Fe, Ni, Mn, Cu, Cd and As were observed in soil of Red spinach field whereas Pb concentration was recorded maximum in soil from Brinjal field. Appearance of relatively lower concentrations of heavy metals in the arable soil of long range contaminated area might be attributed to the absence of industrial establishments in the respective study area and availability of pure and non-contaminated water which is being used in irrigation and cultivation of crops and vegetables in the long range contaminated site. When heavy and toxic metals from industrial effluents are mixed into nearby water bodies, they may be deposited onto the sediment of river in the adjacent areas before mobilizing and migrating to the long range contaminated study area or they may get settled down near the point sources by various means. The calculation of soil pollution load index in different soil samples from the long range contaminated site was not significant and meaningful as well since most of the metals analysis data were found below the prescribed permissible levels.

4.2.3 Contamination of crops and vegetables

The results of heavy and toxic metal analysis in different crops and vegetables collected from Kalihati Upazila, Tangail (Long range contaminated site) have been presented in the **Table 4.11**. Agricultural plants were varied in the uptake and accumulation of different metals in their roots to edible parts. All cadmium concentrations determined in both roots and edible parts of different crops and vegetables were found below the detection limit. The highest accumulated metal was Fe (91.83 mg/kg) whereas the lowest metal uptake was realized for arsenic (0.053 mg/kg), and both concentrations were found in Spinach.

The average heavy metal concentrations determined in all crops and vegetables of LCS was in the order of: Fe>Mn>Cu> Ni>Pb>As. In most cases, the roots of the agricultural plants accumulated excessive level of heavy metals in comparison to other parts of the plant bodies. However, in some cases metal concentrations were found higher in the edible parts than roots (**Table 4.11**). Plants were varied to uptake and accumulate different heavy metals in various parts of their bodies. Highest concentration of Fe (91.83 mg/kg), Ni (9.1 mg/kg), Mn (47.47 mg/kg), Cu (13.52 mg/kg) were found in Spinach whereas maximum Pb concentration (4.58 mg/kg), and As concentration (0.236 mg/kg) were observed in Lady's finger and Rice respectively (**Table 4.11**). Highest accumulation of Fe in edible part of all the crops and vegetable might be due the presence of elevated quantity of Fe in the respective soil and irrigation water (Latif *et al.*)[12]. Relatively lower uptake of As in different crops and vegetables might be attributed to the presence of lesser quantity of As in arable soil as well as in irrigation water in the long range contaminated area which is also supported from the results of another study conducted in Barcelona, Spain by Margenat *et al.*[13]. Appearance of the lowest As concentrations in the agricultural plant samples may also be due to the absence of manufacturing industries such as paper, glass, petroleum and coal products in the long range contaminated site. Fe concentrations measured in crops and vegetables in the LCS under the present study were higher than the data reported previously from similar studies conducted in Tamale Municipal, Ghana (Ametepey *et al.*) [17] but lower than those observed in agricultural plants grown around industrial areas in Pakistan (Latif *et al.*)[12]. Arsenic concentrations in agricultural plants of LCS were lower than the research findings of Gebeyehu *et al.*[11] in Mojo, Ethiopia but higher than those obtained by Margenat *et al.*[13] in similar food plants cultivated in Barcelona, Spain. All crops and vegetables samples in LCS displayed Ni and Pb concentrations relatively higher than the permissible levels of JECFA and Indian. Ni and Pb concentrations data were also highly comparable with other similar research findings (Margenat *et al.*; Islam *et al.*)[13, 23]. Mn contents in all crops and vegetable samples were lower than FAO/WHO permissible limits but the observed data were relatively higher than those found previously in crops and vegetables grown in other countries (Gebeyehu *et al.*; Latif *et al.*; Margenat *et al.*)[11, 12, 13].

Table 4.10: Heavy metal concentrations (mg kg^{-1}) in soil contaminated by waste water in the long range contaminated site (LCS): Mean ± SD and (range)

Sample type	Fe	Ni	Mn	Pb	Cu	Cd	As
Soil (from rice field)	1045.52±101.00 (943.03-1144.96)	28.53±3.25 (25.08-31.53)	398.50±33.21 (368.07-433.92)	9.11±0.72 (8.47-9.89)	27.54±3.81 (23.38-30.87)	0.145±0.011 (0.133-0.154)	4.470±0.439 (4.048-4.924)
Soil (from brinjal field)	943.99±89.29 (853.34-1031.85)	35.17±4.04 (30.55-38.04)	354.68±37.29 (316.81-391.37)	11.99±0.82 (11.46-12.93)	30.24±3.82 (26.04-33.51)	0.085±0.013 (0.074-0.099)	4.632±0.388 (4.242-5.018)
Soil (from lady's finger field)	933.85±101.99 (829.05-1032.78)	35.82±3.53 (32.26-39.31)	345.89±30.52 (315.36-376.40)	10.50±0.98 (9.84-11.63)	27.76±2.25 (25.43-29.92)	0.053±0.009 (0.046-0.063)	3.601±0.313 (3.282-3.907)
Soil (from water spinach field)	964.14±95.39 (864.02-1053.97)	35.08±2.71 (32.28-37.68)	360.84±36.78 (323.05-396.51)	10.97±0.90 (10.17-11.94)	27.97±1.95 (25.95-29.84)	0.095±0.010 (0.084-0.103)	3.661±0.238 (3.441-3.914)
Soil (from red spinach field)	1441.42±135.15 (1308.04-1578.27)	38.47±3.61 (34.87-42.08)	441.79±41.47 (400.01-482.94)	9.81±0.75 (9.11-10.60)	31.88±3.93 (28.17-35.99)	0.147±0.011 (0.137-0.158)	4.721±0.302 (4.393-4.989)
Soil (from green spinach field)	1250.22±175.99 (1080.04-1431.49)	34.46±4.31 (30.39-38.98)	345.05±34.89 (311.68-381.28)	8.83±0.76 (8.05-9.56)	26.08±2.37 (23.68-28.41)	0.051±0.009 (0.043-0.061)	3.486±0.311 (3.175-3.796)
Soil (from spinach field)	1190.52±96.01 (1093.02-1284.96)	32.39±3.89 (28.18-35.86)	430.96±39.30 (392.24-470.82)	10.84±0.85 (10.07-11.75)	29.39±3.32 (26.10-32.73)	0.095±0.012 (0.085-0.108)	4.642±0.354 (4.278-4.985)
Safe limit[a]	40000	50	-	35	30	0.35	6
Safe limit[b]	-	60	-	250	100	0.6	40
Safe limit[c]	-	50	2000	100	100	3	-

[a]Coskun *et al.* (2006); [b]MAC National Environmental Protection Agency of China, GB 15618 (1995); [c]European Union Standards European Union (2006)

Table 4.11: Heavy metal concentrations (mg kg^{-1}) in crops and vegetables grown in grown in long range contaminated site (LCS): Mean ± SD and (range)

