

Chapter 1

Introduction

A major concerning issue has been noticed that a serious environmental problem associated with rapid urbanization and industrialization which is being increasing day by day and ultimately results in heavy metal pollution to the environment. Heavy metals originating from various anthropogenic and natural sources, are eventually released into aquatic or atmospheric systems, although the anthropogenic inputs in environments have increased dramatically since the Industrial Revolution (Nriagu *et al.*, 1979; Thevenon *et al.*, 2011). Being a rapid growing country, Bangladesh is experiencing rapid industrial developments and unplanned urban growth in recent years (Mia *et al.*, 2015), but pollutants produced by these activities are triggering environmental problems on an unprecedented scale, primarily due to different toxic heavy metal pollution (Tareq *et al.*, 2003; Bhuiyan *et al.*, 2011; Islam *et al.*, 2015a; Sharifuzzaman *et al.*, 2016). For example, Chattogram, which is the second largest city, main seaport and economic nerve-center of the country, whose ecosystems is under multiple stresses due to discharge of effluents from various heavy industrial sites of Chattogram region like oil refineries, ship recycling, textile and cement industries, tanneries, paint manufacturing and dyeing plants, paper and rayon mills, naval and merchant ships, steel and engineering factories, food and fertilizer industries, chemical industries and other small-scale and agro-based industries as well as disposal of sewage and solid wastes directly into the adjacent Karnaphuli River (KR) and coastal waters of Bay of Bengal (Chowdhury *et al.*, 1999; Hossain and Khan 2002; Ali *et al.*, 2016).

The Karnaphuli River is the principal and the largest river in Chattogram district of Bangladesh. The Karnaphuli is very important because the people of Chattogram city depend on Karnaphuli for variety of aspects. The river originates from the Lushai Hills of Mizoram of India, flows through Rangamati and the port city of Chattogram and discharges into the Bay of Bengal at latitude 22°12'N and longitude 91°47'E near Patenga (Sujan Dey *et al.*, 2015). Most of the industries in Chattogram, are located mainly at Sagorika, Fauzdarhat, Kaptai, Nasirabad, Barabkunda, Bhatiary, Sholashahar, Patenga and Kalurghat, Oxygen, Kotwali. The

wastewater from these heavy industrial sites is discharged into surface drains that ultimately carry it to the Karnaphuli River. Especially it was noticed, wastewater from Nasirabad and Kalurghat industrial area (mainly chemical, leather, textile and steel re-rolling industries) drain that wastewater into drainage canals, which is ultimately discharged into the Karnaphuli River (Sujan Dey *et al.*, 2015). It is obvious that, heavy metal pollution of river is a major problem which is caused by the disposal of untreated toxic effluent, sewage discharges, industrial pollutants, land washout, city run-off and urban wastages into rivers. Moreover, as being the business capital of Bangladesh, in space and time Chattogram is becoming more industrialized and populated day by day. This because these potential sources of contamination not only comes from these industrial sites but also it comes from the sources of municipal and household wastage materials through different sewage and drainage system ultimately which is discharged into the Karnaphuli River (KR).

The industries produce huge amounts of toxic effluents everyday which are being directly discharged into the agricultural fields, surrounding land, irrigation channels, surface water and finally into the Karnaphuli River after primary or without any treatment. The uncontrolled dumping of huge wastes from heavy industrial sites is even extremely poisonous when the pollutants are heavy metals which cannot be treated easily by conventional methods. This water is distributed into the Karnaphuli River through several ways. These sources of pollution are mainly from gas production plants, cement production plants, oil refining plants, ship-breaking yard, port activities, other nearby industries, and untreated urban wastes from metropolitan. Moreover some industries are discharging untreated waste water directly to the main water body of the river causing serious damage to marine ecology and aquatic lives along with the health of peoples who are exposed to this environment for a long term.

In these circumstances, it is very necessary to evaluate the prevalence of heavy metal contamination in the Karnaphuli River water. In this Consideration, the importance of studying heavy metal pollution for understanding suitability of river water for aquatic life and for the purpose of human activities the study is designed to determine the levels of some toxic heavy metals (Pb, Ni, Cr) of seven selected sites of the Karnaphuli River and to evaluate the water quality parameters in aspects heavy metal contamination of KR as affected by industrial pollution. Although a

number of studies investigated the heavy metal contamination of Karnaphuli River (KR) and within the river catchment (Ali *et al.*, 2016; Islam *et al.*, 2013, 2015b; Dey *et al.*, 2015) but only few studies were carried out to check the overall view of heavy metal contamination profile in Karnaphuli River basically flows through the metropolitan city of Chattogram at a time. This because the study was especially designed to determine the heavy metal contamination of the river at different points covered the sites from the entering point of metropolitan city to the point of estuarine site of the river including Chattogram port. This study also includes the sampling from the main body of the river at different points throughout the metropolitan city of Chattogram as well as the study reveals the view of estuarine environment of the river.

Therefore, the objectives of this research are to estimate the contamination with heavy metals and reveal their potential sources including accumulation history in different sites of KR sediment, and further discuss the results in relation to catastrophic events and human activities. Moreover, this study of heavy metal contamination in KR does not only indicate the environment health issue (Li *et al.*, 2007) but also reveals information on relevant human activities in the surrounding areas (Delgado *et al.*, 2012). This study also includes the analysis of samples from some selected non-industrial sites (residential, households, populated area) to compare the degree of contamination between industrial and non-industrial sites of KR flows through the Chattogram.

1.1 Objectives:

- To determine the level of lead, chromium and nickel in both industrial and non-industrial sites of the Karnaphuli River.
- To evaluate the chemical profile of the water of the Karnaphuli River.
- To investigate the main water quality parameters by determining heavy metals concentration in water.
- To determine the risk factors associated with the prevalence of the selected heavy metals in Karnaphuli River.

1.2. Anticipated outcomes

- Estimated level of lead, chromium and nickel in water of both industrial and non-industrial sites of Karnaphuli River.
- Identified risk factors associated with the level of the selected heavy metals in sites of Karnaphuli River, Chattogram.
- Recommended public health risk according to the level of concentration of the heavy metals recorded from selected the sites of Karnaphuli River, Chattogram.
- Recommended environmental management systems on the level of heavy metal pollution in Karnaphuli River, Chattogram, Bangladesh.

Chapter 2

Review of Literature

Relevant literatures on heavy metals (lead, chromium, nickel) in different rivers have been discussed and reviewed in this chapter.

2.1 Water quality

The quality of water refers to the physical, chemical and biological characteristics of the water. Usually it involves in the evaluation process of the physical, chemical and biological properties in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and aquatic system. The most universal standards used to assess water quality which are related to health of ecosystems, safety of human contact and drinking water. Usually the quality of water depends on the local geology and ecosystem, as well as human activities such as use of water bodies as sink (Johnson *et al.*, 1997).

The parameters which are used to assess the water quality are determined by the intended use. Water quality supposed to be focused on water that is treated for industrial uses, water for human consumption, or in the environment. The pollutants of water may be present in untreated water include microorganisms such as bacteria and viruses; inorganic contaminants such as salts and metals; organic chemical contaminants from industrial processes and petroleum use; pesticides and herbicides; and radioactive contaminants. There are some standards have been established to assess the quality of water to regulate the elements that potentially affect human health, environment and aesthetic qualities of water. The World Health Organization (WHO) guideline for Drinking Water Standards, United States Specification for Drinking Water and European Union Specification for Drinking Water are the organizational bodies which established recognized water quality standards.

The suitability of water for using household and industrial purposes may largely affected by dissolved minerals. The most common of these is the presence of ions

of calcium and magnesium which interpose with the cleaning action of soap, and can form hard sulphate and soft carbonate which deposits in water heaters or boilers.

Environmental water quality, also known as ambient water quality which is related to water bodies such as lakes, rivers, and oceans. The quality standards for surface waters vary significantly because of different environmental conditions, ecosystems, and intended human uses. Poisonous substances and vast concentration of certain harmful microorganisms can cause a health hazard for non-drinking purposes such as irrigation, fishing, rafting, swimming, boating and other industrial uses.

With the rapid grow of industrialization and increasing population the extent of requirements for water has increased together with greater demands for higher quality water. It has been considered that water is the most competent medium to clean, disperse, transport and dispose of wastes (domestic and industrial wastes, mine drainage waters, irrigation returns, etc.). These actions have undesirable effects on the natural environment. Further, uncontrolled use of land, industrialization, urbanization, deforestation, unexpected (or unauthorized) release of chemical substances and discharge of untreated wastes or leaching of noxious liquids from solid waste deposits have impacted badly on the quality of water resources (UNESCO, 2003).

2.2 Water pollution

Pollution of water is one of the most talked of topics in recent years because of its significant on human and aquatic life system. Water can be deemed polluted when its composition or quality gets changed either naturally or as a result of human activities so as to become less suitable for drinking, domestic, agricultural, industrial, recreational, wildlife and other uses for which it would have been otherwise suitable in its natural or unmodified state (Goel *et al.*, 2009). Gross pollution of water mainly because of urbanization, industrialization, agriculture and increase in human population being observed (Calhoun *et al.*, 2005; Goel *et al.*, 2009). In addition to microbial contamination, excess use of fertilizers, trash floating on rivers, streams, lakes and beaches including toxic chemicals, water pollutants occur in many other forms in surface and groundwater. Heavy metals

pollution of water is becoming more concerning issues day by day because of its adverse effects on environment and human life system. Increasing number of human population, urbanization, industrialization are the main possible causes of heavy metals contamination of water. Industrial sites produces huge amount of toxic effluents which are mostly untreated, finally discharged into the river through different canals results in water pollution. Water pollution threatens our health and environment and therefore we need to implement an expanding array of techniques for its assessment, prevention and remediation (Calhoun *et al.*, 2005).

2.3 Heavy metals

2.3.1 Introduction

Heavy metals are the naturally occurring elements can be defined as a subset of elements that exhibit metallic properties such as hard, opaque, shiny, and having good electrical as well as thermal conductivity. Heavy metals are inorganic in nature and having a high atomic weight and high density which is five times greater than that of water (Banfalvi G *et al.*, 2011). Heavy metal also refers to those having a specific density of more than 5 g/cm³ (Suciu *et al.*, 2008). They can also be defined as chemical elements with the density greater than 4 g/cm³ found in all kinds of soils, rocks and water in terrestrial and freshwater ecosystem (Adelekan and Abegunde, 2011).

Contamination of water with heavy metals have received a great concern to environmental chemists due to their toxic nature among any other pollutants. Naturally heavy metals are present in minor quantity in natural waters but many of them are toxic even at very low concentrations (Herawati N *et al.*, 2000). Metals such as lead, chromium, arsenic, cadmium, nickel, mercury, chromium, cobalt, zinc and selenium are highly toxic even in trace amounts. Now-a-days increasing quantity of heavy metals in our resources is becoming a great concern, especially since a large number of industries are discharging their waste water containing toxic effluents into fresh water without any efficient treatment (Salomons W. *et al.*, 1995). Surface and underground water sources when gets contaminated with these untreated waste water from heavy industrial sites which can cause considerable soil and water pollution.

In small amounts, some specific heavy metals are nutritionally essential for a healthy life. Some of these agents (e.g., iron, copper, manganese, and zinc) or some forms of them are commonly found naturally in foodstuffs, fruits and vegetables, and in commercially available multivitamin products. Heavy metals have some common application in different purposes which include diagnostic medical applications i.e. direct injection of gallium during radiological procedures, dosing with chromium in parenteral nutrition mixtures, and the use of lead as a radiation shield around x-ray equipment (Roberts *et al.*, 1999). Heavy metals are also significant in industrial applications.

2.3.2 Influence of heavy metals on human and environmental pollution

Heavy metals become poisonous to the human body when they are consumed above the bio-recommended limits. This because when heavy metals they are consumed in excess amount are not metabolized by the organs and accumulate in the soft tissues causing harmful biotoxic effects to the body. The nature of effects could be toxic ((acute, chronic or sub-chronic), neurotoxic, carcinogenic, teratogenic or mutagenic. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper and aluminium poisoning: gastrointestinal (GI) disorders, diarrhoea stomatitis, tremor, hemoglobinuria causing a rust-red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled (McCluggage *et al.*, 1991). They may enter the human body via food, water, air, or absorption through the skin in agriculture, manufacturing, pharmaceutical, industrial, or residential settings.

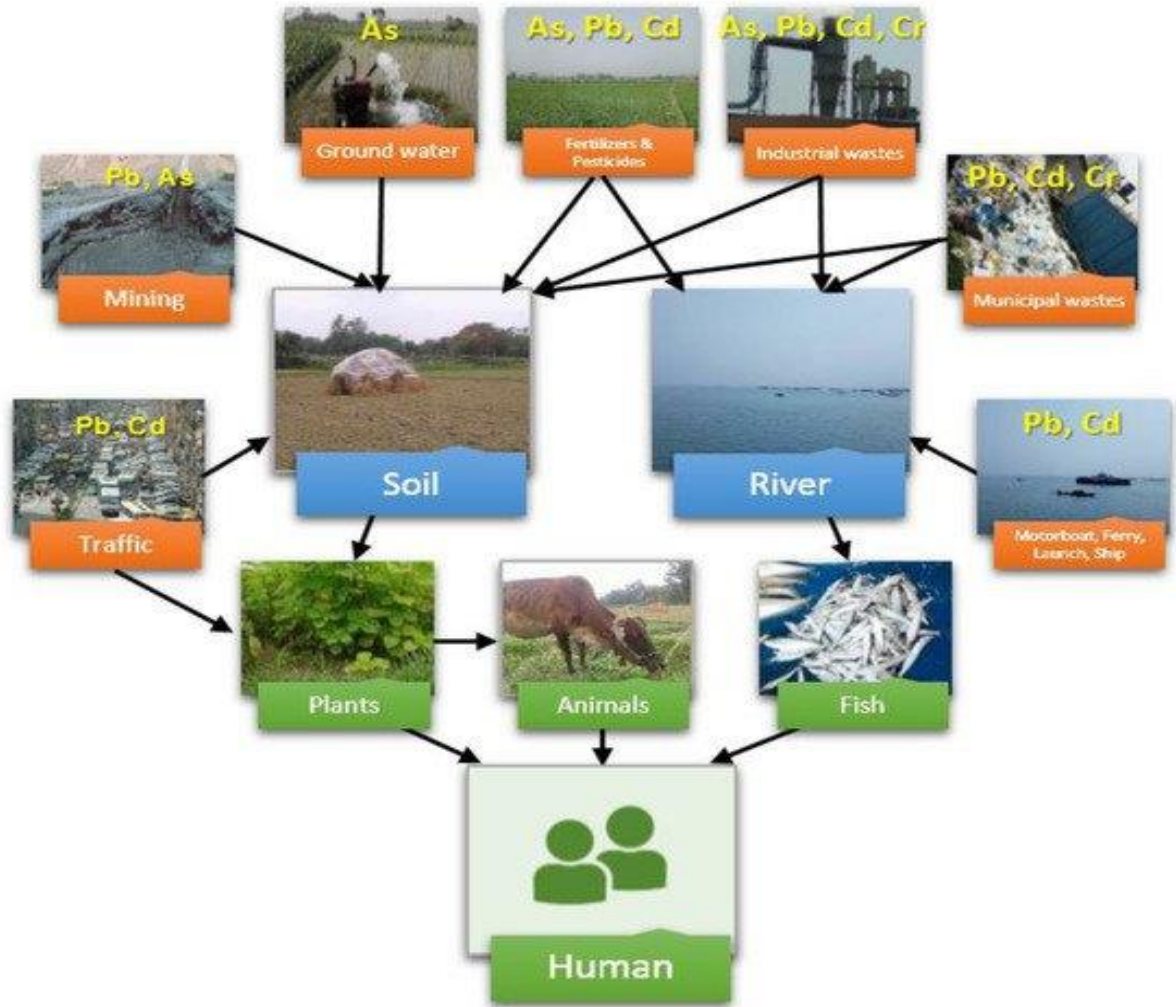


Figure 2.1: major pathways of heavy metal and metalloid dispersion and human exposure in Bangladesh (M. Mominul Islam et al., 2018)

Industrial exposure is common in adults and ingestion the most common route in children (Roberts *et al.*, 1999). Children may improve toxic levels from normal hand-to mouth activity (i.e. coming in contact with polluted soil or eating objects that are not food such as dirt or paint chips). Less common routes of exposure include a radiological procedure, inappropriate dosing or monitoring during intravenous (parenteral) nutrition, a broken thermometer or a suicide or homicide attempt (Lupton *et al.*, 1985; Smith, *et al.*, 1997).