Samples	Plant Parts	Fe	Ni	Mn	Pb	Cu	Cd	As
Rice	Root	537.44±51.73 (485.25-588.69)	16.44±1.24 (15.46-17.84)	55.61±5.24 (50.74-61.16)	3.28±0.41 (2.96-3.74)	29.78±3.03 (26.93-32.97)	BDL	0.426±0.013 (0.412-0.437)
	Edible Part	77.07±5.58 (71.86-82.96)	6.39±0.57 (5.83-6.96)	44.57±4.01 (40.74-48.74)	4.05±0.51 (3.57-4.59)	4.51±0.34 (4.12-4.74)	BDL	0.236±0.007 (0.227-0.241)
Brinjal	Root	163.92±18.73 (144.91-182.36)	6.53±0.54 (6.02-7.09)	47.16±4.99 (42.01-51.97)	3.93±0.30 (3.67-4.26)	30.13±3.69 (26.47-33.85)	BDL	0.443±0.007 (0.437-0.451)
	Edible Part	47.25±4.91 (42.17-51.98)	4.36±0.45 (3.96-4.85)	15.43±1.19 (14.09-16.35)	3.48±0.48 (3.02-3.97)	13.47±1.47 (12.03-14.97)	BDL	0.156±0.008 (0.148-0.163)
Lady's finger	Root	353.31±29.16 (323.63-381.92)	2.94±0.82 (2.23-3.84)	49.81±4.78 (45.07-54.62)	3.53±0.46 (3.05-3.97)	28.33±2.67 (25.75-31.08)	BDL	0.493±0.008 (0.486-0.502)
	Edible Part	82.81±8.46 (74.04-90.92)	3.39±0.21 (3.26-3.63)	15.65±1.32 (14.34-16.98)	4.58±0.38 (4.22-4.98)	10.11±0.78 (9.31-10.87)	BDL	0.185±0.009 (0.176-0.193)
Water spinach	Root	484.63±51.34 (433.27-535.94)	9.20±0.78 (8.32-9.83)	52.79±4.66 (48.40-57.68)	4.12±0.48 (3.69-4.63)	36.08±3.42 (32.68-39.52)	BDL	0.390±0.008 (0.382-0.398)
	Edible Part	75.71±8.13 (67.72-83.97)	8.71±0.85 (7.77-9.42)	46.08±4.49 (41.62-50.59)	3.22±0.37 (2.95-3.64)	10.04±0.84 (9.19-10.86)	BDL	0.055±0.003 (0.053-0.058)
Red spinach	Root	483.43±49.56 (434.16-533.28)	3.92±0.37 (3.53-4.27)	18.57±1.75 (16.63-20.04)	7.97±0.81 (7.37-8.89)	34.92±2.77 (31.91-37.37)	BDL	0.856±0.009 (0.846-0.864)
	Edible Part	52.50±5.54 (46.97-58.05)	7.09±0.79 (6.47-7.98)	22.85±1.88 (21.18-24.89)	3.93±0.43 (3.53-4.38)	10.16±0.93 (9.12-10.93)	BDL	0.097±0.007 (0.091-0.104)
Green spinach	Root	636.00±57.71 (577.92-693.33)	11.21±0.87 (10.28-11.99)	32.50±2.53 (29.97-35.03)	5.67±0.57 (5.14-6.28)	34.41±2.55 (31.93-37.03)	BDL	1.273±0.009 (1.264-1.281)
	Edible Part	45.79±6.57 (38.87-51.93)	2.48±0.45 (2.05-2.94)	12.17±1.23 (10.98-13.44)	4.25±0.46 (3.84-4.74)	6.82±0.55 (6.27-7.37)	BDL	0.097±0.002 (0.095-0.099)
Spinach	Root	296.18±31.21 (265.27-327.68)	7.78±0.71 (7.06-8.48)	33.46±3.26 (30.43-36.91)	9.70±1.39 (8.27-11.04)	28.59±3.33 (25.18-31.84)	BDL	1.472±0.010 (1.463-1.482)
	Edible Part	91.83±8.04 (83.97-100.03)	9.10±0.89 (8.12-9.85)	47.47±4.81 (42.43-52.01)	4.28±0.68 (3.58-4.94)	13.52±1.31 (12.04-14.53)	BDL	0.053±0.008 (0.046-0.062)
Safe limit[abc]		425[a]	0.5[b]	500[c]	0.2[b]	20[b]	0.3[a]	0.1[b]
Safe limit[d]		-	1.5	-	2.5	30	1.5	-
Safe limit[f]		-	1.5	-	2.5	30	1.5	-

[a]FAO/WHO standard (Codex Alimentarious Commission 1984); [b]WHO/FAO (2007); [c](JECFA 2005); [c](FAO/WHO 2002b); [d]European Union Standards European Union (2006); [e]Gebeyehu *et al.*)[11]; [f]Indian Standard (Awashthi 2000

Pb concentrations in crops and vegetables of LCS was also showed higher than those obtained from other research works conducted earlier by Islam *et al.* and Kormoker *et al.*[23, 26] whereas the extents of Pb were relatively lower in comparison to the metal concentrations determined in similar agricultural plants by Proshad *et al.*[16]. Smaller accumulation of Cu was realized in the agricultural plants grown in LCS and thus all Cu concentrations in the respective crops and vegetables in LCS were within the safety limits of FAO/WHO, EU, USEPA, China, and India. However, Cu contents determined in the agricultural samples from LCS were highly comparable to those found in similar studies on agricultural plants by: Gebeyehu *et al.*[11] in Ethiopia; Latif *et al.*[12] in Pakistan; Ametepey *et al.*[17] in Ghana. **Figure 4.7** shows the Pollution Load Index (PLI) values of crops and vegetables grown in long range contaminated site (LCS), Kalihati Upazila, Tangail (Study area-2). In this case, PLI values of lead and nickel in all crops and vegetables samples were observed to be larger than the permissible levels. PLI values of arsenic in some crops and vegetables were also found above the tolerable limits (**Table 4.11** & **Figure 4.7**). All other meals showed PLI values in crops and vegetables which were smaller than the prescribed safety limits (**Figure 4.7**).

4.2.4 Mobilization of heavy metals

BCF values of different metals determined in various crops and vegetables of LCS are presented in the **Figure 4.8**. In case of mobilization of metals from soil to agricultural plants, the maximum BCF value was 0.481 recorded for Pb in Green spinach and lowest value was 0.011 observed for As in spinach. BCF values of different metals were highly varied among various crops and vegetables samples. This might be due to the differences in heavy metal concentrations in various arable soils from different sampling sites and variation in the accumulation capacity of different crops and vegetables (Cui *et al.*)[19]. According to WHO/FAO, 2011, heavy metal contamination may occur if the BCF value exceeds 0.2. **Figure 4.8** revealed that higher accumulation rate of lead and copper was higher in most of the studied samples. The order of average BCF values for different metals is: Pb>Cu>Ni> Mn>Fe>As. BCF values associated with nickel suggest a moderate rate of nickel accumulation in agricultural plants. All other metals showed smaller BCF values indicating the reduced accumulation rate in the plants. However, most of the plant samples showed a tendency of lowest accumulation for arsenic.

Table 4.12: Comparison of the results of metals analysis in crops and vegetables from the present study with other research reported in the literatures

District (Country)	Fe	Ni	Mn	Pb	Cu	Cd	As	References
Kalihati Area (Bangladesh)	91.83 (45.79-91.83)	9.1 (2.48-9.1)	47.47 (12.17-47.47)	4.28 (3.22-4.58)	13.52 (4.51-13.52)	BDL	0.053 (0.053-0.236)	This study
Jhenidah and Kustia (Bangladesh)	-	8.96 (1.71–37.78)	-	4.30 (1.04–10.88)	7.61 (1.97–16.67)	1.39 (0.0–4.02)	1.85 (0.36–3.72)	Kormoker *et al.* [26]
Dera Ghazi Khan (Pakistan)	384.35 (129.00-968.25)	3.63 (1.8-5.05)	47.36 (18.67-137.30)	-	34.9 (22.25-65.24)	0.26 (0.04-0.39)	-	Latif *et al.* [12]
Tangail (Bangladesh)	-	16.11 (1.41–37.52)	-	7.93 (0.84–28.14)	13.99 (2.97–25.45)	1.86 (0.093–4.09)	2.28 (1.31–3.89)	Proshad *et al.* [16]
Barcelona (Spain)	-	0.06	2.25	0.08	1.33	0.009	0.0003	Margenat *et al.*[13]
Tamale Municipal (Ghana)	3.71 (3.04-4.47)	-	0.17 (0.06-0.95)	BDL (BDL-0.04)	0.07 (0.04-0.09)	0.05 (0.01-0.07)	-	Ametepey *et al.* [17]
Mojo (Ethiopia)	287.78	2.995	164.715	5.595	12.845	1.06	3.83	Gebeyehu *et al.* [11]
Bogra (Bangladesh)	-	0.46 (0.01–1.55)	-	0.49 (0.04–1.39)	1.70 (0.09–3.47)	0.06 (0.004–0.25)	0.24 (0.02–1.51)	Islam *et al.* [23]

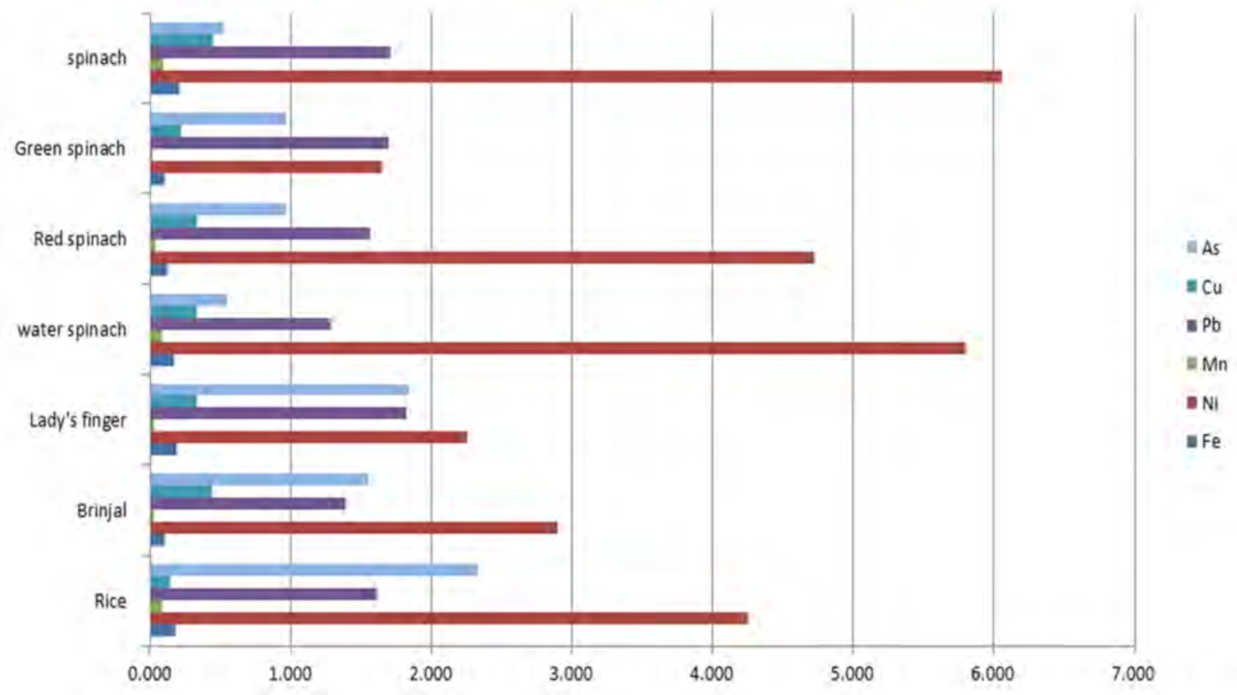


Figure 4.7: Pollution load index of crops and vegetables

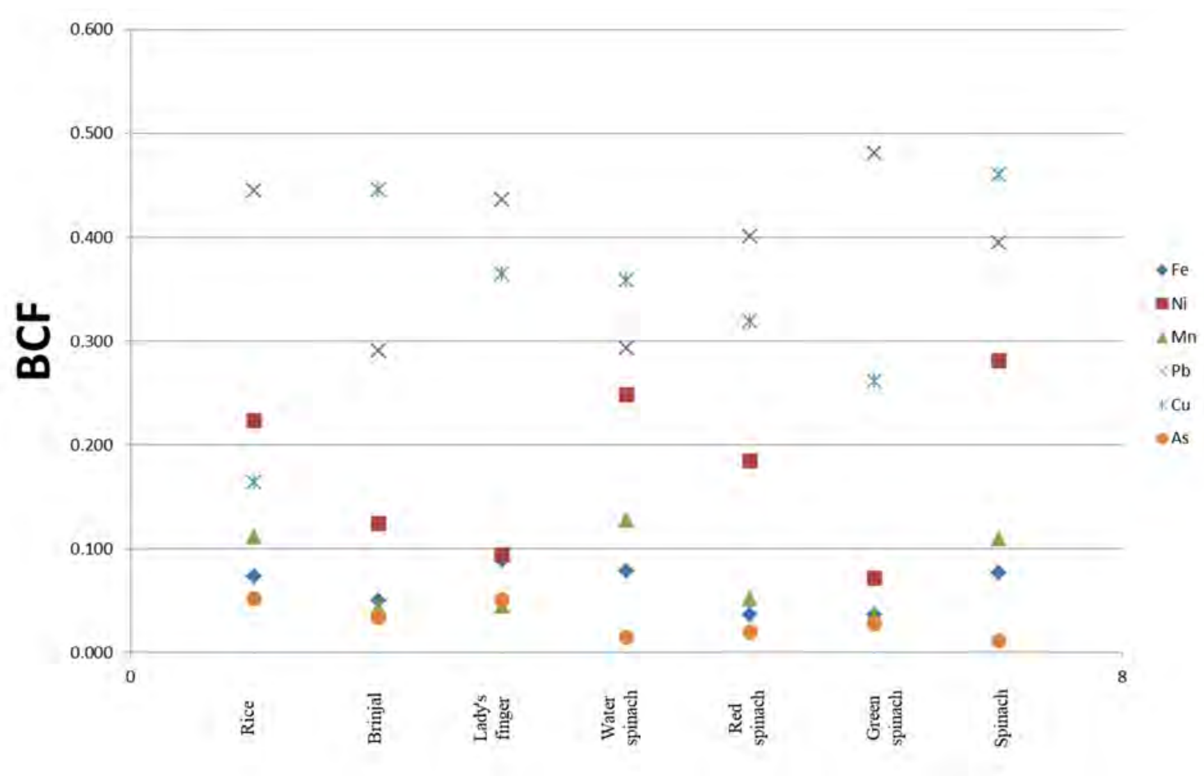


Figure 4.8: Bioconcentration factor (BCF) of heavy metals in different crops and vegetables

Higher level of heavy metals uptake by different crops and vegetables may be due to the availability of metals in soil and water, speciation of metals, moisture content and growth of the plants (Sultana *et al.*)[22].

4.2.5 Human health risk assessment

Both carcinogenic and non-carcinogenic risks of different metals in all crops and vegetables samples from LCS were evaluated. Non-carcinogenic risks are expressed in terms of Target hazard quotient (THQ), Total target hazard quotient (TTHQ), and Hazard index (HI). Total target hazard quotient (TTHQ) describes the total non-carcinogenic risks due to the consumption of specific crops or vegetables.

4.2.5.1 Estimated daily intake

Health risks associated with direct or indirect exposures of heavy metals through various agricultural food items are determined by calculating estimated daily intake (EDI) (Latif *et al.*)[12]. The calculated EDI values for different metals in various crops and vegetables from the long range contaminated site are presented in the **Table 4.13**. EDI for both adult and children associated with individual metal for specific food item were investigated in this case and the corresponding data are displayed in **Table 4.13**. Most of the EDI values were found higher than the maximum tolerable daily intake (MTDI). The TEDI (total estimated daily intake) values of all metals in different crops and vegetables samples were significantly more than maximum tolerable daily intake of those corresponding metals. For all metals the EDI values for children were found to be higher than those obtained for adult suggesting greater risk for children than adult. The calculated maximum TEDI was 918.38 recorded for Fe in children whereas the minimum value was 1.81 observed for As in adult. The results indicate high risk for both adults and children due to the consumption of contaminated food items. The TEDI values for adults associated with different metals were Cu(14.48), Pb(173.05), Fe(42.97), Ni(59.83), Mn(65.45), As(0.91) which were considerably larger than the corresponding MTDI values as well as were 5.77% (Cu), 3.22% (Pb), 57.09% (Fe), 4.77% (Ni), 28.99% (Mn), 0.16 % (As) of total heavy metal intake respectively.

Table 4.13: Estimated daily intake (EDI) of different metals in different crops and vegetables

Samples	EDI											
	Cu		Pb		Fe		Ni		Mn		As	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Rice	26.21	37.23	23.54	33.43	447.94	636.14	37.12	52.72	259.06	367.90	1.36	1.93
Brinjal	21.43	29.66	5.53	7.66	75.14	104.00	6.93	9.60	24.53	33.96	0.25	0.34
Lady's finger	5.78	9.32	2.61	4.22	47.30	76.29	1.94	3.12	8.94	14.42	0.11	0.17
Water spinach	2.34	3.86	0.75	1.24	17.67	29.10	2.03	3.35	10.75	17.71	0.01	0.02
Red spinach	4.48	4.72	1.73	1.83	23.13	24.41	3.13	3.30	10.07	10.62	0.04	0.05
Green spinach	1.99	3.00	1.24	1.87	13.34	20.15	0.72	1.09	3.54	5.35	0.03	0.04
Spinach	2.94	4.16	0.93	1.32	20.00	28.29	1.98	2.80	10.34	14.63	0.01	0.02
TEDI	65.17	91.95	36.34	51.56	644.52	918.38	53.85	75.98	327.23	464.59	1.81	2.57
MTDI	**4.50**[a]		**0.21**[b]		**15**[b]		**0.90**[a]		**5**[b]		**2.00**[a]	

[a]Islam *et. al.* [(FAO/WHO 2002) [23], (FAO/WHO 2004), (JECFA 2005)]; [b] Gebeyehu, *et.al.*[11]

Similarly for children the estimated TEDI values for different metals were Cu(20.43), Pb(245.52), Fe(61.23), Ni(84.42), Mn(92.92), As(1.29) which were also relatively higher than the corresponding MTDI values and were 5.73% (Cu), 3.21% (Pb), 57.22% (Fe), 4.73% (Ni), 28.95% (Mn), 0.16 % (As) of total heavy metal intake respectively.