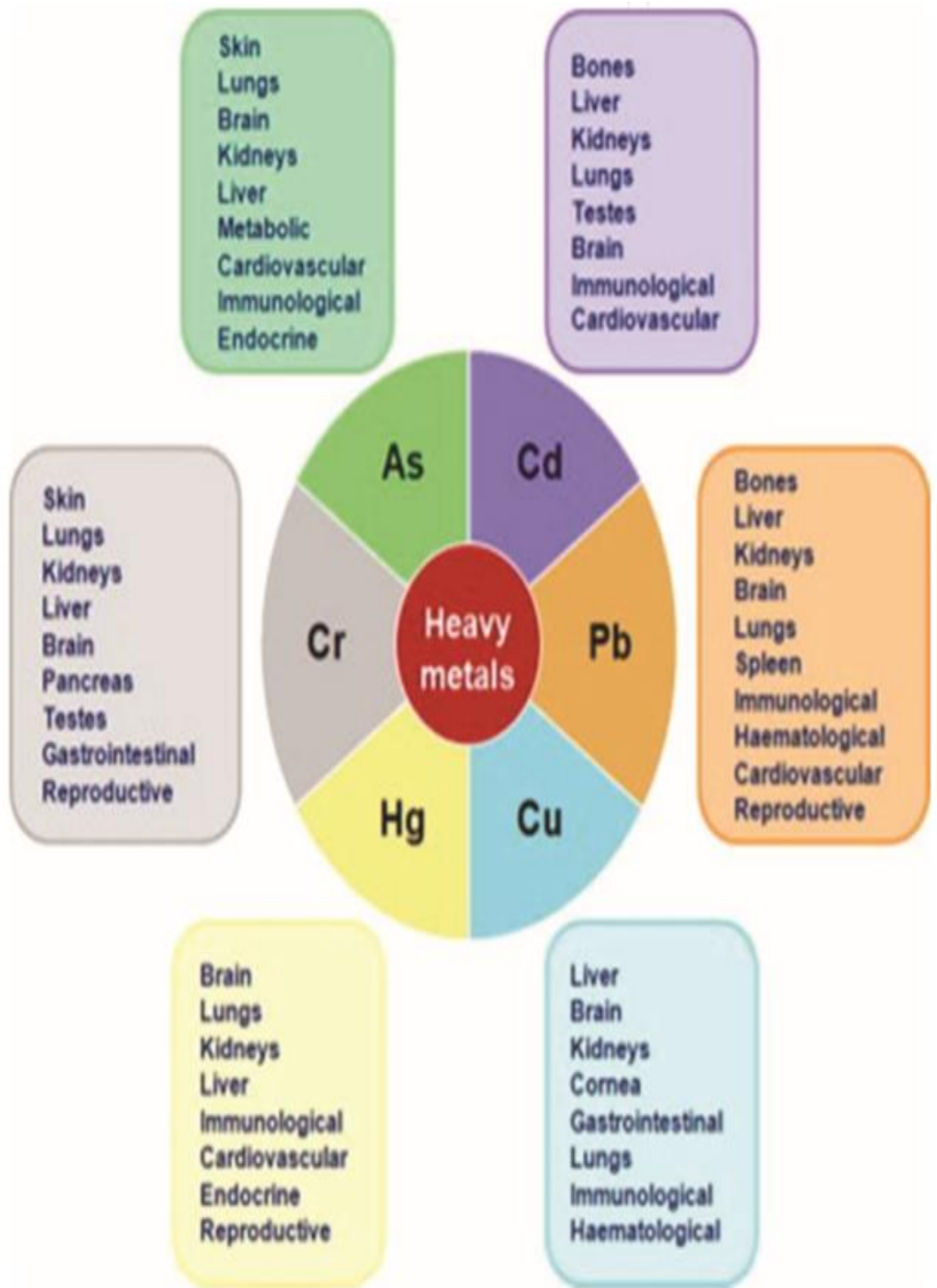


Figure 2.2: Impacts of heavy metals on the environment (Garcia-Niño WR, 2014).

Heavy metals once discharged into the environment can remain in waterways for decades or even centuries, in concentrations that are high enough to cause a health risk. Several methods are used to sanctify the environment from these kinds of pollutants, but most of them are more expensive and troublesome to get optimum results. In modern times, phytoremediation is an effective and affordable technological solution used to extract or remove inactive metals and metal pollutants from contaminated soil and water. This technology is environmental friendly and potentially cost effective (Bieby *et al.*, 2011).

However, it is very emergent to note that the concentrations of individual metals in living tissues must be kept in very low and should be maintained within appropriate limits to permit the optimum biological performance of most organisms (Misra and Mani, 2009). Because heavy metals are considered serious contaminants because of their toxicity, persistence and non-biodegradable natures in the environment, thereby constituting a threat to human beings and other forms of biological life (Adeleken and Abegunde, 2011).

Adeleken and Abegumde (2011) have noticed that heavy metals have low environmental mobility resulting a single contamination could set a stage for a long term exposure of human, microbial, fauna, flora and other edaphic communities to heavy metals. It can be said that the problem of this atmospheric heavy metal pollution is not going to disappear overnight. On the other hand it will remain a succession of mass industrial activity for many generations and is likely to increase swiftly further in future. In this regard, the compilation of past and present catalogues of atmospheric heavy metal concentration is an activity of great importance (Shrivastav *et al.*, 2001).



Figure 2.3: Neurotoxic effects of heavy metal

2.3.3 Heavy metals effect on water quality

The pollution of fresh waters with a wide range of contaminants has become a matter of great concern over the last few decades (Al-Weher *et al.*, 2008). Water pollution refers to the contamination of water by foreign matter that deteriorates the quality of the water. Water pollution covers pollutions in liquid forms like ocean pollution and river pollution. As the term applies, water pollution occurs in the oceans, lakes, streams, rivers, underground water and bays, in short liquid-containing areas. Basically water is being polluted by both organic and inorganic pollutants. In normal situation organic pollutants are biodegraded by microbes and converted to a form that brings benefits to the aquatic life and in contrast the inorganic pollutants can become hazardous when they are discharged in excessive amounts to the environment. Some of the pollutants like lead (Pb), arsenic (As), mercury (Hg), chromium (Cr) specially hexavalent chromium, nickel (Ni), barium (Ba), cadmium (Cd), cobalt (Co), selenium (Se), vanadium (V), oils and grease, pesticides, etc are very harmful, toxic and poisonous even in ppb (parts per billion) range (Rashmi Verma *et al.*, 2013). These large amount of heavy metals are being received by the aquatic systems from natural occurring deposits and natural processes and anthropogenic activities (Wogu and Okaka, 2011). Anthropogenic sources coming from human activities such as industrial, urbanization, municipal

effluents, as well as non-point source run off are the main sources of metals in rivers (Sonayei *et al.*, 2009).

Although there are many sources of water contamination, industrialization and urbanization are two of the culprits for the increased level of heavy metal water contamination. Heavy metals are deported by runoff from municipalities, industries and urban areas. Most of these metals end up accumulating in the soil and sediments of water bodies (Musilova J *et al.*, 2016).

Heavy metals can be found in traces in water sources and still be very poisonous and causes serious health problems to humans and other ecosystems. This is because the toxicity level of a metal depends on various factors such as the type of organisms which are exposed to it, its nature, its biological role and the period at which the organisms are exposed to the metal. Food chains and food webs symbolize the relationships amongst organisms. Therefore, the pollution of water by heavy metals actually affects all organisms. Humans, an example of organisms feeding at the highest level, are more prone to serious health problems because the concentrations of heavy metals increase in the food chain (Lee G *et al.*, 2002).

Releasing heavy metals into rivers or any other aquatic environment can change both aquatic species diversity and ecosystems because of their toxicity and accumulative behaviour (Al-Weher *et al.*, 2008). Heavy metals dissolved in water also endanger the lives of the public who use it for drinking and also irrigation. When used for irrigation heavy metals have the danger of being incorporated in food chain and therefore ingested by the public (Wogu and Okaka, 2011).

Heavy metals accrue in the soils at toxic levels as a result of long term application of untreated waste water and therefore soils irrigated by wastewater accumulate heavy metals in their soil surface (Sonayei *et al.*, 2009). When the strength of the soil to retain heavy metals is reduced due to repeated application of waste water, the metals leach into ground water or soil solution available for uptake (Sonayei *et al.*, 2009). Table 2.1 shows metal limits in water set by national and international organizations.

Table 2.1: Shows metal limits ($\mu\text{g/l}$) in water set by national and international organization

	Cd	Cr	Mn	Pb	Zn
USEPA	5	100	50	10	5000
EU	5	50	50	10	Nm
WHO	3	50	400	10	NGL
Iranian	10	50	500	50	Nm
Australian	2	50	500	10	3000
Indian	10	50	100	100	5000
New Zealand	4	50	400	10	1500

Nm- not mentioned

NGL – No guideline, because it occurs in drinking water at concentrations well below those at which toxic effects may occur

Source; Mebrahtu and Zerabruk (2011)

2.4 Sources of heavy metals

Heavy metals in the atmosphere arise from both natural and anthropogenic activities and end up in different environmental segments (soil, water, air and their interface) (Figure 2). Mainly, among the natural processes like rock weathering, soil erosion, dissolution of water-soluble salts etc. as well as anthropogenic processes such as municipal waste-water treatment plants, manufacturing industries, and agricultural activities etc. are most vital sources of heavy metals. In general, metals permeate the aquatic environment through atmospheric deposition, erosion of geological milieu or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining waste (Aderinola *et al.*, 2009; Adelekan *et al.*, 2011).

2.4.1 Natural processes

Many studies have revealed various natural sources of heavy metals. Under certain and different environmental conditions, natural emissions of heavy metals occur in the atmosphere. Such emissions include volcanic eruptions, sea-salt sprays, forest

fires, rock weathering, biogenic sources and wind-borne soil particles. Besides, natural weathering processes can lead to the release of metals from their endemic spheres to different environment 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 tiny amounts, they still cause serious health problems to human and other mammals (Herawati N *et al.*, 2000). In addition, heavy metals naturally get into waters by chemical weathering of minerals and soil leaching (El-Bouraie et al., 2010).

Table 2.2: Sources of heavy metal pollutants in water

Heavy metals	Sources of Heavy metals	Toxic effects
Pb	<ol style="list-style-type: none"> 1. Vehicles. 2. PbCrO₄ or lead (II) chromate. 3. Tobacco products. 4. Colour paints. 5. Antiknocking agents. 6. Lead pipe. 7. Lead utensils. 	<ol style="list-style-type: none"> 1. High-pressure. 2. Problems in nervous system, kidney and liver. 3. Gastrointestinal hemorrhage. 4. Hemolysis (red blood cell destruction). 5. Acute renal failure.
Cr	<ol style="list-style-type: none"> 1. Tannery waste [Cr₂(SO₄)₃]. 2. Poultry feed. 3. Waste from chemical laboratory. 4. Textile waste. 5. Earth's crust. 	<ol style="list-style-type: none"> 1. Skin problems. 2. Lung, bladder, skin cancer. 3. Toxicity in blood. 4. Problem in embryo.
Ni	<ol style="list-style-type: none"> 1. Earth's crust. 2. Industrial waste (Metal). 3. Urea fertilizer industry. 4. Nickel-plated faucets. 	<ol style="list-style-type: none"> 1. Dermatitis. 2. Problems in male reproductive system. 3. Problems in urinary system. 4. Problems in enzyme system.

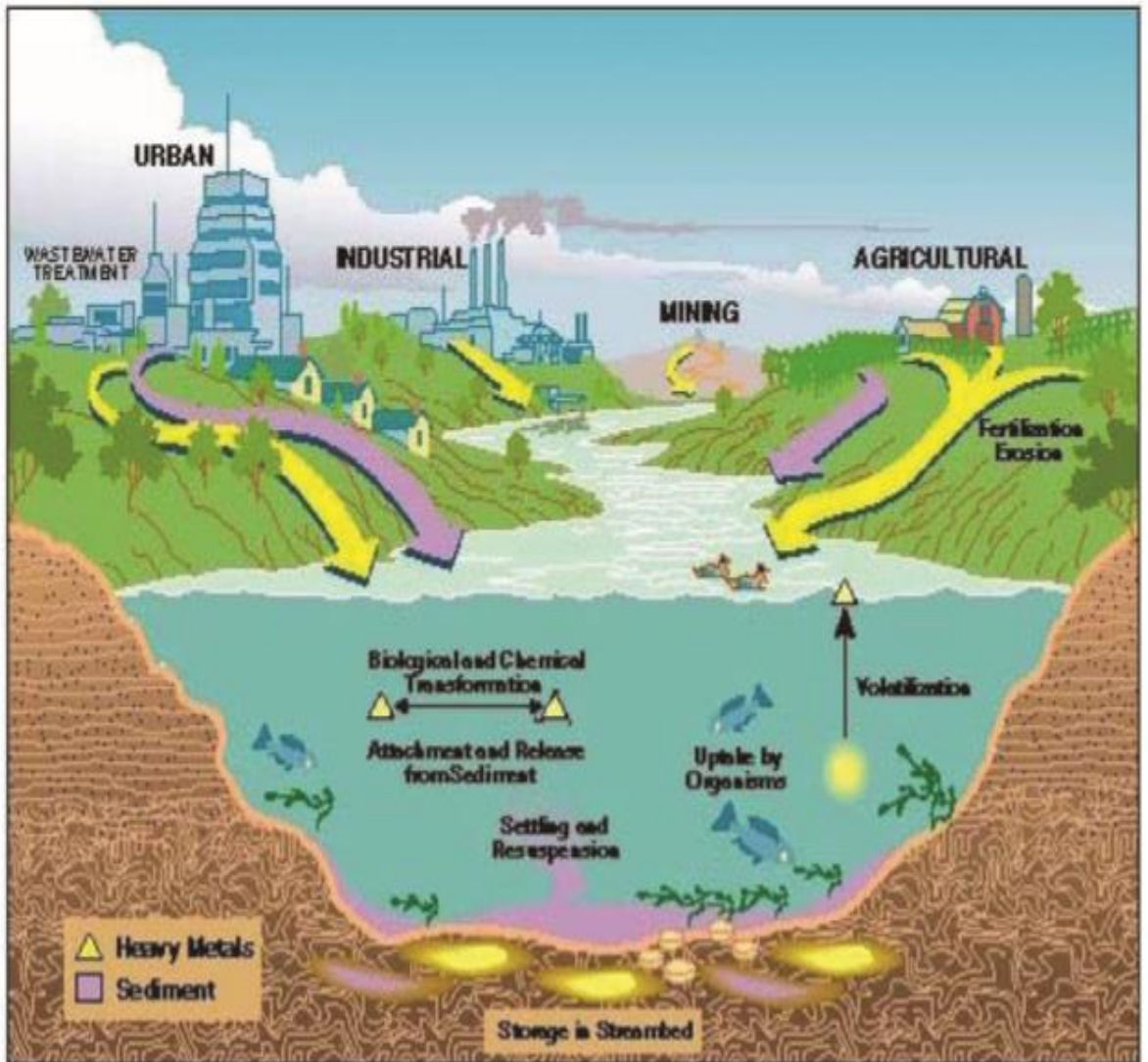


Figure 2.4: Sources and sinks of heavy metals (Garbarino JR et al., 1995).