4.2.5.2 Non carcinogenic risk

Non-carcinogenic risk associated with metal contaminated specific food item is given by THQ. Total target hazard quotient (TTHQ) is the total non-carcinogenic risk associated with the consumption of crops and vegetables. Hazard index (HI) is the total non-carcinogenic risk recorded from the overall study. THQ, TTHQ, and HI values of different metals are presented in the **Table 4.14**. Maximum THQ value was 12.41 for Cu in children from the consumption of rice whereas the minimum value was 0.02 recorded for adult in Green spinach (**Table 4.14)**. The values of TTHQ also showed a large variation (33.38-1.15). The lowest TTHQ value was obtained for adult in Green spinach whereas the highest value was observed for children in rice. HI values of different metals observed in children were significantly more than those determined in adult which revealed the grater non-carcinogenic risk for children. THQ values associated with Cu in most of the crops and vegetables from LCS were realized to be higher than the acceptable value 1 for both adult and children. However, few exceptions were found in Water spinach, Green spinach, Spinach for adult. The results health risks analysis in this case was significantly more than those obtained from several previous studies (Li *et al.*; Margenat *et al.*)[24, 13]. Pb shows THQ values larger than 1, in Rice and Brinjal for adult whereas in the case of children the THQ data were found more in Lady's finger as well as in Rice and Brinjal. Non-carcinogenic risks associated with Fe, Ni, Mn, and As were within the permissible limits for all studied crops and vegetables samples with both adult and children (**Table 4.14**). However, THQ values of Ni, Mn, and As in Rice was observed to be above the safety limits for both adult and children. In addition the THQ for As in Brinjal was also noticed to be greater than 1. THQ values for Mn were smaller than 1 in most of the crops and vegetables which were comparable to the findings of Margenat *et al.*[13]. Rice exhibited the highest non carcinogenic risks for both adult and children among all the crops and vegetables studied (**Table 4.14**) which showed a good agreement with the previous research finding of Real *et al.*[27].

Table 4.14: Non-carcinogenic risk assessments (THQ, TTHQ and HI) for Adult and Children for the consumption of crops and vegetables

Samples	Adult							Children						
	Cu	Pb	Fe	Ni	Mn	As	**TTHQ**	Cu	Pb	Fe	Ni	Mn	As	**TTHQ**
Rice	8.74	5.88	0.64	1.86	1.85	4.54	23.50	12.41	8.36	0.91	2.64	2.63	6.44	33.38
Brinjal	7.14	1.38	0.11	0.35	0.18	0.83	9.98	9.89	1.92	0.15	0.48	0.24	1.14	13.82
Lady's finger	1.93	0.65	0.07	0.10	0.06	0.35	3.16	3.11	1.05	0.11	0.16	0.10	0.57	5.09
Water spinach	0.78	0.19	0.03	0.10	0.08	0.04	1.22	1.29	0.31	0.04	0.17	0.13	0.07	2.00
Red spinach	1.49	0.43	0.03	0.16	0.07	0.14	2.33	1.57	0.46	0.03	0.16	0.08	0.15	2.46
Green spinach	0.66	0.31	0.02	0.04	0.03	0.09	1.15	1.00	0.47	0.03	0.05	0.04	0.14	1.73
Spinach	0.98	0.23	0.03	0.10	0.07	0.04	1.45	1.39	0.33	0.04	0.14	0.10	0.05	2.06
HI							42.79	**HI**						60.54

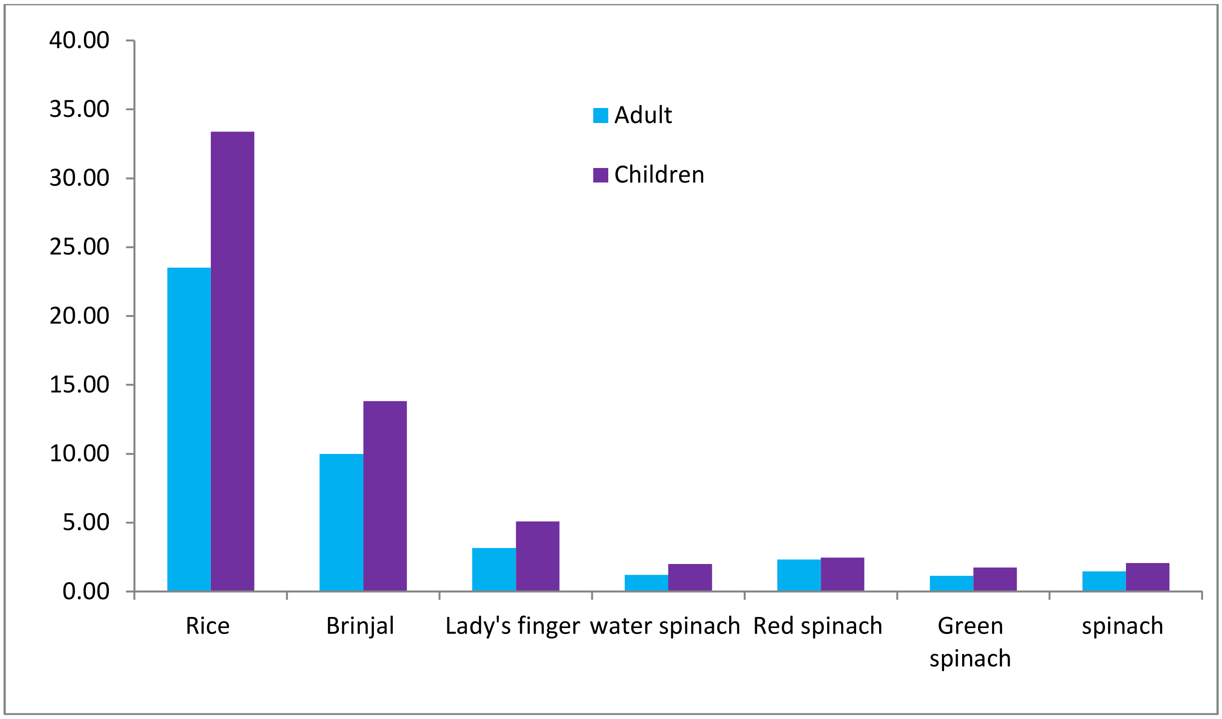


Figure 4.9: TTHQ values for adult and children for the consumption of crops and vegetables

Elevated TTHQ and HI values in this case indicate high non carcinogenic risk for both adult and children due to the consumption of the food items analyzed in the present investigation. TTHQ values determined in different crops and vegetables also suggested that children are more vulnerable to non-carcinogenic risks in comparison to adult (**Figure 4.9**).

4.2.5.3 Carcinogenic risk

Carcinogenic risks data calculated for both adult and children for the consumption of crops and vegetables from LCS is displayed **Table 4.15.** Target carcinogenic risks (TCR) associated with different metals in different crops and vegetables samples were also determined. The results showed a wide range of variation among TCR values of different metals. The maximum TCR value was 0.089621 measured in rice for Ni which was associated with children. However, minimum value was 0.000006 observed in Water spinach for Pb associated with adult. The results of total target carcinogenic risk (TTCR) analysis suggested that children are in danger of higher cancer risk than adult due to consumption of studied agricultural food items.

Table 4.15: Carcinogenic risk assessments (TCR, TTCR) for Adult and Children from the consumption of crops and vegetables from LCS

Samples	**Nickel**		**Lead**		**Arsenic**	
	Adult	Children	Adult	Children	Adult	Children
Rice	0.063106	0.089621	0.000200	0.000384	0.002041	0.002898
Brinjal	0.011788	0.016316	0.000047	0.000019	0.000372	0.000515
Lady's finger	0.003292	0.005309	0.000022	0.000035	0.000158	0.000255
Water spinach	0.003454	0.005689	0.000006	0.000022	0.000019	0.000032
Red spinach	0.005314	0.005607	0.000015	0.000023	0.000064	0.000068
Green spinach	0.001227	0.001853	0.000011	0.000027	0.000043	0.000064
Spinach	0.003369	0.004765	0.000008	0.000434	0.000017	0.000024
TTCR	0.091548	0.129159	0.000309	0.000943	0.002715	0.003857

All target cancer risks (TCR) values were found quite smaller, however, they still are considerable because of higher probability of having the cancer risks in near future (**Table 4.15**). This is also illustrated in other research works performed previously by different authors (Rahman *et al.*; Islam *et al.*)[28, 29].

4.2.6 Metal pollution index (MPI) in crops and vegetables

Metal pollution index data determined in each crop and vegetable samples collected from LCS are presented in the **Figure 4.10.** Metal pollution index (MPI) values determined in different crops and vegetables from the long range contaminated site (LCS) ranges from 1.84 (Green spinach) to 2.08 (Spinach). The order of estimated metal pollution index in this case was: Spinach > Water spinach > Rice > Lady's finger > Red spinach > Brinjal > Green spinach which demonstrated that the highest risk associated with heavy metals ingestion was due to the consumption of Spinach whereas Green spinach poses a minimum health risk to the people of the respective areas.

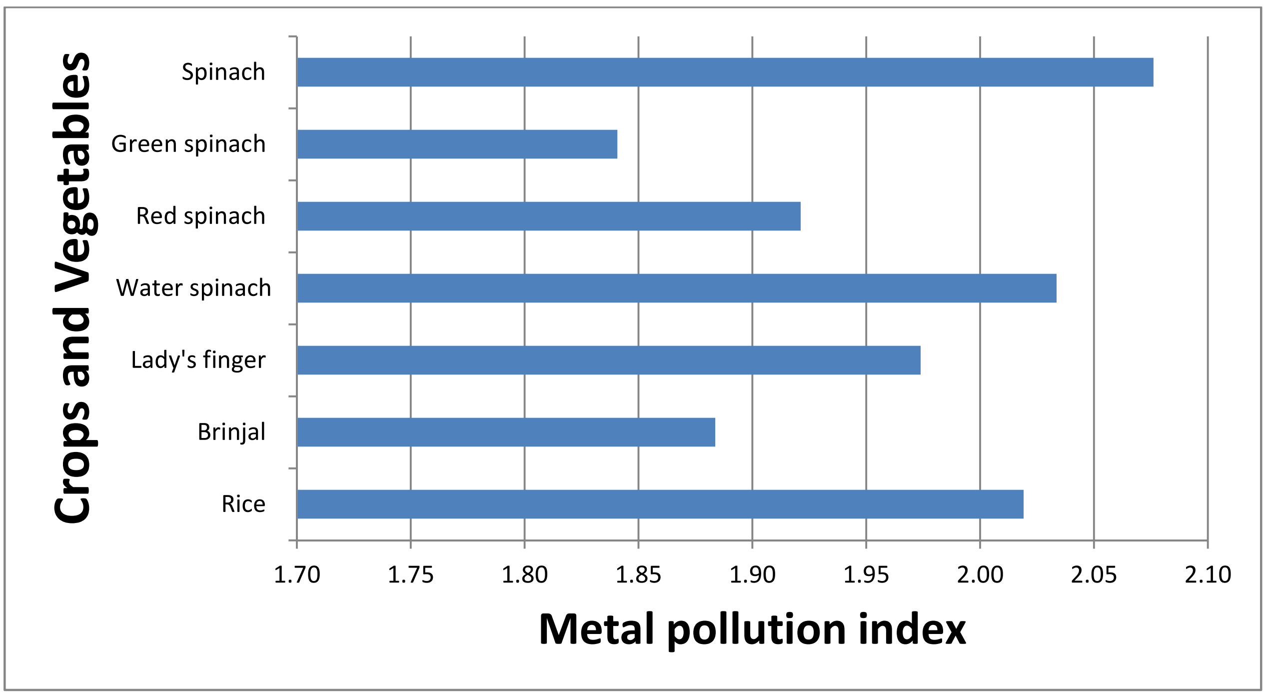


Figure 4.10: Metal pollution index (MPI) in crops and vegetables

4.2.7 Correlation analysis of heavy metals in crops and vegetables

A correlation analysis was performed using the average concentration of different metals in various crops and vegetables of LCS. The results of Pearson correlation analysis is presented in the **Table 4.16**. A significant positive correlation was realized among heavy metals contents determined in crops and vegetables samples which suggest that they might have similar or almost identical accumulation properties and they might be released into the surrounding environments from similar sources (Abbasi *et al.*; Ahmed *et al.*)[32, 33]. Mn concentration showed a strong positive correlation with Ni and Fe (Table 4.16) which demonstrated that with the increase in manganese concentration in crops and vegetables both iron and nickel concentrations will also be increased and vice versa.

Table 4.16: Correlation analysis among the heavy metals contents in crops and vegetables

Correlations	Fe	Ni	Mn	Pb	Cu	As
Fe	1					
Ni	.534	1				
Mn	.702*	.876**	1			
Pb	.298	-.388	-.256	1		
Cu	.086	.279	-.050	-.204	1	
As	.005	-.480	-.213	.275	-.487	1

*. Correlation is significant at the 0.05 level

**. Correlation is significant at the 0.01 level

4.3 Comparison study between heavy and toxic metal contamination status in highly contaminated site (HCS) and long range contaminated site (LCS)

The results of heavy and toxic metal pollution in crops, vegetables, soil, and water bodies from Savar area [Highly contaminated site(HCS)-study area-1) have been compared with the metal contamination data obtained from the same environmental samples collected from Kalihati Upazila, Tangail [Long range contaminated site (LCS)-study area-2]. Relative comparisons between the research findings of highly contaminated site (HCS) and long range contaminated site (LCS) have been described in terms of heavy metal concentrations, bioconcentration factor, non-carcinogenic risk, carcinogenic risk, metals pollution index etc.

4.3.1 Comparison in terms of heavy metal concentrations

The data on the comparison between heavy metals analysis in crops and vegetables from highly contaminated site (study area-1) and long range contaminated site (study area-2) are given in **Table 4.17** and **Table 4.18.** Heavy metal concentrations in the edible parts of crops and vegetables plants from highly contaminated site (HCS) were found significantly higher than those observed in the samples collected from the long range contaminated site (LCS). However, few exceptions were realized in one crop and one vegetable species. In case of Rice, manganese concentration was found higher in the long range contaminated area than those obtained from the highly contaminated area. Another exception was recorded for Spinach. Copper concentration in Spinach from highly contaminated area was observed lower than the metal content measured in Spinach from the long range contaminated site. In general heavy and toxic metal contents in different environmental samples of highly contaminated area were substantially higher than those found in the same samples collected from the long range contaminated area.

4.3.2 Comparison in terms of bioconcentration factor

Comparison results of bioconcentration factors of heavy metals in different crops and vegetables samples from the two sampling areas (HCS and LCS) are illustrated in the **Figure 4.11**. From this figure one can easily understand that, BCF values of metals in the various samples from highly contaminated area are much greater than the BCF values measured in the same samples from the long range contaminated site. The results indicate that crops and vegetables of highly contaminated area are accumulating toxic metals at much higher rate than the similar agricultural plants grown in the long range contaminated site.

Table 4.17: Comparison between heavy metal concentrations in crops and vegetables from highly contaminated site (study area-1) and long range contaminated site (study area-2)

Samples	Concentration of Iron (mg kg^{-1})		Concentration of Nickel (mg kg^{-1})		Concentration of Manganese (mg kg^{-1})		Concentration of Lead (mg kg^{-1})	
	HCS	**LCS**	**HCS**	**LCS**	**HCS**	**LCS**	**HCS**	**LCS**
Rice (DEPZ)	345.47	77.07	14.30	6.39	26.24	44.57	5.47	4.05
Rice (BT)	509.74	77.07	16.83	6.39	19.61	44.57	5.89	4.05
Brinjal (DEPZ)	150.38	47.25	22.71	4.36	21.06	15.43	8.74	3.48
Lady's finger (DEPZ)	125.58	82.81	30.33	3.39	92.99	15.65	5.83	4.58
Water spinach (DEPZ)	432.91	75.71	26.16	8.71	66.20	46.08	8.75	3.22
Red spinach (DEPZ)	246.23	52.50	20.23	7.09	174.23	22.85	7.28	3.93
Green spinach (DEPZ)	305.52	45.79	49.00	2.48	125.99	12.17	6.18	4.25
Green spinach (BT)	510.31	45.79	17.66	2.48	40.39	12.17	6.69	4.25
Spinach (DEPZ)	435.45	91.83	20.83	9.50	62.62	47.47	9.02	4.28
Safe limit[abc]	425[a]		0.5[b]		500[c]		0.2[b]	
Safe limit[d]	-		1.5		-		2.5	

[a]FAO/WHO standard (Codex Alimentarious Commission 1984; [b](JECFA 2005); [c]European Union Standards European Union (2006); [d]Indian Standard (Awashthi 2000); DEPZ means Dhaka Export Processing Zone and BT means Bank Town area.