2.4.2. Anthropogenic processes

Anthropogenic processes includes municipal waste-water treatment plants, industrial activities, agriculture, wastewater, mining and metallurgical processes, and runoffs which lead to the release of pollutants to different environmental compartments. Heavy metals sources from anthropogenic activities have been noted to go beyond the natural fluxes for some metals. In natural, metals emitted in wind-blown dusts are mostly from industrial areas. Some principal anthropogenic sources which significantly contribute to the heavy metal pollution in the environment include automobile exhaust which releases lead; smelting which releases arsenic,

copper and zinc; insecticides which release arsenic and burning of fossil fuels which release nickel, vanadium, mercury, selenium and tin. Human activities have been found to contribute more to environmental pollution due to the everyday manufacturing of goods to meet the demands of the huge population (He ZL *et al.*, 2000).

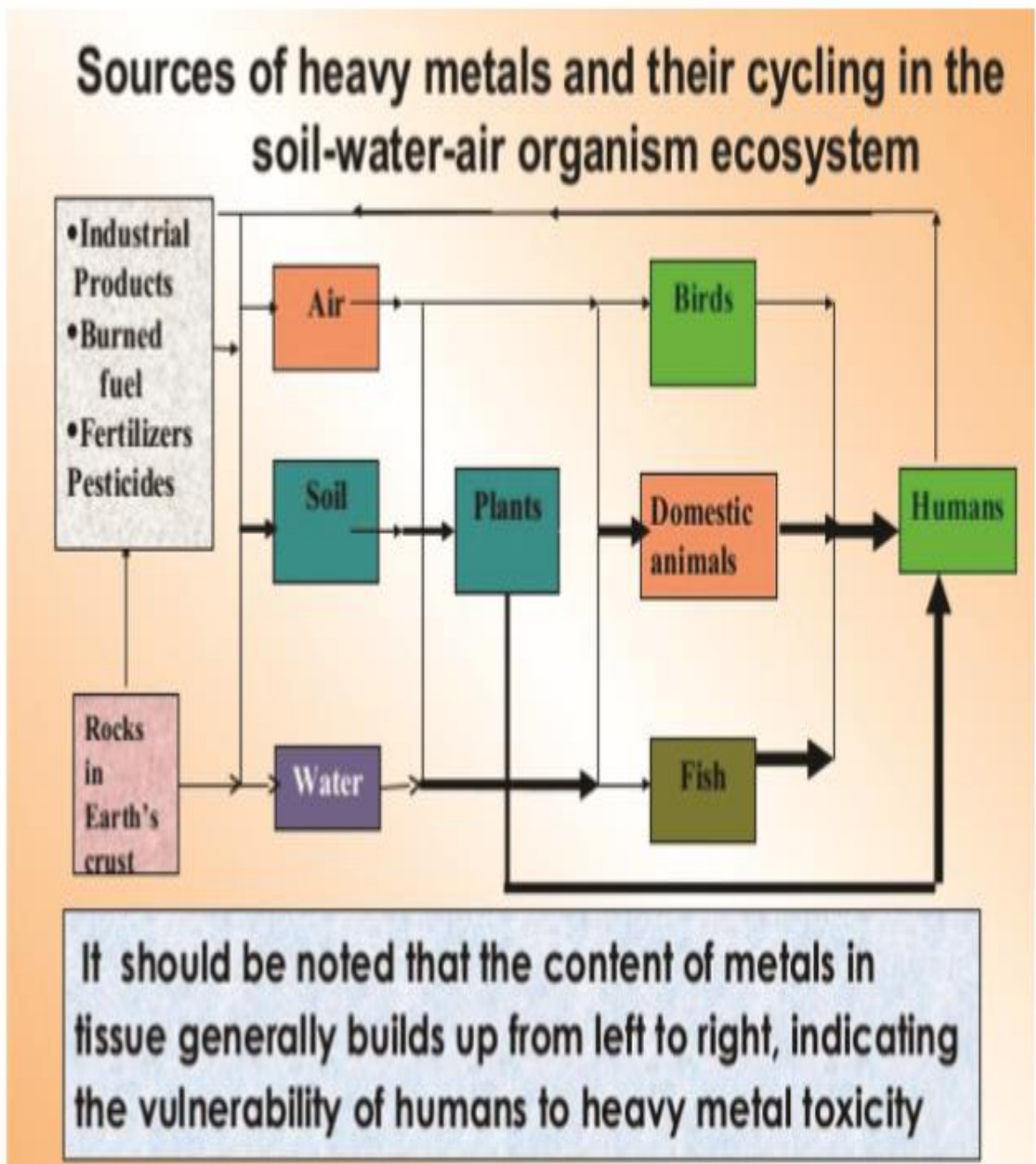


Figure 2.5: Sources of heavy metals and their cycle in the environment (Brady D, 1994).

2.5 Heavy metals and their effects

2.5.1 Lead

Exposure to lead (Pb) is accretive over time. High concentrations of lead in the body can cause death or serious damage to the central nervous system, the brain, and kidneys (Jennings *et al.*, 1996). Commonly, this damage due to Pb results in behavior and learning problems (such as hyperactivity), memory and concentration problems, high blood pressure, headaches, slowed growth, hearing problems, digestive problems, reproductive problems in men and women, muscle and joint pain. Lead is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Not only does lead poisoning extenuates a child's growth, damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children (USGAO). Children are very prone to lead because developing skeletal systems require high calcium levels (ESI SAAWA DADZIE, 2012). Lead that is deposited in bone is not harmful, but if high concentration of calcium (Ca) are ingested later, the Pb in the bone may be replaced by Ca and mobilized. Once free in the system, lead may cause neurotoxicity, nephrotoxicity and hypertension (Salem *et al.*, 2000). Salem *et al.*, (2000), also recorded that strong relationship between contaminated drinking water with heavy metals from some of the Great Cairo Cities, Egypt and chronic diseases such as renal failure, liver cirrhosis, hair loss, and chronic anemia was identified in their study. These diseases were apparently connected to contaminant drinking water with heavy metals such as Pb, Ni, Cr, Cd, Mo and Cu. Liver cirrhosis was subjected to contaminant drinking water with copper and molybdenum, renal failure to lead and cadmium, hair loss to nickel and chromium and chronic anemia to copper and cadmium. Several researches of these diseases suggested that abnormal diffusion in specific areas was related to industrial wastes and agriculture activities that have released hazardous and poisonous materials in the groundwater and thereby led to the contamination of drinking water in those respected areas.

2.5.2 Chromium

Chromium (Cr) is one of those heavy metals in the environment whose concentration is firmly increasing due to industrial growth, especially the development of metals, chemicals and tanning industries (Adeleken and Abegunde, 2011). The most common forms of chromium are chromium VI and chromium III (Hilgenkamp *et al.*, 2006). Chromium III is a significant element of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipid metabolism in humans while chromium VI is carcinogenic (Chernoff *et al.*, 2005). Although chromium toxicity in the environment is rare, it still causes some risks to human health since chromium can be accumulated on skin, dorsal spin, hair, nails, lungs, muscle fat, in liver, and placenta where it is traceable to various health conditions (Adeleken and Abegunde, 2011). Among the health effects brought about by the exposure to chromium VI include lung cancer, chromium dermatitis, malignant neoplasia and skin ulcers (Sarkar *et al.*, 2005). Ulcerations and perforations of the nasal septum and bronchial asthma have also been reported. Sarkar *et al.*, (2005) also demonstrated in their study that a fourfold increase in childhood leukemia was attributed to possible consumption of water with chromium VI levels above standard recommended value. According to Adeleken and Abegunde (2011), the prevalence of chromium in drinking water above 5 mg/l results in bleeding of the gastrointestinal tract, cancer of the respiratory tract, ulcers of the skin and mucus membrane. The sources of chromium in the environment include dyes, textiles, paints, cement, leather, plastics, printing ink, cutting oils, photographic materials, wood preservatives, detergents, among others (Hilgenkamp *et al.*, 2006). Other sources of chromium are water erosion of power plants, rocks, liquid fuels, brown and hard coal and industrial and municipal wastes. Adeleken and Abegunde (2011) have demonstrated that the non-biodegradability properties of chromium is responsible for its persistence in the environment and once united with soil, it undergoes transformation into various mobile forms before ending into environmental sink.

2.5.3 Nickel

Exposure of human to environments highly polluted with nickel (Ni) causes a variety of pathologic effects. The poisonous effects of nickel on the lung were recognized first by Agricola in the 16th century. Some fatal cases were recorded following exposure to nickel carbonyl and nickel was a recognized cause of contact dermatitis by the early 1930s. Ascended incidences of lung and nasal cancer in workers exposed to nickel were also observed (SUNDERMAN *et al.*, 1988, SEILKOP and OLLER 2003). In 2008, nickel avowed the shameful name of “Allergen of the Year” (GILLETTE *et al.*, 2008). According to the dermatologist the frequency of nickel allergy is still flourishing, and it can't be explained only by fashionable piercing and nickel devices used in medicine (like endoprostheses and coronary stents). All those investigations caused that the interest in the nickel impact on human health increased (SIVULKA *et al.*, 2005).

Albumin is the main transport protein of nickel in blood but nickel can bind also to histidine and α 2-macroglobulin (GLENNON and SARKAR, 1982; KASPRZAK *et al.*, 2003), and in this form is distributed throughout the tissues. Moreover, some important number of nickel-binding proteins including α 1-antitrypsin, α 1-lipoprotein and prealbumin were also described (NIELSEN *et al.*, 1994). Commonly, the highest concentrations of Ni are found in the bone, lung, kidney, liver, endocrine glands and brain. Nickel is also found in saliva, breast milk, hair and nails. Nickel transplacental transfer has been demonstrated in rodents. Nickel does not accumulate in the body; it is excreted in the urine, feces, bile and sweat (VALKO *et al.*, 2005).

Human exposure to nickel compounds can cause a variety of adverse effects on health, such as nickel allergy in the form of contact dermatitis, cardiovascular and lung fibrosis, kidney diseases and cancer of the respiratory tract (OLLER *et al.*, 1997, MCGREGOR *et al.*, 2000, SEILKOP and OLLER, 2003). Chronic noncancerous health effects may result from long-term exposure to relatively low concentrations of pollutants and acute health effects generally result from short-term exposure to high concentrations of pollutants. It manifests as a variety of clinical symptoms (nausea, vomiting, abdominal discomfort, diarrhea, visual disturbance, headache, giddiness, and cough). Skin rash is the most common type

of reaction to nickel exposure at the site of contact. Skin contact with metallic or soluble nickel compounds can cause responsible for allergic dermatitis in human. This health problem caused by exposure to nickel affects people both at and away from work. Studies of data from some authors indicate that women have greater risk for dermatitis, possibly due to a more frequent contact with nickel-containing items: jewelry, buttons, watches, zippers, coins, certain shampoos and pigments and detergents etc. (VAHTER *et al.*, 2002, SZCZEPANIAK and PROKOP, 2004). It is also reported that about 10% of women and 2% of men in the population are highly sensitive to nickel. Generally, metal sensitization is caused by direct and prolonged skin contact with items that release nickel ions. It was also noted that nickel (II) chloride with a classical carcinogen, such as UV radiation (UVR) had synergistic effect on skin cancer induction in Skh1 hairless mice (UDDIN *et al.*, 2007). The findings of UDDIN *et al.*, 2007 also reported that since humans are exposed to both UVR from sunlight and to nickel via environmental exposure, there is a potential co-carcinogenic hazard posed by environmental metals (arsenic, chromium, nickel) with UVR, which may be more serious than the hazard of the metals alone.

2.6 Prevalence of lead, nickel and chromium in water

The prevalence of lead, nickel and chromium in water has been reported to be 100% each in India and in Bangladesh (Ahmad and Goni, 2010) and all of the samples crossed the reference values (lead: 0.05 mg/L, nickel: 0.01 mg/L and copper: 0.005 mg/L). Another investigation has also been reported the prevalence of nickel of 100% in water of which 30% samples crossed the reference value (0.01 mg/L) in India (Reddy *et al.*, 2012).

2.7 Risk factors for the presence of lead, nickel and chromium in water

Metropolis and industrial areas and agricultural activities (such as heavy metals used as therapeutics, fertilizers) have been considered as risk factors for the presence of heavy metals at high concentration in water. Transhumance along roads and/or motorways, fodder contamination, climatic factors, such as gusty winds, and the use of pesticide compounds, contaminated pasture with industrial effluents and

mining area may be associated with the presence of lead in water. Solano (2007) have stated that sources arising from cattle rustling, military trainings which have led to heavy use and disposal of arms, a growing population without proper sewerage facilities, increase in the number of aging automobiles and fertilizers from the wheat and barley farms in the highlands are the biggest contributors of heavy metals in the soil and water in Samburu County, Kenya. Chattogram is the second largest and rapid economic growing city in Bangladesh. Due to rapid ascension of these city industrial activities, population growth, agricultural practices, other manufactures, industrial effluents and oil and gas are discharged in a river named Karnaphuli and in early day's pollution was never even felt in this healthy city. Most of the industries located in the shore of the rivers in Bangladesh have no effective effluent treatment plant which results in discharging untreated toxic wastewater in the rivers causing heavy metal pollution. Moreover, as the largest port city, oil tankers are capsized and sank in the Karnaphuli River at a jetty in the port of Chittagong, Bangladesh. This is also majorly responsible for contributing toxic heavy metals in water of the Karnaphuli River. Factors associated with the presence of heavy metals in water have not previously been attempted to explore in Bangladesh. Besides this, lack of planning especially in Chittagong city, has resulted in overcrowding with no proper sewerage disposal system for waste and this could contribute to heavy metal contamination of soil and water. Therefore, the present study has been justified to conduct determining risk factors that influence high prevalence of heavy metals in water.

Chapter 3

Materials and Methods

3.1 Study Area

Water samples were collected from some selected sites of the Karnafully River during dry seasons in January 2019 and tested for toxic heavy metals (Pb, Cr, and Ni) content in water. There are ten sampling points were selected before collecting the samples. Sampling locations are shown in Fig. 3.1 and the sampling conditions are illustrated in Table 3.1. Standard procedures were used to analyze the parameters of the water sample. All laboratory works were performed at Chattogram Veterinary and Animal Sciences University, Bangladesh.

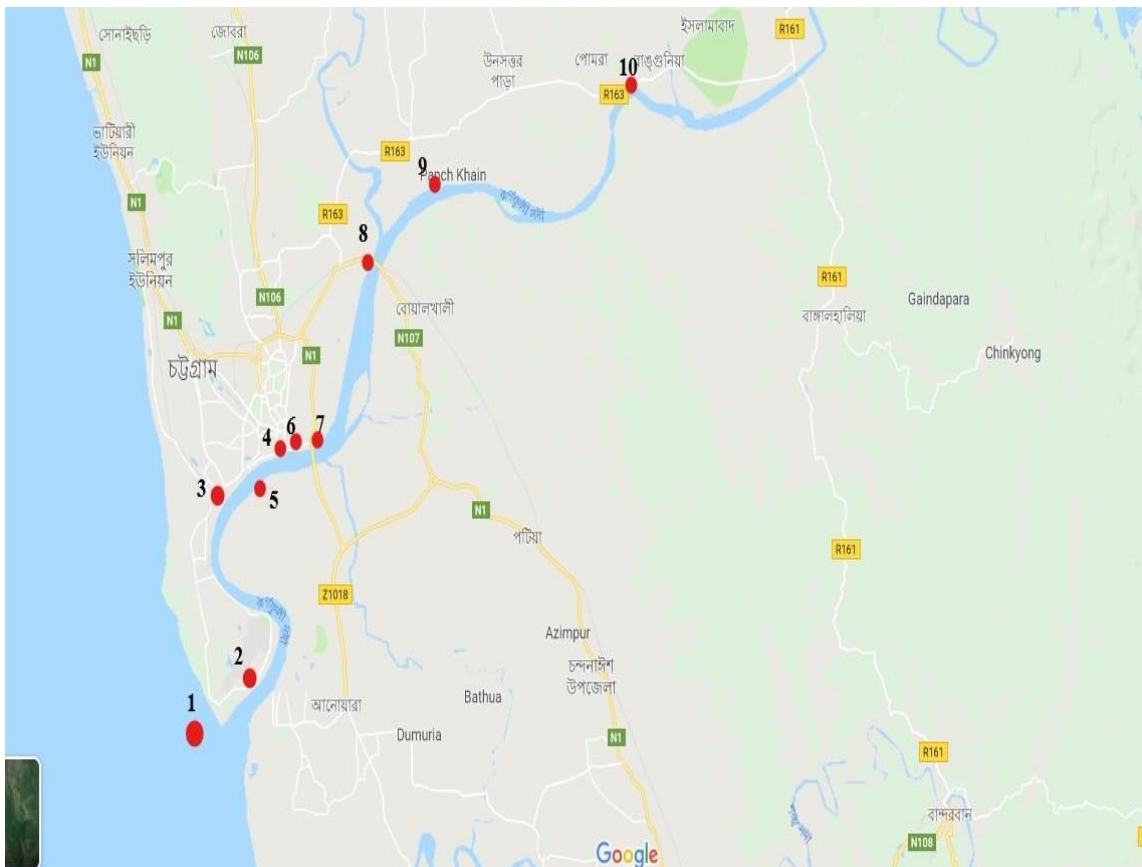


Figure 3.1: Geographical location of study area and sampling points

Table 3.1: The sampling locations and its tidal condition

S.No	Sampling sites / sources	Sample ID	Condition
01	Patenga sea beach	S-1	High tide
02	15 No. ghat, (opposite of the	S-2	High tide
03	KAFCO)	S-3	High tide
04	Shipping corporation	S-4	Low tide
05	Sadarghat jetty	S-5	Low tide
06	Banglabazar ghat	S-6	Low tide
07	Firingibazar ghat	S-7	High tide
08	Chaktai New Bridge	S-8	Low tide
09	Kalurghat industrial area (west	S-9	Low tide
10	side) Lamburhat Rangunai sadar (nearby CUET)	S-10	Low tide

3.2 Study period

The study was conducted from January to May, 2019 and the study sites were purposively selected for collecting the water samples.

3.3 Water samples collection

Water samples were collected from ten selected sites of Karnaphuli River at dry seasonal period. During collection of water 1.5 liter polypropylene bottles were used. Before using the bottles for sample collection, all bottles were washed with dilute acid followed by distilled water and were dried in an oven. For heavy metal analysis the primary sampling point was in the surface water layer (0-5 cm from the surface) at main flow. Before taking final water samples, the bottles were rinsed three times with the water to be collected. The sample bottles were labeled carefully with date and sampling source and chilled immediately to 3° to 4°C.

3.4 Sample analysis

3.4.1 Preliminary treatment of samples for heavy metal determination

Preliminary treatments of collected water samples were done by following international standard method given by APHA (American Public Health Association). To obtain homogeneous suspension of solids water Samples were agitated very carefully. 500 ml for each sample was measured and transferred to an evaporating dish after which sample was acidified with 5 ml HNO₃ and evaporated on a steam bath to 15 to 20 ml. Then the solution was transferred, together with any solids remaining in the dish, to a 125 ml conical flask. 5 ml additional HNO₃, 10ml H₂SO₄ and few glass beads (to prevent bumping) were added into the solution and it was evaporated on a hot plate until dense fumes of SO₃ appear in the flask. A clear solution was observed and all the HNO₃ was removed. The solution was cooled to room temperature, carefully diluted to about 50 ml and filtered through a porcelain filter crucible & washed the residue with 2 small portion of water. Then the filtrate was transferred to a 100 ml volumetric flask and made up to the mark with distilled water. Finally, a aliquots of this solution were taken for the determination of metals.

3.4.2 Analytical Techniques

The samples were analyzed by an atomic absorption spectrophotometer (Type: AA-6200, Shimadzu, Japan) using an air acetylene flame. All the spectroscopic measurements of the standard metal solutions as well as the sample solutions were done at their respective wavelength of maximum absorptions λ max.

3.4.2.1 Atomic Absorption Spectrometry (AAS)

The basic principle of AAS is based on if a sample containing metal element is heated on high temperature, vapor is produced which contains the atoms of the same element. Gaseous metal atom absorbs energy in the form of radiation of characteristic wavelength and amount of absorbed radiation/energy proportional to the concentration of the metal atom in the solution. The measurement of the

radiation transmitted (using Beer-Lambert's law) in such a transition form the basis of AAS. Beer-Lambert's law relates absorbance, a to the concentration of metallic atoms in the atom cell, c as follows-

$$\text{Log}T-1 = a b c$$

Where

a is the absorptivity in grams per litre-centimetre

b is the atom width in centimeters

c is the concentration of atoms

The AAS involves the measurement of the drop in light intensity of initial radiation I_0 to final radiation I depending on the concentration of the metal. Modern instruments automatically convert logarithmic values into absorbance (Nollet *et al.*, 2011). Figure 3.1 below illustrates AAS instrumentation.

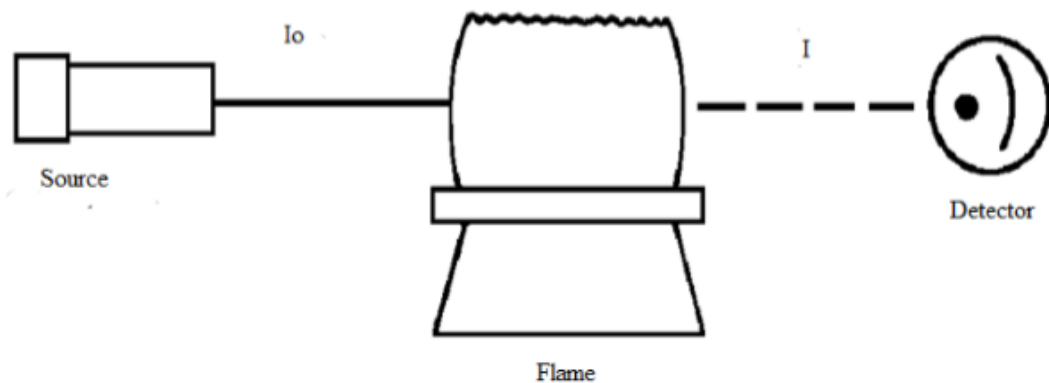


Figure 3.2: Diagram to illustrate instrumentation of AAS (Salano et al., 2007)

During sample analysis all the samples were evaluated by Atomic Absorption Spectrophotometer as per protocol described by (Ahmad *et al.*, 2010). Approximately 12 ml of processed samples were taken in a cup suitable to fit into the sample tray of the Atomic Absorption Spectrophotometer (AA-6200, Shimadzu, Japan). On starting the machine around 2-3 ml processed sample were automatically

drawn for a single metal detection (lead/nickel/chromium). The sample solution was aspirated by a pneumatic analytical nebulizer and transformed into an aerosol, which was then introduced into a spray chamber, where the sample was mixed with the flame gases and conditioned in a way that only the finest aerosol droplets (less than 10 μm) entered into the flame. This conditioning process was responsible that only about 5% of the aspirated sample solution reached the flame.

On top of the spray chamber was a burner head that produced a flame that was laterally long (usually 5–10 cm) and only a few mm deep. The radiation beam passed through this flame at its longest axis, and the flame gas flow-rates was adjusted to generate the highest concentration of free atoms. The burner height was also adjusted, so that the radiation beam passed through the zone of highest atom cloud density in the flame, resulting in the highest sensitivity.

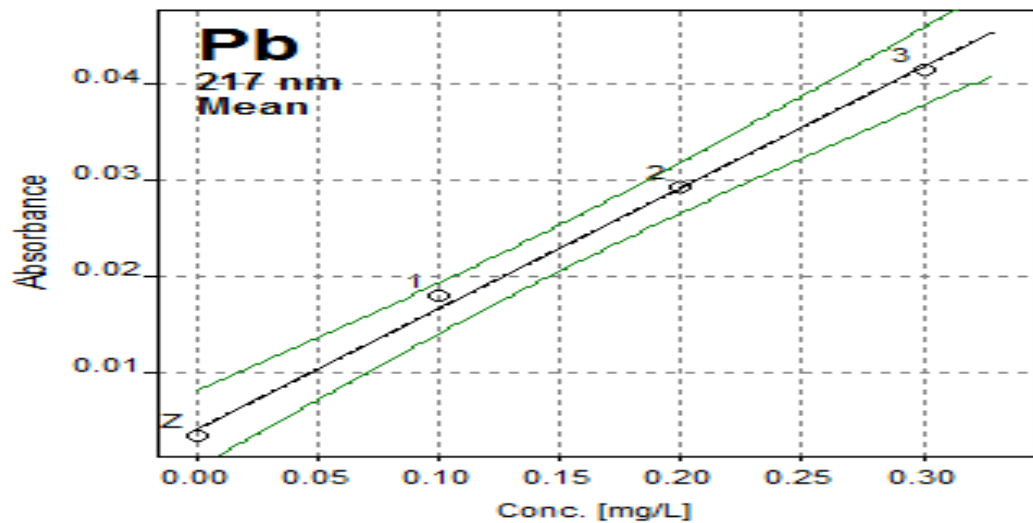


Figure 3.3: Calibration curve of Lead (Pb)

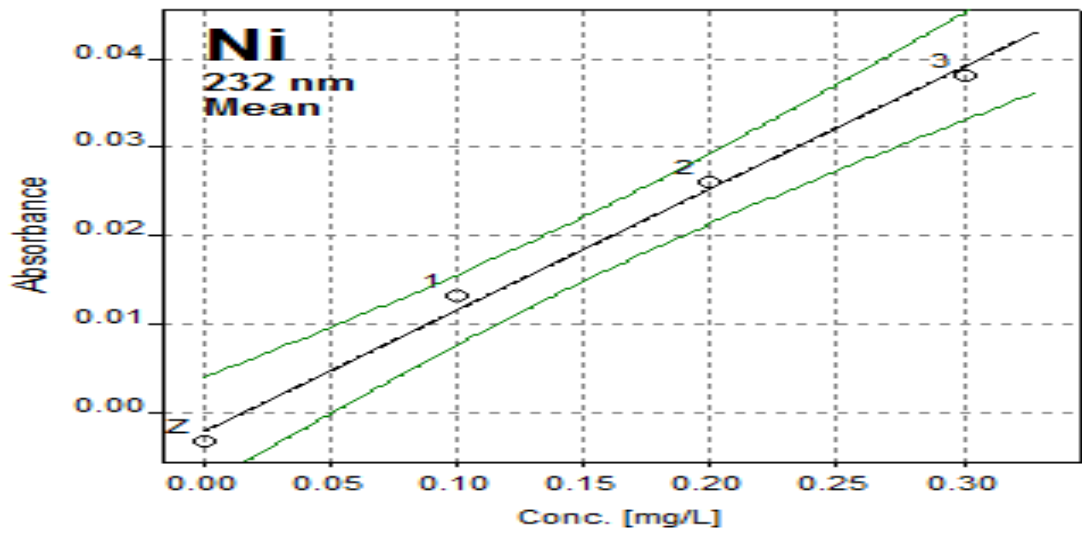


Figure 3.4: Calibration curve of Nickel (Ni)

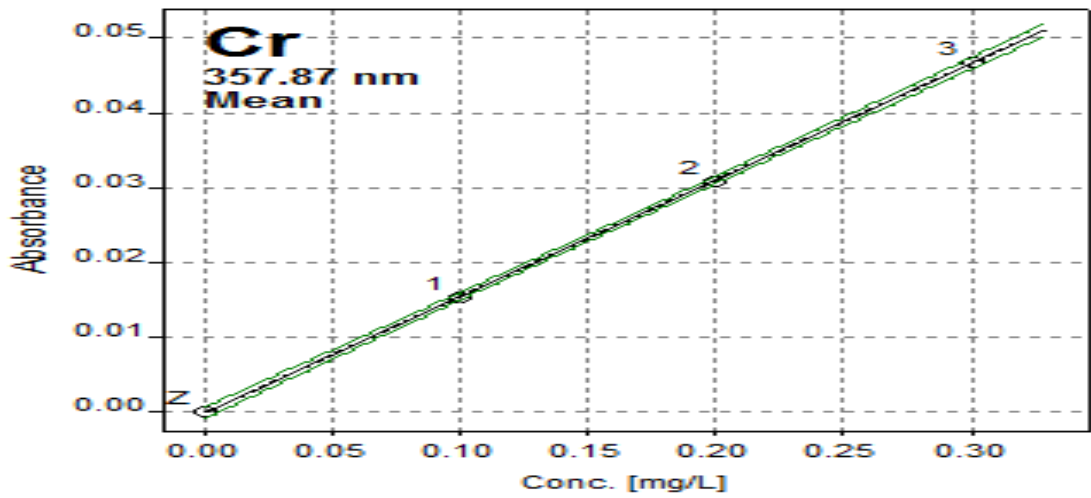


Figure 3.5: Calibration curve of Chromium (Cr)

The processes in a flame include the following stages:

1. Desolation (drying): The solvent was evaporated and the dry sample nanoparticles were remained.
2. Vaporization (transfer to the gaseous phase): The solid particles were converted into gaseous molecules.
3. Atomization: The molecules were dissociated into free atoms.
4. Ionization: Depending on the ionization potential of the analytic atoms and the energy available in a particular flame, atoms in part converted to gaseous ions. In flame Atomic Absorption Spectrometry a steady-state signal was generated during the time when the sample was aspirated and read the results on the screen of the machine concentration of metals was expressed in average mg/L.