Table 4.18: Comparison between heavy metal concentrations in crops and vegetables from highly contaminated site (study area-1) and long range contaminated site (study area-2)

Samples	Concentration of Copper (mg kg^{-1})		Concentration of Cadmium (mg kg^{-1})		Concentration of Arsenic (mg kg^{-1})	
	HCS	**LCS**	**HCS**	**LCS**	**HCS**	**LCS**
Rice (DEPZ)	19.73	4.510	1.57	BDL	0.86	0.234
Rice (BT)	10.97	4.510	2.75	BDL	0.78	0.234
Brinjal (DEPZ)	16.51	13.473	3.05	BDL	0.93	0.156
Lady's finger (DEPZ)	14.54	10.113	2.58	BDL	1.33	0.185
Water spinach (DEPZ)	18.25	10.040	1.36	BDL	0.84	0.055
Red spinach (DEPZ)	15.43	10.160	1.00	BDL	1.45	0.097
Green spinach (DEPZ)	9.54	6.820	2.76	BDL	1.18	0.097
Green spinach (BT)	11.20	6.820	2.23	BDL	0.95	0.097
Spinach (DEPZ)	8.90	13.517	1.46	BDL	0.63	0.053
Safe limit[ab]	20[b]		0.3[a]		0.1[b]	
Safe limit[c]	30		1.5		-	

[a]FAO/WHO standard (Codex Alimentarious Commission 1984; [b](JECFA 2005); DEPZ means Dhaka Export Processing Zone and BT means Bank Town area.

However, there was an exception which was found for the bioaccumulation of iron. Accumulation of Fe in the agricultural plants of highly contaminated area was lower than that observed in the same plants grown in the long range contaminated area.

4.3.3 Comparison in terms of non-carcinogenic risk

Comparison results between non-carcinogenic risk of crops and vegetables (TTHQ) from highly contaminated site and long range contaminated site for both the adult and children is presented in the **Figure 4.12**. TTHQ data gives us information about non-carcinogenic risks associated with specific food item from two study areas. Most of the crops and vegetables samples collected from HCS and LCS displayed similar order non-carcinogenic risks.

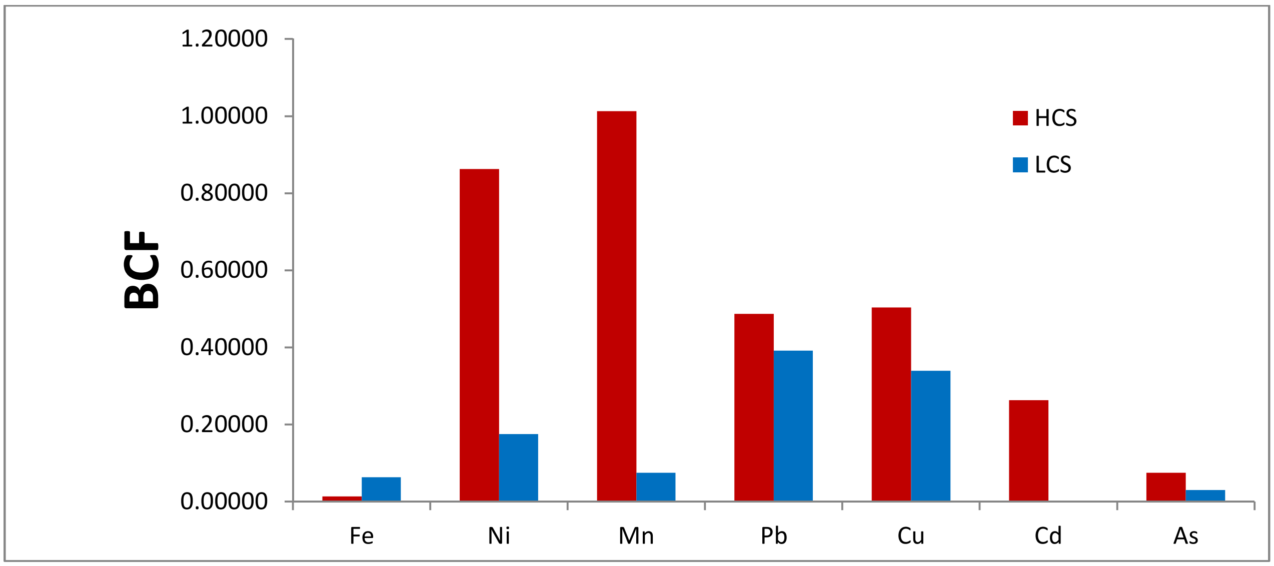


Figure 4.11: Comparison between BCF values for highly contaminated site and long range contaminated site

However, crops and vegetables from the highly contaminated site poses greater non-carcinogenic risk in comparison to agricultural plants collected from the long range contaminated site. Two samples [Rice (BT) and Brinjal (DEPZ)] showed the opposite order for both adult and children i.e. non-carcinogenic risk involved with these two agricultural plants from highly contaminated site were relatively smaller than the non-carcinogenic risks associated with the Rice and Brinjal collected from the long range contaminated site.

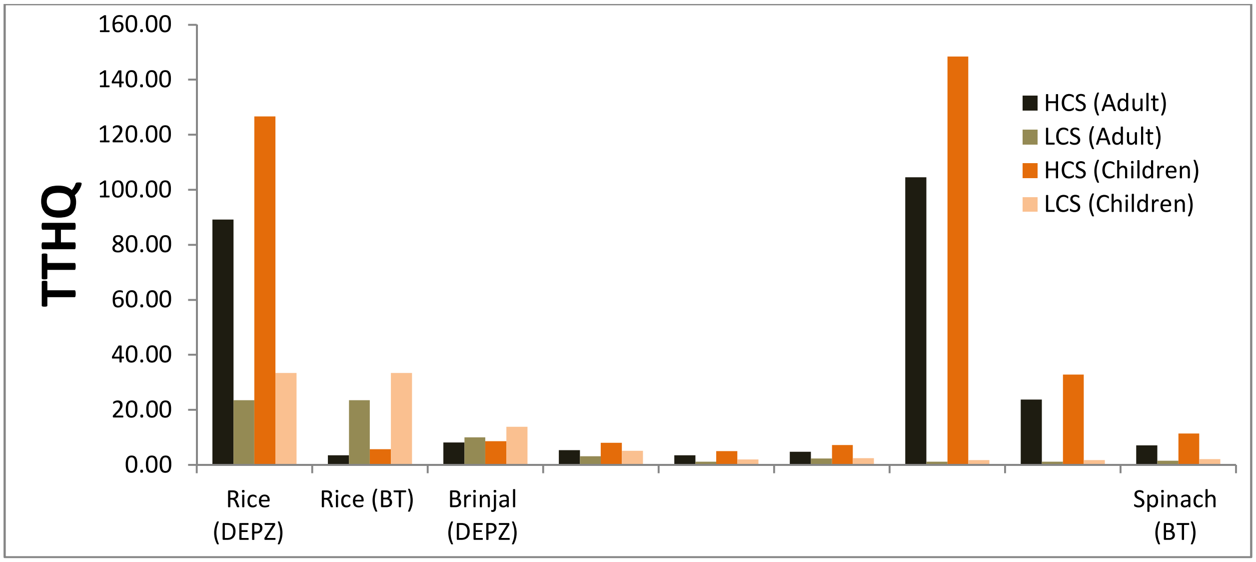


Figure 4.12: Comparison between TTHQ values for highly contaminated site and long range contaminated site

4.3.4 Comparison in terms of carcinogenic risk

Total target cancer risk (TTCR) values of different metals determined in crops and vegetables associated both children and adults from two study areas are being displayed in the **Table 4.19**. From this data table it is revealed that carcinogenic risk associated with all four studied carcinogenic metals for both adult and children are significantly more in the highly contaminated site than those observed in different samples of the long range contaminated site. TTCR values of Cd associated with crops and vegetables for both adult and children are found below the detection limit (**Table 4.19**).