3.5 Statistical analysis

Data were stored in Microsoft Excel 2007 and then exported into STATATM 11.0 (Stata Corporation, College Station, TX, USA) for statistical analysis. Descriptive analysis was performed by using percentages, mean and standard deviation for different variables. Finally one way ANOVA was used to compare the level of heavy metal contents in water of different sites of the Karnaphuli River, Chattogram. The level of significance was set ≤ 0.05 .

Chapter 4

Results

4.1 level of toxic metals in water

The present study revealed the concentrations of trace metals like lead, nickel, chromium which have been estimated in samples collected from the mentioned zone (Fig.3.1) on one occasion only in the winter season and are listed in Table-3.1. Findings of this study along with the recommended standards of World Health Organization (WHO) have been summarized in Fig.4.1-4.3 and Table 4.1. The heavy metal concentration of the Karnaphuli River showed varied from one place to another. Most of the dissolved heavy metals were found to be in slightly higher concentrations in heavy industrial areas than that of lower industrial sites of Karnaphuli River. In this study, the concentration levels ranged from BDL (Below Detection Limit) to 0.131 ± 0.0014 mg/L for Pb, from BDL to 0.050 ± 0.0014 mg/L for Ni and that of BDL to 0.115 ± 0.00212 mg/L for chromium (Cr).

4.2 Mean concentration of heavy metals in water

Table 4.1: Mean concentration of heavy metals in water of KR at selected sites

Sample	Chromium (mg/L)	Nickel (mg/L)	Lead (mg/L)
	Mean \pm SD	Mean \pm SD	Mean \pm SD
01	BDL	BDL	BDL
02	0.0264 ± 0.00015	BDL	0.0455 ± 0.00015
03	0.0123 ± 0.00015	BDL	BDL
04	0.115 ± 0.00212	0.012 ± 0.003	0.131 ± 0.0014
05	0.0091 ± 0.0003	0.0072 ± 0.00015	0.0152 ± 0.00015
06	0.024 ± 0.0015	0.012 ± 0.0015	0.0172 ± 0.00014
07	0.0186 ± 0.00014	0.016 ± 0.0015	BDL
08	0.092 ± 0.0014	0.050 ± 0.0014	0.072 ± 0.0014
09	BDL	BDL	BDL
10	BDL	BDL	BDL
p-value	<0.001	<0.001	<0.001
WHO standard	0.05	0.07	0.01

BDL= Below Detection Limit (Detection Limit of the instrument is 0.001mg/L)

In this study, the mean concentration of lead (Pb) showed varied from one place to another. This might be due to the degree of deterioration of water quality which may differ from one place to another of the Karnaphuli River. Moreover, the extent of deterioration of water quality largely influenced by the seasonal variation, human activities and catastrophic events presents in the sites of the river. The concentration of Pb levels showed huge variation which ranging from nil to 0.131 ± 0.0014 mg/L. The highest contents of Pb (0.0131 ± 0.0014 , 0.072 ± 0.0014 and 0.0455 ± 0.00015 mg/L) were found in samples collected from sadarghat jetty, kalurghat industrial area and 15 no. ghat (opposite of the KAFCO) respectively. However, Pb contents were found below detection limit (BDL) in several points during analysis which is showed in (Fig. 4.1). This might be due to low solubility of Pb containing compound in water. This findings is in well agreement with the findings of Venugopal et al., 2009 also found non- detectable level of Pb in their study. The overall concentration profiles of Pb in water samples are displayed in Fig. 4.1 comparing with WHO standard.

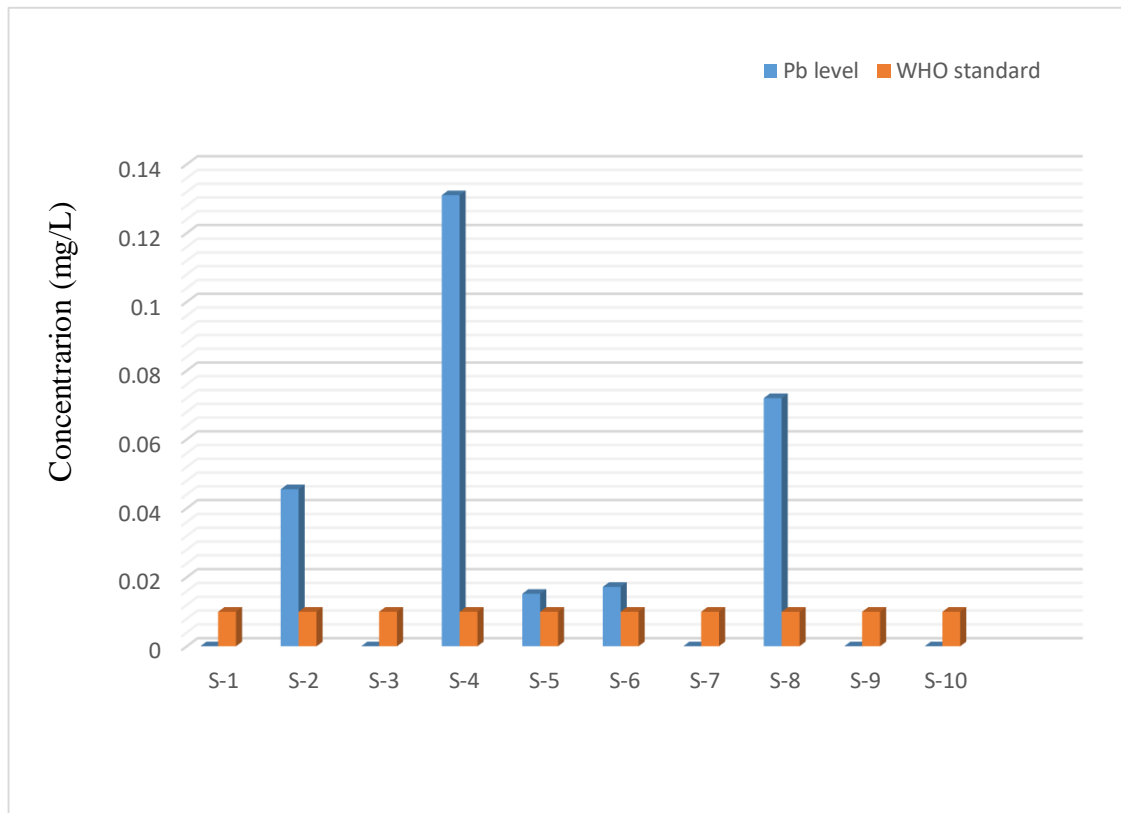


Figure 4.1: Mean concentration of lead (Pb) in samples compared with WHO standard

The concentration of Chromium, in this study were found to be within the detection level in most cases and several points it showed below the permissible limit of WHO standard (1993, 2004 and 2011,WHO). However, in some points it exceeds the permissible limits which is shown in Fig. 4.2 and the highest concentration of Cr (0.115 ± 0.00212 and 0.092 ± 0.0014 mg/L) were found in samples collected from sadarghat jetty and kalurghat industrial area respectively. This findings is also compliance with (F. Islam *et.al.* 2013) they also found an appreciable amount of Cr contents 0.09 mg/L in their study from kalurghat west industrial area. The level of Cr contents in Patenga sea beach, Lamburghat and Rangunai were found below the detection limit (0.001 mg/L) which is in well agreement with the findings of (Mamun *et al.*, 2013) in which they demonstrated that Cr content was below the detection level in KR.

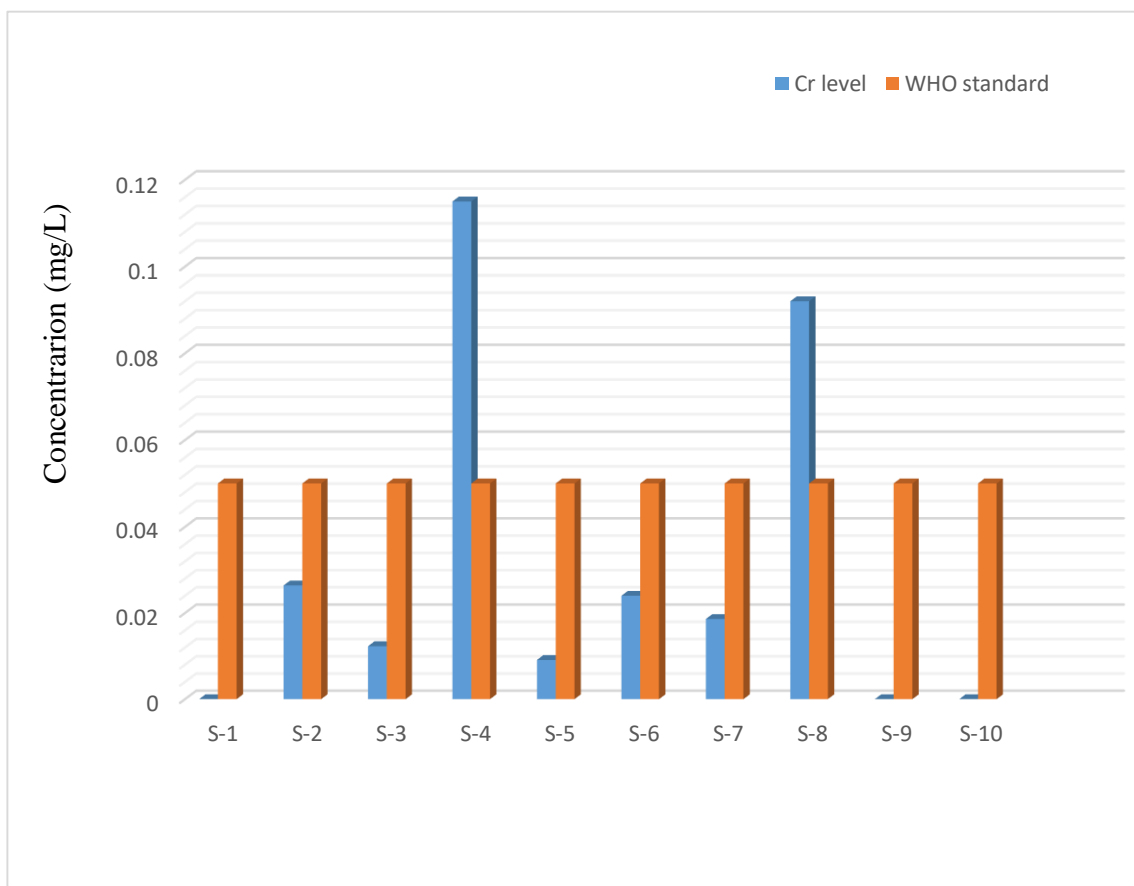


Figure 4.2: Mean concentration of Cr in samples compared with WHO standard

The present study also revealed the status of nikel (Ni) which is shown and mentioned in the table 4.1 and Fig. 4.3. The concentration of Ni was found below the permissible limit of WHO standard of drinking water (WHO, 1993, 2004 and 2011). The overall concentration status of Ni in water samples along with the recommended standards of World Health Organization (WHO) are shown in Fig. 4.3. The present study revealed that that the Ni contents found in almost all samples were considerably higher in heavy industrial sites than that of non-industrial sites. This because the highest concentration of Ni 0.050 ± 0.0014 mg/L was found in sample collected from kalurghat industrial areas than that of other sites of KR. However, in several points the concentration of Ni were found below the detection limit (0.001 mg/L).

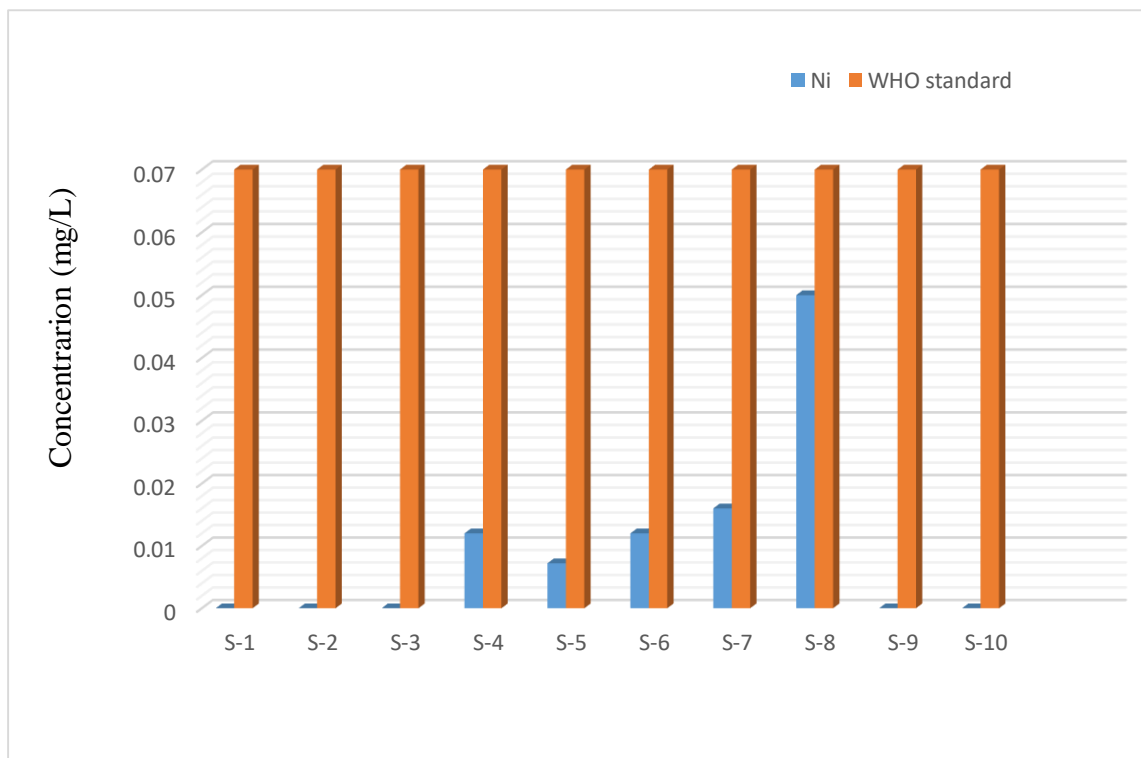


Figure 4.3: Mean concentration of Nickel (Ni) in samples compared with WHO standard

Chapter 5

Discussion

5.1 General

Heavy metal pollution is one of the most talked of topics in recent years because of its detrimental effects in human and aquatic life system. The recent chemical profiles of Karnaphuli River water in several studies indicate that the water quality beyond the acceptable limit which becomes the serious threats to humans and aquatic life. So it is very important to determine the concentration of heavy metal in KR water and evaluation of heavy metal pollution with respect to their sources. This chapter has discussed the main findings of the present study under some broad headings.