Table 4.19: Comparison between carcinogenic risk of crops and vegetables (TTCR) from highly contaminated site and long range contaminated site

	Ni		Pb		Cd		As	
	Adult	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**
HCS	0.7422	1.0537	0.0008	0.0011	0.1990	0.2813	0.0227	0.0322
LCS	0.0915	0.1292	0.0003	0.0009	-	-	0.0027	0.0039

4.3.5 Comparison in terms of metal pollution index (MPI)

The metal pollution index (MPI) data measured in crops and vegetables of the two study areas and their comparisons are presented in the **Figure 4.13**. MPI values of different metals in all crops and vegetables samples from the long range contaminated site were substantially lower than the corresponding MPI values determined in the similar environmental samples collected from the highly contaminated area. Different metals concentrations data obtained from crops, vegetables, soil, and water bodies of two study areas and the corresponding heavy and toxic metal analysis using various factors and parameters such as bioconcentration factor, non-carcinogenic risks, carcinogenic risks, metals pollution index etc revealed that crops and vegetables grown in Savar area near Dhaka city are significantly contaminated and are posing severe health risks to the people who are continuously consuming these metal contaminated food items. On the other hand, considerable metal pollution was not realized in water, arable soil, crops, and vegetables cultivated in Kalihati Upazila, Tangail and thus are relatively safe for human consumption with some exceptions.

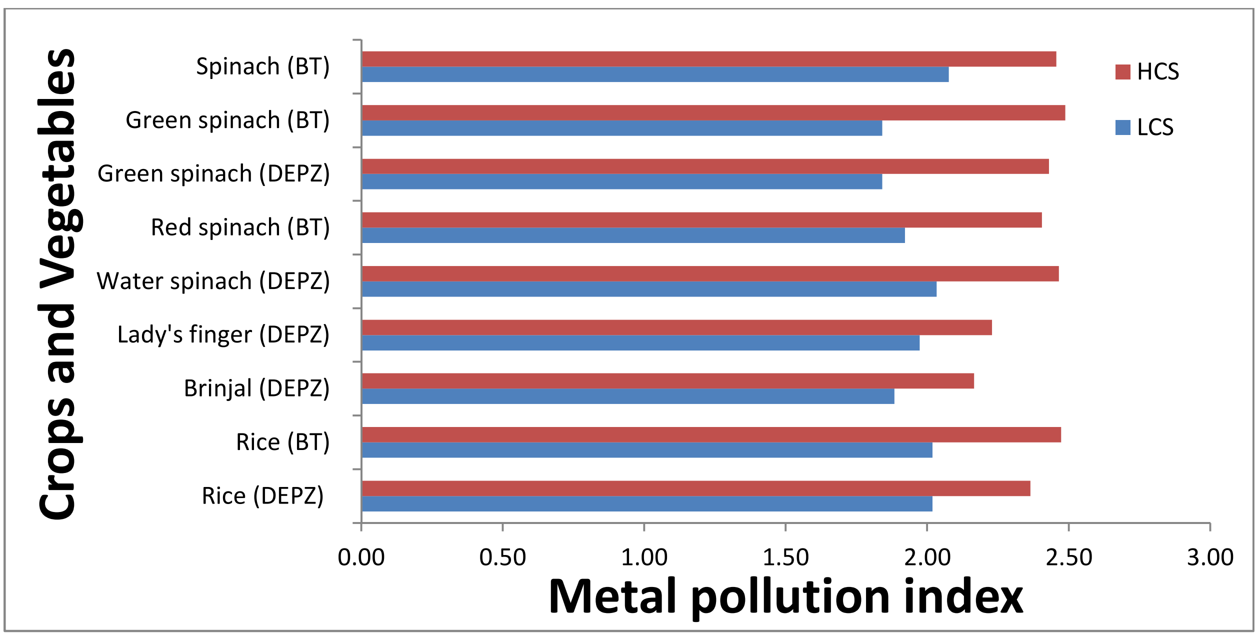


Figure 4.13: Comparison between MPI values for highly contaminated site and long range contaminated site

References

1. M. Maiolo, G. Mendicino, Pantusa, A. Senatore, "Optimization of drinking water distribution systems in relation to the effects of climate change", *Water*, Vol. 9:10, pp. 803(2017).
2. M.I. Hussain, A. Muscolo, M. Farooq, W. Ahmad, "Sustainable use and management of non-conventional water resources for rehabilitation of marginal lands in arid and semiarid environments", *Agricultural Water Management*, Vol. 221, pp. 462–476(2019).
3. I. Ugulu, Z. I. Khan, S. Rehman, K. Ahmad, M. Munir, H. Bashir, K. Nawaz, "Trace Metal Accumulation in Trigonella foenum-graecum Irrigated with Wastewater and Human Health Risk of Metal Access Through the Consumption", *Bulletin of Environmental Contamination and Toxicology*, (2019).
4. H. Rashid, M.N. Hasan, M.B. Tanu, R. Parveen, Z.P. Sukhan, M.S. Rahman, Y. Mahmud, "Heavy metal pollution and chemical profile of Khiru River, Bangladesh", *International Journal of Environment* , Vol. 2:1, pp. 57–63(2012).
5. M.A.H. Bhuiyan, N.I. Suruvi, S.B. Dampare, M.A. Islam, S.B. Quraishi, S. Ganyaglo, S. Suzuki, "Investigation of the possible sources of heavy metal contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangladesh", *Environmental Monitoring and Assessment,* Vol. 175(1-4), pp.633–649(2011).
6. M.A. Islam, D. Romic, M.A. Akber, M. Romic, "Trace metals accumulation in soil irrigated with polluted water and assessment of human health risk from vegetable consumption in Bangladesh", *Environmental Geochemistry and Health*, (2017).
7. A. Sardar, M. Shahid, Natasha, S. Khalid, H. Anwar, M. Tahir, G.M. Shah, M. Mubeen, "Risk assessment of heavy metal(loid)s via Spinacia oleracea ingestion after sewage water irrigation practices in Vehari District", *Environmental Science and Pollution Research*, (2020).
8. J.U. Ahmad, M.A. Goni, "Heavy metal contamination in water, soil, and vegetables of the industrial areas in Dhaka, Bangladesh", *Environmental Monitoring and Assessment*, Vol. 166, pp. 347–357(2010).

9. Z. Leblebici, M. Kar, L. Başaran, "Assessment of the heavy metal accumulation of various green vegetables grown in Nevşehir and their risks human health", *Environmental Monitoring and Assessment,* Vol. 192, pp. 483.
10. M. Coskun, E. Steinnes, M.V. Frontasyeva, T.E. Sjobakk, S. Demkina, "Heavy metal pollution of surface soil in the Thrace region, Turkey", *Environmental Monitoring and Assessment,* Vol. 119, pp. 545–556(2006).
11. H.R. Gebeyehu, D. Curation, "Formal analysis, Investigation and Leta Danno Bayissa; Levels of heavy metals in soil and vegetables and associated health risks in Mojo area, Ethiopia", *PLOS One* , Vol. 15, pp. 1(2020).
12. A. Latif, M. Bilal, W. Asghar, M. Azeem, M.I. Ahmad, A. Abbas, M.Z. Ahmad, T. Shahzad, "Heavy metal accumulation in vegetables and assessment of their potential health risk", *Journal of Environmental Analytical Chemistry*, Vol. 5, pp. 1(2018).
13. A. Margenat, V. Matamoros, S. Díez , N. Cañameras, J. Comas , J. M. Bayona, "Occurrence and human health implications of chemical contaminants in vegetables grown in peri-urban agriculture", *Environment International*, vol. 124, pp. 49–57 (2019).
14. S. Bo, L. Mei, C. Tongbin, Z. Yuanming, X. Yunfeng, L. Xiaoyan, G. Ding, "Assessing the health risk of heavy metals in vegetables to the general population in Beijing, China", *Journal of Environmental Sciences,* Vol. 21, pp. 1702–1709(2009).
15. A. Mahmood, R.N. Malik, "Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from different irrigation sources in Lahore, Pakistan", *Arabian Journal of Chemistry,* Vol. 7, pp. 91–99(2013).
16. R. Proshad, T. Kormoker, M.S. Islam, K. Chandra, "Potential health risk of heavy metals via consumption of rice and vegetables grown in the industrial areas of Bangladesh", *Human and Ecological Risk Assessment*, (2019).
17. S.T. Ametepey, S.J. Cobbina, F.J. Akpabey, A.B. Duwiejuah, Z.N. Abuntori, "Health risk assessment and heavy metal contamination levels in vegetables from Tamale Metropolis, Ghana", *International Journal of Food Contamination,* Vol. 5, pp. 5(2018).
18. M.M. Rahman, M. Asaduzzaman, R. Naidu, "Consumption of arsenic and other elements from vegetables and drinking water from an arsenic-contaminated area of Bangladesh", *Journal of Hazardous Materials,* Vol. 262, pp. 1056–1063(2013).