5.2 Variation of heavy metal concentration among different sites of KR

The concentration of heavy metals in water showed variation from place to place during analysis of the samples. A similar study was carried by (F. Islam *et. Al.*, 2013), they also showed that the heavy metal concentration of the Karnaphuli river varied in place to place as wide range from 4.3 to 0.003 ppm in their study. In this study, the samples were selected from both industrial and non-industrial sites of KR. The investigative results showed that the metals concentration found in water from industrial sites were considerably higher than that of non-industrial sites which is shown in table-5.1. This might be due to the water collected from industrial sites are being greatly polluted by industrial activities. Moreover, most of the industries developed in the vicinity of the Karnaphuli River have no effective effluent treatment plants as a result of this the water of the river are being greatly contaminated with these untreated toxic wastewater. The findings of the study has demonstrated in the table 5.1 which showed that the toxic metals contents found in all most all samples from heavily industrial areas like Sadarghat jetty, Banglabazar ghat, Firingibazar ghat, Chaktai New Bridge, Kalurghat industrial areas were considerably higher than that of non-industrial sites like Patenga sea beach, 15 No.

ghat, Lamburhat, Rangunai sadar. A study also carried out by (Ahmed MK et al.,2010) in which the concentrations of toxic metal in the water of Buriganga River, Bangladesh were reported to be 65.45, 9.34, 8.08, 163.09 and 587.20 mgL⁻¹ for Pb, Cd, Ni, Cu and Cr, respectively; levels were much higher than the permissible limit. In Cauvery River, India concentrations were found to be 0.32, 2.23, 1.12 1.25, 5.25, 10.70 and 9.95 mg/L for Cr, Co, Cu, Mn, Ni, Zn and Pb, respectively; some parameter found within the recommended limit and some parameters beyond the permissible limit (Begum A *et al.*, 2009). High heavy metal concentration in the Karnaphuli River water may have been resulted from the direct discharge of untreated wastes from the leather, textiles, dyeing, glass and plastic industries situated in the presence of the river. During this study a visit along the river, it was established that most of the industries discharging of raw, untreated, hot and opaque wastewater directly into the river. The similar findings were also reported by (H. Rashid *et al.*, 2012) in Khiru River, Bangladesh and by (Ahmed MK *et al.*, 2010) in Buriganga River, Bangladesh.

Table 5.1: Variation of heavy metal concentration among different regions

Sl. No.	Location	Concentration with respect to different sites of KR (mg/L)		
		Cr	Ni	Pb
01	Patenga sea beach	BDL	BDL	BDL
02	15 No. ghat	0.0264±0.00015	BDL	0.0455±0.00015
03	Shipping corporation	0.0123±0.00015	BDL	BDL
04	Sadarghat jetty	0.115±0.00212	0.012±0.003	0.131±0.0014
05	Banglabazar ghat	0.0091±0.0003	0.0072±0.00015	0.0152±0.00015
06	Firingibazar ghat	0.024±0.0015	0.012±0.0015	0.0172±0.00014
07	Chaktai New Bridge	0.0186±0.00014	0.016±0.0015	BDL
08	Kalurghat industrial area	0.092±0.0014	0.050±0.0014	0.072±0.0014
09	Lamburhat	BDL	BDL	BDL
10	Rangunai sadar	BDL	BDL	BDL

However, the analysis also shows variation in the mean concentration of heavy metals in water from one place to another depending on their tidal condition of geographical areas. The sampling point with their tidal status are shown in the table 3.1. The findings of the analysis showed that in most cases the concentration of metals found in low tidal areas were considerably higher than that of high tidal area. Moreover, some previous studies also recorded that heavy metal concentrations in the water of Karnaphuli River showed little seasonal variation. The present study was conducted on one occasion only in the dry winter season. Obasohan and Eguavoen (2008) have also stated in their research that dry seasons have an effect on the accumulation of heavy metals in water and its reared fish of Obga River in Nigeria. Most of the dissolved heavy metals were found to be in slightly higher concentrations during winter than that of the rainy season in the previous studies. This aptitude indicates that during low flow condition of river, the accumulation of the metal concentration increases. This finding is in well agreement with the findings of several authors (Sujan Dey *et al.*, 2015; E.E. *et al.*, 2008 and M.J. Ahmed *et al.*, 2010). The findings of the study is also consent with their studies.

5.3 Concentration of Lead (Pb) in water

Lead (Pb) has detrimental effects on both human and aquatic life system. In this study among the detectable limits, the highest and lowest content of Pb were found in the samples collected from Sadarghat jetty (0.131 ± 0.0014 mg/L) and Kalurghat industrial area (0.072 ± 0.0014 mg/L) respectively (Fig. 4.1). Samples collected from Patenga sea beach, Shipping Corporation, Chaktai New Bridge, Lamburhat, Rangunai sadar shows below detection limit (BDL) during analysis. This might be due to low solubility of Pb containing compound in water in these sites. T. Venugopal *et al.*, (2009) and Sujan Dey *et al.*, (2015) also found non-detectable level of Pb in their study.

The present study revealed that Pb contents were found in an appreciable amount in the sites with higher industrial areas. In this way Kalurghat heavy industrial area shows a considerable amount of Pb contents (0.072 ± 0.0014 mg/L) in this study which exceeds the permissible WHO standard limits (0.01 mg/L). This findings is in well agreement with the findings of F. Islam *et al.*, (2013) who also found

prominent amount of Pb (0.177 mg/L) in Kalurghat area in their study. The concentration of Pb were detected in the Patenga sea beach, Shipping Corporation and Chaktai New Bridge also showed below the detection limit during analysis. A similar study was conducted by H. Rashid *et al.*, (2012) also reported that the concentrations of Pb in the water from Khiru River was within the permissible limit. The areas with lower industrial sites like Lamburhat, Rangunai sadar also shows non detectable limit (BDL) of Pb in this study. This trend indicates that samples collected from higher industrialized zones shows considerably higher Pb contents than that of non-industrialized zones. This statement compliance with the findings of Wang *et al.*, (2016).

5.4 Concentration of Chromium (Cr) in water

The accumulation of chromium (Cr) in all sources from KR water was within the permissible limits except Sadarghat jetty and Kalurghat industrial area is shown on the Fig. 4.2. The samples collected from Patenga sea beach, Lamburhat, Rangunai sadar were reported below detection limit in this study. The highest amount of Cr were found in samples collected from Sadarghat jetty and Kalurghat industrial areas are 0.115 ± 0.00212 and 0.092 ± 0.0014 mg/L respectively which exceeds the permissible limit (0.05 mg/L) of WHO drinking water standard (WHO, 1993, 2004 and 2011). Some other previous authors also reported similar findings in their studies (F. Islam *et al.*, 2013; H. Rashid *et al.*, 2012; Wang *et al.*, 2016). This might be due to the presence of potential sources of Cr contamination from those sites. The potential sources of Cr include wastes from tannery waste, waste from chemical laboratory, textile waste and earth's crust. Chromium solutions are widely used in tannery industries for leather processing purposes in Bangladesh. These liquid wastages from the tanneries are being mixed into the drain without any primary treatment which is ultimately discharged into the river and sea water (Abedin *et al.*, 2014). A field survey study under the Sarwar, Majumder and Islam (2010) found that, from Kalurghat to the Chattogram Port around 713 industries directly or indirectly throwing their untreated waste or wastewater in Karnafully River. Out of that around 156 are situated very close to the Karnafully. List of such industrial locations and type of industries are noted in Table 5.2 and 5.3 respectively.

However, Cr concentration in other locations included 15 No. ghat, Shipping corporation, Banglabazar ghat, Firingibazar ghat, Chaktai New Bridge were detected within the permissible limits of WHO standard is shown in Fig. 4.2. A previous study also reported that Cr concentration was below the detection level in their findings (Sujan Dey *et al.*, 2015).

5.5 Concentration of Nickel (Ni) in water

The present study demonstrated that Ni was found below the permissible limit of WHO standard of drinking water (WHO, 1993, 2004 and 2011) in all stations during the analysis. The findings of the study exhibits that Ni concentration varied from one place to another depending on the presence of industrial zones on the side of the Karnaphuli River. The peak concentration of Ni was found in sample collected from kalurghat industrial area (0.050 ± 0.0014 mg/L) and the relatively low industrial sites included Patenga sea beach, 15 No. ghat, Shipping Corporation, Lamburhat, Rangunai sadar were showed below detection level during analysis. This trend indicates that the areas with heavy industrialized zones having higher Ni contamination than that of low industrialized zones.

In general, the sources of nickel comes from urea fertilizer industry as a catalyst during the breakdown on methane gas. So urea fertilizer and their waste contain nickel at a certain level. By the use of urea fertilizer and disposal of waste from fertilizer industry pollute the environment. This statement is supported by many other studies (Klan *et al.*, 2011; Pirsahab *et al.*, 2013). A field survey was studied by Sarwar and *et al.*, (2010), reported that about 98 industries are located in the kalurghat industrial area which acting as potential sources of heavy metal contamination of water. The major sources of toxic heavy metals which are responsible for water pollution are listed in Table 5.2 and 5.3 respectively.

However, the concentration of Ni in the sites included Sadarghat jetty, Banglabazar ghat, Firingibazar ghat, Chaktai New Bridge were found to be within the detection level but below the permissible limit of WHO standard of drinking water (WHO, 1993, 2004 and 2011) shown in the Fig. 4.3. This findings is in well agreement with the findings of (Sujan Dey *et al.*, 2015), they stated the similar judgment in their study.

Table 5.2: The location of the water pollution responsible industries

Location	Numbers of industries
Kalurghat	98
Mohra	85
Chandraghona	10
Chaktai	76
Sadarghat	71
Firingibazar	60
Fisheryghat	69
Dry-dock	89
Katgore	40
Jaldia	30
Gohira	20
Port	65
Total	713

Source: Sarwar, Majumder and Islam (2010)

Table 5.3: The type and number of industries close to Karnaphuli River

Sl. No	Industry	Number
01	Tannery	11
02	Textile	26
03	Oil refinery	01
04	T.S.P. plant	01
05	Urea plant	02
06	D.D.T. plant	01
07	Chemical industry	02
08	Fish processing plant	20
09	Asphalt bitumen plant	01
10	Steel Mill	01
11	Paper and rayon mill	01
12	Soft drinks industry	03
13	Cement factory	03
14	Soap and detergent	02
15	Insect killer production plant	02
16	Paint and X-ray production unit	04
17	Others industry	75
Total		156

Source: Sarwar, Majumder and Islam (2010)

5.6 Comparison of average mean concentration of metals with international standard

The average mean concentration of heavy metals found in the present study along with the recommended standards of World Health Organization (WHO) have been summarized in the Table 5.4. The findings shows that total mean concentration of Ni and Cr were 0.0108 ± 0.0155 and 0.0331 ± 0.043 mg/L respectively found to be within the detection level but below the permissible limit of WHO standard of drinking water (WHO, 1993, 2004 and 2011). This findings is similar to the findings of Sujan Dey (2015), also reported that Ni and Cr were found to be within the detection level but below the permissible limit of WHO standard in their study. However, the present study revealed that the average concentration of Pb (0.04242 ± 0.0627 mg/L) was found above the permissible limit of WHO drinking water standard. This findings is supported by (Samad M.A *et al.*, 2015), they also recorded that the average concentration of Pb found in the Rupsha River above the permissible limit of WHO standard (0.01 mg/L). A previous study was performed by F. Islam and M. Rahman (2013) with the Karnaphuli River in which they have also stated that the average Pb lead concentration was above the WHO standard limit (0.01mg/L).

Table 5.4: Comparing total mean concentration of metals in all stations with WHO standards.

Heavy metals	No. of samples (N)	Concentration (mg/L) Mean \pm SD	WHO standard (mg/L)
Pb	10	0.04242 ± 0.0627	0.01
Cr	10	0.0331 ± 0.043	0.05
Ni	10	0.0108 ± 0.0155	0.07

5.7 Impact of human activities and catastrophic events on heavy metal accumulation

Estuary of the Karnaphuli River is located in the city of Chattogram which is passing through rapid and frequent economic development activities (Mia *et al.*, 2015), and human activities reported to conflict with nature that eventually affecting the estuarine environment and ecosystems. A survey data reported that since early 1980s, Chattogram experienced an extensive urbanization (Fig. 5.1). As Chattogram is the economic capital of Bangladesh, the industrial zones of the city has been expanding dramatically. As a rapid growing economic zone, Chattogram city is also experiencing a large number of population since last 30 years. The urban population by residence in Chattogram increased from 0.42 million in 1974 to 3.15 million in 2011, and the urban population density by residence increased from 1413 Person/km² in 1981 to 6992 Person/km² in 2011 (Bangladesh Bureau of Statistics 2015), while the urban area/built-up (including commercial, residential, industrial, and other infrastructure) increased from 1309.68 hm² in 1977 to 9401.85 hm² in 2013 (Hassan and Nazem, 2015). As the city expanded, the industries (such as spinning mills, dyeing, cotton, textile, steel mills, oil refineries, leather, paints, fertilizer, and others) were constructed along the river correspondingly, and these industries discharged a vast amount of untreated effluents to KR which induce high concentration of heavy metals in the water and sediments, especially for Pb (Majid *et al.*, 2003; Ali *et al.*, 2016). In addition, a field survey under the Sarwar and Majumder (2010) reported that, from Kalurghat to the Chattogram Port around 713 industries directly or indirectly throwing their untreated waste or wastewater in Karnaphully River. Out of that around 156 are situated very close to the Karnaphuli which is already demonstrated on the Table 5.2 and 5.3. Moreover, these most the industries have no effective effluent treatment plant which results these industries discharged a huge amount of untreated wastewater to KR causing serious heavy metal pollution of water. Previous studies reported that the concentrations of heavy metals in surface water of KR showed little indication of metal pollution in 1997–1998 that did not reach alarming levels (Das *et al.*, 2002; Majid *et al.*, 2003), and the metal contamination continued slowly to 2011–2012 (Dey *et al.*, 2015). Nevertheless, since 2011, the water quality of KR has decreased notably, mainly due to elevated levels of heavy metals that rendered

the waters from this river unsuitable for direct drinking and/or cooking in 2015 (Ali *et al.*, 2016). Hossain and Khan (2002) also displayed that the Karnaphuli is now faced with terrible deterioration of natural water characteristics and it made most significant change in its course from Kalurghat downwards and the change has been taking place for more than a century (M. Iqbal Sarwar *et al.*, 2010).

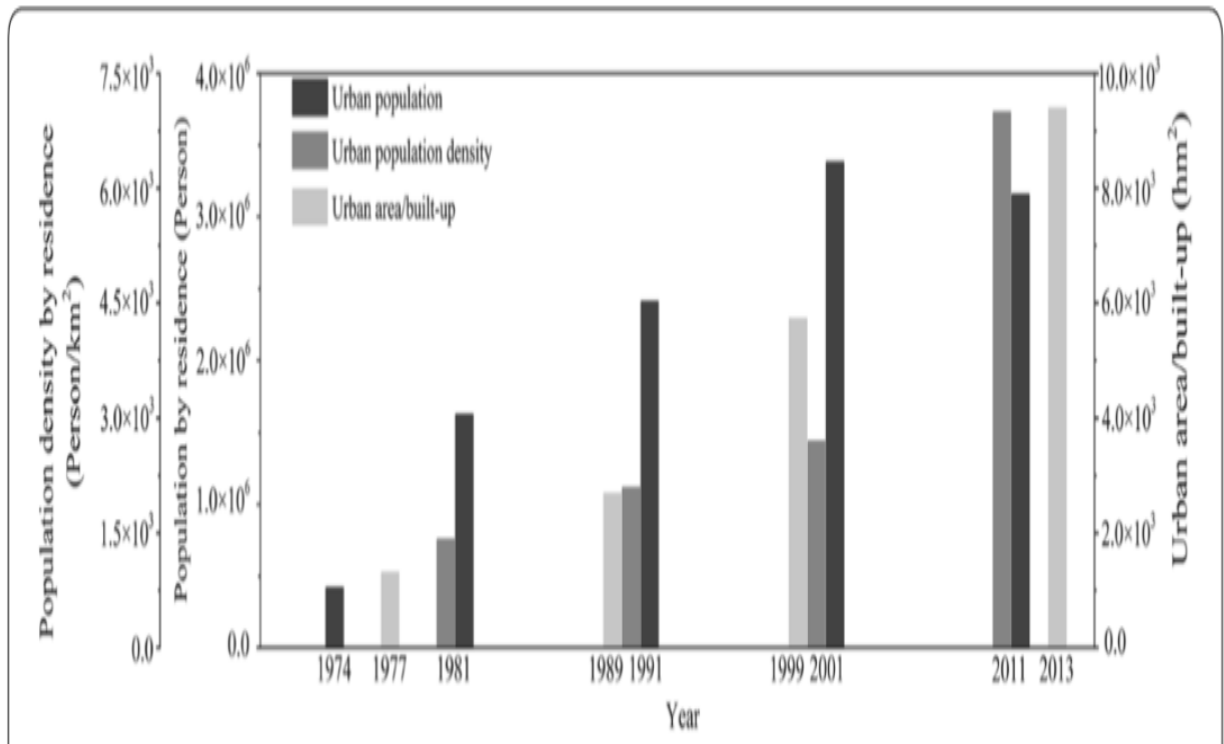


Figure 5.1: Population, population density by residence and urban area/built-up in Chattogram in the last 30 years (Wang et al., 2016)

Chapter 6

Conclusion

Karnaphuli is the largest and an important river in Chattogram, Bangladesh. It is fostering the Chattogram city in many ways and plays a vital role in the communication system of the whole region. At present, the pollution of water as well as aquatic ecosystems of KR by heavy metals is emerging as a serious issue in Bangladesh. Day by day, river Karnaphuli is losing its water quality like other city belts. Several studies revealed that the river is under severe pollution threat. This is mainly due to various human activities and catastrophic events on it. The analysis of the present study represents that among three metals (Pd, Cr and Ni) only Ni was within the recommended values for all sampling points but Pb and Cr were found beyond permissible limits of WHO in several points. However, in the overall concentration of these three metals only Pb (0.04242 ± 0.0627 mg/L) exceeded the recommended values of WHO (0.01 mg/L). This might be due to the presence of higher Pb contamination sources around the respected sites of the Karnaphuli. This exceeded level of Pb recommends a sign of presence of metal pollution which is an alarming environmental issue. If this trend of contamination continues it may make an impact on the quality of water of the Karnaphuli River and in the long run can cause a serious threat for aquatic organisms and human livelihood. Some other previous studies also showed that the chemical profile of the water samples exceeded tolerance limits in their findings (M. Iqbal Sarwar et al., 2010; Wang et al., 2016). In the present study, the mean concentration of the three metals (Pb, Cr, Ni) were found comparatively higher in heavy industrial sites than that of lower industrial sites (Table 5.1). The concentration of metals found in samples collected from the Sadarghat jetty (0.115 ± 0.00212 , 0.012 ± 0.003 and 0.131 ± 0.0014 mg/L for Cr, Ni and Pb respectively) and Kalurgaht area (0.092 ± 0.0014 , 0.050 ± 0.0014 and 0.072 ± 0.0014 mg/L for Cr, Ni and Pb respectively) were showed considerable higher than that of other points in this study. This because the Sadarghat jetty and Kalurgaht areas are highly industrialized zone among other sites selected in this study. This trend indicates that the water in industrial areas are being highly contaminated with toxic untreated effluents which are discharged by the industries located in the bank of river Karnaphuli resulting in the heavy metal pollution. Based

on the results obtained from the present study, metal concentrations in the water which serve as a basis for the announcement of the state of alert and calls for precautions to be taken in order to prevent the pollution of the water as habitat for fish and other aquatic animals of the Karnaphuli River.

As a riverine country, life and river are closely integrated in most parts of Bangladesh. The country depends on its river system for agriculture, fishery, navigation and even sanitation. Therefore, an appropriate management and maintenance of river is very necessary not just because of their crucial role in maintaining ecological balance but to increase fisheries production as well as to provide people of Bangladesh who largely depends on the river for their livelihood. In this perspective of degenerating water quality in most of the rivers during the recent days, it is now important to keep healthy state of rivers for supporting life and livelihood on their banks. The findings of the present study indicate that the water of the Karnaphuli River is being polluted mainly by the untreated discharges from industrial sources. Wang et al., 2016 also reported the same results in their findings in the Kharnaphuli River. The findings of the H. Rashid (2012) also stated that the water and sediment of Khiru River are polluted mainly by the discharges from industrial sources.

Now it becomes so crucial to monitor and enforce environmental laws and regulations on the industries and to enforce installation of effluent treatment plants for preserving the environment of the River Karnaphuli and other rivers of Bangladesh. So therefore, to prevent future adverse impact on the river a restriction must be imposed on the discharge of trace metals and sewages through different sources.

Chapter 7

Recommendations and Future perspectives

This chapter provides the recommendations and future perspectives of the present study on the basis of the prevalence of heavy metal in water of different selected sites of the Karnaphuli River, Chattogram, Bangladesh as follows:

- The levels of lead and Cr in the water should be continuously monitored to check on their levels. Lead levels in both the surface and ground water is already beyond the WHO recommended maximum limit. The two heavy metals are very poisonous even in trace amounts.
- More intensive sampling and analysis, including sampling from different tidal areas, different sections of the river and more special locations, may be carried out which would better describe the heavy metal quality in water.
- The study was conducted on one occasion only in the winter season. So, further investigations to be carried out at different seasonal periods to check the seasonal variation of heavy metals concentration in the Karnaphuli River.
- Sources of heavy metals in water like inorganic fertilizers, pesticides and acaricides need to be controlled. Fertilizers, pesticides and acaricides are known to be the sources of some of the heavy metals like lead, zinc and Cd which have been detected both in soils and water at high levels.
- Kalurghat industrial area had a notable contamination levels of Pb and Cr in water. So, there is need to institute mechanisms to reduce the level of contamination including building the effective ETP, fixing drainage system and checking on the conditions of automobiles that ply the town routes.

- This investigation found higher concentration of metals in the Sadarghat jetty and kalurghat industrial sites. So, further studies should continue for monitoring of the water quality around these sites.
- This present research reveals that the areas with higher industrial zones shows relatively higher concentration of heavy metals than that of lower industrial sites. So therefore, further investigations should be carried out with higher industrial zones around KR to monitor the chemical profile of water.
- The present study was carried out to determine the heavy metals concentration only in water. A similar further research similar to be carried out check the metals concentration in water along with sediments of KR.
- Further research similar to this one be carried out in other areas of the Chittagong, especially the remotest parts that are densely populated around the Karnaphuli River.
- A further study should be done to include metals like cadmium, copper, arsenic and mercury to determine their contamination. This is because their anthropogenic origins like acaricides, and lack of recommended dumpsites within the Chattogram metropolitan city.
- Assessment of heavy metal contamination in deep tube well water and river water samples can be carried out and correlation of heavy metal contamination between green river water, tube well water and sea water samples can be prepared.
- Similar researches to this present one be carried out with other important rivers in Bangladesh to establish correlation of heavy metal contamination between the Karnaphuli and other rivers of Bangladesh.

- Since there was a considerable level of the heavy metals studied in water, a research should be carried out in food crops to determine whether similar levels are reflected in the food stuffs especially in Chattogram where the contamination of poisonous metals like Pb, Cr and Ni in water is high.
- Further investigations on the bioaccumulations and effects of heavy metals, insecticides and other persistent organic and inorganic pollutants on fish and other aquatic biota are required to understand the effects of pollutants on riverine environment.
- To this end research and monitoring of the water flow in the Karnaphuli must continue.
- People should be aware of the possible threats on water pollution in the river.

Chapter 8

References

- Abedin MJ, Akter S, Arafin SAK. (2014). Chromium Toxicity in Soil around Tannery Area, Hazaribagh, Dhaka, Bangladesh, and its Impacts on Environment as well as Human Health. 11(33).
- Adelekan B, Abegunde K. (2011). Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria. *International Journal of Physical Sciences*. 6(5): 1045-1058.
- Aderinola O, Clarke E, Olarinmoye O, Kusemiju V, Anatekhai M. (2009). Heavy metals in surface water, sediments, fish and periwinkles of Lagos Lagoon. *American-Eurasian Journal of Agricultural and Environmental Sciences*. 5(5): 609-617.
- Ahmad JU, Goni MA. (2010). Heavy metal contamination in water, soil, and vegetables of the industrial areas in Dhaka, Bangladesh. *Environmental Monitoring and Assessment*. 166(1-4): 347-357.
- Ahmed MK, Rahman S, Haque MR and Islam MM. (2010). Heavy metals in water, sediment and some fishes of Buriganga River, Bangladesh. *Int. J. Environ. Res.*, 4(2): 321-332.
- Ai-jun Wang, Ahmed Kawser, Yong-hang Xu, Xiang Ye, Seema Rani and Ke-liang Chen (2016). Heavy metal accumulation during the last 30 years in the Karnaphuli River estuary, Chittagong, Bangladesh. *SpringerPlus* (2016). 5:2079 DOI 10.1186/s40064-016-3749-1.
- Ali MM, Ali ML, Islam MS, Rahman MZ (2016). Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. *Environ Nanotechnol Monitor Manag* 5: 27–35.
- Aleksandra Duda-Chodak, Urszula Baszczyk (2008). The impact of nickel on human health: Review paper. Department of Fermentation Technology and

Technical Microbiology Agricultural University in Krakow. J. Elementol. 2008, 13(4): 685-696.

Al-Weher, M. (2008). Levels of heavy metal Cd, Cu and Zn in three fish species collected from the Northern Jordan Valley. Jordan Journal of Biological Sciences; 1: 41-46.

APHA (American Public Health Association), Inc., New York, (1955) .Standard methods for the examination of water, sewage and industrial wastes, 10th edition: 303-305.

Banfalvi G. (2011). Cellular Effects of Heavy Metals. Netherlands, London, NewYork: Springer. "In press".

Bangladesh Bureau of Statistics (2015). Population and Housing Census-2011 (Zila Report: Chittagong). Statistics and Informatics Division, Ministry of Planning, Government of the People's Republic of Bangladesh.

Begum A, Ramaiah M, Khan HI and Veena K. (2009). Heavy metal pollution and chemical profile of Cauvery River Water. E-J. Chem., 6(1): 47-52.

Bhuiyan MAH, Suruvi NI, Dampare SB, Islam MA, Quraishi SB, Ganyaglo S, Suzuki S. (2011). Investigation of the possible sources of heavy metal contamination in lagoon and canal water in the tannery industrial area in Dhaka, Bangla- desh. Environ Monit Assess 175: 633–649.

Bieby V.T., Abdullah S. R .S Basri H, Idris M, Anuar N, and Mukhlisin M. (2011). A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation, International Journal of Chemical Engineering 1: Bangin, Malaysia.

Brady D, Stoll AD, Starke L, Duncan JR. (1994). Bioaccumulation of metal cations by *Saccharomyces cerevisiae*. Applied Microbiology and Biotechnology. 41:149-154.

Calhoun, Y. (2005). Water pollution. New York, USA: Chelsea House Publishers: 1-7.

- Chernoff, R. (2005). Geriatric nutrition: the health professional's handbook. Ontario, Canada: Jones and Bartlett Publishers. Pp: 102.
- Chowdhury MI, Alam MN, Hazari SKS (1999). Distribution of radionuclides in the river sediments and coastal soils of Chittagong, Bangladesh and evaluation of the radiation hazard. *Appl Radiat Isot* 51:747–755.
- Das B, Khan YSA, Sarker MAK (2002). Trace metal concentration in water of the Karnaphuli River estuary of the Bay of Bengal. *Pak J Biol Sci* 5(5): 607–608.
- Delgado J, Boski T, Nieto JM, Pereira L, Moura D, Gomes A, Sousa C, Garcia-Tenorio R (2012). Sea-level rise and anthropogenic activities recorded in the late Pleistocene/Holocene sedimentary infill of the Guadiana Estuary (SW Iberia). *Quat Sci. Rev* 33:121–141.
- Dey S, Das J, Manchur MA (2015). Studies on heavy metal pollution of Karnaphuli River, Chittagong, Bangladesh. *IOSR J Environ Sci Toxicol Food Technol* 9(8):79–83.
- Dey S, Das J, Manchur MA (2015). Studies on heavy metal pollution of Karnaphuli River, Chittagong, Bangladesh. *IOSR J Environ Sci Toxicol Food Technol* 9(8):79–83.
- E.E., Obasohan and O.I. Eguavoen (2008). Seasonal variations of bioaccumulation of heavy metals in a freshwater fish (*Erpetoichthys calabaricus*) from Ogba River, Benin City, Nigeria. *Indian Journal of Animal Research*, 42(30), 171–179.
- El-Bourae M, El-Barbary A, Yehia M, Motawea E. (2010). Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. 61(1): 1-12.
- ESI SAAWA DADZIE (2012). Assessment of heavy metal contamination of the Densu River, weija from leachate: 18-21; “In press”.

- F. Islam, M. Rahman, S.S.A. Khan, B. Ahmed, A. Bakar and M. Halder (2013). Heavy metals in water, sediment and some fishes of Karnofuly river, Bangladesh. *Poll Res.* 32 (4): 715-721; ISSN 0257-8050.
- Garbarino JR, Hayes HC, Roth DA, Antweiler RC, Brinton TI, Taylor HE. (1995). Contaminants in the Mississippi River: Heavy metals in the Mississippi River. Reston, Virginia: U.S. GEOLOGICAL SURVEY CIRCULAR; pp. 1133.
- García-Niño WR, Pedraza-Chaverrí J. (2014). Protective effect of curcumin against heavy metals-induced liver damage. *Food and Chemical Toxicology.* 69:182-201.
- GILLETTE B. (2008). Nickel named «Allergen of the Year». ACDS adds to list of substances warranting more attention. *Dermat. Times*, 4: 15-16.
- GLENNON J.D., SARKAR B. (1982). Nickel (II) transport in human blood serum: studies of nickel (II)-binding human albumin and to native-sequence peptide, and ternary complex formation with L-histidine. *Biochem. J.*, 203: 15-23.
- Goel, P. (2009). Water pollution. New Delhi, India: New Age International: 1-2.
- Harunur Rashid, Md. Nazmul Hasan, Mohosena Begum Tanu, Rawshan Parveen, Zahid Parvez Sukhan, Md. Shahidur Rahman and Yahia Mahmud (2012). Heavy Metal Pollution and Chemical Profile of Khiru River, Bangladesh. *International Journal of Environment*, 2(1): 57-63. ISSN: 2186- 6872.
- Hassan MM, Nazem MNI (2015). Examination of land use/land cover change, urban growth dynamics, and environmental sustainability in Chittagong city, Bangladesh. *Environ Dev Sustain.* Doi: 10.1007/s10668-015-9672-8.
- He ZL, Yang XE, Stoffella PJ. Trace elements in agroecosystems and impacts on the environment (2005). *Journal of Trace Elements in Medicine and Biology.* 19(2-3):125-140.