19. Y.J. Cui, Y.G. Zhu, R.H. Zhai, D.Y. Chen, Y.Z. Huang, Y. Qiu, J.Z. Liang, "Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China", *Environment International,* Vol. 30, pp. 785–791(2004).
20. M.S Ahmed, M.M.H. Biswas, M.A. Mottalib, M.N. Alam, M. Khan, "Translocation of heavy metals from industry into vegetables and crops through water and soil of Mokesh Beel in Bangladesh and their impact on human body", *JESTFT*, Vol. 13:5, pp. 59-71(2019).
21. F.T. Gemeda, D.D. Guta, F.S. Wakjira, G. Gebresenbet, "Occurrence of heavy metal in water, soil, and plants in fields irrigated with industrial wastewater in Sabata town, Ethiopia", *Environ Sci Pollut Res*, (2020).
22. M.S. Sultana, S. Rana, S. Yamazaki, T. Aono, S. Yoshida, "Health risk assessment for carcinogenic and noncarcinogenic heavy metal exposures from vegetables and fruits of Bangladesh", *Cogent Environmental Science,* Vol. 3:1291107.
23. M.S. Islam, M.K. Ahmed, H.A.M. Mamun, M. Raknuzzaman, M.M. Ali, D.W. Eaton, "Health risk assessment due to heavy metal exposure from commonly consumed fish and vegetables", *Environment Systems and Decisions*, (2016).
24. X. Li, Z. Li, C.-J. Lin, X. Bi, J. Liu, X. Feng, H. Zhang, J. Chen, T. Wu, "Health risks of heavy metal exposure through vegetable consumption near a large-scale Pb/Zn smelter in central China", *Ecotoxicology and Environmental Safety,* Vol. 161, pp. 99–110(2018) .
25. S. Kladsomboon, C. Jaiyen, C. Choprathumma, T. Tusai, A. Apilux, "Heavy metals contamination in soil, surface water, crops, and resident blood in Uthai District, Phra Nakhon Si Ayutthaya, Thailand", *Environ Geochem Health*, (2019).
26. T. Kormoker, R. Proshad, M.S. Islam, T.R. Tusher, M. Uddin, S. Khadka, K. Chandra, A. Sayeed, "Presence of toxic metals in rice with human health hazards in Tangail district of Bangladesh", *International Journal of Environmental Health Research*, (2020).
27. M.I.H. Real, H.M. Azam, N. Majed, "Consumption of heavy metal contaminated foods and associated risks in Bangladesh", *Environ Monit Assess,* Vol. 189, pp. 651(2017).
28. M. Rahman, M.A. Islam, M.M. Zaved, "Assessment of Essential and Potentially Toxic Elements and Possible Health Risks in Hylocereus undatus and Punica granatum", *Biological Trace Element Research*, (2020).

29. M.S. Islam, M.K. Ahmed, M.H.A. Mamun, M. Raknuzzaman, "The concentration, source and potential human health risk of heavy metals in the commonly consumed foods in Bangladesh", *Ecotoxicology and Environmental Safety,* Vol. 122, pp. 462–469(2015).
30. M. Miri, E. Akbari, A. Amrane, S.J. Jafari, H. Eslami, E. Hoseinzadeh, M. Zarrabi, J. Salimi, M.S. Arbabi, M. Taghavi, "Health risk assessment of heavy metal intake due to fish consumption in the Sistan region, Iran", *Environ Monit Assess,* Vol. 189, pp. 583(2017).
31. A.A. Mohammadi, A. Zarei, S. Majidi, A. Ghaderpoury, Y. Hashempour, M.H. Saghi, A. Alinejad, M. Yousefi, N.H. Gholizadeh, M. Ghaderpoori, "Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran", *MethodsX*, Vol. 6, pp. 1642–1651(2019).
32. A.M. Abbasi, J. Iqbal, M.A. Khan, M.H. Shah, "Health risk assessment and multivariate apportionment of trace metals in wild leafy vegetables from Lesser Himalayas, Pakistan", *Ecotoxicology and Environmental Safety,* Vol. 92, pp. 237–244(2013).
33. M. Ahmed, M. Matsumoto, K. Kurosawa, "Heavy metal contamination of irrigation water, soil, and vegetables in a multi-industry district of Bangladesh", *International Journal of Environmental Research,* Vol. 12, pp 531–542(2018).

CHAPTER-5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

The present study has investigated the heavy and toxic metals contamination in different crops, vegetables, grown in and around industrial areas of Savar, Dhaka which was identified as highly contaminated area. The study also determined the heavy and toxic metal pollution status in crops, vegetables, soil, and water bodies of Kalihati Upazila, Tangail which has been recognized as a long range contaminated site. The present research work also evaluated the mobilization and transportation of heavy and toxic metals from soil, roots to different parts of the agricultural plant bodies. The significant outcomes of the present study are highlighted below:

1. Heavy and toxic metal concentrations in the studied water and soil samples from highly contaminated area were found much higher than the permissible limits of FAO, WHO, Indian and China whereas the metal concentrations determined in the most of the water and soil samples from long range contaminated area were found lower than the permissible limit.

2. Pollution Load Index (PLI) values suggested the occurrence of significant water and soil pollution by manganese, copper, cadmium and lead in the highly contaminated area. The data also revealed that, soil is highly polluted with cadmium, moderately polluted with arsenic, and slightly polluted with nickel, iron and copper in the same area.

3. Metal concentrations in different crops and vegetables from highly contaminated area were found substantially higher than the safety limits of FAO, WHO, USEPA, EU, and others.

4. Pollution load index (PLI) values in crops and vegetables were also much higher than the prescribed maximum allowable levels.

5. Heavy metals uptake by each part of the crops and vegetables plant bodies were investigated in this study and plants were varied in accumulating metals in their body parts.

6. Mobilization and transportation of heavy metals from roots to shoots of different crops and vegetables plants were also examined.

7. Most of the crops and vegetables plants accumulated and deposited maximum level of heavy metals in their roots. However, some food plants showed maximum accumulation of the respective heavy and toxic metals in their edible parts.

8. Higher Bioconcentration Factors (BCF) data revealed that the metals transfer rate from contaminated soil to plant was considerably higher.

9. BCF values in crops and vegetables plants from the highly contaminated site were found significantly higher than those observed in the long range contaminated site.

10. TTHQ values demonstrated the potential non carcinogenic health risks in all the studied crops and vegetables grown in the study areas.

11. Non carcinogenic risks associated with crops and vegetables were found higher in highly contaminated area. However, in some cases the values were higher in some vegetables plants in the long range contaminated area.

12. TTCR values indicated considerable carcinogenic health risks in all the studied crops and vegetables grown in the study areas.

13. Carcinogenic risks associated with crops and vegetables were found higher in highly contaminated area then those observed in the same environmental samples from the long range contaminated site.
14. For all the studied crops and vegetables, Metal Pollution Index (MPI) and the corresponding Carcinogenic Risks were substantially higher for the consumption of contaminated crops and vegetables grown in the highly contaminated area in comparison to those observed in the same agricultural plants cultivated in the long range contaminated area.

5.2 Recommendations

1. Higher BCF values, considerable TCR values, and $THQ \geq 1$ of metals found in the present study suggested that crops and vegetables should not be cultivated in the contaminated study areas.

2. All industries should be equipped with proper effluent treatment plants (ETP) and they should operate those ETP units during entire period of the manufacturing processes.

3. People awareness about health risks due to the consumption of contaminated food, should be increased.

4. Continuous monitoring of industrial activities should be done by Department of Environment (DoE) to minimize the discharge of untreated industrial effluents.

5. Finally, all the necessary steps should be taken to minimize the heavy and toxic metals pollution in the study areas.