- Herawati N, Suzuki S, Hayashi K, Rivai IF, Koyoma H (2000). Cadmium, copper and zinc levels in rice and soil of Japan, Indonesia and China by soil type. *Bulletin of Environmental Contamination and Toxicology*. 64:33-39.
- Hilgenkamp, K. (2006). *Environmental health: ecological perspective*. Toronto, Canada: Jones and Bartlett Publishers. Pp 83.
- Hossain MS, Khan YSA (2002). An environmental assessment of metal accumulation in the Karnaphuli estuary, Bangladesh. In: Ratnasiri J (ed) *Proceedings of the south Asia regional workshop on 'Assessment of material fluxes to the coastal zone in south Asia and their impacts'*. APN/SASCOM/LOICZ Regional Workshop, Negombo, Sri Lanka.
- Islam F, Rahman M, Khan SSA, Ahmed B, Bakar A, Halder M (2013). Heavy metals in water, sediment and some fishes of Karnofuly River, Bangladesh. *Int J Environ Res* 32(2):715–721.
- Islam MR, Das NG, Barua P, Hossain MB, Venkatramanan S, Chung SY (2015b). Environmental assessment of water and soil contamination in Rajakhali Canal of Karnaphuli River (Bangladesh) impacted by anthropogenic influences: a preliminary case study. *Apply Water Sci*. doi: 10.1007/s13201-015-0310-2.
- Islam MS, Ahmed MK, Habibullah-Al-Mum M, Hoque MF (2015a). Preliminary assessment of heavy metal contamination in surface sediments from a river in Bangladesh. *Environ Earth Sci* 73:1837–1848.
- Jennings, G., D.; Sneed, R., E.; Clair, M., B., St. (1996). *Metals in drinking water*, North Carolina Cooperative Extension service Publication no.: AG-473-1.
- Jigam AA, Dauda BE, Jimoh T, Yusuf HN, Umar Z. (2011). Determination of copper, zinc, lead and some biochemical parameters in fresh cow milk from different locations in Niger State, Nigeria. *African Journal of Food Science*. 5(3): 156-160.

- Johnson, D.L., Ambrose S.H., Bassett T.J., Bowen M.L., Crummey D.E., Isaacson J.S., Johnson D.N., Lamb P., Saul M., and Winter-Nelson A.E. (1997). Meanings of environmental terms. *Journal of Environmental Quality*. 26: 581-589.
- KASPRZAK K.S., SUNDERMAN JR. F.W., SALNIKOW K. (2003). Nickel carcinogenesis. *Mutat. Res.*, 533: 67-97.
- Klan S, Zahoor D, Ihsanulla A, Zubair A. (2011). Levels of selected heavy metals in drinking water of Peshawar city. *Nature*. 2: 648-652.
- Lee G, Bigham JM, Faure G. (2002). 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*. 17(5): 569-581.
- Li QS, Wu ZF, Chu B, Zhang N, Cai SS, Fang JH (2007). Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. *Environ Pollut* 149:158–164.
- Lupton, G.P., Kao, G.F., Johnson, F.B., Graham, J.H. and Helwig, E.B. (1985). Cutaneous mercury granuloma. A clinicopathologic study and review of the literature. *J. Am. Acad. Dermatol.* Feb; 12(2, Pt. 1): 296-303.
- M. Iqbal Sarwar, Ahmad Kamruzzaman Majumderb and M. Nurul Islamc (2010). Water Quality Parameters: A Case Study of Karnafully River Chittagong, Bangladesh. *Bangladesh journal of scientific and industrial research*. Bangladesh J. Sci. Ind. Res. 45(2): 177-181.
- M.J. Ahmed, M.R. Haque, A. Ahsan, S. Siraj, M.H.R. Bhuiyan, S.C. Bhattacharjee, and S. Islam (2010). Physicochemical Assessment of Surface and Groundwater Quality of the Greater Chittagong Region of Bangladesh. *Pak. J. Anal. Environ. Chem*, 11(2):1 – 11.

- M. Mominul Islam, Md. Rezaul Karim, Xin Zheng and Xiaofang (2018). Heavy Metal and Metalloid Pollution of Soil, Water and Foods in Bangladesh: A Critical Review. *Int. J. Environ. Res. Public Health*, 15(12), 2825.
- Majid MA, Rahman IMM, Bhuiyan MIH (2003). Environmental impact assessment of the effluents from Kalurghat Industrial Area of Chittagong on the Karnaphuli River water. *Chittagong U J Sci* 27(1&2): 61–69.
- Mamun, A.; Sumon, K. A.; Sukhan, Z. P.; Hoq, E.; Alam, M. W.; Haq, M. S; Rashid, F. and Rashid, H. (2013). Heavy metal contamination in water and sediments of the river Karnafuli from south-east coast of Bangladesh. Conference paper, 4th the International Conference on Environmental Aspects of Bangladesh, at Fukuoka, Japan: 113-116.
- McCluggage, D. (1991). Heavy Metal Poisoning, *NCS Magazine*. The Bird Hospital, Columbus.
- MCGREGOR D.B., BAAN R.A., PARTENSKY C., RICE J.M., WILBOURN J.D. (2000). Evaluation of the carcinogenic risks to humans associated with surgical implants and other foreign bodies – a report of an IARC Monographs Programme Meeting. *Eur. J. Cancer.*, 36: 307-313.
- Mebrahtu, G. and zebrabruk, S. (2011). Concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia. *Maejo international Journal of Science and Technology*; 3: 105-121.
- Mia MA, Nasrin S, Zhang M, Rasiah R (2015). Chittagong, Bangladesh. *Cities* 48: 31–41.
- Misra, S. and Mani, D. (2009). *Soil pollution*. New Delhi, India: S. B Nangia APH Publishing Corporation: 29-59.
- Musilova J, Arvay J, Vollmannova A, Toth T, Tomas J. Environmental contamination by heavy metals in region with previous mining activity

- (2016). *Bulletin of Environmental Contamination and Toxicology*. 97: 569-575.
- NIELSEN J.L., POULSEN O.M., ABILDTRUP A. (1994). Studies of serum protein complexes with nickel using crossed immunoelectrophoresis. *Electrophoresis*, 15: 666-71.
- Nollet M. (2011). *Hand book on analysis of edible animal by product*. New York, USA: Taylor and Francis: 193-197.
- Nriagu JO (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature* 279: 409–410.
- Nriagu JO (1990). Global metal pollution: poisoning the biosphere? *Environ Sci Policy Sustain Dev*. 32:7–33.
- OLLER A.R., COSTA M., OBERDÖRSTER G. (1997). Carcinogenicity assessment of selected nickel compounds. *Toxicol. Appl. Pharmacol.*, 143: 152-166.
- Pirsaheb M, Khosravi T, Sharafi K, Babajani L, Rezaei M. (2013). Measurement of heavy metals concentration in drinking water from source to consumption site in Kermanshah—Iran. *World Applied Sciences Journal*. 21(3): 416-423.
- Rashmi Verma¹ and Pratima Dwivedi (2013). Heavy metal water pollution- A case study. *Recent Research in Science and Technology* 2013, 5(5): 98-99. ISSN: 2076-5061.
- Reddy VH, Prasad P, Reddy AR, Reddy YR. (2012). Determination of heavy metals in surface and ground water in and around Tirupati, Chittoor (Di), Andhra Pradesh, India. *Der Pharma Chemica*. 4 (6): 2442-2448.
- Roberts, J.R. (1999). Metal toxicity in children. In *Training Manual on Pediatric Environmental Health: Putting It into Practice* Jun. Emeryville, CA: Children's 56 Environmental Health Network.

- Salano, Erick Miheso (2007). Assessment of heavy metal pollution in soils and water of samburu county, Kenya. Department of chemistry, Kenyatta University. I56/CE/11204/2007.
- Salem, H. M., Eweida, A., and Azza, F. (2000). Heavy metals in drinking water and their environmental impact on human health, Center for Environmental Hazards Mitigation: 542- 556.
- Salomons W, Forstner U, Mader P (1995). Heavy Metals: Problems and Solutions. Berlin, Germany: Springer-Verlag.
- Samad M.A., Mahmud Y., Adhikary R.K., Rahman S.B.M., Haq M., Rashid H. (2015). Chemical Profile and Heavy Metal Concentration in Water and Freshwater Species of Rupsha River, Bangladesh. American Journal of Environmental Protection, Vol. 3, No. 6: 180-186.
- Sarkar, B. (2005). Heavy metals in the environment. New York, USA: Taylor and Francis: 33-41.
- SEILKOP S.K., OLLER A.R. (2003). Respiratory cancer risks associated with low-level nickel exposure: an integrated assessment based on animal, epidemiological, and mechanistic data. Regul. Toxicol. Pharmacol. 37: 173-190.
- Sharifuzzaman SM, Rahman H, Ashekuzzaman SM, Islam MM, Chowdhury SR, Hossain MS (2016). Heavy metals accumulation in coastal sediments. In: Hasegawa H, Rahman IMM, Rahman MA (eds) Environmental remediation technologies for metal-contaminated soils. Springer, Japan: 21–42.
- Shrivastav, R. (2001). Atmospheric heavy metal pollution, development of chronological records and geological monitoring. Accessed from www.ias.ac.in.
- SIVULKA D.J. (2005). Assessment of respiratory carcinogenicity associated with exposure to metallic nickel: A review. Regul. Toxicol. Pharmacol. 43: 117-133.

- Smith, S.R., Jaffe, D.M., and Skinner M.A, (1997). Case report of metallic mercury injury. *Pediatr. Emer. Care*; 13: 114-6.
- Sonayei, Y.; Ismail, N. and Talebi, S. (2009). Determination of heavy metals in Zayandeh Road River, Isfahan-Iran. *World Applied Sciences Journal*; 6: 1204-1214.
- Sujan Dey, Jewel Das and M. A. Manchur (2015). Studies on Heavy Metal Pollution of Karnaphuli River, Chittagong, Bangladesh. *Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)* e-ISSN: 2319-2402, p- ISSN: 2319-2399. Volume 9, Issue 8 Ver. I (Aug. 2015): 79-83.
- SUNDERMAN F.W. JR., DINGLE B., HOPFER S.M., SWIFT T. (1988). Acute nickel toxicity in electroplating workers who accidentally ingested a solution of nickel sulfate and nickel chloride. *Am. J. Indust. Med.*, 14: 257-266.
- SZCZEPANIAK E., PROKOP J. (2004). Wyprysk kontaktowy. *Post. Dermatol. Alergol.* 21(4): 205-210.
- T. Venugopal, L. Giridharan, M. Jayaprakash, and P.M. Velmurugan (2009). A comprehensive geochemical evaluation of the water quality of River Adyar, India, *Bull. Environ. Contam. Toxicol.* 82 (2): 211-217.
- Tareq SM, Safiullah S, Anawar HM, Rahman MM, Ishizuka T (2003). Arsenic pollution in groundwater: a self-organizing complex geochemical process in the deltaic sedimentary environment, Bangladesh. *Sci Total Environ* 313: 213–226.
- Thevenon F, Guedron S, Chiaradia M, Loizeau JL, Pote J (2011). (Pre-) historic changes in natural and anthropogenic heavy metals deposition inferred from two contrasting Swiss Alpine lakes. *Quat Sci Rev* 30: 224–233.

- UDDIN A.N., BURNS F.J., ROSSMAN T.G., CHEN H., KLUZ T., COSTA M. (2007). Dietary chromium and nickel enhance UV-carcinogenesis in skin of hairless mice. *Toxicol. Appl. Pharmacol.*, 221: 329-338.
- UNESCO (2003). *Water for people, water for life: UN world water development report, executive summary*. Paris: United Nations Educational, Scientific and Cultural Organization.
- VAHTER M., BERGLUND M., ÅKESSON A., LIDÉN C. (2002). Metals and women's health. *Environ. Res.*, 88: 145-155.
- VALKO M., MORRIS H., CRONIN M.T.D. (2005). Metals, toxicity and oxidative stress. *Curr. Med. Chem.*, 12: 1161-1208.
- WHO (World Health Organization). (2004). *Guidelines for drinking water quality. Vol.1. Recommendations*, Geneva.
- WHO (World Health Organization). (2011). *Guidelines, Standard and Health*. Edited by Lorna Fewtrell and Jamie Bartram. Published by IWA Publishing, London, UK.
- WHO (World Health Organization). (1993). *Guidelines for drinking water quality*. World Health Organization, Geneva, Switzerland.
- Wogu, D. and Okaka, E. (2011). Pollution studies on Nigerian rivers: Heavy metals in surface water of warri River, Delta state. *Journal of Biodiversity and Environmental Sciences*; 1: 7-12.

APPENDIX
Picture Gallery



Figure: Collected raw water samples



Figure: Filtration of water samples



Figure: Filtrated of water samples



Figure: Filtrated of water samples



Figure: Addition of HNO_3 into filtrated water



Figure: Addition of H_2SO_4 into filtrated water

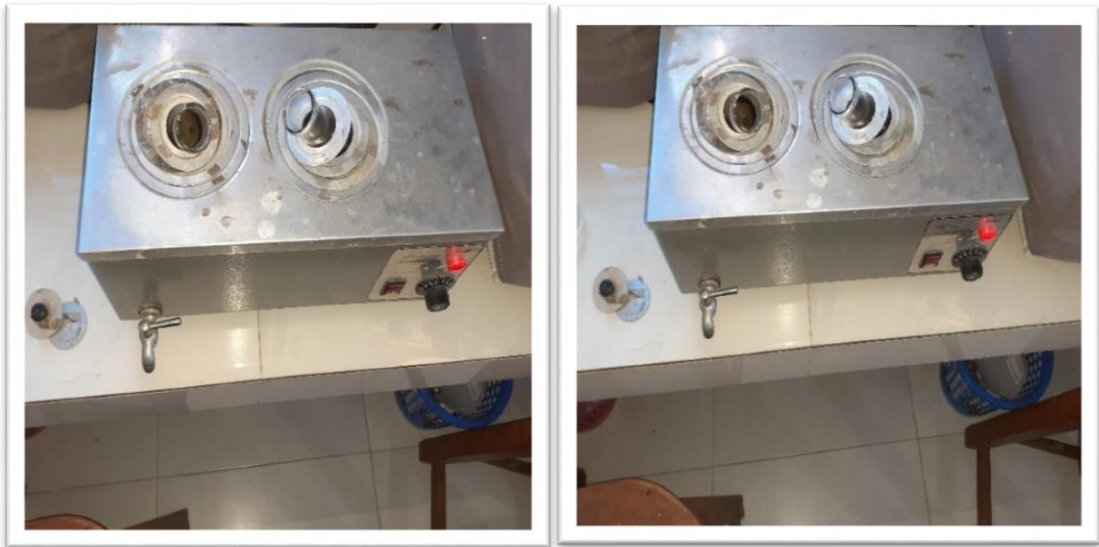


Figure: Evaporation of water samples into water bath



Figure: Digestion of water samples



Figures: Filtration of digested of water samples



Figures: Filtration of digested of water samples



Figure: Final digested of water samples



Figure: Numbering of digested of samples



Figures: Untreated toxic effluents in the Karnaphuli



Figure: Karnaphuli in death throes



Figures: Pollution of the Karnaphuli from dyeing and tannery industries



Figure: The oil tanker capsized and sank in the Karnaphuli River at a jetty in the port of Chittagong, Bangladesh.

BRIEF BIOGRAPHY

Md. Shakhawat Hossain passed the Secondary School Certificate Examination in 2009 and then Higher Secondary Certificate Examination in 2011. Md. Shakhawat Hossain obtained his B.Sc. (Hons.) in Food Science & Technology in 2016 from Chittagong Veterinary and Animal Sciences University (CVASU), Bangladesh. Now, he is a candidate for the degree of MS in Department of Applied Chemistry and Chemical Technology in Food Chemistry and Quality Assurance under Food Science & Technology Faculty; CVASU. He has immense interest to work in food safety issues including food chemistry, quality assurance, food quality control, environmental chemistry, product development and processing, malnutrition, reduction of nutritional changes in food processing etc.